DISSERTATION

Titel der Dissertation

„Quantum Field Theoretical Green Functions

and

Electronic Structure“

Verfasser

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angestrebter akademischer Grad

Doktor der Naturwissenschaften (Dr. rer. nat.)

Wien, 2012

Abstract

The present thesis is a purely theoretical study, the main goal of which is the theoretical development of Electronic Structure Theory from the quantum field theoretical and many-body theory point of view.[1] I have tried to introduce all concepts and definitions in the quantum field theoretical framework. The independent electron approximation is always treated as a special case of the general many-body theory, but does not play any conceptual role. Another goal of this thesis has been the elucidation of various analogies between Electronic Structure Theory and other branches of physics.

The concrete topic of this thesis is the application of Green function methods to the quantum theory of materials properties in the solid state, in particular to Electronic Structure Theory. The thesis is divided into two parts, (i) a review and discussion of some aspects of the general Many-Body Theory and non-relativistic Quantum Field Theory background and (ii) electronic Green functions methods.

The first three Sections of Chapter 1 are included to make this document as self-contained as possible. In the first section of Chapter 1, I review the fundamental Hamiltonian of solid state physics and briefly discuss its limitations. In the second section, I investigate the role of Green functions (or propagators) in standard Quantum Mechanics. This will be useful for the application of Green functions in many-body physics because Green functions in standard Quantum Mechanics display a number of analogies to their many-body (or quantum field theoretical) counterparts. In the third section, I give a very condensed review of Density Functional Theory.

In the fourth section, I deal with Linear Response Theory in both classical electrodynamics and thermodynamics and discuss its quantum mechanical formulation within the Kubo formalism. I placed some emphasis on the interpretation of electrodynamics in continuous media in terms of internal fields and its relation to the so-called Modern Theory of Polarization. A master formula is derived which allows for the determination of all electrodynamic materials properties from the microscopic conductivity. I also comment on the connection between quantum mechanical response functions and thermodynamic susceptibilities, on the classification of response functions in general, and on the derivation of so-called relaxed re-

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[1] Electronic Structure Theory can be defined as non-relativistic, fermionic Quantum Field Theory at temperature $T = 0$. P.C. Martin and J. Schwinger [67] are credited with the introduction of field-theoretical methods for quantum many-body systems.

sponse functions from Mean Field Theory.

As all these topics can be treated without ever taking recourse to field theoretical methods, the first Chapter is called "First Quantization". In the second Chapter, I then review the formulation of multi-particle Quantum Mechanics in the Fock space and discuss its relation to Quantum Field Theory. Some effort is devoted to a field-theoretical formulation of quantized lattice oscillations which displays numerous analogies to the electronic Green function theory. In particular, I have emphasized the formulation of phononic Field Theory in real space.

The second part of this thesis, "Green Function Theory", is dedicated to the theory of Green functions in Electronic Structure Theory. At the beginning, I introduce the notion of many-body Green functions in its most general form, discuss some of their elementary properties and review the equation of motion theory for Green functions as well as the Lehmann representation. Some minor lemmata about the Lehmann representation are proven. For the convenience of the reader, a final subsection treats some aspects of solid state physics. This paves the way for a discussion of the definition and measurement of band structures and Fermi surfaces from a many-body point of view. The fourth Chapter starts with an introduction of Green function perturbation theory. Although this introduction is rather sketchy in other respects, a detailed proof of the Gell-Mann and Low theorem is given in which several arguments which have been treated only cursorily in the standard reference [21] have been worked out in detail. After a short review of the Bethe-Salpeter equation, I derive a self-consistent set of three equations which encapsulates the whole Green function theory and show its equivalence to the well-known Hedin equations. This set of three equations, henceforth called the self-consistent set of equations, is a central result of this thesis.[2] The second part of Chapter 4 is dedicated to a discussion of several standard approximations within the context of the self-consistent set of equations.[3]

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[2]R. Starke, G. Kresse: Phys Rev B **85** 7 075119 (2012)

[3]I want to remark that the renormalization of Feynman graphs is a topic which has been completely skipped in this work while it is actually highly relevant. The reason for this is that this thesis is centered around the Electronic Structure Theory as it is implemented in modern computer codes, e.g. VASP. These codes ultimately calculate everything in finite dimensional Hilbert spaces where all Feynman graphs collapse to matrix products. Usually, it is then investigated empirically whether the resulting values stay roughly constant as a function of a suitably defined cut-off momentum. In other words, the Feynman graphs are supposed to converge anyway. Intuitively, this has the smack of truth to it in that condensed matter physics is low-energy physics and therefore the high-energy degrees of freedom may somehow become irrelevant leaving us with a (finite-dimensional) Hilbert space of low-lying degrees of freedom. We stress, however, that in principle the necessity of renormalization is in no way restricted to high energy physics.

A decisive conceptual advantage of the self-consistent set of equations developed in Chapter 4 is that it is independent of the concrete form of the two-particle interaction and of the orbital basis in the one-particle Hilbert space. This motivates the fifth Chapter in which effective electron-electron interactions are introduced. They are not included in the standard model of solid state physics discussed in Chapter 1. The first part of Chapter 5 discusses some general aspects of the theory of effective Lagrangeans. The application of this theory to classical electrodynamics shows that effective theories are in general non-local field theories. I then discuss the equivalence of the effective Lagrangean approach in classical Field Theory to a quantum mechanical approach through the Gell-Mann and Low theorem. After a short discussion of non-local field theories, the central result of which is the derivation of the connection between the non-local interaction Lagrangean and the interaction Hamiltonian, the effective Lagrangean approach is applied to the full electromagnetic interaction of electrons, yielding a purely electronic but time-dependent Hamiltonian containing current-current terms. I then derive a static approximation to this Hamiltonian and the corresponding Hartree-Fock equations. Finally, the results from the electromagnetic case are used as a motivation to derive and discuss effective electron-electron interactions mediated by phonons. A relation between the effective, phonon-mediated electron-electron interaction and the nuclear polarizability is derived and discussed. This allows for a rederivation of effective interactions in general from a mean-field theoretical point of view. Within this context it becomes possible to introduce a new way to decouple electronic and nuclear degrees of freedom and to generalize the standard phononic Hamiltonian, which is recovered in a suitable zero-frequency limit. This leads to the ultimate goal of this thesis: the unification of electronic and phononic propagator theories into one self-consistent system of equations.

The appendix mainly assembles conventions and formulas of the ubiquitous theory of Fourier transforms and related topics.

Chapter 4 follows the paper: R. Starke, G. Kresse, Phys Rev B **85** 7 075119 (2012).

(Cf. e.g. [86]) A systematic investigation of Feynman graph theory in Electronic Structure Theory with regard to the possible necessity of renormalization would of course constitute a dissertation in its own right.

Kurzbeschreibung

Die vorliegende Arbeit stellt eine rein theoretische Untersuchung dar, deren Hauptziel darin besteht, die Theorie der elektronischen Struktur vom Standpunkt der Quantenfeld- und Vielteilchentheorie aus zu entwickeln. Dabei habe ich versucht, alle Konzepte und Definitionen im quantenfeldtheoretischen Rahmen einzuführen.[4] Die Einteilchennäherung hingegen wird nur als Spezialfall behandelt, spielt jedoch keine konzeptionelle Rolle. Ein weiteres Ziel dieser Arbeit besteht darin, Analogien zwischen der "Electronic Structure Theory" und anderen Gebieten der Physik zu erhellen.

Das konkrete Thema dieser Dissertation ist die Anwendung von Greenschen Funktionen auf die Quantentheorie der Materialeigenschaften des Festkörpers, insbesondere der elektronischen Struktur. Die Arbeit ist in zwei Teile gegliedert: (i) eine Zusammenfassung und Diskussion des allgemeinen vielteilchen- und quantenfeldtheoretischen Rahmens und (ii) die Theorie der elektronischen Green-Funktionen.

Die ersten drei Abschnitte von Kapitel 1 wurden aufgenommen, um diese Arbeit möglichst in sich abgeschlossen zu halten. Im ersten Abschnitt definiere ich den fundamentalen Hamilton-Operator eines Festkörpers und diskutiere die Grenzen seiner Anwendbarkeit. Im zweiten Abschnitt wird die Rolle der Greenschen Funktionen in der Standard-Quantenmechanik untersucht, was sich als nützlich im Vielteilchenfall herausstellen wird, da die quantenmechanischen Greenschen Funktionen einige Analogien zu ihren quantenfeldtheoretischen Pendants aufweisen. Der dritte Abschnitt stellt eine kurze Einführung in die Dichtefunktionaltheorie dar.

Der vierte Abschnitt widmet sich der "Linear Response Theory" sowohl vom Standpunkt der klassischen Elektrodynamik, als auch aus der Sicht der Thermodynamik und Quantenmechanik. Ein Schwerpunkt liegt hierbei auf der Interpretation der Elektrodynamik kontinuierlicher Medien im Sinne einer Unterteilung in externe und induzierte Felder und ihrem Zusammenhang mit der sogenannten "Modern Theory of Polarization". Es wird eine Schlüsselformel abgeleitet zur Berechnung aller elektrodynamischen Response-Eigenschaften aus der mikroskopischen Leitfähigkeit. Weiterhin untersuche ich den Zusammenhang zwischen quantenmechanischen Response-Funktionen und thermodynamischen Suszeptibilitäten,

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[4]Elektronische Strukturtheorie kann als nichtrelativistische, fermionische Quantenfeldtheorie bei Temperatur $T = 0$ definiert werden. Die Einführung feldtheoretischer Methoden in die Vielteilchenquantenmechanik wird P.C. Martin und J. Schwinger [67] zugeschrieben.

die allgemeine Klassifikation von Response-Funktionen und die Ableitung von relaxierten Response-Funktionen aus der "Mean Field Theory".

Da alle diese Themen im Grunde ohne Zuhilfenahme quantenfeldtheoretischer Methoden behandelt werden können, wurden sie im ersten Kapitel unter der Überschrift "First Quantization" zusammengefasst. Im zweiten Kapitel bespreche ich dann die Formulierung der Vielteilchen-Quantenmechanik im Fock-Raum und deren Zusammenhang mit der Quantenfeldtheorie. Dem folgt eine feld-theoretische Formulierung von Gitterschwingungen, die viele Analogien zur elektronischen Green-Funktionen-Theorie aufweist. Insbesondere habe ich im Gegensatz zur üblichen Darstellung von Gitterschwingungen – insbesondere des Phononen-Propagators – im Fourier-Raum alles konsequent im Ortsraum behandelt.

Der zweite Teil dieser Dissertation, "Green Function Theory", gilt der Theorie der Greenschen Funktionen im Rahmen der elektronischen Strukturtheorie. Zunächst führe ich noch einmal den Begriff der Greenschen Funktion ein und diskutiere einige elementare Eigenschaften sowie die Bewegungsgleichung und die Lehmann-Darstellung der Greenschen Funktion, wobei einige kleinere Lemmata formuliert werden. Im Sinne des Lesers fasst ein weiterer Unterabschnitt einige Schlüsselformeln der Festkörperphysik zusammen, die dann im Weiteren verwendet werden, um die Begriffe der Bandstruktur und der Fermi-Fläche vom quantenfeldtheoretischen Standpunkt aus zu diskutieren. Das vierte Kapitel gibt zunächst eine Wiederholung der störungstheoretischen Behandlung von Greenschen Funktionen. Obwohl sich dieses Kapitel im Allgemeinen eher als skizzenhafter Überblick versteht, wurden einige Argumente, die in dem Standardwerk [21] nur oberflächlich erwähnt wurden, im vollen Detail ausgeführt. Nach einer kurzen Besprechung der Bethe-Salpeter-Gleichung folgt dann die Ableitung eines selbstkonsistenten Gleichungssystems, welches die komplette elektronische Green-Funktionen-Theorie enthält. Dieses System dreier Gleichungen, im Folgenden das selbskonsistente Gleichungssystem genannt, ist ein zentrales Ergebnis dieser Arbeit.[5] Der zweite Abschnitt des vierten Kapitels diskutiert dementsprechend die gängigen Näherungen im Rahmen dieses Gleichungssystems.[6]

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[5]R. Starke, G. Kresse: Phys Rev B **85** 7 075119 (2012)

[6]An dieser Stelle möchte ich anmerken, dass die Renormierung von Feynman-Graphen ein Thema ist, das in der vorliegenden Dissertation völlig ausgelassen wurde, obwohl es eigentlich hochgradig relevant ist. Der Grund dafür besteht darin, dass diese Arbeit sich um die elektronische Strukturtheorie dreht, so wie sie in modernen Computer-Programmen, beispielsweise VASP, implementiert wurde. Dergleichen Programme berechnen letzten Endes alle Größen in endlichdimensionalen Hilberträumen, was zur Folge hat, dass sich Feynman-Graphen zu bloßen Matrixprodukten reduzieren. Es wird dann üblicherweise empirisch untersucht, ob die resultierenden Ergebnisse in Abhängigkeit eines entsprechend definierten Cut-Off-Impulses konstant bleiben. Mit anderen Worten, es wird davon ausgegangen, dass die Feynman-Graphen

Ein Hauptvorteil des selbstkonsistenten Gleichungssystems, so wie es im vierten Kapitel entwickelt wurde, besteht in seiner Forminvarianz unter Basiswechseln im Hilbertraum und seiner Unabhängigkeit von der konkreten Form der Zweiteilchen-Wechselwirkung. Dieses mag als Motivation des fünften Kapitels dienen, in welchem effektive, elektronische Wechselwirkungen eingeführt werden, die nicht Teil des Standardmodells der Festkörperphysik sind, so wie es im ersten Kapitel diskutiert wurde. Im ersten Abschnitt des fünften Kapitels werden zunächst einige allgemeine Züge effektiver Lagrange-Funktionen diskutiert. Die Anwendung dieser Erkenntnisse auf die klassische Elektrodynamik erweist effektive Theorien als nicht-lokale Feldtheorien. Ich diskutiere weiterhin die Verbindung zwischen effektiven Lagrangeans und dem Gell-Mann-Low-Theorem. Nach einer Ableitung nicht-lokaler Euler-Lagrange-Gleichungen wird die effektive Feldtheorie dann auf die volle elektromagnetische Wechselwirkung der Elektronen angewendet, was zu einem rein elektronischen, jedoch zeitabhängigen Hamiltonian führt, der Strom-Strom-Wechselwirkungen berücksichtigt. Für diesen leite ich dann eine statische Näherung und die daraus resultierenden Hartree-Fock-Gleichungen ab. Schließlich werden die Erkenntnisse aus der effektiven elektromagnetischen Wechselwirkung verwendet, um eine effektive, phononen-induzierte Elektron-Elektron-Wechselwirkung sowie deren Verhältnis zur nuklearen Polarisierbarkeit abzuleiten. Diese ermöglicht dann eine Neuinterpretation effektiver Wechselwirkungen im Sinne einer dann zu erläuternden "Mean Fluctuation Theory". In diesem Zusammenhang ergibt sich auch ein neues Entkopplungsschema für elektronische und nukleare Freiheitsgrade. Der Standard-Hamiltonian der Phononen ergibt sich daraus dann als ein statischer Limes. Damit gelingt es schließlich, phononische und elektronische Freiheitsgrade in einem geschlossen, selbstkonsistenten Propagator-Gleichungssystem zusammenzufassen.

Der Anhang fasst hauptsächlich Formeln und Konventionen der allgegenwärtigen Fourier-Transformation zusammen.

Kapitel 4 folgt der Publikation: R. Starke, G. Kresse, Phys Rev B **85** 7 075119 (2012).

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ohnehin konvergieren. Das klingt intuitiv plausibel, da Festkörperphysik auch Niedrigenergiephysik bedeutet und man folglich vermuten mag, dass die Hochenergiefreiheitsgrade irgendwie verschwinden und dabei einen (endlichdimensionalen) Hilbertraum der Niedrigenergiefreiheitsgrade zurücklassen. Es ist jedoch zu betonen, dass im Prinzip die Notwendigkeit der Renormierung in keiner Weise auf den Bereich der Hochenergiephysik beschränkt ist. (siehe beispielsweise [86]) Eine systematische Untersuchung der Feynman-Graphen-Theorie in der elektronischen Strukturtheorie im Hinblick auf die Notwendigkeit der Renormierung wäre natürlich eine Dissertation für sich.

Danksagung

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Part I.

Many-Body Theory

1. First Quantization

1.1. Quantum Mechanics of the Solid State

1.1.1. Standard Model

Hilbert Space for Solid State Physics We begin this work by reviewing the first-quantized, non-relativistic Hamiltonian of a system of N nuclei with charge Ze and $Z \times N$ electrons ($Z, N \in \mathbb{N}$) where N is large ($\geq 10^{23}$). The Hilbert space of this system is a subspace of $\mathcal{H}_{\mathrm{nucl}}^{N} \otimes \mathcal{H}_{\mathrm{el}}^{ZN}$ which is spanned by functions of the form

$$\Psi(\mathbf{y}_1, \ldots, \mathbf{y}_N, \mathbf{x}_1, \ldots, \mathbf{x}_{ZN}) = \psi(\mathbf{y}_1, \ldots, \mathbf{y}_N)\phi(\mathbf{x}_1, \ldots, \mathbf{x}_{ZN}) \tag{1.1}$$

where the arguments are to be understood as joint spin and space variables. The electronic one-particle Hilbert space $\mathcal{H}_{\mathrm{el}} \equiv \mathcal{H}$ is given by

$$\mathcal{H} \simeq \mathbb{C}^2 \otimes \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \simeq \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \oplus \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \simeq \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}^2, \mathrm{d}\mathbf{x}). \tag{1.2}$$

The definition of the nuclear one-particle Hilbert space depends on the spin s of the nucleus. For the eigenvalue m_s of the spin operator in a given direction, we have the inequality

$$-s \leq m_s \leq s \tag{1.3}$$

which gives $2s + 1$ possible values. The spinorial space is therefore $\mathbb{C}^{2s+1}$ and the nuclear one-particle Hilbert space is given by

$$\mathcal{H}_{\mathrm{nucl}} \simeq \mathbb{C}^{2s+1} \otimes \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{y}) \simeq \bigoplus_{-s}^{s} \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{y}) \simeq \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}^{2s+1}, \mathrm{d}\mathbf{y}). \tag{1.4}$$

The ZN-electron Hilbert space $\mathcal{H}^{ZN}$ is given in terms of $\mathcal{H}$ as $\wedge^{ZN}\mathcal{H}$ and the N-nuclei Hilbert space is given by $\wedge^N \mathcal{H}_{\mathrm{nucl}}$ for $s \in \frac{1}{2}\mathbb{N}$ and $\vee^N \mathcal{H}_{\mathrm{nucl}}$ for $s \in \mathbb{N}$. In other words, the Hilbert space restricted to the subspace of functions which are totally antisymmetric with respect to the $\mathbf{x}_i$ and totally symmetric or antisymmetric with respect to the $\mathbf{y}_j$ depending on the spin of the nuclei (symmetric for integer spin, antisymmetric for half-integer spin).

Hamiltonian for Solid State Physics The Hamiltonian of the system reads[1]

$$
\hat{H} = (\hat{T}_{\mathrm{nucl}} + \hat{V}_{\mathrm{nucl-nucl}}) + (\hat{T}_{\mathrm{el}} + \hat{V}_{\mathrm{el-el}}) + \hat{V}_{\mathrm{el-ion}} \tag{1.5}
$$

$$
\equiv -\frac{\hbar^2}{2M}\sum_{i=1}^{N}\Delta_{\mathbf{y}_i} + \frac{Z^2 e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{1}{|\mathbf{y}_i-\mathbf{y}_j|} \tag{1.6}
$$

$$
-\frac{\hbar^2}{2m}\sum_{i=1}^{ZN}\Delta_{\mathbf{x}_i} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i<j}\frac{1}{|\mathbf{x}_i-\mathbf{x}_j|} - \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{N}\sum_{j=1}^{ZN}\frac{1}{|\mathbf{y}_i-\mathbf{x}_j|}. \tag{1.7}
$$

The model consisting of this Hamiltonian and the Hilbert space $\mathcal{H}_{\mathrm{nucl}}^{N}\otimes\mathcal{H}^{ZN}$ will be called *standard model of solid-state physics*. In fact, the above Hamiltonian describes more generally any non-relativistic system of electrons and nuclei interacting through the Coulomb potential, e.g. the corresponding liquid would have the same Hamiltonian. Surprisingly enough, the ground-state is in most cases crystalline. The dynamics of the system is described by a Schrödinger equation

$$
\mathrm{i}\hbar\partial_t\Psi(\mathbf{y}_1,\ldots,\mathbf{y}_N,\mathbf{x}_1,\ldots,\mathbf{x}_{ZN};t) = \hat{H}\Psi(\mathbf{y}_1,\ldots,\mathbf{y}_N,\mathbf{x}_1,\ldots,\mathbf{x}_{ZN};t). \tag{1.8}
$$

Here, the time t enters as parameter. That means, for t being given $\Psi\in\mathcal{H}$ but Ψ is not square-integrable with respect to $\mathrm{d}t$. In practice, one is not interested in the full dynamics. In most cases, one wants to find the values of certain observables in the ground-state

$$
E_0\Psi_0(\mathbf{y}_1,\ldots,\mathbf{y}_N,\mathbf{x}_1,\ldots,\mathbf{x}_{ZN}) = \hat{H}\Psi_0(\mathbf{y}_1,\ldots,\mathbf{y}_N,\mathbf{x}_1,\ldots,\mathbf{x}_{ZN}) \tag{1.9}
$$

or the canonical ensemble, i.e. the density-matrix

$$
\hat{\rho} = \frac{1}{Z}\exp\left(-\frac{\hat{H}}{k_{\mathrm{B}}T}\right) \tag{1.10}
$$

with $Z = \mathrm{Tr}\exp\left(-\frac{\hat{H}}{k_{\mathrm{B}}T}\right)$.

Usually, the full Hamiltonian of the electrons and nuclei is too complicated. One therefore tries to eliminate the nuclear degrees of freedom in favor of a purely electronic Hamiltonian which, although being inequivalent, entails for many realistic situations the most important information. For this purpose, one usually proceeds in the following way:

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[1] e denotes the charge of an electron including the sign. The advantage of this definition is that all formulas generalize with the simple replacement $e\mapsto q$.

1. One introduces the so-called *Born-Oppenheimer approximation* (see e.g. [55]), an expansion of the fundamental Hamiltonian in the parameter

$$\kappa = \left(\frac{m}{M}\right)^{1/4} \tag{1.11}$$

where $\frac{m}{M}$ is the mass ratio of nuclei and electrons. One writes the time-dependent wave-function as

$$\Psi(\mathbf{y}_1, \ldots, \mathbf{y}_N, \mathbf{x}_1, \ldots, \mathbf{x}_{ZN}; t) = \sum_i \psi_i(\mathbf{y}_1, \ldots, \mathbf{y}_N; t)\phi_i(\mathbf{y}_1, \ldots, \mathbf{y}_N, \mathbf{x}_1, \ldots, \mathbf{x}_{ZN}). \tag{1.12}$$

This form of the wave-function is still completely general. Now one assumes that the $\phi_i(\mathbf{y}_1, \ldots, \mathbf{y}_N, \mathbf{x}_1, \ldots, \mathbf{x}_{ZN}) \equiv \phi_i(\mathbf{Y}, \mathbf{X})$ are determined by the Schrödinger equation

$$(\hat{T}_{\text{el}} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{el-ion}}(\mathbf{Y}))\phi_i(\mathbf{Y}, \mathbf{X}) = E_i(\mathbf{Y})\phi_i(\mathbf{Y}, \mathbf{X}). \tag{1.13}$$

This assumes that the $\phi_i(\mathbf{Y}, \mathbf{X}) \equiv \phi_{i\mathbf{Y}}(\mathbf{X})$ are the electronic eigenstates corresponding to the fixed nuclear position eigenstate configuration $\mathbf{Y} = (\mathbf{y}_1, \ldots, \mathbf{y}_N)$. One can now plug this ansatz in the Schrödinger equation. The $\psi_i(\mathbf{Y})$ then have to obey ([55], p.9, equation (1.7))

$$\begin{aligned} i\hbar\partial_t\psi_i(\mathbf{Y}, t) &= (\hat{T}_{\text{nucl}} + \hat{V}_{\text{nucl-nucl}} + E_i(\mathbf{Y}))\psi_i(\mathbf{Y}, t) + \\ &\quad - \sum_j \langle\phi_i|\hat{T}_{\text{el}}|\phi_j\rangle\psi_j(\mathbf{Y}, t) - 2\sum_j\sum_{k=1}^N \frac{\hbar^2}{2M}\nabla_k\psi_j(\mathbf{Y}, t)\langle\phi_i|\nabla_k|\phi_j\rangle \end{aligned}$$

where $\nabla_k = \nabla_{\mathbf{y}_k}$.[2] One now assumes that the system if suitably prepared at an initial time stays the whole time in a state of the form $\psi\phi$. This is not general any more. The loss of generality comes in because the electronic wave-functions $\phi_{\mathbf{Y}}(\mathbf{X})$ are not wave-functions with respect to nuclear coordinates $\mathbf{Y}$. These enter only as parameters. If such a diagonal expansion works the system is said to be *adiabatic* because under the time-evolution the electrons run through a sequence of energy eigenstates of the instantaneous nuclear configuration. The crucial point is now that a perturbative inclusion of the non-adiabatic effects leads to a formal Taylor series in κ. However, even within this adiabatic approximation, the nuclei are still delocalized. Although the electronic states $\phi_i(\mathbf{Y}, \mathbf{X})$ correspond to fixed nuclear configurations $\mathbf{Y}$, the total state is still a superposition of such electronic states with expansion coefficients $\psi_i(\mathbf{Y})$.

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[2]As this equation couples different nuclear eigenfunctions, the resulting theory is not of Schrödinger form any more and will therefore not be considered in the sequel. An alternative decoupling will be proposed in the last Chapter.

One therefore proceeds further by introducing the *classical nuclei approximation* which neglects $\hat{T}_{\mathrm{nucl}}$. Furthermore, one momentarily neglects $\hat{V}_{\mathrm{el-ion}}$. The eigenstates of the resulting Hamiltonian for the nuclei are position eigenstates. In principle, any configuration of eigenstates would solve the corresponding Schrödinger equation for the nuclei. From experiments we know that the atoms in a crystal form regular arrays. Therefore, we choose nuclei to form a Bravais lattice

$$\mathbf{x_{n0}} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3 \tag{1.14}$$

with $\mathbf{n} \in \mathbb{Z}^3$ and $|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)| = V_c \neq 0$. That means, the nth nucleus is in state $\psi(\mathbf{x}) = \delta(\mathbf{x} - \mathbf{x_{n0}})$ and the total nuclear state is a Slater determinant or permanent.

2. From experiments we know that low lying electronic spectral lines in a crystal are only slightly shifted with respect to the spectral lines of the corresponding free atoms. It therefore seems plausible to group the electrons into core electrons and valence electrons. The core electrons are described by solutions of the atomic Schrödinger equations centered around a nucleus of the lattice. Thus, the nuclei become ions. The influence of the core electrons on the valence electrons is taken into account by the introduction of the so-called *pseudo-potentials*. The simplest and most intuitive way to do this is to compute the core electronic density $n(\mathbf{x})$ from the atomic solutions and include an operator of the form

$$v(\mathbf{x}) = \frac{e^2}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.15}$$

in the Schrödinger equation for the valence electrons. This corresponds to a purely classical interaction between core electrons and valence electrons. In actual fact, however, there is not even a basis to say that an electron is core or valence because the all-electron solution would be antisymmetrized. Therefore, a proper core-valence interaction would include exchange effects. As all-electron calculations are usually unfeasible, one tries to compensate for this with more involved pseudo-potentials. (see e.g. [66]) Finally, one replaces the initial $\hat{V}_{\mathrm{el-ion}}$ by the effective, external potential of the static regular lattice and the valence-electrons. This new potential then obeys in the limit $N \to \infty$

$$\forall (n_1, n_2, n_3) \in \mathbb{Z}^3 : \ v_{\mathrm{ext}}(\mathbf{x} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) = v_{\mathrm{ext}}(\mathbf{x}). \tag{1.16}$$

With these approximations, we get a purely electronic Hamiltonian of the form

$$\hat{H} \quad = \quad (\hat{T}_{\mathrm{el}} + \hat{V}_{\mathrm{ext}}) + \hat{V}_{\mathrm{el-el}} = \sum_{i=1}^{N} \left(-\frac{\hbar^2}{2m}\Delta_{\mathbf{x}_i} + v_{\mathrm{ext}}(\mathbf{x}_i) \right) + \frac{e^2}{4\pi\varepsilon_0} \sum_{i<j}^{N} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} \tag{1.17}$$

where we renamed the electron number into N. Note, that this Hamiltonian is not translationally invariant anymore. The model consisting of the Hamiltonian (1.17) and the Hilbert space $\mathcal{H}^N = \wedge^N \mathcal{H}$ will be called *standard model of Electronic Structure Theory*. Even for the full standard model of solid-state theory, the standard model of Electronic Structure Theory is a good starting point. The nuclear degrees of freedom are then reintroduced by the concept of phonons (for details and definitions see sections 2.3 and 3.3 or [15]) with a free Hamiltonian

$$\hat{H}_{\mathrm{ph}} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} \left(b_{\mathbf{k}\lambda}^\dagger b_{\mathbf{k}\lambda} + \frac{1}{2} \right) \qquad (1.18)$$

and a photon-electron interaction Hamiltonian typically written in the form ([15], Chapter 3)

$$\hat{V}_{\mathrm{el-ph}} = \frac{1}{V} \sum_{\mathbf{k}} \sum_{\mathbf{q}\in\Gamma^*} \sum_{\mathbf{G}\in\tilde{\Gamma}} g_{\mathbf{q}\mathbf{G}} \; a_{\mathbf{k}+\mathbf{q}+\mathbf{G}}^\dagger a_{\mathbf{k}} (b_{\mathbf{q}}^\dagger + b_{-\mathbf{q}}). \qquad (1.19)$$

The full (all-electron) electron-phonon system $\hat{T}_{\mathrm{el}} + \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{el-el}} + \hat{H}_{\mathrm{ph}} + \hat{V}_{\mathrm{el-ph}}$ differs from the standard model of solid-state physics only in that the ionic potential operator is expanded linearly around a Bravais lattice of equilibrium positions. The introduction of phonons regroups the nuclear degrees of freedom. The Hamiltonian with (1.19) is called the Fröhlich-Hamiltonian.

1.1.2. Limitations of the Standard Model

The standard models have a number of restrictions:

1. Nuclei are completely described by their position and spin. In other words, the internal structure of the nuclei is neglected in the description of the solid state. In actual fact, every nucleus is a complicated many-body system in its own right. On an intuitive level, disregarding the nuclear structure can be justified by the mental picture of a nucleus which is highly localized on the electronic length scale (the length scale at which the electronic wave-function typically varies). This localization makes it plausible to treat the nuclei as point-particles. Within this approximation, the only vestige of the complicated internal structure of the nucleus is the nuclear spin which, of course, is the total spin of the nuclear many-body system and cannot be associated with the individual elementary constituents of the nucleus. The effect of nuclear spins on the electronic structure makes itself felt through spin-spin interactions of electrons and nuclei. On an experimental level, disregarding the nuclear structure is justified because the spectrum of nuclei in the bulk practically coincides with the spectrum of the free nuclei. Nonetheless, the fact that the nucleus is not a point particle and displays a

rich internal structure can make itself felt, e.g. by quadrupole terms in the interaction potential $\hat{V}_{\mathrm{el-ion}}$.

2. The standard model is completely non-relativistic. Surprising as it may be at first sight, relativistic effects make themselves felt in a broad variety of solid-state experiments and therefore cannot generally be neglected. In principle, there are two different kinds of relativistic corrections:

a) First, relativistic corrections stem from the fact that the Schrödinger equation (or rather the Pauli equation) is the non-relativistic approximation to the Dirac equation. In other words, these corrections come from a modification of the wave-equation as such. In solid state physics, this is usually taken into account by expanding the relativistic dispersion relation

$$E = \sqrt{c^2\mathbf{p}^2 + m^2c^4} \simeq mc^2 + \frac{\mathbf{p}^2}{2m} - \frac{1}{8}\frac{(\mathbf{p}^2)^2}{m^3c^2} + \dots \qquad (1.20)$$

The term $\frac{1}{8}\frac{(\mathbf{p}^2)^2}{m^3c^2}$ – the so-called *mass-velocity term* – is then promoted to an operator through the replacement $\mathbf{p} \mapsto -i\hbar\nabla$ and treated as a perturbation to the Schrödinger equation. In hydrogen-like systems this leads to a first-order shift given by

$$\Delta E_{nml} = \frac{Z\alpha^2}{n^2}\left(\frac{n}{l+1/2} - \frac{3}{4}\right)E_n \qquad (1.21)$$

where $\alpha = e^2/4\pi\varepsilon_0\hbar c \simeq 1/137$ denotes the fine structure constant (cf. [20] p.23f). The connection to the relativistic Dirac theory consists in the fact that the mass-velocity term corresponds to a term in a Foldy-Wouthuysen transformed Dirac Hamiltonian (cf. [47] p.69f).

b) Secondly, relativistic corrections stem from the fact that within the relativistic regime new force terms arise. In other words, the inclusion of these corrections does not consist in a modification of the wave-equation as such but only in the additional inclusion of new potential terms. The most notable of these effects is the so-called spin-orbit coupling which stems from the relativistic transformation properties of the electric field (cf. [48] p.364f; [47] p.16). This leads to the inclusion of a potential term

$$\hat{V}_{\mathrm{SO}} = \frac{1}{m^2}\hat{\mathbf{S}}\cdot\hat{\mathbf{L}}\frac{1}{r}\frac{\partial v(r)}{\partial r} \qquad (1.22)$$

where $v(r)$ is the Coulomb potential of the nucleus, r being the relative coordinate.

1.2. Green Functions in Standard Quantum Mechanics

1.2.1. Definition and Properties

Definition For a particle with associated Hilbert space $\mathcal{H} = \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x})$ and Hamiltonian $\hat{H} = -\frac{\hbar^2}{2m}\Delta + v(\mathbf{x})$ a single-particle Green function in the space-time domain is a distribution obeying

$$\left(\mathrm{i}\hbar\partial_t - \hat{H}(\mathbf{x}, \partial_\mathbf{x})\right) G(\mathbf{x}t, \mathbf{x}'t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{1.23}$$

Remarks

1. For time-independent external potentials $v(\mathbf{x})$, the Green function can be chosen such that it depends only on the difference $\tau = t - t'$.

2. A Green function is in general not uniquely defined by equation (1.23). Therefore, (1.23) has to be supplemented by initial or boundary conditions. We postulate $G^{\mathrm{R}} \to 0$ for $\tau \to -\infty$ and $G^{\mathrm{A}} \to 0$ for $\tau \to \infty$ and the initial-value condition

$$\mathrm{i}\hbar G^{\mathrm{R/A}}(\mathbf{x}, \mathbf{x}'; \tau = 0^\pm) = \pm\delta(\mathbf{x} - \mathbf{x}'). \tag{1.24}$$

3. The importance of the Green Function lies in the following:

    Theorem 1.2.1 *Consider the inhomogeneous Schrödinger equation*

    $$\mathrm{i}\hbar\partial_t\psi(\mathbf{x}t) = \hat{H}\psi(\mathbf{x}t) + f(\mathbf{x}t) \tag{1.25}$$

    subject to the initial (final) condition

    $$\psi(\mathbf{x}t_0) = \psi_0(\mathbf{x}). \tag{1.26}$$

    The unique solution of this problem is given by the Duhamel Formula:

    $$\psi(\mathbf{x}t) = \mathrm{i}\hbar \int \mathrm{d}\mathbf{x}'\, G(\mathbf{x}t, \mathbf{x}'t_0)\psi_0(\mathbf{x}') + \int_{t_0}^{\pm\infty} \mathrm{d}t' \int \mathrm{d}\mathbf{x}'\, G(\mathbf{x}t, \mathbf{x}'t')f(\mathbf{x}'t') \tag{1.27}$$

    where $G = \pm G^{R/A}$ for $t > t_0$ or $t \le t_0$ respectively.

    The Duhamel formula shows that the Green function has two different roles: one is to relate the solution to the inhomogeneity (the original meaning of "Green function"), the second is to relate the solution to the initial value condition ("propagator").

Green Functions as Propagators Consider now the homogeneous Schrödinger equation and suppose we know $\psi(\mathbf{x}'t')$ at some initial time t'. Then, we can obtain ψ at a later time t by

$$\psi(\mathbf{x}t) = i\hbar \int d\mathbf{x}' \, G^{\mathrm{R}}(\mathbf{x}, \mathbf{x}'; t - t')\psi(\mathbf{x}'t'). \tag{1.28}$$

On the other hand, expanding ψ with respect to a complete system of energy eigenstates yields

$$\psi(\mathbf{x}t) = \sum_n \psi_n(\mathbf{x})\langle\psi_n|\psi(t')\rangle e^{-\frac{i}{\hbar}\varepsilon_n(t-t')}. \tag{1.29}$$

This implies that the time-dependent integral operator

$$\sum_n \psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')e^{-\frac{i}{\hbar}\varepsilon_n(t-t')} \tag{1.30}$$

propagates ψ from t to t'. We rewrite the last expression as

$$\langle\mathbf{x}| \sum_n |\psi_n\rangle\langle\psi_n|e^{-\frac{i}{\hbar}\varepsilon_n(t-t')}|\mathbf{x}'\rangle \tag{1.31}$$

and interpret

$$\sum_n e^{-\frac{i}{\hbar}\varepsilon_n(t-t')}|\psi_n\rangle\langle\psi_n| \tag{1.32}$$

as the spectral resolution of $\hat{U}(t - t') = \exp(-i\hat{H}(t - t'))$. Hence, the propagator can be recast as

$$\langle\mathbf{x}|\hat{U}(t', t)|\mathbf{x}'\rangle = \langle\mathbf{x}| \exp\left(-\frac{i}{\hbar}H(t - t')\right)|\mathbf{x}'\rangle \equiv \langle\mathbf{x}t|\mathbf{x}'t'\rangle. \tag{1.33}$$

Consequently, the propagator can also be interpreted as the amplitude for propagation from $(\mathbf{x}t)$ to $(\mathbf{x}'t')$. This can also be deduced from the theorem of Stone according to which the time evolution of the wave-function is given by the one-parameter unitary group generated by $\hat{H}$, i.e.

$$\psi(t) = \exp\left(-\frac{i}{\hbar}\hat{H}(t - t')\right)\psi(t'). \tag{1.34}$$

Writing this in the position state representation, we get

$$\langle\mathbf{x}|\psi(t)\rangle = \psi(\mathbf{x}t) = \int d\mathbf{x}' \, \langle\mathbf{x}| \exp\left(-\frac{i}{\hbar}\hat{H}(t - t')\right)|\mathbf{x}'\rangle\langle\mathbf{x}'|\psi(t')\rangle. \tag{1.35}$$

As it stands, the propagator propagates the state both into the future and the past. In accordance with the conventions met above, we define a retarded and an advanced propagator by means of:

$$i\hbar G^{\mathrm{R}}(\mathbf{x}, \mathbf{x}'; t - t') = \theta(t - t')\langle\mathbf{x}| \exp\left(-\frac{i}{\hbar}\hat{H}(t - t')\right)|\mathbf{x}'\rangle \tag{1.36}$$

$$-i\hbar G^{\mathrm{A}}(\mathbf{x}, \mathbf{x}'; t - t') = \theta(t' - t)\langle\mathbf{x}| \exp\left(-\frac{i}{\hbar}\hat{H}(t - t')\right)|\mathbf{x}'\rangle. \tag{1.37}$$

1.2.2. Examples

Free Green Functions The free Hamiltonian reads

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}. \tag{1.38}$$

The corresponding Green functions fulfill in the respective domains:

$$\left(\frac{\hbar^2}{2m}\Delta + \mathrm{i}\hbar\partial_t\right)G(\mathbf{x}t, \mathbf{x}'t') = \delta(\mathbf{x}-\mathbf{x}')\delta(t-t'). \tag{1.39}$$

$$\left(-\frac{\hbar^2|\mathbf{k}|^2}{2m} + \mathrm{i}\hbar\partial_t\right)G(\mathbf{k}, t) = \delta(t-t'). \tag{1.40}$$

$$\left(\frac{\hbar^2}{2m}\Delta + \varepsilon\right)G(\mathbf{x}, \mathbf{x}', \varepsilon) = \delta(\mathbf{x}-\mathbf{x}'). \tag{1.41}$$

$$\left(-\frac{\hbar^2|\mathbf{k}|^2}{2m} + \varepsilon\right)G(\mathbf{k}, \varepsilon) = 1. \tag{1.42}$$

The last equation can be solved easily:

$$G(\mathbf{k}, \varepsilon) = \frac{1}{\varepsilon - \varepsilon(\mathbf{k})} = \frac{1}{\hbar\omega - \frac{\hbar^2|\mathbf{k}|^2}{2m}}. \tag{1.43}$$

The remaining domains can be regained by Fourier backtransforms. However, these transforms are not well defined because there are different distributions which can be considered to be the regularization of $1/(\varepsilon - \hbar^2 k^2/2m)$. Therefore, we redefine

$$G(\mathbf{k}, \varepsilon) = \frac{1}{\varepsilon - \varepsilon(\mathbf{k})} := \lim_{\eta \to 0} \frac{1}{\hbar\omega - \frac{\hbar^2|\mathbf{k}|^2}{2m} \pm \mathrm{i}\eta} \tag{1.44}$$

with the limit in the distributional sense. The choice $+\mathrm{i}\eta$ corresponds to the retarded Green function whereas $-\mathrm{i}\eta$ corresponds to the advanced Green function. In particular, in the retarded case we have

$$\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}'t') = \theta(t-t')\left(\frac{m}{2\pi\mathrm{i}\hbar(t-t')}\right)^{\frac{3}{2}}\exp\left(\frac{\mathrm{i}m(\mathbf{x}-\mathbf{x}')^2}{2\hbar(t-t')}\right) \tag{1.45}$$

$$\mathrm{i}\hbar G(\mathbf{k}t, \mathbf{k}'t') = \theta(t-t')\delta_{\mathbf{k}\mathbf{k}'}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\varepsilon(\mathbf{k})(t-t')} \tag{1.46}$$

$$\mathrm{i}\hbar G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \mathrm{i}\hbar\int\frac{\mathrm{d}\mathbf{k}}{(2\pi)^3}\frac{\exp(\mathrm{i}\mathbf{k}(\mathbf{x}-\mathbf{x}'))}{\varepsilon - \frac{\hbar^2|\mathbf{k}|^2}{2m} + \mathrm{i}\eta} = -\frac{m}{2\pi\hbar^2}\frac{\exp(-\mathrm{i}k|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.47}$$

where $k = \sqrt{2m\varepsilon}/\hbar$.

Spectral Resolution We now suppose the Hamiltonian to be of the form:

$$\hat{H} = \hat{H}_0 + \hat{V} \tag{1.48}$$

with the multiplicative potential $(\hat{V}\psi)(\mathbf{x}) = v(\mathbf{x})\psi(\mathbf{x})$. A formal expression for G can be easily found, if we express $\delta(\mathbf{x} - \mathbf{x}')$ in terms of a complete set of eigenfunctions of $\hat{H}$:

$$\delta(\mathbf{x} - \mathbf{x}') = \sum_n \psi_n(\mathbf{x})\psi_n^*(\mathbf{x}'). \tag{1.49}$$

Similarly, G can be expanded as:

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_{n,m} G_{nm}\psi_n(\mathbf{x})\psi_m^*(\mathbf{x}'). \tag{1.50}$$

Plugging this into the Schrödinger equation, we get:

$$G_{nm} = \frac{\delta_{nm}}{\varepsilon - \varepsilon_n} \tag{1.51}$$

or

$$G(\mathbf{x}, \mathbf{x}'; \varepsilon) = \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\varepsilon - \varepsilon_n}. \tag{1.52}$$

In general, for the time-dependent Green function

$$\left(\mathrm{i}\hbar\frac{\partial}{\partial t} - \hat{H}\right) G(\mathbf{x}t, \mathbf{x}'t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{1.53}$$

we now have the formal solution:

$$\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}'t') = \int \frac{\mathrm{d}\varepsilon}{2\pi} \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\varepsilon - \varepsilon_n} \exp\left(-\frac{\mathrm{i}}{\hbar}\varepsilon(t - t')\right). \tag{1.54}$$

Again as it stands, this integral is undefined due to the integration over the poles ε_n. Hence, we redefine the integral according to

$$\mathrm{i}\hbar G(\mathbf{x}, \mathbf{x}'; t - t') = \lim_{\eta \to 0} \int \frac{\mathrm{d}\varepsilon}{2\pi} \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\varepsilon - \varepsilon_n \pm \mathrm{i}\eta} \exp\left(-\frac{\mathrm{i}}{\hbar}\varepsilon(t - t')\right), \tag{1.55}$$

i.e.

$$G^{\mathrm{R}}(\mathbf{x}, \mathbf{x}', \varepsilon) = \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\varepsilon - \varepsilon_n + \mathrm{i}\eta} \tag{1.56}$$

$$G^{\mathrm{A}}(\mathbf{x}, \mathbf{x}', \varepsilon) = \sum_n \frac{\psi_n(\mathbf{x})\psi_n^*(\mathbf{x}')}{\varepsilon - \varepsilon_n - \mathrm{i}\eta} \tag{1.57}$$

leading to

$$\mathrm{i}\hbar G^{\mathrm{R}}(\mathbf{x},\mathbf{x}';t-t') \;=\; \theta(t-t')\sum_{n}\psi_{n}(\mathbf{x})\psi_{n}^{*}(\mathbf{x}')\exp\left(-\mathrm{i}\frac{\varepsilon_{n}}{\hbar}(t-t')\right) \qquad (1.58)$$

$$-\mathrm{i}\hbar G^{\mathrm{A}}(\mathbf{x},\mathbf{x}';t-t') \;=\; \theta(t'-t)\sum_{n}\psi_{n}(\mathbf{x})\psi_{n}^{*}(\mathbf{x}')\exp\left(-\mathrm{i}\frac{\varepsilon_{n}}{\hbar}(t-t')\right). \qquad (1.59)$$

Perturbation Theory for Green Functions The equation

$$(\mathrm{i}\hbar\partial_{t}-\hat{H}_{0})\psi(\mathbf{x}t)=f(\mathbf{x}t), \qquad (1.60)$$

can be solved by the Green function as

$$\psi(\mathbf{x}t)=\psi_{0}(\mathbf{x}t)+\int \mathrm{d}\mathbf{x}'\mathrm{d}t'\,G_{0}(\mathbf{x}t,\mathbf{x}'t')f(\mathbf{x}'t') \qquad (1.61)$$

where ψ_{0} is a solution of the homogeneous equation. Now, consider the homogeneous Schrödinger equation

$$(\mathrm{i}\hbar\partial_{t}-\hat{H})\psi(\mathbf{x}t)=0 \qquad (1.62)$$

with the Hamiltonian $\hat{H}=\hat{H}_{0}+\hat{V}$. We rewrite this equation as

$$(\mathrm{i}\hbar\partial_{t}-\hat{H}_{0})\psi(\mathbf{x}t)=v(\mathbf{x})\psi(\mathbf{x}t). \qquad (1.63)$$

This can again be treated like an inhomogeneous equation with perturbation $f(\mathbf{x}t)=v(\mathbf{x})\psi(\mathbf{x}t)$. Hence,

$$\psi(\mathbf{x}t)=\psi_{0}(\mathbf{x}t)+\int \mathrm{d}\mathbf{x}'\,G_{0}(\mathbf{x}t,\mathbf{x}'t')v(\mathbf{x}')\psi(\mathbf{x}'t') \qquad (1.64)$$

where ψ_{0} is a solution of the unperturbed, homogeneous equation. By iteration it follows

$$\begin{aligned}\psi(\mathbf{x}t) \;=\;& \psi_{0}(\mathbf{x}t)+\int \mathrm{d}\mathbf{x}'\mathrm{d}t'\,G_{0}(\mathbf{x}t,\mathbf{x}'t')v(\mathbf{x}')\psi_{0}(\mathbf{x}t')+\\ & \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\mathrm{d}\mathbf{x}''\mathrm{d}t''\,G_{0}(\mathbf{x}t,\mathbf{x}'t')v(\mathbf{x}')G_{0}(\mathbf{x}'t',\mathbf{x}''t'')v(\mathbf{x}'')\psi_{0}(\mathbf{x}''t'')+\dots\end{aligned} \qquad (1.65)$$

This means, in terms of Green functions that

$$\begin{aligned}G(\mathbf{x}t,\mathbf{x}'t') \;=\;& G_{0}(\mathbf{x}t,\mathbf{x}'t')+\int \mathrm{d}\mathbf{x}''\mathrm{d}t''\,G_{0}(\mathbf{x}t,\mathbf{x}''t'')v(\mathbf{x}'')G_{0}(\mathbf{x}''t'',\mathbf{x}'t')+\\ & \int \mathrm{d}\mathbf{x}''\mathrm{d}t''\mathrm{d}\mathbf{x}'''\mathrm{d}t'''\,G_{0}(\mathbf{x}t,\mathbf{x}''t'')v(\mathbf{x}'')G_{0}(\mathbf{x}''t'',\mathbf{x}'''t''')v(\mathbf{x}''')G_{0}(\mathbf{x}'''t''',\mathbf{x}'t')\dots\end{aligned}$$

or symbolically

$$G=G_{0}+G_{0}\hat{V}G_{0}+G_{0}\hat{V}G_{0}\hat{V}G_{0}+\dots. \qquad (1.66)$$

By factoring out G_0, we find

$$G = G_0 + G_0\hat{V}G. \tag{1.67}$$

This is the so-called *Dyson equation*. For one-particle Green functions, it is a rigorous identity which can be seen as follows: if we interpret $\delta(\mathbf{x} - \mathbf{x}')$ as the integral kernel of the identity $\mathbb{1}_{\mathcal{H}}$, then we get in the frequency domain

$$(\varepsilon - \hat{H})G(\varepsilon) = \mathbb{1}_{\mathcal{H}}. \tag{1.68}$$

In other words, $G(\varepsilon)$ is (minus) the resolvent of $\hat{H}$ at $\varepsilon \in \mathbb{C} \setminus \sigma(\hat{H})$, σ denoting the spectrum. If we now have two self-adjoint operators $\hat{H}_1$, $\hat{H}_2$ with resolvents $G_1(\varepsilon)$ and $G_2(\varepsilon)$, then the so-called second resolvent identity says that

$$G_1(\varepsilon) - G_2(\varepsilon) = G_1(\varepsilon)(\hat{H}_1 - \hat{H}_2)G_2(\varepsilon). \tag{1.69}$$

In particular, for $\hat{H}_2 = \hat{H}$ and $\hat{H}_1 = \hat{H}_0$, we retrieve the Dyson equation because we have $\hat{H}_2 - \hat{H}_1 = \hat{V}$, $G_1(\varepsilon) = G_0(\varepsilon)$, $G_2(\varepsilon) = G(\varepsilon)$. In other words, for one-particle Green functions, the Dyson equation is equivalent to the second resolvent identity. This would not be obvious if we had worked in the space-time domain.

1.3. Density Functional Theory

1.3.1. Hohenberg-Kohn Theorem

Introduction We consider a family of many-electron Hamiltonians of the form

$$\hat{H} = \hat{T} + \hat{V}_{\text{el}-\text{el}} + \hat{V}_{\text{ext}} \tag{1.70}$$

where $\hat{T}$ corresponds to the kinetic energy of the electrons, $\hat{V}_{\text{el}-\text{el}}$ to the electron-electron Coulomb interaction and $\hat{V}_{\text{ext}}$ is an external potential (typically the potential of the classical nuclei) of the form

$$\hat{V}_{\text{ext}} = \int d\mathbf{x} \, v_{\text{ext}}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}). \tag{1.71}$$

In the N-particle sector, this reduces to

$$\hat{V}_{\text{ext}} = \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{x}_i) \tag{1.72}$$

where $\hat{V}_{\text{ext}}$ acts in $\mathcal{H}$ via $(\hat{V}_{\text{ext}}\psi)(\mathbf{x}) = v_{\text{ext}}(\mathbf{x})\psi(\mathbf{x})$. In particular, for $\Psi \in \mathcal{H}^N$ we have the identity

$$\langle \Psi | \hat{V}_{\text{ext}} | \Psi \rangle = \int d\mathbf{x} \, n(\mathbf{x})v_{\text{ext}}(\mathbf{x}). \tag{1.73}$$

We think of the external potential as indexing the family of Hamiltonians. Furthermore, we assume a fixed particle number N. The ground-state energy $E = E_0^N$ is the absolute minimum of the functional

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \tag{1.74}$$

where Ψ varies in $\mathcal{H}^N$ and is subject to the constraint $\|\Psi\| = 1$.

Definition An electronic density $n(\mathbf{x})$ is called $v - representable$ if it can be written as

$$n(\mathbf{x}) = \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) | \Psi \rangle = N \int \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N \ \Psi^*(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \tag{1.75}$$

where Ψ is the ground-state of some Hamiltonian $\hat{H}$ of the form (1.70) with a suitably chosen external potential v.

Theorem 1.3.1 *(Hohenberg-Kohn) If Ψ_1 and Ψ_2 are ground-states of the many-electron Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ of the form (1.70) respectively which yield the same density $n(\mathbf{x})$, then the respective external potentials entering in the Hamiltonians H_i differ only by a constant (which of course can be set zero). Put differently, the ground-state density uniquely determines the external potential which gives rise to it.*

Lemma 1.3.2 *The ground-state wave-functions of two Hamiltonians $\hat{H}_1$ and $\hat{H}_2$ of the form (1.70) with external potentials which differ by more than a constant cannot coincide.*

Proof Assume the contrary:

$$
\begin{aligned}
(\hat{T} + \hat{V}_{\text{el}-\text{el}} + \hat{V}_{\text{ext1}})\Psi_0 &= E_0^1 \Psi_0 \\
(\hat{T} + \hat{V}_{\text{el}-\text{el}} + \hat{V}_{\text{ext2}})\Psi_0 &= E_0^2 \Psi_0.
\end{aligned}
$$

Consequently, Ψ_0 would be an eigenfunction of $\hat{V}_{\text{ext1}} - \hat{V}_{\text{ext2}}$ with eigenvalue $E_0^1 - E_0^2$ which is impossible, because an eigenfunction of a Hamiltonian of the standard form vanishes only at a set of measure zero. [99]

Proof of the Hohenberg-Kohn Theorem Assume $\hat{H}_1$ and $\hat{H}_2$ are Hamiltonians with essentially different external potentials $v_{\text{ext1}}(\mathbf{x})$ and $v_{\text{ext2}}(\mathbf{x})$ and ground-state wave-functions Ψ_1 and Ψ_2 (which by the lemma have to be different) such that

$$n(\mathbf{x}) = \langle \Psi_1 | \hat{n}(\mathbf{x}) | \Psi_1 \rangle \equiv \langle \Psi_2 | \hat{n}(\mathbf{x}) | \Psi_2 \rangle. \tag{1.76}$$

Consequently,

$$\begin{aligned}
\langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle \quad & < \quad \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle && (1.77) \\
& = \quad \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{H}_1 - \hat{H}_2 | \Psi_2 \rangle && (1.78) \\
& = \quad \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \langle \Psi_2 | \hat{V}_{\text{ext1}} - \hat{V}_{\text{ext2}} | \Psi_2 \rangle && (1.79) \\
& = \quad \langle \Psi_2 | \hat{H}_2 | \Psi_2 \rangle + \int d\mathbf{x}\, n(\mathbf{x})(v_{\text{ext1}}(\mathbf{x}) - v_{\text{ext2}}(\mathbf{x})). && (1.80)
\end{aligned}$$

That means

$$E_1 < E_2 + \int d\mathbf{x}\, n(\mathbf{x})(v_{\text{ext1}}(\mathbf{x}) - v_{\text{ext2}}(\mathbf{x})) \qquad (1.81)$$

By symmetry,

$$E_2 < E_1 + \int d\mathbf{x}\, n(\mathbf{x})(v_{\text{ext2}}(\mathbf{x}) - v_{\text{ext1}}(\mathbf{x})). \qquad (1.82)$$

Therefore

$$E_1 + E_2 < E_1 + E_2. \qquad (1.83)$$

This contradiction shows the impossibility of the assumption.

Remarks

1. The converse is not true. Different ground-states of one and the same Hamiltonian (in the case of a degenerate ground-state energy) can give rise to different densities.

2. The proof of the Hohenberg-Kohn theorem shows that, more generally, the ground-state density determines the Hamiltonian uniquely within an equivalence class of Hamiltonians differing by external potentials.

3. Since the Hamiltonian is fully determined (up to a constant) by the ground-state density, it follows that in principle all properties (all time-independent many-particle wave-functions and the corresponding values of observables) of the system are determined by the ground-state density.

Energy Functional We define the energy functional $E \equiv E[n]$ by

$$E : \quad \{\tilde{n}(\mathbf{x})\} \to \mathbb{R} \qquad (1.84)$$

$$\tilde{n}(\mathbf{x}) \mapsto E_{v_{\text{ext}}}[\tilde{n}] = F[\tilde{n}] + \int d\mathbf{x}\, \tilde{n}(\mathbf{x}) v_{\text{ext}}(\mathbf{x}) \qquad (1.85)$$

where $\tilde{n}$ is non-negative and normalized to the total particle number ($\int d\mathbf{x}\, n(\mathbf{x}) = N$), $\{\tilde{n}\}$ denotes the set of v-representable densities and F is is given by

$$F[\tilde{n}] = \langle \Psi_0[\tilde{n}] | \hat{T} + \hat{V}_{\text{el}-\text{el}} | \Psi_0[\tilde{n}] \rangle \qquad (1.86)$$

where $\Psi_0[\tilde{n}]$ is the ground-state of a Hamiltonian of the form (1.70) with an external potential which has $\tilde{n}$ as its corresponding ground-state density.

Theorem 1.3.3 *The exact ground-state energy corresponding to $\hat{V}_{\text{ext}}$ is given by the global minimum value of this functional, and the respective minimizing density equals to the ground-state density.*

Proof First, we prove that the value $F[\tilde{n}]$ does not depend on which of the possibly degenerate ground-state wave-functions is chosen: let Ψ_1 and Ψ_2 be two ground-state wave-functions corresponding to $\tilde{n}$ and the Hamiltonian $\hat{T} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext }\tilde{n}}$. Then

$$\langle\Psi_1|\hat{H}|\Psi_1\rangle = \langle\Psi_2|\hat{H}|\Psi_2\rangle$$

$$\Rightarrow \quad \langle\Psi_1|\hat{T} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext }\tilde{n}}|\Psi_1\rangle = \langle\Psi_2|\hat{T} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext }\tilde{n}}|\Psi_2\rangle$$

$$\Rightarrow \quad \langle\Psi_1|\hat{T} + \hat{V}_{\text{el-el}}|\Psi_1\rangle + \int \mathrm{d}\mathbf{x}\,\tilde{n}(\mathbf{x})v_{\text{ext }\tilde{n}}(\mathbf{x}) = \langle\Psi_2|\hat{T} + \hat{V}_{\text{el-el}}|\Psi_2\rangle + \int \mathrm{d}\mathbf{x}\,\tilde{n}(\mathbf{x})v_{\text{ext }\tilde{n}}(\mathbf{x})$$

$$\Rightarrow \quad \langle\Psi_1|\hat{T} + \hat{V}_{\text{el-el}}|\Psi_1\rangle = \langle\Psi_2|\hat{T} + \hat{V}_{\text{el-el}}|\Psi_2\rangle$$

which shows the equality. In particular, this shows that $E[\tilde{n}]$ is the evaluation of the Hamiltonian $\hat{T} + \hat{V}_{\text{el-el}} + \hat{V}_{\text{ext}}$ in the ground-state corresponding to $\tilde{n}$. Finally, $\hat{V}_{\text{ext}}$ is the uniquely determined potential which has n as a ground-state density. Therefore, by the Rayleigh-Ritz principle $\forall\,\tilde{n} \neq n:\ E_0 = E_{v_{\text{ext}}}[n]$ satisfies

$$E_0 \leq E_{v_{\text{ext}}}[\tilde{n}]. \tag{1.87}$$

1.3.2. Kohn-Sham Equations

Introduction Obviously, it is impossible to write down $F[n]$ explicitly. Kohn and Sham therefore proposed to introduce a non-interacting many-electron reference system with the property that the non-interacting ground-state has the same density as the ground-state of the interacting system under consideration. In principle, it is not clear whether such a non-interacting system exists, but if it exists, then the external potential which gives rise to it is uniquely determined. This is because by the remark to the Hohenberg-Kohn theorem, the ground-state density determines the Hamiltonian uniquely within an equivalence class of Hamiltonians differing by external potentials, i.e. the proof of the Hohenberg-Kohn theorem works also for a family of Hamiltonians of the form $\hat{H}_0 = \hat{T} + \hat{V}_{\text{ext}}$.

Constrained Search Algorithm We consider now a reformulation of the Rayleigh-Ritz variational principle. In the first step, we fix an electron density $n(\mathbf{x})$, consider all wave-functions Ψ that yield this very density and search for the constrained minimum of the

functional

$$E_{v_{\text{ext}}}[n] = F[n] + \int d\mathbf{x} \, v_{\text{ext}}(\mathbf{x})n(\mathbf{x}) \tag{1.88}$$

where

$$F[n] = \min_{\langle \Psi | \hat{n}(x) | \Psi \rangle = n(x)} \langle \Psi | \hat{T} + \hat{V}_{\text{el}-\text{el}} | \Psi \rangle. \tag{1.89}$$

We then minimize $E_{v_{\text{ext}}}[n]$ with respect to $n(\mathbf{x})$. This allows for an alternative definition of the functional $F[n]$. The different definitions read explicitly:

1. $F[n]$ is given by $\langle \Psi[n] | \hat{T} + \hat{V}_{\text{el}-\text{el}} | \Psi[n] \rangle$ where $\Psi[n]$ is an arbitrary ground-state of the uniquely (within its equivalence class) determined Hamiltonian with ground-state density n.

2. $F[n]$ is given by the global minimum of $\langle \Psi | \hat{T} + \hat{V}_{\text{el}-\text{el}} | \Psi \rangle$ where the variation goes over all many-body wave-functions with density n (no matter whether they are a ground-state of some Hamiltonian or not).

The equivalence of the two definitions can be seen as follows: Consider a given set of many-electron wave-functions yielding the same density n. For all Ψ in this set the expectation value of an arbitrary external $\hat{V}_{\text{ext}}$ yields the same value $\int d\mathbf{x} \, v_{\text{ext}}(\mathbf{x})n(\mathbf{x})$. In particular, this applies to the uniquely determined external potential corresponding to the density n. The minimization of the expectation value $\langle \Psi | \hat{H} | \Psi \rangle$ of the thus defined Hamiltonian within the fixed class of wave-functions with the same density is therefore completely determined by the minimization of the functional $\langle \Psi[n] | \hat{T} + \hat{V}_{\text{el}-\text{el}} | \Psi[n] \rangle$ because on $\hat{V}_{\text{ext}}$ all wave-functions give the same value. On the other hand, this minimum is (by the Rayleigh-Ritz principle) obtained for the ground-state of the Hamiltonian with the given ground-state density. The Constrained Search definition of $F[n]$ suggests to consider the functional variation of $E_{v_{\text{ext}}}[n]$:

$$E_{v_{\text{ext}}}[n + \eta \delta n] - E_{v_{\text{ext}}}[n] = \eta \int d\mathbf{x} \left(\frac{\delta F[n]}{\delta n(\mathbf{x})} + v_{\text{ext}}(\mathbf{x}) \right) \delta n(\mathbf{x}) + \mathcal{O}(\eta^2) \tag{1.90}$$

Hence, the ground-state energy satisfies:

$$\frac{\delta F[n]}{\delta n(\mathbf{x})} = -v_{\text{ext}}(\mathbf{x}) \tag{1.91}$$

under the constraint:

$$\int d\mathbf{x} \, n(\mathbf{x}) = N. \tag{1.92}$$

Derivation of Kohn-Sham Equations One introduces a new energy functional:

$$E_{\text{KS}}^0[\tilde{n}] = T_s[\tilde{n}] + \int d\mathbf{x} \, v_{\text{KS}}(\mathbf{x})\tilde{n}(\mathbf{x}) \tag{1.93}$$

with

$$T_s[\tilde{n}] = \min_{\langle \Psi | \hat{n}(x) | \Psi \rangle = \tilde{n}(x)} \langle \Psi | \hat{T} | \Psi \rangle \tag{1.94}$$

and an external potential $v_{\mathrm{KS}}(\mathbf{x})$ yet to be defined. The stationarity condition for the functional $E_{\mathrm{KS}}^0[\tilde{n}]$ reads:

$$\frac{\delta T_s[\tilde{n}]}{\delta \tilde{n}(\mathbf{x})} = -v_{\mathrm{KS}}(\mathbf{x}). \tag{1.95}$$

On the other hand, the minimization of $E_{\mathrm{KS}}^0[n]$ is equivalent to minimizing $\langle \Psi | \hat{H}_0 | \Psi \rangle$ with the non-interacting Hamiltonian $\hat{H}_0 = \hat{T} + \hat{V}_{\mathrm{KS}}$. We therefore have the following equivalences:

1. minimizing E_{KS}^0 is equivalent to

2. finding the ground-state density of a non-interacting electron system subject to the external potential v_{KS} which in turn is equivalent to

3. solving the *Kohn-Sham equations*

$$\left(-\frac{\hbar^2}{2m} \Delta + v_{\mathrm{KS}}(\mathbf{x}) \right) \psi_i(\mathbf{x}) = \varepsilon_i \psi_i(\mathbf{x}) \tag{1.96}$$

for the lowest-lying energies $\epsilon_1 \leq \ldots \leq \epsilon_N$, the ground-state density being given by

$$n(\mathbf{x}) = \sum_{i=1}^{N} |\psi_i(\mathbf{x})|^2. \tag{1.97}$$

Now, we return the exact functional $F[n]$ for which we can make without loss of generality the ansatz

$$F[n] = T_s[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] \tag{1.98}$$

where

$$E_{\mathrm{H}} = \frac{e^2}{8\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.99}$$

whereas E_{xc} is defined by this ansatz, that is

$$E_{\mathrm{xc}} = F - T_s - E_{\mathrm{H}}. \tag{1.100}$$

The stationarity condition for the exact functional F then implies

$$\frac{\delta T_s[n]}{\delta n(\mathbf{x})} = -v_{\mathrm{ext}}(\mathbf{x}) - v_{\mathrm{H}}(\mathbf{x}) - v_{\mathrm{xc}}(\mathbf{x}) \tag{1.101}$$

where

$$v_{\mathrm{H}}(\mathbf{x}) = \frac{e^2}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.102}$$

and

$$v_{\mathrm{xc}}(\mathbf{x}) \equiv \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{x})}. \tag{1.103}$$

We now define

$$v_{\mathrm{KS}} = v_{\mathrm{ext}} + v_{\mathrm{H}} + v_{\mathrm{xc}}. \tag{1.104}$$

This definition (1.104) makes the stationarity conditions (1.95) and (1.101) coincide. The non-interacting reference energy functional and the exact functional therefore have the same stationarity conditions. Furthermore, as the minimizing densities correspond to the ground-state densities of the respective systems, the density (1.97) of the Kohn-Sham system coincides with the exact ground-state density. In other words, the Kohn-Sham system is the uniquely determined non-interacting system which has the same ground-state density as a given interacting system.

Remarks

1. The ground-state energy of the many-electron system is not given as the evaluation of the Kohn-Sham Hamiltonian in the respective ground-state, but by the evaluation of the energy-functional at the Kohn-Sham ground-state density. The relation between the ground-state energy of the many-electron system and the ground-state energy of the Kohn-Sham system (sum of eigenvalues) is given by

$$E = \sum_{i=1}^{N} \epsilon_i - \frac{e^2}{8\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} - \int \mathrm{d}\mathbf{x} \, n(\mathbf{x})v_{\mathrm{xc}}(\mathbf{x}) + E_{\mathrm{xc}}[n]. \tag{1.105}$$

   In particular, the Kohn-Sham orbitals have to be chosen such that they minimize this energy functional. These do not necessarily correspond to the Kohn-Sham orbitals with the lowest Kohn-Sham eigenvalues.

2. The fundamental band gap is defined as

$$\Delta = E_0^{N+1} + E_0^{N-1} - 2E_0^{N}. \tag{1.106}$$

   For a non-interacting system, this yields the difference between the lowest unoccupied and the highest occupied orbital energy. In the case of the Kohn-Sham system, we have the problem that $v_{\mathrm{KS}}(\mathbf{x})$ per constructionem depends on the particle number (through the density whose integral equals N). Therefore, the difference between the lowest unoccupied and the highest occupied Kohn-Sham orbital energy does not equal the band-gap. However, in the spirit of a thermodynamic limit, the Kohn-Sham potential may be roughly independent of the particle number (for large N). If this approximation holds, the Kohn-Sham system may be used to compute the band-gap.

3. Thermodynamic susceptibilities at temperature $T = 0$ – being second derivatives of the ground-state energy with respect to external fields – can be calculated from the Kohn-Sham ground-state.

4. The exchange correlation potential is unknown as a functional of the density. In practice, there are several ansätze. [35, 55, 66, 74]

5. One may drop the assumption about the existence of a non-interacting reference system because the definition of v_{KS} is independent of this assumption. However, it is then not clear whether the ground-state density is given by the ground-state of the reference system because any eigenstate fulfills the stationarity condition.

Adiabatic Connection Theorem Consider the many-body Hamiltonian

$$\hat{H} = \hat{H}_\lambda = \hat{T} + \hat{V}(\lambda) + \lambda\hat{V}_{\mathrm{el-el}} \tag{1.107}$$

where $\lambda \in [0, 1]$. The λ-dependence of

$$\hat{V} = \int \mathrm{d}\mathbf{x}\, v_\lambda(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) \tag{1.108}$$

is defined in the following way:

1. For $\lambda = 1$, the system reverts to the full, interacting system, i.e. $v_{\lambda=1}(\mathbf{x}) = v_{\mathrm{ext}}(\mathbf{x})$.

2. For $\lambda \in [0, 1)$, $v_\lambda(\mathbf{x})$ is such that the corresponding ground-state density has the same value as in the case $\lambda = 1$. If such a potential exists, it is unique. In particular, for $\lambda = 0$ we have $v_{\lambda=0}(\mathbf{x}) = v_{\mathrm{KS}}(\mathbf{x})$.

Theorem 1.3.4 *Let $\Psi(\lambda)$ be the ground-state of $\hat{H}_\lambda$ and assume that the ground-state energy is non-degenerate. Then the sum of the Hartree and the exchange correlation energy of the full, interacting system can be written as*

$$E_{\mathrm{H}} + E_{\mathrm{xc}} = \int_0^1 \mathrm{d}\lambda\, \langle\Psi(\lambda)|\hat{V}_{\mathrm{el-el}}|\Psi(\lambda)\rangle. \tag{1.109}$$

Proof The total ground-state energy is defined by

$$E_0 = \langle\Psi(1)|\hat{H}_{\lambda=1}|\psi(1)\rangle. \tag{1.110}$$

On the other hand E_0 is given within DFT as

$$
\begin{aligned}
E_0 &= T_s[n] + E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] \tag{1.111}\\
&= \langle\Psi(0)|\hat{H}_{\lambda=0}|\Psi(0)\rangle - E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] - \int \mathrm{d}\mathbf{x}\, n(\mathbf{x})v_{\mathrm{xc}}(\mathbf{x}). \tag{1.112}
\end{aligned}
$$

Equating these expressions for the ground-state energy, we get

$$\langle\Psi(1)|\hat{H}_{\lambda=1}|\psi(1)\rangle - \langle\Psi(0)|\hat{H}_{\lambda=0}|\Psi(0)\rangle = -E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n] - \int \mathrm{d}\mathbf{x}\, n(\mathbf{x})v_{\mathrm{xc}}(\mathbf{x}). \quad (1.113)$$

For the RHS we make a formal ansatz and using the Hellmann-Feynman theorem we get:

$$
\begin{aligned}
\langle\Psi(1)|\hat{H}_{\lambda=1}|\psi(1)\rangle - \langle\Psi(0)|\hat{H}_{\lambda=0}|\Psi(0)\rangle &= \int_0^1 \mathrm{d}\lambda\, \frac{\partial}{\partial\lambda}\langle\Psi(\lambda)|\hat{H}_\lambda|\Psi(\lambda)\rangle \\
&= \int_0^1 \mathrm{d}\lambda\, \langle\Psi(\lambda)|\partial_\lambda\hat{H}_\lambda|\Psi(\lambda)\rangle \\
&= \int_0^1 \mathrm{d}\lambda\, \langle\Psi(\lambda)|\hat{V}_{\mathrm{el-el}}|\Psi(\lambda)\rangle \\
&\quad + \int_0^1 \mathrm{d}\lambda\, \langle\Psi(\lambda)|\partial_\lambda\hat{V}_\lambda|\Psi(\lambda)\rangle.
\end{aligned}
$$

The last integral can be transformed as

$$
\begin{aligned}
\int_0^1 \mathrm{d}\lambda\, \langle\Psi(\lambda)|\partial_\lambda\hat{V}_\lambda|\Psi(\lambda)\rangle &= \langle\Psi(1)|\hat{V}_{\lambda=1}|\Psi(1)\rangle - \langle\Psi(0)|\hat{V}_{\lambda=0}|\Psi(0)\rangle - \int \mathrm{d}\mathbf{x}\, v_\lambda(\mathbf{x})\partial_\lambda n_\lambda(\mathbf{x}) \\
&= \langle\Psi(1)|\hat{V}_{\mathrm{ext}}|\Psi(1)\rangle - \langle\Psi(0)|\hat{V}_{\mathrm{KS}}|\Psi(0)\rangle \\
&= -\langle\Psi(1)|\hat{V}_{\mathrm{H}}|\Psi(1)\rangle - \langle\Psi(0)|\hat{V}_{\mathrm{xc}}|\Psi(0)\rangle \\
&= -2E_{\mathrm{H}} - \langle\Psi(0)|\hat{V}_{\mathrm{xc}}|\Psi(0)\rangle.
\end{aligned}
$$

In the first line, the last integral accounts for the difference between $\langle\Psi(\lambda)|\partial_\lambda\hat{V}_\lambda|\Psi(\lambda)\rangle$ and $\partial_\lambda\langle\Psi(\lambda)|\hat{V}_\lambda|\Psi(\lambda)\rangle$. This difference vanishes because n_λ equals the ground-state density for all λ and hence $\partial_\lambda n_\lambda(\mathbf{x}) \equiv 0$. Collecting everything together yields the theorem.

Reformulation The electron-electron interaction reads explicitly

$$\hat{V}_{\mathrm{el-el}} = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, v(\mathbf{x} - \mathbf{x}')\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}). \quad (1.114)$$

This translates into the expression

$$\langle\Psi_0|\hat{V}_{\mathrm{el-el}}|\Psi_0\rangle = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, v(\mathbf{x} - \mathbf{x}')\langle\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x})\rangle \quad (1.115)$$

for the expectation value. On the other hand, the pair correlation function $g(\mathbf{x}, \mathbf{x}')$ is defined in second quantization :

$$\frac{\langle\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\hat{\psi}(\mathbf{x}')\rangle}{\langle\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})\rangle\langle\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\rangle} = \frac{n_2(\mathbf{x}, \mathbf{x}')}{n(\mathbf{x})n(\mathbf{x}')} = \frac{\langle\hat{n}(\mathbf{x})\hat{n}(\mathbf{x}')\rangle - \delta(\mathbf{x} - \mathbf{x}')n(\mathbf{x})}{n(\mathbf{x})n(\mathbf{x}')} \quad (1.116)$$

where $n(\mathbf{x}) = \langle \hat{n}(\mathbf{x}) \rangle = \langle \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}) \rangle$ etc. Therefore, we can rewrite $\langle \hat{V}_{\mathrm{el-el}} \rangle$ in terms of the pair-correlation function as

$$\langle \Psi_0 | \hat{V}_{\mathrm{el-el}} | \Psi_0 \rangle = \frac{e^2}{8\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} g(\mathbf{x}, \mathbf{x}'). \qquad (1.117)$$

Let $g_\lambda(\mathbf{x}, \mathbf{x}')$ denote the pair correlation function with respect to the ground-state of $\hat{H}(\lambda)$. The adiabatic-connection theorem can then be written as

$$E_{\mathrm{H}} + E_{\mathrm{xc}} = \frac{e^2}{8\pi\varepsilon_0} \int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} g_\lambda(\mathbf{x}, \mathbf{x}') \qquad (1.118)$$

or

$$E_{\mathrm{xc}} = \frac{e^2}{8\pi\varepsilon_0} \int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x})n(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} (g_\lambda(\mathbf{x}, \mathbf{x}') - 1). \qquad (1.119)$$

On the other hand, according to equation (1.116) we have:

$$\langle \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x})\hat{\psi}(\mathbf{x}') \rangle = \langle \hat{n}(\mathbf{x})\hat{n}(\mathbf{x}') \rangle - \delta(\mathbf{x} - \mathbf{x}')n(\mathbf{x}). \qquad (1.120)$$

But, $\langle \hat{n}(\mathbf{x})\hat{n}(\mathbf{x}') \rangle$ equals the time-ordered density-density response-function evaluated at equal times:

$$\langle \hat{n}(\mathbf{x})\hat{n}(\mathbf{x}') \rangle = \mathrm{i}\hbar\chi(\mathbf{x}, \mathbf{x}'; \tau = 0^+). \qquad (1.121)$$

$\chi(\mathbf{x}, \mathbf{x}'; \tau = 0)$ can be expressed in terms of the Fourier transform $\tilde{\chi}(\mathbf{x}, \mathbf{x}'; \omega)$ as

$$\chi(\mathbf{x}, \mathbf{x}'; \tau = 0) = \int \frac{\mathrm{d}\omega}{2\pi} \, \chi(\mathbf{x}, \mathbf{x}'; \omega). \qquad (1.122)$$

Using all this, we get the *Adiabatic-Connection-Fluctuation-Dissipation Theorem*:

$$E_{\mathrm{H}} + E_{\mathrm{xc}} = \frac{e^2}{8\pi\varepsilon_0} \int_0^1 \mathrm{d}\lambda \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, \frac{1}{|\mathbf{x} - \mathbf{x}'|} \left(\int \frac{\mathrm{d}\omega}{2\pi} \, \mathrm{i}\hbar\chi^\lambda(\mathbf{x}, \mathbf{x}'; \omega) - \delta(\mathbf{x} - \mathbf{x}')n(\mathbf{x}) \right).$$

This expression is apparently divergent due to the Dirac delta which enforces $\mathbf{x} = \mathbf{x}'$. One can show, however, that this divergence is cancelled by the term involving $\chi(\mathbf{x}, \mathbf{x}')$ (see e.g. [88]).

1.3.3. Time-Dependent Density Functional Theory

Runge-Gross Theorem Again we consider a many-body system with a Hamilonian of the form (1.70) where the external potential $\hat{V}_{\mathrm{ext}}$ is now given by a *time-dependent* function $v_{\mathrm{ext}}(\mathbf{x}t)$. Time-dependent solutions $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N, t)$ of the Schrödinger equation give rise to time-dependent densities $n(\mathbf{x}t)$ explicitly given by

$$n(\mathbf{x}t) = \langle \Psi | \hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}(\mathbf{x}t) | \Psi \rangle = N \int \mathrm{d}\mathbf{x}_2 \ldots \mathrm{d}\mathbf{x}_N \, (\Psi^* \cdot \Psi)(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N) \qquad (1.123)$$

In this situation, the analog of the Hohenberg-Kohn theorem is the Runge-Gross theorem which we state without proof. (see e.g. [64])

Theorem 1.3.5 *If the densities $n(\mathbf{x}t)$ and $n'(\mathbf{x}t)$ evolving from a common initial state $\Psi(t = 0)$ under the influence of external potentials $v_{\text{ext}}(\mathbf{x}t)$ and $v'_{\text{ext}}(\mathbf{x}t)$ agree for all t and all $\mathbf{x}$ then*

$$v_{\text{ext}}(\mathbf{x}t) - v_{\text{ext}}(\mathbf{x}t) = f(t), \tag{1.124}$$

i.e. the respective external potentials differ by a purely time-dependent function.

As in the time-independent case, this has the consequence that the external potential is a functional of the density. However, there are also some new features which have to be commented.

1. External potentials which differ by a function $f(t)$ essentially coincide: a purely time-dependent function $f(t)$ in the Schrödinger equation leads only to a purely time-dependent phase factor $\exp(-\mathrm{i}/\hbar \int^t \mathrm{d}t' f(t'))$. This phase-factor cancels out in all expectation values $\langle \Psi | \cdot | \Psi \rangle$ because observables are operators in a Hilbert space and hence act only on the spatial variables.

2. The functional of the density giving the external potential would in principle be different for every initial wave function $\Psi(t = 0)$. In practice, one therefore considers non-degenerate instantaneous ground-states.

3. The functionals of the density are to be understood as functionals of the whole function $n(\mathbf{x}t)$, i.e. of the entire history of n, not as a family of functionals which for every t give $v_{\text{ext}}(\mathbf{x}t)$ in terms of $n(\mathbf{x}t)$.

Precisely as in the time-independet case, one now considers an auxiliary Schrödinger equation:

$$\mathrm{i}\hbar\partial_t\psi_i(\mathbf{x}t) = \left(-\frac{\hbar^2}{2m}\Delta + v_{\text{KS}}(\mathbf{x}t)\right)\psi_i(\mathbf{x}t) \tag{1.125}$$

with the condition that

$$n(\mathbf{x}t) = \sum_{i=1}^{N} |\psi_i(\mathbf{x}t)|^2. \tag{1.126}$$

From the details of the proof of the Runge-Gross theorem, one can establish that the uniqueness of the external potential v_{KS} is also guaranteed in the non-interacting case. Similarly, one makes again the ansatz

$$v_{\text{KS}}(\mathbf{x}t) = v_{\text{ext}}(\mathbf{x}t) + v_{\text{H}}(\mathbf{x}t) + v_{\text{xc}}(\mathbf{x}t) \tag{1.127}$$

with

$$v_{\text{H}}(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}' \, \frac{n(\mathbf{x}'t)}{|\mathbf{x} - \mathbf{x}'|} \tag{1.128}$$

which corresponds to a time-dependent, self-consistent Hartree kernel.

Pseudo-Dyson Equation for the Density Response Function Recall that the time-dependent density-density response function is defined by

$$\chi(\mathbf{x}t, \mathbf{x}'t') = \frac{\delta n(\mathbf{x}t)}{\delta v_{\text{ext}}(\mathbf{x}'t')}. \tag{1.129}$$

Consider the change of the time-dependent exchange-correlation potential under the density variation $\delta n(\mathbf{x}t)$:

$$v_{\text{xc}}[n + \delta n](\mathbf{x}t) - v_{\text{xc}}[n](\mathbf{x}t) = \int \mathrm{d}t' \int \mathrm{d}\mathbf{x}' \; f_{\text{xc}}(\mathbf{x}, \mathbf{x}'; t - t')\delta n(\mathbf{x}'t') \tag{1.130}$$

or

$$f_{\text{xc}}(\mathbf{x}, \mathbf{x}'; t - t') = \frac{\delta v_{\text{xc}}(\mathbf{x}'t')}{\delta n(\mathbf{x}t)} = \frac{\delta^2 E_{\text{xc}}[n]}{\delta n(\mathbf{x}t)\delta n(\mathbf{x}'t')}. \tag{1.131}$$

The density-density response function χ_{KS} of the Kohn-Sham auxiliary system is defined by

$$\delta n(\mathbf{x}t) = \int \mathrm{d}\mathbf{x}'\mathrm{d}t' \; \chi_{\text{KS}}(\mathbf{x}t, \mathbf{x}'t')(\delta v_{\text{ext}}(\mathbf{x}'t') + \delta v_{\text{H}}(\mathbf{x}'t') + \delta v_{\text{xc}}(\mathbf{x}'t')) \tag{1.132}$$

or

$$\chi_{\text{KS}}(\mathbf{x}t, \mathbf{x}'t') = \frac{\delta n(\mathbf{x}t)}{\delta v_{\text{KS}}(\mathbf{x}'t')}. \tag{1.133}$$

Using the chain-rule in the form

$$\frac{\delta n(\mathbf{x}t)}{\delta v_{\text{ext}}(\mathbf{x}'t')} = \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \; \frac{\delta n(\mathbf{x}t)}{\delta v_{\text{KS}}(\mathbf{x}''t'')} \frac{\delta v_{\text{KS}}(\mathbf{x}''t'')}{\delta v_{\text{ext}}(\mathbf{x}'t')}, \tag{1.134}$$

the definition of f_{xc} as well as

$$\frac{\delta v_{\text{ext}}(\mathbf{x}t)}{\delta v_{\text{ext}}(\mathbf{x}'t')} = \delta(x - x') \tag{1.135}$$

$$\frac{\delta v_{\text{H}}(\mathbf{x}t)}{\delta v_{\text{ext}}(\mathbf{x}'t')} = \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \; v(\mathbf{x}, \mathbf{x}'')\delta(t - t'')\chi(\mathbf{x}''t'', \mathbf{x}'t') \tag{1.136}$$

$$\frac{\delta v_{\text{xc}}(\mathbf{x}t)}{\delta v_{\text{ext}}(\mathbf{x}'t')} = \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \; \frac{\delta v_{\text{xc}}(\mathbf{x}t)}{\delta n(\mathbf{x}''t'')} \frac{\delta n(\mathbf{x}''t'')}{\delta v_{\text{ext}}(\mathbf{x}'t')} \tag{1.137}$$

one finds for $\chi(\mathbf{x}t, \mathbf{x}'t')$

$$\chi_{\text{KS}}(\mathbf{x}t, \mathbf{x}'t') + \int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{x}''' \; \chi_{\text{KS}}(\mathbf{x}t, \mathbf{x}''t'') \times (v(\mathbf{x}''t'', \mathbf{x}'''t''') + f_{\text{xc}}(\mathbf{x}''t'', \mathbf{x}'''t''')) \, \chi(\mathbf{x}'''t''', \mathbf{x}'t').$$

Neglecting the exchange-correlation kernel in this equation and using the formal density response function from time-independent DFT is known as *Random Phase Approximation*

(RPA),[3] an approximation which in combination with the Adiabatic Connection Theorem is now at the very heart of a great deal of progress in complex problems of materials science. (see e.g. [88])

1.4. Linear Response Theory

1.4.1. Classical Electrodynamics

Maxwell's equations read

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \tag{1.138}$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B} \tag{1.139}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{1.140}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \varepsilon_0 \mu_0 \partial_t \mathbf{E}. \tag{1.141}$$

They determine the fields $\mathbf{E}(\mathbf{x}t)$, $\mathbf{B}(\mathbf{x}t)$ as functionals of the sources $\rho(\mathbf{x}t)$, $\mathbf{j}(\mathbf{x}t)$.

Splitting into External and Internal Quantities Due to the linearity of the homogeneous Maxwell equations, we can without loss of generality arbitrarily split the source term $\rho, \mathbf{j} \equiv \rho_{\text{tot}}, \mathbf{j}_{\text{tot}}$ into

$$\rho_{\text{tot}} = \rho_{\text{ext}} + \rho_{\text{int}} \tag{1.142}$$

$$\mathbf{j}_{\text{tot}} = \mathbf{j}_{\text{ext}} + \mathbf{j}_{\text{int}}. \tag{1.143}$$

such that

$$\mathbf{E} \equiv \mathbf{E}_{\text{tot}} = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{int}} \tag{1.144}$$

$$\mathbf{B} \equiv \mathbf{B}_{\text{tot}} = \mathbf{B}_{\text{ext}} + \mathbf{B}_{\text{int}} \tag{1.145}$$

where the external fields fulfill Maxwell's equations with the external sources and the internal fields fulfill Maxwell's equations with the internal sources. For a fixed splitting of the sources, the splitting into external and internal fields is unique up to a solution of the homogeneous

---

[3]Note, however, that this RPA has only a formal resemblance to the RPA within the context of Green Function Theory. After all, where is the Random Phase in neglecting f_{xc}? Strictly speaking, a random phase approximation is an approximation of the form $\langle \hat{A}(t)\hat{B}(t')\rangle \approx \langle \hat{A}(t)\rangle \langle \hat{B}(t')\rangle$. Inserting a complete system of energy eigenstates shows that this corresponds indeed to neglecting the relative phases which one may think of averaging to zero. Now, *the* RPA is really of this kind in that it approximates the four-point propagator by a product of two-point propagators. This kind of RPA is therefore the quantum analog of Boltzmann's famous stoßzahlenansatz.

Maxwell equations which can be arbitrarily partitioned between the external and the internal fields. Physically, we think of the internal field $\mathbf{E}_{\text{int}}, \mathbf{B}_{\text{int}}$ as belonging to the system we study whereas the external fields $\mathbf{E}_{\text{ext}}, \mathbf{B}_{\text{ext}}$ are prescribed. Furthermore, we may think of $\rho_{\text{int}}, \mathbf{j}_{\text{int}}$ as somehow localized (e.g. in a probe) whereas we think of $\rho_{\text{ext}}, \mathbf{j}_{\text{ext}}$ as "far away". We stress, however, that the source splitting as such is indepedindependent of such an interpretation. For example, we could also split the sources into high frequency and low frequency components. Furthermore, it is noteworthy that a spatial separation between the external and the internal sources implies that external and internal sources separately obey continuity equations

$$\partial_t \rho_{\text{int}} + \nabla \cdot \mathbf{j}_{\text{int}} = 0 \tag{1.146}$$
$$\partial_t \rho_{\text{ext}} + \nabla \cdot \mathbf{j}_{\text{ext}} = 0. \tag{1.147}$$

Note that in the standard parlance of classical electrodynamics

$$-\varepsilon_0 \mathbf{E}_{\text{int}} = \mathbf{P}$$
$$\varepsilon_0 \mathbf{E}_{\text{ext}} = \mathbf{D}$$
$$\mathbf{E}_{\text{tot}} = \mathbf{E}$$

$$\mathbf{B}_{\text{int}} = \mu_0 \mathbf{M}$$
$$\mathbf{B}_{\text{ext}} = \mu_0 \mathbf{H}$$
$$\mathbf{B}_{\text{tot}} = \mathbf{B}.$$

Historically, this comes about because one thinks of $\mathbf{P}$ and $\mathbf{M}$ as electric and magnetic dipole densities. The reason for this is a topic in its own right.[4] First, we assemble some mathematical prerequisites.

Helmholtz Decomposition The energy of the free electromagnetic field $(\mathbf{E}, \mathbf{B})$ is given by

$$E(t) = \frac{1}{2} \int d\mathbf{x} \left(\varepsilon_0 \mathbf{E}^2(\mathbf{x}t) + \frac{1}{\mu_0} \mathbf{B}^2(\mathbf{x}t) \right). \tag{1.148}$$

We conclude that for the energy to be finite, the fields have to be square-integrable. The state space for $\mathbf{E}$ and $\mathbf{B}$ respectively is given by $\mathcal{H}_V = \mathcal{L}(\mathbb{R}^3) \otimes \mathbb{R}^3$ at fixed time t. Any vector field $\mathbf{F} \in \mathcal{L}(\mathbb{R}^3) \otimes \mathbb{R}^3$ can be decomposed uniquely into a divergence and rotation free part (the so-called longitudinal and transversal part) according to

$$\mathbf{F} = \mathbf{F}_{\text{T}} + \mathbf{F}_{\text{L}} \tag{1.149}$$

[4]Modern textbooks as [26, 57] introduce electrodynamics in media in terms of internal and external fields whereas classical textbooks as [37, 48] rely on dipole densities. In condensed matter and many-body theory [15, 35, 50], the partition in external and internal fields is common practice.

with

$$\mathbf{F}_{\mathrm{T}} = \frac{1}{4\pi} \nabla \times \int \mathrm{d}\mathbf{x}' \, \frac{\nabla \times \mathbf{F}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.150}$$

$$\mathbf{F}_{\mathrm{L}} = -\frac{1}{4\pi} \nabla \int \mathrm{d}\mathbf{x}' \, \frac{\nabla \cdot \mathbf{F}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.151}$$

such that

$$\nabla \cdot \mathbf{F}_{\mathrm{T}} = 0 \tag{1.152}$$

$$\nabla \times \mathbf{F}_{\mathrm{L}} = \mathbf{0}. \tag{1.153}$$

The longitudinal and the transversal part can be shown to be orthogonal in $\mathcal{H}_{\mathrm{V}}$. In other words, we have an orthogonal decomposition $\mathcal{H}_{\mathrm{V}} = \mathcal{H}_{\mathrm{T}} \oplus \mathcal{H}_{\mathrm{L}}$. The respective projectors P_{T} and P_{L} are given through equations (1.150, 1.151). It follows that $P_{\mathrm{L}} + P_{\mathrm{T}} = \mathbb{1}_{\mathcal{L}^2 \otimes \mathbb{R}^3}$ which can also be read off from $-\nabla \times \nabla \times + \nabla \nabla \cdot = \Delta$ and $\Delta(1/|\mathbf{x} - \mathbf{x}'|) = -4\pi\delta(\mathbf{x} - \mathbf{x}')$. In the following, we perform a lot of partial integrations which strictly would require the inclusion of boundary or surface terms. As we require the fields to be square-integrable, these surface terms vanish. On the other hand, such a mathematical assumption on the decay behaviour seems to be the right idealization for conceptual matters as the real solid can always be thought of as embedded in $\mathbb{R}^3$ without any sharp boundary. Systems in a finite volume V with definite conditions on the behaviour at ∂V constitute an idealization.

Internal Field vs Dipole Moment Density Standard textbooks define $\mathbf{P}(\mathbf{x})$ and $\mathbf{M}(\mathbf{x})$ respectively as the densities of electric and magnetic dipoles. To clarify this we have to define the notion of electric and magnetic dipole densities in the first place. We begin with the electric case. The dipole moment of a charge density $\rho(\mathbf{x})$ is defined as the constant vector

$$\mathbf{P} = \int \mathrm{d}\mathbf{x} \, \mathbf{x}\rho(\mathbf{x}). \tag{1.154}$$

The potential $\varphi(\mathbf{x})$ corresponding to the charge density $\rho(\mathbf{x})$ is given by

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}' \, \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.155}$$

The Taylor expansion (around the origin) of the Coulomb kernel under the integral leads to the multipole expansion

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0} \frac{q}{|\mathbf{x}|} + \frac{1}{4\pi\varepsilon_0} \frac{\mathbf{P} \cdot \mathbf{x}}{|\mathbf{x}|^3} + \dots \tag{1.156}$$

where $q = \int \mathrm{d}\mathbf{x} \, \rho(\mathbf{x})$ denotes the total charge. The first term in this infinite expansion – the so-called monopole term – corresponds to the field resulting from the whole charge

concentrated at the origin. The second term corresponds to a pure dipole field. Consider now a charge distribution

$$\rho(\mathbf{x}) = q\delta(\mathbf{x}) + (-q)\delta(\mathbf{x} + \mathbf{l}). \tag{1.157}$$

This charge distribution has a dipole moment given by

$$\mathbf{P} = q\mathbf{l}. \tag{1.158}$$

The charge distribution of a point dipole (located at the origin) is obtained from the charge distribution (1.157) by performing $\mathbf{l} \rightarrow 0$ such that $\mathbf{P} = \mathbf{const}$. This limit can be easily performed by considering

$$\rho_\eta(\mathbf{x}) = \frac{q}{\eta}\delta(\mathbf{x}) + \frac{(-q)}{\eta}\delta(\mathbf{x} + \eta\mathbf{l}). \tag{1.159}$$

We then have

$$\lim_{\eta \rightarrow 0} \rho_\eta(\mathbf{x}) = -(\mathbf{P} \cdot \nabla\delta)(\mathbf{x}). \tag{1.160}$$

This is the charge distribution of a point dipole. From

$$\begin{align}
\varphi(\mathbf{x}) &= \frac{1}{4\pi\varepsilon_0} \int d\mathbf{x}' \, \frac{\rho(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|} \tag{1.161} \\
&= -\frac{1}{4\pi\varepsilon_0} \int d\mathbf{x}' \, (\mathbf{P} \cdot \nabla\delta)(\mathbf{x}')\frac{1}{|\mathbf{x} - \mathbf{x}'|} \tag{1.162} \\
&= -\frac{1}{4\pi\varepsilon_0}(\mathbf{P} \cdot \nabla)\frac{1}{|\mathbf{x}|} \tag{1.163} \\
&= \frac{1}{4\pi\varepsilon_0} \frac{\mathbf{P} \cdot \mathbf{x}}{|\mathbf{x}|^3} \tag{1.164}
\end{align}$$

we read off that the charge density of a point dipole gives rise to a pure dipole field. The charge distribution of a point dipole makes it plausible to define the charge distribution of a continuous dipole density $\mathbf{P}(\mathbf{x})$ as

$$\rho(\mathbf{x}) = \int d\mathbf{x}' \, \mathbf{P}(\mathbf{x}') \cdot (\nabla\delta')(\mathbf{x} - \mathbf{x}'). \tag{1.165}$$

This charge distribution gives rise to the electric field

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0} \int d\mathbf{x}' \, \frac{\mathbf{P}(\mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3}. \tag{1.166}$$

Of course, in general this is not a pure dipole field. We now come to the magnetic case. The dipole moment $\mathbf{M}$ of a current density $\mathbf{j}(\mathbf{x})$ is defined by the constant vector

$$\mathbf{M} = \frac{1}{2} \int d\mathbf{x} \, \mathbf{x} \times \mathbf{j}(\mathbf{x}). \tag{1.167}$$

The vector potential $\mathbf{A}(\mathbf{x})$ corresponding to the current density $\mathbf{j}(\mathbf{x})$ is given by

$$\mathbf{A}(\mathbf{x}) = \frac{\mu_0}{4\pi} \int \mathrm{d}\mathbf{x}' \, \frac{\mathbf{j}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.168}$$

The Taylor expansion (around the origin) of the Coulomb kernel under the integral leads to the multipole expansion

$$\mathbf{A}(\mathbf{x}) = \frac{\mu_0}{4\pi} \frac{\mathbf{M} \times \mathbf{x}}{|\mathbf{x}|^3} + \dots, \tag{1.169}$$

i.e. in the magnetic case the first non-vanishing term corresponds to a pure dipole field. Consider now the constant current distribution of a circular loop with radius r_0 centered around the origin in the x-y-plane. This current distribution is given by

$$\mathbf{j}(\mathbf{x}) \;=\; I \int_C \mathrm{d}t \frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} \, \delta(\mathbf{x} - \mathbf{x}(t)) \tag{1.170}$$

$$\;=\; Ir_0\delta(z) \int_0^{2\pi} \mathrm{d}t \, \mathbf{e}_\varphi(t)\delta(x - r_0\cos t)\delta(y - r_0\sin t) \tag{1.171}$$

where $C : \mathbb{R} \to \mathbb{R}^3$ is given by

$$\mathbf{x}(t) = r_0(\cos t, \sin t, 0) \tag{1.172}$$

and

$$\mathbf{e}_\varphi(t) = -\sin t \, \mathbf{e}_x + \cos t \, \mathbf{e}_y. \tag{1.173}$$

With $\mathbf{x} = |\mathbf{x}|\mathbf{e}_r$ and

$$\mathbf{e}_r \times \mathbf{e}_\varphi(t) = \mathbf{const}. = \mathbf{e}_z \tag{1.174}$$

we then find for the corresponding magnetic moment

$$\mathbf{M} \;=\; \frac{1}{2} \int \mathrm{d}\mathbf{x} \, \mathbf{x} \times \mathbf{j}(\mathbf{x}) \tag{1.175}$$

$$\;=\; \frac{I}{2}r_0^2\mathbf{e}_z \int \mathrm{d}\mathbf{x} \int_0^{2\pi} \mathrm{d}t \, \delta(x - r_0\cos t)\delta(y - r_0\sin t)\delta(z) \tag{1.176}$$

$$\;=\; \frac{I}{2}r_0^2\mathbf{e}_z \int_0^{2\pi} \mathrm{d}t \int \mathrm{d}\mathbf{x} \, \delta(x - r_0\cos t)\delta(y - r_0\sin t)\delta(z) \tag{1.177}$$

$$\;=\; \frac{I}{2}r_0^2\mathbf{e}_z \int_0^{2\pi} \mathrm{d}t \tag{1.178}$$

$$\;=\; I\pi r_0^2\mathbf{e}_z. \tag{1.179}$$

Hence, the resulting magnetic moment is given by

$$\mathbf{M} = IA\mathbf{e}_z \tag{1.180}$$

where $A = \pi r_0^2$. The charge distribution of a magnetic point dipole (located at the origin) is obtained from the charge distribution (1.170) by performing $r_0 \to 0$ such that $\mathbf{M} = \mathbf{const}$. This limit can be performed by considering the rescaling $I \mapsto I/\eta^2$, $r_0 \mapsto \eta r_0$ and performing $\lim_{\eta \to 0} \mathbf{j}_\eta$. The concrete calculation is somewhat more complicated than in the electric case. First consider

$$
\begin{aligned}
\mathbf{j}_\eta(\mathbf{x}) &= I r_0^2 \int_0^{2\pi} \mathrm{d}t\ \mathbf{e}_\varphi(t) \frac{1}{\eta r_0} \delta(x - \eta r_0 \cos t) \delta(y - \eta r_0 \sin t) \delta(z) \\
&= I r_0^2 \int_0^{2\pi} \mathrm{d}t\ (-\sin t\ \mathbf{e}_x + \cos t\ \mathbf{e}_y) \frac{1}{\eta r_0} (\delta(x - \eta r_0 \cos t) \delta(y - \eta r_0 \sin t) \delta(z) - \delta(\mathbf{x}))
\end{aligned}
$$

where we inserted a t-independent term $\delta(\mathbf{x})$ because

$$
\int_0^{2\pi} \mathrm{d}t\ \mathbf{e}_\varphi(t) \equiv 0. \tag{1.181}
$$

Now, in the limit $\eta \to 0$ the delta terms in the integrand simply yield

$$
-\cos t\ \delta'(x)\delta(y)\delta(z) - \sin t\ \delta(x)\delta'(y)\delta(z). \tag{1.182}
$$

With

$$
\int_0^{2\pi} \mathrm{d}t\ \sin t \cos t = 0 \tag{1.183}
$$

$$
\int_0^{2\pi} \mathrm{d}t\ \cos^2 t = \pi \tag{1.184}
$$

$$
\int_0^{2\pi} \mathrm{d}t\ \sin^2 t = \pi \tag{1.185}
$$

we get multiplying out

$$
\mathbf{j}_{\eta \to 0}(\mathbf{x}) = I\pi r_0^2 (\mathbf{e}_x \partial_y - \mathbf{e}_y \partial_x)\delta(\mathbf{x}). \tag{1.186}
$$

Obviously, this generalizes to the formula

$$
\mathbf{j}(\mathbf{x}) = -(\mathbf{M} \times \nabla\delta)(\mathbf{x}) \tag{1.187}
$$

for the current density of a magnetic point dipole at the origin in the plane orthogonal to $\mathbf{M}$. With the formulas for electric and magnetic point dipole charge and current density we can now define electric and magnetic dipole densities $\mathbf{P}(\mathbf{x})$ and $\mathbf{M}(\mathbf{x})$ through the corresponding charge and current densities as

$$
\rho(\mathbf{x}) = \int \mathrm{d}\mathbf{x}'\ \mathbf{P}(\mathbf{x}') \cdot (\nabla\delta')(\mathbf{x} - \mathbf{x}') \tag{1.188}
$$

$$
\mathbf{j}(\mathbf{x}) = \int \mathrm{d}\mathbf{x}'\ \mathbf{M}(\mathbf{x}') \times (\nabla\delta')(\mathbf{x} - \mathbf{x}'). \tag{1.189}
$$

With

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}'\, \frac{\rho(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}$$

$$\mathbf{A}(\mathbf{x}) = \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\mathbf{j}(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}$$

these densities give rise to the fields

$$\varphi(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}'\, \frac{\mathbf{P}(\mathbf{x}')\cdot(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3} \tag{1.190}$$

$$\mathbf{A}(\mathbf{x}) = \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\mathbf{M}(\mathbf{x}')\times(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3}. \tag{1.191}$$

For continuous media, one assumes that these equations also hold in the time-dependent case in the sense that

$$\varphi(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}'\, \frac{\mathbf{P}(\mathbf{x}'t)\cdot(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3} \tag{1.192}$$

$$\mathbf{A}(\mathbf{x}t) = \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\mathbf{M}(\mathbf{x}'t)\times(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3}. \tag{1.193}$$

In principle, these relations are the definition of the time-dependent dipole densities $\mathbf{P}(\mathbf{x}t)$ and $\mathbf{M}(\mathbf{x}t)$. Now, the fields $\mathbf{E}, \mathbf{B}$ are given in terms of the potentials as

$$\mathbf{E}(\mathbf{x}t) = -\nabla\varphi(\mathbf{x}t) - \partial_t\mathbf{A}(\mathbf{x}t) \tag{1.194}$$

$$\mathbf{B}(\mathbf{x}t) = \nabla\times\mathbf{A}(\mathbf{x}t) \tag{1.195}$$

and hence with the idenities

$$\frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}'\, \frac{\mathbf{P}(\mathbf{x}'t)\cdot(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3} = -\frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}'\, \frac{\nabla'\cdot\mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.196}$$

$$\frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\mathbf{M}(\mathbf{x}'t)\times(\mathbf{x}-\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|^3} = \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\nabla'\times\mathbf{M}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.197}$$

we find that

$$\mathbf{E}(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0}\nabla\int d\mathbf{x}'\, \frac{\nabla'\cdot\mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} - \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\nabla'\times\partial_t\mathbf{M}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.198}$$

$$\mathbf{B}(\mathbf{x}t) = \frac{\mu_0}{4\pi}\nabla\times\int d\mathbf{x}'\, \frac{\nabla'\times\mathbf{M}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.199}$$

Within the realm of electrodynamics in continuous media, this is to be interpreted as

$$\mathbf{E}_{\text{int}}(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0}\nabla\int d\mathbf{x}'\, \frac{\nabla'\cdot\mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} - \frac{\mu_0}{4\pi}\int d\mathbf{x}'\, \frac{\nabla'\times\partial_t\mathbf{M}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.200}$$

$$\mathbf{B}_{\text{int}}(\mathbf{x}t) = \frac{\mu_0}{4\pi}\nabla\times\int d\mathbf{x}'\, \frac{\nabla'\times\mathbf{M}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.201}$$

where $\mathbf{P}(\mathbf{x}t), \mathbf{M}(\mathbf{x}t)$ denote the dipole densities in the medium. On the other hand, the so-called macroscopic Maxwell equations say that

$$\nabla \times \mathbf{E}_{\text{tot}}(\mathbf{x}t) \equiv \nabla \times \mathbf{E}(\mathbf{x}t) = -\partial_t \mathbf{B}_{\text{tot}}(\mathbf{x}t) \tag{1.202}$$

and with

$$\mathbf{E}(\mathbf{x}t) = \frac{1}{\varepsilon_0}\mathbf{D}(\mathbf{x}t) - \frac{1}{\varepsilon_0}\mathbf{P}(\mathbf{x}t) \tag{1.203}$$

$$\mathbf{B}(\mathbf{x}t) = \mu_0 \mathbf{H}(\mathbf{x}t) + \mu_0 \mathbf{M}(\mathbf{x}t) \tag{1.204}$$

and the fact that the $\mathbf{D}(\mathbf{x}t), \mathbf{H}(\mathbf{x}t)$ fulfill the vacuum Maxwell equations, it follows that

$$\frac{1}{\varepsilon_0}\nabla \times \mathbf{P}(\mathbf{x}t) = \mu_0 \partial_t \mathbf{M}(\mathbf{x}t) \tag{1.205}$$

which we now reinterpret as a microscopic equation. Independently from electrodynamics in continuous media, one could argue that the expression of $\varphi(\mathbf{x}t), \mathbf{A}(\mathbf{x}t)$ in terms of the dipole densities shows that $\mathbf{P}(\mathbf{x}t)$, $\mathbf{M}(\mathbf{x}t)$ can be altered by transversal/longitudinal vectors fields without effect on the observable fields. We use this "gauge freedom" to *postulate*

$$\nabla \times \mathbf{P}(\mathbf{x}t) = \varepsilon_0 \mu_0 \partial_t \mathbf{M}(\mathbf{x}t), \tag{1.206}$$

$$\nabla \cdot \mathbf{M}(\mathbf{x}t) = 0. \tag{1.207}$$

All in all, we have

$$\mathbf{E}(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0}\nabla \int d\mathbf{x}' \frac{\nabla' \cdot \mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} - \frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}' \frac{\nabla' \times (\nabla' \times \mathbf{P})(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.208}$$

$$= \frac{1}{4\pi\varepsilon_0}\nabla \int d\mathbf{x}' \frac{\nabla' \cdot \mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|} - \frac{1}{4\pi\varepsilon_0}\nabla \times \int d\mathbf{x}' \frac{\nabla' \times \mathbf{P}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.209}$$

Comparison with the Helmholtz decomposition shows that

$$\mathbf{E}(\mathbf{x}t) = -\frac{1}{\varepsilon_0}\mathbf{P}(\mathbf{x}t). \tag{1.210}$$

Similarly it follows that

$$\mathbf{B}(\mathbf{x}t) = \mu_0 \mathbf{M}(\mathbf{x}t) \tag{1.211}$$

where one has to use $\nabla \cdot \mathbf{M}(\mathbf{x}t) = 0$ which again follows from the Maxwell equations. In summary, we say: electric and magnetic dipole densities are – up to conversion factors – identical to electric and magnetic fields. This has nothing to do with electrodynamics in continuous media. Instead, it is a mathematical identity which applies in particular to the fields inside the medium. For the special case of electrodynamics in continuous media, this

means: $\mathbf{P}(\mathbf{x}t), \mathbf{M}(\mathbf{x}t)$ are the dipole densities of the medium, $-\mathbf{D}(\mathbf{x}t), \mathbf{H}(\mathbf{x}t)$ are the dipole densities without the medium and $-\varepsilon_0\mathbf{E}(\mathbf{x}t), 1/\mu_0\mathbf{B}$ are the total dipole densities. With the introduction of the notion "dipole density" we simply recover the fields. Furthmore, the equations of motion for the dipole densities which are derived for continuous media are simply the Maxwell equations for the internal fields and therefore do not need any derivation.

Local Fields The simple interpretation of $\mathbf{E}$ as the total field in the medium seems to be in contradiction with well-known arguments leading to the Clausius-Mosotti formula. The standard reference [48] p.116 argues that in order to calculate the induced electric dipole moment of a molecule, one cannot simply take the "macroscopic" $\mathbf{E}$-field. Instead one has to introduce still another quantity (in addition to $\mathbf{D}, \mathbf{P}, \mathbf{E}$), namely the so-called local field at the molecule ("internal field" as by Jackson; in german: "Nahfeld"). How does this square with the fact that $\mathbf{E}$ actually is the total field in the medium? To answer this question, we first have to note that although $\mathbf{P}$ simply is the electromagnetic field generated by the charges in the medium, this does not imply that its contribution to the total field $\mathbf{E}$ is restricted to the domain "where the medium is". Instead, the field $\mathbf{P}$ outside the medium is determined by the facts that (i) it has to obey the vacuum Maxwell equations $\nabla\cdot\mathbf{P} = 0$, $\nabla\times\mathbf{P} = 0$ because its sources lie in the medium and (ii) it has to fit the boundary condition that it equals $\mathbf{P}$ within the medium at the surface. In the case of the Clausius-Mosotti model, one thinks of a given molecule the dipole moment of which is to be calculated as enclosed in a little cavity (typically a sphere) which contains only the molecule under consideration. One then thinks of $\mathbf{P}$ as the field inside the medium (which means in particular outside the cavity) and calculates the resulting field in the center of the cavity. In other words, one calculates the field inside an empty cavity embedded in a (homogeneously) polarized material. The logic behind this is that the macroscopically measurable bulk $\mathbf{P}$ describes the field inside the sample only on very large length scales. Obviously, this is due to the fact that in standard treatments $\mathbf{P}$ is thought of as a macroscopic quantity resulting from a suitable averaging. This loss of information is then compensated for by introducing yet another quantity, the local field, which roughly reinstalls the original internal field $\mathbf{P}(\mathbf{x})$. Without the transition to macroscopic fields, the field which induces the dipole moment of a given molecule located at $\mathbf{x}$ is of course simply $\mathbf{E}(\mathbf{x})$.

Caveat about Singular Dipole Densities The equations

$$\mathbf{E}(\mathbf{x}t) = -\frac{1}{\varepsilon_0}\mathbf{P}(\mathbf{x}t) \tag{1.212}$$

$$\mathbf{B}(\mathbf{x}t) = \mu_0\mathbf{M}(\mathbf{x}t) \tag{1.213}$$

constitute rigorous identities relating the smooth, integrable dipole densities to "their" fields. If we consider instead a singular dipole density, e.g. a point dipole, then these identities seem to imply that the field would be zero everywhere except for where the dipole is and there it is given by $-1/\varepsilon_0 \mathbf{P}$ or $\mu_0 \mathbf{M}$ respectively. Of course, this is not true. Instead, the fields generated by an electric or magnetic point dipole at the origin are given by the well-known formulas [29, 30, 37]

$$
\mathbf{E}(\mathbf{x}) = \frac{1}{4\pi\varepsilon_0} \frac{3(\mathbf{P} \cdot \mathbf{x})\mathbf{x} - |\mathbf{x}|^2 \mathbf{P}}{|\mathbf{x}|^5} - \frac{1}{3\varepsilon_0} \mathbf{P}\delta(\mathbf{x}) \tag{1.214}
$$

$$
\mathbf{B}(\mathbf{x}) = \frac{\mu_0}{4\pi} \frac{3(\mathbf{M} \cdot \mathbf{x})\mathbf{x} - |\mathbf{x}|^2 \mathbf{M}}{|\mathbf{x}|^5} + \frac{2\mu_0}{3} \mathbf{M}\delta(\mathbf{x}). \tag{1.215}
$$

Indeed, for a singular dipole density the field is singular where the dipole is. Intuitively, one has to think about this in the following way: at the location of the dipole the singular contribution "dominates". This singular contribution is just proportional to the dipole moment. So, if one goes to the limit where one has such a dipole $\mathbf{P}$ or $\mathbf{M}$ at every point in space, then the contribution from the singular term ultimately dominates at every point yielding a contribution proportional to $\mathbf{P}(\mathbf{x})$ or $\mathbf{M}(\mathbf{x})$. In fact, we can also start with equations (1.214, 1.215) and define the fields corresponding to continuous dipole densities as

$$
\mathbf{E}(\mathbf{x}) = \int d\mathbf{x}' \left(\frac{1}{4\pi\varepsilon_0} \frac{3(\mathbf{P}(\mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}'))(\mathbf{x} - \mathbf{x}') - |\mathbf{x} - \mathbf{x}'|^2 \mathbf{P}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^5} - \frac{1}{3\varepsilon_0} \mathbf{P}(\mathbf{x}')\delta(\mathbf{x} - \mathbf{x}') \right)
$$

$$
\mathbf{B}(\mathbf{x}) = \int d\mathbf{x}' \left(\frac{\mu_0}{4\pi} \frac{3(\mathbf{M}(\mathbf{x}') \cdot (\mathbf{x} - \mathbf{x}'))(\mathbf{x} - \mathbf{x}') - |\mathbf{x} - \mathbf{x}'|^2 \mathbf{M}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^5} + \frac{2\mu_0}{3} \mathbf{M}(\mathbf{x}')\delta(\mathbf{x} - \mathbf{x}') \right).
$$

An elementary reasoning using the same vector identities as above then yields

$$
\mathbf{E}_{\mathrm{L}}(\mathbf{x}) = -\frac{1}{\varepsilon_0} \mathbf{P}(\mathbf{x}) \tag{1.216}
$$

$$
\mathbf{B}(\mathbf{x}) = \mu_0 \mathbf{M}_{\mathrm{T}}(\mathbf{x}). \tag{1.217}
$$

As the point dipole fields correspond to an electrostatic or magnetostatic situation, this implies precisely

$$
\mathbf{E}(\mathbf{x}) = -\frac{1}{\varepsilon_0} \mathbf{P}(\mathbf{x}) \tag{1.218}
$$

$$
\mathbf{B}(\mathbf{x}) = \mu_0 \mathbf{M}(\mathbf{x}). \tag{1.219}
$$

In fact, this breakdown of the dipole-densiy identification as electromagnetic field is at the very heart of the present argumentation. For singular point dipoles, the dipole density as a discrete sum over point dipoles divided by the volume is a well-defined distributional object which is not identical to the electromagnetic field. These singular densities are motivated

by classical physics where one can imagine them to be created by point particles. If, however, we are confronted with a continuous, microscopic charge density (as we expect it in Quantum Mechanics), then it is not so obvious what the dipole density corresponding to this continuous charge density is (as opposed to the total dipole moment of the charge density which is well-known). The above arguments made it clear that the dipole density corresponding to a continuous charge density is the electromagnetic field generated by that very density.

Alternative Definition of Dipole Densities involving Retardation Effects The definition of the dipole densities through the corresponding fields via equations (1.192, 1.193) seems to imply that the time-dependent dipole densities cannot – as in the static case – literally interpreted as continuous distributions of "oscillating" dipoles because these latter would lead to radiation, retardation effects etc. The derivation of the electromagnetic fields starting from the fields of time-dependent point-dipoles as in radiation theory and then making the transition to continuous distributions is an interesting problem in its own right. It has been solved explicitly by Vrejoiu and Zus [101] leading to the result[5]

$$\varphi(\mathbf{x}t) \;=\; -\frac{1}{4\pi\varepsilon_0}\int d\mathbf{x}' \, \frac{(\nabla\cdot\mathbf{P})(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x}-\mathbf{x}'|} \tag{1.220}$$

$$\mathbf{A}(\mathbf{x}t) \;=\; \frac{\mu_0}{4\pi}\int d\mathbf{x}' \, \frac{(\nabla\times\mathbf{M})(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x}-\mathbf{x}'|}$$

$$+\; \frac{\mu_0}{4\pi}\int d\mathbf{x}' \, \frac{(\partial_{t_{\mathrm{ret}}}\mathbf{P})(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.221}$$

where

$$t_{\mathrm{ret}} = t - \frac{|\mathbf{x}-\mathbf{x}'|}{c}. \tag{1.222}$$

and in an expression like $(\nabla\cdot\mathbf{P})(\mathbf{x}'t_{\mathrm{ret}})$, the brackets mean that the operation is performed for $\mathbf{P}(\mathbf{x}'t')$ which is afterwards evaluated at $t' = t_{\mathrm{ret}}$. We will now show that this definition of the dipole densities agrees with our approach. First, observe that with

$$G(\mathbf{x}t,\mathbf{x}'t') = \frac{1}{4\pi}\frac{\delta\left(t-t'-\frac{|\mathbf{x}-\mathbf{x}'|}{c}\right)}{|\mathbf{x}-\mathbf{x}'|} \tag{1.223}$$

the equations for φ and $\mathbf{A}$ can be rewritten as

$$\varphi(\mathbf{x}t) \;=\; -\frac{1}{\varepsilon_0}\int d\mathbf{x}'dt' \, G(\mathbf{x}t,\mathbf{x}'t')\nabla\cdot\mathbf{P}(\mathbf{x}'t')$$

$$\mathbf{A}(\mathbf{x}t) \;=\; \mu_0\int d\mathbf{x}'dt' \, G(\mathbf{x}t,\mathbf{x}'t')\nabla\times\mathbf{M}(\mathbf{x}'t')$$

$$+\; \mu_0\int d\mathbf{x}'dt' \, G(\mathbf{x}t,\mathbf{x}'t')\partial_{t'}\mathbf{P}(\mathbf{x}'t').$$

---

[5]This corresponds to equations (11) and (13) in [101]. The surface term has been neglected because here we deal with square-integrable functions for which we can move the surface infinitely far off.

On the other hand, G is just the retarded Green function for the d'Alembert operator $\Box$, i.e. an "inverse" operator $\Box^{-1}$ in the sense that

$$\Box G(\mathbf{x}t, \mathbf{x}'t') = \delta(\mathbf{x} - \mathbf{x}')\delta(t - t'). \tag{1.224}$$

Therefore, acting on the above equation with $\Box$ yields

$$\Box\varphi(\mathbf{x}t) = -\frac{1}{\varepsilon_0}\nabla \cdot \mathbf{P}(\mathbf{x}t) \tag{1.225}$$

$$\Box\mathbf{A}(\mathbf{x}t) = \mu_0\nabla \times \mathbf{M}(\mathbf{x}t) + \mu_0\partial_t\mathbf{P}(\mathbf{x}t). \tag{1.226}$$

In the Lorentz gauge, we can identify

$$\Box\varphi(\mathbf{x}t) = \frac{\rho(\mathbf{x}t)}{\varepsilon_0} \tag{1.227}$$

$$\Box\mathbf{A}(\mathbf{x}t) = \mu_0\mathbf{j}(\mathbf{x}t). \tag{1.228}$$

A comparison shows that $\mathbf{P}$ and $\mathbf{M}$ fulfill the Maxwell equations in the sense that $\mathbf{P} = -\varepsilon_0\mathbf{E}$ and $\mu_0\mathbf{M} = \mathbf{B}$. Therefore, also in the retarded approach, the dipole densities can be identified with the fields. At first sight, it seems to be astonishing that the definition of electric and magnetic dipole densities in terms of the retarded expressions (1.220, 1.221) should be equivalent to the naive approach given by the instantaneous expressions (1.192, 1.193). Once we understand the general identities $\mathbf{P} = -\varepsilon_0\mathbf{E}$, $\mu_0\mathbf{M} = \mathbf{B}$, the reason for this apparent paradox becomes clear: it resides of course in the gauge freedom $A^\mu \mapsto A^\mu - \partial^\mu f$.[6] In fact, through the identification of the dipole densities with the electromagnetic fields, the definitions (1.220, 1.221) and (1.192, 1.193) simply correspond to different expressions in different gauges for the potentials $(\varphi/c, \mathbf{A})$ through the fields $(\mathbf{E}, \mathbf{B})$. Concretely, $(\varphi/c, \mathbf{A})$ can be represented as

$$\varphi(\mathbf{x}t) = -\frac{1}{4\pi}\int \mathrm{d}\mathbf{x}' \frac{\mathbf{E}(\mathbf{x}'t) \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3} \tag{1.229}$$

$$\mathbf{A}(\mathbf{x}t) = \frac{1}{4\pi}\int \mathrm{d}\mathbf{x}' \frac{\mathbf{B}(\mathbf{x}'t) \times (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3}. \tag{1.230}$$

in the Coulomb gauge and as

$$\varphi(\mathbf{x}t) = -\frac{1}{4\pi}\int \mathrm{d}\mathbf{x}' \frac{\nabla \cdot \mathbf{E}(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x} - \mathbf{x}'|} \tag{1.231}$$

$$\mathbf{A}(\mathbf{x}t) = \frac{1}{4\pi}\int \mathrm{d}\mathbf{x}' \frac{\nabla \times \mathbf{B}(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x} - \mathbf{x}'|}$$
$$+ \frac{1}{4\pi}\int \mathrm{d}\mathbf{x}' \frac{\partial_{t_{\mathrm{ret}}}\mathbf{E}(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.232}$$

---

[6]This settles the dispute Leung/Ni vs Vrejoiu/Zus. [60, 101]

in the Lorentz gauge as will be shown now. These formulas prove that the different definitions of dipole densities (through equations (1.192, 1.193) and equations (1.220, 1.221)) correspond to different gauges. We begin with the Lorentz gauge for which the equations of motion simply read

$$\Box A^\mu(x) = \mu_0 j^\mu(x). \tag{1.233}$$

Expressing then $A^\mu(x)$ in terms of $j^\mu(x)$ through the retarded Green function and using Maxwell equations in the form

$$\rho = \varepsilon_0 \nabla \cdot \mathbf{E} \tag{1.234}$$

$$\mathbf{j} = \frac{1}{\mu_0} \nabla \times \mathbf{B} - \varepsilon_0 \partial_t \mathbf{E} \tag{1.235}$$

immediately leads to the expressions (1.220, 1.221) under the identification $\mathbf{P} = -\varepsilon_0 \mathbf{E}$, $\mu_0 \mathbf{M} = \mathbf{B}$. In the Coulomb gauge, things are only slightly more complicated. The equations of motion in the Coulomb gauge read

$$\Delta \varphi = -\frac{\rho}{\varepsilon_0} \tag{1.236}$$

$$\Box \mathbf{A} = \mu_0 \mathbf{j}_{\mathrm{T}} \tag{1.237}$$

where $\mathbf{j}_{\mathrm{T}}$ denotes the transversal part. Using Gauss' law, the first equation immediately leads to the expression of φ in terms of the dipole density. In order to reproduce the instantaneous relations between $\mathbf{A}$ and $\mathbf{M}$ (or $\mathbf{B}$) we rewrite the second equation as

$$\Delta \mathbf{A} = -\mu_0 \mathbf{j}_{\mathrm{T}} + \partial_t^2 \mathbf{A} \tag{1.238}$$

and replace $\partial_t^2 \mathbf{A}$ by $-\partial_t \mathbf{E}_{\mathrm{T}}$ because in the Coulomb gauge, the vector potential is purely transversal and hence the transversal part of the electric field is given by $-\partial_t \mathbf{A}$. Now, the last equation can be solved for $\mathbf{A}$ using the inverse Laplace operator, i.e. the Coulomb kernel. It remains to show that the integrand $-\mu_0 \mathbf{j}_{\mathrm{T}} - \partial_t \mathbf{E}_{\mathrm{T}}$ equals $-\nabla \times \mathbf{B}$. This follows easily by considering the Maxwell equation

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \mu_0 \varepsilon_0 \partial_t \mathbf{E}. \tag{1.239}$$

The continuity equation $\partial_\mu j^\mu = 0$ implies that the longitudinal part of the RHS vanishes (as it is in fact necessary on grounds of consistency). Still we have to emphasize that also in the Lorentz gauge, only the inhomogeneous equations

$$\nabla \cdot \mathbf{P} = -\rho \tag{1.240}$$

$$\nabla \times \mathbf{M} = \mathbf{j} - \partial_t \mathbf{P} \tag{1.241}$$

follow rigorously whereas the longitudinal part of $\mathbf{M}$ and the transversal part $\mathbf{P}$ remain arbitrary. The reason behind this is that even within a given gauge, the potentials $(\varphi, \mathbf{A})$ uniquely fix the fields $(\mathbf{E}, \mathbf{B})$ but not vice versa.

Maxwell Equations for Dipole Densities Once we identify $\mathbf{P}(\mathbf{x}t), \mathbf{M}(\mathbf{x}t)$ as the electric and magnetic fields of the medium, we can write down the Maxwell equations for them in the form

$$\nabla \cdot \mathbf{P}(\mathbf{x}t) = -\rho(\mathbf{x}t) \tag{1.242}$$

$$\nabla \times \mathbf{P}(\mathbf{x}t) = \varepsilon_0 \mu_0 \partial_t \mathbf{M}(\mathbf{x}t) \tag{1.243}$$

$$\nabla \cdot \mathbf{M}(\mathbf{x}t) = 0 \tag{1.244}$$

$$\nabla \times \mathbf{M}(\mathbf{x}t) = \mathbf{j}(\mathbf{x}t) - \partial_t \mathbf{P}(\mathbf{x}t). \tag{1.245}$$

Note that this implies that in the general time-dependent case, the relations

$$\rho(\mathbf{x}) = \int d\mathbf{x}' \, \mathbf{P}(\mathbf{x}') \cdot (\nabla \delta')(\mathbf{x} - \mathbf{x}')$$

$$\mathbf{j}(\mathbf{x}) = \int d\mathbf{x}' \, \mathbf{M}(\mathbf{x}') \times (\nabla \delta')(\mathbf{x} - \mathbf{x}').$$

do not hold any more. In fact, the above equations can be integrated by parts yielding

$$\rho(\mathbf{x}) = -\nabla \cdot \mathbf{P}(\mathbf{x}) \tag{1.246}$$

$$\mathbf{j}(\mathbf{x}) = \nabla \times \mathbf{M}(\mathbf{x}). \tag{1.247}$$

Obviously, these are just the static Maxwell equations. In particular, they imply $\nabla \cdot \mathbf{j} = 0$ and hence $\partial_t \rho = 0$. This shows again that in the time-dependent case, the static connection between dipole densities and sources does not constitute the definition of the dipole densities. Instead, the defining equations of time-dependent dipole densities are the aforementioned equations

$$\varphi(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0} \int d\mathbf{x}' \, \frac{\mathbf{P}(\mathbf{x}'t) \cdot (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3}$$

$$\mathbf{A}(\mathbf{x}t) = \frac{\mu_0}{4\pi} \int d\mathbf{x}' \, \frac{\mathbf{M}(\mathbf{x}'t) \times (\mathbf{x} - \mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|^3}.$$

These equations determine $\mathbf{P}(\mathbf{x}t)$ and $\mathbf{M}(\mathbf{x}t)$ only up to transversal and longitudinal vector fields respectively. This "gauge" freedom allows one to determine $\mathbf{P}(\mathbf{x}t)$ and $\mathbf{M}(\mathbf{x}t)$ such that they fulfill the Maxwell equations.

Modern Theory of Polarization We define the macroscopic electric and magnetic polarization as

$$\mathbf{P}(t) = \int \mathrm{d}\mathbf{x}\, \mathbf{P}(\mathbf{x}t), \tag{1.248}$$

$$\mathbf{M}(t) = \int \mathrm{d}\mathbf{x}\, \mathbf{M}(\mathbf{x}t), \tag{1.249}$$

In fact, it is well-known that the volume integrals of electromagnetic fields generated by localized sources yield the corresponding dipole moments [49, 57].[7] In the electric case this can be shown easily by considering the Gauss law in the form

$$\mathbf{x}\,\nabla\cdot\mathbf{P}(\mathbf{x}t) = -\mathbf{x}\,\rho(\mathbf{x}t), \tag{1.250}$$

integrating this over the volume and performing a partial integration. This leads to

$$\int \mathrm{d}\mathbf{x}\, \mathbf{P}(\mathbf{x}t) = \int \mathrm{d}\mathbf{x}\, \mathbf{x}\rho(\mathbf{x}t). \tag{1.251}$$

Similar arguments hold for the magnetic case. ([57], p.78f) On the other hand, the constitutive equation of the Modern Theory of Polarization reads

$$\mathbf{P}(t) = \int^{t} \mathrm{d}t'\, \mathbf{j}(t'), \tag{1.252}$$

where $\mathbf{j}(t') = \int \mathrm{d}\mathbf{x}\, \mathbf{j}(\mathbf{x}, t')$. We now show this equation directly from the Maxwell equations for the microscopic quantities $\mathbf{P}(\mathbf{x}t)$ and $\mathbf{M}(\mathbf{x}t)$. Integrating the fourth Maxwell equation (Ampère's law) yields

$$\int \mathrm{d}\mathbf{x}\, \nabla\times\mathbf{M}(\mathbf{x}t) = \mathbf{j}(t) - \partial_t\mathbf{P}(t). \tag{1.253}$$

If we can show that the LHS vanishes under realistic assumptions, then a time integration yields immediately

$$\mathbf{P}(t) = \int \mathrm{d}t'\, \mathbf{j}(t'). \tag{1.254}$$

This is the fundamental equation of the modern theory of polarizability. [77, 78, 79] The equation of motion for $\mathbf{M}(\mathbf{x}t)$ in terms of $\mathbf{j}(\mathbf{x}t)$ reads

$$\Box\mathbf{M}(\mathbf{x}t) = \nabla\times\mathbf{j}(\mathbf{x}t). \tag{1.255}$$

This can be solved for $\mathbf{M}$ using the retarded Green function as

$$\mathbf{M}(\mathbf{x}, t) = \frac{1}{4\pi}\int \mathrm{d}\mathbf{x}\, \frac{(\nabla\times\mathbf{j})(\mathbf{x}'t_{\mathrm{ret}})}{|\mathbf{x}-\mathbf{x}'|} \tag{1.256}$$

---

[7]Kovetz uses these formulas to motivate the identification of dipole densities with internal fields.

where $(\nabla \times \mathbf{j})(\mathbf{x}'t_{\mathrm{ret}})$ means $(\nabla \times \mathbf{j})(\mathbf{x}'t')$ evaluated at $t' = t_{\mathrm{ret}}$. In condensed matter systems, it is reasonable to assume that $\mathbf{j}$ stays inside a finite volume V for all times. Furthermore, considering typical measurement setups for induced polarizations, we may assume that the current starts to flow at a finite time t_0. This implies that for all times t, there exists $R > 0$ such that for $\mathbf{x}' \in V$ and all $\mathbf{x}$ with $|\mathbf{x}| \geq R$, we have $t_{\mathrm{ret}} < t_0$ and consequently $\mathbf{M}(\mathbf{x}t) = 0$. Consider now

$$\int \mathrm{d}\mathbf{x} \, (\nabla \times \mathbf{M})^i(\mathbf{x}t) = \int \mathrm{d}\mathbf{x} \, \delta_{ik}(\nabla \times \mathbf{M})^k(\mathbf{x}t). \tag{1.257}$$

Using $\delta_{ij} = \partial_i x_j$ and performing a partial integration yields

$$\int \mathrm{d}\mathbf{x} \, x_i \partial_k (\nabla \times \mathbf{M})^k(\mathbf{x}t) + \int \mathrm{d}\mathbf{x} \, \partial_k (x_i(\nabla \times \mathbf{M})^k(\mathbf{x}t)). \tag{1.258}$$

The first integral vanishes since it involves the divergence of a rotational vector field. The second integral can be converted into a surface integral by Gauss' theorem leading to

$$\lim_{R \to \infty} \int_{|\mathbf{x}|=R} \mathrm{d}A \, x_i \, \mathbf{n} \cdot (\nabla \times \mathbf{M})(\mathbf{x}, t). \tag{1.259}$$

This equals zero as $\mathbf{M}(\mathbf{x}, t) = 0$ for sufficiently large R.

Permittivity Consider now Gauss' law (1.138) in the form

$$\nabla \cdot \mathbf{E}_{\mathrm{ext}} = \frac{\rho_{\mathrm{ext}}}{\varepsilon_0} \tag{1.260}$$

$$\nabla \cdot \mathbf{E}_{\mathrm{int}} = \frac{\rho_{\mathrm{int}}}{\varepsilon_0}. \tag{1.261}$$

In many situations it is then a well justified hypothesis to assume a linear relation between $\mathbf{E}_{\mathrm{ext}}$ and $\mathbf{E}_{\mathrm{tot}}$ in the general form

$$E_{\mathrm{ext}}^i(\mathbf{x}t) = \int \mathrm{d}t' \mathrm{d}\mathbf{x}' \, \varepsilon^i_{\;j}(\mathbf{x}t, \mathbf{x}'t') E_{\mathrm{tot}}^j(\mathbf{x}'t') \tag{1.262}$$

where ε is called *permittivity tensor*. In the case of an isotropic permittivity $\varepsilon^i_{\;j} \propto \delta^i_{\;j}$, it is more convenient to work with the potential φ such that

$$\mathbf{E} = -\nabla \varphi \tag{1.263}$$

$$\Delta \varphi = -\frac{\rho}{\varepsilon_0}. \tag{1.264}$$

Due to linearity, for homogeneous systems the splitting carries over to the potential as

$$\varphi_{\mathrm{tot}} = \varphi_{\mathrm{ext}} + \varphi_{\mathrm{int}} \tag{1.265}$$

$$\varphi_{\mathrm{ext}}(\mathbf{x}t) = \int \mathrm{d}\mathbf{x}' \mathrm{d}t' \, \varepsilon(\mathbf{x}t, \mathbf{x}'t') \varphi_{\mathrm{tot}}(\mathbf{x}'t') \tag{1.266}$$

because

$$
\begin{align}
\mathbf{E}_{\text{ext}}(\mathbf{x}t) &= -\nabla\varphi_{\text{ext}}(\mathbf{x}t) \tag{1.267} \\
&= -\nabla \int d\mathbf{x}'dt' \; \varepsilon(\mathbf{x}t, \mathbf{x}'t')\varphi_{\text{tot}}(\mathbf{x}'t') \tag{1.268} \\
&= -\int d\mathbf{x}'dt' \; \nabla\varepsilon(\mathbf{x}-\mathbf{x}'; t-t')\varphi_{\text{tot}}(\mathbf{x}'t') \tag{1.269} \\
&= \int d\mathbf{x}'dt' \; \nabla'\varepsilon(\mathbf{x}-\mathbf{x}'; t-t')\varphi_{\text{tot}}(\mathbf{x}'t') \tag{1.270} \\
&= -\int d\mathbf{x}'dt' \; \varepsilon(\mathbf{x}-\mathbf{x}'; t-t')\nabla'\varphi_{\text{tot}}(\mathbf{x}'t') \tag{1.271} \\
&= \int d\mathbf{x}'dt' \; \varepsilon(\mathbf{x}-\mathbf{x}'; t-t')\mathbf{E}_{\text{tot}}(\mathbf{x}'t') \tag{1.272}
\end{align}
$$

where suitable boundary conditions have been assumed. Recalling the fundamental solution for the Laplace operator, one sees that the internal potential can be written in terms of the internal charge density as

$$
\varphi_{\text{int}}(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0} \int d\mathbf{x}' \; \frac{\rho_{\text{int}}(\mathbf{x}'t)}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.273}
$$

This ansatz removes the arbitrariness in the definition of φ_{int}. The external density response function $\chi(\mathbf{x}t, \mathbf{x}'t')$ is defined by the linear ansatz

$$
\begin{align}
\rho_{\text{int}}(\mathbf{x}t) &= \int d\mathbf{x}'dt' \; \chi(\mathbf{x}t, \mathbf{x}'t')\varphi_{\text{ext}}(\mathbf{x}'t') \tag{1.274} \\
\chi(\mathbf{x}t, \mathbf{x}'t') &= \frac{\delta\rho_{\text{int}}(\mathbf{x}t)}{\delta\varphi_{\text{ext}}(\mathbf{x}'t')}. \tag{1.275}
\end{align}
$$

Again, we stress that the second equation is the more general definition which also applies for non-linear systems. Comparison with the defining equation for the permittivity yields

$$
\varepsilon^{-1}(\mathbf{x}, \mathbf{x}'; \omega) = \delta(\mathbf{x}-\mathbf{x}') + \int d\mathbf{x}'' \; v(\mathbf{x}, \mathbf{x}'')\chi(\mathbf{x}'', \mathbf{x}'; \omega) \tag{1.276}
$$

with

$$
v(\mathbf{x}, \mathbf{x}') = \frac{1}{4\pi\varepsilon_0} \frac{1}{|\mathbf{x}-\mathbf{x}'|}. \tag{1.277}
$$

Analogously, the total density response function $\tilde{\chi}(\mathbf{x}t, \mathbf{x}'t')$ is defined by relating the internal charge density to the total potential

$$
\begin{align}
\rho_{\text{int}}(\mathbf{x}t) &= \int_{-\infty}^{\infty} d\mathbf{x}'dt' \; \tilde{\chi}(\mathbf{x}t, \mathbf{x}'t')\varphi_{\text{tot}}(\mathbf{x}'t') \tag{1.278} \\
\tilde{\chi}(\mathbf{x}t, \mathbf{x}'t') &= \frac{\delta\rho_{\text{int}}(\mathbf{x}t)}{\delta\varphi_{\text{tot}}(\mathbf{x}'t')} \tag{1.279}
\end{align}
$$

In terms of the total density response function[8], the permittivity reads

$$\varepsilon(\mathbf{x}, \mathbf{x}; \omega) = \delta(\mathbf{x} - \mathbf{x}') - \int \mathrm{d}\mathbf{x}'' \, v(\mathbf{x}, \mathbf{x}'') \tilde{\chi}(\mathbf{x}'', \mathbf{x}'; \omega). \tag{1.280}$$

Comparing (1.276) and (1.280) in the compact form

$$\varepsilon = 1 - v\tilde{\chi} \tag{1.281}$$
$$\varepsilon^{-1} = 1 + v\chi \tag{1.282}$$

and using the geometric summation formula we see that χ and $\tilde{\chi}$ are interrelated by

$$\chi = \tilde{\chi} + \tilde{\chi}v\tilde{\chi} + \tilde{\chi}v\tilde{\chi}v\tilde{\chi} + \dots \tag{1.283}$$

which can also be written as a Dyson-like equation $\chi = \tilde{\chi} + \tilde{\chi}v\chi$, i.e.

$$\chi(\mathbf{x}, \mathbf{x}'; \omega) = \tilde{\chi}(\mathbf{x}, \mathbf{x}'; \omega) + \int \mathrm{d}\mathbf{x}''\mathrm{d}\mathbf{x}''' \, \tilde{\chi}(\mathbf{x}, \mathbf{x}''; \omega) v(\mathbf{x}'', \mathbf{x}''') \chi(\mathbf{x}''', \mathbf{x}'; \omega). \tag{1.284}$$

This equation can also be shown directly through a functional chain rule as

$$\chi(x, x') \equiv \frac{\delta \rho_{\mathrm{int}}(x)}{\delta \varphi_{\mathrm{ext}}(x')} \tag{1.285}$$

$$= \int \mathrm{d}x'' \, \frac{\delta \rho_{\mathrm{int}}(x)}{\delta \varphi_{\mathrm{tot}}(x'')} \frac{\delta \varphi_{\mathrm{tot}}(x'')}{\delta \varphi_{\mathrm{ext}}(x')} \tag{1.286}$$

$$= \int \mathrm{d}x'' \, \frac{\delta \rho_{\mathrm{int}}(x)}{\delta \varphi_{\mathrm{tot}}(x'')} \frac{\delta(\varphi_{\mathrm{ext}}(x'') + \varphi_{\mathrm{int}}(x''))}{\delta \varphi_{\mathrm{ext}}(x')} \tag{1.287}$$

$$= \int \mathrm{d}x'' \, \frac{\delta \rho_{\mathrm{int}}(x)}{\delta \varphi_{\mathrm{tot}}(x'')} \left(\delta(x'' - x') + \frac{\delta \varphi_{\mathrm{int}}(x'')}{\delta \varphi_{\mathrm{ext}}(x')} \right) \tag{1.288}$$

$$= \tilde{\chi}(x, x') + \int \mathrm{d}x''\mathrm{d}x''' \, \tilde{\chi}(x, x'') v(x'', x''') \frac{\delta \rho_{\mathrm{int}}(x''')}{\delta \varphi_{\mathrm{ext}}(x')} \tag{1.289}$$

$$= \tilde{\chi}(x, x') + \int \mathrm{d}x''\mathrm{d}x''' \, \tilde{\chi}(x, x'') v(x'', x''') \chi(x''', x'). \tag{1.290}$$

Alternatively, assuming suitable invertibility properties, we can write

$$\tilde{\chi}^{-1} = \chi^{-1} + v. \tag{1.291}$$

For a homogeneous systems, some equations become particularly lucid in the Fourier domain, e.g.

$$\varphi_{\mathrm{tot}}(\mathbf{k}, \omega) = \frac{\varphi_{\mathrm{ext}}(\mathbf{k}, \omega)}{\varepsilon(\mathbf{k}, \omega)}. \tag{1.292}$$

---

[8]The terms "total" and "external density response function" are shorthand for "response function for variations with respect to the total/external field". This does not imply that the total response function is the sum of the external response function plus some rest. Instead, as we will see shortly, the relation between the total and the external response function is given by a Dyson-like equation.

Therefore, we can write mode-wise

$$
\begin{aligned}
\varphi_{\text{ext}} &= \varepsilon \varphi_{\text{tot}} \\
\varphi_{\text{int}} &= (1 - \varepsilon)\varphi_{\text{tot}} \\
\varphi_{\text{int}} &= \frac{1 - \varepsilon}{\varepsilon}\varphi_{\text{ext}}
\end{aligned}
$$

or multiplying through with $-|\mathbf{k}|^2$ (cf. [51], p.345)

$$
\begin{aligned}
\rho_{\text{ext}} &= \varepsilon \rho_{\text{tot}} \\
\rho_{\text{int}} &= (1 - \varepsilon)\rho_{\text{tot}} \\
\rho_{\text{int}} &= \frac{1 - \varepsilon}{\varepsilon}\rho_{\text{ext}}.
\end{aligned}
$$

Conductivity In order to turn Maxwell's equations into a fully consistent and self-contained theory, one has to specify the equation of motion of the sources in terms of the fields. Within the realm of solid-state physics, one often assumes a simple, linear relation between $\mathbf{j}$ and $\mathbf{E}$. The most general linear relation is given by

$$
j^i(\mathbf{x}t) = \int \mathrm{d}t'\mathrm{d}\mathbf{x}' \; \sigma^i{}_j(\mathbf{x}t, \mathbf{x}'t')E^j(\mathbf{x}'t'). \tag{1.293}
$$

σ is called *microscopic conductivity tensor*. We read off that the conductivity tensor can also be characterized as

$$
\sigma^i{}_j(\mathbf{x}t, \mathbf{x}'t') = \frac{\delta j^i(\mathbf{x}t)}{\delta E^j(\mathbf{x}'t')}. \tag{1.294}
$$

This relation can be reinterpreted as the definition of the conductivity for a system in which the current and the electric field are not linearly related. A special case is the homogeneous, local, isotropic, time-independent conductivity

$$
\sigma^i{}_j(\mathbf{x}t, \mathbf{x}'t') = \sigma_0 \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')\delta^i{}_j \tag{1.295}
$$

leading to

$$
\mathbf{j} = \sigma_0 \mathbf{E}. \tag{1.296}
$$

Of course, on a fundamental level such a relation cannot be true already because it is at odds the transformation properties ($\mathbf{E}$ is a spatial three-vector whereas $\mathbf{j}$ is the spatial part of a four-vector). In the spirit of the above distinction between external and induced quantities we now reinterpret Ohm's law as

$$
\mathbf{j}_{\text{int}} = \sigma \mathbf{E}_{\text{ext}}. \tag{1.297}
$$

mode-wise. The external and the induced quantities fulfill the local current conservation law separately yielding in the Fourier domain

$$-\mathrm{i}\omega\rho_{\mathrm{int}}(\mathbf{k},\omega) + \mathrm{i}\mathbf{k}\cdot\mathbf{j}_{\mathrm{int}}(\mathbf{k},\omega) = 0. \tag{1.298}$$

On the other hand

$$\rho_{\mathrm{int}}(\mathbf{k},\omega) = \frac{1-\varepsilon}{\varepsilon}\rho_{\mathrm{ext}} = \frac{1-\varepsilon}{\varepsilon}|\mathbf{k}|^2\varepsilon_0\varphi_{\mathrm{ext}}(\mathbf{k},\omega). \tag{1.299}$$

Using $\mathbf{E} = -\mathrm{i}\mathbf{k}\varphi$, the combination of these leads to

$$\varepsilon^{-1}(\mathbf{k},\omega) = 1 - \mathrm{i}\frac{\sigma(\mathbf{k},\omega)}{\omega\varepsilon_0}. \tag{1.300}$$

It is noteworthy that sometimes the conductivity is also defined with respect to the total electric field

$$\mathbf{j}_{\mathrm{int}} = \tilde{\sigma}\mathbf{E}_{\mathrm{tot}}. \tag{1.301}$$

It is moot to discuss which of these is the "right" definition. Instead, we state that these notions of conductivity are related by

$$\tilde{\sigma} = \sigma\varepsilon. \tag{1.302}$$

Finally, we note that within the realm of classical electrodynamics, conductivity and permittivity are concepts which are introduced ad hoc and which should be considered as the introduction of free parameters characterizing materials. That is, classical electrodynamics alone does not provide a basis to calculate these quantities.

Induced vs Macroscopic Quantites In the derivation of many relations we assumed the material (described by $\rho_{\mathrm{int}}, \mathbf{j}_{\mathrm{int}}$) to behave linearly. The linear relationship between φ_{ext} and ρ_{int} implies that the charge density of the system vanishes in the absence of an external field. This cannot be true for a system composed of charged particles. Instead, it is realistic to assume that the difference between the charge density of the system in the absence of an external field and in the presence of an external field responds linearly to that very external field. We call that difference the *induced charge density* ρ_{ind}. In other words, $\rho_{\mathrm{int}} = \rho_0 + \rho_{\mathrm{ind}}$ where only the second term responds (linearly) to the external field. This distinction is sometimes blurred by the usage of macroscopic fields. Here, we have to stress that in principle the introduction of external and internal fields has nothing to do with the distinction between microscopic and macroscopic fields: the first distinction results from a splitting of the source terms in Maxwell's equations, the second distinguishes between averaged and non-averaged fields. By an averaged field we mean

$$\bar{\mathbf{F}}(\mathbf{x}t) = \int \mathrm{d}\mathbf{x}\, f(\mathbf{x}-\mathbf{x}')\mathbf{F}(\mathbf{x}'t) \tag{1.303}$$

where the averaging function f fulfills some natural properties (e.g. f is symmetric, localized around the origin and integrates to 1). Now, within the realm of Linear Response Theory one defines the averaging process such that the charge density in the absence of the external field just vanishes (where we assume that the overall charge of the system vanishes anyway). Therefore, if one works with the macroscopic quantities, the system behaves linear in the sense that Linear Response Theory provides a first-order functional Taylor expansion of the internal fields in terms of the external fields. The higher order terms are usually (but not always) negligible because the external fields are very weak as compared to the field strenghts in the vicinity of the atomic nuclei which constitute the material. However, an explicit treatment of the averaging is unnecessary if one interprets from the very outset the linear relations as referring to the induced instead of the internal quantities. In this text, we therefore do not perform any averaging process of the fields. Instead, we reinterpret the linear relations as referring to the induced quantites.

General Theory of Electromagnetic Response Functions We now come to the problem of the anisotropy and the inhomogeneity. For anistropic, inhomogeneous systems, the relation between induced and external fields cannot be given by scalar quantities which in the Fourier domain essentially depend on only one $\mathbf{k}$-vector. The response of a system to an external electromagnetic perturbation is usually described by a very huge number of quantities:

- The conductivity tensor σ describes the response of the current density $\mathbf{j}_{\mathrm{ind}}$ to an external electric field $\mathbf{E}_{\mathrm{ext}}$.

- The electric susceptibility tensor χ_{e} describes the response of the polarization $\mathbf{P}$ to the total electric field $\mathbf{E}_{\mathrm{tot}}$.

- The magnetic susceptibility χ_{m} describes the response of the magnetization $\mathbf{M}$ to an external magnetic field $\mathbf{B}_{\mathrm{ext}}$.

All in all, this makes $3 \cdot 9 = 27$ material parameters. Empirically, this way of describing materials has proven to be highly effective. On the other hand, in view of the fact that all electromagnetic quantities of the system can ultimately be traced back to the induced electromagnetic 4-current $j^{\mu} = (c\rho_{\mathrm{ind}}, \mathbf{j}_{\mathrm{ind}})$ whereas all external quantities ultimately result from an external 4-potential $A^{\mu} = (\varphi_{\mathrm{ext}}/c, \mathbf{A})$, the $4 \cdot 4 = 16$ response functions

$$\chi^{\mu}{}_{\nu}(x, x') = \frac{\delta j^{\mu}_{\mathrm{ind}}(x)}{\delta A^{\nu}_{\mathrm{ext}}(x')} \tag{1.304}$$

corresponding to the effect of A_{ext}^{μ} on j_{ind}^{ν} – we will henceforth call them the *fundamental electromagnetic response functions* – suffices to deduce all the different responses.[9] Apart from reducing the total number of independent response functions, focussing on the fundamental response functions in the first place bears several advantages. First of all, the fundamental response functions constitute a second-rank Lorentz tensor and therefore yield a relativistic description of the materials responses, in particular a relativistic generalization of Ohm's law,

$$j_{\text{ind}}^{\mu}(x) = \int \mathrm{d}x' \chi^{\mu}_{\ \nu}(x, x') A_{\text{ext}}^{\nu}(x'). \tag{1.305}$$

It will later become apparent that the thus determined induced current is independent of the gauge in the external field. The transformation property of the fundamental response functions reads explicitly

$$\chi^{\mu}_{\ \nu}(x, x') = \Lambda^{\mu}_{\ \alpha} \Lambda_{\nu}^{\ \beta} \chi^{\alpha}_{\ \beta}(\Lambda^{-1}x, \Lambda^{-1}x') \tag{1.306}$$

with a proper, orthochronous Lorentz transformation $\Lambda \in \mathcal{L}_{+}^{\uparrow} \subset \mathrm{O}(3, 1)$. The transformation property w.r.t the current coordinates is obvious whereas the transformation properties with respect to electromagnetic potential can be shown by a functional chain rule. Another important advantage is that, as opposed to the fields $(\mathbf{E}, \mathbf{B})$ the coupling of A^{μ} to a Hamiltonian can easily be written down on the most fundamental level. It is given by the minimal coupling prescription $p^{\mu} \mapsto p^{\mu} - eA^{\mu}$. As this corresponds to a field theoretical interaction Hamiltonian $j_{\mu}A^{\nu}$, a quantum mechanical expression for the fundamental response function can easily be calculated from the Kubo formula, i.e.,

$$\frac{\delta j_{\text{ind}}^{\mu}(x)}{\delta A_{\text{ext}}^{\nu}(x')} = -\frac{\mathrm{i}}{\hbar} \theta(t - t') \langle [\hat{j}^{\mu}(x), \hat{j}_{\nu}(x')] \rangle. \tag{1.307}$$

As the current operator is bilinear in the field operator, this implies that the fundamental response function can be calculated from the four-point propagator by taking suitable equal-time limits[10]. However, the crucial question is whether or not one can derive a closed analytical formula which expresses the usual response functions in terms of the fundamental response functions. Now, we are facing two different problems: (i) how can we relate the response of the induced 4-current to the response of $\mathbf{P}, \mathbf{M}$ and (ii) how do we express the reaction with respect to the external fields $\mathbf{E}_{\text{ext}}, \mathbf{B}_{\text{ext}}$ in terms of the response to the external four-potential A_{ext}^{μ}. We start with the first problem which is the trivial one. In fact, we

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[9]These response functions are indeed standard in the electronic structure community. [35]

[10]Usually, one works with the time-ordered four-point propagator instead of its retarded counterpart. This does not affect our argument because in the frequency domain the time ordered and the retarded response function differ only by infinitesimal $\mathrm{i}\eta$ in the denominator and therefore carry the same information.

argued that $\mathbf{P}$ and $\mathbf{M}$ can be identified with the microscopic fields $\mathbf{E}_{\text{ind}}, \mathbf{B}_{\text{ind}}$ generated by the current j^μ_{ind}. The first problem therefore simply amounts to the calculation of the fields in terms of the sources. That means, if e.g. the magnetic field $\mathbf{B}$ is given in terms of the current $\mathbf{j}$ as

$$\mathbf{B}(x) = \int \mathrm{d}x'\ \mathbf{G}(x, x')\mathbf{j}(x') \tag{1.308}$$

where $\mathbf{G}$ is an appropriate (matrix valued) integral operator, then the response χ_{m} of $\mu_0\mathbf{M} = \mathbf{B}_{\text{ind}}$ can be expressed in terms of the response of $\mathbf{j}$ as

$$\mu_0 \frac{\delta M^i(x)}{\delta B^j_{\text{ext}}(x')} = \sum_k \int \mathrm{d}y\ G^i{}_k(x, y)\frac{\delta j^k(y)}{\delta B^j_{\text{ext}}(x')}. \tag{1.309}$$

On the most fundamental level, the integral operator which relates the fields to the sources can be calculated as follows. We fix a gauge (e.g. the Lorentz gauge) and observe that $\Box A^\mu = \mu_0 j^\mu$ and

$$\mathbf{E}(\mathbf{x}t) = -\nabla\varphi(\mathbf{x}t) - \partial_t\mathbf{A}(\mathbf{x}t) \tag{1.310}$$
$$\mathbf{B}(\mathbf{x}t) = \nabla \times \mathbf{A}(\mathbf{x}t). \tag{1.311}$$

implies

$$\Box\mathbf{E}(\mathbf{x}t) = -\frac{1}{\varepsilon_0}\nabla\rho(\mathbf{x}t) - \mu_0\partial_t\mathbf{j}(\mathbf{x}t) \tag{1.312}$$
$$\Box\mathbf{B}(\mathbf{x}t) = \mu_0\nabla \times \mathbf{j}(\mathbf{x}t). \tag{1.313}$$

These equations can also be shown directly from the Maxwell equations. Choosing a Green function for the d'Alembert operator then gives the fields in terms of the sources. Of course, usually the precedure is way to complicated for solid-state physics because there retardation effects usually do not matter. For example, in most cases it will sufficient to simply set $\mathbf{E} = -\nabla\varphi,\ \mathbf{B} = \nabla \times \mathbf{A}$ where

$$\varphi(\mathbf{x}t) = \frac{1}{4\pi\varepsilon_0} \int \mathrm{d}\mathbf{x}' \frac{\rho(\mathbf{x}'t)}{|\mathbf{x} - \mathbf{x}'|} \tag{1.314}$$
$$\mathbf{A}(\mathbf{x}t) = \frac{\mu_0}{4\pi} \int \mathrm{d}\mathbf{x}' \frac{\mathbf{j}(\mathbf{x}'t)}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.315}$$

We now come to the second problem. Indeed, this problem also seems to be trivial if one considers the functional chain rule

$$\frac{\delta j^\mu_{\text{ind}}(x)}{\delta E^i_{\text{ext}}(x')} = \sum_\alpha \int \mathrm{d}y\ \frac{\delta j^\mu_{\text{ind}}(x)}{\delta A^\alpha_{\text{ext}}(y)}\frac{\delta A^\alpha_{\text{ext}}(y)}{\delta E^i_{\text{ext}}(x')} \tag{1.316}$$
$$\frac{\delta j^\mu_{\text{ind}}(x)}{\delta B^i_{\text{ext}}(x')} = \sum_\alpha \int \mathrm{d}y\ \frac{\delta j^\mu_{\text{ind}}(x)}{\delta A^\alpha_{\text{ext}}(y)}\frac{\delta A^\alpha_{\text{ext}}(y)}{\delta B^i_{\text{ext}}(x')}. \tag{1.317}$$

However, the problem is now that the explicit dependence of the four-potential on the fields depends on the gauge. We therefore have to show that equations (1.316), (1.317) do not depend on the gauge. It is well-known that A^μ and $A^\mu - \partial^\mu f$ give rise to the same fields. The converse also holds true: if two potentials A^μ and A'^μ determine the same fields $\mathbf{E}, \mathbf{B}$ they differ by a gauge transform. It is then sufficient for the equations (1.316), (1.317) to be gauge independent if

$$\sum_\alpha \int \mathrm{d}y \; \frac{\delta j_{\mathrm{ind}}^\mu(x)}{\delta A_{\mathrm{ext}}^\alpha(y)} \frac{\delta \partial^\alpha f(y)}{\delta E_{\mathrm{ext}}^i(x')} = 0 \tag{1.318}$$

and similarly for the second equation. As the functional derivative commutes with the partial derivative we conclude that – assuming partial integrability – that

$$\partial'^\alpha \frac{\delta j_{\mathrm{ind}}^\beta(x)}{\delta A_{\mathrm{ext}}^\alpha(x')} = \partial'^\alpha \chi^\beta{}_\alpha(x, x') = 0 \tag{1.319}$$

is sufficient for the gauge independence. This will be shown now. For this purpose, we use again the functional chain rule

$$\frac{\delta j^\mu(x)}{\delta A^\nu(x')} = \sum_{\alpha, \beta} \int \mathrm{d}y \; \frac{\delta j^\mu(x)}{\delta F^{\alpha\beta}(y)} \frac{\delta F^{\alpha\beta}(y)}{\delta A^\nu(x')} \tag{1.320}$$

where the field strength tensor is given by $F^{\mu\nu} = \partial^\mu A^\nu - \partial^\nu A^\mu$. We can calculate explicitly

$$\frac{\delta F^{\alpha\beta}(x)}{\delta A^\nu(x')} = \delta^\beta{}_\nu (\partial^\alpha \delta)(x - x') - \delta^\alpha{}_\nu (\partial^\beta \delta)(x - x'). \tag{1.321}$$

This yields

$$\frac{\delta j^\mu(x)}{\delta A^\nu(x')} = -2\partial'^\alpha \frac{\delta j^\mu(x)}{\delta F^{\alpha\nu}(x')} \tag{1.322}$$

and hence

$$\partial'^\nu \frac{\delta j^\mu(x)}{\delta A^\nu(x')} = -2\partial'^\nu \partial'^\alpha \frac{\delta j^\mu(x)}{\delta F^{\alpha\nu}(x')} = 0 \tag{1.323}$$

because this corresponds to the contraction of a symmetric with an antisymmetric tensor.

Conductivity as the Fundamental Response Function We now compute the conductivity in terms of the fundamental response. As we have shown that the overall result is gauge independent, we may choose any gauge we want. For the conductivity, it seems to be particularly suitable to work with a gauge where $\varphi = 0$ (Weyl or axial gauge), i.e.

$$\mathbf{E}(\mathbf{x}t) = -\partial_t \mathbf{A}(\mathbf{x}t). \tag{1.324}$$

This leads to

$$\mathbf{A}(\mathbf{x}t) = -\int^t \mathrm{d}t' \; \mathbf{E}(\mathbf{x}t') \tag{1.325}$$

and to the formal functional derivative

$$\frac{\delta A^i(x)}{\delta E^j(x')} = -\delta^i{}_j \left(\int^t \delta\right)(x - x').$$

(1.326)

Here, we introduced an integrated Dirac distribution via the prescription

$$\left(\int^t \delta\right)[f] = \int_{-\infty}^t \mathrm{d}t' \ f(t').$$

(1.327)

In four dimension, this means explicitly

$$\left(\int^t \delta\right)(x - x') = \theta(t - t')\delta(\mathbf{x} - \mathbf{x}').$$

(1.328)

We now find

$$\sigma^i{}_j(x, x') = \frac{\delta j^i(x)}{\delta E^j(x')}$$

(1.329)

$$= -\int \mathrm{d}y \, \frac{\delta j^i(x)}{\delta A^j(y)} \left(\int^t \delta\right)(y - x')$$

(1.330)

$$= -\int_{t'} \mathrm{d}t'' \, \frac{\delta j^i(x)}{\delta A^j(\mathbf{x}'t'')}.$$

(1.331)

Observing that[11]

$$\mathcal{F}\left(\int^t f\right)(\omega) = \frac{1}{\mathrm{i}\omega}\tilde{f}(\omega)$$

(1.332)

we find that in the Fourier domain we have

$$\sigma^i{}_j(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\mathrm{i}\omega}\chi^i{}_j(\mathbf{x}, \mathbf{x}'; \omega).$$

(1.333)

Within the Kubo formalism, we can identify $\chi^i{}_j$ with the current-current response function. This yields the standard formula for the conductivity.[12] The above discussion makes it clear that the microscopic, frequency dependent conductivity already contains the complete information about all electromagnetic response functions. Trivially, $\chi^i{}_j$ can be reconstructed from $\sigma^i{}_j$. Using the constraints

$$\partial_\mu \chi^\mu{}_\nu(x, x') = 0$$
$$\partial'^\nu \chi^\mu{}_\nu(x, x') = 0$$

---

[11]Operator kernels transform as $\int \mathrm{d}t\mathrm{d}t' \ \mathrm{e}^{\mathrm{i}\omega t}\chi(t, t')\mathrm{e}^{-\mathrm{i}\omega' t'}$.

[12]Compare Bruus/Flensberg [15], equation (6.28). The second term stems from the non-classical contribution $\rho(x)\mathbf{A}(x)$, which is not consiered here. The different sign is due to $\chi^i{}_j = -\chi^{ij}$.

and observing $-\partial_0' = \partial_0,$[13] we can express $\chi^i{}_0$, $\chi^0{}_j$ and $\chi^0{}_0$ in terms of $\sigma^i{}_j$ as

$$\chi^0{}_j(\omega) = \partial_i \sigma^i{}_j(\omega) \tag{1.334}$$

$$\chi^i{}_0(\omega) = -\partial'^j \sigma^i{}_j(\omega) \tag{1.335}$$

$$\chi^0{}_0(\omega) = -\frac{1}{i\omega}\partial_i \partial'^j \sigma^i{}_j(\omega). \tag{1.336}$$

On the other hand, $\chi^0{}_0 = \chi = \delta\rho/\delta\varphi_{\mathrm{ext}}$ is just the usual density response function related to the (scalar) permittivity through $\varepsilon^{-1} = 1 + v\chi$ and hence

$$\varepsilon^{-1} = 1 - v\frac{1}{i\omega}\partial_i \partial'^j \sigma^i{}_j(\omega). \tag{1.337}$$

In the particular case of an isotropic, homogeneous material, we have $\sigma^i{}_j \propto \delta^i_j$ and $\sigma(\mathbf{x}, \mathbf{x}') = \sigma(\mathbf{x} - \mathbf{x}')$. The partial derivative ∂'^j can then be replaced with $-\partial_i$ and thus $\partial_i \partial'^j \mapsto -\partial_i \partial^i = \partial_i \partial_i$ reverts to the Laplace operator which cancels after convolution with its inverse, minus the Coulomb potential. We therefore recover the well-known formula

$$\varepsilon^{-1}(\mathbf{k}; \omega) = 1 - \frac{i}{\omega\varepsilon_0}\sigma(\mathbf{k}; \omega). \tag{1.338}$$

Finally, we express the microscopic magnetic susceptibility in terms of the microscopic conductivity. To do this, we start from the fundamental relation

$$\begin{aligned}
\mu_0 \frac{\delta M^i(x)}{\delta B^j_{\mathrm{ext}}(x')} &= \int \mathrm{d}y\,\mathrm{d}y'\, \frac{\delta M^i(x)}{\delta j^k_{\mathrm{ind}}(y)} \frac{\delta j^k_{\mathrm{ind}}(y)}{\delta A^l_{\mathrm{ext}}(y')} \frac{\delta A^l_{\mathrm{ext}}(y')}{\delta B^j_{\mathrm{ext}}(x')} \\
&= \int \mathrm{d}y\,\mathrm{d}y'\, \frac{\delta M^i(x)}{\delta j^k_{\mathrm{ind}}(y)} \chi^k{}_l(y, y') \frac{\delta A^l_{\mathrm{ext}}(y')}{\delta B^j_{\mathrm{ext}}(x')}.
\end{aligned}$$

For $\delta M^i(x)/\delta j^k_{\mathrm{ind}}(y)$ we find

$$\frac{\delta M^i(x)}{\delta j^k_{\mathrm{ind}}(y)} = \frac{\mu_0}{4\pi}\varepsilon_{ijk}\partial_j \frac{\delta(t - t')}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.339}$$

For A^μ we impose the Coulomb gauge such that $\delta A^0/\delta B^j = 0$ and $\nabla \cdot \mathbf{A} = 0$. With the Helmholtz decomposition theorem we get

$$\mathbf{A}(\mathbf{x}t) = \frac{1}{4\pi}\nabla \times \int \mathrm{d}\mathbf{x}'\, \frac{\mathbf{B}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.340}$$

We then find again

$$\frac{\delta A^i(x)}{\delta B^k_{\mathrm{ind}}(y)} = \frac{1}{4\pi}\varepsilon_{ijk}\partial_j \frac{\delta(t - t')}{|\mathbf{x} - \mathbf{x}'|}. \tag{1.341}$$

---

[13]The response functions depend on the time differences.

Now, a double partial integration shows that

$$(\chi_{\mathrm{m}})^i{}_j(\mathbf{x}t, \mathbf{x}'t') = -\frac{\mu_0}{(4\pi)^2} \int \mathrm{d}\mathbf{y}\mathrm{d}\mathbf{y}' \frac{1}{|\mathbf{x}-\mathbf{y}|} \varepsilon_{imk}\, \varepsilon_{jnl} \frac{\partial}{\partial y^m} \frac{\partial}{\partial y'^n} \chi^k{}_l(\mathbf{y}t, \mathbf{y}'t') \frac{1}{|\mathbf{y}'-\mathbf{x}'|}. \quad (1.342)$$

Defining the current-rotation response function

$$\chi_{\nabla\times\mathbf{j},\nabla\times\mathbf{j}}(x, x') = \varepsilon_{imk}\, \varepsilon_{jnl} \frac{\partial}{\partial x^m} \frac{\partial}{\partial x'^n} \chi^k{}_l(x, x'), \quad (1.343)$$

and using the Coulomb kernel v, the result can be written compactly as[14]

$$\chi_{\mathrm{m}} = -\mu_0 \int \mathrm{d}y\mathrm{d}y'\, v(x, y)\, \chi_{\nabla\times\mathbf{j},\nabla\times\mathbf{j}}(y, y')\, v(y', x'). \quad (1.344)$$

Substituting back the expression for $\chi^i{}_j$ in terms of $\sigma^i{}_j$, we obtain a closed formula for the magnetic susceptibility tensor in terms of the microscopic conductivity tensor. Furthermore, expressing the above result in the Fourier domain and specializing to homogeneous and isotropic systems leads to

$$(\chi_{\mathrm{m}})^i{}_j = \mu_0 \frac{1}{|\mathbf{k}|^4} \varepsilon_{imk}\, \varepsilon_{jnl}\, k_m k_n\, \delta^k{}_l \chi(\mathbf{k}), \quad (1.345)$$

or equivalently,

$$(\chi_{\mathrm{m}})^i{}_j = \mu_0 \frac{1}{|\mathbf{k}|^2} \left(\frac{k_i k_j}{|\mathbf{k}|^2} - \delta_{ij} \right) \chi(\mathbf{k}). \quad (1.346)$$

By noticing that the term in brackets corresponds to minus the projector on the transversal part of $\chi(\mathbf{k})$, we recover the well-known relation between the magnetic susceptibility and the transversal current response function[15]:

$$\chi_{\mathrm{m}} = -\mu_0 \lim_{k\to 0} \frac{\chi_{\mathrm{T}}(\mathbf{k}, \omega = 0)}{k^2}. \quad (1.347)$$

Here, the limit $k \to 0$ corresponds to integrating out spatial dependence whereas $\omega = 0$ corresponds to the transition from response functions to thermodynamic susceptibilities at temperature $T = 0$.

Maxwell Equations in Matter per definitionem give the total fields in terms of the external sources. Now, in principle the external fields fulfill the Maxwell equations with the external sources. Therefore, in order to express the total fields in terms of the external sources, one has to express the external fields in terms of the total fields and feed this

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[14]A Fourier space version of this equation for homogeneous materials has been found by a different method by Takimoto. [94]
[15]Cf. Giuliani/Vignale [35], p. 147.

expression back into the Maxwell equations. This necessitates e.g. the introduction of the somewhat counterintuitive quantity ε which is actually not a response function because the external field does not respond to the total field but vice versa. Consequently, ε is not retarded either. Macroscopically, one restricts oneself to the case where the induced electric field only depends on the external electric field and the induced magnetic field on the external magnetic field. The dependence is given by a constant (tensor). Microscopically, things get more complicated. The constant tensors are to be replaced by time and non-locally space dependent integral operators and furthermore the induced fields depend on all external fields. Therefore, it is more convenient to work with the fundamental response functions. First we derive the connection between the external field A^μ_{ext} and the total field A^μ_{tot}.[16] We have

$$\Box A^\mu_{\text{ind}} = \mu_0 j^\mu_{\text{ind}} \tag{1.348}$$

and hence

$$A^\mu_{\text{ind}} = \mu_0 G j^\mu_{\text{ind}} = (G\chi)^\mu{}_\nu A^\nu_{\text{ext}} \tag{1.349}$$

where χ denotes the fundamental response function and G is a Green function for the d'Alembert operator. Therefore

$$A^\mu_{\text{ext}} = ((1 + G\chi)^{-1})^\mu{}_\nu A_{\text{tot}}. \tag{1.350}$$

Maxwell equation in matter therefore read in their most general form

$$\Box (1 + G\chi)^{-1} A_{\text{tot}} = \mu_0 j_{\text{ext}}. \tag{1.351}$$

Of course these equations are in general highly complicated integro-differential equations and therefore not of Maxwellian form any more.

1.4.2. Thermodynamics

Thermodynamic Systems or macroscopic systems in equilibrium are characterized by a set of degrees of freedom $(E, T, \{X_i\}_{i=1,\ldots,n})$, where E is called *energy*, T *temperature* and the X_i are the so-called *extensive* or *external* parameters. The space $\mathbb{R}^{n+2}$ spanned by the degrees of freedom is called *state space*. In equilibrium, not the whole state-space is accessible, but the possible combinations of the $(E, T, \{X_i\}_{i=1,\ldots,n})$ are restricted to fulfill a so-called equation of state

$$f(E, T, \{X_i\}) = 0. \tag{1.352}$$

---

[16]In the following we use a formal notation.

Under suitable regularity conditions on f,[17] this equation defines a manifold $\mathcal{M}$, the manifold of states. Any (sufficiently regular[18]) function $f : \mathcal{M} \to \mathbb{R}$ is called *state variable*. State variables form an algebra. In particular, $E = E(T, \{X_i\})$ is a state variable. In this form, the energy dependence is called *caloric equation of state* and the $(T, \{X_i\})$ can be interpreted as local coordinates on the manifold of states. For any function f on a manifold, we can form the corresponding one-form $\mathrm{d}f$ (also called "differential"). It is a fundamental tenet that the differential of the energy can be written as

$$\mathrm{d}E = T\mathrm{d}S + \sum_{i=1}^{n} A_i \mathrm{d}X_i \tag{1.353}$$

with states variables $(S, \{A_i\}_{i=1,\dots,n})$. This is called *Gibbsian fundamental form*. S is called *entropy*. It is noteworthy that this form of writing $\mathrm{d}E$ is completely general in the sense that it does not depend on the local coordinates on the manifold. Instead it relates in a coordinate independent way the differential of the energy to the differentials of the state variables $(S, \{X_i\})$. If we use indeed $(T, \{X_i\})$ as local coordinates (as we did in the caloric equation of state), then with $S = S(T, \{X_i\})$ we have

$$\frac{\partial E}{\partial T} = T\frac{\partial S}{\partial T} \tag{1.354}$$

$$\frac{\partial E}{\partial X_i} = T\frac{\partial S}{\partial X_i} + A_i. \tag{1.355}$$

If we have a set of functions $f, x_1, \dots, x_n, y_1, \dots, y_n$ on a manifold $\mathcal{M}$ with $\dim \mathcal{M} = n$ such that the differentials are related via

$$\mathrm{d}f = \sum_{i=1}^{n} x_i \mathrm{d}y_i, \tag{1.356}$$

then the y_i are called *natural coordinates* for f and the $\{x_i\}$. In the natural coordinate system $x_i = \partial f/\partial y_i$ necessarily holds. (We assume tacitly that the lines of constant y_i define a local coordinate chart.) Consequently, in the natural coordinates for the energy we have $E = E(S, \{X_i\})$ and

$$\frac{\partial E}{\partial S} = T \tag{1.357}$$

$$\frac{\partial E}{\partial X_i} = A_i. \tag{1.358}$$

---

[17]In particular, f should be differentiable with non-vanishing gradient on the niveau surface. (cf. e.g. [83] Chapter 1, [43] Chapter 2)

[18]Usually, on a manifold, one considers smooth functions $f \in C^\infty(\mathcal{M})$. Physically, however, this is far from being a necessity. Quite to the contrary, when it comes to phase transitions, it might just be the non-regularity of a state variable which turns out to be the decisive feature. As this is not our concern here, we will always tacitly assume sufficient regularity to compute formally.

The A_i are the so-called *generalized forces*. Conversely, from the Gibbsian fundamental form, we read off that

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E - \sum_{i=1}^{n}\frac{A_i}{T}\mathrm{d}X_i \qquad (1.359)$$

i.e. the natural coordinates are given by $S = S(E, \{X_i\})$ and

$$\frac{\partial S}{\partial E} = \frac{1}{T} \qquad (1.360)$$

$$\frac{\partial S}{\partial X_i} = -\frac{A_i}{T}. \qquad (1.361)$$

Next, we introduce the *Helmholtz free energy*

$$F = E - TS. \qquad (1.362)$$

Note that at $T = 0$ (the relevant case for Electronic Structure Theory), $E = F$. For the associated one-form, we find using the Gibbsian fundamental form

$$\mathrm{d}F = -S\mathrm{d}T + \sum_{i=1}^{n} A_i\mathrm{d}X_i. \qquad (1.363)$$

Therefore, in the natural coordinates $F = F(T, \{X_i\})$. The

$$\chi_{ij}(T, \{X_i\}) = \frac{\partial A_i(T, \{X_i\})}{\partial X_j} = \frac{\partial^2 F(T, \{X_i\})}{\partial X_i \partial X_j} \qquad (1.364)$$

are the so-called *generalized susceptibilities*. This terminology stems from the study of magnetism: for a thermodynamic system in an external magnetic field $\mathbf{B}_{\mathrm{ext}} = \mu_0 \mathbf{H}$, the magnetization (in the i-th direction) and the susceptibility are defined as

$$M_i = \frac{\partial F}{\partial B_i} \qquad (1.365)$$

$$\chi_{ij} = \frac{\partial M_i}{\partial B_j}. \qquad (1.366)$$

The extensivity of E in the sense that

$$E(\lambda S, \{\lambda X_i\}) = \lambda E(S, \{X_i\}) \qquad (1.367)$$

for $\lambda \in \mathbb{R}_+$ is a frequent assumption which will certainly not hold in general. It leads to the so-called *Gibbs-Duhem equation*

$$E(S, \{X_i\}) = TS + \sum_{i=1}^{n} X_i A_i. \qquad (1.368)$$

By the Gibbsian fundamental form we obtain the Euler equation

$$S\mathrm{d}T + \sum_{i=1}^{n} X_i \mathrm{d}A_i = 0. \tag{1.369}$$

The Gibbs-Duhem equation for the Helmholtz free energy reads

$$F = \sum_{i=1}^{n} A_i X_i. \tag{1.370}$$

Linear Response Theory is defined by the ansatz

$$\chi_{ij} = f_{ij}(T) \tag{1.371}$$

or $A_i = A_{i0}(T) + \sum_{j=1}^{n} \chi_{ij}(T) X_j$. Within Linear Response Theory, the Helmholtz free energy is given by the simple expression

$$F(T, \{X_i\}) = \sum_i A_{i0}(T) X_i + \frac{1}{2} \sum_{i,j} \chi_{ij}(T) X_i X_j. \tag{1.372}$$

This can be interpreted as the leading term of a Taylor expansion

$$F(T, \{X_i\}) = \sum_i A_{i0}(T) X_i + \frac{1}{2!} \sum_{i,j} \chi_{ij}(T) X_i X_j + \frac{1}{3!} \sum_{i,j,k} \chi_{ijk}(T) X_i X_j X_k + \ldots \tag{1.373}$$

around $X_i = 0$. This latter ansatz is of course independent of the validity of the Gibbs-Duhem relation.

Work done on the System by the External Field The formula

$$E = \frac{1}{2} \int \mathrm{d}\mathbf{x}\, \rho(\mathbf{x})\varphi(\mathbf{x}) = \frac{\varepsilon_0}{2} \int \mathrm{d}\mathbf{x}\, |\mathbf{E}(\mathbf{x})|^2 \tag{1.374}$$

for the energy of the static charge density in the field created by itself is of unrestricted generality.[19] Within the realm of thermodynamics, we interpret the splitting $\rho = \rho_{\mathrm{ext}} + \rho_{\mathrm{int}}$; $\varphi \equiv \varphi_{\mathrm{tot}} = \varphi_{\mathrm{ext}} + \varphi_{\mathrm{int}}$ such that the induced quantities refer to the thermodynamic system under consideration whereas the external quantites are to be interpreted as a continuous family (indexed by $i \mapsto \mathbf{x}$)[20] of external parameters X_i. The total energy then splits into four terms proportional to $\varphi_{\mathrm{ext}}\rho_{\mathrm{ext}}, \varphi_{\mathrm{ext}}\rho_{\mathrm{int}}, \varphi_{\mathrm{int}}\rho_{\mathrm{ext}}, \varphi_{\mathrm{int}}\rho_{\mathrm{int}}$. The first term is simply not considered because it does not refer to the thermodynamic system. The third term describes the

[19]The characterization of the electric field energy as an integral of the square of the field strength actually goes beyond the static realm.
[20]Strictly speaking, this would require the introduction of infinite-dimensional state manifolds.

back-reaction of the system on the external source and is therefore neglected (otherwise the source would not be external). The remaining terms give

$$E = \frac{1}{2} \int d\mathbf{x} \; \rho_{\text{int}}(\mathbf{x}) \varphi_{\text{tot}}(\mathbf{x}) \tag{1.375}$$

As in the general case, we can use $\nabla \cdot \mathbf{E}_{\text{int}} = \rho_{\text{int}}/\varepsilon_0$ and $-\nabla\varphi = \mathbf{E}$ to get

$$E = E_{\text{el}} = \frac{\varepsilon_0}{2} \int d\mathbf{x} \; \mathbf{E}_{\text{int}}(\mathbf{x}) \cdot \mathbf{E}_{\text{tot}}(\mathbf{x}) = -\frac{1}{2} \int d\mathbf{x} \; \mathbf{P}(\mathbf{x}) \cdot \mathbf{E}(\mathbf{x}) \tag{1.376}$$

by a partial integration. Similar arguments starting from the expression for the static magnetic field generated by a static current

$$E_{\text{m}} = -\frac{1}{2} \int d\mathbf{x} \; \mathbf{j}(\mathbf{x}) \cdot \mathbf{A}(\mathbf{x}) = \frac{1}{2\mu_0} \int d\mathbf{x} \; |\mathbf{B}(\mathbf{x})|^2 \tag{1.377}$$

lead to the expression

$$E_{\text{m}} = \frac{1}{2} \int d\mathbf{x} \; \mathbf{M}(\mathbf{x}) \cdot \mathbf{B}(\mathbf{x}) \tag{1.378}$$

for the energy of a magnetized medium in a total field $\mathbf{B}$. A main advantage of these formulas is that they allow for a characterization of the polarization $\mathbf{P}$ and the induced charge density ρ_{int} as suitable functional derivatives of the energy with respect to fields or potentials. This paves the way for a connection with thermodynamics. Note that if only the energy in the external field is relevant (i.e. the self-energy of the induced charge can be neglected as in dilute systems), then we can even replace the total quantities with the external. The quantity

$$F = \frac{1}{2} \int d\mathbf{x} \; \rho_{\text{int}}(\mathbf{x}) \varphi_{\text{ext}}(\mathbf{x}) = \frac{\varepsilon_0}{2} \int d\mathbf{x} \; \mathbf{E}_{\text{int}}(\mathbf{x}) \cdot \mathbf{E}_{\text{ext}}(\mathbf{x}) = -\frac{1}{2\varepsilon_0} \int d\mathbf{x} \; \mathbf{P}(\mathbf{x}) \cdot \mathbf{D}(\mathbf{x}) \tag{1.379}$$

can be identified with the Helmholtz free energy for a system with external parameters $\varepsilon_0 \mathbf{E}_{\text{ext}} = \mathbf{D}$ within the limits of the Gibbs-Duhem equation for F. In particular, this implies

$$TS = \frac{1}{2} \int d\mathbf{x} \; \rho_{\text{int}}(\mathbf{x}) \varphi_{\text{int}}(\mathbf{x}) = \frac{\varepsilon_0}{2} \int d\mathbf{x} \; \mathbf{E}_{\text{int}}(\mathbf{x}) \cdot \mathbf{E}_{\text{int}}(\mathbf{x}). \tag{1.380}$$

Indeed, the integral is positive definite. We now think of the induced charge density ρ_{int} as a temperature-dependent functional

$$\rho_{\text{int}} = \rho_{\text{int}}([\mathbf{E}_{\text{ext}}], T)(\mathbf{x}). \tag{1.381}$$

Now, F depends on its natural coordinates and we have

$$dF = \frac{1}{2} \int d\mathbf{x} \; \delta\rho_{\text{int}}(\mathbf{x}) \varphi_{\text{ext}}(\mathbf{x}) + \frac{1}{2} \int d\mathbf{x} \; \rho_{\text{int}}(\mathbf{x}) \delta\varphi_{\text{ext}}(\mathbf{x}). \tag{1.382}$$

Identifying this with $= -S\mathrm{d}T + \sum_i A_i \mathrm{d}X_i$ and using

$$A_i = \frac{\partial F}{\partial X_i} \tag{1.383}$$

as well as

$$
\begin{aligned}
\frac{\delta F}{\delta \varphi_{\mathrm{ext}}(\mathbf{x})} &= \frac{1}{2}\rho_{\mathrm{int}}(\mathbf{x}) + \frac{1}{2}\int \mathrm{d}\mathbf{x}' \, \frac{\delta \rho_{\mathrm{int}}(\mathbf{x}')}{\delta \varphi_{\mathrm{ext}}(\mathbf{x})}\varphi_{\mathrm{ext}}(\mathbf{x}') \\
&= +\frac{1}{2}\rho_{\mathrm{int}}(\mathbf{x}) + \frac{1}{2}\int \mathrm{d}\mathbf{x}' \, \chi(\mathbf{x},\mathbf{x}')\varphi_{\mathrm{ext}}(\mathbf{x}') \\
&= \frac{1}{2}\rho_{\mathrm{int}}(\mathbf{x}) + \frac{1}{2}\rho_{\mathrm{int}}(\mathbf{x})
\end{aligned}
$$

or

$$\rho_{\mathrm{int}}(\mathbf{x}) = \frac{\delta F}{\delta \varphi_{\mathrm{ext}}(\mathbf{x})} \tag{1.384}$$

leads to

$$\chi(\mathbf{x},\mathbf{x}') = \frac{\delta^2 F}{\delta \varphi_{\mathrm{ext}}(\mathbf{x})\delta \varphi_{\mathrm{ext}}(\mathbf{x}')} \tag{1.385}$$

for the generalized susceptibilities.[21] Similar formulas hold in the magnetic case.

1.4.3. Quantum Mechanics

Quantum Mechanics can be related to classical thermodynamics by identifying the energy E at temperature T and external parameters $\{X_i\}$ with the expectation value

$$E = \langle \hat{H} \rangle \tag{1.386}$$

in the canonical ensemble

$$\hat{\rho} = \frac{\exp\left(-\frac{\hat{H}}{k_B T}\right)}{\mathrm{Tr}\ \exp\left(-\frac{\hat{H}}{k_B T}\right)} \tag{1.387}$$

where the Hamiltonian is of the form

$$\hat{H} = \hat{H}_0 + \sum_{i=1}^{n} X_i \hat{A}_i. \tag{1.388}$$

In particular, the partition function

$$Z(T,\{X_i\}) = \mathrm{Tr}\ \exp\left(-\frac{\hat{H}}{k_B T}\right) \tag{1.389}$$

---

[21]If the Gibbs-Duhem equation does not hold, this equality is to understood as a definition where the funtional derivative is evaluated at $\varphi_{\mathrm{ext}} = 0$.

formally depends on the natural variables of the Helmholtz free energy. Indeed, we have the well-known formula

$$F(T, \{X_i\}) = -k_B T \ln Z \tag{1.390}$$

and hence

$$E(T, \{X_i\}) = -\frac{\partial \ln Z}{\partial \beta} \tag{1.391}$$

$$A_i(T, \{X_i\}) = \frac{\partial F}{\partial X_i}. \tag{1.392}$$

where $\beta = (k_B T)^{-1}$. In particular, this shows that the Gibbs-Duhem equations in general do not hold because

$$-k_B T \ln Z \neq \sum_i X_i A_i. \tag{1.393}$$

Furthermore, as

$$S = \frac{1}{T}(E - F) \tag{1.394}$$

and

$$\ln \hat{\rho} = -\beta \hat{H} - \text{Tr } \exp(-\beta \hat{H}) \tag{1.395}$$

implying

$$\langle \ln \hat{\rho} \rangle = -\beta \langle \hat{H} \rangle - \text{Tr } \exp(-\beta \hat{H}) \tag{1.396}$$

$$= \frac{1}{k_B T}(-E + F) \tag{1.397}$$

we have

$$S(T, \{X_i\}) = -k_B \text{Tr } \hat{\rho} \ln \hat{\rho}. \tag{1.398}$$

This is the famous *von-Neumann entropy*.

Kubo Formula Consider a quantum system which is initially described by the time-independent Hamiltonian $\hat{H}_0$. Suppose, that at some time $t = t_0$ an external perturbation is applied to the system:

$$\hat{H}(t) = \hat{H}_0 + \theta(t - t_0) X_j(t) \hat{A}_j. \tag{1.399}$$

with some real-valued function $X_j(t)$. Furthermore, consider the observable $\hat{A}_i$ and suppose, the system is initially in thermal equilibrium. Then the expectation value of $\hat{A}_i$ is given by

$$A_i = \langle \hat{A}_i \rangle_{t \leq t_0} = \frac{\text{Tr}(\hat{\rho}_0 \hat{A}_i)}{Z_0} = \frac{1}{Z_0} \sum_r \langle \Psi_r | \hat{A}_i | \Psi_r \rangle e^{-\beta E_r} \tag{1.400}$$

with

$$\hat{\rho}_0 = \frac{\exp\left(-\frac{\hat{H}_0}{k_B T}\right)}{\mathrm{Tr}\ \exp\left(-\frac{\hat{H}_0}{k_B T}\right)} \tag{1.401}$$

After the perturbation is turned on, the system is in a non-equilibrium state. That means, initially, the states are distributed according to the canonical ensemble, but after the perturbation is switched on, the distribution is still the same, but the states are now time-dependent and evolve according to the perturbed Hamiltonian. This leads to a time-dependent change in the expectation value of $\hat{A}_i$ given by

$$\delta A_i(t) = \langle \hat{A}_i \rangle_t - \langle \hat{A}_i \rangle_{t_0}. \tag{1.402}$$

Theorem 1.4.1 *Up to linear order in the perturbation the change in the expectation value is given by:*

$$\delta A_i(t) = -\frac{\mathrm{i}}{\hbar} \int_{t_0}^t \mathrm{d}t'\ \langle [\hat{A}_i(t), \hat{A}_j(t')] \rangle_0 X_j(t') \tag{1.403}$$

$$= -\frac{\mathrm{i}}{\hbar} \int_{t_0}^\infty \mathrm{d}t'\ \theta(t - t')\langle [\hat{A}_i(t), \hat{A}_j(t')] \rangle_0 X_j(t') \tag{1.404}$$

$$= -\frac{\mathrm{i}}{\hbar} \int_{-\infty}^\infty \mathrm{d}t'\ \theta(t - t')\theta(t' - t_0)\langle [\hat{A}_i(t), \hat{A}_j(t')] \rangle_0 X_j(t') \tag{1.405}$$

where $\langle \cdot \rangle_0$ refers to the expectation value in the unperturbed ensemble $\hat{\rho}_0$ (which will not be written explicitly in the sequel) and the time-dependence of $\hat{A}_i(t)$ and $\hat{A}_j(t)$ is given by the unperturbed Hamiltonian $\hat{H}_0$.

Remark Equation (1.403) is the famous *Kubo formula.* (see e.g. [15] or [35])

Proof We make a transition to the interaction picture where $\hat{H}_{\mathrm{pert}} = \theta(t - t_0)X_j(t)\hat{A}_j$ is the perturbation. In the interaction picture, we have

$$\Psi_r^I(t) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}_0 t}\Psi_r(t) \tag{1.406}$$

$$\Psi_r^I(t) = \Psi_r\ \text{for } t \le t_0 \tag{1.407}$$

$$\hat{H}^I(t) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}_0 t}\hat{H}(t)\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t} \tag{1.408}$$

$$\hat{U}^I(t, t_0) \simeq \mathbb{1} - \frac{\mathrm{i}}{\hbar}\int_{t_0}^t \mathrm{d}t'\ \hat{H}_{\mathrm{pert}}^I(t') \tag{1.409}$$

$$\hat{H}_{\mathrm{pert}}^I(t) = \theta(t - t_0)X_j(t)\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}_0 t}\hat{A}_j\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t} \tag{1.410}$$

$$\frac{1}{Z_0}\sum_r \mathrm{e}^{-\beta E_r(t_0)}\langle \Psi_r(t)|\hat{A}_i|\Psi_r(t)\rangle = \frac{1}{Z_0}\sum_r \mathrm{e}^{-\beta E_r(t_0)}\langle \Psi_r^I(t)|\hat{A}_i^I(t)|\Psi_r^I(t)\rangle. \tag{1.411}$$

The Kubo formula now follows from plugging the time evolution operator in the interaction picture into this formula and retaining only terms up to first oder in X_j.

Definition The quantities

$$\chi_{ij}^{\mathrm{R}}(t, t') = -\frac{\mathrm{i}}{\hbar}\theta(t - t')\langle[\hat{A}_i(t), \hat{A}_j(t')]\rangle \quad (1.412)$$

$$\chi_{ij}^{\mathrm{A}}(t, t') = \frac{\mathrm{i}}{\hbar}\theta(t' - t)\langle[\hat{A}_i(t), \hat{A}_j(t')]\rangle \quad (1.413)$$

$$\chi_{ij}(t, t') = -\frac{\mathrm{i}}{\hbar}\langle\mathcal{T}\hat{A}_i(t)\hat{A}_j(t')\rangle \quad (1.414)$$

are called *retarded, advanced* and *time-ordered response function*. $\mathcal{T}$ denotes the time-ordering operator.

Remark The importance of the time-ordered response function lies in the fact that it can be calculated from the time-ordered Green functions for which there exists a perturbation theory in terms of the electron-electron interaction. For the retarded and advanced response functions, this is not the case. On the other hand, the following formulas show that the time-ordered response functions being given, one can reconstruct the retarded and advanced response functions.

Explicit Form By inserting complete systems of energy eigenstates of the reference Hamiltonian, we read off that in the frequency domain the response functions read

$$\chi_{ij}^{\mathrm{R}}(\omega) = \frac{1}{Z_0}\sum_{r,s}\mathrm{e}^{-\beta E_r(t_0)}\left(\frac{\langle\Psi_r|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_r\rangle}{\hbar\omega - (E_s - E_r) + \mathrm{i}\eta} - \frac{\langle\Psi_r|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_r\rangle}{\hbar\omega + (E_s - E_r) + \mathrm{i}\eta}\right) \quad (1.415)$$

$$\chi_{ij}^{\mathrm{A}}(\omega) = \frac{1}{Z_0}\sum_{r,s}\mathrm{e}^{-\beta E_r(t_0)}\left(\frac{\langle\Psi_r|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_r\rangle}{\hbar\omega - (E_s - E_r) - \mathrm{i}\eta} - \frac{\langle\Psi_r|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_r\rangle}{\hbar\omega + (E_s - E_r) - \mathrm{i}\eta}\right) \quad (1.416)$$

$$\chi_{ij}(\omega) = \frac{1}{Z_0}\sum_{r,s}\mathrm{e}^{-\beta E_r(t_0)}\left(\frac{\langle\Psi_r|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_r\rangle}{\hbar\omega - (E_s - E_r) + \mathrm{i}\eta} - \frac{\langle\Psi_r|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_r\rangle}{\hbar\omega + (E_s - E_r) - \mathrm{i}\eta}\right) \quad (1.417)$$

In particular, the response functions at temperature $T = 0$ read

$$\chi_{ij}^{\mathrm{R}}(\omega) = \sum_s\frac{\langle\Psi_0|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_0\rangle}{\hbar\omega - (E_s - E_0) + \mathrm{i}\eta} - \sum_s\frac{\langle\Psi_0|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_0\rangle}{\hbar\omega + (E_s - E_0) + \mathrm{i}\eta} \quad (1.418)$$

$$\chi_{ij}^{\mathrm{A}}(\omega) = \sum_s\frac{\langle\Psi_0|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_0\rangle}{\hbar\omega - (E_s - E_0) - \mathrm{i}\eta} - \sum_s\frac{\langle\Psi_0|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_0\rangle}{\hbar\omega + (E_s - E_0) - \mathrm{i}\eta} \quad (1.419)$$

$$\chi_{ij}(\omega) = \sum_s\frac{\langle\Psi_0|\hat{A}_i|\Psi_s\rangle\langle\Psi_s|\hat{A}_j|\Psi_0\rangle}{\hbar\omega - (E_s - E_0) + \mathrm{i}\eta} - \sum_s\frac{\langle\Psi_0|\hat{A}_j|\Psi_s\rangle\langle\Psi_s|\hat{A}_i|\Psi_0\rangle}{\hbar\omega + (E_s - E_0) - \mathrm{i}\eta} \quad (1.420)$$

where the sum goes over a complete system Ψ_s of energy eigenstates in the N-particle space and $E_r = E_r(t_0)$. This explicit form of the response functions is analogous to the Lehmann

representation of the Green function which will be treated later.

Response Function vs Fluctuation Response Function The response function gives the reaction of the expectation value $A_i(t) = \langle\Psi(t)|\hat{A}_i|\Psi(t)\rangle$ upon a switch in the perturbation $X_j(t)\hat{A}_j$ at time t'. Equivalently, one could say that the response function gives the reaction of the expectation value of the fluctuation operator

$$\delta\hat{A}_i = \hat{A}_i - \langle\hat{A}_i\rangle_0 \mathbb{1}. \tag{1.421}$$

Furthermore, the perturbation can also be redefined as

$$\hat{A}_j \mapsto \delta\hat{A}_j = \hat{A}_j - \langle\hat{A}_j\rangle_0 \mathbb{1} \tag{1.422}$$

because this would yield an extra perturbation $X_j(t)\langle\hat{A}_j\rangle\mathbb{1}$ which only leads to time-dependent phase factor, but does not change the eigenvectors Ψ_r. We conclude that the response function and the fluctuation response function coincide, i.e.

$$\chi^{\mathrm{R}}_{ij}(t,t') = -\frac{\mathrm{i}}{\hbar}\theta(t-t')\langle[\delta\hat{A}_i(t),\delta\hat{A}_j(t')]\rangle \tag{1.423}$$

$$\chi^{\mathrm{A}}_{ij}(t,t') = \frac{\mathrm{i}}{\hbar}\theta(t'-t)\langle[\delta\hat{A}_i(t),\delta\hat{A}_j(t')]\rangle \tag{1.424}$$

This can also be read off from the explicit form of the response function or from the defining formulas where one has to note that a term proportional to the identity has a vanishing commutator with every operator. For the time-ordered response function, however, this does not hold true. There, we earn the extra term

$$-\mathbb{E}_{\mathrm{thermal}}(A_iA_j)\int_{t_0}^{t}\mathrm{d}t'\ X_j(t') \tag{1.425}$$

with

$$\mathbb{E}_{\mathrm{thermal}}(A_iA_j) = \frac{1}{Z_0}\sum_r \mathrm{e}^{-\beta E_r(t_0)}\langle\Psi_r|\hat{A}_i|\Psi_r\rangle\langle\Psi_r|\hat{A}_j|\Psi_r\rangle \tag{1.426}$$

if we make the replacements $\hat{A}_i \mapsto \delta\hat{A}_i$. This fact should be interpreted as a mathematical pathology because for the time being the importance of the time-ordered response function consists in that it allows for the reconstruction of the retarded or advanced response function. In fact, the time-ordered response function is the only one for which the terms $r = s$ in the sum $\sum_{r,s}$ do not cancel between the first and the second expression. It is these terms that are responsible for the inequality

$$\langle\mathcal{T}\hat{A}_i(t)\hat{A}_j(t')\rangle \neq \langle\mathcal{T}\delta\hat{A}_i(t)\delta\hat{A}_j(t')\rangle. \tag{1.427}$$

We are therefore free to *redefine* the time-ordered response function as

$$\chi_{ij}(t, t') = -\frac{\mathrm{i}}{\hbar} \langle \mathcal{T} \delta \hat{A}_i(t) \delta \hat{A}_j(t') \rangle \tag{1.428}$$

whenever it suits our purposes. In particular, with the time-ordered density response function χ, we introduce the time-ordered fluctuation response function which is often denoted by P and called *polarizability*.[22]

Kubo Response Function and Susceptibility From the Kubo-formula, we read off that the retarded response function can also be characterized as

$$\chi_{ij}^{\mathrm{R}}(t, t') = \frac{\delta A_i(t)}{\delta X_j(t')}, \quad t \geq t' \geq t_0 \tag{1.429}$$

where it is understood that the derivative is evaluated at $X_j(t) \equiv 0$.[23] In other words, up to linear order in the perturbation we have

$$A_i(t) = A_i(0) + \int \mathrm{d}t' \; \chi_{ij}^{\mathrm{R}}(t, t') X_j(t') \tag{1.430}$$

or more generally

$$A_i(t) = A_i(0) + \int \mathrm{d}t' \sum_j \chi_{ij}^{\mathrm{R}}(t, t') X_j(t') \tag{1.431}$$

for a perturbation $\sum X_j(t)\hat{A}_j(t)$. As the response functions depend only on the time-difference, a Fourier transform with respect to $\tau = t - t'$ yields

$$A_i(\omega) = A_{i0}\delta(\omega) + \sum_j \chi_{ij}^{\mathrm{R}}(\omega) X_j(\omega) \tag{1.432}$$

giving the response of the mode $A_i(\omega)$ to a perturbation with the same frequency. In particular, $\chi_{ij}^{\mathrm{R}}(\omega = 0)$ yields a constant shift in A_i due to a constant perturbation. It is therefore plausible to consider the Fourier transform of $\chi_{ij}^{\mathrm{R}}(t, t') = \chi_{ij}^{\mathrm{R}}(\tau)$ with respect to $\tau = t - t'$ at frequency $\omega = 0$ and to interpret $\chi_{ij}^{\mathrm{R}}(\omega = 0)$ as the thermodynamic susceptibility χ_{ij}. Obviously, numerically $\chi_{ji}^{\mathrm{R}}(\omega = 0) = \chi_{ij}^{\mathrm{A}}(\omega = 0) = \chi_{ij}^{\mathrm{R}}(\omega = 0)$, i.e. χ_{ij}^{R} is symmetric in the indices. Furthermore, $\chi_{ij}^{R/A}(\omega = 0) < 0$. To check this idea, we have to calculate

$$\chi_{ij} = \frac{\partial^2 F}{\partial X_i \partial X_j}.$$

---

[22] As we will see later, the distinction between $\chi, \tilde{\chi}, P, \tilde{P}$ has a clearcut interpretation in Quantum Field Theory. The transition from $\chi, \tilde{\chi}$ to $P, \tilde{P}$ corresponds to the transition from the four-point propagator $G(1, 2, 3, 4)$ to $L(1, 2, 3, 4) = G^4(1, 2, 3, 4) - G(1, 3)G(2, 4)$ whereas the distinction between χ, P and $\tilde{\chi}, \tilde{P}$ corresponds to the difference between reducible and irreducible quantities in the sense of a Feynman graph summation.

[23] This condition garantuees that our definitions also hold true for non-linear systems.

We find

$$
\begin{aligned}
\partial_j F &= -k_B T \partial_j \ln Z && (1.433)\\
&= -k_B T \frac{\partial_j Z}{Z} && (1.434)\\
&= \frac{\sum_r \partial_j E_r \, \mathrm{e}^{-\beta E_r}}{Z}. && (1.435)
\end{aligned}
$$

For the second derivatives $\partial_i \partial_j F$, we get

$$
= \beta \frac{\sum_r \partial_i E_r \, \mathrm{e}^{-\beta E_r}}{Z} \frac{\sum_s \partial_j E_s \, \mathrm{e}^{-\beta E_s}}{Z} + \frac{\sum_r \partial_i \partial_j E_r \, \mathrm{e}^{-\beta E_r}}{Z} - \beta \frac{\sum_r \partial_i E_r \partial_j E_r \, \mathrm{e}^{-\beta E_r}}{Z}.
$$

With the Hellmann-Feynman theorem we get

$$
\begin{aligned}
\partial_i E_r &= \partial_i \langle \Psi_r(\{X_i\}) | \hat{H}(\{X_i\}) | \Psi_r(\{X_i\}) \rangle\\
&= \langle \Psi_r(\{X_i\}) | \partial_i \hat{H}(\{X_i\}) | \Psi_r(\{X_i\}) \rangle\\
&= \langle \Psi_r(\{X_i\}) | \hat{A}_i | \Psi_r(\{X_i\}) \rangle\\
&= A_{ir}(\{X_i\})
\end{aligned}
$$

and therefore

$$
\begin{aligned}
\partial_i \partial_j E_r &= \partial_i \langle \Psi_r(\{X_i\}) | \hat{A}_j | \Psi_r(\{X_i\}) \rangle && (1.436)\\
&= \langle \partial_i \Psi_r(\{X_i\}) | \hat{A}_j | \Psi_r(\{X_i\}) \rangle + \langle \Psi_r(\{X_i\}) | \hat{A}_j | \partial_i \Psi_r(\{X_i\}) \rangle && (1.437)\\
&= 2\mathfrak{Re} \langle \Psi_r(\{X_i\}) | \hat{A}_j | \partial_i \Psi_r(\{X_i\}) \rangle. && (1.438)
\end{aligned}
$$

We assume that $\Psi_r(\{X_i\})$ can be treated perturbatively as

$$
\Psi_r(\{X_k + \delta_{ik}\eta\}) = \Psi_r(\{X_k\}) + \eta \sum_{s \neq r} \frac{\langle \Psi_r | \hat{A}_i | \Psi_s \rangle}{E_r - E_s} \Psi_s + \ldots \tag{1.439}
$$

and hence

$$
\partial_i \Psi_r(\{X_k\}) = \sum_{s \neq r} \frac{\langle \Psi_r(\{X_k\}) | \hat{A}_i | \Psi_s(\{X_k\}) \rangle}{E_r - E_s} \Psi_s(\{X_k\}). \tag{1.440}
$$

We now find

$$
\partial_i \partial_j E_r = \sum_{s \neq r} \left(\frac{\langle \Psi_r | \hat{A}_i | \Psi_s \rangle \langle \Psi_s | \hat{A}_j | \Psi_r \rangle}{E_r - E_s} + \frac{\langle \Psi_r | \hat{A}_j | \Psi_s \rangle \langle \Psi_s | \hat{A}_i | \Psi_r \rangle}{E_r - E_s} \right). \tag{1.441}
$$

It is this term which obviously coincides with $\chi^{\mathrm{R}}(\omega = 0)$. (Note in this context again that the divergent contributions to $\chi^{\mathrm{R}}(\omega = 0)$ resulting from the terms $r = s$ just cancel between

the two sums.) The remaining terms which can be compactly written as the thermal expectation values $\beta(-\mathbb{E}_{\text{thermal}}(A_i A_j) + \mathbb{E}_{\text{thermal}}(A_i)\mathbb{E}_{\text{thermal}}(A_j))$ are in general neither zero nor even negligible.[24]

Susceptibility and Response Function at Zero Temperature The surprising difference between the static response function $\chi_{ij}(\omega = 0)$ and the susceptibility χ_{ij} results from the fact that the susceptibility involves effects due to the thermal weighting $\mathrm{e}^{-\beta E_r}/Z$. Upon a perturbation, not only the expectation values A_i, but also the weighting factors change. The Kubo formula ignores this in that it works with a constant partition function Z_0. It is intuitively clear that the difference vanishes at zero temperature because there the thermal weighting does not matter. We now show this explicitly by prooving that

$$\beta \frac{\sum_r \partial_i E_r \ \mathrm{e}^{-\beta E_r}}{Z} \frac{\sum_r \partial_j E_r \ \mathrm{e}^{-\beta E_r}}{Z} - \beta \frac{\sum_r \partial_i E_r \partial_j E_r \ \mathrm{e}^{-\beta E_r}}{Z} \tag{1.442}$$

goes to zero as $\beta \to \infty$. We find

$$\lim_{\beta \to \infty} \left(\beta \frac{\sum_r \partial_i E_r \ \mathrm{e}^{-\beta E_r}}{Z} \frac{\sum_s \partial_j E_s \ \mathrm{e}^{-\beta E_s}}{Z} - \beta \frac{\sum_r \partial_i E_r \partial_j E_r \ \mathrm{e}^{-\beta E_r}}{Z} \right) \tag{1.443}$$

$$= \lim_{\beta \to \infty} \left(\beta \frac{\sum_r \partial_i E_r \ \mathrm{e}^{-\beta E_r}}{Z} \frac{\sum_s \partial_j E_s \ \mathrm{e}^{-\beta E_s}}{Z} - \beta \frac{\sum_{r,s} \partial_i E_r \partial_j E_r \ \mathrm{e}^{-\beta E_r}\mathrm{e}^{-\beta E_s}}{Z^2} \right) \tag{1.444}$$

$$= \lim_{\beta \to \infty} \frac{\sum_{r,s}(\partial_i E_r \partial_j E_s - \partial_i E_r \partial_j E_r) \ \beta\mathrm{e}^{-\beta E_r - \beta E_s}}{Z^2} \tag{1.445}$$

$$= \lim_{\beta \to \infty} \frac{\sum_{r,s}(\partial_i E_r \partial_j E_s - \partial_i E_r \partial_j E_r) \ \beta\mathrm{e}^{-\beta (E_r - E_0) - \beta(E_s - E_0)}}{\sum_r \mathrm{e}^{-\beta(E_r - E_0)} \sum_r \mathrm{e}^{-\beta(E_r - E_0)}} \tag{1.446}$$

$$= \frac{\sum_{r,s} \lim_{\beta \to \infty}(\partial_i E_r \partial_j E_s - \partial_i E_r \partial_j E_r) \ \beta\mathrm{e}^{-\beta (E_r - E_0) - \beta(E_s - E_0)}}{\sum_r \lim_{\beta \to \infty} \mathrm{e}^{-\beta(E_r - E_0)} \sum_r \lim_{\beta \to \infty} \mathrm{e}^{-\beta(E_r - E_0)}} \tag{1.447}$$

$$= \frac{\sum_{r,s} \lim_{\beta \to \infty}(\partial_i E_r \partial_j E_s - \partial_i E_r \partial_j E_r) \ \beta\mathrm{e}^{-\beta (E_r - E_0) - \beta(E_s - E_0)}}{\sum_r \lim_{\beta \to \infty} \mathrm{e}^{-\beta(E_r - E_0)} \sum_r \lim_{\beta \to \infty} \mathrm{e}^{-\beta(E_r - E_0)}} \tag{1.448}$$

$$= 0 \tag{1.449}$$

because

$$\lim_{\beta \to \infty} \beta\mathrm{e}^{-\beta(E_r - E_0) - \beta(E_s - E_0)} = 0 \tag{1.450}$$

---

[24]This result coincides with equation (3.119) of [35] p.135 which there goes under the name "adiabatic versus isothermal response" and has been derived within a different setup.

except when $E_r = E_s = E_0$ in which case $\partial_i E_r \partial_j E_s - \partial_i E_r \partial_j E_r = 0$.[25]

Classification of Response Functions The above discussion made it clear that the response function

$$\chi_{ij}(t, t') = \frac{\delta A_i(t)}{\delta X_j(t')} \tag{1.453}$$

is not a well-defined object without further specifications. In fact, if the response function is to be calculated from a thermal ensemble, then for the response function to be well-defined it is necessary to fix

1. the perturbation theory by which the states evolve and

2. the evolution of the weighting factors of the states.

The Kubo response theory specifies the first point by the ordinary time-dependent perturbation theory. An alternative choice would be the adiabatic approximation[26] (cf. [28], [68])

$$\Psi_r(t) = \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t} dt' E_r(t')\right) \Psi_{E_r}(t) + \sum_{s \neq r} \frac{\langle \Psi_{E_s}(t)|\hat{H}_{\text{pert}}|\Psi_{E_r}(t)\rangle}{E_s(t) - E_r(t)} \Psi_{E_s}(t) \tag{1.454}$$

where

$$\Psi_r(t \leq t_0) = \Psi_{E_r} \tag{1.455}$$

---

[25]In this proof we interchanged such limits as e.g.

$$\lim_{\beta \to \infty} \lim_{N \to \infty} \sum_{r=0}^{N} = \lim_{N \to \infty} \sum_{r=0}^{N} \lim_{\beta \to \infty} \tag{1.451}$$

$$\lim_{N \to \infty} \lim_{M \to \infty} \sum_{r=0}^{N} \sum_{s=0}^{M} = \lim_{M \to \infty} \lim_{N \to \infty} \sum_{r=0}^{N} \sum_{s=0}^{M}. \tag{1.452}$$

For this it would be sufficient if the $f_r^i(\beta) = \sqrt{\beta}\partial_i E_r \frac{e^{-\beta E_r}}{Z}$ and $f_r^{ij}(\beta) = \beta\partial_i E_r \partial_j E_r \frac{e^{-\beta E_r}}{Z^2}$ constituted uniformly convergent series, i.e. $F^i(\beta) = \sum_{r=0}^{\infty} f_r^i(\beta)$ converges uniformly for, say, $0 < \beta_0 < \beta \leq \infty$. A sufficient criterion for the uniform convergence would be the normal convergence, i.e. the convergence of the supremum norms $\sum_{r=0}^{\infty} \|f_r^i\|_0$ within the domain of definition $[\beta_0, \infty]$. For the supremum norm, we have $\|f_r^i\|_0 = |\partial_i E_r| e^{-\beta_0 E_r}$. Convergence cannot be proven without further assumptions on the functional dependence $E_r(X_1, \ldots, X_N)$. In any case, it would be sufficient if the $\hat{A}_i$ were bounded. Accepting free interachangebility of all limits (including the derivatives ∂_i), the equality $\chi_{ij}^{T=0}(\omega = 0) = \chi_{ij}^{T=0}$ becomes trivial if we identify $F = E$ for $T = 0$ in the first place. Therefore, the formal calculation yields the right physical result.

[26]We follow the formula given by Fradkin [28] p.274 which does not include a "quantal phase factor accompanying adiabatic changes" ([10], [71]) In fact, it has been the merit of the Modern Theory of Polarization to relate the concept of Polarization to a Berry Phase. Fradkin's formula can be recovered by writing the scalar product in the interaction picture and replacing the perturbation by $i\hbar\partial_t$.

---

and

$$\hat{H}(t)\Psi_{E_r}(t) = E_r(t)\Psi_{E_r}(t), \qquad (1.456)$$

i.e. the $\Psi_{E_r}(t)$ are the instantaneous eigenstates.[27] In fact, it is this approximation which is used for the derivation of the so-called Kubo formula[28] for the Hall conductance, as used for example in the famous TKNN paper [96] on the quantization of the Hall conductivity. As to the second point, a priori everything is possible, but in praxi only two cases seem to be relevant: (i) the weighting factors remain constant $\mathrm{e}^{-\beta E_r(t_0)}/Z(t_0)$ or (ii) the weighting factors are given by the instantaneous Boltzmann factors $\mathrm{e}^{-\beta E_r(t)}/Z(t)$. In the last case, the response function should be called isothermal because it corresponds to a system always being in the instantaneous canonical ensemble corresponding to the fixed temperature T.[29]

Isothermal Response Function and Susceptibility We now calculate explicitly the isothermal Kubo response function. The expectation value A_i is now given by

$$A_i(t) = \sum_r \frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} \langle \Psi_r(t)|\hat{A}_i|\Psi_r(t)\rangle. \qquad (1.457)$$

Consequently,

$$\frac{\delta A_i(t)}{\delta X_j(t')} = \sum_r \left(\frac{\delta}{\delta X_j(t')} \frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} \right) \langle \Psi_r(t)|\hat{A}_i|\Psi_r(t)\rangle + \sum_r \frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} \frac{\delta}{\delta X_j(t')} \langle \Psi_r(t)|\hat{A}_i|\Psi_r(t)\rangle.$$

For the second term, we find as in the case of the Kubo formula

$$-\frac{\mathrm{i}}{\hbar}\theta(t-t') \sum_r \frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} \langle \Psi_r|[\hat{A}_i(t), \hat{A}_j(t')]|\Psi_r\rangle \qquad (1.458)$$

which corresponds to the ordinary Kubo response but with the thermal weighting determined by the instantaneous Hamiltonian.[30] For the first term we calculate

$$\frac{\delta}{\delta X_j(t')} \frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} = -\beta\delta(t-t')A_{jr}(t)\frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)} + \beta\delta(t-t')\frac{\mathrm{e}^{-\beta E_r(t)}}{Z^2(t)} \sum_s A_{js}(t)\mathrm{e}^{-\beta E_s(t)}.$$

---

[27]The adiabatic approximation simply corresponds to a formal *time-independent*, first-order perturbative expansion where the eigenvectors and eigenstates have been replaced by the instantaneous eigenvectors and eigenstates.

[28]The Kubo formula therefore does not give a Kubo response function but rather an "adiabatic" response function.

[29]Note in this context that in the ordinary Kubo response, T is only a parameter after the perturbation is switched on.

[30]Per definitionem, one has to set $X_j(t) = 0$ after performing the functional derivative. Therefore, in the end this expression really collapses to the ordinary Kubo response.

leading to the overall contribution

$$-\beta\delta(t-t')\sum_r A_{jr}(t)A_{ir}(t)\frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)}+\beta\delta(t-t')\sum_r\frac{\mathrm{e}^{-\beta E_r(t)}}{Z(t)}A_{ir}(t)\sum_s A_{js}(t)\frac{\mathrm{e}^{-\beta E_s(t)}}{Z(t)}. \quad (1.459)$$

to the isothermal response function. Obviously, this is indeed the time-dependent generalization of the thermodynamic susceptibility calculated from the quantum mechanical partition function.

Frozen vs Relaxed Response Functions Up to now, we considered a fixed reference Hamiltonian $\hat{H}_0$ which beginning at some time t_0 is perturbed such that the overall Hamiltonian reads

$$\hat{H}(t)=\hat{H}_0+\sum_j\theta(t-t_0)X_j(t)\hat{A}_j. \quad (1.460)$$

In the special case of Electronic Structure Theory, the unperturbed Hamiltonian reads

$$\hat{H}_0=-\frac{\hbar^2}{2m}\sum_{i=1}^N\Delta_i+\sum_{i+1}^N v_{\mathrm{ext}}(\mathbf{x}_i)+\mathrm{el}-\mathrm{el\ interaction\ terms} \quad (1.461)$$

where v_{ext} is to be understood as the external potential generated by the nuclei. In other words, the external potential depends parametrically on the positions of nuclei $\mathbf{X}_i$. These classical nuclear positions are to be understood as the equilibrium positions of the nuclei or, in a more quantum mechanical parlance, as the expectation value

$$\mathbf{x_n}=\langle\hat{\mathbf{x}}_\mathbf{n}\rangle \quad (1.462)$$

of the nuclear position operator evaluated in the nuclear state (typically the ground-state). This makes it clear that the nuclei constitute a complicated quantum mechanical system of its own right and the external perturbation does in general not naively couple to the electronic system by an operator of the form $\sum_j\theta(t-t_0)X_j(t)\hat{A}_j$. Instead, the external perturbation also influences v_{ext}. A response functions which also takes into account the effect of the perturbation on the external potential will be called a *relaxed response function*. We now develop a simple theory of relaxed response functions. For this purpose, we expand the external potential

$$v_{\mathrm{ext}}(\mathbf{x};\{\mathbf{x_n}(t)\}) = v_{\mathrm{ext}}(\mathbf{x};\{\mathbf{x_{n0}}\})+\sum_i(\nabla_{\mathbf{x_n}}v_{\mathrm{ext}})(\mathbf{x};\{\mathbf{x_n}\})\cdot(\mathbf{x_n}(t)-\mathbf{x_{n0}}) \quad (1.463)$$

$$= v_{\mathrm{ext}}(\mathbf{x})-\sum_{\mathbf{n}\in\Gamma}\mathbf{F}(\mathbf{x}-\mathbf{x_n})\cdot\mathbf{u}(\mathbf{x_{n0}},t) \quad (1.464)$$

with the displacement field $\mathbf{u}(\mathbf{x_{n0}}, t)$ which is defined on the Bravais lattice $\mathbf{x_{n0}}$. We assume that the electronic perturbation $\sum_j \theta(t - t_0) X_j(t) \hat{A}_j$ couples to the nuclear system in the form

$$\sum_j \theta(t - t_0) X_j(t) \hat{B}_j \tag{1.465}$$

with an appropriate operator $\hat{B}_j$. For the expectation values $\mathbf{u}(\mathbf{x}_{i0}, t)$ we use again the Kubo response formalism

$$\mathbf{u}(\mathbf{x_{n0}}; t) = -\frac{\mathrm{i}}{\hbar} \int_{t_0}^{t} \mathrm{d}t' \ \sum_j \langle [\hat{\mathbf{u}}(\mathbf{x_{n0}}, t), \hat{B}_j(t')] \rangle X_j(t'). \tag{1.466}$$

This leads to an additional electronic perturbation of the form

$$\sum_{\mathbf{n}} \sum_{k=1}^{3} \theta(t - t_0) Y_{\mathbf{n}}^{k}(t) \hat{C}_{\mathbf{n}}^{k} \tag{1.467}$$

where

$$\hat{C}_{\mathbf{n}}^{k} = -\int \mathrm{d}\mathbf{x} \ F^k(\mathbf{x} - \mathbf{x_{n0}}) \hat{\rho}(\mathbf{x}) \tag{1.468}$$

and

$$Y_{\mathbf{n}}^{k}(t) = u^k(\mathbf{x_{n0}}; t). \tag{1.469}$$

We therefore get an additional term in the response formula for A_i given by

$$
\begin{aligned}
\frac{\delta A_i(t)}{\delta X_j(t')}\big|_{\text{relax}} &= \int \mathrm{d}t'' \sum_{\mathbf{n}} \sum_{k=1}^{3} \frac{\delta A_i(t)}{\delta Y_{\mathbf{n}}^{k}(t'')} \frac{\delta Y_{\mathbf{n}}^{k}(t'')}{\delta X_j(t')} \\
&= \left(\frac{\mathrm{i}}{\hbar}\right)^2 \theta(t - t') \int_{t'}^{t} \mathrm{d}t'' \sum_{\mathbf{n}} \sum_{k=1}^{3} \langle [\hat{A}_i(t), \hat{C}_{\mathbf{n}}^{k}(t'')] \rangle \langle [\hat{u}^k(\mathbf{x_{n0}}, t''), \hat{B}_j(t')] \rangle \\
&= -\left(\frac{\mathrm{i}}{\hbar}\right)^2 \theta(t - t') \int_{t'}^{t} \mathrm{d}t'' \int \mathrm{d}\mathbf{x} \ \sum_{\mathbf{n}} \langle [\hat{A}_i(t), \hat{\rho}(\mathbf{x}t'')] \rangle (\nabla_{\mathbf{x_{n0}}} v_{\text{ext}})(\mathbf{x}) \cdot \\
&\quad \langle [\hat{\mathbf{u}}(\mathbf{x_{n0}}, t''), \hat{B}_j(t')] \rangle \\
&= -\left(\frac{\mathrm{i}}{\hbar}\right)^2 \theta(t - t') \int_{t'}^{t} \mathrm{d}t'' \int \mathrm{d}\mathbf{x} \ \sum_{\mathbf{n}} \langle [\hat{A}_i(t), \hat{\rho}(\mathbf{x}t'')] \rangle \langle [\mathbf{F}(\mathbf{x} - \mathbf{x_{n0}}) \cdot \\
&\quad \hat{\mathbf{u}}(\mathbf{x_{n0}}, t''), \hat{B}_j(t')] \rangle.
\end{aligned}
$$

This formula will get important later when it comes to electron-phonon interactions. With hindsight to these later applications, we specify this formula to the case of the density response with respect to an external potential which couples to both electrons and nuclei. In that case, $\hat{A}_i$ to be replaced with the electronic density (fluctuation) and $\hat{B}_j$ with the nuclear

density (fluctuation). It will later be shown that the nuclear density fluctuation operator
can be written as

$$\delta\hat{\rho}_{\text{nucl}}(\mathbf{x}t) = -\sum_{\mathbf{n}} \hat{\mathbf{u}}(\mathbf{x_{n0}}t)(\nabla'\delta)(\mathbf{x} - \mathbf{x_{n0}}). \tag{1.470}$$

We therefore get

$$\sum_{\mathbf{n}\in\Gamma} \mathbf{F}(\mathbf{x} - \mathbf{x_{n0}}) \cdot \hat{\mathbf{u}}(\mathbf{x_{n0}}, t'') \tag{1.471}$$

$$= -\sum_{\mathbf{n}\in\Gamma} (\nabla v_{\text{ext}})(\mathbf{x} - \mathbf{x_{n0}}) \cdot \hat{\mathbf{u}}(\mathbf{x_{n0}}, t'') \tag{1.472}$$

$$= -\sum_{\mathbf{n}\in\Gamma} \int d\mathbf{x}' \, (\nabla v_{\text{ext}})(\mathbf{x} - \mathbf{x}')\delta(\mathbf{x}' - \mathbf{x_{n0}}) \cdot \hat{\mathbf{u}}(\mathbf{x_{n0}}, t'') \tag{1.473}$$

$$= \sum_{\mathbf{n}\in\Gamma} \int d\mathbf{x}' \, v_{\text{ext}}(\mathbf{x} - \mathbf{x}')(\nabla\delta)(\mathbf{x}' - \mathbf{x_{n0}}) \cdot \hat{\mathbf{u}}(\mathbf{x_{n0}}, t'') \tag{1.474}$$

$$= -\int d\mathbf{x}' \, v_{\text{ext}}(\mathbf{x} - \mathbf{x}')\delta\hat{\rho}(\mathbf{x}'t). \tag{1.475}$$

Identifying A_i with the electronic charge density, B_j with the nuclear charge density and X_j with an external field, this leads to the intriguing formula

$$\frac{\delta\rho_{\text{el}}(x)}{\delta\varphi_{\text{ext}}(x')}|_{\text{relax}} \equiv \chi_{\text{el}}^{\text{relax}}(x, x') = \int dx''dx'' \chi_{\text{el}}^{\text{frozen}}(x, x'')v(x'', x''')\chi_{\text{nucl}}(x''', x') \tag{1.476}$$

or

$$\chi_{\text{el}}^{\text{tot}} \equiv \chi_{\text{el}}^{\text{frozen}} + \chi_{\text{el}}^{\text{relax}} = \chi_{\text{el}}^{\text{frozen}} + \chi_{\text{el}}^{\text{frozen}}v\chi_{\text{nucl}}^{\text{tot}}. \tag{1.477}$$

This formula is actually of a more fundamental nature and its validity is in now way restricted to the Kubo regime. Instead, this general formula follows directly from a functional chain rule of the form

$$\chi_{\text{el}}^{\text{relax}} \equiv \frac{\delta\rho_{\text{el}}(x)}{\delta\varphi_{\text{ext}}(x')}|_{\text{relax}} \tag{1.478}$$

$$= \int dx'' \, \frac{\delta\rho_{\text{el}}(x)}{\delta v_{\text{ext}}(x'')}\frac{\delta v_{\text{ext}}(x'')}{\delta\varphi_{\text{ext}}(x')} \tag{1.479}$$

$$= \int dx''dx''' \, \frac{\delta\rho_{\text{el}}(x)}{\delta v_{\text{ext}}(x'')}\frac{\delta}{\delta\varphi_{\text{ext}}(x')}v(x'', x''')\rho_{\text{nucl}}(x''') \tag{1.480}$$

$$= \int dx''dx''' \, \chi_{\text{el}}^{\text{frozen}}(x, x'')v(x'', x''')\chi_{\text{nucl}}^{\text{tot}}(x''', x'). \tag{1.481}$$

Behind this formula lurks a still more general structure which can best be elucidated within the Mean Field Theory formalism.

Relaxed Response Theory from the Abstract Mean-Field Theoretical Point of View Mean Field Theory considers two coupled systems with the fundamental Hamiltonian

$$\hat{H}_0^{\mathrm{A}} \otimes \mathbb{1}_{\mathcal{H}_2} + \mathbb{1}_{\mathcal{H}_1} \otimes \hat{H}_0^{\mathrm{B}} + \hat{A}_k \otimes \hat{B}_k. \tag{1.482}$$

The goal of Mean Field Theory is to formulate standard Quantum Mechanics with a time-independent Hamiltonian for the, say, first system. Of course, for such a coupled system this can only be approximately true. As the name suggests, Mean Field Theory achieves this by replacing $\hat{B}_k$ by its "mean field" $B_k = \langle \hat{B}_k \rangle$. The mean field Hamiltonian for the first system then simply reads

$$\hat{H}_0^{\mathrm{A}} + B_k \hat{A}_k. \tag{1.483}$$

To this system, we can now couple a time-dependent perturbation

$$\theta(t - t_0) X_j(t) \hat{A}_j. \tag{1.484}$$

The "naive" or "frozen" Kubo formalism now has it that the expectation value of still another observable, $\delta \hat{A}_i$ say, fluctuates as

$$\delta A_i(t) = \int \mathrm{d}t' \; \chi_{ij}^{\mathrm{A}}(t, t') X_j(t'). \tag{1.485}$$

The relaxed Kubo formalism assumes instead that associated with the perturbation

$$\theta(t - t_0) X_j(t) \hat{A}_j \tag{1.486}$$

of the first system, we have a perturbation

$$\theta(t - t_0) X_j(t) \hat{B}_j \tag{1.487}$$

of the second system. We therefore get the fluctuation

$$\delta B_k(t) = \int \mathrm{d}t' \; \chi_{kj}^{\mathrm{B}}(t, t') X_j(t') \tag{1.488}$$

or

$$\frac{\delta B_k(t)}{\delta X_j(t')} = \chi_{kj}^{\mathrm{B}}(t, t'). \tag{1.489}$$

The total perturbation of of the first system then reads

$$\theta(t - t_0) X_j(t) \hat{A}_j + \theta(t - t_0) \delta B_k(t) \hat{A}_k. \tag{1.490}$$

leading to an additional "relaxed" fluctuation in A_i given by

$$\int \mathrm{d}t' \; \chi_{ik}(t, t') \delta B_k(t'). \tag{1.491}$$

Consequently, the relaxed contribution is

$$\frac{\delta A_i(t)}{\delta X_j(t')}|_{\text{relax}} = \sum_k \int \mathrm{d}t'' \; \chi_{ik}^{\text{A}}(t, t'')\chi_{kj}^{\text{B}}(t'', t'). \tag{1.492}$$

This formula generalizes to

$$\frac{\delta A_i(t)}{\delta X_j(t')}|_{\text{relax}} = \sum_{k,l} \int \mathrm{d}t'' \; \chi_{ik}^{\text{A}}(t, t'')L_{kl}\chi_{lj}^{\text{B}}(t'', t') \tag{1.493}$$

for a fundamental interaction Hamilonian

$$\hat{H}_{\text{int}} = \sum_{i,j} L_{ij}\hat{A}_i \otimes \hat{B}_j. \tag{1.494}$$

This formula will be important in the context of effective interactions.

Self-consistent Equations for Relaxed Response We already showed that

$$\frac{\delta \rho_{\text{el}}(x)}{\delta \varphi_{\text{ext}}(x')}|_{\text{relax}} \equiv \chi_{\text{el}}^{\text{relax}}(x, x') = \int \mathrm{d}x'' \mathrm{d}x''' \chi_{\text{el}}^{\text{frozen}}(x, x'')v(x'', x''')\chi_{\text{nucl}}(x''', x').$$

We will later discuss in detail that the decoupled Hamiltonian is completely symmetric in the electronic und nuclear degrees of freedom. We therefore conclude in anticipation of this result that

$$\frac{\delta \rho_{\text{nucl}}(x)}{\delta \varphi_{\text{ext}}(x')}|_{\text{relax}} \equiv \chi_{\text{nucl}}^{\text{relax}}(x, x') = \int \mathrm{d}x'' \mathrm{d}x'' \chi_{\text{nucl}}^{\text{frozen}}(x, x'')v(x'', x''')\chi_{\text{el}}(x''', x') \tag{1.495}$$

or in an obvious shorthand notation

$$\chi_{\text{el}} = \chi_{\text{el}}^{\text{frozen}} + \chi_{\text{el}}^{\text{frozen}}v\chi_{\text{nucl}} \tag{1.496}$$

$$\chi_{\text{nucl}} = \chi_{\text{nucl}}^{\text{frozen}} + \chi_{\text{nucl}}^{\text{frozen}}v\chi_{\text{el}}. \tag{1.497}$$

Iterating this system of equations shows that we have a formal solution for the total response functions in terms of the frozen response functions given by

$$\chi_{\text{el}} = (1 - v\chi_{\text{nucl}}^{\text{frozen}}v\chi_{\text{el}}^{\text{frozen}})^{-1}(\chi_{\text{el}}^{\text{frozen}} + \chi_{\text{el}}^{\text{frozen}}v\chi_{\text{nucl}}^{\text{frozen}}) \tag{1.498}$$

$$\chi_{\text{nucl}} = (1 - v\chi_{\text{el}}^{\text{frozen}}v\chi_{\text{nucl}}^{\text{frozen}})^{-1}(\chi_{\text{nucl}}^{\text{frozen}} + \chi_{\text{nucl}}^{\text{frozen}}v\chi_{\text{el}}^{\text{frozen}}). \tag{1.499}$$

Furthermore, with $v_{\text{phon}} = v\chi_{\text{nucl}}v$, we find immediately

$$\chi_{\text{el}}^{\text{relax}}v = \chi_{\text{el}}^{\text{frozen}}v_{\text{phon}} \tag{1.500}$$

where $\chi_{\text{el}}^{\text{relax}} = \chi_{\text{el}}^{\text{tot}} - \chi_{\text{el}}^{\text{frozen}}$.

2. Second Quantization

2.1. Many-Body Quantum Mechanics

2.1.1. Fock Space

Quantization of Multiparticle Systems The quantization of a system of one particle with position degree of fredom $\mathbf{x}$, conjugate momentum $\mathbf{p}$ and phase space $\mathbb{R}^3 \times \mathbb{R}^3$ is implemented by postulating the commutator relations

$$
\begin{aligned}
[\hat{x}^i, \hat{p}_j] &= \mathrm{i}\hbar \delta^i{}_j \\
[\hat{x}^i, \hat{x}^j] &= 0 \\
[\hat{p}_i, \hat{p}_j] &= 0.
\end{aligned}
$$

The John-von-Neumann uniqueness theorem says that these commutator relations have – up to unitary equivalence – an unique irreducible Hilbert space representation given by

$$
\begin{aligned}
(\hat{x}^i \psi)(\mathbf{x}) &= x^i \psi(\mathbf{x}) & (2.1) \\
(\hat{p}_i \psi)(\mathbf{x}) &= -\mathrm{i}\hbar \partial_i \psi(\mathbf{x}). & (2.2)
\end{aligned}
$$

where $\psi \in \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x})$. If we deal instead with two particles, the commutator relations read

$$
\begin{aligned}
[\hat{x}^{i\alpha}, \hat{p}_j^\beta] &= \mathrm{i}\hbar \delta^i{}_j \delta^{\alpha\beta} \\
[\hat{x}^{i\alpha}, \hat{x}_j^\beta] &= 0 \\
[\hat{p}_i^\alpha, \hat{p}_j^\beta] &= 0,
\end{aligned}
$$

(with $\alpha, \beta \in \{1, 2\}$) and the (up to unitary equivalence) uniquely defined representation reads

$$
\begin{aligned}
(\hat{x}^{i\alpha} \psi)(\mathbf{x}_1, \mathbf{x}_2) &= x^{i\alpha} \psi(\mathbf{x}_1, \mathbf{x}_2) & (2.3) \\
(\hat{p}_i^\beta \psi)(\mathbf{x}_1, \mathbf{x}_2) &= -\mathrm{i}\hbar \partial_i^\beta \psi(\mathbf{x}_1, \mathbf{x}_2). & (2.4)
\end{aligned}
$$

This makes it clear that the state is now a function on the configuration space $\mathbb{R}^6$. In other words, such a two particle system can by no means considered as a classical Field Theory

(dealing with fields in ordinary three-dimensional space). We can formalize as follows: if there are two systems with Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$, then the total system has the Hilbert space $\mathcal{H}_1 \otimes \mathcal{H}_2$. In particular, if the two particles have Hilbert spaces $\mathcal{H}_1 = \mathcal{H}_2 = \mathcal{H} = \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x})$, then the two-particle system has the Hilbert space

$$\mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \otimes \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \simeq \mathcal{L}^2(\mathbb{R}^3 \oplus \mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x}) \simeq \mathcal{L}^2(\mathbb{R}^6, \mathbb{C}, \mathrm{d}\mathbf{x}). \tag{2.5}$$

If $\{\varphi_\alpha\}$ denotes a complete orthonormal system in $\mathcal{H}$, then $\{\varphi_\alpha \otimes \varphi_\beta\}$ is a complete orthonormal system in $\mathcal{H} \otimes \mathcal{H}$, where

$$\langle \mathbf{x}_1 \otimes \mathbf{x}_2 | \varphi_\alpha \otimes \varphi_\beta \rangle \equiv \langle \mathbf{x}_1 \mathbf{x}_2 | \varphi_\alpha \varphi_\beta \rangle = \varphi_\alpha(\mathbf{x}_1) \varphi_\beta(\mathbf{x}_2). \tag{2.6}$$

Fock Space We can be easily generalize to a system of N particles by defining the corresponding Hilbert space as

$$\mathcal{H}^N = \bigotimes_{i=1}^{N} \mathcal{H}. \tag{2.7}$$

Furthermore, we introduce a zero particle space defined as $\mathcal{H}^0 = \mathbb{C}$. The unit vector which spans $\mathcal{H}^0$ is denoted by $|0\rangle$ and called vacuum. If we want to consider states with arbitrary particle number (including in particular superpositions of states with different particle number), we have to introduce the *Fock space* over $\mathcal{H}$ defined as

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}^N = \bigoplus_{N=0}^{\infty} \bigotimes_{i=1}^{N} \mathcal{H}. \tag{2.8}$$

Elements of $\mathcal{F}$ are infinite sequences $\Psi = (\Psi_0, \Psi_1, \Psi_2, \ldots)$ where every Ψ_N is a N-particle wave-function in $\mathcal{H}^N$ and

$$\|\Psi\|_{\mathcal{F}}^2 = \sum_{i=0}^{\infty} \|\Psi_i\|_{\mathcal{H}^i}^2 < \infty. \tag{2.9}$$

In this parlance, $|0\rangle = (1, 0, 0, \ldots)$. The metric in the N-particle Hilbert space is given in terms of the scalar product as $\|\Psi_N\|_{\mathcal{H}^N} = \sqrt{\langle \Psi_N | \Psi_N \rangle_{\mathcal{H}^N}}$ where

$$\langle \Psi_N | \Phi_N \rangle_{\mathcal{H}^N} = \int \mathrm{d}\mathbf{x}_1 \ldots \mathbf{x}_N \; \Psi_N^*(\mathbf{x}_1, \ldots, \mathbf{x}_N) \Phi_N(\mathbf{x}_1, \ldots, \mathbf{x}_N). \tag{2.10}$$

The following exposition and the corresponding proofs are sketchy (for details, see e.g. [31, 39, 86, 87, 89]).

Completely Symmetric and Completely Antisymmetric States By the Bose-Fermi alternative, states of indistinguishable particles have to be either completely symmetric or completely antisymmetric. Therefore, the states of N indistinguishable particles are actually

restricted to a subspace of $\otimes^N \mathcal{H}$. It can easily be shown that the completely (anti)symmetric elements of $\otimes^N \mathcal{H}$ form a Hilbert subspace, i.e. a subspace which is closed in the norm induced by the scalar product. From now on, the completely symmetric subspace of $\otimes^N \mathcal{H}$ will be denoted by $\vee^N \mathcal{H}$ and the completely antisymmetric subspace will be denoted by $\wedge^N \mathcal{H}$. The corresponding subspaces of $\mathcal{F}$ are called *bosonic Fock space* and *fermionic Fock space*. We introduce the (anti)symmetrizing operator $\mathbb{A}_\pm^N \equiv \mathbb{A}_\pm : \otimes^N \mathcal{H} \to \otimes^N \mathcal{H}$ defined by

$$\mathbb{A}_\pm(\varphi_1 \otimes \ldots \otimes \varphi_N) = \frac{1}{N!} \sum_{\pi \in S^N} (\pm 1)^\pi \varphi_{\pi(1)} \otimes \ldots \otimes \varphi_{\pi(N)} \tag{2.11}$$

where $(-1)^\pi$ means -1 up to the sign of the respective permutation. In the position state basis, the action of the (anti)-symmetrizer reads

$$\langle \mathbf{x}_1 \ldots \mathbf{x}_N | \mathbb{A}_\pm(\varphi_1 \otimes \ldots \otimes \varphi_N) \rangle = \frac{1}{N!} \sum_{\pi \in S^N} (\pm 1)^\pi \varphi_1(\mathbf{x}_{\pi(1)}) \cdot \ldots \cdot \varphi_N(\mathbf{x}_{\pi(N)}). \tag{2.12}$$

Completely symmetrized, normalized products will be denoted by $\varphi_{\alpha_1} \vee \ldots \vee \varphi_{\alpha_N}$ and completely antisymmetrized, normalised products will be denoted by $\varphi_{\alpha_1} \wedge \ldots \wedge \varphi_{\alpha_N}$. That implies

$$\varphi_1 \vee \ldots \vee \varphi_N = \sqrt{\frac{N!}{n_1! \ldots n_i!}} \mathbb{A}_+ \varphi_1 \otimes \ldots \otimes \varphi_N \tag{2.13}$$

$$\varphi_1 \wedge \ldots \wedge \varphi_N = \sqrt{N!} \mathbb{A}_- \varphi_1 \otimes \ldots \otimes \varphi_N \tag{2.14}$$

where $n_1 + \ldots + n_i = N$ and are n_j the occupation numbers ≥ 1 of orbitals entering into the tensor product $\varphi_1 \otimes \ldots \otimes \varphi_N$. $\mathbb{A}_\pm$ is the *projector* on $\vee^N \mathcal{H}$ or $\wedge^N \mathcal{H}$ respectively. In particular, this means

$$\mathbb{A} = \mathbb{A}^2 = \mathbb{A}^\dagger \tag{2.15}$$

and

$$\mathbb{A}_+|_{\vee^N \mathcal{H}} = \mathbb{1} \tag{2.16}$$

$$\mathbb{A}_-|_{\wedge^N \mathcal{H}} = \mathbb{1}, \tag{2.17}$$

i.e. $\mathbb{A}_\pm \Psi = \Psi$ if $\Psi \in \otimes^N \mathcal{H}$ is already (anti)symmetric. Furthermore, if $\{\varphi_\alpha\}$ denotes a complete orthonormal system in $\mathcal{H}$, then $\{\varphi_{\alpha_1} \vee \ldots \vee \varphi_{\alpha_N}\}$ is a complete orthonormal system in $\vee^N \mathcal{H}$ and $\{\varphi_{\alpha_1} \wedge \ldots \wedge \varphi_{\alpha_N}\}$ is a complete orthonormal system in $\wedge^N \mathcal{H}$. $\varphi_{\alpha_1} \wedge \ldots \wedge \varphi_{\alpha_N}$ is called a *Slater determinant* and reads in the position state basis

$$\langle \mathbf{x}_1 \ldots \mathbf{x}_N | \varphi_{\alpha_1} \wedge \ldots \wedge \varphi_{\alpha_N} \rangle = \frac{1}{\sqrt{N!}} \det(\varphi_{\alpha_i}(\mathbf{x}_j)). \tag{2.18}$$

Equation (2.10) induces (by restriction) a scalar product on $\wedge^N \mathcal{H}$ which reads in terms of the orbitals

$$\langle \psi_1 \wedge \ldots \wedge \psi_N | \varphi_1 \wedge \ldots \wedge \varphi_N \rangle_{\wedge^N \mathcal{H}} = \det(\langle \psi_i | \varphi_j \rangle_{\mathcal{H}}). \tag{2.19}$$

In particular, for two Slater determinants $\Psi = \varphi_{i_1} \wedge \ldots \wedge \varphi_{i_N}$ and $\Psi = \varphi_{j_1} \wedge \ldots \wedge \varphi_{j_N}$ over the same complete, orthonormal set of orbitals $\{\varphi_i \in \mathcal{H} | i \in \mathbb{N}\}$ we have

$$\langle \varphi_{i_1} \wedge \ldots \wedge \varphi_{i_N} | \varphi_{j_1} \wedge \ldots \wedge \varphi_{j_N} \rangle_{\wedge^N \mathcal{H}} = \det(\delta_{i_k j_l}) = \begin{cases} (-1)^\pi & \text{if } \{i_1, \ldots, i_N\} = \{j_1, \ldots, j_N\} \\ 0 & \text{otherwise.} \end{cases}$$

where π is the permutation which translates the tupel $(i_1, \ldots, i_N)$ into $(j_1, \ldots, j_N)$.

Creators and Annihilators Finally, for Hilbert space functions $\varphi \in \mathcal{H}$, we introduce creators $a^\dagger(\varphi) : \mathcal{H}^N \to \mathcal{H}^{N+1}$ and annihilators $a(\varphi) : \mathcal{H}^N \to \mathcal{H}^{N-1}$ which are componentwise defined by

$$a(\varphi)(\varphi_1 \otimes \ldots \otimes \varphi_N) = \sqrt{N} \langle \varphi | \varphi_1 \rangle \, \varphi_2 \otimes \ldots \otimes \varphi_N \tag{2.20}$$

$$a^\dagger(\varphi)(\varphi_1 \otimes \ldots \otimes \varphi_N) = \sqrt{N+1} \, \varphi \otimes \varphi_1 \otimes \varphi_2 \otimes \ldots \otimes \varphi_N. \tag{2.21}$$

These operators push forward to operators $\mathcal{F} \to \mathcal{F}$. From the explicit definition, we read off that $\varphi \mapsto a^\dagger(\varphi)$ is a linear mapping whereas $\varphi \mapsto a(\varphi)$ is antilinear. Fermionic creators and annihilators are defined by

$$a^\dagger_-(\varphi) = \mathbb{A}_- a^\dagger(\varphi) \mathbb{A}_- \tag{2.22}$$

$$a_-(\varphi) = \mathbb{A}_- a(\varphi) \mathbb{A}_-. \tag{2.23}$$

Bosonic creators and annihilators are defined by replacing $\mathbb{A}_-$ with $\mathbb{A}_+$. From now on, we will omit creator and annihilator indices hoping that the character of the operators will be clear from the context.

Lemma 2.1.1 *For* $\mathrm{SLATER}(\varphi_1, \ldots, \varphi_N) \equiv \varphi_1 \wedge \ldots \wedge \varphi_N$ *we have*

$$a^\dagger(\varphi_{N+1}) \mathrm{SLATER}(\varphi_1, \ldots, \varphi_N) = (-1)^N \mathrm{SLATER}(\varphi_1, \ldots, \varphi_{N+1}) \tag{2.24}$$

$$a(\varphi_i) \mathrm{SLATER}(\varphi_1, \ldots, \varphi_N) = (-1)^{i-1} \mathrm{SLATER}(\varphi_1, \ldots, \widehat{\varphi_i}, \ldots, \varphi_{N+1}) \tag{2.25}$$

where $\{\varphi_i\}_{i \in \mathbb{N}}$ *is a complete, orthonormal system. Furthermore,*

$$a^\dagger(\varphi_i) \mathrm{SLATER}(\varphi_1, \ldots, \varphi_N) = 0 \tag{2.26}$$

$$a(\varphi_j) \mathrm{SLATER}(\varphi_1, \ldots, \varphi_N) = 0 \tag{2.27}$$

for $i \in \{1, \ldots, N\}$ *and* $j > N$.

Proof The last statement is trivial because it follows directly from the construction of the creators and annihilators. We come to

$$a^\dagger(\varphi_{N+1})\text{SLATER}(\varphi_1, \ldots, \varphi_N) = \text{SLATER}(\varphi_1, \ldots, \varphi_{N+1}).$$

First, note that $a^\dagger(\varphi)$ is linear in φ. Furthermore, the whole expression is completely anti-symmetric due to the construction of the fermionic operators. As $\text{SLATER}(\varphi_1, \ldots, \varphi_N)$ is linear in every slot anyway, the whole expression is completely antisymmetric and linear and therefore has to be proportional to $\text{SLATER}(\varphi_1, \ldots, \varphi_{N+1})$. The only thing to be checked is the normalisation. This, however, follows from the fact that $\sqrt{N+1}\mathbb{A}_-\varphi_1 \otimes \ldots \otimes \varphi_{N+1}$ is normalized to one. A similar argument works for $a(\varphi)$. The prefactor can be shown from the definition of the antisymmetrization operator.

Lemma 2.1.2 *For $\Psi \in \wedge^N\mathcal{H}$ and $\varphi \in \mathcal{H}$ with $\|\Psi\|_{\wedge^N\mathcal{H}} = \|\varphi\|_{\mathcal{H}} = 1$, we have*

$$\|a^\dagger(\varphi)\Psi\|_{\wedge^{N+1}\mathcal{H}} \leq 1 \tag{2.28}$$

$$\|a(\varphi)\Psi\|_{\wedge^N\mathcal{H}} \leq 1. \tag{2.29}$$

Proof Expand Ψ in the Slater determinants Φ_I over $\{\varphi_i\}_{i\in\mathbb{N}}$ and assume without loss of generality that $\varphi \in \{\varphi_i\}_{i\in\mathbb{N}}$, i.e. $\Psi = \sum_I c_I \Phi_I$ with $\sum_I |c_I|^2 = 1$. Therefore $a^\dagger(\varphi)\Psi = \sum_I c_I a^\dagger(\varphi)\Phi_I = \sum_I c_I \Phi_I'$. Now, with the Φ_I being orthonormal (in $\wedge^N\mathcal{H}$), the Φ_I' are again orthonormal (in $\wedge^{N+1}\mathcal{H}$) or zero. Therefore $\|\sum_I c_I \Phi_I'\| \leq 1$ which proves the lemma. A similar argument works in the annihilator case.

Remark Note that the lemma shows in particular that creators and annihilators are bounded operators $\mathcal{H}^N \to \mathcal{H}^{N\pm 1}$ and bounded operators $\mathcal{F} \to \mathcal{F}$. (This last statement does not hold true for bosonic creators and annihilators which are unbounded on $\mathcal{F}$.) Furthermore, the lemma is in accord with[1]

$$\langle\Psi|a_i^\dagger a_i\Psi\rangle = \langle a_i\Psi|a_i\Psi\rangle \leq 1 \tag{2.30}$$

implying that the occupation number of state i is never bigger than 1.

Commutation and Anticommutation Rules It is straightforward to show that for fermionic creators and annihilators the following anticommutation relations (CAR) hold:

$$[a(\varphi), a^\dagger(\psi)]_+ = \langle\varphi|\psi\rangle_{\mathcal{H}} \, \mathbb{1}_{\mathcal{F}} \tag{2.31}$$

$$[a(\varphi), a(\psi)]_+ = 0 \tag{2.32}$$

$$[a^\dagger(\varphi), a^\dagger(\psi)]_+ = 0. \tag{2.33}$$

---

[1] If the function φ created or annihilated by $a^\dagger(\varphi)$ or $a(\varphi)$ respectively can be characterized by some index (tupel) of quantum number, k say, we write concisely $a^\dagger(\varphi_k) = a_k^\dagger$.

The bosonic operators fulfill the corresponding commutation relations (CCR).

Field Operators For the creators and annihilators of the (generalized) position eigenstates, we write

$$a^\dagger(\delta_\mathbf{x}) \;=\; \hat{\psi}^\dagger(\mathbf{x}) \tag{2.34}$$

$$a(\delta_\mathbf{x}) \;=\; \hat{\psi}(\mathbf{x}). \tag{2.35}$$

For reasons which will become clear later, the $\hat{\psi}^{(\dagger)}(\mathbf{x})$ are called *field operators* (corresponding to the Schrödinger field and its complex conjugate). The CAR for the field operators reads

$$[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{x}')]_+ = \delta(\mathbf{x} - \mathbf{x}'). \tag{2.36}$$

As the action of the annihilator $a(\varphi)$ on $\mathcal{H}^N$ reads in the position state basis explicitly

$$(a(\varphi)\Psi)(\mathbf{x}_2, \ldots, \mathbf{x}_N) = \sqrt{N} \int \mathrm{d}\mathbf{x}_1 \; \varphi^*(\mathbf{x}_1)\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{2.37}$$

we find for $\varphi = \delta_\mathbf{x}$ the important formula

$$(\hat{\psi}(\mathbf{x})\Psi)(\mathbf{x}_2, \ldots, \mathbf{x}_N) = \sqrt{N}\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N). \tag{2.38}$$

Note, however, that this formula is a typical non-relativistic result which in no way generalizes to all kinds of field operators.

Quantum Harmonic Oscillator as a Many-Body System Consider a particle with no degree of freedom. The corresponding state space $\mathcal{H}$ is obviously $\mathbb{C}$ and the Hamiltonian operator is a constant, E_0 say. The one-particle Schrödinger equation then reads

$$\mathrm{i}\hbar\partial_t\varphi(t) = E_0\varphi(t) \tag{2.39}$$

where $\forall t \in \mathbb{R} : \varphi(t) \in \mathbb{C}$. Now, consider the system of arbitrarily many, indistinguishable particles without degree of freedom. This system has a degree of freedom, namely the particle number N. As we have the general relation

$$\bigotimes_{i=1}^{N} \mathbb{C} = \mathbb{C} \tag{2.40}$$

the Fock space turns out to be ℓ^2, i.e. the set of all sequences $(c_0, c_1, \ldots, c_n, \ldots)$ with $\sum_{i=0}^{\infty} |c_i|^2 < \infty$. As there is now only one state in the one-particle Hilbert space, the only nontrivial CCR reads

$$[a, a^\dagger] = 1 \tag{2.41}$$

which is obviously the harmonic oscillator CCR. This gives an intuitive justification for the fact that the spectrum of the harmonic oscillator consists of infinitely many equidistant levels. The usual representation on $\mathcal{L}^2(\mathbb{R}, \mathbb{C}, \mathrm{d}\mathbf{x})$ given by

$$
\begin{aligned}
a &= \frac{1}{\sqrt{2}}(\hat{x} + \mathrm{i}\hat{p}) \\
a^\dagger &= \frac{1}{\sqrt{2}}(\hat{x} - \mathrm{i}\hat{p})
\end{aligned}
$$

is equivalent to the Fock space representation. The action of a and $a^\dagger$ reads in the Fock space

$$
\begin{aligned}
a(c_0, c_1, c_2, \ldots) &= (\sqrt{1}c_1, \sqrt{2}c_2, \ldots) \\
a^\dagger(c_0, c_1, c_2, \ldots) &= (0, \sqrt{1}c_0, \sqrt{2}c_1, \sqrt{3}c_2, \ldots).
\end{aligned}
$$

This is – up to the prefactors – the so-called shift-algebra well-known from functional analysis. A similar construction using $[a, a^\dagger]_+ = 1$ yields the 2-level system.

2.1.2. Second Quantization of Operators

Self-Adjoint Operators Let $\hat{A}$ be a self-adjoint operator on the one-particle Hilbert space $\mathcal{H}$. Second Quantization is an algebra homomorphism of the self-adjoint operators in $\mathcal{H}$ into the linear operators in $\mathcal{F}(\mathcal{H})$ which is explicitly given by:

$$
q(\hat{A}) = \mathbf{0} \oplus A \oplus (A \otimes \mathbb{1} + \mathbb{1} \otimes A) \oplus (A \otimes \mathbb{1} \otimes \mathbb{1} + \mathbb{1} \otimes A \otimes \mathbb{1} + \ldots) \oplus \ldots \tag{2.42}
$$

It can be shown that $q(\hat{A})$ is indeed essentially self-adjoint on $\mathcal{F}$. A simple example is the projection operator $|\varphi_i\rangle\langle\varphi_i|$, $\varphi_i \in \mathcal{H}$, the second quantization of which is the occupation number operator $\hat{n}_i$. Correspondingly, the second quantization of the identity (sum over projectors) yields the total number operator $\hat{N}$. The homomorphism property means that

$$
q(\lambda\hat{A} + \mu\hat{B}) = \lambda q(\hat{A}) + \mu q(\hat{B}) \tag{2.43}
$$

and, as a simple calculation shows, that the commutator relation

$$
[\hat{A}, \hat{B}] = \hat{C} \tag{2.44}
$$

implies

$$
[q(\hat{A}), q(\hat{B})] = q(\hat{C}). \tag{2.45}
$$

In other words, second quantization preserves commutator relations. Note, however, that even for bounded $\hat{A}$, $q(\hat{A})$ is in general unbounded. ($\mathbb{1} \in \mathcal{B}(\mathcal{H})$ bounded; $q(\mathbb{1}) = \hat{N}$ unbounded.)

Unitary Operators In the case of a unitary operator, $\hat{U}$, we define:

$$q(\hat{U}) = \mathbb{1} \oplus \hat{U} \oplus (\hat{U} \otimes \hat{U}) \oplus \ldots \oplus (\otimes_{i=1}^{n} \hat{U}) \oplus \ldots \tag{2.46}$$

This definition is consistent with the fact the self-adjoint operators generate one-parameter unitary groups. In fact, if $\hat{H}$ generates the time-evolution $\hat{U}(t) = \exp(-\mathrm{i}/\hbar \hat{H}t)$ then the second quantized (free) time evolution $q(\hat{U})$ is generated by $q(\hat{H})$. Similarly, one can define the second quantization of two-particle operators (e.g. the two particle potential). With these definitions, one shows easily that

$$\hat{U}a^{\dagger}(\varphi)\hat{U}^{-1} = a^{\dagger}(\hat{U}\varphi) \tag{2.47}$$

$$\hat{U}a(\varphi)\hat{U}^{-1} = a(\hat{U}\varphi). \tag{2.48}$$

In particular, if $\hat{U}(t) = \exp(-\frac{\mathrm{i}}{\hbar}\hat{H}t)$, then

$$a^{\dagger}(\varphi, t) = \hat{U}^{\dagger}(t)a^{\dagger}(\varphi)\hat{U}(t) = a^{\dagger}(\hat{U}(-t)\varphi) \tag{2.49}$$

$$\mathrm{i}\hbar\partial_t a^{\dagger}(\varphi, t) = [a^{\dagger}(\varphi), \hat{H}]. \tag{2.50}$$

For the field operators this implies

$$\hat{\psi}^{\dagger}(\mathbf{x}t) = \hat{U}^{-1}a^{\dagger}(\delta_{\mathbf{x}})\hat{U} = a^{\dagger}(\hat{U}(-t)\delta_{\mathbf{x}}), \tag{2.51}$$

i.e. $\hat{\psi}^{\dagger}(\mathbf{x}t)$ creates the wave-function $\hat{U}(-t)\delta_{\mathbf{x}}$ which after a time lapse t will take the form of a Dirac delta $\hat{U}(t)\hat{U}(-t)\delta_{\mathbf{x}} = \delta_{\mathbf{x}}$ localized at $\mathbf{x}$. In other words, $\hat{\psi}(\mathbf{x}t)$ creates a particle at the space-time point $(\mathbf{x}t)$. Indeed, for an energy eigenstate $\varphi_n(\mathbf{x}t) = \varphi_n(\mathbf{x})\mathrm{e}^{-\mathrm{i}/\hbar\varepsilon_n t}$ we find

$$
\begin{aligned}
\langle \mathbf{x}t | \varphi_n \rangle &= \langle 0 | \hat{\psi}(\mathbf{x}t) | \varphi_n \rangle \\
&= \langle 0 | \hat{\psi}(\mathbf{x}t) a_n^{\dagger} | 0 \rangle \\
&= \langle 0 | \sum_m \mathrm{e}^{-\mathrm{i}\frac{\varepsilon_n}{\hbar}t} \varphi_m(\mathbf{x}) a_m a_n^{\dagger} | 0 \rangle \\
&= \sum_m \mathrm{e}^{-\mathrm{i}\frac{\varepsilon_n}{\hbar}t} \varphi_m(\mathbf{x}) \langle 0 | a_m a_n^{\dagger} | 0 \rangle \\
&= \sum_m \mathrm{e}^{-\mathrm{i}\frac{\varepsilon_n}{\hbar}t} \varphi_m(\mathbf{x}) \langle 0 | \delta_{mn} | 0 \rangle \\
&= \mathrm{e}^{-\mathrm{i}\frac{\varepsilon_n}{\hbar}t} \varphi_n(\mathbf{x}) \langle 0 | 0 \rangle \\
&= \mathrm{e}^{-\mathrm{i}\frac{\varepsilon_n}{\hbar}t} \varphi_n(\mathbf{x}).
\end{aligned}
$$

Normal Form Usually (at least for all bounded operators; cf. [9]), it is possible to write $\hat{A}$ in terms of creation and annihilation operators (normal form). The normal form of the second-quantized operator $q(\hat{A})$ where $\hat{A} \in \mathcal{B}(\mathcal{H})$ reads

$$q(\hat{A}) = \sum \langle \varphi_i | \hat{A} | \varphi_j \rangle a_i^\dagger a_j \tag{2.52}$$

where i, j index a complete orthogonal system in $\mathcal{H}$. This can be easily seen by thinking of $\hat{A}$ as replacing every φ with $\hat{A}\varphi$ and using the important formula

$$q\left(|\varphi_i\rangle\langle\varphi_j|\right) = a^\dagger(\varphi_i) a(\varphi_j). \tag{2.53}$$

Consequently,

$$q(\hat{A}) = \sum_i a^\dagger(\hat{A}\varphi_j) a(\varphi_j) = \sum_i a^\dagger(\langle\varphi_i|\hat{A}|\varphi_j\rangle\varphi_i) a(\varphi_j) \tag{2.54}$$

where we used the linearity of $\varphi \mapsto a^\dagger(\varphi)$. The restriction of $q(\hat{A})$ to $\mathcal{H}$ then coincides with $\hat{A}$. If we allow for generalized coefficients (i.e. distribution valued), then every second quantization $q(\hat{A})$ can be written in terms of creators and annihilators. For example, the second quantized kinetic energy operators reads:

$$q(\hat{T}) = -\frac{\hbar^2}{2m} \int d\mathbf{x} \ \hat{\psi}^\dagger(\mathbf{x}) \Delta_{\mathbf{x}} \hat{\psi}(\mathbf{x}). \tag{2.55}$$

Of course,

$$q(\hat{T})|_{\mathcal{H}^N} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_{\mathbf{x}_i}. \tag{2.56}$$

From the expression for $q(\hat{T})$ we read off the following rule of thumb for the construction of the second quantization in terms of the field operators: (i) write the expectation value of the first quantized one-particle operator in some state and (ii) replace in this formal expression the orbital with the field operator (annihilator) and the complex conjugate orbital with the adjoint field operator (creator). If we promote a one-particle Hamiltonian $\hat{H}$ to a second quantized Hamiltonian $q(\hat{H})$ and postulate a Schrödinger equation

$$i\hbar\partial_t \Psi(t) = q(\hat{H})\Psi(t) \tag{2.57}$$

for $\Psi(t) \in \mathcal{F} \ \forall t \in \mathbb{R}$, then the resulting theory is componentwise equivalent to standard Quantum Mechanics (cf. [89] Chapter 6), i.e.

$$i\hbar\partial_t \ \mathrm{pr}_{\mathcal{H}^N} \Psi(t) = q(\hat{H})|_{\mathcal{H}^N} \ \mathrm{pr}_{\mathcal{H}^N} \Psi(t) \tag{2.58}$$

where $\mathrm{pr}_{\mathcal{H}^N} \Psi(t)$ is an ordinary N-particle wave-function. This result loses its validity as soon as $[\hat{H}, \hat{N}] \neq 0$, i.e. as soon as the Hamiltonian does not conserve the particle number. For a typical two-body multiplicative potential $v(\mathbf{x}_1 - \mathbf{x}_2)$, we can write the second quantization:

$$\hat{V} = q(v) = \frac{1}{2} \sum \langle i_1 i_2 | v | i_3 i_4 \rangle a_{i_1}^\dagger a_{i_2}^\dagger a_{i_4} a_{i_3}. \tag{2.59}$$

The restriction of $\hat{V}$ on $\mathcal{H}^2$ then coincides with the multiplicative potential $v(\mathbf{x}_1 - \mathbf{x}_2)$. On $\mathcal{H} = \mathcal{H}^1$, the operator $\hat{V}$ vanishes identically.

Density Operator The second quantized *density operator* is given by

$$\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x}). \tag{2.60}$$

In the pure N-particle state Ψ the expectation value equals

$$n(\mathbf{x}) = \langle\Psi|\hat{n}(\mathbf{x})|\Psi\rangle = N \int d\mathbf{x}_2 \dots d\mathbf{x}_N \ \Psi^*(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N)\Psi(\mathbf{x}, \mathbf{x}_2, \dots, \mathbf{x}_N). \tag{2.61}$$

This shows that $\hat{n}(\mathbf{x})$ is the second-quantization of the first quantized integral operator $\delta(\mathbf{x} - \hat{\mathbf{x}})$, i.e.:

$$\hat{n}(\mathbf{x}) = \delta(\mathbf{x} - \hat{\mathbf{x}}_1) \oplus (\delta(\mathbf{x} - \hat{\mathbf{x}}_1) \otimes \mathbb{1}_{\mathcal{H}_2} + \mathbb{1}_{\mathcal{H}_1} \otimes \delta(\mathbf{x} - \hat{\mathbf{x}}_2)) \oplus \dots \tag{2.62}$$

The density operator can also be considered as the occupation number operator for the position eigenstate. In particular, the density-operator evaluated in the one-particle state ψ gives $n(\mathbf{x}) = \langle\psi|\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}(\mathbf{x})|\psi\rangle = \psi^*(\mathbf{x})\psi(\mathbf{x})$.[2] Now, consider the Fourier transform of the expectation value of the density

$$n(\mathbf{k}) = \int d\mathbf{x} \ \exp(-i\mathbf{k}\mathbf{x})n(\mathbf{x}). \tag{2.63}$$

One shows easily, that $n(\mathbf{k})$ is the expectation value of the operator

$$\hat{n}(\mathbf{k}) = \sum_\mathbf{q} a^\dagger_{\mathbf{k}-\mathbf{q}} a_\mathbf{q}. \tag{2.64}$$

Finally, the time derivative of the density operator yields

$$\partial_t \hat{n}(\mathbf{x}) = -\nabla \cdot \hat{\mathbf{j}}(\mathbf{x}) \tag{2.65}$$

which implies current-conservation for the respective expectation values. Note that the derivation of the current conservation in standard (one-particle) Quantum Mechanics would imply for a N-particle system a conserved current on the configuration space $\mathbb{R}^N$.

Density Matrices A density matrix $\hat{\rho}$ is a bounded operator, i.e. $\rho \in \mathcal{B}(\mathcal{H})$, with (i) $\hat{\rho}^\dagger = \hat{\rho}$ (self-adjointness), (ii) $\hat{\rho} \geq 0$ (positive definiteness) and (iii) $\mathrm{Tr}_\mathcal{H}\ \hat{\rho} = 1$ (trace-class-property).

---

[2]Often, $\sum_{i=1}^N \delta(\mathbf{x} - \mathbf{x}_i)$ is adressed as the (second quantized) density operator. Strictly speaking, this is only the integral kernel. By contrast, $\delta(\mathbf{x} - \hat{\mathbf{x}})$ is rarely identified as the (first quantized) density operator. Notable exceptions include [35, 70].

Such an operator is necessarily compact and hence has a discrete spectrum. Consequently, $\hat{\rho}$ has a spectral resolution of the form

$$\hat{\rho} = \sum_s \rho_s |\Psi_s\rangle\langle\Psi_s| \tag{2.66}$$

where $\rho_s > 0$ and $\sum_s \rho_s = 1$. ρ_s can be interpreted as the "classical probability" (incoherent superposition) for the system to be in the state Ψ_s. The expectation value of the observable $\hat{A}$ in the state $\hat{\rho}$ is defined via

$$\langle\hat{A}\rangle_{\hat{\rho}} = \mathrm{Tr}_{\mathcal{H}}\ \hat{\rho}\hat{A}. \tag{2.67}$$

The trace-class operators form a two-sided ideal in $\mathcal{B}(\mathcal{H})$. Therefore, with $\hat{\rho}$ the operator $\hat{\rho}\hat{A}$ is again trace-class and hence $\mathrm{Tr}_{\mathcal{H}}\ \hat{\rho}\hat{A}$ converges. The density matrix corresponding to a pure state $\Psi \in \mathcal{H}$ is given by the projector $|\Psi\rangle\langle\Psi|$.

Reduced Density Matrices Now, let $\mathcal{H} = \mathcal{H}_1 \otimes \mathcal{H}_2$. The reduced density matrix $\hat{\rho}_1$ is defined by the partial trace

$$\hat{\rho}_1 = \mathrm{Tr}_{\mathcal{H}_2}\ \hat{\rho}. \tag{2.68}$$

Then, $\hat{\rho}_1$ is a density matrix on $\mathcal{H}_1$. $\hat{\rho}_1$ corresponds to the measurement of observables of the form $\hat{A} = \hat{A}_1 \otimes \mathbb{1}_{\mathcal{H}_2}$ in the sense that

$$\mathrm{Tr}_{\mathcal{H}}\ \hat{\rho}\hat{A} = \mathrm{Tr}_{\mathcal{H}_1}\ \hat{\rho}_1\hat{A}_1. \tag{2.69}$$

Multi-Electron Reduced Density Matrices Consider now a many-electron state $\Psi \in \mathcal{H}^N = \wedge^N \mathcal{H}$. The *s-particle reduced density matrix* is defined by

$$\hat{\rho}_s = \mathrm{Tr}_{\mathcal{H}^{N-s}}\ |\Psi\rangle\langle\Psi| \tag{2.70}$$

Evaluating the trace in the position-state basis shows that

$$\langle \mathbf{x}_1 \ldots \mathbf{x}_s|\hat{\rho}_s|\mathbf{x}_1' \ldots \mathbf{x}_s'\rangle = \rho_s(\mathbf{x}_1, \ldots, \mathbf{x}_s, \mathbf{x}_1', \ldots, \mathbf{x}_s')$$
$$= \int d\mathbf{x}_{s+1} \ldots d\mathbf{x}_N\ \Psi^*(\mathbf{x}_1, \ldots, \mathbf{x}_s, \mathbf{x}_{s+1}, \ldots, \mathbf{x}_N)\Psi(\mathbf{x}_1', \ldots, \mathbf{x}_s', \mathbf{x}_{s+1}, \ldots, \mathbf{x}_N).$$

As with every operator, the time-evolution of $\hat{\rho}$ is defined by the Heisenberg equation of motion, which due to a different sign, in the case of the density matrix is called *Liouville equation*. That means

$$i\hbar\partial_t\hat{\rho}(t) = [\hat{H}, \hat{\rho}(t)] \tag{2.71}$$

whereas time-dependent operators evolve according to

$$i\hbar\partial_t\hat{A}(t) = [\hat{A}(t), \hat{H}]. \tag{2.72}$$

For the pure state Ψ, the Liouville equation for $|\Psi\rangle\langle\Psi|$ is of course equivalent to the Schrödinger equation $i\hbar\partial_t\Psi = \hat{H}\Psi$. The general case can be obtained from the spectral resolution, the components of which get their induced time-dependence from the Schrödinger equation $i\hbar\partial_t\Psi_s = \hat{H}\Psi_s$. In particular, the time evolution for Ψ induces time dependences $\rho_s(\mathbf{x}_1, \ldots, \mathbf{x}_s, \mathbf{x}'_1, \ldots, \mathbf{x}'_s; t)$. By taking the derivative $i\hbar\partial_t$, one can then derive equations of motion for the ρ_s. If the time-evolution of Ψ is governed by a Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}$ containing a one-particle part $\hat{H}_0$ and a two-particle part $\hat{V}$, then every equation of motion for ρ_s involves a term with ρ_{s+2}. (cf. [17]) In other words, the ρ_s form a hierarchy, the so-called quantum BBGKY hierarchy (the quantum analogon of the classical BBGKY hierarchy [46]). With the ρ_s we introduce the n_s by

$$n_s = \frac{N!}{(N-s)!}\rho_s. \tag{2.73}$$

For example, if the N-particle wave-function is given by a Slater-Determinant

$$\Psi_0(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det \varphi_i(\mathbf{x}_j) \tag{2.74}$$

the corresponding free n_1 is given by

$$\hat{n}_1 = \sum_{i=1}^{N} |\varphi_i\rangle\langle\varphi_i| \tag{2.75}$$

$$n_1(\mathbf{x}', \mathbf{x}) = \sum_{i=1}^{N} \varphi_i^*(\mathbf{x}')\varphi_i(\mathbf{x}). \tag{2.76}$$

In general, the free n_s factorize as

$$n_s(\mathbf{x}_1, \ldots, \mathbf{x}_s, \mathbf{x}'_1, \ldots, \mathbf{x}'_s) = \det(n_1(\mathbf{x}_i, \mathbf{x}'_j)). \tag{2.77}$$

With the normalization of the n_s it is possible to write

$$n_s(\mathbf{x}_1, \ldots, \mathbf{x}_s, \mathbf{x}'_1, \ldots, \mathbf{x}'_s) = \langle\Psi|\hat{\psi}^\dagger(\mathbf{x}_1)\ldots\hat{\psi}^\dagger(\mathbf{x}_s)\hat{\psi}(\mathbf{x}'_s)\ldots\hat{\psi}(\mathbf{x}'_1)|\Psi\rangle. \tag{2.78}$$

The equation of motion for n_1 (first equation in the BBGKY hierarchy) reads

$$i\hbar\partial_t\hat{n}_1(t) = [\hat{n}_1, \hat{H}_0] + \mathrm{Tr}_{\mathcal{H}_2}[\hat{n}_2, \hat{V}]. \tag{2.79}$$

Later, we will work with a time-dependent generalization of these expressions, where every field operator $\hat{\psi}(\mathbf{x})$ is replaced with a time-dependent field operator $\hat{\psi}(\mathbf{x}t)$, the time-dependence being given by the Heisenberg equation of motion. This will lead to the notion of Green functions. The BBGKY hierarchy for the reduced density matrices will then turn

out to be a special case of the corresponding hierarchy of equations of motion for the Green functions and the factorization property for the reduced density matrices will turn out to be a special case of the so-called Wick theorem.

Second Quantized Coulomb Potential In the N-particle sector, the first quantized Coulomb potential reads

$$\hat{V}_{\mathrm{Coul}} = \frac{1}{2} \sum_{i,j=1}^{N} v(\mathbf{x}_i, \mathbf{x}_j) \equiv \frac{1}{8\pi\varepsilon_0} \sum_{i,j=1}^{N} \frac{e^2}{|\mathbf{x}_i - \mathbf{x}_j|} \tag{2.80}$$

This translates into the second quantized form

$$q(\hat{V}_{\mathrm{Coul}}) \equiv \hat{V} = \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')v(\mathbf{x}, \mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}). \tag{2.81}$$

The matrix elements of $\hat{V}$ in $\mathcal{H}^2$ can be calculated as

$$\begin{aligned}
V^{ij}_{\ kl} &= \langle \varphi_i \otimes \varphi_j | \hat{V} | \varphi_k \otimes \varphi_l \rangle_{\mathcal{F}} \\
&= \langle \varphi_i \otimes \varphi_j | \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')v(\mathbf{x}, \mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) | \varphi_k \otimes \varphi_l \rangle_{\mathcal{F}} \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ v(\mathbf{x}, \mathbf{x}') \langle \varphi_i \otimes \varphi_j | \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) \varphi_k \otimes \varphi_l \rangle_{\mathcal{H}^2} \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ v(\mathbf{x}, \mathbf{x}') \langle \hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x})\varphi_i \otimes \varphi_j | \hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x})\varphi_k \otimes \varphi_l \rangle_{\mathcal{H}^0} \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ v(\mathbf{x}, \mathbf{x}') \langle \sqrt{2!}\varphi_i(\mathbf{x})\varphi_j(\mathbf{x}') | \sqrt{2!}\varphi_k(\mathbf{x})\varphi_l(\mathbf{x}') \rangle_{\mathbb{C}} \\
&= \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\ \varphi_i^*(\mathbf{x})\varphi_j^*(\mathbf{x}')v(\mathbf{x}, \mathbf{x}')\varphi_k(\mathbf{x})\varphi_l(\mathbf{x}').
\end{aligned}$$

The matrix element $V^{ij}_{\ kl}$ is neither symmetric with respect to the upper nor to with respect to the lower indices but only with respect to a simultaneous switch in the sense that

$$V^{ij}_{\ kl} = V^{ji}_{\ lk} \tag{2.82}$$

This is to be compared with the hermiticity of $\hat{V}$ which translates into the orbital basis as

$$(V^*)^{ij}_{\ kl} = V^{kl}_{\ ij}. \tag{2.83}$$

Equally important is the expectation value $\langle \hat{V} \rangle_\Phi$ evaluated in a Slater determinant $\Phi = \mathrm{SLATER}(\varphi_1, \ldots, \varphi_N)$. We calculate at first $\langle \hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x}) \rangle$ for which we find (de-

noting $(-1)^\pi = \epsilon(\pi))$

$$
\begin{aligned}
&= \frac{N(N-1)}{\sqrt{N!}\sqrt{N!}} \sum_{\pi,\sigma \in S^N} \epsilon(\pi \cdot \sigma) \varphi_{\sigma(1)}^*(\mathbf{x}) \varphi_{\sigma(2)}^*(\mathbf{x}') \varphi_{\pi(1)}(\mathbf{x}) \varphi_{\pi(2)}(\mathbf{x}') \langle \varphi_{\sigma(3)} | \varphi_{\pi(3)} \rangle \cdot \ldots \cdot \langle \varphi_{\sigma(N)} | \varphi_{\pi(N)} \rangle \\
&= \frac{1}{(N-2)!} \sum_{\pi,\sigma \in S^N} \epsilon(\pi \cdot \sigma) \varphi_{\sigma(1)}^*(\mathbf{x}) \varphi_{\sigma(2)}^*(\mathbf{x}') \varphi_{\pi(1)}(\mathbf{x}) \varphi_{\pi(2)}(\mathbf{x}') \delta_{\sigma(3)\pi(3)} \cdot \ldots \cdot \delta_{\sigma(N)\pi(N)} \\
&= \sum_{\pi,\sigma \in S^N,\ \pi(3)=\sigma(3),\ldots,\pi(N)=\sigma(N)} \epsilon(\pi \cdot \sigma) \varphi_{\sigma(1)}^*(\mathbf{x}) \varphi_{\sigma(2)}^*(\mathbf{x}') \varphi_{\pi(1)}(\mathbf{x}) \varphi_{\pi(2)}(\mathbf{x}') \\
&= \sum_{\pi(1)=\sigma(1),\pi(2)=\sigma(2),\pi(3)=\sigma(3),\ldots,\pi(N)=\sigma(N)} \epsilon(\pi \cdot \sigma) \varphi_{\sigma(1)}^*(\mathbf{x}) \varphi_{\sigma(2)}^*(\mathbf{x}') \varphi_{\pi(1)}(\mathbf{x}) \varphi_{\pi(2)}(\mathbf{x}') + \\
&\qquad\qquad \sum_{\pi(1)=\sigma(2),\pi(2)=\sigma(1),\pi(3)=\sigma(3),\ldots,\pi(N)=\sigma(N)} \epsilon(\pi \cdot \sigma) \varphi_{\sigma(1)}^*(\mathbf{x}) \varphi_{\sigma(2)}^*(\mathbf{x}') \varphi_{\pi(1)}(\mathbf{x}) \varphi_{\pi(2)}(\mathbf{x}') \\
&= \sum_{i,j}^{N} \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}') - \sum_{i,j}^{N} \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') \varphi_j(\mathbf{x}) \varphi_i(\mathbf{x}')
\end{aligned}
$$

For $\langle \Psi_0 | \hat{V}_{\text{Coul}} | \Psi_0 \rangle$, we now have

$$
\frac{1}{2} \sum_{i,j=1}^{N} \int d\mathbf{x}d\mathbf{x}' \ \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') v(\mathbf{x},\mathbf{x}') \varphi_i(\mathbf{x}) \varphi_j(\mathbf{x}') - \frac{1}{2} \sum_{i,j=1}^{N} \int d\mathbf{x}d\mathbf{x}' \ \varphi_i^*(\mathbf{x}) \varphi_j^*(\mathbf{x}') v(\mathbf{x},\mathbf{x}') \varphi_j(\mathbf{x}) \varphi_i(\mathbf{x}')
$$

Consequently, the expectation value in the state $\text{SLATER}(\varphi_1, \ldots, \varphi_N)$ can be expressed in terms of the matrix elements with respect to $\{\varphi_i\}$ as

$$
\langle \hat{V}_{\text{Coul}} \rangle = \frac{1}{2} \sum_{i,j}^{N} V^{ij}{}_{ij} - \frac{1}{2} \sum_{i,j}^{N} V^{ij}{}_{ji}. \tag{2.84}
$$

The first term is usually called *direct term* whereas the second is called *exchange term*. One shows easily (in the case of the exchange contribution by taking the Fourier transform) that both the direct term and the exchange term are positive definite. Therefore, the total Coulomb energy is always smaller than the Hartree energy.

Spin in Second Quantization Until now, we never treated the spin explicitly. The formulary worked out automatically carries over to systems with spin if we implicitly understand by the orbitals φ_i elements of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C}^2, d\mathbf{x})$. When dealing with spin systems, however, it comes in handy to write down a spin index explicitly, e.g.

$$
\hat{\psi}_\sigma^\dagger(\mathbf{x}) \tag{2.85}
$$

with $\sigma \in \{\uparrow, \downarrow\}$ denotes the creator of $\delta_{\mathbf{x}}(1,0)^{\mathrm{T}}$ or $\delta_{\mathbf{x}}(0,1)^{\mathrm{T}}$ respectively. This allows for the definition of a spin density operator via

$$\hat{\rho}_\sigma(\mathbf{x}) = \hat{\psi}_\sigma^\dagger(\mathbf{x})\hat{\psi}_\sigma(\mathbf{x}). \tag{2.86}$$

The first quantized spin observable $\hat{\mathbf{S}} = \frac{\hbar}{2}\boldsymbol{\sigma}$, $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ reads in second quantization

$$q(\hat{\mathbf{S}}) = \frac{\hbar}{2}\sum_i \left(a_{i\downarrow}^\dagger a_{i\uparrow} + a_{i\uparrow}^\dagger a_{i\downarrow}, \mathrm{i}a_{i\downarrow}^\dagger a_{i\uparrow} - \mathrm{i}a_{i\uparrow}^\dagger a_{i\downarrow}, a_{i\uparrow}^\dagger a_{i\uparrow} - a_{i\downarrow}^\dagger a_{i\downarrow} \right) \tag{2.87}$$

where the sum goes over a complete system $\{\varphi_i\}$ in the one-particle Hilbert space. The vector valued quantity

$$\mathbf{M} = \frac{e}{m}\langle\Psi|q(\hat{\mathbf{S}})|\Psi\rangle \tag{2.88}$$

can then be identified with the classical magnetization. This will now be discussed.

General Form of the Electromagnetic Current Operator in Nonrelativistic Electronic Quantum Field Theory In many parts of this thesis we will start with a classical model and deduce from it interaction terms which contain the classical (electronic) density and current. These models are then quantized by replacing the classical density and current by their quantum field theoretical operator counterparts. This raises immediately the question, which one are the right operator counterparts? To answer this question one has to go back to the classical theory of fields where one considers a classical (one-electron) field interacting with the electromagnetic field. This model is then quantized by replacing the classical field with the quantized field operator (as determined by the CAR). This replacement then carries over to all observables (up to possible ordering ambiguities, normal order prescriptions etc.). Therefore, in order to find the general form of the current operator one has to write down the general classical, free, electronic Field Theory in the first place. One then couples the electro-magnetic field to the free theory via the gauge principle. The expression for the current is then determined by the postulates that

1. the interaction Lagrangean density is of the form $-A^\mu j_\mu$[3] and;

2. the current is conserved in the sense that $\partial_\mu j^\mu = 0$.

The first condition implies that the inclusion of a term $-1/4\mu_0 F^{\mu\nu}F_{\mu\nu}$ into the Lagrangean leads to Maxwell's equations with j^μ as source terms.[4] Of course, it is the very definition of an electromagnetic current that it acts as a source in Maxwell's equations. The second condition

---

[3]Alternatively, one defines $j_\mu = \delta S/\delta A^\mu$; see e.g. [91] p.75.

[4]Strictly speaking, we run into trouble here because already the usual conserved current of the Schrödinger equation depends on A^μ. The formal Maxwell equation $\partial_\mu F^{\mu\nu} = \mu_0 j^\nu$ would then imply a "gauge break-

is necessary because the Maxwell's equations are only compatible with converved currents and the conservation of j_μ in an interaction Lagrangean $A^\mu j_\mu$ implies gauge invariance. Now, the general (= comprising all degrees of freedom) classical, nonrelativistic, electronic theory is given by the Pauli equation

$$i\hbar\partial_t \mathbb{1}_{\mathbb{C}^2}\psi = \frac{(\mathbf{p}\cdot\boldsymbol{\sigma})^2}{2m}\psi \tag{2.89}$$

with $\psi \in \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}^2, \mathrm{d}\mathbf{x})$, $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ and

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

The Pauli equation can be derived from the Lagrangean density

$$\mathcal{L}(x) = \psi^*(x)\mathrm{i}\hbar\partial_t\psi(x) - \psi^*(x)\frac{(\mathbf{p}\cdot\boldsymbol{\sigma})^2}{2m}\psi(x). \tag{2.90}$$

The action reads

$$S = \int \mathrm{d}^4x\, \mathcal{L}(x) = \int \mathrm{d}^4x\, \left(\psi^*(x)\mathrm{i}\hbar\partial_t\psi(x) + \frac{1}{2m}(\mathbf{p}\cdot\boldsymbol{\sigma}\psi^*(x))(\mathbf{p}\cdot\boldsymbol{\sigma}\psi(x)) \right) \tag{2.91}$$

where $\psi^*(x)\psi(x)$ denotes the scalar product in $\mathbb{C}^2$. Variation with respect to $\psi^*(x)$ then directly yields the Pauli equation. The electromagnetic field now couples to the free Pauli system by virtue of the gauge principle

$$p^\mu \mapsto p^\mu - eA^\mu. \tag{2.92}$$

Defining the spin-density as

$$\mathbf{S}(\mathbf{x}t) = \psi^*(x)\frac{\hbar}{2}\boldsymbol{\sigma}\psi(x) \equiv \langle\psi(x)|\frac{\hbar}{2}\boldsymbol{\sigma}|\psi(x)\rangle_{\mathbb{C}^2}, \tag{2.93}$$

we get the action S as the integral $\int \mathrm{d}^4x$ of

$$\psi^*(x)\mathrm{i}\hbar\partial_t\psi(x) - eA^0(x)\psi^*(x)\psi(x) - \frac{1}{2m}((\mathbf{p}-e\mathbf{A})\psi^*(x))((\mathbf{p}-e\mathbf{A})\psi(x)) - \frac{e}{m}\mathbf{B}(x)\cdot\mathbf{S}(x). \tag{2.94}$$

---

ing". Presently, I am not sure about the interpretation of this fact. It may be a non-relativistic artefact because the Dirac current is given by $j^\mu(x) = e\bar{\psi}(x)\gamma^\mu\psi(x)$ even in the presence of an external field. On the other hand, one may argue that the vector potential entering the non-relativistic current cannot be identified with the vector potential generated by that current within a semi-classical approximation. However, the prescription to write the interaction Lagrangean in the form $-A^\mu j_\mu$ leads to the right definition of the current even for the case of the Schrödinger equation in an external four-potential.

Factoring out A^μ in the interaction term and observing that $\mathbf{B} = \nabla \times \mathbf{A}$ we get with a partial integration an interaction Lagrangean of the form $-A^\mu j_\mu$ where the Pauli current is given by

$$
\begin{aligned}
j^0(x) &= e\psi^*(x)\psi(x) \\
\mathbf{j}(x) &= \frac{e\hbar}{2m\mathrm{i}}(\psi^*(x)(\mathbf{p} - e\mathbf{A}(x))\psi(x) - ((\mathbf{p} - e\mathbf{A}(x)\psi^*(x))\psi(x)) + \frac{e}{m}\nabla \times \mathbf{S}(x).
\end{aligned}
$$

The last term is obviously the spinorial contribution to the current. This current is conserved as can be easily shown by the equation of motion. In fact, the divergence of the spinorial contribution vanishes identically. Consequently, the continuity equation can be proven precisely as in the case of the Schrödinger equation.[5] In other words, the spinorial source of magnetism *is* a current, namely a current term corresponding to the Pauli equation. Finally, a word of warning is in order here. In general, the quantity $\mathbf{S}(\mathbf{x}t)$ cannot be identified with the classical magnetization. In other words, $\mu_0\mathbf{S}(\mathbf{x}t)$ is not (the spinorial contribution to) the internal magnetic field, already because in general $\nabla \cdot \mathbf{S} \neq 0$. This suggests to consider instead the projection on the transversal part. This intuition is right indeed. In order to find the classical magnetization, one has to consider the magnetic field generated by the spinorial current $\mathbf{j}_\mathrm{s} = e/m\nabla \times \mathbf{S}$. This is given by

$$
\mathbf{B}(\mathbf{x}) = \frac{\mu_0}{4\pi}\nabla \times \int \mathrm{d}\mathbf{x}' \; \frac{\mathbf{j}_\mathrm{s}(\mathbf{x}')}{|\mathbf{x} - \mathbf{x}'|}. \tag{2.95}
$$

A comparison with the Helmholtz decomposition theorem shows that the magnetization density is given by the projection of $\mathbf{S}$ on the transversal part, i.e. $\mathbf{M}(\mathbf{x}t) = e/m\mathbf{S}_\mathrm{T}(\mathbf{x}t)$. Note, however, that in products of the form

$$
\int \mathrm{d}\mathbf{x} \; \mathbf{B}_\mathrm{ext}(\mathbf{x}) \cdot \mathbf{S}(\mathbf{x}) \tag{2.96}
$$

we can identify $\mathbf{S}$ with the magnetization because the rotational vector field $\mathbf{B}_\mathrm{ext}$ automatically projects out the longitudinal component of $\mathbf{S}$.

Spin Current As

$$
(\mathbf{p} \cdot \boldsymbol{\sigma})^2 = \mathbf{p}^2 \mathbb{1}_{2\times 2} \tag{2.97}
$$

the action for the Pauli equation is $\mathrm{SU}(2, \mathbb{C})$ invariant. The most general $\mathrm{SU}(2, \mathbb{C})$ transformation reads

$$
U(\varphi, \mathbf{n}) = \exp\left(\mathrm{i}\varphi\mathbf{n} \cdot \frac{\boldsymbol{\sigma}}{2}\right) = \cos(\varphi/2) + \mathrm{i}\mathbf{n} \cdot \boldsymbol{\sigma}\sin(\varphi/2). \tag{2.98}
$$

---

[5]The "spinor current" term $\nabla \times \mathbf{S}(x)$ is usually not mentioned in the literature. I found two references which contain it. ([56], [73]) The reference [73] derives the spinor current of the Pauli equation from the usual current of the Dirac equation in the nonrelativistic limit, whereas in [56] p.107 the spinor current term comes somehow out of the blue.

This leads to the infinitesimal transformation

$$\delta\psi(x) = \left(\frac{\partial U}{\partial\varphi}|_{\varphi=0}\delta\varphi\right)\psi(x) = \left(\frac{\mathrm{i}}{2}\mathbf{n}\cdot\boldsymbol{\sigma}\delta\varphi\right)\psi(x). \tag{2.99}$$

From the Noether theorem ([40, 47, 63, 102]) we get the general formula for the conserved current

$$j^\mu\delta\varphi = \sum_a \frac{\partial\mathcal{L}}{\partial(\partial_\mu\psi_a)}\delta\psi_a \tag{2.100}$$

where the sum goes over all fields entering the Lagrangean (in this case the Pauli field and its complex conjugate). As the resulting current has to be conserved for every $\mathbf{n}$, we conclude that we have a vector-valued conserved current

$$\mathbf{j}^0(x) = \frac{\hbar}{2}\psi^*(x)\boldsymbol{\sigma}\psi(x) = \mathbf{S}(\mathbf{x}t) \tag{2.101}$$

$$\mathbf{j}^i(x) = \frac{\hbar^2}{4m\mathrm{i}}(\psi^*(x)\boldsymbol{\sigma}\partial_i\psi(x) - (\partial_i\psi)^*(x)\boldsymbol{\sigma}\psi(x)) \tag{2.102}$$

such that

$$\partial_t\mathbf{j}^0 + \partial_i\mathbf{j}^i = 0. \tag{2.103}$$

This equation can also be shown directly from the equation of motion. The proof is analogous to the proof of current conservation in elementary Quantum Mechanics if one observes $[\boldsymbol{\sigma}, \partial_i] \equiv [\boldsymbol{\sigma}\otimes\mathbb{1}_{\mathcal{L}^2}, \mathbb{1}_{\mathbb{C}^2}\otimes\partial_i] = 0$. We conclude that the SU$(2,\mathbb{C})$-invariance implies the conservation of the spin current.

2.2. Field Quantization

2.2.1. Canonical Quantization of Fields

Canonical Quantization of Point-Particles A point-particle is described by a Lagrangean L which is a function on some manifold (typically the tangent bundle to some configuration space $\mathcal{Q}$). The Lagrangean may depend on the position and its derivatives (velocity). The transition to Hamiltonian mechanics is implemented by identifying the canonical momentum

$$p^i = \frac{\partial L}{\partial\dot{x}_i} \tag{2.104}$$

and performing a Legendre transform

$$H = p^i\dot{x}_i - L. \tag{2.105}$$

The resulting Hamiltonian is to be understood as a function of $\mathbf{x}$ and the canonical momentum $\mathbf{p}$.[6] For the sake of simplicity, we suppose the phase space to be $\mathbb{R}^3 \times \mathbb{R}^3$. The time evolution of an arbitrary time-independent function $f : \mathcal{M} \to \mathbb{R}$ on the phase space is given by the Poisson bracket [3, 36]:

$$\dot{f} = \{f, H\}. \tag{2.106}$$

In classical mechanics, the state of the point particle is completely described by the instantaneous values $\mathbf{x}(t)$ and $\mathbf{p}(t)$. These are identical to the respective observables. In short:

1. State of the system: $(\mathbf{x}, \mathbf{p}) \in \mathcal{M} = \mathbb{R}^3 \times \mathbb{R}^3$.

2. Observable: function $f : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}$ on the phase space.

3. Time evolution of the state: $\dot{x}_i = \{x_i, H\} = \frac{\partial H}{\partial p_i}$, $\dot{p}_i = \{p_i, H\} = -\frac{\partial H}{\partial x_i}$.

By contrast, the framework of Quantum Mechanics reads:

1. The state of the system is described by a function $\psi \in \mathcal{H}$ where $\mathcal{H}$ is a Hilbert space.

2. Expectation values of observables are given by $\langle \psi | \hat{A} | \psi \rangle$, where $\hat{A}$ is a self-adjoint operator on $\mathcal{H}$.

3. Position and momentum operator obey $[\hat{\mathbf{x}}, \hat{\mathbf{p}}] = \mathrm{i}\hbar \mathbb{1}_{\mathcal{H}}$. By the von-Neumann theorem, for irreducible representations this is equivalent to

$$\begin{aligned} \mathcal{H} &= \mathcal{L}(\mathbb{R}^3, \mathbb{C}) \tag{2.107} \\ (\hat{\mathbf{x}}\psi)(\mathbf{x}) &= \mathbf{x}\psi(\mathbf{x}) \tag{2.108} \\ (\hat{\mathbf{p}}\psi)(\mathbf{x}) &= \frac{\hbar}{\mathrm{i}}(\nabla \psi)(\mathbf{x}) \tag{2.109} \end{aligned}$$

up to unitary transformations. We interpret $\psi(\mathbf{x})$ to be the amplitude for the particle to be at $\mathbf{x}$.

4. The time-dependence of the operators is given by

$$\mathrm{i}\hbar \partial_t \hat{A}(t) = [\hat{A}(t), \hat{H}]. \tag{2.110}$$

This time-dependence of the operators can be pulled back onto the states yielding the Schrödinger equation.

---

[6]The case where the velocities cannot be expressed in terms of the momenta is indeed physically relevant; see the illuminating discussion in [34].

Consider now the space of polynomials in x and p up to second order. Let f, g be such polynomials. By $\hat{f}$ we denote the operator resulting from f by the replacement $x \mapsto \hat{x}$ and $p \mapsto \hat{p}$. Then

$$\widehat{\{f, g\}} = -\frac{\mathrm{i}}{\hbar}[\hat{f}, \hat{g}] \tag{2.111}$$

irrespective of the ordering ambiguities. That means: the quantization of the Poisson bracket is identical to the commutator of the quantization up to second order. For third order polynomials, this correspondence breaks down.[7] In other words, for polynomials up to second order, the canonical commutator ensures that under quantization classical Poisson brackets go over into commutators. On the other hand, the time-dependence of operators is given by their commutators with the Hamiltonian. For free field it is required to be of second order. Consequently, the (second order) operators fulfill the classical equations of motion as operator identities. These identities can be sandwiched between Heisenberg states. Hence, the classical theory is recovered in the limit of expectation values.

Field Quantization Consider now a classical Field Theory given by a Lagrangean density $\mathcal{L}(\psi(x), \partial_\mu \psi(x))$. Usually, the Lagrangean depends on the field and its derivatives up to first order.[8] The classical equations of motion are then determined by the Euler-Lagrange equations

$$\frac{\partial \mathcal{L}}{\partial \psi} - \frac{\partial}{\partial x^\mu} \frac{\partial \mathcal{L}}{\partial \psi_\mu} = 0 \tag{2.112}$$

where $\psi_\mu = \partial_\mu \psi$ and $x = (\mathbf{x}t)$. We identify the canonically conjugate variable to $\psi(x)$ as

$$\pi(x) = \frac{\delta S}{\delta \partial_t \psi(x)} = \frac{\partial \mathcal{L}(\psi(x), \partial_\mu \psi(x))}{\partial(\partial_t \psi(x))} \tag{2.113}$$

where $S = \int \mathrm{d}^4 x \, \mathcal{L}$ denotes the action. A straightforward adaption of the canonical quantization procedure to the quantization of a classical field reads:

1. The state of the field is described by a functional $\Psi = \Psi[\psi]$. We interpret $\Psi[\psi]$ to be the amplitude for the field to be in the classical field configuration ψ.[9]

---

[7] This is known as Groenewold-Van-Hove theorem. [38] Another way to put it is to say that the correspondence between Poisson brackets and commutators only holds to first order in $\hbar$.

[8] The Euler-Lagrange equations generalize easily to higher order derivatives. (cf. [52, 53])

[9] This field-functional point of view is not so widespread in field theory as it is very hard to perform real calculations with the functional. (For explicit calculations with the functional see e.g. [40] Chapters 9-11. The functional point of view is also emphasised in [46, 89].) However, the field-functional point of view is imperative, when one wants to interpret Quantum Field Theory as Quantum Mechanics applied to systems with infinitely many degrees of freedom. Then, the functional is the direct analog of the wave-function. Another problem with the functional point of view is that the functional Schrödinger equation breaks manifest Lorentz invariance. Finally, the field functional point of view is important in the context of canonical quantum gravity and the Wheeler-deWitt equation. [34, 72]

2. Expectation values of observables are given by $\langle \Psi | \hat{A} | \Psi \rangle$ where

$$\langle \Psi | \Phi \rangle = \int \mathcal{D}\psi \; \Psi^*[\psi] \Phi[\psi]. \tag{2.114}$$

3. The field operator and its canonical momentum obey the (equal-time[10]) CCR or CAR

$$[\hat{\psi}(\mathbf{x}t), \hat{\pi}(\mathbf{x}'t)]_\pm = \mathrm{i}\hbar\delta(\mathbf{x} - \mathbf{x}'). \tag{2.115}$$

For the canonical commutator, we usually write shortly $[\cdot, \cdot] \equiv [\cdot, \cdot]_-$. In the case of CCR, this can be realized by

$$\hat{\psi}(\mathbf{x})\Psi[\psi] = \psi(\mathbf{x})\Psi[\psi] \tag{2.116}$$

$$\hat{\pi}(\mathbf{x})\Psi[\psi] = \frac{\hbar}{\mathrm{i}} \frac{\delta}{\delta\psi(\mathbf{x})} \Psi[\psi] \tag{2.117}$$

The Schrödinger field can be quantized using the CAR or the CCR. This is because the spin-statistics theorem is a relativistic effect. (see e.g. [2])

4. The state of the field obeys a functional Schrödinger equation (also called Schwinger-Dyson equation; see e.g. [40, 46, 70])

$$\int \mathrm{d}\mathbf{x} \; \hat{H}(\mathbf{x}t)\Psi(t) = \mathrm{i}\hbar\partial_t\Psi(t). \tag{2.118}$$

where the Hamiltonian $\hat{H}(\mathbf{x}t)$ density is given in terms of $\hat{\psi}(\mathbf{x}t)$ and $\hat{\pi}(\mathbf{x}t)$ by the classical expression for the field energy density (disregarding ordering ambiguities). The classical expression for the Hamiltonian density can be found by a Legendre transformation of the Lagrangean density:

$$\mathcal{H}(x) = \pi(x)\dot{\psi}(x) - \mathcal{L}(\psi(x), \partial_\mu\psi(x)) \tag{2.119}$$

On a fundamental level, the Lagrangean does not explicitly depend on space and time. The Noether theorem then implies the existence of four conserved currents[11]

$$\partial_\mu T^{\mu\nu} = 0 \tag{2.124}$$

---

[10]Within the non-relativistic regime, we do not have to care about a Lorentz invariant form of the (anti)commutator relations as there is a preferred time variable.

[11]This can also be shown directly. (cf. e.g. [70]) If $\mathcal{L}$ depends on x only through the fields, then

$$\partial_\nu \delta^\nu_\mu \mathcal{L} = \partial_\mu \mathcal{L} \tag{2.120}$$

$$= \frac{\partial\mathcal{L}}{\partial\psi(x)}\partial_\mu\psi(x) + \frac{\partial\mathcal{L}}{\partial(\partial_\nu\psi(x))}\partial_\mu\partial_\nu\psi(x) \tag{2.121}$$

$$= \left(\partial_\nu \frac{\partial\mathcal{L}}{\partial(\partial_\nu\psi(x))}\right)\partial_\mu\psi(x) + \frac{\partial\mathcal{L}}{\partial(\partial_\nu\psi(x))}\partial_\mu\partial_\nu\psi(x) \tag{2.122}$$

$$= \partial_\nu \left(\frac{\partial\mathcal{L}}{\partial(\partial_\nu\psi(x))}\partial_\mu\psi(x)\right). \tag{2.123}$$

where

$$T^{\mu}{}_{\nu} \equiv \frac{\partial \mathcal{L}}{\partial(\partial_{\mu}\psi)}\partial_{\nu}\psi - \delta^{\mu}{}_{\nu}\mathcal{L} \tag{2.125}$$

T is called energy-momentum tensor. T^{00} equals the Hamiltonian. In non-relativistic Quantum Field Theory, we usually have systems in external potentials which destroys spatial translation invariance. Although unusual, in principle also in non-relativistic quantum physics the Hamiltonian can be interpreted as the 00-component of the energy-momentum derived from a suitable Lagrangean. (see e.g. [16])

5. Equivalently, one can postulate Heisenberg time evolution for the field operators. The Heisenberg equation of motion then implies that the field operators formally fulfill the classical equation of motion as operator identities, which can be sandwiched directly between state vectors. This ensures that the classical theory is recovered in the limit of expectation values.[12] In the case of standard Quantum Mechanics, this is known as Ehrenfest theorem. The importance of the Heisenberg picture is that it allows to get rid of the Schrödinger picture which sometimes – not only in the relativisitic domain – leads to conceptual problems.

2.2.2. Quantization of the Schrödinger Field

Heuristic Approach to the Quantization of the Schrödinger Field Consider a quantum system with Hilbert space $\mathcal{H} = \mathcal{L}^2(\mathbb{R}^3, \mathbb{C}, \mathrm{d}\mathbf{x})$ and a Hamiltonian $\hat{H}$ with a purely discrete spectrum. A solution $\psi(\mathbf{x}t)$ of the Schrödinger equation can then be expanded in the complete system $\{\varphi_n(\mathbf{x}): n \in \mathbb{N}_0\}$ of eigenfunctions of the Hamiltonian:

$$\psi(\mathbf{x}t) = \sum_{n=0}^{\infty} \varphi_n(\mathbf{x})a_n(t) \tag{2.126}$$

$$a_n(t) = \int \mathrm{d}\mathbf{x}\, \varphi_n^*(\mathbf{x})\psi(\mathbf{x}t). \tag{2.127}$$

If $\psi(\mathbf{x}t)$ is to fulfill the Schrödinger equation $\mathrm{i}\hbar\partial_t\psi(\mathbf{x}t) = \hat{H}\psi(\mathbf{x}t)$, then the time dependence of the expansion coefficients a_n has to be given by $a_n(t) = a_n(0)\mathrm{e}^{-\mathrm{i}\varepsilon_n/\hbar t}$. The expectation value of the energy reads:

$$H = \langle\psi|\hat{H}|\psi\rangle = \sum_{n=0}^{\infty} \varepsilon_n a_n^* a_n = \sum_{n=0}^{\infty} \hbar\omega_n a_n^* a_n. \tag{2.128}$$

---

[12]This statement is to be understood cum grano salis. For example, for a one-particle system the expectation values fulfill $\dot{\mathbf{p}} = -\nabla\varphi$ but in general $\langle\varphi(\mathbf{x})\rangle \neq \varphi(\langle\mathbf{x}\rangle)$

This is reminiscent of the Hamiltonian operator of independent harmonic oscillators with frequencies ω_n which would formally read

$$\hat{H} = \sum_{n=0}^{\infty} \hbar\omega_n \left(a_n^{\dagger} a_n + \frac{1}{2} \right).$$

(2.129)

This harmonic oscillator analogy can be pushed further by investigating the equation of motion for $a_n(t)$

$$i\hbar\partial_t a_n(t) = \varepsilon_n a_n(t).$$

(2.130)

Now, in general a_n is a complex amplitude which we write as

$$a_n = \frac{1}{\sqrt{2}} (r_n + \mathrm{i}s_n)$$

(2.131)

with $r_n, s_n \in \mathbb{R}$. The equation of motion for a_n then implies

$$\partial_t r_n = \omega_n s_n$$

(2.132)

$$\partial_t s_n = -\omega_n r_n$$

(2.133)

which after eliminating yields

$$\ddot{r}_n = -\omega_n^2 r_n$$

(2.134)

$$\ddot{s}_n = -\omega_n^2 s_n.$$

(2.135)

The coupled equations of motion show that r_n and s_n are conjugate in the sense that

$$\dot{r}_n = \frac{\partial H_n}{\partial s_n}$$

(2.136)

$$\dot{s}_n = -\frac{\partial H_n}{\partial r_n}$$

(2.137)

if we set

$$H_n = \frac{\omega_n}{2} \left(s_n^2 + r_n^2 \right) = \omega_n a_n^* a_n.$$

(2.138)

On a heuristic level, we quantize by replacing these classical harmonic oscillators with quantum harmonic oscillators. The commutation relation for the conjugate variables

$$[\hat{r}_n, \hat{s}_n] = \mathrm{i}$$

(2.139)

then translates into

$$[a_n, a_n^{\dagger}] = 1.$$

(2.140)

To quantize the whole Schrödinger field, we suppose that through second quantization all the $a_n(t)$ are replaced by harmonic oscillator annihilators as above whereas the φ_n remain classical fields. We then have for the commutator:

$$[\hat{\psi}(\mathbf{x}t), \hat{\psi}^{\dagger}(\mathbf{x}'t)] = \sum_{m,n} [a_n(t), a_m^{\dagger}(t)]\varphi_n(\mathbf{x})\varphi_m^*(\mathbf{x}'). \tag{2.141}$$

It follows that

$$[\hat{\psi}(\mathbf{x}t), \hat{\psi}^{\dagger}(\mathbf{x}'t)] = \delta(\mathbf{x} - \mathbf{x}') \tag{2.142}$$

is equivalent to

$$[a_n(t), a_m^{\dagger}(t)] = \delta_{nm}. \tag{2.143}$$

The Hamiltonian operator for the field now reads:

$$\hat{H} = \sum_n \varepsilon_n a_n^{\dagger} a_n. \tag{2.144}$$

From this we read off that the quantized field can be interpreted as an infinite ensemble of independent harmonic oscillators. The quantum harmonic oscillators are the amplitudes of the respective field modes.

Canonical Quantization Consider the classical Lagrangean density for a classical complex valued field $\psi: \mathbb{R}^4 \to \mathbb{C}$ in the external potential $v(x) = v(\mathbf{x}t)$:

$$\mathcal{L}(\psi, \partial_\mu \psi; x) = i\hbar \psi^*(x)\partial_t \psi(x) - \frac{\hbar^2}{2m}\nabla\psi^*(x) \cdot \nabla\psi(x) - v(x)\psi^*(x)\psi(x). \tag{2.145}$$

The corresponding Hamiltonian density reads:

$$\mathcal{H}(\psi, \partial_\mu \psi; x) = \frac{1}{i\hbar}\left(\frac{\hbar^2}{2m}\nabla\pi(x) \cdot \nabla\psi(x) + v(x)\pi(x)\psi(x)\right) \tag{2.146}$$

with the conjugate momentum

$$\pi(x) = \frac{\delta S}{\delta \partial_t \psi(x)} = i\hbar\psi^*(x). \tag{2.147}$$

The Euler-Lagrange equation for the classical field ψ leads to the classical equation of motion:

$$i\hbar\partial_t \psi(x) = -\frac{\hbar^2}{2m}\Delta\psi(x) + v(x)\psi(x). \tag{2.148}$$

The transition to the corresponding Quantum Field Theory (cf. [76, 89, 95]) is implemented by replacing the classical fields with operators such that the operators corresponding to

conjugate variables fulfill the canonical (anti)commutation rule (CCR/CAR). For the field operators of the Schrödinger Field, the nontrivial CCR or CAR at fixed time t read:

$$[\hat{\psi}(\mathbf{x}t), \hat{\pi}(\mathbf{x}'t)]_\pm = \mathrm{i}\hbar\delta(\mathbf{x} - \mathbf{x}').$$ (2.149)

This obviously agrees with the result we already found by the heuristic approach. The main advantage of the canonical approach is that it works for any system which allows for a Lagrangean description and is not dependent on the identification of harmonic modes.

General Connection between Quantum Field Theory and Many-Body Physics
We now want to represent the CAR for the field operators on some concrete Hilbert space $\mathcal{F}$. Therefore, we consider the operator $a_\mathbf{x}^\dagger$ on the fermionic Fock space creating a particle in the state $\psi(\mathbf{x}') = \delta(\mathbf{x}' - \mathbf{x})$. The corresponding annihilator is written $a_\mathbf{x}$. Clearly these operators fulfill the CAR (see Chapter 2.1.1):

$$[a_\mathbf{x}, a_{\mathbf{x}'}^\dagger]_+ = \delta(\mathbf{x} - \mathbf{x}').$$ (2.150)

Therefore, we can represent the field operator $\hat{\psi}(\mathbf{x})$ on the Fock space $\mathcal{F}$ by the replacement $\hat{\psi}(\mathbf{x}) \mapsto a_\mathbf{x}$. Indeed, within the realm of non-relativistic Quantum Field Theory, one can even prove that any irreducible representation of the CCR/CAR is unitarily equivalent to the bosonic/fermionic Fock space representation. [87] This is in sharp contrast to the relativistic case where in general (in the interacting case) one does not have a Fock space at all. (see e.g. [39]) Furthermore, it is impossible to find a relativistic transformation law for an N-particle state of the form $\Psi_N(\mathbf{x}_1, \ldots, \mathbf{x}_N; t)$ which depends on N spatial arguments but only one time argument[13]. Clearly this leads to a conflict with Lorentz transformations which in general mix spatial and temporal coordinates.

We conclude that the quantization of the Schrödinger field corresponds to the transition from one-particle Quantum Mechanics to Many-Body Quantum Mechanics (with arbitrary particle number[14]). In particular, this explains why the creators and annihilators of position eigenstates are referred to as field operators.

---

[13]Indeed, in the early days of Quantum Field Theory, Dirac developed a multi-time formalism within which a generic n-particle wave-function depends on n different times; cf. [90].

[14]The deeper reason for this is that both many-particle systems with variable particle number and classical fields are systems with an infinite number of degrees of freedom.

2.3. Phononic Field Theory

2.3.1. Quantization of Lattice Oscillations

Classical Lattice Dynamics Consider a one-dimensional, finite, classical, harmonic lattice, i.e. a discrete collection $\{u_n\}$ of classical degrees of freedom indexed by $n \in \mathbb{Z}_N = \mathbb{Z}/N\mathbb{Z}$. The advantage of interpreting the indices n as a group is that this automatically implies the periodic boundary conditions $u_{n+N} = u_n$. In the context of Electronic Structure Theory the lattice is interpreted as the crystal lattice and the $\{u_n\}$ as the nuclear (or ionic) elongations (or displacements). In principle, the u_n can also be interpreted as some more general quantity associated with the lattice site n. In the latter case, u_n actually denotes a discretized field, i.e. a field $u = u(x_{n0})$ on a discretized space:

$$u_n = u(an) = u(x_{n0}). \tag{2.151}$$

The interpretation of this equation is that the "elongation" at lattice site x_{n0} is given by the evaluation of the ("elongation" or "displacement") field at that very point na. The position of the n-th particle is then given by

$$x_n = x_{n0} + u_n. \tag{2.152}$$

"Classical" means in this context that the system has a configuration space $\mathbb{R}^N$ corresponding to the N positions of the particles or (in the more general interpretation) of the N values which determine the field configuration. The state of the system is at every instant t given by a point in the phase space $\mathbb{R}^N \times \mathbb{R}^N$ and the time-evolution is given by Hamilton's equations

$$\frac{\mathrm{d}x_n(t)}{\mathrm{d}t} = \frac{\partial H}{\partial p_n} \tag{2.153}$$

$$\frac{\mathrm{d}p_n(t)}{\mathrm{d}t} = -\frac{\partial H}{\partial x_n}. \tag{2.154}$$

In the harmonic approximation, the Hamiltonian is given by

$$H = \sum_{n=1}^{N} \frac{p_n^2}{2M} + \frac{\kappa}{2} \sum_{n=1}^{N} (u_n - u_{n+1})^2 \tag{2.155}$$

corresponding to the equation of motion

$$M\frac{\mathrm{d}^2 u_n(t)}{\mathrm{d}t^2} = \kappa(u_{n-1}(t) - 2u_n(t) + u_{n+1}(t)). \tag{2.156}$$

This equation has solutions of the form

$$u_n(t) = u_n(0) \exp(-\mathrm{i}\omega_k t + \mathrm{i}kx_{n0}) \tag{2.157}$$

where

$$k \in \{0, \frac{2\pi}{aN}, \ldots, (N-1)\frac{2\pi}{aN}\} \tag{2.158}$$

and

$$\omega(k) \equiv \omega_k = \sqrt{\frac{4\kappa}{M}} |\sin\left(\frac{ak}{2}\right)| = \sqrt{\frac{2\kappa}{M}} |\cos ka - 1|. \tag{2.159}$$

In the following, summations over the wavevector k always denote a summation over the finite set

$$\frac{2\pi}{L}\mathbb{Z}_N, \tag{2.160}$$

with $L = Na$, i.e.

$$\sum_k = \sum_{k \in \frac{2\pi}{L}\mathbb{Z}_N} \tag{2.161}$$

The general solution of the equation of motion is given by

$$x_n(t) = \frac{1}{\sqrt{N}} \sum_k q_k \exp(-i\omega_k t + ikx_{n0}) \tag{2.162}$$

where the q_k have to be fixed by the initial conditions. For later purposes, we note that the inclusion of an additional coupling of the particles

$$\frac{\lambda}{2} u_n^2 \tag{2.163}$$

to their equilibrium positions leads to a modification of the dispersion relation as

$$\omega_k^2 = \frac{2\kappa}{M}(1 - \cos ka) + \frac{\lambda}{M}. \tag{2.164}$$

The original Hamiltonian leads to a wave-equation in the continuum limit $a \to 0$ whereas the coupling to the equilibrium positions modifies this wave-equation to a Klein-Gordon equation. The coupling constant corresponds to an effective mass μ of the quasiparticles given by

$$\mu = \frac{\hbar}{c}\sqrt{\frac{\lambda}{M}}. \tag{2.165}$$

This fact is sometimes used as a heuristic introduction for the Klein-Gordon equation. (cf. e.g. [95])

Quantization The quantization is now implemented by replacing the classical observables x_n and p_m with operators $\hat{x}_n$ and $\hat{p}_m$ such that

$$[\hat{x}_n, \hat{p}_m] = i\hbar\delta_{nm} \tag{2.166}$$

where

$$\hat{x}_n = x_{n0}\mathbb{1} + \hat{u}_n. \tag{2.167}$$

The state of the lattice is then described by a wave-function

$$\Psi(x_1, \ldots, x_N; t) \in \mathcal{L}^2(\mathbb{R}^N, \mathbb{C}) \tag{2.168}$$

which obeys a Schrödinger equation

$$\mathrm{i}\hbar\partial_t \Psi(x_1, \ldots, x_N; t) = \hat{H}\Psi(x_1, \ldots, x_N; t) \tag{2.169}$$

where the Hamiltonian operator $\hat{H}$ is given by

$$\hat{H} = \sum_{n=1}^{N} \frac{\hat{p}_n^2}{2M} + \frac{\kappa}{2}\sum_{n=1}^{N}(\hat{u}_n - \hat{u}_{n+1})^2. \tag{2.170}$$

So far, this is simply the canonical quantization of a system of N particles. The role of the lattice consists in making plausible the concrete form of the Hamiltonian. We will now perform a transition to normal coordinates which will pave the way to the field-theoretical point of view. Equation (2.162) suggests to use the expansion coefficients of the general solution as coordinates, i.e. we define the coordinates q_k by the point transformation

$$u_n = \frac{1}{\sqrt{N}}\sum_k q_k \exp(\mathrm{i}k x_{n0}) \tag{2.171}$$

or

$$\mathbf{u} = \mathbf{U}\mathbf{q} \tag{2.172}$$

with

$$U_{ij} = \frac{1}{\sqrt{N}}\exp(\mathrm{i}k_j x_{i0}) = \frac{1}{\sqrt{N}}\exp(\mathrm{i}ak_j i) = \frac{1}{\sqrt{N}}\exp\left(\frac{2\pi\mathrm{i}}{N}ij\right) \tag{2.173}$$

$$k_j = \frac{2\pi}{L}j \tag{2.174}$$

where $L = Na$. As $p = m\dot{x}$, this induces the transformation

$$p_n = \frac{1}{\sqrt{N}}\sum_k \pi_k \exp(\mathrm{i}k x_{n0}) \tag{2.175}$$

for the momenta $\pi_k(t) = m\dot{q}_k(t)$. As x_n and p_n are real, the new coordinates fulfill

$$q_k^* = q_{-k} \equiv q_{2\pi N/L - k} \tag{2.176}$$

$$\pi_k^* = \pi_{-k} \equiv \pi_{2\pi N/L - k} \tag{2.177}$$

because

$$u_n^* = \frac{1}{\sqrt{N}} \sum_k q_k^* \exp(-\mathrm{i}kx_{n0}) \tag{2.178}$$

$$= \frac{1}{\sqrt{N}} \sum_k q_{2\pi N/L - k} \exp\left(\mathrm{i}\frac{2\pi}{L}Nx_{n0} - \mathrm{i}kx_{n0}\right) \tag{2.179}$$

$$= \frac{1}{\sqrt{N}} \sum_{2\pi N/L - k} q_{2\pi N/L - k} \exp\left(\mathrm{i}\left(\frac{2\pi}{L}N - k\right)x_{n0}\right). \tag{2.180}$$

The matrix $\mathbf{U}$ is a discrete Fourier transform (cf. appendix (A.2.2)), therefore induces a unitary transformation $\mathbb{C}^N \to \mathbb{C}^N$ and hence preserves the standard norm. In particular, we have

$$\sum_{i=1}^N u_i^2 = \sum_{k \in \frac{2\pi}{L}\mathbb{Z}_N} q_k^* q_k. \tag{2.181}$$

This implies immediately

$$\frac{1}{2M} \sum p_n^2 = \frac{1}{2M} \sum_k \pi_k^* \pi_k \tag{2.182}$$

$$\sum u_n^2 = \sum u_{n+1}^2 = \sum q_k^* q_k. \tag{2.183}$$

For the mixed term $\sum u_{n+1} u_n$ we find

$$\sum_{n=1}^N u_{n+1} u_n = \frac{1}{N} \sum_n \sum_{k,l} q_k q_l \mathrm{e}^{\mathrm{i}kx_{n0}} \mathrm{e}^{\mathrm{i}lx_{n0}} \mathrm{e}^{\mathrm{i}la} \tag{2.184}$$

$$= \frac{1}{N} \sum_{k,l} q_k q_l \mathrm{e}^{\mathrm{i}la} \sum_n \mathrm{e}^{\mathrm{i}(k+l)x_{n0}} \tag{2.185}$$

$$= \frac{1}{N} \sum_{k,l} q_k q_l \mathrm{e}^{\mathrm{i}la} N\delta_{k,-l} \tag{2.186}$$

$$= \sum_k q_k q_{-k} \mathrm{e}^{-\mathrm{i}ka} \tag{2.187}$$

$$= \sum_k q_k q_k^* \mathrm{e}^{-\mathrm{i}ka}. \tag{2.188}$$

Furthermore, the reality conidition $\sum u_{n+1} u_n \in \mathbb{R}$ implies

$$\sum_k q_k q_k^* \mathrm{e}^{-\mathrm{i}ka} = \sum_k q_k q_k^* \mathrm{e}^{\mathrm{i}ka}. \tag{2.189}$$

In the new coordinates, the Hamiltonian therefore reads:

$$
\begin{aligned}
H &= \sum_{n=1}^{N} \frac{p_n^2}{2M} + \frac{\kappa}{2} \sum_{n=1}^{N} (u_n - u_{n+1})^2 & \text{(2.190)}
\end{aligned}
$$

$$
= \sum_{n=1}^{N} \frac{p_n^2}{2M} + \frac{\kappa}{2} \sum_{n=1}^{N} (u_n^2 - 2u_n u_{n+1} + u_{n+1}^2) \qquad \text{(2.191)}
$$

$$
= \sum_{k} \frac{\pi_k^* \pi_k}{2M} + \frac{\kappa}{2} \sum_{k} (q_k^* q_k - q_k q_k^* e^{ika} - q_k q_k^* e^{-ika} + q_k^* q_k) \qquad \text{(2.192)}
$$

$$
= \sum_{k} \frac{\pi_k^* \pi_k}{2M} - \frac{\kappa}{2} \sum_{k} q_k^* q_k (e^{ika} - 2 + e^{-ika}) \qquad \text{(2.193)}
$$

$$
= \sum_{k} \left(\frac{\pi_k^* \pi_k}{2M} + \frac{M\omega_k^2}{2} q_k^* q_k \right). \qquad \text{(2.194)}
$$

Introducing yet again new coordinates a_k and a_k^* via

$$
q_k = \sqrt{\frac{\hbar}{2M\omega_k}} (a_k + a_{-k}^*) \qquad \text{(2.195)}
$$

$$
\pi_k = i\sqrt{\frac{\hbar M\omega_k}{2}} (a_k^* - a_{-k}) \qquad \text{(2.196)}
$$

the Hamiltonian takes the particularly simple form

$$
H = \sum_{k} \hbar\omega_k \left(a_k^* a_k + \frac{1}{2} \right). \qquad \text{(2.197)}
$$

The quantization procedure $x_n, p_n \mapsto \hat{x}_n, \hat{p}_n$ now translates into a replacement of the classical coordinates a_k, a_k^* by operators $a_k, a_k^\dagger$ which fulfill

$$
\begin{aligned}
[a_k, a_l^\dagger] &= \delta_{kl} \\
[a_k, a_l] &= 0 \\
[a_k^\dagger, a_l^\dagger] &= 0
\end{aligned}
$$

and the Hamiltonian can be rewritten as

$$
\hat{H} = \sum_{k} \hbar\omega_k \left(a_k^\dagger a_k + \frac{1}{2} \right). \qquad \text{(2.198)}
$$

This shows that in the new coordinates the system is a collection of independent harmonic oscillators. Consequently, the ground-state can easily be written down

$$
\Psi_0 = \otimes_{k \in \frac{2\pi}{L} \mathbb{Z}_N} |0_k\rangle \qquad \text{(2.199)}
$$

where $|0_k\rangle$ is the ground-state of the k-th harmonic oscillator characterized by:

$$a_k|0_k\rangle = 0. \tag{2.200}$$

However, it is worth noting that all this is still completely equivalent to the canonical quantization of N non-relativistic particles with Hamiltonian (2.170). In fact

$$\Psi_0(x_1, \ldots, x_N) = \langle x_1, \ldots, x_N| \otimes_{k \in \frac{2\pi}{L}\mathbb{Z}_N} |0_k\rangle \tag{2.201}$$

is the ground-state of the Hamiltonian (2.170). This is to be understood in the following sense: $|0_k\rangle$ is the function

$$\varphi_0(q_k) = \left(\frac{M\omega_k}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{M\omega_k}{2\hbar}q_k^*q_k\right) \tag{2.202}$$

(ground-state of the harmonic oscillator in the position state representation) with

$$q_k = q_k(x_1, \ldots, x_N). \tag{2.203}$$

Ψ_0 is then given by

$$\Psi_0(x_1, \ldots, x_N) \propto \varphi_0(q_1(x_1, \ldots, x_N)) \cdot \ldots \cdot \varphi_0(q_N(x_1, \ldots, x_N)). \tag{2.204}$$

This shows that the quantization of a ("displacement") field on a lattice with N lattice points is completely equivalent to the standard Quantum Mechanics of N particles.

Lattice Dynamics of One-Quasiparticle Wave-function Denoting $\Psi_0 = |0\rangle$, we now consider a general one-quasiparticle state

$$|1\rangle = \sum_k f_k a_k^\dagger |0\rangle \tag{2.205}$$

with the wave-function in Fourier space f_k. The dynamics of the whole lattice implies

$$i\hbar\partial_t|1\rangle = \hat{H}|1\rangle = \frac{3}{2}\sum_k f_k \hbar\omega_k a_k^\dagger |0\rangle. \tag{2.206}$$

As the free Hamiltonian preserves the functional form of $|1\rangle$ (does not change the quasiparticle number), the time-dependence of the state $|1\rangle$ can be completely absorbed into the expansion coefficient $f_k := f_k(t)$ which implies for these

$$i\hbar\partial_t f_k(t) = \frac{3}{2}\hbar\omega_k f_k(t) \tag{2.207}$$

or

$$f_k(t) = f_{k0}e^{-i3/2\hbar\omega_k t}. \tag{2.208}$$

We now define a quasiparticle wave-function in real space by

$$\psi(x_{i0}) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp\left(i\frac{2\pi}{N}ij\right) f_{k_j} = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp\left(i\frac{2\pi}{Na}jia\right) f_{k_j} = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp(ik_j x_{i0}) f_{k_j}$$

and the respective time-dependence by

$$\psi(x_{i0}, t) = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp(ik_j x_{i0}) f_{k_j}(t) \tag{2.209}$$

Our goal is now to derive an equation of motion in real space for the wave-function $\psi(x_{i0}, t)$. We therefore introduce the operators

$$(\nabla_a^+ f)(x_{n0}) = \frac{f(x_{(n+1)0}) - f(x_{n0})}{a} \tag{2.210}$$

$$(\nabla_a^- f)(x_{n0}) = \frac{f(x_n) - f(x_{(n-1)0})}{a} \tag{2.211}$$

which we call forward and backward lattice derivative. From this definition, we find

$$((\nabla_a^+ \nabla_a^-)(f))(x_{n0}) = \frac{f(x_{(n+1)0}) - 2f(x_{n0}) + f(x_{(n-1)0})}{a^2} \tag{2.212}$$

In particular, for $f(x_{n0}) = e^{ikx_{n0}}$ we find

$$(\nabla_a^+ f)(x_{n0}) = \frac{e^{ika} - 1}{a} f(x_{n0}) \tag{2.213}$$

$$(\nabla_a^- f)(x_{n0}) = \frac{1 - e^{-ika}}{a} f(x_{n0}) \tag{2.214}$$

$$((\nabla_a^+ \nabla_a^-)(f))(x_{n0}) = \frac{2}{a^2}(\cos ka - 1) \tag{2.215}$$

We now compute

$$
\begin{aligned}
\partial_t^2 \psi(x_{i0}, t) &= \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp(\mathrm{i} k_j x_{i0}) \partial_t^2 f_{k_j}(t) \\
&= -\frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp(\mathrm{i} k_j x_{i0}) \frac{9}{4} \omega_k^2 f_{k_j}(t) \\
&= -\frac{9}{\sqrt{16N}} \sum_{j=0}^{N-1} \omega_k^2 \exp(\mathrm{i} k_j x_{i0}) f_{k_j}(t) \\
&= -\frac{9}{\sqrt{16N}} \sum_{j=0}^{N-1} \frac{2\kappa}{M} (1 - \cos ka) \exp(\mathrm{i} k_j x_{i0}) f_{k_j}(t) \\
&= \frac{18\kappa a^2}{\sqrt{64 N M^2}} \sum_{j=0}^{N-1} \nabla_a^+ \nabla_a^- \exp(\mathrm{i} k_j x_{i0}) f_{k_j}(t) \\
&= \frac{9\kappa a^2}{4M} \nabla_a^+ \nabla_a^- \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} \exp(\mathrm{i} k_j x_{i0}) f_{k_j}(t) \\
&= \frac{9\kappa a^2}{4M} \nabla_a^+ \nabla_a^- \psi(x_{i0}, t)
\end{aligned}
$$

or

$$
\left(\frac{1}{v_q^2} \partial_t^2 - \nabla_a^+ \nabla_a^- \right) \psi(x_{i0}, t) = 0. \tag{2.216}
$$

with

$$
v_q = \sqrt{\frac{9\kappa a^2}{4M}} = \frac{3}{2} \sqrt{\frac{\kappa a^2}{M}}. \tag{2.217}
$$

We now compare this one-quasiparticle wave-equation with the original equation (2.156) for the classical displacement field $x_{i0}(t) - x_{i0} = u(x_{i0}, t)$. By the help of the lattice derivatives, the equation of motion can be rewritten as

$$
\left(\frac{1}{v_c^2} \partial_t^2 - \nabla_a^+ \nabla_a^- \right) u(x_{i0}, t) = 0. \tag{2.218}
$$

where

$$
v_c = \sqrt{\frac{\kappa a^2}{M}}. \tag{2.219}
$$

In the continuum limit $a \to 0$, both equations become wave-equations of the standard form

$$
\left(\frac{1}{v^2} \partial_t^2 - \Delta \right) f(x, t) = \Box f(x, t) = 0 \tag{2.220}
$$

where the divergence in $1/v^2$ has to be absorbed in a suitable dependence $\kappa = \kappa(a)$. The astonishing difference in the velocities v_c and v_q due to the factor $\sqrt{9/4} = 3/2$ is a quantum

effect which is is caused by the zero point energy $1/2\hbar\omega_k$. Without this zero-point energy, the equation of motion for the Fourier mode would read

$$\mathrm{i}\hbar\partial_t f_k(t) = \hbar\omega_k f_k(t) \tag{2.221}$$

and a similar calculation would yield $v_q = v_c$. In other words, due to the zero-point energy phonons do not move we the speed of sound!

Hilbert Space of One-Phonon Wave-functions, Local Phonon Creation and Annihilation Operators The Hilbert space $\mathcal{H}$ of one-phonon states is given by $\mathbb{C}^N$. In the reciprocal space, a one-phonon state $f : \mathbb{Z}_N \to \mathbb{C}$ is a function on the FBZ with the interpretation that f_k is the amplitude for the phonon to have the lattice wave vector k. The induced scalar product reads

$$\langle f|g\rangle = \sum_{k,k'} f_k^* g_{k'} \langle 0|a_k a_{k'}^\dagger|0\rangle = \sum_k f_k^* g_k. \tag{2.222}$$

With the one-phonon Hilbert space being given, one can easily construct the (bosonic) Fock space for arbitrarily many phonons. A general eigenstate of the phonon number operator

$$\hat{N} = \sum_k a_k^\dagger a_k \tag{2.223}$$

reads

$$|\Psi_n^f\rangle = \sum_{k_1,\ldots,k_n} f(k_1,\ldots,k_n)a_{k_1}^\dagger \ldots a_{k_n}^\dagger|0\rangle. \tag{2.224}$$

Due to the commutation rule $[a_k^\dagger, a_l^\dagger] = 0 \ \forall k,l$ the many-quasiparticle wave-function

$$f(k_1,\ldots,k_n)$$

can without restriction of generality be chosen totally symmetric. In other words, on the level of the quasiparticles the quantum dynamics of the lattice induces a bosonic theory with arbitrarily many particles in contrast to the constituent lattice N-particle wave-function $\Psi(x_1,\ldots,x_N)$ (N fixed!) which in general is neither symmetric nor antisymmetric (the constituent particles can be distinguished by their lattice number). Furthermore, the quasiparticle number is in general neither conserved nor bounded (disregarding the physical fact that for too high energies, the lattice may be blown apart) as opposed to the constituent particles, whose number is fixed. Note that phonons are not quite quantized lattice oscillations (whatever this actually means), but quantum states of the lattice which can be written

in the form (2.224). Starting from the phonon creation and annihilation operators a_k and $a_k^\dagger$ we can construct local creation and annihilation operators

$$\hat{\psi}^\dagger(x_{n0}) \;=\; \frac{1}{\sqrt{N}} \sum_k \exp(-\mathrm{i}kx_{n0})a_k^\dagger \tag{2.225}$$

$$\hat{\psi}(x_{n0}) \;=\; \frac{1}{\sqrt{N}} \sum_k \exp(\mathrm{i}kx_{n0})a_k \tag{2.226}$$

which we can sloppily interpret as operators creating or annihilating a phonon at x_{n0}, i.e. a phonon with the real space wave-function $\psi(x_{m0}) = \delta_{mn}$.

2.3.2. Phonon Propagator

Quantum Displacement Field We want to compute expectation values of the displacement field operator

$$\hat{x}_n = \hat{u}(x_{n0}) + x_{n0} \tag{2.227}$$

and its products in various states, in particular in the field theoretical vacuum state $|0\rangle$ (ground-state of the lattice). Using equations (2.171, 2.195) and replacing $-k \mapsto k$ under the sum, we can write

$$\hat{x}_n - x_{n0} = \hat{u}(x_{n0}) = \sqrt{\frac{\hbar}{2NM}} \sum_k \frac{1}{\sqrt{\omega_k}}(a_k \mathrm{e}^{\mathrm{i}kx_{n0}} + a_k^\dagger \mathrm{e}^{-\mathrm{i}kx_{n0}}). \tag{2.228}$$

We call $\hat{u}(x_{n0})$ the quantum phonon field. In the language of first quantization, it is the indexed position operator of the constituent particles. Note that the quantum phonon field $\hat{u}(x_{n0})$ does not create a phonon at x_{n0} because (i) it contains both creators and annihilators and (ii) it contains $\frac{1}{\sqrt{\omega_k}}$.[15] Obviously $\hat{x}_n^\dagger = \hat{x}_n$. From $\langle 0|a_k|0\rangle = \langle 0|a_k^\dagger|0\rangle = 0$, we conclude $\langle \hat{x}_n \rangle = 0$. This result generalizes to any phonon number eigenstate. By equation (2.228) one easily establishes the following equal-time commutators

$$[\hat{u}_n(t), \hat{u}_m(t)] \;=\; 0 \tag{2.229}$$

$$[\partial_t \hat{u}_n(t), \partial_t \hat{u}_m(t)] \;=\; 0 \tag{2.230}$$

$$[\hat{u}_n(t), \partial_t \hat{u}_m(t)] \;=\; \frac{\mathrm{i}\hbar}{M}\delta_{nm}. \tag{2.231}$$

---

[15]In this respect, the quantum phonon field behaves as almost all quantized fields, in particular in the relativistic domain. Only the quantized Schrödinger field has the property of creating/annihilating particles at a certain point stricto sensu, i.e. in the sense of the many-body Fock space. This is due to the fact that the Schrödinger equation is first order in time.

This shows that the phonon field fulfills the canonical commutators of a a quantum field on a lattice. We now establish the time dependence of the operator

$$\hat{u}_n(t) \;=\; \sqrt{\frac{\hbar}{2NM}}\sum_k \frac{1}{\sqrt{\omega_k}}\big(a_k(t)\mathrm{e}^{\mathrm{i}kx_{n0}} + a_k^\dagger(t)\mathrm{e}^{-\mathrm{i}kx_{n0}}\big). \tag{2.232}$$

From

$$\mathrm{i}\hbar\partial_t a_k \;=\; -[\hat{H}, a_k] = \hbar\omega_k a_k \tag{2.233}$$

$$\mathrm{i}\hbar\partial_t a_k^\dagger \;=\; -[\hat{H}, a_k^\dagger] = -\hbar\omega_k a_k^\dagger \tag{2.234}$$

we conclude

$$a_k(t) \;=\; a_k\mathrm{e}^{-\mathrm{i}\omega_k t} \tag{2.235}$$

$$a_k^\dagger(t) \;=\; a_k^\dagger\mathrm{e}^{\mathrm{i}\omega_k t}. \tag{2.236}$$

This implies

$$\hat{x}_n(t) - x_{n0} = \hat{u}(x_{n0}t) \;=\; \sqrt{\frac{\hbar}{2NM}}\sum_k \frac{1}{\sqrt{\omega_k}}\big(a_k\mathrm{e}^{-\mathrm{i}\omega_k t+\mathrm{i}kx_{n0}} + a_k^\dagger\mathrm{e}^{\mathrm{i}\omega_k t-\mathrm{i}kx_{n0}}\big). \tag{2.237}$$

By the dispersion relation $\omega = \omega_k$, it follows that the phonon field operator fulfills the classical equation of motion (2.218).

Phonon Propagator The phononic Green function is defined by

$$-\mathrm{i}\hbar D_{\mathrm{phon}}(x_{n0}t, x_{m0}t') = \langle 0|\mathcal{T}\hat{u}(x_{n0}t)\hat{u}(x_{m0}t')|0\rangle \tag{2.238}$$

Using $\partial_t\theta(t) = \delta(t)$, the CCR (2.229, 2.230, 2.231) and the fact that $\hat{x}_n(t)$ fulfills the classical equation for the displacement field, one shows easily that the phonon Green function fulfills the equation of motion

$$\big(M\partial_t^2 - a^2\kappa\nabla_a^+\nabla_a^-\big) D_{\mathrm{phon}}(x_{n0}t, x_{m0}t') = \delta(t - t')\delta_{nm}. \tag{2.239}$$

An explicit calculation yields for $-\mathrm{i}\hbar D_{\mathrm{phon}}(x_{n0}t, x_{m0}t')$

$$= \frac{\hbar}{2NM}\sum_k \left(\frac{\theta(t - t')}{\omega_k}\mathrm{e}^{\mathrm{i}k(x_{n0}-x_{m0})-\mathrm{i}\omega_k(t-t')} + \frac{\theta(t' - t)}{\omega_k}\mathrm{e}^{\mathrm{i}k(x_{m0}-x_{n0})-\mathrm{i}\omega_k(t'-t)}\right)$$

$$= \frac{\mathrm{i}\hbar}{2NM}\sum_k \int\frac{\mathrm{d}\omega}{2\pi}\left(\frac{1}{\omega_k}\frac{\mathrm{e}^{\mathrm{i}k(x_{n0}-x_{m0})-\mathrm{i}\omega(t-t')}}{\omega - \omega_k + \mathrm{i}\eta} + \frac{1}{\omega_k}\frac{\mathrm{e}^{\mathrm{i}k(x_{m0}-x_{n0})-\mathrm{i}\omega(t-t')}}{\omega + \omega_k - \mathrm{i}\eta}\right)$$

$$= \frac{\mathrm{i}\hbar}{NM}\sum_k \int\frac{\mathrm{d}\omega}{2\pi}\frac{\mathrm{e}^{\mathrm{i}k(x_{n0}-x_{m0})-\mathrm{i}\omega(t-t')}}{\omega^2 - \omega_k^2 + \mathrm{i}\eta}$$

where we again substituted $k \mapsto -k$ under the sum $\sum_k$. The transformation from the second to the third line holds in the limit $\eta \to 0$. We read off that

$$D_{\text{phon}}(k, k'; \omega) = \frac{1}{M} \frac{-\delta_{kk'}}{\omega^2 - \omega_k^2 + i\eta}. \tag{2.240}$$

Recall in this context that k varies over the finite set of wave vectors in the FBZ.

Generalization to 3 Dimensions In the case of three dimensions, the most general harmonic Hamiltonian reads

$$H = T + V = \sum_{\mathbf{n}} \frac{M}{2}(\partial_t \mathbf{u})^2(\mathbf{x}_{\mathbf{n}0}, t) + \frac{1}{2}\sum_{\mathbf{n}, \mathbf{m}} \langle \mathbf{u}(\mathbf{x}_{\mathbf{n}0}, t) | \mathbf{K}(\mathbf{x}_{\mathbf{n}0}, \mathbf{x}_{\mathbf{m}0}) \mathbf{u}(\mathbf{x}_{\mathbf{m}0}, t) \rangle_{\mathbb{R}^3}$$

where we think of $\mathbf{K}$ as the Hessian matrix of some kind of potential energy $E(\{\mathbf{x}(\mathbf{x}_{\mathbf{n}0})\})$. In other words, the Hamiltonian corresponds to a truncated Taylor expansion around the equilibrium positions $\mathbf{x}_{\mathbf{n}0}$. In general, the potential energy $E(\{\mathbf{x}(\mathbf{x}_{\mathbf{n}0})\})$ includes the static nuclear Coulomb interaction and the electronic ground-state energy as a function of the nuclear positions. Therefore, $E(\{\mathbf{x}(\mathbf{x}_{\mathbf{n}0})\})$ does not have a classical origin and instead represents an "electron-mediated" interaction. Interactions of nuclei at arbitrary distance $\mathbf{x}_{\mathbf{n}0} - \mathbf{x}_{\mathbf{m}0}$ correspond to higher order lattice derivatives in the field-theoretical picture (as opposed to nearest neighbor interactions which imply first-order lattice derivatives). The potential term of the Hamiltonian reads in full detail

$$\frac{1}{2}\sum_{\mathbf{n}, \mathbf{m}}\sum_{i,j=1}^3 K_{ij}(\mathbf{x}_{\mathbf{n}0}, \mathbf{x}_{\mathbf{m}0})u^i(\mathbf{x}_{\mathbf{n}0}, t)u^j(\mathbf{x}_{\mathbf{m}0}, t). \tag{2.241}$$

and has a number of well-known symmetries. These will be derived in the following. We start with a some of definitions. The Bravais lattice of the crystal under consideration can be written as

$$\Gamma_{\mathbf{a}_i, L} = \{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3; \ (n_1, n_2, n_3) \in \mathbb{Z} \times \mathbb{Z} \times \mathbb{Z}; \ \mathbf{a}_i \ i = 1, 2, 3 \ \text{lin. indt.}\}. \tag{2.242}$$

We interpret $\Gamma_{\mathbf{a}_i, L}$ as a subset of $\mathbb{R}^3$. Let $\mathbf{R}$ be an element of the euclidean group of $\mathbb{R}^3$. If $\mathbf{R}$ enjoys the property

$$\mathbf{R}(\Gamma_{\mathbf{a}_i, L}) = \Gamma_{\mathbf{a}_i, L} \tag{2.243}$$

it is called a *symmetry of the lattice*. A lattice function

$$f : \Gamma \times \ldots \times \Gamma \quad \to \quad \mathbb{K} \in \{\mathbb{R}, \mathbb{C}\} \tag{2.244}$$

$$(\mathbf{x}_{n_10}, \ldots, \mathbf{x}_{n_m0}) \quad \mapsto \quad f(\mathbf{x}_{n_10}, \ldots, \mathbf{x}_{n_m0}) \tag{2.245}$$

is said to be Bravais invariant if for any lattice symmetry transformation $\mathbf{R}$, the equation

$$f(\mathbf{x}_{n_10}, \ldots, \mathbf{x}_{n_m0}) = f(\mathbf{R}\mathbf{x}_{n_10}, \ldots, \mathbf{R}\mathbf{x}_{n_m0}) \tag{2.246}$$

holds. (In particular, if $f(\mathbf{x}_{n0})$ is Bravais invariant, it is constant.) Furthermore, the lattice function f being given, we define its pull back $\mathbf{R}^*f$ to be given by

$$(\mathbf{R}^*f)(\mathbf{x}_{n_10}, \ldots, \mathbf{x}_{n_m0}) = f(\mathbf{R}\mathbf{x}_{n_10}, \ldots, \mathbf{R}\mathbf{x}_{n_m0}). \tag{2.247}$$

Bravais invariance then simply means $\mathbf{R}^*f = f$. For a vector valued lattice function $\mathbf{f}$, we define the push forward $\mathbf{R}_*\mathbf{f}$ through

$$(\mathbf{R}_*\mathbf{f})(\mathbf{x}_{n_10}, \ldots, \mathbf{x}_{n_m0}) = \mathbf{R}'\mathbf{f}(\mathbf{R}^{-1}\mathbf{x}_{n_10}, \ldots, \mathbf{R}^{-1}\mathbf{x}_{n_m0}) \tag{2.248}$$

where $\mathbf{R}'$ denotes the differential (tangential map) of $\mathbf{R}$. A vector valued function on the lattice is said to be Bravais contravariant if $\mathbf{R}_*\mathbf{f} = \mathbf{f}$. The generalization to Bravais covariant and contravariant tensors of various degrees is obvious. Finally, a functional $E[\mathbf{f}, \mathbf{g}, \ldots]$ of vector valued lattice functions is called Bravais invariant iff

$$E[\mathbf{f}, \mathbf{g}, \ldots] = E[\mathbf{R}_*\mathbf{f}, \mathbf{R}_*\mathbf{g}, \ldots]. \tag{2.249}$$

Lemma 2.3.1 *The potential energy*

$$\frac{1}{2} \sum_{\mathbf{n},\mathbf{m}} \langle \mathbf{u}(\mathbf{x}_{\mathbf{n}0}, t) | \mathbf{K}(\mathbf{x}_{\mathbf{n}0}, \mathbf{x}_{\mathbf{m}0}) \mathbf{u}(\mathbf{x}_{\mathbf{m}0}, t) \rangle_{\mathbb{R}^3} \tag{2.250}$$

is a Bravais invariant functional.

Corollary 2.3.2 *With* $\mathbf{u}(\mathbf{x}_{\mathbf{n}0}, t)$*, the push-forward* $(\mathbf{R}_*\mathbf{u})(\mathbf{x}_{\mathbf{n}0}, t)$ *is a solution of the equation of motion.*

Proof For this to hold true, it suffices that

$$\mathbf{K}(\mathbf{x}_{\mathbf{n}0}, \mathbf{x}_{\mathbf{m}0}) = \frac{\partial^2 E(\{\mathbf{x}_{\mathbf{l}}\})}{\partial \mathbf{x}_{\mathbf{n}} \partial \mathbf{x}_{\mathbf{m}}}\Big|_{\{\mathbf{u}(\mathbf{x}_{\mathbf{l}0})=0,\ \forall \mathbf{l}\}} \tag{2.251}$$

is a Bravais covariant tensor. The energy is explicitly given as

$$E(\{\mathbf{x}_{\mathbf{l}}\}) = \langle \Psi_0(\{\mathbf{x}_{\mathbf{l}}\}) | \hat{H}(\{\mathbf{x}_{\mathbf{l}}\}) | \Psi_0(\{\mathbf{x}_{\mathbf{l}}\}) \rangle + \frac{Z^2 e^2}{8\pi\varepsilon_0} \sum_{\mathbf{m},\mathbf{n}} \frac{1}{|\mathbf{x}_{\mathbf{n}} - \mathbf{x}_{\mathbf{m}}|} \tag{2.252}$$

where $\hat{H}$ depends on $\mathbf{x}_{\mathbf{n}}$ through $v_{\text{ext}}(\mathbf{x})$. Using second-order perturbation theory and the Hellman-Feynman theorem, we find

$$\begin{aligned}
K_{ij}(\mathbf{x}_{\mathbf{n}0}, \mathbf{x}_{\mathbf{m}0}) &= 2\mathfrak{Re} \sum_s \frac{\langle \Psi_0 | \frac{\partial \hat{V}_{\text{ext}}}{\partial x_{\mathbf{n}}^i} | \Psi_s \rangle \langle \Psi_s | \frac{\partial \hat{V}_{\text{ext}}}{\partial x_{\mathbf{m}}^j} | \Psi_0 \rangle}{E_0 - E_s} + \delta_{\mathbf{nm}} \langle \Psi_0 | \frac{\partial^2 \hat{V}_{\text{ext}}}{\partial x_{\mathbf{n}}^i \partial x_{\mathbf{m}}^j} | \Psi_0 \rangle \\
&\quad + \frac{Z^2 e^2}{8\pi\varepsilon_0} \sum_{\mathbf{m},\mathbf{n}} \frac{\partial^2}{\partial x_{\mathbf{n}}^i \partial x_{\mathbf{m}}^j} \frac{1}{|\mathbf{x}_{\mathbf{n}} - \mathbf{x}_{\mathbf{m}}|}
\end{aligned}$$

where all electronic eigenvectors, energies and derivatives of the external potential are evaluated at $\mathbf{x_n} = \mathbf{x_{n0}}$. The lattice symmetry is also a symmetry of $\hat{H}(\{\mathbf{x_{l0}}\})$ and the derivatives of $\hat{V}_{\text{ext}}$ evaluated at the equilibrium positions are lattice covariant. The same applies to the derivatives of the electrostatic energy of the ions. (The derivatives of the potentials are even covariant under the full euclidean group.) Therefore, every of the terms involved possesses the lattice symmetry and we conclude that $K_{ij}(\mathbf{x_{n0}}, \mathbf{x_{m0}})$ is a lattice covariant tensor.

$\square$

In particular, $\mathbf{K}$ is invariant under inversion and lattice translation $\mathbf{K}(\mathbf{x}+\mathbf{a}, \mathbf{x'}+\mathbf{a}) = \mathbf{K}(\mathbf{x}, \mathbf{x'})$ and can therefore be written as

$$K_{ij}(\mathbf{x_{n0}} - \mathbf{x_{m0}}) \tag{2.253}$$

with

$$K_{ij}(\mathbf{x_{n0}}) = K_{ij}(-\mathbf{x_{n0}}) \tag{2.254}$$

$$K_{ji}(\mathbf{x_{n0}}) = K_{ij}(\mathbf{x_{n0}}) \tag{2.255}$$

where we used the trivial identity

$$K_{ij}(\mathbf{x_{n0}}, \mathbf{x_{m0}}) = K_{ji}(\mathbf{x_{m0}}, \mathbf{x_{n0}}) \tag{2.256}$$

which follows from the characterization of $\mathbf{K}$ as a second derivative tensor. Using the symmetry properties, we see that the equation of motion for the classical displacement field reads

$$M\partial_t^2 u^i(\mathbf{x_{n0}}, t) = -\sum_{\mathbf{m}, j} K^i{}_j(\mathbf{x_{n0}} - \mathbf{x_{m0}}) u^j(\mathbf{x_{m0}}, t). \tag{2.257}$$

We consider a pure Fourier mode

$$u^i_{\mathbf{k}\lambda}(\mathbf{x_{n0}}, t) = \mathbf{e}^i_{\mathbf{k}\lambda} e^{-i\omega_{\mathbf{k}\lambda} t + i\mathbf{k}\cdot\mathbf{x_{n0}}} \tag{2.258}$$

with $\mathbf{k} \in$ FBZ. We then have

$$M\partial_t^2 u^i_{\mathbf{k}\lambda}(\mathbf{x_{n0}}, t) = -M\omega^2_{\mathbf{k}\lambda} u^i_{\mathbf{k}\lambda}(\mathbf{x_{n0}}, t) \tag{2.259}$$

and

$$
\begin{aligned}
\sum_{\mathbf{m}, j} K^i{}_j(\mathbf{x_{n0}} - \mathbf{x_{m0}}) u^j_{\mathbf{k}\lambda}(\mathbf{x_{m0}}, t) &= \sum_{\mathbf{m}, j} K^i{}_j(\mathbf{x_{n0}} - \mathbf{x_{m0}}) \mathbf{e}^j_{\mathbf{k}\lambda} e^{-i\omega_{\mathbf{k}\lambda} t + i\mathbf{k}\cdot\mathbf{x_{m0}}} \\
&= \sum_j e^{-i\omega_{\mathbf{k}\lambda} t + i\mathbf{k}\cdot\mathbf{x_{n0}}} \mathbf{e}^j_{\mathbf{k}\lambda} \sum_{\mathbf{m}} K^i{}_j(\mathbf{x_{n0}} - \mathbf{x_{m0}}) e^{i\mathbf{k}\cdot(\mathbf{x_{m0}} - \mathbf{x_{n0}})} \\
&= \sum_j e^{-i\omega_{\mathbf{k}\lambda} t + i\mathbf{k}\cdot\mathbf{x_{n0}}} \mathbf{e}^j_{\mathbf{k}\lambda} \sum_{\mathbf{m}} K^i{}_j(\mathbf{x_{m0}}) e^{-i\mathbf{k}\cdot\mathbf{x_{m0}}} \\
&= \sum_j \tilde{K}^i{}_j(\mathbf{k}) \mathbf{e}^j_{\mathbf{k}\lambda} e^{-i\omega_{\mathbf{k}\lambda} t + i\mathbf{k}\cdot\mathbf{x_{n0}}}.
\end{aligned}
$$

In other words, $\mathbf{u}_{\mathbf{k}\lambda}(\mathbf{x}_{\mathbf{n}0}, t)$ is a solution of the equation of motion iff $\mathbf{e}_{\mathbf{k}\lambda}$ is an eigenvector of the dynamical matrix

$$\tilde{K}^i{}_j(\mathbf{k}) = \sum_{\mathbf{m}} K^i{}_j(\mathbf{x}_{\mathbf{m}0}) \mathrm{e}^{-\mathrm{i}\mathbf{k}\cdot\mathbf{x}_{\mathbf{m}0}} \tag{2.260}$$

with eigenvalue $M\omega_{\mathbf{k}\lambda}^2$. The phononic field (3-dimensional quantum displacement operator) can then be expanded as

$$\hat{\mathbf{x}}_{\mathbf{n}}(t) - \mathbf{x}_{\mathbf{n}0} = \hat{\mathbf{u}}(\mathbf{x}_{\mathbf{n}0}, t) = \sqrt{\frac{\hbar}{2NM}} \sum_{\lambda, \mathbf{k} \in \mathrm{FBZ}} \frac{1}{\sqrt{\omega_{\mathbf{k}\lambda}}} (a_{\mathbf{k}\lambda}\mathbf{e}_{\mathbf{k}\lambda}\mathrm{e}^{-\mathrm{i}\omega_{\mathbf{k}\lambda}t + \mathrm{i}\mathbf{k}\cdot\mathbf{x}_{\mathbf{n}0}} + \mathbf{e}_{\mathbf{k}\lambda}^* a_{\mathbf{k}\lambda}^\dagger \mathrm{e}^{\mathrm{i}\omega_{\mathbf{k}\lambda}t - \mathrm{i}\mathbf{k}\cdot\mathbf{x}_{\mathbf{n}0}})$$
$$\tag{2.261}$$

and is an operator-valued solution of the equation of motion, i.e.

$$M\partial_t^2 \hat{u}^i(\mathbf{x}_{\mathbf{n}0}, t) = -\sum_{\mathbf{m}, j} K^i{}_j(\mathbf{x}_{\mathbf{n}0} - \mathbf{x}_{\mathbf{m}0}) \hat{u}^j(\mathbf{x}_{\mathbf{m}0}, t). \tag{2.262}$$

or

$$(M\partial_t^2 + \mathbf{K})\hat{\mathbf{u}}_{(\mathbf{x}_{\mathbf{n}0}, t)} = 0 \tag{2.263}$$

where

$$(\mathbf{Ku})(\mathbf{x}_{\mathbf{n}0}) \equiv \sum_{\mathbf{m}} \mathbf{K}(\mathbf{x}_{\mathbf{n}0} - \mathbf{x}_{\mathbf{m}0})\mathbf{u}(\mathbf{x}_{\mathbf{m}0}, t). \tag{2.264}$$

The creators and annihilators fulfill

$$[a_{\mathbf{k}\lambda}, a_{\mathbf{l}\mu}] = 0 \tag{2.265}$$

$$[a_{\mathbf{k}\lambda}^\dagger, a_{\mathbf{l}\mu}^\dagger] = 0 \tag{2.266}$$

$$[a_{\mathbf{k}\lambda}, a_{\mathbf{l}\mu}^\dagger] = \delta_{\mathbf{k}\mathbf{l}}\delta_{\lambda\mu} \tag{2.267}$$

which is equivalent to the equal-time commutators

$$[\hat{\mathbf{u}}(\mathbf{x}_{\mathbf{n}0}, t), \hat{\mathbf{u}}(\mathbf{x}_{\mathbf{m}0}, t)] = 0 \tag{2.268}$$

$$[\partial_t \hat{\mathbf{u}}(\mathbf{x}_{\mathbf{n}0}, t), \partial_t \hat{\mathbf{u}}(\mathbf{x}_{\mathbf{m}0}, t)] = 0 \tag{2.269}$$

$$[\hat{\mathbf{u}}(\mathbf{x}_{\mathbf{n}0}, t), \partial_t \hat{\mathbf{u}}(\mathbf{x}_{\mathbf{m}0}, t)] = \frac{\mathrm{i}\hbar}{M}\delta_{\mathbf{n}\mathbf{m}}\mathbb{1}_{3\times3}. \tag{2.270}$$

The Hamiltonian can be written as

$$\hat{H} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda}\left(a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda} + \frac{1}{2}\right). \tag{2.271}$$

In 3 dimensions, we define the phonon propagator as

$$-\mathrm{i}\hbar\mathbf{D}_{\mathrm{phon}}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') = \langle 0|\mathcal{T}\hat{\mathbf{u}}(\mathbf{x}_{\mathbf{n}0}t)\hat{\mathbf{u}}(\mathbf{x}_{\mathbf{m}0}t')|0\rangle. \tag{2.272}$$

For $\partial_t^2 \langle 0|\mathcal{T}\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')|0\rangle$, we find

$$\partial_t(\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle + \theta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle)$$
$$\partial_t(-\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle)$$
$$= \partial_t(\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle + \theta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle)$$
$$\partial_t(-\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle)$$
$$= \delta'(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle + \delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle + \delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle$$
$$+\delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle + \theta(t-t')\langle\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle$$
$$-\delta'(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle - \delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle - \delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$-\delta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle) + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle)$$
$$= \delta'(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle + 2\delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle + \theta(t-t')\langle\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle$$
$$+\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\rangle - \delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$-\delta'(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle - 2\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$= \theta(t-t')\langle\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$2\delta(t-t')\langle\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t) - \hat{\mathbf{u}}(\mathbf{x_{m0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$+\delta(t-t')\langle\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t) - \partial_t\hat{\mathbf{u}}(\mathbf{x_{m0}}t)\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$= \theta(t-t')\langle\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\rangle + \theta(t'-t)\langle\hat{\mathbf{u}}(\mathbf{x_{m0}}t')\partial_t^2\hat{\mathbf{u}}(\mathbf{x_{n0}}t)\rangle$$
$$-\frac{\mathrm{i}\hbar}{M}\delta(t-t')\delta_{\mathbf{nm}}.$$

We read off that the phonon propagator fulfills

$$\left(M\partial_t^2 + \mathbf{K}\right)\mathbf{D}_{\text{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t') = \delta(t-t')\delta_{\mathbf{nm}}\mathbb{1}_{3\times3} \qquad (2.273)$$

or in full detail

$$\left(M\partial_t^2 + \sum_{\mathbf{l}\in\Gamma}\mathbf{K}(\mathbf{x_{n0}}, \mathbf{x_{l0}})\right)\mathbf{D}_{\text{phon}}(\mathbf{x_{l0}}, \mathbf{x_{m0}}; t-t') = \delta(t-t')\delta_{\mathbf{nm}}\mathbb{1}_{3\times3}. \qquad (2.274)$$

This implies for the Fourier domain

$$\left(-M\omega^2 + \sum_{\mathbf{k''}\in\Gamma^*}\tilde{\mathbf{K}}(\mathbf{k}, \mathbf{k''})\right)\mathbf{D}_{\text{phon}}(\mathbf{k''}, \mathbf{k}; \omega) =$$

$$\left(-M\omega^2 + \sum_{\mathbf{k''}\in\Gamma^*;\lambda}M\omega_{\mathbf{k}\lambda}^2\delta_{\mathbf{kk''}}\mathbf{e}_\lambda(\mathbf{k})\otimes\mathbf{e}_\lambda^*(\mathbf{k})\right)\mathbf{D}_{\text{phon}}(\mathbf{k''}, \mathbf{k}; \omega) = \mathbb{1}_{3\times3}.$$

Using

$$\sum_{\lambda=1}^{3}\mathbf{e}_\lambda(\mathbf{k})\otimes\mathbf{e}_\lambda^*(\mathbf{k}) = \mathbb{1}_{3\times3} \qquad (2.275)$$

we see that the phonon propagator in the Fourier domain therefore reads

$$\mathbf{D}_{\text{phon}}(\mathbf{k}, \mathbf{k}'; \omega) = \frac{1}{M} \sum_{\lambda=1}^{3} \frac{-\delta_{\mathbf{k}\mathbf{k}'}}{\omega^2 - \omega_{\mathbf{k}\lambda}^2 + \mathrm{i}\eta} \mathbf{e}_\lambda(\mathbf{k}) \otimes \mathbf{e}_\lambda^*(\mathbf{k}). \qquad (2.276)$$

The regularization factor $\mathrm{i}\eta$ has been inserted ad-hoc to recover the time-ordered propagator. This framework can be generalized to polyatomic bases by introducing a number of displacement fields $\mathbf{u}_i(\mathbf{x}_{\mathbf{n}0}t)$ (one for each sort of atom) and including a suitable (linear) interaction between these.

Remark about the Dependence of the Green Function on the Quantum State
In the proof for the quantum field theoretical propagator constituting a Green function of the classical equation of motion, we used only the derivative of the Heaviside function, the fact that field operator fulfills the classical equation of motion and the linearity of the expectation value functional $\langle \cdot \rangle$ (which allows one to pull the equation of motion into the expectation value). The fact that the time-ordered product is evaluated in the ground-state has not been used. Any other (time-indepedendent) state (even mixed!) would do. On the other hand, the general form of the Green function in terms of $\mathbf{e}_\lambda(\mathbf{k})$, $\omega_{\mathbf{k}\lambda}$ etc. can be deduced from purely classical considerations. At first sight, this seems to imply that the quantum field theoretical Green function is indepedendent of the quantum state. This, however, is not true. In fact, the quantum state comes into play when one is to fix the regularization $\mathrm{i}\eta$ of the poles which in principle has to be done separately for each pole. Even real-valued superpositions of different regularizations are possible which becomes relevant in the case of mixed states. Classically, the regularization is completely undetermined and therefore has to be fixed by so-called physical considerations ("causality"). Quantum mechancially, the regularization is fixed by the underlying quantum state.[16]

Phonon Propagator vs Lagrangean A straightforward calculation shows that in terms of the phonon propagator, the classical Lagrangean of the displacement can be written succinctly as

$$L(t) = T - V = -\frac{1}{2} \int \mathrm{d}t' \sum_{\mathbf{n},\mathbf{m}} \langle \mathbf{u}(\mathbf{x}_{\mathbf{n}0}, t) | \mathbf{D}_{\text{phon}}^{-1}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \mathbf{u}(\mathbf{x}_{\mathbf{m}0}, t') \rangle_{\mathbb{R}^3} \qquad (2.277)$$

the action being given by $S = \int \mathrm{d}t \ L(t)$. This formula will become extremely important for the derivation of effective phonon-mediated interactions. It is a lattice analogon of well-known field-theoretical facts (cf. e.g. [54, 85, 86]): the (free) propagator is the inverse of the

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[16]As we will see later, mutatis mutandis the same applies the electronic Green function where the regularization prescription can be expressed in terms of occupied and unoccupied one-particle states.

operator in the quadratic part of the Lagrangean.

Phonon Propagator vs Density Response Functions In order to express the nuclear density and current response functions in terms of the phonon propagator we first take a somewhat alternative route to the density and current operators. Consider a quantum one-particle system with wave-function $\psi(\mathbf{x})$ which we interpret as the quantization of some classical one-particle system described by the Hamiltonian function $H(\mathbf{x}, \mathbf{p})$. Classically, the density is given by

$$n(\mathbf{x}t) = \delta(\mathbf{x} - \mathbf{x}(t)), \tag{2.278}$$

where $\mathbf{x}(t)$ denotes the classical trajectory. We postulate that the density operator simply results from the classical density by the replacement $\mathbf{x}(t) \mapsto \hat{\mathbf{x}}(t)$ where $\hat{\mathbf{x}}(t)$ is the position operator in the Heisenberg picture. Using the spectral resolution, this yields the operator

$$\hat{n}(\mathbf{x}t) = \int \mathrm{d}\mathbf{y} \; \delta(\mathbf{x} - \mathbf{y})|\mathbf{y}t\rangle\langle\mathbf{y}t| \tag{2.279}$$

where $|\mathbf{y}t\rangle = \hat{\psi}^\dagger(\mathbf{y}t)|0\rangle$. The evaluation of this operator in the state ψ yields indeed the standard expression

$$n(\mathbf{x}t) = \langle\psi|\hat{n}(\mathbf{x}t)|\psi\rangle = \psi^*(\mathbf{x}t)\psi(\mathbf{x}t). \tag{2.280}$$

Similarly, for the current we have the classical expression

$$\mathbf{j}(\mathbf{x}t) = \frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t}\delta(\mathbf{x} - \mathbf{x}(t)) \tag{2.281}$$

which translates into the quantum operator

$$\hat{\mathbf{j}}(\mathbf{x}t) = \frac{\mathrm{d}\hat{\mathbf{x}}(t)}{\mathrm{d}t}\delta(\mathbf{x} - \hat{\mathbf{x}}(t)) \tag{2.282}$$

$$= -\frac{\mathrm{i}}{\hbar}[\hat{\mathbf{x}}(t), \hat{H}]\delta(\mathbf{x} - \hat{\mathbf{x}}(t)) \tag{2.283}$$

$$= \frac{\hat{\mathbf{p}}}{m}\delta(\mathbf{x} - \hat{\mathbf{x}}(t)) \tag{2.284}$$

$$= \int \mathrm{d}\mathbf{y} \; \frac{\hat{\mathbf{p}}}{m}\delta(\mathbf{x} - \mathbf{y})|\mathbf{y}t\rangle\langle\mathbf{y}t|. \tag{2.285}$$

The evaluation of this expression in the state ψ shows that the resulting current is in general not real-valued. Of course, this is due to ordering ambiguities and can therefore easily be remedied by starting from the classically equivalent expression

$$\hat{\mathbf{j}}(\mathbf{x}t) = \frac{1}{2}\left(\frac{\mathrm{d}\hat{\mathbf{x}}(t)}{\mathrm{d}t}\delta(\mathbf{x} - \hat{\mathbf{x}}(t)) + \delta(\mathbf{x} - \hat{\mathbf{x}}(t))\frac{\mathrm{d}\hat{\mathbf{x}}(t)}{\mathrm{d}t}\right) \tag{2.286}$$

which leads to the standard current

$$\mathbf{j}(\mathbf{x}t) = \langle \psi | \hat{\mathbf{j}}(\mathbf{x}t) | \psi \rangle = \frac{\hbar}{2m\mathrm{i}} (\psi^*(\mathbf{x}) \nabla \psi(\mathbf{x}) - (\nabla \psi^*(\mathbf{x})) \psi(\mathbf{x})). \tag{2.287}$$

This result can now be applied to solid state physics. The charge density of the nuclei is given by

$$\rho_{\mathrm{nucl}}(\mathbf{x}t) = \sum_{\mathbf{n}} Ze\delta(\mathbf{x} - \mathbf{x_n}(t)). \tag{2.288}$$

The first order deviation from the equilibrium density is then given[17]

$$\delta\rho_{\mathrm{nucl}}(\mathbf{x}t) = -\sum_{\mathbf{n}} Ze\mathbf{u}(\mathbf{x_{n0}}, t) \cdot (\nabla\delta)(\mathbf{x} - \mathbf{x_{n0}}). \tag{2.289}$$

This translates into the operator

$$\delta\hat{\rho}_{\mathrm{nucl}}(\mathbf{x}t) = -\sum_{\mathbf{n}} Ze\hat{\mathbf{u}}(\mathbf{x_{n0}}, t) \cdot (\nabla\delta)(\mathbf{x} - \mathbf{x_{n0}}). \tag{2.290}$$

The (time-ordered) polarizability

$$\chi_{\mathrm{nucl}}(\mathbf{x}t, \mathbf{x}'t') = -\frac{\mathrm{i}}{\hbar} \langle \mathcal{T} \delta\hat{\rho}_{\mathrm{nucl}}(\mathbf{x}t) \delta\hat{\rho}_{\mathrm{nucl}}(\mathbf{x}'t') \rangle \tag{2.291}$$

can then be expressed in terms of the phonon propagator as

$$\chi_{\mathrm{nucl}}(\mathbf{x}t, \mathbf{x}'t') = Z^2 e^2 \sum_{\mathbf{n},\mathbf{m}} \langle (\nabla\delta)(\mathbf{x} - \mathbf{x_{n0}}) | \mathbf{D}_{\mathrm{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t)(\nabla\delta)(\mathbf{x_{m0}} - \mathbf{x}') \rangle_{\mathbb{R}^3}. \tag{2.292}$$

A similar formula can be written down for the current response function in terms of the phonon propagator. These formulas will become relevant in the theory of effective phonon-mediated interactions. The formula $\hat{n}(\mathbf{x}) = \delta(\mathbf{x} - \hat{\mathbf{x}}) \approx \delta(\mathbf{x} - \mathbf{x_0}) - (\hat{\mathbf{x}} - \mathbf{x_0}) \cdot (\nabla\delta)(\mathbf{x} - \mathbf{x_0})$ can also be used to derive the standard dipolar Hamiltonian $\mathbf{E}_{\mathrm{ext}} \cdot \hat{\mathbf{x}}$ for an atom in an external electric field as

$$\hat{H}_{\mathrm{int}} = \int \mathrm{d}\mathbf{x} \; \varphi_{\mathrm{ext}}(\mathbf{x}) \hat{\rho}(\mathbf{x}) \tag{2.293}$$

$$= \varphi_{\mathrm{ext}}(0) - \hat{\mathbf{x}} \cdot \int \mathrm{d}\mathbf{x} \; e\varphi_{\mathrm{ext}}(\mathbf{x})(\nabla\delta)(\mathbf{x}) \tag{2.294}$$

$$= \varphi_{\mathrm{ext}}(0) - e\mathbf{E}_{\mathrm{ext}}(0) \cdot \hat{\mathbf{x}} \tag{2.295}$$

$$= \varphi_{\mathrm{ext}}(0) - \mathbf{E} \cdot \hat{\mathbf{P}} \tag{2.296}$$

---

[17]The Taylor expansion of the Dirac distribution ultimately has the meaning of a Taylor expansion of the respective test functions which in this context are assumed to be analytical. The first order Taylor expansion therefore does not mean that the Dirac distribution is really approximated by its Taylor series of a certain order. Instead, it means that the first order expansion is a good approximation for the state on which it acts.

where $\hat{\mathbf{P}}$ denotes the dipole operator. Note that in this context $\hat{\mathbf{x}}$ is an abstract operator in the Hilbert and therefore does not "feel" the integration over $\mathbf{x}$.

Condensed Matter vs Quantum Gravity The classical displacement field $\mathbf{u} : \Gamma \to \mathbb{R}^3$ is naturally defined on the lattice Γ. For the moment, we consider the displacement field on large length scales which allows one to perform the continuum limit. In that case, the "source space" becomes $\Gamma = \mathbb{R}^3$. Equipping the "target space" $\mathbb{R}^3$ with the usual euclidean metric, we consider the pull back under $\mathbf{u}$ of the metric on the source space.[18] It is well-known [58] that the induced metric on the source space reads

$$g_{ij} = \delta_{ij} + u_{ij} \tag{2.297}$$

with

$$u_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \tag{2.298}$$

Physically, the induced metric on the source space gives the distances of the displaced "atoms" in terms of the undisplaced coordinates. One can now consider field theories on the (original, undisplaced) lattice, e.g. Ising-like spin models. These will contain terms which involve the lattice spacings (e.g. nearest neighbor interactions). In principal, one can consider modifications of such models in which these lattice spacing are to be calculated with the non-trivial, induced metric, i.e. in which the lattice-field "interacts" with the metric (at least the metric acts on the spin field). Now, under quantization, the displacement field becomes an operator and so do all derived concepts such as the metric itself and possible geometric operators (length, area, volume) which one can form with the metric. (cf. e.g. [82] p.42) The resulting theory, even if of poor relevance in condensed matter physics, would be analogous to quantum gravity.[19] Nonetheless, one also has to stress some crucial differences: as opposed to gravity [98], in condensed matter, (i) the fields interacting with the metric naturally live on a predetermined lattice, (ii) the metric is a derived concept and therefore does not carry independent degrees of freedom, (iii) consequently, there is no analogon of the Einstein equations, (iv) the metric is Riemannian, (v) the time coordinate is not involved.

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[18]"Target space" and "source space" is actually string theoretical parlance [40, 102], but seems to be highly intuitive in this case. In fact, the present problem *is* analogous to the usual bosonic string theory provided one identifies the physical space not with the 26-dimensional target space but with the 2-dimensional source space of the string. In other words, $u^i(\mathbf{x}_{n0}, t)$ is the analogon of the classical string $X^\mu(\sigma, \tau)$. From this point of view, string theory simply describes a Field Theory in 2 dimensions, actually even quantum gravity (apart from the fact that the string dynamics is defined by the Nambu-Goto action and not by the Einstein-Hilbert action which would yield a topological constant in 2 dimensions). Needless to say, this analogy has been stressed time and again by the string theorists themselves. (cf. e.g. [97] p.19)

[19]A "world crystal" theory of gravitation has been proposed by Hagen Kleinert. [52, 53, 54]

Field Theoretical Language	Particle Picture
Field Degrees of Freedom	Particles position and momentum at Lattice Sites
$\psi(x_{n0}) = \psi(na)$	x_n
$\pi(x_{n0}) = \pi(na)$	p_n
Field Quantization	Many-Body Quantum Mechanics
$[\hat{\psi}(x_{n0}), \hat{\pi}(x_{m0})] = i\hbar\delta_{nm}$	$[\hat{x}_n, \hat{p}_m] = i\hbar\delta_{nm}$
State of the Field = Functional of the classical field ψ	State of the Particles = Many-Body Wave Function
$\Psi[\psi] = \Psi(\psi(x_{10}), \ldots, \psi(x_{N0}))$	$\Psi(x_1, \ldots, x_N)$
Lattice Functional Integral	Scalar Product
$\langle\Psi|\Phi\rangle = \int \mathcal{D}\psi\ \Psi^*[\psi]\Phi[\psi]$	$\langle\Psi|\Phi\rangle = \int dx_1 \ldots dx_N\ (\Psi^* \cdot \Phi)(x_1, \ldots, x_N)$
Explicit Form of Field Operators	Explicit Form of Position and Momentum Operator
$\hat{\psi}(x_{n0})\Psi[\psi] = \psi(x_{n0})\Psi[\psi]$	$\hat{x}_n\Psi(x_1, \ldots, x_N) = x_n\Psi(x_1, \ldots, x_N)$
$\hat{\pi}(x_{n0})\Psi[\psi] = \frac{\hbar}{i}\frac{\delta}{\delta\psi(x_{n0})}\Psi[\psi]$	$\hat{p}_n\Psi(x_1, \ldots, x_N) = \frac{\hbar}{i}\frac{\partial}{\partial x_n}\Psi(x_1, \ldots, x_N)$
Expectation Value of the Field at x_{n0}	Expectation value of the position of particle n
$\langle\psi(x_{n0})\rangle = \langle\Psi|\hat{\psi}(x_{n0})|\Psi\rangle$	$\langle x_n\rangle = \langle\Psi|\hat{x}_n|\Psi\rangle$
Field Quanta	Quasiparticles
$\int dk\ f(k)a_k^\dagger|0\rangle$	$\sum_k f(k)a_k^\dagger|\Psi_0\rangle$
Excitation of Oscillation	Particle Creation
Deexcitation of Oscillation	Particle Annihilation
Multiple Excitation	Many Particle State
$\int dk_1 \ldots dk_i\ f(k_1, \ldots, k_i)a_{k_i}^\dagger \ldots a_{k_1}^\dagger|0\rangle$	$\sum_{k_1 \ldots k_i} f(k_1, \ldots, k_i)a_{k_i}^\dagger \ldots a_{k_1}^\dagger|\Psi_0\rangle$
Continuum Limit	Thermodynamic Limit
$a \to 0$	$N \to \infty$
classical field $\psi(x)$	continuous matter distribution displacement field $u(x)$
Quantum State of the Field	Quantum State of the Matter Distribution
Functional $\Psi[\psi]$	Function of infinitely many variables
Field Theoretical Vacuum $|0\rangle$	Quantum Mechanical Groundstate $|\Psi_0\rangle$ of the Matter Distribution (here: formal infinite product of harmonic oscillator ground-states)

Table 2.1.: Particles vs Fields

Part II.

Green Function Theory

3. Green Functions and Quasiparticles

3.1. Quantum Field Theoretical Green Functions

3.1.1. Definition and Properties

Definition The expectation values

$$(\mathrm{i}\hbar)^n G^{2n}(1,\ldots,n;n+1,\ldots,2n) = \langle\Psi_0|\mathcal{T}\hat{\psi}(1)\ldots\hat{\psi}(n)\hat{\psi}^\dagger(2n)\ldots\hat{\psi}^\dagger(n+1)|\Psi_0\rangle. \qquad (3.1)$$

are called $2n$-point (n-particle) *Green functions*.

Remarks

1. $\mathcal{T}$ denotes the time-ordering operator. The explicit formula for the time-ordering of $2n$ field operators reads:

$$\mathcal{T}\hat{\psi}(\mathbf{x}_1 t_1)\ldots\hat{\psi}(\mathbf{x}_n t_n)\hat{\psi}^\dagger(\mathbf{x}_{n+1}t_{n+1})\ldots\hat{\psi}^\dagger(\mathbf{x}_{2n}t_{2n}) = \sum_\pi (-1)^\pi \times$$

$$\theta(t_{\pi(1)} - t_{\pi(2)})\theta(t_{\pi(2)} - t_{\pi(3)})\ldots\theta(t_{\pi(2n-1)} - t_{\pi(2n)})\hat{\psi}^{(\dagger)}(\mathbf{x}_{\pi(1)}t_{\pi(1)})\ldots\hat{\psi}^{(\dagger)}(\mathbf{x}_{\pi(2n)}t_{\pi(2n)})$$

   In general, the arguments of the field operators are composite variables: $(1) = (\mathbf{x}_1, t_1, \sigma_1)$. In particular, $\hat{\psi}^{(\dagger)}(1) \equiv \hat{\psi}_{\sigma_1}^{(\dagger)}(\mathbf{x}_1 t_1)$ denotes a Heisenberg operator with the time-evolution being induced by:

$$\mathrm{i}\hbar\partial_t\hat{\psi}^{(\dagger)} = [\hat{\psi}^{(\dagger)}, \hat{H}] \qquad (3.2)$$

   i.e.

$$\hat{\psi}^{(\dagger)}(\mathbf{x}t) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}t}\hat{\psi}^{(\dagger)}(\mathbf{x})\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}t}. \qquad (3.3)$$

   Ψ_0 denotes an N-particle ground-state $\Psi_0 \in \mathcal{H}^N \subset \mathcal{F}$ of some Hamiltonian $\hat{H}$ to be specified later. We will suppress the spin indices whenever possible. In the following formulas, the spin degree of freedom can be remade explicit by substituting $\hat{\psi}(\mathbf{x}) \mapsto \hat{\psi}_\sigma(\mathbf{x})$; $\varphi(\mathbf{x}) \mapsto \varphi_\sigma(\mathbf{x})$; $\int \mathrm{d}\mathbf{x} \mapsto \sum_\sigma \int \mathrm{d}\mathbf{x}$ etc. The prefactor $(\mathrm{i}\hbar)^n$ in the definition of the n-particle Green function is of importance for the conventions in the equation of motion theory. In particular, it has the effect of turning the two-particle Green function

of a non-interacting system into a Green function in the sense of standard Quantum Mechanics. The inverse numbering of the second n arguments in the definition of the n-particle Green function is not imperative, but will turn out to be a good convention.

2. In particular, the two-point Green function

$$i\hbar G^2(\mathbf{x}t, \mathbf{x}'t') \equiv i\hbar G(\mathbf{x}t, \mathbf{x}'t') = \langle \Psi_0 | \mathcal{T}\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') | \Psi_0 \rangle. \qquad (3.4)$$

is simply called *Green function* or *propagator*.

3. We introduce a non-interacting ground-state Φ_0 of the n-particle system: $\hat{H}_0 \Phi_0 = E_0 \Phi_0$ where $\hat{H}_0$ is the one-particle operator part of $\hat{H}$. The corresponding Green function will be denoted by $G_0(\mathbf{x}t, \mathbf{x}'t')$.

4. The formal correspondence between quantum field theoretical and single-particle Green functions (= Green functions in standard Quantum Mechanics) is elucidated by observing that

$$\langle \mathbf{x}' | \hat{U}(t', t) | \mathbf{x} \rangle = \langle \mathbf{x}'t' | \mathbf{x}t \rangle = \langle 0 | \hat{\psi}(\mathbf{x}'t')\hat{\psi}^\dagger(\mathbf{x}t) | 0 \rangle \qquad (3.5)$$

where $|0\rangle$ refers to the Fock vacuum. Therefore, both single-particle and many-body (two-point) Green functions can – up to prefactors and time ordering – be written in the form

$$\langle \text{state} | \hat{\psi}(\mathbf{x}'t')\hat{\psi}^\dagger(\mathbf{x}t) | \text{state} \rangle. \qquad (3.6)$$

As $\psi(\mathbf{x}t)|0\rangle \equiv 0$, one can even introduce a time-ordering operator in the single-particle Green function.

5. We define the *retarded Green function*, the *advanced Green function*, the *greater Green function* and the *lesser Green function* through:

$$i\hbar G^{\mathrm{R}}(\mathbf{x}t, \mathbf{x}'t') = \theta(t - t')\langle \{\hat{\psi}(\mathbf{x}t), \hat{\psi}^\dagger(\mathbf{x}'t')\} \rangle \qquad (3.7)$$

$$-i\hbar G^{\mathrm{A}}(\mathbf{x}t, \mathbf{x}'t') = \theta(t' - t)\langle \{\hat{\psi}(\mathbf{x}t), \hat{\psi}^\dagger(\mathbf{x}'t')\} \rangle \qquad (3.8)$$

$$i\hbar G^{>}(\mathbf{x}t, \mathbf{x}'t') = \langle \hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') \rangle \qquad (3.9)$$

$$i\hbar G^{<}(\mathbf{x}t, \mathbf{x}'t') = \langle \hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t) \rangle. \qquad (3.10)$$

In particular, we have

$$G^{\mathrm{R}} = \theta(t - t')(G^{>} + G^{<}) \qquad (3.11)$$

$$-G^{\mathrm{A}} = \theta(t' - t)(G^{<} + G^{>}) \qquad (3.12)$$

$$G^2 = \theta(t - t')G^{>} - \theta(t' - t)G^{<}. \qquad (3.13)$$

Note, however, that the so-called greater and lesser Green functions actually are not Green functions because they fulfill the homogeneous equations.

6. The definition of Green functions as ground-state expectation values corresponds to the zero-temperature case $T = 0$. The definition can be generalized to arbitrary temperatures $T > 0$ by replacing the ground-state expectation value $\langle \Psi_0 | \cdot | \Psi_0 \rangle$ with the expectations with respect to the canonical ensemble $\hat{\rho} \propto \exp\left(-\frac{\hat{H}}{k_B T}\right)$. The corresponding Green functions are called *temperature Green functions*. As the temperature Green functions depend on the Hamiltonian in a complicated manner (through the time evolution and through the Boltzmann factor), their perturbation theory becomes clumsy. One therefore often considers the temperature Green functions in imaginary time. These imaginary-time Green functions are called *Schwinger functions*. (cf. [15, 21]) Fortunately, in Electronic Structure Theory, one can restrict attention to the ordinary Green functions (i.e. the Green functions at zero-temperature). This is due to the fact that the natural temperature scale for a metal is given by the Fermi temperature which is usually of order 10^4 K. On this scale room temperature is roughly zero.

Elementary Properties Due to

$$
\begin{aligned}
(\mathrm{i}\hbar)G^i{}_j(t,t') &= \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \; \varphi_i^*(\mathbf{x})G(\mathbf{x}t,\mathbf{x}'t')\varphi_j(\mathbf{x}') \\
&= \langle \Psi_0 | \mathcal{T} \int \mathrm{d}\mathbf{x} \; \varphi_i^*(\mathbf{x})\hat{\psi}(\mathbf{x}t) \int \mathrm{d}\mathbf{x}' \; \varphi_j(\mathbf{x}')\hat{\psi}^\dagger(\mathbf{x}'t') | \Psi_0 \rangle \\
&= \langle \Psi_0 | \mathcal{T} a_i(t)a_j^\dagger(t') | \Psi_0 \rangle
\end{aligned}
$$

the Green function (as well as its higher-order counterparts) is a well-defined distribution. Using the explicit time-dependence $\hat{\psi}(t) = \mathrm{e}^{\mathrm{i}\hat{H}t/\hbar}\hat{\psi}\mathrm{e}^{-\mathrm{i}\hat{H}t/\hbar}$, we see that we can write

$$
\mathrm{i}\hbar G^>(\mathbf{x}t,\mathbf{x}'t') = \mathrm{e}^{\mathrm{i}E_0(t-t')/\hbar}\langle \Psi_0 | \hat{\psi}(\mathbf{x})\hat{U}(t,t')\hat{\psi}^\dagger(\mathbf{x}') | \Psi_0 \rangle \tag{3.14}
$$

with the time-evolution operator

$$
\hat{U}(t,t') = \exp\left(-\frac{\mathrm{i}}{\hbar}\hat{H}(t-t')\right). \tag{3.15}
$$

Therefore, for the time-dependent family of integral operators $G^>(t,t') : \mathcal{H} \to \mathcal{H}$; $\varphi(\mathbf{x}) \mapsto \int \mathrm{d}\mathbf{x}' \; G^>(\mathbf{x}t,\mathbf{x}'t')\varphi(\mathbf{x}')$, we find

$$
\begin{aligned}
\|G^>(t,t')\| &= \sup_{\varphi \in \mathcal{H}} \frac{\|G^>(t,t')\varphi\|}{\|\varphi\|} \\
&= \hbar^{-1} \sup_{\Phi \in \mathfrak{P}^{N+1}} \frac{\|\hat{U}(t,t')\Phi\|}{\|\Phi\|} \\
&\leq \hbar^{-1} \sup_{\Phi \in \mathcal{H}^{N+1}} \frac{\|\hat{U}(t,t')\Phi\|}{\|\Phi\|} \\
&= \hbar^{-1}\|\hat{U}(t,t')\| \\
&= \hbar^{-1}
\end{aligned}
$$

where $\mathfrak{P}$ denotes the one-particle excitation space associated with the N-particle ground-state Ψ_0 given by $\{\Phi \in \mathcal{H}^{n+1} | \exists \varphi \in \mathcal{H} : \Phi = a^{\dagger}(\varphi)\Psi_0\}$. Hence, $G^{>}$ is bounded. Analogously, one shows that $G^{<}$ is bounded and by (3.11), $G^{\mathrm{R}}, G^{\mathrm{A}}$ and G are bounded integral operators for t, t' fixed. Finally, as fermionic field operators within the range of a time-ordering anti-commute, we conclude that $G(1, \ldots, n; n+1, \ldots, 2n)$ is totally antisymmetric with respect to permutations of the first n or the second n arguments (but not with respect to arbitrary permutations).

Evaluation of Observables in Terms of Green Functions Every second-quantized observable of normal form (expansion in terms of creators and annihilators) can be evaluated in terms of Green functions by taking suitable equal-time limits. For example, the density operator

$$\hat{n}(\mathbf{x}) = \hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}(\mathbf{x}) \tag{3.16}$$

has the expectation value

$$n(\mathbf{x}) = \langle \hat{n}(\mathbf{x}) \rangle = -\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}t^{+}). \tag{3.17}$$

For the second-quantized current observable

$$\hat{\mathbf{j}}(\mathbf{x}) = \frac{e\hbar}{2m\mathrm{i}}(\hat{\psi}^{\dagger}(\mathbf{x})\nabla\hat{\psi}(\mathbf{x}) - (\nabla\hat{\psi}^{\dagger}(\mathbf{x}))\hat{\psi}(\mathbf{x})) \tag{3.18}$$

we find

$$\mathbf{j}(\mathbf{x}) = \frac{e}{2m}\left(-\lim_{t'\to t^{+}}\lim_{\mathbf{x}'\to\mathbf{x}}\frac{\hbar}{\mathrm{i}}\nabla G(\mathbf{x}t, \mathbf{x}'t') + \lim_{t'\to t^{+}}\lim_{\mathbf{x}'\to\mathbf{x}}\frac{\hbar}{\mathrm{i}}\nabla' G(\mathbf{x}t, \mathbf{x}'t')\right). \tag{3.19}$$

For the Coulomb potential

$$\hat{V}_{\mathrm{Coul}} = \frac{1}{2}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, v(\mathbf{x} - \mathbf{x}')\hat{\psi}^{\dagger}(\mathbf{x}')\hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}(\mathbf{x})\hat{\psi}(\mathbf{x}') \tag{3.20}$$

we find

$$\langle \hat{V}_{\mathrm{Coul}} \rangle = \frac{(\mathrm{i}\hbar)^2}{2}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}' \, v(\mathbf{x} - \mathbf{x}') \lim_{t_3\to t_1^{+}}\lim_{t_4\to t_3^{+}}\lim_{t_1\to t_2^{+}} G^4(\mathbf{x}t_1, \mathbf{x}'t_2, \mathbf{x}t_3, \mathbf{x}'t_4). \tag{3.21}$$

Although the standard Hamiltonian contains a two-particle operator part (namely $\hat{V}_{\mathrm{Coul}}$), it is possible to evaluate $\hat{H}$ in terms of $G^2 \equiv G$ alone (instead of using G^4 as in the above formula for the expectation value of the Coulomb potential). For this purpose, one uses the equation of motion for the Heisenberg operator $\hat{\psi}(\mathbf{x}t)$ in the form

$$(\mathrm{i}\hbar\partial_t - \hat{H}_0)\hat{\psi}(\mathbf{x}t) = \int \mathrm{d}\mathbf{x}' \, v(\mathbf{x}' - \mathbf{x})\hat{\psi}^{\dagger}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}t). \tag{3.22}$$

Consequently,

$$
\begin{aligned}
\langle \hat{V}_{\mathrm{Coul}} \rangle &= \frac{1}{2} \int \mathrm{d}\mathbf{x}\,\mathrm{d}\mathbf{x}'\; v(\mathbf{x}' - \mathbf{x}) \langle \hat{\psi}^{\dagger}(\mathbf{x}t) \hat{\psi}^{\dagger}(\mathbf{x}'t) \hat{\psi}(\mathbf{x}'t) \hat{\psi}(\mathbf{x}t) \rangle \\
&= \frac{1}{2} \int \mathrm{d}\mathbf{x}\; \lim_{t'' \to t^+} \lim_{\mathbf{x}'' \to \mathbf{x}} (\mathrm{i}\hbar \partial_t - \hat{H}_0) \langle \hat{\psi}^{\dagger}(\mathbf{x}''t'') \hat{\psi}(\mathbf{x}t) \rangle \\
&= -\frac{\mathrm{i}\hbar}{2} \int \mathrm{d}\mathbf{x}\; \lim_{t'' \to t^+} \lim_{\mathbf{x}'' \to \mathbf{x}} (\mathrm{i}\hbar \partial_t - \hat{H}_0) G(\mathbf{x}t, \mathbf{x}''t'').
\end{aligned}
$$

The one-particle operator part $\hat{H}_0$ can trivially be evaluated in terms of G as

$$
\langle \hat{H}_0 \rangle = -\mathrm{i}\hbar \int \mathrm{d}\mathbf{x}\; \lim_{t'' \to t^+} \lim_{\mathbf{x}'' \to \mathbf{x}} \hat{H}_0 G(\mathbf{x}t, \mathbf{x}''t'') \tag{3.23}
$$

and therefore

$$
\langle \hat{H} \rangle = \langle \hat{H}_0 \rangle + \langle \hat{V}_{\mathrm{Coul}} \rangle = -\frac{\mathrm{i}\hbar}{2} \int \mathrm{d}\mathbf{x}\; \lim_{t'' \to t^+} \lim_{\mathbf{x}'' \to \mathbf{x}} (\mathrm{i}\hbar \partial_t + \hat{H}_0) G(\mathbf{x}t, \mathbf{x}''t''). \tag{3.24}
$$

This is the so-called *Migdal formula*.

3.1.2. Equation of Motion Theory

Introduction In this subsection, the equation of motion theory is reviewed. The most intuitive approach to calculate the Green function consists in deriving an equation of motion. This is done by differentiating the defining equation for the Green function with respect to t. By linearity this differentiation ∂_t is pulled under the expectation value where it acts on a field operator $\hat{\psi}(\mathbf{x}t)$. The equation of motion for a Heisenberg operator $\hat{\psi}(\mathbf{x}t)$ reads:

$$
\begin{aligned}
\mathrm{i}\hbar \partial_t \hat{\psi}(\mathbf{x}t) &= -\frac{\hbar^2}{2m} \Delta \hat{\psi}(\mathbf{x}t) + v_{\mathrm{ext}}(\mathbf{x}) \hat{\psi}(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\; v(\mathbf{x}' - \mathbf{x}) \hat{\psi}^{\dagger}(\mathbf{x}'t) \hat{\psi}(\mathbf{x}'t) \hat{\psi}(\mathbf{x}t) \\
&= -\frac{\hbar^2}{2m} \Delta \hat{\psi}(\mathbf{x}t) + [\hat{\psi}(\mathbf{x}t), \hat{V}].
\end{aligned}
$$

One then plugs this into the expectation value and reorders the formulas in terms of Green functions. The appearance of a term with three field operators in the time-derivative for one field operator signals that the equation of motion for G^2 contains a term proportional to G^4. From the Heisenberg equation of motion we conclude that this is a general feature: the equation of motion for G^{2n} involves G^{2n+2}. In other words, the Green functions form an infinite hierarchy. We now calculate the equation of motion for G^2 explicitly.

Lemma 3.1.1 $G(\mathbf{x}t, \mathbf{x}'t')$ *fulfills the following equation of motion:*

$$
(\mathrm{i}\hbar \partial_t + \frac{\hbar^2}{2m} \Delta_{\mathbf{x}}) G(\mathbf{x}t, \mathbf{x}'t') = \delta(t - t') \delta(\mathbf{x} - \mathbf{x}') + \frac{1}{\mathrm{i}\hbar} \langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}] \hat{\psi}^{\dagger}(\mathbf{x}'t') \rangle. \tag{3.25}
$$

Proof We use

$$
\begin{aligned}
[\hat{\psi}(\mathbf{x}), \hat{H}_0] &= -\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\hat{\psi}(\mathbf{x}) & (3.26) \\
\mathcal{T}\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') &= \theta(t-t')\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') - \theta(t'-t)\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t) & (3.27) \\
\partial_t\theta(t) &= \delta(t) & (3.28) \\
\{\hat{\psi}(\mathbf{x}t), \hat{\psi}^\dagger(\mathbf{x}'t)\} &= \delta(\mathbf{x}-\mathbf{x}'). & (3.29)
\end{aligned}
$$

Therefore, we get:

$$
\begin{aligned}
(\mathrm{i}\hbar)^2\partial_t G(\mathbf{x}t, \mathbf{x}'t') &= \mathrm{i}\hbar\partial_t\langle\theta(t-t')\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') - \theta(t'-t)\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)\rangle \\
&= \mathrm{i}\hbar\delta(t-t')\langle\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\rangle \\
&\quad -\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\theta(t-t')\langle\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\rangle \\
&\quad +\theta(t-t')\langle[\hat{\psi}(\mathbf{x}t),\hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle \\
&\quad +\mathrm{i}\hbar\delta(t-t')\langle\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)\rangle \\
&\quad +\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\theta(t-t')\langle\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)\rangle \\
&\quad -\theta(t-t')\langle\hat{\psi}^\dagger(\mathbf{x}'t')[\hat{\psi}(\mathbf{x}t),\hat{V}]\rangle \\
&= \mathrm{i}\hbar\delta(t-t')\langle\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\rangle \\
&\quad +\mathrm{i}\hbar\delta(t-t')\langle\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)\rangle \\
&\quad -\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}'t') \\
&\quad \langle\mathcal{T}[\hat{\psi}(\mathbf{x}t),\hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle \\
&= \mathrm{i}\hbar\delta(t-t')\delta(\mathbf{x}-\mathbf{x}') \\
&\quad -\frac{\hbar^2}{2m}\Delta_{\mathbf{x}}\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}'t') \\
&\quad \langle\mathcal{T}[\hat{\psi}(\mathbf{x}t),\hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle.
\end{aligned}
$$

In the last step we used the equal-time commutator because the Dirac-delta enforces equal-time arguments on the operators. (All expressions have to be interpreted as distributions acting on test functions $f(\mathbf{x}t)$.) Furthermore, note that derivatives can be pulled under the expectation value because the scalar product $\langle\Psi|\cdot|\Phi\rangle$ is a continuous (in the operator norm) functional mapping of operators into numbers.

Interaction Term We now turn to the potential. First, consider the case of an external potential:

$$
\hat{V}_{\text{ext}} = \int \mathrm{d}\mathbf{y}\; v_{\text{ext}}(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}). \tag{3.30}
$$

We then have

$$
\begin{aligned}
[\hat{\psi}(\mathbf{x}), \hat{V}_{\text{ext}}] &= [\hat{\psi}(\mathbf{x}), \int d\mathbf{y}\, v_{\text{ext}}(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})] \\
&= \int d\mathbf{y}\, v_{\text{ext}}(\mathbf{y})[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})] \\
&= \int d\mathbf{y}\, v_{\text{ext}}(\mathbf{y}) \left(\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) - \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x}) \right) \\
&= \int d\mathbf{y}\, v_{\text{ext}}(\mathbf{y}) \left(\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) + \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{x})\hat{\psi}(\mathbf{y}) \right) \\
&= \int d\mathbf{y}\, v_{\text{ext}}(\mathbf{y}) \left(\{\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\}\hat{\psi}(\mathbf{y}) \right) \\
&= v_{\text{ext}}(\mathbf{x})\hat{\psi}(\mathbf{x})
\end{aligned}
$$

and hence

$$
\begin{aligned}
\langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}_{\text{ext}}]\hat{\psi}^\dagger(\mathbf{x}'t') \rangle &= v_{\text{ext}}(\mathbf{x})\langle \mathcal{T}\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') \rangle \\
&= v_{\text{ext}}(\mathbf{x})i\hbar G(\mathbf{x}t, \mathbf{x}'t').
\end{aligned}
$$

Consequently in the presence of an external potential, the equation of motion for the Green function reads:

$$
\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_\mathbf{x} - v_{\text{ext}}(\mathbf{x}) \right) G_0(\mathbf{x}t, \mathbf{x}'t') = \delta(t - t')\delta(\mathbf{x} - \mathbf{x}') \tag{3.31}
$$

For later purposes, we note that the *conjugate equation of motion* reads

$$
\left(-i\hbar\partial_t' + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}'} - v_{\text{ext}}(\mathbf{x}') \right) G_0(\mathbf{x}t, \mathbf{x}'t') = \delta(t - t')\delta(\mathbf{x} - \mathbf{x}'), \tag{3.32}
$$

which can be shown analogously. We conclude that for non-interacting systems, the Green function reverts to a Green function in the sense of standard Quantum Mechanics (or partial differential equations). Now, we consider a two-particle interaction:

$$
\hat{V} = \int d\mathbf{y}d\mathbf{y}'\, \frac{1}{2}v(\mathbf{y}, \mathbf{y}')\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{y}'). \tag{3.33}
$$

We calculate

$$
\begin{aligned}
[\hat{\psi}(\mathbf{x}), \hat{V}] &= [\hat{\psi}(\mathbf{x}), \int d\mathbf{y}d\mathbf{y}'\, \frac{1}{2}v(\mathbf{y}, \mathbf{y}')\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y})] \\
&= \int d\mathbf{y}d\mathbf{y}'\, \frac{1}{2}v(\mathbf{y}, \mathbf{y}')[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y})].
\end{aligned}
$$

For the commutator $[\hat{\psi}(\mathbf{x}), \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{y}')]$, we get:

$$
\begin{aligned}
&= \hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) - \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{x}) \\
&= \hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) - \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{x})\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) \\
&= \hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y})\hat{\psi}(\mathbf{y}') + \hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{x})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) \\
&\quad - \hat{\psi}^\dagger(\mathbf{y})\delta(\mathbf{y}' - \mathbf{x})\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) \\
&= \delta(\mathbf{x} - \mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) - \delta(\mathbf{y}' - \mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y})
\end{aligned}
$$

Consequently, $[\hat{\psi}(\mathbf{x}), \hat{V}]$ yields:

$$
\begin{aligned}
&= \int \mathrm{d}\mathbf{y}\mathrm{d}\mathbf{y}' \, \frac{1}{2}v(\mathbf{y}, \mathbf{y}') \left(\delta(\mathbf{x} - \mathbf{y})\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) - \delta(\mathbf{y}' - \mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}')\hat{\psi}(\mathbf{y}) \right) \\
&= \left(\int \mathrm{d}\mathbf{y}' \, \frac{1}{2}v(\mathbf{x}, \mathbf{y}')\hat{\psi}^\dagger(\mathbf{y}')\hat{\psi}(\mathbf{y}') \right) \hat{\psi}(\mathbf{x}) + \left(\int \mathrm{d}\mathbf{y}\frac{1}{2}v(\mathbf{y}, \mathbf{x})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) \right) \hat{\psi}(\mathbf{x})
\end{aligned}
$$

Using the symmetry of the potential $\frac{1}{2}v(\mathbf{x}, \mathbf{y}) = \frac{1}{2}v(\mathbf{y}, \mathbf{x})$, we get

$$
\left(\int \mathrm{d}\mathbf{y} \, v(\mathbf{x}, \mathbf{y})\hat{\psi}^\dagger(\mathbf{y})\hat{\psi}(\mathbf{y}) \right) \hat{\psi}(\mathbf{x}). \tag{3.34}
$$

Hence, $\langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle$ yields

$$
\begin{aligned}
&= \left\langle \mathcal{T}\left(\int \mathrm{d}\mathbf{y} \, v(\mathbf{x}, \mathbf{y})\hat{\psi}^\dagger(\mathbf{y}t)\hat{\psi}(\mathbf{y}t) \right) \hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t') \right\rangle \\
&= \int \mathrm{d}\mathbf{y} \, v(\mathbf{x}, \mathbf{y})\langle \mathcal{T}(\hat{\psi}^\dagger(\mathbf{y}t)\hat{\psi}(\mathbf{y}t)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t'))\rangle
\end{aligned}
$$

In general, when there are both external potentials and interactions, the equation of motion reads:

$$
(\mathrm{i}\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_\mathbf{x} - v_{\text{ext}}(\mathbf{x}))G(\mathbf{x}t, \mathbf{x}'t') = \delta(t - t')\delta(\mathbf{x} - \mathbf{x}') + \frac{1}{\mathrm{i}\hbar}\langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle.
$$

Generalization to Arbitrary Green Functions The general equation of motion formula for $2n$-point Green functions is gained by considering

$$
(\mathrm{i}\hbar\partial_{t_1} + \frac{\hbar^2}{2m}\Delta - v_{\text{ext}}(\mathbf{x}_1))G(\mathbf{x}_1 t_1, \ldots, \mathbf{x}_n t_n; \mathbf{x}_{n+1}t_{n+1}, \ldots, \mathbf{x}_{2n}t_{2n}). \tag{3.35}
$$

A somewhat lengthy calculation (analogous to the one-particle Green function) shows that ([67], equation (5.4))

$$
(\mathrm{i}\hbar\partial_{t_1} + \frac{\hbar^2}{2m}\Delta - v_{\text{ext}}(\mathbf{x}_1))G^{2n}(\mathbf{x}_1 t_1, \ldots, \mathbf{x}_{2n}t_{2n}) =
$$

$$
\sum_{i=n+1}^{2n} \delta(t_1 - t_i)\delta(\mathbf{x}_1 - \mathbf{x}_i)(-1)^{i-1}G^{2n-2}(\widehat{\mathbf{x}_1 t_1}, \ldots, \mathbf{x}_n t_n; \mathbf{x}_{n+1}t_{n+1}, \ldots, \widehat{\mathbf{x}_i t_i}, \ldots, \mathbf{x}_{2n}t_{2n}) +
$$

$$
(\mathrm{i}\hbar)^{-n}\langle \mathcal{T}[\hat{\psi}(\mathbf{x}_1 t_1), \hat{V}]\hat{\psi}(\mathbf{x}_2 t_2)\ldots\hat{\psi}(\mathbf{x}_n t_n)\hat{\psi}^\dagger(\mathbf{x}_{n+1}t_{n+1})\ldots\hat{\psi}^\dagger(\mathbf{x}_{2n}t_{2n})\rangle.
$$

where the last term can be written as

$$(\mathrm{i}\hbar)^{-n} \int \mathrm{d}\mathbf{x}'\, v(\mathbf{x}_1 - \mathbf{x}')\langle \mathcal{T}\hat{\psi}^\dagger(\mathbf{x}'t_1)\hat{\psi}(\mathbf{x}'t_1)\hat{\psi}(\mathbf{x}_1t_1)\hat{\psi}(\mathbf{x}_2t_2)\ldots\hat{\psi}(\mathbf{x}_nt_n)\hat{\psi}^\dagger(\mathbf{x}_{n+1}t_{n+1})\ldots\hat{\psi}^\dagger(\mathbf{x}_{2n}t_{2n})\rangle$$

$$= -\mathrm{i}\hbar \int \mathrm{d}\mathbf{x}'\, v(\mathbf{x}_1 - \mathbf{x}')G^{2n+2}(\mathbf{x}'t_1, \mathbf{x}_1t_1, \ldots, \mathbf{x}_nt_n, ; \mathbf{x}'t_1, \mathbf{x}_{2n}t_{2n}, \ldots, \mathbf{x}_{n+1}t_{n+1}).$$

This shows that in general the equation of motion for the $2n$-function involves the expectation value of a product of $2n + 2$ operators. (This is due to the fact that the interaction is given by a pair potential. For arbitrary interactions there could be contributions of even higher order.) For later purposes we state the

Theorem 3.1.2 *The free $2n$-point functions $G_0^{2n}(1, \ldots, n; n+1, \ldots, 2n)$ factorize as*

$$G_0^{2n}(1, \ldots, n; n+1, \ldots, 2n) = \det G_0(i, n+j)|_{i,j=1,\ldots,n} \qquad (3.36)$$

Remark This is a Green function version of the so-called Wick theorem, which will be treated later. Here, we state this theorem because it has the same structure as the equation of motion for a free $2n$-point Green function. As the free Green function $G_0(\mathbf{x}t, \mathbf{x}'t')$ is the right-inverse integral operator to the free Hamiltonian $\mathrm{i}\hbar\partial_{t_1} + \frac{\hbar^2}{2m}\Delta - v_{\text{ext}}(\mathbf{x}_1)$, one can immediately gain back the equation of motion of the free $2n$-point Green function from the Wick theorem. Cavalierly accepting the Green function also as a left-inverse[1], a multiplication with $G_0(\mathbf{x}t, \mathbf{x}_1t_1)$ and a subsequent integration $\int \mathrm{d}\mathbf{x}_1\mathrm{d}t_1$ yields

$$G^{2n}(\mathbf{x}_1t_1, \ldots, \mathbf{x}_{2n}t_{2n}) =$$

$$\sum_{i=n+1}^{2n} (-1)^{i-1} G_0(\mathbf{x}_1t_1, \mathbf{x}_it_i)G^{2n-2}(\widehat{\mathbf{x}_1t_1}, \ldots, \mathbf{x}_nt_n; \mathbf{x}_{n+1}t_{n+1}, \ldots, \widehat{\mathbf{x}_it_i}, \ldots, \mathbf{x}_{2n}t_{2n}) +$$

$$- \mathrm{i}\hbar \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\mathrm{d}\mathbf{x}\mathrm{d}t\, G_0(\mathbf{x}_1t_1, \mathbf{x}t)v(\mathbf{x}t, \mathbf{x}'t')G^{2n+2}(\mathbf{x}'t', \mathbf{x}t, \ldots, \mathbf{x}_nt_n; \mathbf{x}'t', \mathbf{x}_{n+1}t_{n+1}, \ldots, \mathbf{x}_{2n}t_{2n}).$$

where after the convolution we have renamed $\mathbf{x}t \mapsto \mathbf{x}_1t_1$ and vice versa. In particular, this applies to the free Green functions G_0^{2n} themselves where the interaction terms vanishes:

$$G_0^{2n}(\mathbf{x}_1t_1, \ldots, \mathbf{x}_{2n}t_{2n}) =$$

$$\sum_{i=n+1}^{2n} (-1)^{i-1} G_0(\mathbf{x}_1t_1, \mathbf{x}_it_i)G_0^{2n-2}(\widehat{\mathbf{x}_1t_1}, \ldots, \mathbf{x}_nt_n; \mathbf{x}_{n+1}t_{n+1}, \ldots, \widehat{\mathbf{x}_it_i}, \ldots, \mathbf{x}_{2n}t_{2n}).$$

Iteration of this formula yields the Wick theorem.

---

[1]This can be shown by by a partial integration and the conjugate equation of motion.

3.1.3. Self-Energy

Introduction The equation of motion for the two-point function reads

$$(\mathrm{i}\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}})G(\mathbf{x}t, \mathbf{x}'t') = \delta(t-t')\delta(\mathbf{x}-\mathbf{x}') + \frac{1}{\mathrm{i}\hbar}\langle\mathcal{T}[\hat{\psi}(\mathbf{x}t),\hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle$$

The fundamental drawback of the equation of motion is that it cannot be used to calculate G because it is not a closed equation. One therefore assumes that the equation of motion for $G(\mathbf{x}t, \mathbf{x}'t')$ can be rewritten in the form:

$$\left(\mathrm{i}\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}} - v_{\mathrm{ext}}(\mathbf{x})\right)G(\mathbf{x}t, \mathbf{x}'t') = \delta(t-t')\delta(\mathbf{x}-\mathbf{x}') +$$

$$\int \mathrm{d}t''\mathrm{d}\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}t, \mathbf{x}''t'')G(\mathbf{x}''t'', \mathbf{x}'t')$$

where $\tilde{\Sigma} = \tilde{\Sigma}[G]$ is (highly non-linear) functional of G.

Definition The integral operator $\tilde{\Sigma}(\mathbf{x}t, \mathbf{x}'t')$ is called *irreducible* or *proper self energy*.

Remarks

1. Remembering that $\left(\mathrm{i}\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}} - v_{\mathrm{ext}}(\mathbf{x})\right)$ is the inverse of $G_0(\mathbf{x}t, \mathbf{x}'t')$, we see that the equation of motion in terms of $\tilde{\Sigma}$ can be rewritten as

$$G(\mathbf{x}t, \mathbf{x}'t') = G_0(\mathbf{x}t, \mathbf{x}'t') + \int \mathrm{d}\mathbf{x}''\mathrm{d}t''\mathrm{d}\mathbf{x}'''\mathrm{d}t''' \ G_0(\mathbf{x}t, \mathbf{x}''t'')\tilde{\Sigma}(\mathbf{x}''t'', \mathbf{x}'''t''')G(\mathbf{x}'''t''', \mathbf{x}'t')$$

   or symbolically

$$G = G_0 + G_0\tilde{\Sigma}G \tag{3.37}$$

   This is called *Dyson equation* and constitutes the many-body analog of (1.67).

2. We reproduce this introduction of the self-energy through a redefinition of the equation of motion because it is a standard trick in the literature. It should be stressed, however, that the introduction of $\tilde{\Sigma}$ has no meaning as long as it is not clear how $\tilde{\Sigma}$ can be actually calculated as a functional of G. We will later see that typical ansätze can be derived from Green function perturbation theory.

3. External potentials can be absorbed in a redefinition of the self energy via

$$\tilde{\Sigma}(\mathbf{x}, \mathbf{x}'t') \mapsto \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'t') - v_{\mathrm{ext}}(\mathbf{x}')\delta(\mathbf{x}-\mathbf{x}')\delta(t-t'). \tag{3.38}$$

   This becomes important if one starts with a DFT reference Green function. The self-energy then has to be redefined as $\tilde{\Sigma} - v_{\mathrm{xc}} - v_{\mathrm{H}}$, because the exchange-correlation potential is not present in the original Hamiltonian. $\tilde{\Sigma}_{\mathrm{xc}} = \tilde{\Sigma} - v_{\mathrm{H}}$ is called *exchange-correlation self-energy*.

4. Per constructionem, the self-energy is defined through the equation:

$$\langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}]\hat{\psi}^{\dagger}(\mathbf{x}'t')\rangle = i\hbar \int dt'' d\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}t, \mathbf{x}''t'')G(\mathbf{x}''t'', \mathbf{x}'t'). \qquad (3.39)$$

The catch here is that the convolution of the self-energy with the two-point function goes over space and time whereas on the LHS there are only spatial integrations. In order to write this equation in a more symmetric fashion, we transform as

$$
\begin{aligned}
\langle \mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}]\hat{\psi}^{\dagger}(\mathbf{x}'t')\rangle &= -(i\hbar)^2 \int d\mathbf{x}''\ v(\mathbf{x} - \mathbf{x}'')G_4(\mathbf{x}t, \mathbf{x}''t, \mathbf{x}'t', \mathbf{x}''t) \\
&= -(i\hbar)^2 \int d\mathbf{x}''dt''\ v(\mathbf{x} - \mathbf{x}'')\delta(t - t'')G_4(\mathbf{x}t, \mathbf{x}''t'', \mathbf{x}'t', \mathbf{x}''t'') \\
&= -(i\hbar)^2 \int d\mathbf{x}''dt''\ v(\mathbf{x}t, \mathbf{x}''t'')G_4(\mathbf{x}t, \mathbf{x}''t'', \mathbf{x}'t', \mathbf{x}''t'')
\end{aligned}
$$

with the instantaneous potential $v(x, x') = v(\mathbf{x}t, \mathbf{x}'t') = v(\mathbf{x} - \mathbf{x}')\delta(t - t')$. The problem of the equal-time limit in G^4 will be treated later. Symbolically, the introduction of the self-energy now amounts to the replacement (cf section 4.1.4)

$$-i\hbar V \cdot G^4 =: \tilde{\Sigma}G. \qquad (3.40)$$

For later purposes, we note in this context that the equation of motion can in this notation be written as

$$G = G_0 - i\hbar G_0 V \cdot G^4. \qquad (3.41)$$

We see that this replacement is possible iff the Green function G is formally invertible (as an operator kernel in $\mathbf{x}t$): if it is invertible, then $\tilde{\Sigma} \propto VG^4G^{-1}$. Conversely, if $\tilde{\Sigma}$ exists, then $i\hbar\partial_t - \hat{H}_0 - \tilde{\Sigma}$ is the inverse of G.

5. For a time-independent Hamiltonian, the self-energy depends only on the time-difference $\tilde{\Sigma} = \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; t - t')$. Consequently, we find

$$
\begin{aligned}
&\int dt'' d\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}t, \mathbf{x}''t'')G(\mathbf{x}''t'', \mathbf{x}'t') \\
&= \int dt'' d\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}, \mathbf{x}''; t - t'')G(\mathbf{x}'', \mathbf{x}'t'' - t') \\
&= \int dt'' d\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}, \mathbf{x}''; t - t'')G(\mathbf{x}'', \mathbf{x}'; t - t' - (t - t'')).
\end{aligned}
$$

Consequently, this integral is a convolution in t the outcome of which is again a function of the time difference $t - t'$ only. (This has to be the case on grounds of consistency.) In the frequency domain, we get for the self-energy contribution

$$\int d\mathbf{x}''\ \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'', \hbar\omega)G(\mathbf{x}'', \mathbf{x}', \hbar\omega). \qquad (3.42)$$

6. The *reducible self-energy* is defined by the ansatz:

$$G(\mathbf{x}t, \mathbf{x}'t') = G_0(\mathbf{x}t, \mathbf{x}'t') + \int d\mathbf{x}''dt''d\mathbf{x}'''dt''' \, G_0(\mathbf{x}t, \mathbf{x}''t'')\Sigma(\mathbf{x}''t'', \mathbf{x}'''t''')G_0(\mathbf{x}'''t''', \mathbf{x}'t')$$

or symbolically

$$G = G_0 + G_0\Sigma G_0. \tag{3.43}$$

By iteration of the Dyson equation, one shows easily the relation

$$\Sigma = \tilde{\Sigma} + \tilde{\Sigma}G_0\Sigma. \tag{3.44}$$

7. In the case of a homogeneous system ($v_{\text{ext}}(\mathbf{x}) = \text{const.}$), both the Green function and the self-energy depend only on the difference of their arguments. A Fourier transformation of the Dyson equation with respect to these differences then yields

$$G(k) = G(k) + G_0(k)\tilde{\Sigma}(k)G(k) \tag{3.45}$$

with $k = (\omega, \mathbf{k})$. In Fourier space, the free Green function reads:

$$G_0(k) = \frac{1}{\hbar\omega - \varepsilon_0(\mathbf{k}) \pm i\eta} \tag{3.46}$$

where $\varepsilon_0(k)$ is the dispersion relation of the free Schrödinger equation. Therefore, the full propagator in Fourier space reads:

$$G(k) = \frac{1}{\hbar\omega - \varepsilon_0(\mathbf{k}) - \tilde{\Sigma}(k)}. \tag{3.47}$$

3.2. Lehmann Representation

3.2.1. Definition

Derivation of the Lehmann Representation In the expression for the two-point Green function we insert the identity on the Fock space $\mathcal{F}$ in the form

$$\mathbb{1}_{\mathcal{F}} = \sum_N \sum_s |N\ s\rangle\langle N\ s| \tag{3.48}$$

between the field operators where $|N\ s\rangle$ denotes a complete system of N-particle energy eigenstates with energy E_s and the sum goes over all particle numbers and all eigenstates for fixed particle numbers. We set $|\Psi_0\rangle \equiv |N\ 0\rangle$ and get

$$i\hbar G(\mathbf{x}t, \mathbf{x}'t') = \sum_s \theta(t - t')\langle N\ 0|\hat{\psi}(\mathbf{x}t)|N+1\ s\rangle\langle N+1\ s|\hat{\psi}^\dagger(\mathbf{x}'t')|N\ 0\rangle$$

$$- \sum_s \theta(t' - t)\langle N\ 0|\hat{\psi}^\dagger(\mathbf{x}'t')|N-1\ s\rangle\langle N-1\ s|\hat{\psi}(\mathbf{x}t)|N\ 0\rangle.$$

Next, we use

$$\hat{\psi}^{(\dagger)}(\mathbf{x}t) = e^{\frac{i}{\hbar}\hat{H}t}\hat{\psi}^{(\dagger)}(\mathbf{x})e^{-\frac{i}{\hbar}\hat{H}t} \tag{3.49}$$

and act with the time-evolution operators directly on the energy eigenstates. This yields

$$
\begin{aligned}
i\hbar G(\mathbf{x}t, \mathbf{x}'t') &= \sum_s \theta(t-t')e^{-\frac{i}{\hbar}(E_s^{N+1}-E_0^N)(t-t')}\langle N\ 0|\hat{\psi}(\mathbf{x})|N+1\ s\rangle\langle N+1\ s|\hat{\psi}^\dagger(\mathbf{x}')|N\ 0\rangle \\
&\quad - \sum_s \theta(t'-t)e^{-\frac{i}{\hbar}(E_s^{N-1}-E_0^N)(t'-t)}\langle N\ 0|\hat{\psi}^\dagger(\mathbf{x}')|N-1\ s\rangle\langle N-1\ s|\hat{\psi}(\mathbf{x})|N\ 0\rangle
\end{aligned}
$$

We define

$$
\begin{aligned}
f_s(\mathbf{x}) = f_s^+(\mathbf{x}) &= \langle N\ 0|\hat{\psi}(\mathbf{x})|N+1\ s\rangle \tag{3.50}\\
f_s(\mathbf{x}) = f_s^-(\mathbf{x}) &= \langle N-1\ s|\hat{\psi}(\mathbf{x})|N\ 0\rangle \tag{3.51}\\
\varepsilon_s^+ &= E_s^{N+1} - E_0^N \tag{3.52}\\
\varepsilon_s^- &= E_s^{N-1} - E_0^N \tag{3.53}
\end{aligned}
$$

The $f_s^\pm$ are called *Lehmann amplitudes* and the $\varepsilon_s^\pm$ are called *quasiparticle energies*. Introducing $\tau = t - t'$, the Green function can be written compactly as

$$i\hbar G(\mathbf{x}, \mathbf{x}'; \tau) = \sum_s \theta(\tau)e^{-\frac{i}{\hbar}\varepsilon_s^+\tau}f_s^+(\mathbf{x})f_s^{+*}(\mathbf{x}') - \sum_s \theta(-\tau)e^{\frac{i}{\hbar}\varepsilon_s^-\tau}f_s^-(\mathbf{x})f_s^{-*}(\mathbf{x}').$$

The Lehmann representation is the direct analog of the Kallen-Lehmann representation for the propagator in relativistic Quantum Field Theory. (see e.g. [92] Chapter 13)

Spectral Representation We define the Fourier transform of the Green function by

$$
\begin{aligned}
G(\omega) &= \int_{-\infty}^{\infty} d\tau\ e^{+\frac{i}{\hbar}E\tau}G(\tau) \tag{3.54}\\
G(\tau) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\ e^{-\frac{i}{\hbar}E\tau}G(\omega) \tag{3.55}
\end{aligned}
$$

with $E = \hbar\omega$ and use the master formula (see e.g. appendix on Fourier transforms and complex analysis)

$$\int_{-\infty}^{\infty} d\tau\ \theta(\pm\tau)e^{\mp\frac{i}{\hbar}(E_0-i\eta)\tau+\frac{i}{\hbar}E\tau} = \mp\frac{\hbar}{i}\frac{1}{E\mp(E_0-i\eta)} \tag{3.56}$$

to get

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \sum_s \frac{f_s^+(\mathbf{x})f_s^{+*}(\mathbf{x}')}{E - \varepsilon_s^+ + i\eta} + \sum_s \frac{f_s^-(\mathbf{x})f_s^{-*}(\mathbf{x}')}{E + \varepsilon_s^- - i\eta} \tag{3.57}$$

This form of the Lehmann representation is the many-body analog of equation (1.52). By the same method, one shows that

$$G^{\mathrm{R}}(\mathbf{x}, \mathbf{x}'; \omega) \;=\; \sum_s \frac{f_s^+(\mathbf{x}) f_s^{+*}(\mathbf{x}')}{E - \varepsilon_s^+ + \mathrm{i}\eta} + \sum_s \frac{f_s^-(\mathbf{x}) f_s^{-*}(\mathbf{x}')}{E + \varepsilon_s^- + \mathrm{i}\eta} \qquad (3.58)$$

$$G^{\mathrm{A}}(\mathbf{x}, \mathbf{x}'; \omega) \;=\; \sum_s \frac{f_s^+(\mathbf{x}) f_s^{+*}(\mathbf{x}')}{E - \varepsilon_s^+ - \mathrm{i}\eta} + \sum_s \frac{f_s^-(\mathbf{x}) f_s^{-*}(\mathbf{x}')}{E + \varepsilon_s^- - \mathrm{i}\eta}. \qquad (3.59)$$

In other words, from a numerical point of view G, G^{R} and G^{A} all have the same Fourier transform. (The $\mathrm{i}\eta$ in the denominator says nothing about the "value" of the Fourier transform at ω but is a way of bookkeeping, i.e. it says to which Fourier preimage the function belongs.)

Introduction of the Chemical Potential The spectral Lehmann representation shows that the Green function has poles at

$$\pm\varepsilon_s^\pm \;=\; \pm(E_s^{N\pm1} - E_0^N) \qquad (3.60)$$

$$=\; \pm(E_s^{N\pm1} - E_0^{N\pm1} + E_0^{N\pm1} - E_0^N) \qquad (3.61)$$

$$=\; \pm(\epsilon_s^{N\pm1} \pm \mu^N) \qquad (3.62)$$

where

$$\epsilon_s^{N\pm1} = E_s^{N\pm1} - E_0^{N\pm1} \qquad (3.63)$$

is the so-called *optical spectrum* and

$$\mu^N = E_0^{N+1} - E_0^N \qquad (3.64)$$

is the chemical potential at temperature $T = 0$. In the spirit of the thermodynamic limit we assume $\mu^N \approx \mu^{N-1} =: \mu$. We have the following inequalities

$$\mu^N \;\geq\; 0 \qquad (3.65)$$

$$\epsilon_s^N \;\geq\; 0 \qquad (3.66)$$

$$\varepsilon_s^+ \;\geq\; \mu \qquad (3.67)$$

$$-\varepsilon_s^- \;\leq\; \mu. \qquad (3.68)$$

Introducing

$$e_s = \begin{cases} \varepsilon_s^+ & \text{if } e_s \geq \mu \\ -\varepsilon_s^- & \text{if } e_s \leq \mu \end{cases} \qquad (3.69)$$

we can write the Green function even more compactly as

$$\mathrm{i}\hbar G(\mathbf{x}, \mathbf{x}'; \tau) \;=\; \sum_{s;\, N\pm1} f_s(\mathbf{x}) f_s^*(\mathbf{x}') \mathrm{e}^{-\frac{\mathrm{i}}{\hbar} e_s \tau} (\theta(\tau)\theta(e_s - \mu) - \theta(-\tau)\theta(\mu - e_s)) \qquad (3.70)$$

$$G(\mathbf{x}, \mathbf{x}'; \omega) \;=\; \sum_{s;\, N\pm1} \frac{f_s(\mathbf{x}) f_s^*(\mathbf{x}')}{\hbar\omega - e_s + \mathrm{sg}(e_s - \mu)\mathrm{i}\eta}. \qquad (3.71)$$

3.2.2. Properties

Lemma 3.2.1 *The Lehmann amplitudes have the following properties:*

1. *The Lehmann amplitudes are square-integrable: $f_s \in \mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$.*

2. *The Lehmann amplitudes are complete.*

3. *The Lehmann amplitudes fulfill $\|f_s\| \leq 1$.*

4. *The Lehmann amplitudes constitute an overcomplete set if $\|f_s\| < 1$ at least for one f_s. In this case, the Lehmann amplitudes are in general not orthogonal.*

Proof

1. We introduce $\Psi^N_{s\mathbf{x}} = \hat{\psi}(\mathbf{x})\Psi^{N+1}_s$. It follows that

$$\langle \Psi^N_{s\mathbf{x}} | \Psi^N_{s\mathbf{x}} \rangle = \langle \Psi^{N+1}_s | \hat{n}(\mathbf{x}) | \Psi^{N+1}_s \rangle = n(\mathbf{x}). \tag{3.72}$$

On the other hand

$$\int d\mathbf{x}\, f_s^{+*}(\mathbf{x}) f_s^+(\mathbf{x}) = \int d\mathbf{x}\, \langle \Psi^N_{\mathbf{x}s} | \Psi_0 \rangle \langle \Psi_0 | \Psi^N_{s\mathbf{x}} \rangle \leq \int d\mathbf{x}\, \langle \Psi^N_{s\mathbf{x}} | \Psi^N_{s\mathbf{x}} \rangle = N + 1. \tag{3.73}$$

This shows $\|f_s^+\| \leq \infty$. The arguments for f_s^- are analogous.

2. Follows from

$$
\begin{aligned}
\sum_s f_s(\mathbf{x}) f_s^*(\mathbf{x}') &= \sum_s \langle N\, 0 | \hat{\psi}^\dagger(\mathbf{x}) | N-1\, s \rangle \langle N-1\, s | \hat{\psi}(\mathbf{x}') | N\, 0 \rangle + \\
&\quad \sum_{s;} \langle N\, 0 | \hat{\psi}(\mathbf{x}) | N+1\, s \rangle \langle N+1\, s | \hat{\psi}^\dagger(\mathbf{x}') | N\, 0 \rangle \\
&= \langle N\, 0 | \hat{\psi}^\dagger(\mathbf{x}) \mathbb{1}_\mathcal{F} \hat{\psi}(\mathbf{x}') | N\, 0 \rangle + \langle N\, 0 | \hat{\psi}(\mathbf{x}) \mathbb{1}_\mathcal{F} \hat{\psi}^\dagger(\mathbf{x}') | N\, 0 \rangle \\
&= \langle N\, 0 | \{ \hat{\psi}^\dagger(\mathbf{x}), \hat{\psi}(\mathbf{x}') \} | N\, 0 \rangle \\
&= \delta(\mathbf{x} - \mathbf{x}') \langle N\, 0 | N\, 0 \rangle \\
&= \delta(\mathbf{x} - \mathbf{x}').
\end{aligned}
$$

3. By the second point

$$\sum_s |f_s\rangle\langle f_s| = \mathbb{1}_\mathcal{H}. \tag{3.74}$$

Assume $\|f_r\| > 1$ for some r. Let e_r be the unit vector in the r-th direction. Then

$$1 = \langle e_r | e_r \rangle = \sum_s \langle e_r | f_s \rangle \langle f_s | e_r \rangle \geq \langle e_r | f_r \rangle \langle f_r | e_r \rangle > 1. \tag{3.75}$$

This contradiction proves $\forall r :\ \|f_r\| \leq 1$.

4. By the second point, the Lehmann amplitudes certainly constitute a complete set. Overcompleteness means: a proper subset of $\{f_s\}$ is already complete. In order to prove that such a subset exists, we show that a generic Lehmann amplitude f with $\|f\| < 1$ is not independent of the remaining amplitudes f_s. It then follows that the set $\{f_s\} \setminus \{f\}$ is already complete. Now, assume that f is linearly independent of the f_s. It follows that there exists some $e \in \mathcal{H}$; $\|e\| = 1$ such that $\langle e|f_s \rangle = 0$ for $f_s \neq f$ and $\langle e|f \rangle \neq 0$. f can be written as $f = g + \langle e|f \rangle e$ where $g \perp e$ and $|\langle e|f \rangle|^2 < 1$. Consequently

$$|f\rangle\langle f| = |g\rangle\langle g| + |\langle e|f\rangle|^2|e\rangle\langle e| + \langle f|e\rangle|g\rangle\langle e| + \langle e|f\rangle|e\rangle\langle g| \tag{3.76}$$

On the other hand

$$|f\rangle\langle f| + \sum_s |f_s\rangle\langle f_s| = \mathbb{1}_{\mathcal{H}} \tag{3.77}$$

Application of the identity in this form on the vector $|e\rangle$ eo ipso yields a contradiction. This proves in particular the last point because in an overcomplete set not all functions can be orthogonal.

Example Let $\varphi_i(\mathbf{x})$ be a complete system of energy eigenstates of a one-particle Hamiltonian $\hat{H}_0$. The corresponding non-interacting, many-body ground-state Φ_0^N is given by a Slater determinant:

$$\Phi_0^N(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det(\varphi_i(\mathbf{x}_j))_{i,j=1\ldots N} \tag{3.78}$$

One shows easily: the f_s^- coincide with the occupied orbitals and the f_s^+ with the unoccupied orbitals. The corresponding quasiparticle energies are given by the respective one-particle energies of the Hamiltonian $\hat{H}_0$.

Lemma 3.2.2 *Let $\hat{U}$ be a symmetry of the Hamiltonian, i.e. a unitary operator with $[\hat{U}, \hat{H}] = 0$. The Lehmann amplitudes can then be chosen as eigenstates of $\hat{U}$.*

Proof In any case, there exists a complete orthonormal system of (possibly generalized) eigenvectors Ψ_s of both $\hat{U}$ and $\hat{H}$ and we are free to define the $f_s^\pm$ with respect to these Ψ_s. Introducing a Hilbert space basis $\{\varphi_n\}$ in the one-particle Hilbert space $\mathcal{H}$, we can then write

$$\hat{\psi}(\mathbf{x}) = \sum_n \varphi_n(\mathbf{x}) a_n \tag{3.79}$$

and hence

$$f_s^+(\mathbf{x}) = \sum_n \langle \Psi_0 | a(\varphi_n) | \Psi_s^{N+1} \rangle \varphi_n(\mathbf{x}). \tag{3.80}$$

By applying the definition of creators and annihilators, one shows easily that for any $\hat{U}$

$$\hat{U}a^{\dagger}(\varphi)\hat{U}^{\dagger} = a^{\dagger}(\hat{U}\varphi) \tag{3.81}$$

$$\hat{U}a(\varphi)\hat{U}^{\dagger} = a(\hat{U}\varphi). \tag{3.82}$$

This implies

$$a(\varphi) = \hat{U}^{\dagger}a(\hat{U}\varphi)\hat{U}. \tag{3.83}$$

On the other hand, as the Hilbert space basis in equation (3.79) is arbitrary, we have

$$\hat{\psi}(\mathbf{x}) = \sum_n (\hat{U}\varphi_n)(\mathbf{x})a(\hat{U}\varphi). \tag{3.84}$$

We therefore find

$$
\begin{aligned}
(\hat{U}f_s)(\mathbf{x}) &= \sum_n \langle\Psi_0|a(\varphi_n)|\Psi_s^{N+1}\rangle(\hat{U}\varphi_n)(\mathbf{x}) & (3.85)\\
&= \sum_n \langle\Psi_0|\hat{U}^{\dagger}a(\hat{U}\varphi_n)\hat{U}|\Psi_s^{N+1}\rangle(\hat{U}\varphi_n)(\mathbf{x}) & (3.86)\\
&= \langle\Psi_0|\hat{U}^{\dagger}\sum_n a(\hat{U}\varphi_n)(\hat{U}\varphi_n)(\mathbf{x})\hat{U}|\Psi_s^{N+1}\rangle & (3.87)\\
&= \langle\Psi_0|\hat{U}^{\dagger}\hat{\psi}(\mathbf{x})\hat{U}|\Psi_s^{N+1}\rangle. & (3.88)
\end{aligned}
$$

Hence,

$$(\hat{U}f_s^+)(\mathbf{x}) = \langle\Psi_0|\hat{U}^{\dagger}\hat{\psi}(\mathbf{x})\hat{U}|\Psi_s^{N+1}\rangle = \mathrm{e}^{\mathrm{i}(g_s^{N+1}-g_0^N)}\langle\Psi_0|\hat{\psi}(\mathbf{x})|\Psi_s^{N+1}\rangle = \mathrm{e}^{\mathrm{i}(g_s^{N+1}-g_0^N)}f_s(\mathbf{x})$$

where $\hat{U}\Psi_s^N = \mathrm{e}^{\mathrm{i}g_s^N}\Psi_s^N$. Similarly one argues for f_s^-.

This result can be easily generalized to the following:

Lemma 3.2.3 *Let G be an abelian symmetry group of the Hamiltonian $\hat{H}$ with unitary representation $\hat{U}_g$; $g \in G$ on $\mathcal{F} = \oplus_{n=0}^{\infty}\mathcal{H}^n$. Then the Lehmann amplitudes can be chosen such that they are eigenvectors of the $\hat{U}_g$.*

The typical application is the abelian group of lattice translations. The lemma then says that the Lehmann amplitudes can be chosen to be of Bloch form. This can also be shown directly. The energy eigenstates Ψ_s^{N+1} and Ψ_0^N can be chosen to diagonalize $\hat{U}_{\mathbf{a}}$ with Bloch vectors $\mathbf{K}$ and $\mathbf{K}_0$ respectively. Therefore, we have

$$
\begin{aligned}
f_s^+(\mathbf{x}+\mathbf{a}) &= \langle\Psi_s^{N+1}|\hat{\psi}(\mathbf{x}+\mathbf{a})|\Psi_0^N\rangle\\
&= \langle\Psi_s^{N+1}|\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{\mathbf{P}}\mathbf{a}}\hat{\psi}(\mathbf{x})\mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{\mathbf{P}}\mathbf{a}}|\Psi_0^N\rangle\\
&= \langle\Psi_s^{N+1}|\hat{U}_{-\mathbf{a}}\hat{\psi}(\mathbf{x})\hat{U}_{\mathbf{a}}|\Psi_0^N\rangle\\
&= \mathrm{e}^{\mathrm{i}\Delta\mathbf{K}\mathbf{a}}f_s^+(\mathbf{x}).
\end{aligned}
$$

with $\Delta \mathbf{K} = \mathbf{K} - \mathbf{K}_0$. Here, $U_{\mathbf{a}}$ is defined to act on $\psi(\mathbf{x})$ as $(U_{\mathbf{a}}\psi)(\mathbf{x}) = \psi(\mathbf{x} + \mathbf{a})$. In particular, for a lattice invariant Hamiltonian, we have:

Corollary 3.2.4 *The self-energy integral operator $\tilde{\Sigma}(\mathbf{x}t, \mathbf{x}'t')$ is invariant under the joint translation* $\mathbf{x}, \mathbf{x}' \mapsto \mathbf{x} - \mathbf{a}, \mathbf{x}' - \mathbf{a}$.

Proof The Green function G is invariant under joint translations as can be seen e.g. from the Lehmann representation using the lattice translation invariance of the amplitudes. With G itself, G^{-1} is also lattice translation invariant as follows from

$$
\begin{aligned}
\delta(\mathbf{x}' - \mathbf{x})\delta(t - t') &= \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \ G^{-1}(\mathbf{x}t, \mathbf{x}''t'')G(\mathbf{x}''t'', \mathbf{x}'t') \\
&= \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \ G^{-1}(\mathbf{x}t, \mathbf{x}''t'')G(\mathbf{x}'' - \mathbf{a}, t''; \mathbf{x}' - \mathbf{a}, t') \\
&= \int \mathrm{d}\mathbf{x}''\mathrm{d}t'' \ G^{-1}(\mathbf{x} + \mathbf{a}, t; \mathbf{x}'' + \mathbf{a}, t'')G(\mathbf{x}''t'', \mathbf{x}'t').
\end{aligned}
$$

The free reference Green function has at least the symmetry group of the Green function. The invariance of the self-energy now follows from the Dyson equation in the form

$$
\tilde{\Sigma}(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega). \tag{3.89}
$$

Lemma 3.2.5 *If we have a set* $\{(f_s^{\pm}(\mathbf{x}), \varepsilon_s^{\pm})\}$ *of functions and numbers ("energies") fulfilling the (in general non-linear) eigenvalue equation*

$$
\left(-\frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^{\pm}(\mathbf{x}) + \int \mathrm{d}\mathbf{x}' \ \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; \pm\varepsilon_s^{\pm}/\hbar)f_s^{\pm}(\mathbf{x}') = \pm\varepsilon_s^{\pm}f_s^{\pm}(\mathbf{x}), \tag{3.90}
$$

then the Green function G constructed from these very $\{(f_s^{\pm}(\mathbf{x}), \varepsilon_s^{\pm})\}$ *by virtue of*

$$
\mathrm{i}\hbar G(\mathbf{x}, \mathbf{x}'; \tau) = \sum_{s; \ N\pm 1} f_s(\mathbf{x})f_s^*(\mathbf{x}')e^{-\frac{\mathrm{i}}{\hbar}e_s\tau}(\theta(\tau)\theta(e_s - \mu) - \theta(-\tau)\theta(\mu - e_s)) \tag{3.91}
$$

fulfills

$$
G = G_0 + G_0\tilde{\Sigma}G. \tag{3.92}
$$

Remarks

1. Equation (3.90) is called *quasiparticle equation.*

2. In order to decide whether a given solution $f_s(\mathbf{x}), \varepsilon_s$ of the quasiparticle equation corresponds to a one-particle excitation or to a one-hole excitation, the chemical potential μ has to be given. Only in special cases, where the self-energy evaluated at fixed amplitudes gives a frequency independent, self-adjoint operator, the solutions of the

quasiparticle equation turn out to be orthogonal and hence the Lehmann amplitudes corresponding to the N lowest lying ε_s can be associated with the "occupied" amplitudes f_s^-. This, however, does not work in general. As the Lehmann amplitudes in general have norm ≤ 1, but nontheless reproduce the correct ground-state energy, there are in the interacting case much more "occupied" amplitudes f_s^- than particles.

3. In general, $\tilde{\Sigma}[(f_s^\pm(\mathbf{x}), \varepsilon_s^\pm)]$ is a functional of G reexpressed in terms of the Lehmann amplitudes and quasiparticle energies. The quasiparticle equation is therefore not only non-linear on the one-particle Hilbert space. It is also non-linear in the frequency: as such the self-energy is a family of Hilbert space operator kernels $\tilde{\Sigma}(\omega)$. In the quasiparticle equation, the frequency at which this family of operators is evaluated has to coincide with the eigenvalue of the respective amplitude.

4. The converse direction – the Lehmann amplitudes fulfill the quasiparticle equation – is a standard theorem. A proof can be found e.g. in ([32], appendix B).

Proof First, we introduce the time-dependent Lehmann amplitudes

$$
\begin{align}
f_s^\pm(\mathbf{x}t) &= f_s(\mathbf{x})\mathrm{e}^{\mp\mathrm{i}\varepsilon_s^\pm t} \tag{3.93}\\
f_s^\pm(\mathbf{x}\omega) &= 2\pi f_s(\mathbf{x})\delta(\hbar\omega \mp \varepsilon_s^\pm) \tag{3.94}
\end{align}
$$

where

$$
\begin{align}
f_s(\mathbf{x}\omega) &= \int \mathrm{d}t\, f_s(\mathbf{x}t)\mathrm{e}^{\mathrm{i}\omega t} \tag{3.95}\\
f_s(\mathbf{x}t) &= \int \frac{\mathrm{d}\omega}{2\pi}\, f_s(\mathbf{x}\omega)\mathrm{e}^{-\mathrm{i}\omega t}. \tag{3.96}
\end{align}
$$

We now multiply the quasiparticle equation with $\mathrm{e}^{-\mathrm{i}e_s t}$ and transform as

$$
\begin{align}
0 &= \left(\mp\varepsilon_s^\pm - \frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^\pm(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\, \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; \pm\varepsilon_s/\hbar)f_s^\pm(\mathbf{x}'t)\\
&= \left(-\mathrm{i}\hbar\partial_t - \frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^\pm(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}' \int \mathrm{d}\omega\, \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; \omega)\delta(\hbar\omega \mp \varepsilon_s^\pm)f_s^\pm(\mathbf{x}')\mathrm{e}^{-\mathrm{i}\omega t}\\
&= \left(-\mathrm{i}\hbar\partial_t - \frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^\pm(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}' \int \frac{\mathrm{d}\omega}{2\pi}\, \mathrm{e}^{-\mathrm{i}\omega t}\tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; \omega)f_s^\pm(\mathbf{x}'\omega)\\
&= \left(-\mathrm{i}\hbar\partial_t - \frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^\pm(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\, \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; t - t')f_s^\pm(\mathbf{x}'t')
\end{align}
$$

i.e.

$$
\mathrm{i}\hbar\partial_t f_s^\pm(\mathbf{x}t) = \left(-\frac{\hbar^2}{2m}\Delta + v_{\mathrm{ext}}(\mathbf{x})\right) f_s^\pm(\mathbf{x}t) + \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\, \tilde{\Sigma}(\mathbf{x}, \mathbf{x}'; t - t')f_s^\pm(\mathbf{x}'t'). \tag{3.97}
$$

We now find

$$
\begin{aligned}
i\hbar\partial_t G(\mathbf{x}t;\mathbf{x}'t') &= \partial_t \sum_{s;\,N\pm1} f_s(\mathbf{x}t)f_s^*(\mathbf{x}'t')(\theta(t-t')\theta(e_s-\mu)-\theta(t'-t)\theta(\mu-e_s)) \\
&= \sum_{s;\,N\pm1} \partial_t f_s(\mathbf{x}t)f_s^*(\mathbf{x}'t')(\theta(t-t')\theta(e_s-\mu)-\theta(t'-t)\theta(\mu-e_s)) + \\
&\quad\ \sum_{s;\,N\pm1} f_s(\mathbf{x}t)f_s^*(\mathbf{x}'t')(\delta(t-t')\theta(e_s-\mu)+\delta(t'-t)\theta(\mu-e_s)) \\
&= \sum_{s;\,N\pm1} \frac{1}{i\hbar}((\hat{H}_0+\tilde{\Sigma})f_s)(\mathbf{x}t)f_s^*(\mathbf{x}'t')(\theta(t-t')\theta(e_s-\mu)-\theta(t'-t)\theta(\mu-e_s)) \\
&\quad\ +\delta(\mathbf{x}-\mathbf{x}')\delta(t-t') \\
&= ((\hat{H}_0+\Sigma)G)(\mathbf{x}t;\mathbf{x}'t') + \delta(\mathbf{x}-\mathbf{x}')\delta(t-t')
\end{aligned}
$$

i.e.

$$
(i\hbar\partial_t - \hat{H}_0)G = \mathbb{1} + \tilde{\Sigma}G
$$

or $G = G_0 + G_0\tilde{\Sigma}G$.

Observables in Terms of Lehmann amplitudes The ground-state density, the one-particle reduced density matrix, the ground-state current and the ground-state energy can be expressed in terms of the ("occupied") Lehmann amplitudes as

$$
n(\mathbf{x}) = \sum_s f_s^-(\mathbf{x})f_s^{-*}(\mathbf{x}) \tag{3.98}
$$

$$
n(\mathbf{x},\mathbf{x}') = \sum_s f_s^-(\mathbf{x})f_s^{-*}(\mathbf{x}') \tag{3.99}
$$

$$
\mathbf{j}(\mathbf{x}) = \frac{e\hbar}{2mi} \sum_s \left(f_s^{-*}(\mathbf{x})\nabla f_s^-(\mathbf{x}) - (\nabla f_s^{-*}(\mathbf{x}))f_s^-(\mathbf{x}) \right) \tag{3.100}
$$

$$
E_0 = \sum_s \int d\mathbf{x}\, f_s^{-*}(\mathbf{x}) \left(\hat{H}_0 + \frac{1}{2}\tilde{\Sigma} \right) f_s(\mathbf{x}). \tag{3.101}
$$

The last equation can be shown easily from the Migdal formula. The prefactor $1/2$ in front of the self-energy is analogous to the Hartree-Fock energy.[2] The equations for the observables in terms of the Lehmann amplitudes are analogous to a system of non-interacting particles. In particular, the formula for the one-particle density matrix allows for the expression of an arbitrary one-particle observable $\hat{A}$ as

$$
\langle \hat{A} \rangle = \sum_{\text{occ}} \langle f_s | \hat{A} | f_s \rangle. \tag{3.102}
$$

---

[2]More precisely, the Hartree-Fock energy formulas are a special case of this.

The Lehmann amplitudes therefore provide an effective independent-particle picture of a many-body system. $\hat{H}_0 + \tilde{\Sigma}$ can be considered as an auxiliary Hamiltonian for these "quasi-particles". Note, however, that $\tilde{\Sigma}$ depends implicitly on the Lehmann amplitudes and quasiparticle energies and is furthermore neither hermitean nor frequency indepedendent. A further difference to a true independent particle system is – as already mentioned – the fact that the total energy is not given by the sum of the one-particle eigenvalues.

Definition The distribution

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \langle \mathbf{x} | \hat{A}(\omega) | \mathbf{x}' \rangle = \sum_{s;\ N \pm 1} f_s(\mathbf{x}) f_s^*(\mathbf{x}') \delta(\hbar\omega - \varepsilon_s) \tag{3.103}$$

is called *spectral function* where

$$\hat{A}(\omega) = \sum_{s;\ N \pm 1} |f_s\rangle \delta(\hbar\omega - \varepsilon_s) \langle f_s| \tag{3.104}$$

is the *quasiparticle density of states operator*.

Lemma 3.2.6 *The following relations hold:*

$$G(\mathbf{x}, \mathbf{x}'; \omega) = \hbar \int_{-\infty}^{\mu} \mathrm{d}\omega' \ \frac{A(\mathbf{x}, \mathbf{x}'; \omega')}{E + \hbar\omega' - \mathrm{i}\eta} + \hbar \int_{\mu}^{\infty} \mathrm{d}\omega' \ \frac{A(\mathbf{x}, \mathbf{x}'; \omega')}{E - \hbar\omega' + \mathrm{i}\eta} \tag{3.105}$$

$$\int_{-\infty}^{\mu} \mathrm{d}\omega \ A(\mathbf{x}, \mathbf{x}'; \omega) = n(\mathbf{x}, \mathbf{x}') \tag{3.106}$$

$$\int_{-\infty}^{\infty} \mathrm{d}\omega \ A(\mathbf{x}, \mathbf{x}'; \omega) = \delta(\mathbf{x} - \mathbf{x}') \tag{3.107}$$

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi} |\mathfrak{Anti}\ G(\mathbf{x}, \mathbf{x}'; \omega)| \tag{3.108}$$

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{2\pi\mathrm{i}} (G^{\mathrm{A}}(\mathbf{x}, \mathbf{x}'; \omega) - G^{\mathrm{R}}(\mathbf{x}, \mathbf{x}'; \omega)) \tag{3.109}$$

where $\mathfrak{Anti}$ denotes the antihermitean part.

Proof The first and the second identity follow trivially from the properties of the Dirac distribution. For the third identity, one has to use the completeness relation for the Lehmann amplitudes in addition. For the fourth identity, we use the standard formula

$$\lim_{\eta \to 0} \frac{1}{E \pm \mathrm{i}\eta} = \mathcal{P}\left(\frac{1}{E}\right) \mp \mathrm{i}\pi\delta(E). \tag{3.110}$$

Therefore, for any Lehmann contribution to the Green function we have

$$\frac{f_s(\mathbf{x}) f_s^*(\mathbf{x}')}{\hbar\omega - e_s + \mathrm{sg}(e_s - \mu)\mathrm{i}\eta} = \mathcal{P}\left(\frac{f_s(\mathbf{x}) f_s^*(\mathbf{x}')}{\hbar\omega - e_s}\right) - \mathrm{sg}(e_s - \mu)\mathrm{i}\pi f_s(\mathbf{x}) f_s^*(\mathbf{x}') \delta(\hbar\omega - e_s)$$

where the first term is obviously the hermitean and the second term the antihermitean part. Similarly one shows the fifth equation.

Definition The distribution

$$N(\omega) = \text{Tr}_{\mathcal{H}} \; \hat{A}(\omega) \tag{3.111}$$

is called *quasiparticle density of states.*

Density of States vs Quasiparticle Density of States For an arbitrary quantum mechanical system with the Hamiltonian $\hat{H}$ and the (not necessarily one-particle) Hilbert space $\mathcal{H}$, the *density of states operator* is defined by the operator valued distribution

$$\hat{\rho}(\omega) = \delta(\hbar\omega - \hat{H}) \tag{3.112}$$

and the *density of states* is given by the distribution

$$\rho(\omega) \equiv \text{Tr}_{\mathcal{H}}\delta(\hbar\omega - \hat{H}) = \sum_n \delta(\hbar\omega - E_n) \tag{3.113}$$

where the sum goes over all energy eigenstates. E.g., the partition function can be written in terms of the density of states as

$$Z(T) = \hbar \int d\omega \; \rho(\omega)\mathrm{e}^{-\frac{\hbar\omega}{k_B T}}. \tag{3.114}$$

The quasiparticle density is therefore not identical to the density of states of the respective many-electron system.

The following lemmata can be easily shown. (Recall that $\langle\varphi_i|f_s^-\rangle = \langle\Psi_s^{N-1}|a(\varphi_i)|\Psi_0\rangle$.)

Lemma 3.2.7 *The occupation number n_i of the state φ_i can be obtained from the quasiparticle density of states via*

$$\int_{-\infty}^{\mu} d\omega \; \langle\varphi_i|\hat{A}(\omega)|\varphi_i\rangle = \langle\Psi_0|\hat{n}_i|\Psi_0\rangle. \tag{3.115}$$

Lemma 3.2.8 *The quasiparticle density of states fulfills*

$$N(\omega) = \sum_s \|f_s\|^2 \delta(\hbar\omega - \varepsilon_s). \tag{3.116}$$

Complex Poles and Life-Times The above lemma shows that the quasiparticle density of states has – apart from a constant shift of value E_0^N – the same singular support as the density of states, but differs from it by the weighting function $\|f_s\|^2$. In a true many-body system, the distance of the energy levels gets very narrow such that in the thermodynamic limit one may think of $N(\omega)$ as a continuous distribution on the ω-axis. If we label the Lehmann amplitudes by the energy itself, then we read off from the last lemma that – neglecting a

possible continuous degeneracy function – the spectral function is the norm squared of the Lehmann amplitude as a function of ω. Now, assume that for some reason or other the quantity which is actually of interest is that very spectral function and that it displays a number of peaks, say of a Lorentzian type. Then, a *model* Green function the role of which consists in that it reproduces roughly the right spectral function can be easily written down by using Lehmann contributions of the form

$$f(\mathbf{x})f^*(\mathbf{x})\mathrm{e}^{-\mathrm{i}\varepsilon_s t - \Gamma t}. \tag{3.117}$$

Promoting

$$A(\mathbf{x}, \mathbf{x}'; \omega) = \frac{1}{\pi}|\mathfrak{Anti}\, G(\mathbf{x}, \mathbf{x}'; \omega)| \tag{3.118}$$

to a defining equation, we see that the above Lehmann contribution leads to a contribution in the spectral function of the form

$$\|f\|^2 \frac{\Gamma}{(\hbar\omega - \varepsilon_s)^2 - \Gamma^2}, \tag{3.119}$$

i.e. to a Lorentz peak. On the other hand, in the corresponding Lehmann contribution to the Green function, Γ^{-1} plays the formal role of a decay rate. This is the famous connection between peak widths and decay rates or life-times. It has led many authors to claim that the Green function itself acquires complex poles. This seems to be wrong because the Lehmann representation shows that the poles (or – in the case of a continuous spectrum – the branch cut) always lie at the real axis.

3.3. Solid State Physics

3.3.1. Lattice Symmetry

Introduction We now deal with a standard electronic Hamiltonian with the external potential $v_{\mathrm{ext}}(\mathbf{x})$. The one-particle Hilbert space of the system under consideration is given by $\mathcal{H} = \mathcal{L}^2([0, L]^3, \mathbb{C}, |\det(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)|\mathrm{d}\mathbf{x};\ \psi(0, x_2, x_3) = \psi(L, x_2, x_3)$ etc.) (Born-von-Karman boundary conditions). The symmetry group

$$\Gamma_{\mathbf{a}_i, L} = \{n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3;\ (n_1, n_2, n_3) \in \mathbb{Z}_{N_1} \times \mathbb{Z}_{N_2} \times \mathbb{Z}_{N_3};\ \mathbf{a}_i,\ i = 1, 2, 3\ \text{lin. indt.}\} \tag{3.120}$$

of the external potential $v_{\mathrm{ext}}(\mathbf{x}_i + \mathbf{a}) = v_{\mathrm{ext}}(\mathbf{x}_i)\ \forall \mathbf{a} \in \Gamma_{a_i, L}$ is called *direct lattice*, *Bravais lattice* or *crystal lattice*. Here, $\mathbf{a}_i = a_i\mathbf{e}_i$ where the $\mathbf{e}_i$ are unit vectors and a_i is the lattice spacing in the i-th direction. The number of points in the direct lattice is given by

$$N = \frac{L^3}{a_1 a_2 a_3} = N_1 N_2 N_3. \tag{3.121}$$

Furthermore, we set

$$\mathbf{b}^i = 2\pi \varepsilon^{ijk} \frac{\mathbf{a}_j \times \mathbf{a}_k}{|\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)|} \tag{3.122}$$

and call

$$\tilde{\Gamma}_{\mathbf{a}_i,L} = \{n_1 \mathbf{b}^1 + n_2 \mathbf{b}^2 + n_3 \mathbf{b}^3;\ (n_1, n_2, n_3) \in \mathbb{Z}^3\} \tag{3.123}$$

reciprocal lattice. Finally,

$$\Gamma^*_{\mathbf{a}_i,L} = \{\frac{n_1}{N_1}\mathbf{b}^1 + \frac{n_2}{N_2}\mathbf{b}^2 + \frac{n_3}{N_3}\mathbf{b}^3;\ (n_1, n_2, n_3) \in \mathbb{Z}_{N_1} \times \mathbb{Z}_{N_2} \times \mathbb{Z}_{N_3}\} \tag{3.124}$$

is called *dual lattice* or *first Brillouin zone* (FBZ). The direct lattice and the dual lattice have the same number of points whereas the reciprocal lattice has infinitely many points. For any $\mathbf{a} \in \Gamma_{\mathbf{a}_i,L}$, the unitary representation $\hat{U}_\mathbf{a}$ on $\mathcal{H}^N$ is given by

$$(\hat{U}_\mathbf{a}\Psi)(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \Psi(\mathbf{x}_1 + \mathbf{a}, \ldots, \mathbf{x}_N + \mathbf{a}) \tag{3.125}$$

The unitary representation of $\hat{U}_\mathbf{a}$ on $\mathcal{F}$ is defined componentwise. Unitarity follows from the translation invariance of the Lebesgue measure. One shows easily that for any such representative $\hat{U}_\mathbf{a}$ we have $\hat{U}_\mathbf{a}\hat{H}\hat{U}_\mathbf{a}^{-1} = \hat{H}$.

Bloch Functions Consider now a unitary representation $\hat{U}_\mathbf{a}$ of the lattice translation group Γ and a complete, orthonormal basis $\{\varphi_i\}_{i \in \mathbb{N}}$ of the separable Hilbert space $\mathcal{H}$. The set $\hat{U}_\mathbf{a}\varphi_i$, i fixed where $\mathbf{a}$ goes over all Γ is finite and invariant under the unitary representation of Γ. On the other hand, the set $\{\hat{U}_\mathbf{a}\varphi_i :\ \mathbf{a} \in \Gamma, i \in \mathbb{N}\}$ is again countable and complete. It follows that the representation of Γ is fully reducible. As the lattice translation group is abelian, so is its representation. By the lemma of Schur, a matrix which commutes with all representatives in an irreducible representation is proportional to the identity. Consequently, all $\hat{U}_\mathbf{a}$ are proportional to the identity which for an irreducible representation is only possible if the representation space is one-dimensional. Such a one-dimensional representation space is necessarily spanned by an eigenvector of all $\hat{U}_\mathbf{a}$. The fact that $\hat{U}_{\mathbf{a}_1}\hat{U}_{\mathbf{a}_2} = \hat{U}_{\mathbf{a}_1+\mathbf{a}_2}$ then implies that the eigenvalues are of the form $e^{i\mathbf{k}\cdot\mathbf{a}}$, $\mathbf{k}$ being the index of the representation. If $\psi_\mathbf{k}(\mathbf{x})$ is an eigenvector of $\hat{U}_\mathbf{a}$ with that very eigenvalue, then $u_\mathbf{k}(\mathbf{x}) = e^{-i\mathbf{k}\cdot\mathbf{x}}\psi_\mathbf{k}(\mathbf{x})$ is invariant under all $\hat{U}_\mathbf{a}$, i.e. $u_\mathbf{k}(\mathbf{x})$ is a lattice periodic function. Put differently, in $\mathcal{H}$ we can choose a basis of the so-called *Bloch form*

$$\psi_\mathbf{k}(\mathbf{x}) = e^{i\mathbf{k}\mathbf{x}}u_\mathbf{k}(\mathbf{x}) \tag{3.126}$$

where $u_\mathbf{k}(\mathbf{x})$ is a lattice periodic function. As the lattice translation group representation and the Hamiltonian commute, they can be diagonalized simultaneously. Plugging the Bloch

form into the Schrödinger equation, we find that $u_{\mathbf{k}}(\mathbf{x})$ then has to obey

$$\left(-\frac{\hbar^2}{2m}(\nabla + \mathrm{i}\mathbf{k})^2 + v_{\mathrm{ext}}(\mathbf{x})\right)u_{\mathbf{k}}(\mathbf{x}) = \varepsilon(\mathbf{k})u_{\mathbf{k}}(\mathbf{x}). \tag{3.127}$$

$\mathbf{k}$ being given, this equation has infinitely many solutions. We label these by the so-called band index n. We conclude that there is a complete set of orthogonal functions diagonalizing both $\hat{H}$ and all $\hat{U}_{\mathbf{a}}$. These functions are of the form:

$$\psi_{n\mathbf{k}}(\mathbf{x}) = \exp(\mathrm{i}\mathbf{k}\mathbf{x})u_{n\mathbf{k}}(\mathbf{x}). \tag{3.128}$$

Due to the lattice periodicity v_{ext} has only Fourier components in the reciprocal lattice:

$$v(\mathbf{x}) = \sum_{\mathbf{G}\in\tilde{\Gamma}} v_{\mathbf{G}}\mathrm{e}^{\mathrm{i}\mathbf{G}\mathbf{x}}, \tag{3.129}$$

Accordingly, for the wave-function we make the ansatz:

$$\psi(\mathbf{x}) = \sum_{\mathbf{k}} \psi_{\mathbf{k}}\mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{x}}. \tag{3.130}$$

Plugging this into the stationary Schrödinger equation, we get:

$$\left(\frac{\hbar^2|\mathbf{k}|^2}{2m} - \varepsilon\right)\psi_{\mathbf{k}} + \sum_{\mathbf{G}\in\tilde{\Gamma}} v_{\mathbf{G}}\psi_{\mathbf{k}-\mathbf{G}} = 0, \tag{3.131}$$

Consequently, only those modes are coupled together, which differ by reciprocal lattice vectors. We can therefore set

$$u_{\mathbf{k}}(\mathbf{x}) = \sum_{\mathbf{G}\in\tilde{\Gamma}} \psi_{\mathbf{k}-\mathbf{G}}\mathrm{e}^{-\mathrm{i}\mathbf{G}\mathbf{x}}. \tag{3.132}$$

This implies the important relation

$$u_{\mathbf{k}+\mathbf{G}}(\mathbf{x}) = u_{\mathbf{k}}(\mathbf{x})\mathrm{e}^{-\mathrm{i}\mathbf{G}\mathbf{x}}. \tag{3.133}$$

As the last factor is again lattice periodic it can be absorbed in the definition of u. This implies that we can restrict attention to those $u_{\mathbf{k}}$ with $\mathbf{k}$ in the first Brillouin zone.

Many-Body System in Periodic Potential The above arguments generalize to the many-body case $\mathcal{H}^N$ for which the energy eigenstates $\Psi_s^N \equiv \Psi_{n\mathbf{K}}^N$ can be chosen as eigenvectors of all $\hat{U}_{\mathbf{a}}$ with eigenvalue $\mathrm{e}^{\mathrm{i}\mathbf{K}\cdot\mathbf{a}}$. The space of eigenvectors with Bloch vector $\mathbf{K}$ is spanned by the Slater determinants of N Bloch functions $\psi_{n_i\mathbf{k}_i}$ with the restriction that $\sum_{i=1}^{N}\mathbf{k}_i = \mathbf{K}$.

Wannier Functions of a given band index are defined by

$$w_{n\mathbf{x_m}}(\mathbf{x}) \;=\; \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\in\Gamma^*} \exp(-\mathrm{i}\mathbf{k}\mathbf{x_m})\psi_{n\mathbf{k}}(\mathbf{x}) \tag{3.134}$$

$$\psi_{n\mathbf{k}}(\mathbf{x}) \;=\; \frac{1}{\sqrt{N}} \sum_{\mathbf{x_m}\in\Gamma} \exp(\mathrm{i}\mathbf{k}\mathbf{x_m})w_{n\mathbf{x_m}}(\mathbf{x}). \tag{3.135}$$

This is a discrete Fourier transform in the finite dimensional Hilbert space spanned by the $\psi_{n\mathbf{k}}$ with n fixed (the Wannier functions are not the Fourier transforms of the Bloch functions in $\mathcal{H}$). It follows that the transitions from the Bloch functions to the Wannier functions is unitary and hence $\langle w_{n\mathbf{x_m}}, w_{n'\mathbf{x_{m'}}}\rangle = \delta_{nn'}\delta_{\mathbf{mm'}}$ and $w_{n\mathbf{x_m}}$ is concentrated about $\mathbf{x_m}$. Furthermore, from the definition of the Wannier functions one shows easily that

$$w_{n(\mathbf{x_m}+\mathbf{x_{m'}})}(\mathbf{x} + \mathbf{x_{m'}}) = w_{n\mathbf{x_m}}(\mathbf{x}) \tag{3.136}$$

for all $\mathbf{x_m}, \mathbf{x_{m'}} \in \Gamma$.

3.3.2. Band-Structure and Fermi Surface

Definition The family (indexed by n) of functions $e_n(\Delta\mathbf{K}) = \pm E_n^{N\pm1}(\mathbf{K}) \mp E_0^N(\mathbf{K}_0)$ is called *band structure*. The hypersurface in the dual "space" (lattice) $e_n(\Delta\mathbf{K}) = \mu_N$ is called *Fermi surface*.

Measurement of band structure by angular resolved Photoemission Spectroscopy
A piece of material is irradiated by photons of well-defined frequency and wave-vector such that electrons are ejected in a certain direction. In the description of the photon absorption process we make the following assumptions:

1. Terms of second order in the electromagnetic field operator can be neglected.

2. The transition rate between initial and final states is roughly given by Fermi's golden rule.

3. One electron is ejected per photon absorbed.

4. The ejected electron is free.

5. The material is initially in its ground-state and finally in an excited energy eigenstate.

The first point says that the interaction Hamiltonian is given by

$$\hat{H}_{\text{int}} = \hat{\mathbf{p}} \otimes \hat{\mathbf{A}} \tag{3.137}$$

resulting from the minimal coupling $\hat{\mathbf{p}} \mapsto \hat{\mathbf{p}} - e\hat{\mathbf{A}}$ after neglecting higher order terms. The second point implies that a current can be detected only if the matrix element

$$\langle f|\hat{H}_{\text{int}}|i\rangle \tag{3.138}$$

does not vanish. By the last three points we conclude that the initial state and the final state can be written as

$$|i\rangle = |\ldots n_{\mathbf{q}\lambda}\ldots\rangle \otimes |\Psi_0^N\rangle \tag{3.139}$$

$$|f\rangle = |\ldots n_{\mathbf{q}\lambda} - 1\ldots\rangle \otimes |\mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{x}} \wedge \Psi_s^{N-1}\rangle \tag{3.140}$$

where $|\ldots n_{\mathbf{q}\lambda}\ldots\rangle$ denotes the photon number eigenstate of the electromagnetic field with $n_{\mathbf{q}\lambda}$ photons of wavelength $\mathbf{q}$ and polarization λ. The operator of the electromagnetic field reads (cf. e.g. [62], Chapter 6)

$$\hat{\mathbf{A}}(\mathbf{x}t) = \sum_{\mathbf{q}'\lambda} \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_{\mathbf{q}'}}} \left(a_{\mathbf{q}'\lambda} \mathbf{e}_{\mathbf{q}'\lambda} \mathrm{e}^{-\mathrm{i}\omega_{\mathbf{q}'}t + \mathrm{i}\mathbf{q}'\mathbf{x}} + a_{\mathbf{q}'\lambda}^\dagger \mathbf{e}_{\mathbf{q}'\lambda}^* \mathrm{e}^{+\mathrm{i}\omega_{\mathbf{q}'}t - \mathrm{i}\mathbf{q}'\mathbf{x}} \right) \tag{3.141}$$

where $\omega_{\mathbf{q}} = c|\mathbf{q}|$ and we assumed the electromagnetic field to be enclosed in the same finite volume with the same boundary conditions as the electrons. Therefore, for $\langle\ldots n_{\mathbf{q}\lambda} - 1\ldots|\hat{\mathbf{A}}|\ldots n_{\mathbf{q}\lambda}\ldots\rangle$ we find

$$\sum_{\mathbf{q}'\lambda} \sqrt{\frac{\hbar}{2\varepsilon_0 V \omega_{\mathbf{q}'}}} \mathbf{e}_{\mathbf{q}'\lambda} \langle\ldots n_{\mathbf{q}\lambda} - 1\ldots|a_{\mathbf{q}'\lambda}|\ldots n_{\mathbf{q}\lambda}\ldots\rangle \mathrm{e}^{-\mathrm{i}\omega_{\mathbf{q}}t + \mathrm{i}\mathbf{q}\mathbf{x}} = \sqrt{\frac{\hbar n_{\mathbf{q}\lambda}}{2\varepsilon_0 V \omega_{\mathbf{q}}}} \mathbf{e}_{\mathbf{q}\lambda} \mathrm{e}^{-\mathrm{i}\omega_{\mathbf{q}}t + \mathrm{i}\mathbf{q}\mathbf{x}}$$

and the transition matrix element is proportional to

$$\langle \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{x}} \wedge \Psi_s^{N-1}|\hat{\mathbf{p}}|\mathrm{e}^{\mathrm{i}\mathbf{q}\mathbf{x}}\Psi_0^N\rangle. \tag{3.142}$$

Now, suppose Ψ_s^{N-1} and Ψ_0^N are lattice translation eigenstates with Bloch vectors $\mathbf{K}$ and $\mathbf{K}_0$ respectively. Then the initial state has total Bloch vector $\mathbf{K}_0 + \mathbf{q}$ and the final state has total Bloch vector $\mathbf{K} + \mathbf{k}$ because a free wave with wave vector $\mathbf{k}$ is also a Bloch function with $u_{n\mathbf{k}} \equiv 1$. The total momentum operator is the generator of the translations and hence commutes with all translations, in particular with the lattice translations. Therefore, for the matrix element not to vanish it is necessary that the total final Bloch vector equals the total initial Bloch vector:

$$\mathbf{K} + \mathbf{k} = \mathbf{K}_0 + \mathbf{q}. \tag{3.143}$$

Furthermore, Fermi's golden rule enforces energy conservation (with respect to the unperturbed Hamiltonian):

$$E_s^{N-1}(\mathbf{K}) + \frac{\hbar^2|\mathbf{k}|^2}{2m} = E_0^N(\mathbf{K}_0) + \hbar c|\mathbf{q}|. \tag{3.144}$$

Now, $\mathbf{q}$ and hence $\hbar\omega_{\mathbf{q}}$ – the energy and wave-vector of the photons – are controlled experimentally and $\mathbf{k}$ and hence $\frac{\hbar^2|\mathbf{k}|^2}{2m}$ – the wave-vector and energy of the ejected electron – is measured. These data then allow for the deduction of $e_n(\Delta\mathbf{K})$.

Independent Electrons and Quasiparticles A non-interacting many-body energy eigenstate of Blochvector $\mathbf{K}$ reads

$$\Psi_{\mathbf{K}}(\mathbf{x}_1, \ldots, \mathbf{x}_N) = \text{SLATER}(\psi_{n_1\mathbf{k}_1}(\mathbf{x}_1), \ldots, \psi_{n_N\mathbf{k}_N}(\mathbf{x}_N)) \tag{3.145}$$

with $\mathbf{K} = \sum_{i=1}^N \mathbf{k}_i$ and energy $E = \sum_{i=1}^N \varepsilon_{n_i\mathbf{k}_i}$. The ground-state is found by choosing the N lowest lying values $\varepsilon_{n_i\mathbf{k}_i}$. In the simplest case, the energy $E_n^{N+1}(\mathbf{K})$ of a singly-excited $(N+1)$-particle state differs from the energy E_0^N of the N-particle ground-state by the energy eigenvalue $\varepsilon_{n\mathbf{k}}$ of a Bloch function. For singly-excited states, we then have $\Delta\mathbf{K} = \mathbf{k}$. Therefore, the band-structure comprises the one-particle energy functions $\varepsilon_n(\Delta\mathbf{K}) = \varepsilon_{n\mathbf{k}}$. Using $\mu_N = E_0^{N+1} - E_0^N$, one sees that the Fermi surface is given by the surface in $\mathbf{k}$-space of the $\mathbf{k}$-vectors of the highest (in energy) occupied Bloch functions. By the quasiparticle equation, this paradigm generalizes to the interacting case: the band-structure is the quasiparticle energy as a function of the Bloch vector of the quasiparticle wave-functions (Lehmann amplitudes) and the Fermi surface is given by the surface in $\mathbf{k}$-space where the quasiparticle energy reaches the chemical potential.

Definition The occupation number operator $\hat{n}_{\mathbf{k}}$ for the Bloch vector $\mathbf{k}$ is given by

$$\hat{n}_{\mathbf{k}} = \sum_n a_{n\mathbf{k}}^\dagger a_{n\mathbf{k}} \tag{3.146}$$

Here, n denotes the band index and the sum goes over all bands.

Lemma 3.3.1 *The occupation number operator is independent of the external potential which determines the band index.*

Proof The total Hilbert space decomposes in an orthogonal sum $\oplus\mathcal{H}_{\mathbf{k}}$ of subspaces indexed by the (total) Bloch momentum $\mathbf{k}$. The lemma then means that the operator $\hat{n}_{\mathbf{k}}$ is invariant under a unitary change of basis in the respective subspace which is true because $\hat{n}_{\mathbf{k}}$ is the

second quantization of the projector onto that subspace. Explicitly, one finds

$$
\begin{aligned}
\hat{n}_{\mathbf{k}} &= \sum_i a^\dagger(\varphi_i) a(\varphi_i) \\
&= \sum_i a^\dagger \left(\sum_j U^i{}_j \psi_j \right) a \left(\sum_k U^i{}_k \psi_k \right) \\
&= \sum_{ijk} (U^*)^i{}_k U^i{}_j a^\dagger(\psi_j) a(\psi_k) \\
&= \sum_{ijk} (U^{*\mathrm{T}})^k{}_i U^i{}_j a^\dagger(\psi_j) a(\psi_k) \\
&= \sum_{jk} \delta^k{}_j a^\dagger(\psi_j) a(\psi_k) \\
&= \sum_j a^\dagger(\psi_j) a(\psi_j)
\end{aligned}
$$

where $\{\varphi_i\}$ and $\{\psi_k\}$ denote othonormal bases in $\mathcal{H}_{\mathbf{k}}$.

Behaviour of $n_{\mathbf{k}}$ at the Fermi Surface In general, for the occupation $n_i = \langle a^\dagger(\varphi_i) a(\varphi_i) \rangle$ we can write

$$
\begin{aligned}
n_i &\equiv \langle \Psi_0 | \hat{n}_i | \Psi_0 \rangle \\
&= \int_{-\infty}^{\mu} \mathrm{d}\omega \, \langle \varphi_i | \hat{A}(\omega) | \varphi_i \rangle \\
&= \int_{-\infty}^{\mu} \mathrm{d}\omega \, |\langle \varphi_i | f_{n\mathbf{k}} \rangle|^2 \delta(e_{n\mathbf{k}} - \omega) \\
&= \sum_{e_{n\mathbf{k}} \leq \mu} |\langle \varphi_i | f_{n\mathbf{k}} \rangle|^2 \\
&= \sum_{n\mathbf{k}} |\langle \varphi_i | f_{n\mathbf{k}}^- \rangle|^2.
\end{aligned}
$$

In the subspace $\mathcal{H}_{\mathbf{k}}$, we can choose the Lehmann amplitudes $f_{n\mathbf{k}}$ as a (non-orthogonal) basis. Further, note that $f_{n\mathbf{k}} \perp f_{m\mathbf{k}'}$ for $\mathbf{k} \neq \mathbf{k}'$ because in this case the Lehmann amplitudes correspond to eigenvectors with different eigenvalues of a unitary operator. One shows easily that in terms of the Lehmann amplitudes $n_{\mathbf{k}} = \sum_n a^\dagger(f_{n\mathbf{k}}) a(f_{n\mathbf{k}})$ and hence

$$
n_{\mathbf{k}} = \sum_n \sum_{m,\mathbf{l}, \, e_m \leq \mu} |\langle f_{n\mathbf{k}} | f_{m\mathbf{l}} \rangle|^2. \tag{3.147}
$$

This shows that if $\mathbf{k}$ traverses the Fermi surface, the Bloch vector occupation number $n_{\mathbf{k}}$ jumps from $\sum_{n,m,\mathbf{l}} |\langle f_{n\mathbf{k}}^- | f_{m\mathbf{l}}^- \rangle|^2$ to $\sum_{n,m,\mathbf{l}} |\langle f_{n\mathbf{k}}^+ | f_{n\mathbf{l}}^- \rangle|^2$.

4. Perturbation Theory, Self-Consistent Equations and Infinite Resummations

4.1. Green Function Perturbation Theory

4.1.1. Time-Dependent Perturbation Theory

Introduction Perturbation Theory for Green functions is based on three fundamental theorems:

1. The *Gell-Mann and Low theorem* connects the interacting Green function to a perturbative series in the non-interacting Green functions.

2. The *Wick theorem* reduces the non-interacting n-point Green function to a sum of products of non-interacting two-point functions and therefore allows for a representation of perturbative expansions in terms of Feynman graphs (the straight lines of which represent free Green functions).

3. The *Cancellation Theorem* restricts this expansion in Feynman graphs to the so-called connected graphs.

Preliminaries We deal with a general many-body Hamiltonian of the form:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \tag{4.1}$$

where $\hat{H}_0$ represents an unperturbed Hamiltonian (typically: kinetic energy + external potential) whereas $\hat{H}_1$ represents some kind of perturbation (typically: a two-particle interaction potential).

Adiabatic Switching On is defined as the replacement of the original, time-independent Hamiltonian $\hat{H}$ with the new time-dependent Hamiltonian

$$\hat{H}(t) = \hat{H}_0 + g\mathrm{e}^{-\eta|t|}\hat{H}_1 \tag{4.2}$$

where $\eta \in \mathbb{R}_+$. A coupling constant g has been drawn out of the interaction Hamiltonian for technical purposes which will later become clear. For large times, $t \to \pm\infty$, the Hamiltonian equals the free Hamiltonian and for $t = 0$ it becomes the full Hamiltonian of the interacting system. We define an interaction picture corresponding to this new Hamiltonian via

$$\Psi_{\mathrm{I}}(t) = \mathrm{e}^{\mathrm{i}\frac{\hat{H}_0}{\hbar}t}\Psi(t) \tag{4.3}$$

where $\Psi(t) \equiv \Psi_{\mathrm{S}}(t)$ is the state-vector in the Schrödinger picture. The time evolution of Ψ_{I} now reads:

$$\mathrm{i}\hbar\partial_t\Psi_{\mathrm{I}} = \hat{H}'_{1\mathrm{I}}(t)\Psi_{\mathrm{I}} \tag{4.4}$$

or

$$\mathrm{i}\hbar\partial_t\Psi_{\mathrm{I}} = g\mathrm{e}^{-\eta|t|}\hat{H}_{1\mathrm{I}}(t)\Psi_{\mathrm{I}} \tag{4.5}$$

where

$$
\begin{aligned}
\hat{H}'_{1\mathrm{I}}(t) &= \mathrm{e}^{\mathrm{i}\frac{\hat{H}_0}{\hbar}t}\hat{H}_1(t)\mathrm{e}^{-\mathrm{i}\frac{\hat{H}_0}{\hbar}t} \tag{4.6} \\
&= g\mathrm{e}^{-\eta|t|}\mathrm{e}^{\mathrm{i}\frac{\hat{H}_0}{\hbar}t}\hat{H}_1\mathrm{e}^{-\mathrm{i}\frac{\hat{H}_0}{\hbar}t} \tag{4.7} \\
&\equiv g\mathrm{e}^{-\eta|t|}\hat{H}_{1\mathrm{I}}(t). \tag{4.8}
\end{aligned}
$$

Time-Evolution Operator in Time-Dependent Perturbation Theory We recall the general formalism in time-dependent perturbation theory for an arbitrary Hamiltonian $\hat{H}(t) = \hat{H}_0 + \hat{H}_1(t)$. The time-evolution operator in the interaction picture is given explicitly by

$$\hat{U}(t, t_0) = \mathrm{e}^{\frac{\mathrm{i}}{\hbar}\hat{H}_0 t}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}(t-t_0)}\mathrm{e}^{-\frac{\mathrm{i}}{\hbar}\hat{H}_0 t_0} \tag{4.9}$$

and obeys the differential equation

$$\mathrm{i}\hbar\partial_t\hat{U}(t, t_0) = \hat{H}_{1\mathrm{I}}(t)\hat{U}(t, t_0). \tag{4.10}$$

This is equivalent to the self-consistent integral equation

$$\hat{U}(t, t_0) - \hat{U}(t_0, t_0) = -\frac{\mathrm{i}}{\hbar}\int_{t_0}^{t}\mathrm{d}t_1\ \hat{H}_{1\mathrm{I}}(t_1)\hat{U}(t_1, t_0). \tag{4.11}$$

A formal perturbation series for $\hat{U}$ is obtained by iterating this self-consistent equation (using $\hat{U}(t_0, t_0) = \mathbb{1}$):

$$\hat{U}(t, t_0) = \mathbb{1} + \left(-\frac{\mathrm{i}}{\hbar}\right)\int_{t_0}^{t}\mathrm{d}t_1\ \hat{H}_{1\mathrm{I}}(t_1) + \left(-\frac{\mathrm{i}}{\hbar}\right)^2\int_{t_0}^{t}\mathrm{d}t_1\int_{t_0}^{t_1}\mathrm{d}t_2\ \hat{H}_{1\mathrm{I}}(t_1)\hat{H}_{1\mathrm{I}}(t_2) + \dots \tag{4.12}$$

It is well-known that integrals of the form

$$\int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \ldots \int_{t_0}^{t_{n-1}} dt_n \; \hat{H}_{1I}(t_1)\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n) \tag{4.13}$$

can be replaced by[1]

$$\frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \; \mathcal{T}\hat{H}_{1I}(t_1)\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n) \tag{4.14}$$

leading to the concise expression

$$\hat{U}(t,t_0) = \sum_{n=0}^{\infty} \hat{U}^{(n)}(t,t_0) = \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{1}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \; \mathcal{T}\hat{H}_{1I}(t_1)\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n). \tag{4.15}$$

This is sometimes symbolically written as

$$\hat{U}(t,t_0) = \mathcal{T}\exp\left(-\frac{i}{\hbar}\int_{t_0}^{t} dt_1 \; \hat{H}_{1I}(t_1)\right). \tag{4.16}$$

If the time-evolution operator for the time-dependent Hamiltonian exists, then it necessarily fulfills the self-consistent integral equation $\hat{U} = \mathbb{1} - i/\hbar \int dt\hat{H}_1\hat{U}$. This, however, does not imply that the formal perturbation exists. For the case of adiabatic switching on, we *define*

$$\hat{U}_\eta(t,t_0) = \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{g^n}{n!} \int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \ldots \int_{t_0}^{t} dt_n \; e^{-\eta(|t_1|+\ldots+|t_n|)}\mathcal{T}\hat{H}_{1I}(t_1)\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n).$$

Gell-Mann and Low Theorem Consider the noninteracting ground-state (supposed to be non-degenerate) Φ_0 at $t \to -\infty$ and let it evolve with $\hat{H}(t)$ up to $t = 0$. That means, we set

$$\Psi_\eta(t=0) = \hat{U}_\eta(t=0,-\infty)\Phi_0 \equiv \hat{U}_\eta\Phi_0 \equiv \Psi_\eta. \tag{4.17}$$

One might now expect that $\Psi_\eta(t=0)$ is somehow related to the eigenstates of the original Hamiltonian $\hat{H}$ at least in the limit $\eta \to 0$. A precise statement about this connection is given by the Gell-Mann-Low theorem:

Theorem 4.1.1 *If the limit*

$$\lim_{\eta\to 0}\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle} \equiv \lim_{\eta\to 0}\frac{\hat{U}_\eta(0,-\infty)\Phi_0}{\langle\Phi_0|\hat{U}_\eta(0,-\infty)|\Phi_0\rangle} =: \frac{\Psi}{\langle\Phi_0|\Psi\rangle} \tag{4.18}$$

exists, then it is an eigenvector of the full (time-independent, original) Hamiltonian $\hat{H} = \hat{H}_0 + \hat{H}_1$, i.e.

$$\hat{H}\Psi = E\Psi, \tag{4.19}$$

for some E.

---

[1] For a fixed time-order this integral yields a contribution which coincides with (4.13). The prefactor then cancels out the overcounting.

In the following, we will need several lemmata.

Lemma 4.1.2 *We have*

$$(\partial_{t_1} + \ldots + \partial_{t_n}) \, \theta(t_{\pi(1)} - t_{\pi(2)}) \ldots \theta(t_{\pi(n-1)} - t_{\pi(n)}) = 0 \tag{4.20}$$

where π is an arbitrary permutation in S^n.

Proof First, observe

$$\partial_{t_1} + \ldots + \partial_{t_n} = \partial_{t_{\pi(1)}} + \ldots + \partial_{t_{\pi(n)}}. \tag{4.21}$$

Therefore, we consider without loss of generality:

$$(\partial_{t_1} + \ldots + \partial_{t_n}) \, \theta(t_1 - t_2) \ldots \theta(t_{n-1} - t_n). \tag{4.22}$$

This equals

$$((\partial_{t_1} + \partial_{t_2})\theta(t_1 - t_2)) \ldots \theta(t_{n-1} - t_n) + \theta(t_1 - t_2)\left((\partial_{t_3} + \partial_{t_4})\theta(t_3 - t_4)\right) \ldots \theta(t_{n-1} - t_n) + \ldots$$

On the other hand,

$$(\partial_{t_1} + \partial_{t_2})\theta(t_1 - t_2) = \delta(t_1 - t_2) - \delta(t_2 - t_1) = 0. \tag{4.23}$$

Therefore, all summands vanish.

Lemma 4.1.3 *We have the distributional identity*

$$\sum_{m=0}^{n} \frac{1}{m!(n-m)!} \sum_{\pi \in S^n} \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t) = 1. \tag{4.24}$$

Proof Clearly,

$$\theta(t - t_i) + \theta(t_i - t) = 1. \tag{4.25}$$

Therefore

$$\prod_{i=1}^{n}(\theta(t - t_i) + \theta(t_i - t)) = 1. \tag{4.26}$$

Let $A = \{1, \ldots, n\}$. We then write for $\prod_{i=1}^{n}(\theta(t - t_i) + \theta(t_i - t))$

$$= \sum_{m=0}^{n} \sum_{\substack{B \subset A \\ |B|=m}} \prod_{i \in B} \theta(t - t_i) \prod_{i \in A-B} \theta(t_i - t)$$

$$= \sum_{m=0}^{n} \frac{1}{m!(n-m)!} \sum_{\substack{B \subset A \\ |B|=m}} \sum_{\pi \in S^m(B)} \prod_{i \in B} \theta(t - t_{\pi(i)}) \sum_{\pi \in S^{n-m}(A-B)} \prod_{i \in A-B} \theta(t_{\pi(i)} - t)$$

$$= \sum_{m=0}^{n} \frac{1}{m!(n-m)!} \sum_{\pi \in S^n} \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t).$$

Lemma 4.1.4 *The integral over a time-ordered operator product can be split according to*

$$\int_{-\infty}^{\infty} dt_1 \ldots dt_n \; \mathcal{T}\hat{O}(t_1)\ldots\hat{O}(t_n) =$$
$$\sum_{l=0}^{n} \binom{n}{l} \int_{-\infty}^{t} dt_1 \ldots dt_l \; \mathcal{T}\hat{O}(t_1)\ldots\hat{O}(t_l) \int_{t}^{\infty} dt_{l+1} \ldots dt_n \; \mathcal{T}\hat{O}(t_{l+1})\ldots\hat{O}(t_n). \quad (4.27)$$

where the $\hat{O}(t_i)$ are supposed to commute for equal times (i.e. they commute within the range of a time-ordering operator).

Proof We calculate explicitly

$$\int_{-\infty}^{\infty} dt_1 \ldots dt_n \; \mathcal{T}\hat{O}(t_1)\ldots\hat{O}(t_n)$$

$$= \int_{-\infty}^{\infty} dt_1 \ldots dt_n \sum_{\sigma \in S^n} \theta(t_{\sigma(1)} - t_{\sigma(2)})\ldots\theta(t_{\sigma(n-1)} - t_{\sigma(n)})\hat{O}(t_{\sigma(1)})\ldots\hat{O}(t_{\sigma(n)})$$

$$= \int_{-\infty}^{\infty} dt_1 \ldots dt_n \sum_{\sigma \in S^n} \theta(t_{\sigma(1)} - t_{\sigma(2)})\ldots\theta(t_{\sigma(n-1)} - t_{\sigma(n)}) \times$$

$$\sum_{m=0}^{n} \frac{1}{m!(n-m)!} \sum_{\pi \in S^n} \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t)\hat{O}(t_{\sigma(1)})\ldots\hat{O}(t_{\sigma(n)})$$

$$= \sum_{m=0}^{n} \frac{1}{m!(n-m)!} \int_{-\infty}^{\infty} dt_1 \ldots dt_n \sum_{\sigma \in S^n} \theta(t_{\sigma(1)} - t_{\sigma(2)})\ldots\theta(t_{\sigma(n-1)} - t_{\sigma(n)}) \times$$

$$\sum_{\pi \in S^n} \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t)\hat{O}(t_{\sigma(1)})\ldots\hat{O}(t_{\sigma(n)})$$

where we used lemma (4.1.3) in the third line. Now, we consider

$$\sum_{\sigma \in S^n} \theta(t_{\sigma(1)} - t_{\sigma(2)})\ldots\theta(t_{\sigma(n-1)} - t_{\sigma(n)}) \sum_{\pi \in S^n} \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t)$$

and fix permutations π and σ. The corresponding contribution reads

$$\theta(t_{\sigma(1)} - t_{\sigma(2)})\ldots\theta(t_{\sigma(n-1)} - t_{\sigma(n)}) \prod_{i=1}^{m} \theta(t - t_{\pi(i)}) \prod_{i=m+1}^{n} \theta(t_{\pi(i)} - t) \quad (4.28)$$

The factor $\prod_{i=1}^{m} \theta(t - t_{\pi(i)})$ is only nonzero if $t_{\pi(i)} < t \; \forall i = 1\ldots, m$ and correspondingly $t_{\pi(i)} > t \; \forall i = m+1, \ldots, n$ and therefore

$$t_{\pi(i)} > t_{\pi(j)} \; \forall j = 1, \ldots, m; \; i = m+1, \ldots, n. \quad (4.29)$$

On the other hand, the first factor enforces

$$t_{\sigma(1)} > t_{\sigma(2)} > \ldots > t_{\sigma(n)}. \quad (4.30)$$

The last two conditions are only consistent if $\{t_{\sigma(1)}, \ldots, t_{\sigma(n-m)}\} = \{t_{\pi(m+1)}, \ldots, t_{\pi(n)}\}$ and all permutations π which fulfill this condition, yield the same contribution (there are $m!(n-m)!$ such permutations). As the θ-factors commute, the contribution of all permutations π which fulfill the above conditions, can be written

$$m!(n-m)!\theta(t_{\sigma(1)} - t_{\sigma(2)}) \ldots \theta(t_{\sigma(n-1)} - t_{\sigma(n)}) \times$$
$$\theta(t_{\sigma(1)} - t) \ldots \theta(t_{\sigma(n-m)} - t) \ldots \theta(t - t_{\sigma(n-m+1)}) \ldots \theta(t - t_{\sigma(n)})$$

Furthermore, as $dt_1 \ldots dt_n = dt_{\sigma(1)} \ldots dt_{\sigma(n)}$, we can write explicitly

$$= \int_{-\infty}^{\infty} dt_1 \ldots dt_n \, \mathcal{T}\hat{O}(t_1) \ldots \hat{O}(t_n)$$

$$= \sum_{m=0}^{n} \sum_{\sigma \in S^n} \int_{-\infty}^{\infty} dt_{\sigma(1)} \ldots dt_{\sigma(n)}$$
$$\theta(t_{\sigma(1)} - t) \ldots \theta(t_{\sigma(n-m)} - t) \ldots \theta(t - t_{\sigma(n-m+1)}) \ldots \theta(t - t_{\sigma(n)}) \times$$
$$\theta(t_{\sigma(1)} - t_{\sigma(2)}) \ldots \theta(t_{\sigma(n-1)} - t_{\sigma(n)})\hat{O}(t_{\sigma(1)}) \ldots \hat{O}(t_{\sigma(n)})$$

$$= \sum_{m=0}^{n} \sum_{\sigma \in S^n} \int_t^{\infty} dt_{\sigma(1)} \ldots dt_{\sigma(n-m)} \int_{-\infty}^{t} dt_{\sigma(n-m+1)} \ldots dt_{\sigma(n)}$$
$$\theta(t_{\sigma(1)} - t_{\sigma(2)}) \ldots \theta(t_{\sigma(n-1)} - t_{\sigma(n)})\hat{O}(t_{\sigma(1)}) \ldots \hat{O}(t_{\sigma(n)})$$

$$= \sum_{m=0}^{n} \sum_{\sigma \in S^n} \int_t^{\infty} dt_{\sigma(1)} \ldots dt_{\sigma(n-m)}$$
$$\theta(t_{\sigma(1)} - t_{\sigma(2)}) \ldots \theta(t_{\sigma(n-m-1)} - t_{\sigma(n-m)}) \times \hat{O}(t_{\sigma(1)}) \ldots \hat{O}(t_{\sigma(n-m)}) \times$$
$$\int_{-\infty}^{t} dt_{\sigma(n-m+1)} \ldots dt_{\sigma(n)}$$
$$\theta(t_{\sigma(n-m+1)} - t_{\sigma(n-m+2)}) \ldots \theta(t_{\sigma(n-1)} - t_{\sigma(n)})\hat{O}(t_{\sigma(n-m+1)}) \ldots \hat{O}(t_{\sigma(n)}).$$

$$= \sum_{m=0}^{n} \binom{n}{m} \sum_{\sigma \in S^{n-m}} \sum_{\sigma' \in S^m} \int_t^{\infty} dt_{\sigma(1)} \ldots dt_{\sigma(n-m)}$$
$$\theta(t_{\sigma(1)} - t_{\sigma(2)}) \ldots \theta(t_{\sigma(n-m-1)} - t_{\sigma(n-m)})\hat{O}(t_{\sigma(1)}) \ldots \hat{O}(t_{\sigma(n-m)}) \int_{-\infty}^{t} dt_{\sigma'(n-m+1)} \ldots dt_{\sigma'(n)}$$
$$\theta(t_{\sigma'(n-m+1)} - t_{\sigma'(n-m+2)}) \ldots \theta(t_{\sigma'(n-1)} - t_{\sigma'(n)})\hat{O}(t_{\sigma'(n-m+1)}) \ldots \hat{O}(t_{\sigma'(n)})$$

$$= \sum_{m=0}^{n} \binom{n}{m} \int_t^{\infty} dt_1 \ldots dt_{n-m} \, \mathcal{T}\hat{O}(t_1) \ldots \hat{O}(t_{n-m}) \int_{-\infty}^{t} dt_{n-m+1} \ldots dt_n \, \mathcal{T}\hat{O}(t_{n-m+1}) \ldots \hat{O}(t_n).$$

Heuristically, the lemma can be proven as follows: dividing equation (4.27) by $n!$ shows that the lemma is equivalent to

$$\hat{U}^{(n)}(-\infty, \infty) = \sum_{l=0}^{n} \hat{U}^{(l)}(-\infty, t)\hat{U}^{(n-l)}(t, \infty). \tag{4.31}$$

This follows from plugging the perturbative expansion into

$$\hat{U}(-\infty, \infty) = \hat{U}(-\infty, t)\hat{U}(t, \infty) \tag{4.32}$$

and equating powers of the coupling constant.

Proof of the Theorem We consider

$$(\hat{H}_0 - E_0)\Psi_\eta \equiv (\hat{H}_0 - E_0)\hat{U}_\eta \Phi_0 = [\hat{H}_0, \hat{U}_\eta]\Phi_0. \tag{4.33}$$

Our general strategy is: rework this equality until it depends on η only through the quantity $\Psi_\eta/\langle\Psi_\eta|\Phi_0\rangle$ (which, by the assumption, exists and whose limit $\eta \to 0$ stays finite) and through η explicitly and then perform the limit $\eta \to 0$. We start by evaluating the commutator $[\hat{H}_0, \hat{U}_\eta]$ within the limits of perturbation theory. The formal expansion of time-evolution operator $\hat{U}_\eta$ is explicitly given by

$$\hat{U}_\eta = \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{1}{n!} \int_{-\infty}^{0} dt_1 \dots dt_n \ \mathcal{T}\hat{H}'_{1I}(t_1) \dots \hat{H}'_{1I}(t_n) \tag{4.34}$$

$$= \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{g^n}{n!} \int_{-\infty}^{0} dt_1 \dots dt_n \ e^{\eta(t_1+\dots+t_n)}\mathcal{T}\hat{H}_{1I}(t_1) \dots \hat{H}_{1I}(t_n). \tag{4.35}$$

We calculate the commutator with every summand separately:

$$[\hat{H}_0, \hat{H}_{1I}(t_1) \dots \hat{H}_{1I}(t_n)]. \tag{4.36}$$

As the commutator is a derivation in the operator algebra (and hence fulfills a Leibniz rule), we find for the last expression

$$[\hat{H}_0, \hat{H}_{1I}(t_1)]\hat{H}_{1I}(t_2) \dots \hat{H}_{1I}(t_n) + \hat{H}_{1I}(t_1)[\hat{H}_0, \hat{H}_{1I}(t_2)]\hat{H}_{1I}(t_3) \dots \hat{H}_{1I}(t_n) + \dots \tag{4.37}$$

By the general time-evolution law of operators

$$i\hbar\partial_t \hat{A}(t) = [\hat{A}(t), \hat{H}], \tag{4.38}$$

every commutator can be replaced by $-i\hbar\partial_{t_i}$ and we get

$$[\hat{H}_0, \hat{H}_{1I}(t_1) \dots \hat{H}_{1I}(t_n)] = \frac{\hbar}{i} \left(\partial_{t_1} + \dots + \partial_{t_n}\right) \hat{H}_{1I}(t_1) \dots \hat{H}_{1I}(t_n). \tag{4.39}$$

It is possible to pull the time-derivatives out of the operating range of the time-ordering operator. This can be seen as follows: if we replace

$$\mathcal{T}\frac{\hbar}{i} \left(\partial_{t_1} + \dots + \partial_{t_n}\right) \hat{H}_{1I}(t_1) \dots \hat{H}_{1I}(t_n) \tag{4.40}$$

by

$$\frac{\hbar}{i}\left(\partial_{t_1}+\ldots+\partial_{t_n}\right)\mathcal{T}\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n) \tag{4.41}$$

and observe

$$\mathcal{T}\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n)=\sum_{\pi\in S^n}\theta(t_{\pi(1)}-t_{\pi(2)})\ldots\theta(t_{\pi(n-1)}-t_{\pi(n)})\hat{H}_{1I}(t_{\pi(1)})\ldots\hat{H}_{1I}(t_{\pi(n)}), \tag{4.42}$$

we earn an extra term where the time-derivatives act on the Heaviside functions. For both expressions to be equal, it is sufficient that

$$\left(\partial_{t_1}+\ldots+\partial_{t_n}\right)\theta(t_{\pi(1)}-t_{\pi(2)})\ldots\theta(t_{\pi(n-1)}-t_{\pi(n)})=0. \tag{4.43}$$

This is indeed true according to lemma (4.1.2). The n-th order term in $[\hat{H}_0,\hat{U}_\eta]$ now reads

$$-\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^n}{n!}\int_{-\infty}^0 dt_1\ldots dt_n\ e^{\eta(t_1+\ldots+t_n)}(\partial_{t_1}+\ldots+\partial_{t_n})\mathcal{T}\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n) \tag{4.44}$$

where the minus sign appears because

$$\left(-\frac{i}{\hbar}\right)^n\frac{\hbar}{i}=-\left(-\frac{i}{\hbar}\right)^{n-1}. \tag{4.45}$$

As the $\hat{H}_{1I}(t_i)$ commute (they are two-particle operators within the range of a time-ordering operator), we can replace this last expression by

$$-\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^n}{(n-1)!}\int_{-\infty}^0 dt_1\ldots dt_n\ e^{\eta(t_1+\ldots+t_n)}\partial_{t_1}\mathcal{T}\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n). \tag{4.46}$$

Integrating by parts now yields

$$\begin{aligned}-\quad&\hat{H}_{1I}(t_1=0)\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^n}{(n-1)!}\int_{-\infty}^0 dt_2\ldots dt_n\ e^{\eta(t_2+\ldots+t_n)}\mathcal{T}\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n)\\+\quad&\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^n\eta}{(n-1)!}\int_{-\infty}^0 dt_1\ldots dt_n\ e^{\eta(t_1+\ldots+t_n)}\mathcal{T}\hat{H}_{1I}(t_1)\ldots\hat{H}_{1I}(t_n).\end{aligned}$$

We begin by considering the first term and sum over all orders:

$$\begin{aligned}&\sum_{n=1}^\infty\hat{H}_{1I}(t_1=0)\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^n}{(n-1)!}\int_{-\infty}^0 dt_2\ldots dt_n\ e^{\eta(t_2+\ldots+t_n)}\mathcal{T}\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n)\\=\ &g\hat{H}_{1I}(t_1=0)\sum_{n=1}^\infty\left(-\frac{i}{\hbar}\right)^{n-1}\frac{g^{n-1}}{(n-1)!}\int_{-\infty}^0 dt_2\ldots dt_n\ e^{\eta(t_2+\ldots+t_n)}\mathcal{T}\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n)\\=\ &g\hat{H}_{1I}(t_1=0)\sum_{n=0}^\infty\left(-\frac{i}{\hbar}\right)^{n}\frac{g^{n}}{n!}\int_{-\infty}^0 dt_2\ldots dt_n\ e^{\eta(t_2+\ldots+t_n)}\mathcal{T}\hat{H}_{1I}(t_2)\ldots\hat{H}_{1I}(t_n)\\=\ &g\hat{H}_{1I}(0)\hat{U}_\eta\end{aligned}$$

The second term is a little bit more complicated and can only be calculated by playing a further trick. Now we use the fact that we assumed $\hat{H}_1$ to be proportional to a coupling constant g (typically, the square of the electron charge). The n-th order term is then proportional to g^n. The prefactor in the n-th order term of the form

$$\frac{g^n}{(n-1)!}$$

can now be rewritten as

$$g\frac{\mathrm{d}}{\mathrm{d}g}\frac{g^n}{n!}.$$

Pulling $g\frac{\mathrm{d}}{\mathrm{d}g}$ to the front and summing all orders in the second term then clearly yields

$$i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\hat{U}_\eta. \tag{4.47}$$

Therefore, we finally get

$$(\hat{H}_0 - E_0)\Psi_\eta = -g\hat{H}_{1\mathrm{I}}(0)\hat{U}_\eta\Phi_0 + i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\hat{U}_\eta\Phi_0 \tag{4.48}$$

or

$$(\hat{H} - E_0)\Psi_\eta = i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\Psi_\eta. \tag{4.49}$$

We now take the scalar product of this expression with the vector

$$\frac{\Phi_0}{\langle\Psi_\eta|\Phi_0\rangle} \tag{4.50}$$

and get

$$\frac{\langle\Phi_0|\hat{H}_1|\Psi_\eta\rangle}{\langle\Phi_0|\Psi_\eta\rangle} = i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\ln\langle\Phi_0|\Psi_\eta\rangle. \tag{4.51}$$

Furthermore, with

$$\left(\hat{H} - E_0 - i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\right)\Psi_\eta = 0$$

we get

$$\left(\hat{H} - E_0 - i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\right)\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle} = -\Psi_\eta i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\frac{1}{\langle\Phi_0|\Psi_\eta\rangle} = \frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle}i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\ln\langle\Phi_0|\Psi_\eta\rangle$$

or

$$\left(\hat{H} - E_0 - i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\ln\langle\Phi_0|\Psi_\eta\rangle\right)\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle} = i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle} \tag{4.52}$$

and therefore

$$\left(\hat{H} - E_0 - \frac{\langle\Phi_0|\hat{H}_1|\Psi_\eta\rangle}{\langle\Phi_0|\Psi_\eta\rangle}\right)\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle} = i\hbar\eta g\frac{\mathrm{d}}{\mathrm{d}g}\frac{\Psi_\eta}{\langle\Phi_0|\Psi_\eta\rangle}. \tag{4.53}$$

The above equation depends on η only through the expression

$$\frac{\Psi_\eta}{\langle \Phi_0 | \Psi_\eta \rangle} \tag{4.54}$$

and through η explicitly on the RHS. As $\frac{\Psi_\eta}{\langle \Phi_0 | \Psi_\eta \rangle}$ exists by assumption, we can now safely perform the limit $\eta \to 0$ to get

$$\left(\hat{H} - E_0 - \frac{\langle \Phi_0 | \hat{H}_1 | \Psi \rangle}{\langle \Phi_0 | \Psi \rangle} \right) \frac{\Psi}{\langle \Phi_0 | \Psi \rangle} = 0. \tag{4.55}$$

In other words $\frac{\Psi}{\langle \Phi_0 | \Psi \rangle}$ is an eigenvector of $\hat{H} - E_0$ with eigenvalue

$$\frac{\langle \Phi_0 | \hat{H}_1 | \Psi \rangle}{\langle \Phi_0 | \Psi \rangle} := \Delta E. \tag{4.56}$$

This proves the theorem.

Remarks

1. In the proof given in [21], equation (6.51) already uses a result inferred from the assumption. The above reformulation shows that this little defect can be easily cured.

2. The proof works equally well if $-\infty$ is replaced by $+\infty$. Furthermore, it can be shown that the respective limiting vectors Ψ coincide.

Adiabatic Assumption From now on we assume that the adiabatic switching on yields in particular the interacting ground-state, i.e. $\Psi = \Psi_0$. Furthermore, we assume that both the interacting and the noninteracting ground-state are non-degenerate.

Corollary 4.1.5 *The interacting ground-state expectation value of the Heisenberg operator $O_\mathrm{H}(t)$ can be related to non-interacting ground-state expectation value of the respective operator in the interaction picture via*

$$\frac{\langle \Psi | \hat{O}_\mathrm{H}(t) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\langle \Phi_0 | \mathcal{T} \hat{O}_\mathrm{I}(t) \exp\left(-\frac{\mathrm{i}}{\hbar} \int_{-\infty}^{\infty} \mathrm{d}t \; \hat{H}_{1\mathrm{I}}(t) \right) | \Phi_0 \rangle}{\langle \Phi_0 | \hat{U}_\eta(\infty, -\infty) | \Phi_0 \rangle}. \tag{4.57}$$

Proof First, we rewrite the denominator $\langle \Psi | \Psi \rangle$. By the adiabatic assumption and the Gell-Mann and Low theorem, we have

$$\lim_{\eta \to 0} \frac{\hat{U}_\eta(0, \pm\infty) \Phi_0}{\langle \Phi_0 | \hat{U}_\eta(0, \pm\infty) | \Phi_0 \rangle} = \lim_{\eta \to 0} \frac{\Psi_\eta}{\langle \Phi_0 | \Psi_\eta \rangle} = \frac{\Psi}{\langle \Phi_0 | \Psi \rangle}. \tag{4.58}$$

Introducing twice the factor $|\langle\Psi_\eta|\Phi_0\rangle|^2$, we rewrite

$$\frac{\langle\Psi|\hat{O}_{\mathrm{H}}(t)|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \lim_{\eta\to 0}\frac{\frac{\langle\Psi_\eta|\hat{O}_{\mathrm{H}}(t)|\Psi_\eta\rangle}{|\langle\Psi_\eta|\Phi_0\rangle|^2}}{\frac{\langle\Psi_\eta|\Psi_\eta\rangle}{|\langle\Psi_\eta|\Phi_0\rangle|^2}} \tag{4.59}$$

Therefore,

$$
\begin{aligned}
\frac{\langle\Psi|\Psi\rangle}{|\langle\Phi_0|\Psi\rangle|^2} &= \lim_{\eta\to 0}\frac{\langle\Phi_0|\hat{U}_\eta^\dagger(0,+\infty)\hat{U}_\eta(0,-\infty)|\Phi_0\rangle}{|\langle\Phi_0|\Psi\rangle|^2} \\[2mm]
&= \lim_{\eta\to 0}\frac{\langle\Phi_0|\hat{U}_\eta(+\infty,0)\hat{U}_\eta(0,-\infty)|\Phi_0\rangle}{|\langle\Phi_0|\Psi\rangle|^2} \\[2mm]
&= \lim_{\eta\to 0}\frac{\langle\Phi_0|\hat{U}_\eta(+\infty,-\infty)|\Phi_0\rangle}{|\langle\Phi_0|\Psi\rangle|^2} \\[2mm]
&=: \frac{\langle\Phi_0|\hat{S}|\Phi_0\rangle}{|\langle\Phi_0|\Psi\rangle|^2}
\end{aligned}
$$

Similarly, for $\langle\Psi|\hat{O}_{\mathrm{H}}(t)|\Psi\rangle$, we get

$$
\begin{aligned}
&= \lim_{\eta\to 0}\frac{\langle\Phi_0|\hat{U}_\eta(\infty,0)\hat{U}_\eta(0,t)\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(t,0)\hat{U}_\eta(0,-\infty)|\Phi_0\rangle}{|\langle\Psi_\eta|\Phi_0\rangle|^2} \\[2mm]
&= \lim_{\eta\to 0}\frac{\langle\Phi_0|\hat{U}_\eta(\infty,t)\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(t,-\infty)|\Phi_0\rangle}{|\langle\Psi_\eta|\Phi_0\rangle|^2}
\end{aligned}
$$

If we now can show that

$$\mathcal{T}\hat{U}_\eta(\infty,t)\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(t,-\infty) = \mathcal{T}\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(\infty,-\infty), \tag{4.60}$$

then we are done. Consider therefore the expansion of $\mathcal{T}\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(\infty,-\infty)$ and use lemma (4.1.4) to get

$$
\begin{aligned}
&= \sum_{n=0}^\infty\left(-\frac{\mathrm{i}}{\hbar}\right)^n\frac{g^n}{n!}\int_{-\infty}^\infty \mathrm{d}t_1\ldots\mathrm{d}t_n\; \mathrm{e}^{-\eta(|t_1|+\ldots+|t_n|)}\mathcal{T}\hat{O}_{\mathrm{I}}(t)\hat{H}_{1\mathrm{I}}(t_1)\ldots\hat{H}_{1\mathrm{I}}(t_n) \\[2mm]
&= \sum_{n=0}^\infty\left(-\frac{\mathrm{i}}{\hbar}\right)^n\frac{g^n}{n!}\sum_{m+l=n}\frac{n!}{m!l!}\int_t^\infty \mathrm{d}t_1\ldots\mathrm{d}t_m\; \mathrm{e}^{-\eta(|t_1|+\ldots+|t_m|)}\mathcal{T}\hat{H}_{1\mathrm{I}}(t_1)\ldots\hat{H}_{1\mathrm{I}}(t_m)\hat{O}_{\mathrm{I}}(t)\times \\[2mm]
&\qquad \int_{-\infty}^t \mathrm{d}t_1\ldots\mathrm{d}t_l\; \mathrm{e}^{-\eta(|t_1|+\ldots+|t_l|)}\mathcal{T}\hat{H}_{1\mathrm{I}}(t_1)\ldots\hat{H}_{1\mathrm{I}}(t_l) \\[2mm]
&= \sum_{m=0}^\infty\left(-\frac{\mathrm{i}}{\hbar}\right)^m\frac{g^m}{m!}\int_t^\infty \mathrm{d}t_1\ldots\mathrm{d}t_m\; \mathrm{e}^{-\eta(|t_1|+\ldots+|t_m|)}\mathcal{T}\hat{H}_{1\mathrm{I}}(t_1)\ldots\hat{H}_{1\mathrm{I}}(t_m)\hat{O}_{\mathrm{I}}(t)\times \\[2mm]
&\qquad \sum_{l=0}^\infty\left(-\frac{\mathrm{i}}{\hbar}\right)^l\frac{g^l}{l!}\int_{-\infty}^t \mathrm{d}t_1\ldots\mathrm{d}t_l\; \mathrm{e}^{-\eta(|t_1|+\ldots+|t_l|)}\mathcal{T}\hat{H}_{1\mathrm{I}}(t_1)\ldots\hat{H}_{1\mathrm{I}}(t_l) \\[2mm]
&= \hat{U}_\eta(\infty,t)\hat{O}_{\mathrm{I}}(t)\hat{U}_\eta(t,-\infty) \to \hat{U}(\infty,t)\hat{O}_{\mathrm{I}}(t)\hat{U}(t,-\infty).
\end{aligned}
$$

This proves the corollary.

Remark The corollary can be generalized to products of operators for which its reads

$$\frac{\langle\Psi|\mathcal{T}\hat{O}_{1\mathrm{H}}(t_1)\dots\hat{O}_{n\mathrm{H}}(t_n)|\Psi\rangle}{\langle\Psi|\Psi\rangle}=\frac{\langle\Phi_0|\mathcal{T}\exp\left(-\frac{\mathrm{i}}{\hbar}\int_{-\infty}^{\infty}\mathrm{d}t\ \hat{H}_{1\mathrm{I}}(t)\right)\hat{O}_{1\mathrm{I}}(t_1)\dots\hat{O}_{n\mathrm{I}}(t_n)|\Phi_0\rangle}{\langle\Phi_0|\hat{S}|\Phi_0\rangle}.$$

Magic Gell-Mann and Low Formula[2] In particular, the Gell-Mann-Low theorem for expectation values allows for an expansion of interacting Green functions in non-interacting Green functions. Explicitly, the formal perturbation series for the interacting Green function reads:

$$\mathrm{i}\hbar G(\mathbf{x}t,\mathbf{x}'t')=\frac{\sum_{n=0}^{\infty}\left(-\frac{\mathrm{i}}{\hbar}\right)^n\frac{g^n}{n!}\int_{-\infty}^{\infty}\mathrm{d}t_1\dots\mathrm{d}t_n\ \langle\Phi_0|\mathcal{T}\hat{H}_I(t_1)\dots\hat{H}_I(t_n)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|\Phi_0\rangle}{\sum_{n=0}^{\infty}\left(-\frac{\mathrm{i}}{\hbar}\right)^n\frac{g^n}{n!}\int_{-\infty}^{\infty}\mathrm{d}t_1\dots\mathrm{d}t_n\ \langle\Phi_0|\mathcal{T}\hat{H}_I(t_1)\dots\hat{H}_I(t_n)|\Phi_0\rangle}$$
(4.61)

where the field operators are taken in the Heisenberg picture, i.e. they evolve according to the free Hamiltonian $\hat{H}_0$. The goal will now be to decompose this formal perturbative expression for G into a sum over free Green functions G_0.

4.1.2. Perturbation Theory for Green Functions

Introduction In this subsection we sketch how the perturbation theory for Green functions can be reworked in order to give an expansion for G^2 in terms of G_0^2 and the Coulomb potential. The aim consists partly in review and partly in the fixation of conventions.

Particles and Holes In the following, we consider a free field $\hat{\psi}(\mathbf{x}t)\equiv\hat{\psi}(x)$ corresponding to a free Hamiltonian (i.e. one-particle operator) $\hat{H}_0$. The free field has an expansion

$$\hat{\psi}(\mathbf{x}) \;=\; \sum_{n=0}^{\infty}\varphi_n(\mathbf{x})a_n \tag{4.62}$$

$$\hat{\psi}^\dagger(\mathbf{x}) \;=\; \sum_{n=0}^{\infty}\varphi_n^*(\mathbf{x})a_n^\dagger \tag{4.63}$$

into the eigenmodes of $\hat{H}_0$. As $\hat{H}_0$ is a one-particle operator, we have the simple time-dependence

$$a_n(t) \;=\; \exp\left(-\frac{\mathrm{i}}{\hbar}\varepsilon_n\right)a_n \tag{4.64}$$

$$a_n^\dagger(t) \;=\; \exp\left(\frac{\mathrm{i}}{\hbar}\varepsilon_n t\right)a_n^\dagger \tag{4.65}$$

---

[2]The magic in this formula will become clear later.

and therefore

$$\hat{\psi}(\mathbf{x}t) = \sum_{n=0}^{\infty} \varphi_n(\mathbf{x}t)a_n \tag{4.66}$$

$$\hat{\psi}^{\dagger}(\mathbf{x}t) = \sum_{n=0}^{\infty} \varphi_n^*(\mathbf{x}t)a_n^{\dagger} \tag{4.67}$$

with $\varphi_n(\mathbf{x}t) = \varphi_n(\mathbf{x})\mathrm{e}^{-\mathrm{i}/\hbar\varepsilon_n t}$. Furthermore, we restrict our attention to the operator algebra generated by the field operators $\hat{\psi}^{(\dagger)}(x)$. Consider now an N-particle ground-state Φ_0 of the non-interacting Hamiltonian $\hat{H}_0$ and let φ_n be the energetically ordered system of orthonormal eigenvectors of $\hat{H}_0$ with energies ε_i. The ground-state can now be written as

$$\Phi_0 = a_N^{\dagger} \ldots a_1^{\dagger}|0\rangle = \frac{1}{\sqrt{N!}} \det(\varphi_i(\mathbf{x}_j))|_{i,j=1,\ldots,N} \tag{4.68}$$

where $a_i^{\dagger} = a^{\dagger}(\varphi_i)$. The energy of this state then is $E_0^N = \sum_{i=1}^{N} \varepsilon_i$. We now have the following annihilation properties:

$$a_i|\Phi_0\rangle = 0, \ i > N \tag{4.69}$$

$$a_i^{\dagger}|\Phi_0\rangle = 0, \ i \leq N. \tag{4.70}$$

For $i \leq N$ we therefore rename

$$b_i := a_i^{\dagger} \tag{4.71}$$

$$b_i^{\dagger} = a_i \tag{4.72}$$

such that we now have $a_i|\Phi_0\rangle = b_i|\Phi_0\rangle = 0$. If we write a_i or b_i it is now understood that $i > N$ or $i \leq N$ respectively. Note that we do not redefine the field operators, in particular, $\hat{\psi}(\mathbf{x})|\Phi_0\rangle \neq 0$. Instead we only rename the harmonic oscillator operators such that all operators which have the property of annihilating the ground-state Φ_0 are formally written as annihilators. We call these operators, i.e. the a_i and b_i, the ground-state annihilators. Furthermore, note that this definition depends on the ground-state under consideration.[3] In particular, this implies that the so-called normal order, which we are now going to define, also depends on the ground-state under consideration, i.e. even for fixed $\hat{H}_0$ it depends on the particle number. One therefore should not speak of *the* normal order but instead of the normal order with respect to a certain ground-state. Finally, for the definition of the normal order it will be convenient to use the symbol c_i for the ground-state annihilators, i.e. $c_i = b_i$ for $i \leq N$ and $c_i = a_i$ for $i > N$. $c_i^{\dagger}$ is defined analogously. In the following, we consider operators which lie in the algebra generated by the field operators $c_i^{\dagger}$ and c_i and can therefore be expanded in monomials of the products in $c_i^{\dagger}$ and c_i.

---

[3]In relativistic Quantum Field Theory, the ground-state is simply replaced with the vacuum.

Definition The normal order $\mathcal{N}$ is a linear mapping of the operator algebra generated by the $c_i^\dagger$ and c_i which is defined by the following two prescriptions:

1. For products of the form

$$c_{i_1}^\dagger \ldots c_{i_n}^\dagger c_{i_{n+1}} \ldots c_{i_{n+m}}$$

   we define

$$
\begin{aligned}
\mathcal{N} c_j^\dagger c_{i_1}^\dagger \ldots c_{i_n}^\dagger c_{i_{n+1}} \ldots c_{i_{n+m}} &= c_j^\dagger c_{i_1}^\dagger \ldots c_{i_n}^\dagger c_{i_{n+1}} \ldots c_{i_{n+m}} \\
\mathcal{N} c_j c_{i_1}^\dagger \ldots c_{i_n}^\dagger c_{i_{n+1}} \ldots c_{i_{n+m}} &= (-1)^n c_{i_1}^\dagger \ldots c_{i_n}^\dagger c_j c_{i_{n+1}} \ldots c_{i_{n+m}}.
\end{aligned}
$$

2. For arbitrary products, the normal order is defined by the recursive prescription:

$$\mathcal{N} c_{i_{n+1}}^{(\dagger)} \ldots c_{i_1}^{(\dagger)} = \mathcal{N}\left(c_{i_{n+1}}^{(\dagger)} \mathcal{N}\left(c_{i_n}^{(\dagger)} \ldots c_{i_1}^{(\dagger)} \right) \right). \tag{4.73}$$

From these rules, one deduces that on monomials which consist exclusively of creators or annihilators, the action of $\mathcal{N}$ is trivial:

$$
\begin{aligned}
\mathcal{N} c_{i_1} \ldots c_{i_n} &= c_{i_1} \ldots c_{i_n} & (4.74) \\
\mathcal{N} c_{i_1}^\dagger \ldots c_{i_n}^\dagger &= c_{i_1}^\dagger \ldots c_{i_n}^\dagger & (4.75)
\end{aligned}
$$

and that for products of two field operators, we have

$$
\begin{aligned}
\mathcal{N} c_i^\dagger c_j &= c_i^\dagger c_j \\
\mathcal{N} c_i c_j^\dagger &= -c_j^\dagger c_i.
\end{aligned}
$$

The rule of thumb for the normal order therefore is: "annihilators to the right, creators to the left, internal order of creators and annihilators unchanged, every transposition yields a factor (-1) (or $(+1)$ for bosonic field operators with which we do not deal here)".

Definition The *contraction* $\mathcal{C}\hat{\psi}^{(\dagger)}(x_1)\hat{\psi}^{(\dagger)}(x_2)$ of two Heisenberg field operators $\hat{\psi}^{(\dagger)}(x_i)$ is given by

$$\mathcal{C}\hat{\psi}^{(\dagger)}(x_1)\hat{\psi}^{(\dagger)}(x_2) = \mathcal{T}\hat{\psi}^{(\dagger)}(x_1)\hat{\psi}^{(\dagger)}(x_2) - \mathcal{N}\hat{\psi}^{(\dagger)}(x_1)\hat{\psi}^{(\dagger)}(x_2) \tag{4.76}$$

Explicit Form of Contraction We now calculate the contraction explicitly. First, we express the field operator in terms of the $c^\dagger, c$:

$$
\begin{aligned}
\hat{\psi}(x) &= \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \varphi_n(x) c_n + \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \varphi_n(x) c_n^\dagger \\
\hat{\psi}^\dagger(x) &= \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_m^*(x) c_m^\dagger + \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_m^*(x) c_m.
\end{aligned}
$$

Therefore, for $\mathcal{N}\hat{\psi}(x_1)\hat{\psi}(x_2)$ we find

$$
\begin{aligned}
= & \; \mathcal{N} \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m + \mathcal{N} \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m^\dagger + \\
& \; \mathcal{N} \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m + \mathcal{N} \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m^\dagger \\
= & \; \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m - \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_m^\dagger c_n + \\
& \; \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m + \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m^\dagger \\
= & \; \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m + \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m^\dagger .
\end{aligned}
$$

Similarly, for $\mathcal{T}\hat{\psi}(x_1)\hat{\psi}(x_2)$ we get

$$
\begin{aligned}
= & \; \mathcal{T} \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m + \mathcal{T} \sum_{\varepsilon_n > \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n c_m^\dagger + \\
& \; \mathcal{T} \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m > \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m + \mathcal{T} \sum_{\varepsilon_n \leq \varepsilon_{\mathrm{F}}} \sum_{\varepsilon_m \leq \varepsilon_{\mathrm{F}}} \varphi_n(x_1)\varphi_m(x_2)c_n^\dagger c_m^\dagger
\end{aligned}
$$

where $\mathcal{T}\varphi_n(x_1)\varphi_m(x_2)c_n c_m^\dagger$ is to be understood as

$$
\mathcal{T}\varphi_n(\mathbf{x}_1)\varphi_m(\mathbf{x}_2)c_n(t_1)c_m^\dagger(t_2) = \varphi_n(\mathbf{x}_1)\varphi_m(\mathbf{x}_2)\mathcal{T}c_n(t_1)c_m^\dagger(t_2). \tag{4.77}
$$

To calculate $\mathcal{C}$, we observe that for non-interacting systems the CAR carry over to the time-dependent case in the sense that

$$
\begin{aligned}
\{c_n(t), c_m(t')\} &= \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(\varepsilon_n t + \varepsilon_m t')}\{c_n, c_m\} \tag{4.78}\\
\{c_n^\dagger(t), c_m^\dagger(t')\} &= \mathrm{e}^{\frac{\mathrm{i}}{\hbar}(\varepsilon_n t + \varepsilon_m t')}\{c_n^\dagger, c_m^\dagger\} \tag{4.79}\\
\{c_n(t), c_m^\dagger(t')\} &= \mathrm{e}^{-\frac{\mathrm{i}}{\hbar}(\varepsilon_n t - \varepsilon_m t')}\{c_n, c_m^\dagger\}. \tag{4.80}
\end{aligned}
$$

Therefore, we find

$$
\begin{aligned}
\mathcal{T}(c_n(t)c_m^\dagger(t') + c_m^\dagger(t')c_n(t)) &= 0 \\
(\mathcal{T} - \mathcal{N})c_n^\dagger(t)c_m(t') &= -\theta(t' - t)\{c_m(t'), c_n^\dagger(t)\} \\
(\mathcal{T} - \mathcal{N})c_n(t)c_m^\dagger(t') &= \theta(t - t')\{c_n(t), c_m^\dagger(t')\} \\
(\mathcal{T} - \mathcal{N})c_n(t)c_m(t') &= 0 \\
(\mathcal{T} - \mathcal{N})c_n^\dagger(t)c_m^\dagger(t') &= 0.
\end{aligned}
$$

From these facts, one reads off that

$$
\begin{aligned}
\mathcal{C}\hat{\psi}(x_1)\hat{\psi}(x_2) &= 0 \tag{4.81}\\
\mathcal{C}\hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_2) &= 0. \tag{4.82}
\end{aligned}
$$

Finally, we calculate

$$\mathcal{C}\hat{\psi}(x_1)\hat{\psi}^\dagger(x_2) = -\mathcal{C}\hat{\psi}^\dagger(x_2)\hat{\psi}(x_1). \tag{4.83}$$

For the product $\hat{\psi}(x_1)\hat{\psi}^\dagger(x_2)$, we find

$$
\begin{aligned}
= \;&\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(x_1)\varphi_m^*(x_2)c_n c_m^\dagger + \sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m\leq\varepsilon_F}\varphi_n(x_1)\varphi_m^*(x_2)c_n c_m + \\
&\sum_{\varepsilon_n\leq\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(x_1)\varphi_m^*(x_2)c_n^\dagger c_m^\dagger + \sum_{\varepsilon_n\leq\varepsilon_F}\sum_{\varepsilon_m\leq\varepsilon_F}\varphi_n(x_1)\varphi_m^*(x_2)c_n^\dagger c_m
\end{aligned}
$$

Now, the action of both $\mathcal{C}$ annihilates the second and the third term. For the first term, we find explicitly

$$
\begin{aligned}
= \;&\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\mathcal{C}c_n(t_1)c_m^\dagger(t_2) \\
= \;&\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)(\mathcal{T}-\mathcal{N})c_n(t_1)c_m^\dagger(t_2) \\
= \;&\theta(t_1-t_2)\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\{c_n(t_1),c_m^\dagger(t_2)\} \\
= \;&\theta(t_1-t_2)\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\mathrm{e}^{-\mathrm{i}/\hbar(\varepsilon_n t_1-\varepsilon_m t_2)}\{c_n,c_m^\dagger\} \\
= \;&\theta(t_1-t_2)\sum_{\varepsilon_n>\varepsilon_F}\sum_{\varepsilon_m>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\mathrm{e}^{-\mathrm{i}/\hbar(\varepsilon_n t_1-\varepsilon_m t_2)}\delta_{nm} \\
= \;&\theta(t_1-t_2)\sum_{\varepsilon_n>\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_n^*(\mathbf{x}_2)\mathrm{e}^{-\mathrm{i}/\hbar\varepsilon_n(t_1-t_2)}
\end{aligned}
$$

and for the fourth term

$$
\begin{aligned}
= \;&\sum_{\varepsilon_n\leq\varepsilon_F}\sum_{\varepsilon_m\leq\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\mathcal{C}c_n^\dagger(t_1)c_m(t_2) \\
= \;&\sum_{\varepsilon_n\leq\varepsilon_F}\sum_{\varepsilon_m\leq\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)(\mathcal{T}-\mathcal{N})c_n^\dagger(t_1)c_m(t_2) \\
= \;&-\theta(t_2-t_1)\sum_{\varepsilon_n\leq\varepsilon_F}\sum_{\varepsilon_m\leq\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_m^*(\mathbf{x}_2)\{c_n^\dagger(t_1),c_m(t_2)\} \\
= \;&-\theta(t_2-t_1)\sum_{\varepsilon_n\leq\varepsilon_F}\varphi_n(\mathbf{x}_1)\varphi_n^*(\mathbf{x}_2)\mathrm{e}^{\mathrm{i}/\hbar\varepsilon_n(t_1-t_2)}.
\end{aligned}
$$

This is precisely the Lehmann representation of G_0. We conclude that

$$\mathcal{C}\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}^\dagger(\mathbf{x}_2 t_2) = \mathrm{i}\hbar G_0(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) \tag{4.84}$$

where G_0 denotes the free reference Green function corresponding to $\hat{H}_0$ and N particles.[4]

---

[4]Note, that this holds in the non-interacting case.

Corollary 4.1.6 $\mathcal{C}\hat{\psi}^{(\dagger)}(x_1)\hat{\psi}^{(\dagger)}(x_2)$ *is a distribution in* (x_1, x_2)*, i.e. acts only as a multiplication operator on* $\mathcal{F}$*. ("the contraction yields a c-number")*

Definition The generalization the action of $\mathcal{C}$ to arbitrary monomials is given by

$$
\begin{aligned}
&\mathcal{C}_{2n}\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_{2n}) \\
=\ &\sum_{i<j}(-1)^{i+j+1}\left(\mathcal{C}\hat{\psi}^{(\dagger)}(x_i)\hat{\psi}^{(\dagger)}(x_j)\right)\hat{\psi}^{(\dagger)}(x_1)\dots\widehat{\hat{\psi}^{(\dagger)}(x_i)}\dots\widehat{\hat{\psi}^{(\dagger)}(x_j)}\dots\hat{\psi}^{(\dagger)}(x_{2n})
\end{aligned}
$$

In particular $\mathcal{C}_2 = \mathcal{C}$.

Definition The sum over all contractions of a product of field operators $\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_{2n})$ is given by the expression

$$
\prod_{i=1}^{n}\mathcal{C}_{2(n-i)}\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_{2n}).
$$

Lemma 4.1.7 *The ground-state expectation value of a product of field operators which is normally ordered with respect to that very ground-state vanishes identically.*

Proof First, note that in general

$$
\mathcal{N}\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_n)|\Phi_0\rangle \neq 0 \tag{4.85}
$$

because in the normally ordered products there are contributions consisting entirely of $c_n^\dagger$. These contributions vanish, however, in the expectation value $\langle\Phi_0|\cdot|\Phi_0\rangle$ because

$$
\langle\Phi_0|c_1^\dagger\dots c_n^\dagger|\Phi_0\rangle = \langle c_n\dots c_1\Phi_0|\Phi_0\rangle = 0. \tag{4.86}
$$

Any contribution in the field operator product whose operator part does not exclusively consist of $c^\dagger$ yields automatically zero because the normal ordering operator will commute the ground-state annihilators to the front where they act on Φ_0 directly.

Theorem 4.1.8 *(Wick) The time-ordered product of field operators can be decomposed into normal ordered products and contractions according to*

$$
\mathcal{T}\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_{2n}) = \mathcal{N}\hat{\psi}^{(\dagger)}(x_1)\dots\hat{\psi}^{(\dagger)}(x_{2n}) + \mathcal{N}(\text{sum over all contractions}). \tag{4.87}
$$

Wick-Theorem for Non-Interacting $2n$-Point Green Functions If we evaluate

$$
\mathcal{T}\hat{\psi}(1)\dots\hat{\psi}(n)\hat{\psi}^\dagger(2n)\dots\hat{\psi}^\dagger(n+1) \tag{4.88}
$$

in the ground-state Φ_0 and use the fact that all non-contracted terms vanish, we regain the *master formula*

$$G_0(1,\ldots,n,2n,\ldots,n+1) = \det(G_0(i,n+j))|_{i=1,\ldots,n;\ j=1,\ldots,n} \tag{4.89}$$

which we already found within the context of the equation of motion theory.

Expansion in Free Propagators We have seen in the last section that the perturbation theory for the two-point Green function can be condensed into the magic Gell-Mann and Low formula which we write compactly as.

$$i\hbar G(\mathbf{x}t,\mathbf{x}'t') = \sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{g^n}{n!}\int_{-\infty}^{\infty} dt_1\ldots dt_n\ \langle \mathcal{T}\hat{H}_I(t_1)\ldots\hat{H}_I(t_n)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\rangle/\langle\hat{S}\rangle.$$

We now discuss how the numerator in this formula can be decomposed in terms of the free propagator. Using the explicit form of the interacting Hamiltonian $\hat{H}_I(t)$ given by $\int d\mathbf{x}d\mathbf{x}'\ v(\mathbf{x}'-\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}'t)\hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}(\mathbf{x}t)\hat{\psi}(\mathbf{x}'t)$, this turns a generic n-th order term in the perturbative expansion of G into a complicated multiple integral of $2n+1$ free propagators and n interaction terms $v(\mathbf{x}-\mathbf{x}')$. Rewriting the interaction term as

$$\hat{H}_I(t) = \int d\mathbf{x}d\mathbf{x}'dt'\ v(\mathbf{x}'-\mathbf{x})\delta(t-t')\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}(\mathbf{x}t)\hat{\psi}(\mathbf{x}'t') \tag{4.90}$$

we see that the n-th order term is given by the integral

$$\sum_{n=0}^{\infty}\left(-\frac{i}{\hbar}\right)^n \frac{g^n}{n!}\int_{-\infty}^{\infty} dx_1 dx_1'\ldots dx_n dx_n'$$

over

$$v(x_1-x_1')\ldots v(x_n-x_n')\langle \mathcal{T}\hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1')\hat{\psi}(x_1)\ldots\hat{\psi}^\dagger(x_n)\hat{\psi}^\dagger(x_n')\hat{\psi}(x_n')\hat{\psi}(x_n)\hat{\psi}(x)\hat{\psi}^\dagger(x')\rangle_c$$

where $x=(\mathbf{x}t)$, $dx=d\mathbf{x}dt$ and $v(x)=v(\mathbf{x})\delta(t)$. One convinces oneself easily that an even permutation transforms

$$\hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_1')\hat{\psi}(x_1')\hat{\psi}(x_1)\ldots\hat{\psi}^\dagger(x_n)\hat{\psi}^\dagger(x_n')\hat{\psi}(x_n')\hat{\psi}(x_n)\hat{\psi}(x)\hat{\psi}^\dagger(x')$$

into

$$\hat{\psi}(x_1')\hat{\psi}(x_1)\ldots\hat{\psi}(x_n')\hat{\psi}(x_n)\hat{\psi}(x)\hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_1')\ldots\hat{\psi}^\dagger(x_n)\hat{\psi}^\dagger(x_n')\hat{\psi}^\dagger(x').$$

and therefore

$$(i\hbar)^{-n}\langle\mathcal{T}\hat{\psi}(x_1')\hat{\psi}(x_1)\ldots\hat{\psi}(x_n')\hat{\psi}(x_n)\hat{\psi}(x)\hat{\psi}^\dagger(x_1)\hat{\psi}^\dagger(x_1')\ldots\hat{\psi}^\dagger(x_n)\hat{\psi}^\dagger(x_n')\hat{\psi}^\dagger(x')\rangle$$

$$= i\hbar G_0^{4n+2}(x_1',x_1,\ldots,x_n',x_n,x;x',x_n',x_n,\ldots,x_1',x_1).$$

The master formula decomposes this $(4n + 2)$-point function G_0^{4n+2} into sums of products of $2n + 1$ two-point functions G_0. An n-th order term in the expansion of G can then be represented by graph: the arguments of the G_0 and v are the *vertices* or *points* and the G_0, v are the *edges* or *lines*. The lines corresponding to G are the *particle lines*, those corresponding to v are the *interaction lines*. At the vertex 1, $G_0(1, 2)$ is called an ingoing line and $G_0(2, 1)$ an outgoing line. The arguments which are integrated over are called *internal points*. x, x' are the *external points*. An internal point is necessarily linked to an incoming particle line, an outgoing particle line and an interaction line (where ingoing and outgoing particle line can be given by the same propagator as in $v(1, 2)G_0(2, 2)$). The edges joining the external points are called *external lines*. A graph in which all points are connected to the external points (through a sequence of lines) is called *connected*. Note that if we have in a certain graph a disconnected contribution, then the same expression necessarily arises also in the denominator of the Gell-Mann and Low formula which can be decomposed analogously to the numerator. One can show that the sum of all these disconnected contributions can be factored out leading to the famous cancellation theorem:

Theorem 4.1.9 *All disconnected contributions in the numerator of the perturbation series for the Green function given by the Gell-Mann and Low theorem in the form (4.61) can be factored out and exactly cancel the respective contributions of the denominator.*

The upshot of this is that we restrict attention in the following to the connected graphs. A graph in which the external lines are omitted is called *amputated* or in the case of G^2 a *self-energy graph*. Clearly, if Σ denotes the sum over all such graphs then

$$G(1, 2) = G_0(1, 2) + \int \mathrm{d}3\mathrm{d}4 \; G_0(1, 3)\Sigma(3, 4)G_0(4, 2). \tag{4.91}$$

This shows that the perturbatively defined Σ is identical to the reducible self-energy. A graph that cannot be separated into two pieces by removing a single G_0-line is called *irreducible* (in G_0). If $\tilde{\Sigma}$ denotes the subset of the Σ-graphs which are irreducible, then

$$\Sigma = \tilde{\Sigma} + \tilde{\Sigma}G_0\tilde{\Sigma} + \tilde{\Sigma}G_0\tilde{\Sigma}G_0\tilde{\Sigma} + \ldots = \tilde{\Sigma} + \tilde{\Sigma}G_0(\tilde{\Sigma} + \tilde{\Sigma}G_0\tilde{\Sigma} + \ldots) = \tilde{\Sigma} + \tilde{\Sigma}G\Sigma \tag{4.92}$$

and hence

$$G = G_0 + G_0\tilde{\Sigma}G \tag{4.93}$$

showing that $\tilde{\Sigma}$ is identical to the proper self-energy.

Feynman Rules We have seen that a given perturbative contribution to G can be represented by a graph. In order to gain back a perturbative contribution from a given (ad-

missible) graph, one has to observe the so-called Feynman rules. Admissible graphs are constructed inductively[5]:

1. The 2 first-order self-energy graphs are: $G(1,2)v(1,2)$ and $v(1,2)G(2,2)$.

2. A $(n+1)$-th order graph is constructed from a n-th order graph according to: (i) choose once or twice a particle line (including the possibility of choosing twice the same line). (ii) Replace the chosen particle lines $G(1,2)$ and $G(4,5)$ by $G(1,3)G(3,2)$ and $G(4,6)G(6,5)$ and join them by $v(3,6)$. If you have choosen only one line, then replace $G(1,2)$ with $G(1,3)G(3,1)v(3,4)G(4,4)$.

In order to evaluate a given n-th order graph (constructed inductively according to the above rules):

1. Integrate out the internal points. (The labelling of the internal points is irrelevant. There are $n!$ labellings corresponding to different contraction schemes in G_0^{4n+2} which all yield the same value. This cancels the prefactor $1/n!$ in the Gell-Mann and Low formula.)

2. Multiply by $(\mathrm{i}\hbar)^n g^n$.[6]

3. Include factor (-1) for every closed fermion loop.

Self-Consistent Methods The two first-order diagrams for the self-energy read in the space-time domain:

$$-\int \mathrm{d}\mathbf{x}'\mathrm{d}t'\ v(\mathbf{x}t,\mathbf{x}'t')\mathrm{i}\hbar G_0(\mathbf{x}'t',\mathbf{x}'t'^+) \tag{4.94}$$

and

$$v(\mathbf{x}t,\mathbf{x}'t')\mathrm{i}\hbar G_0(\mathbf{x}t,\mathbf{x}'t'). \tag{4.95}$$

The first expression is called *Hartree term* and the second is the *Fock term*. Note, that the total first order contribution to G can be written as

$$G = G_0 - \mathrm{i}\hbar G_0 V \cdot G_0^4 \tag{4.96}$$

where $G_0^4(1,2,3,4) = G(1,3)G(2,4) - G(1,4)G(2,3)$. As every n-th order perturbative contribution to the Green function can also be interpreted as a $(n-1)$-th order contribution to the first order contribution, the total perturbation series sums up to

$$G = G_0 - \mathrm{i}\hbar G_0 V \cdot G^4. \tag{4.97}$$

---

[5]The problem of the interpretation of equal-time Green functions will be discussed later.

[6]From now on, the coupling constant will be reabsorbed in the interaction potential.

Multiplication with G_0^{-1} shows that the Gell-mann and Low theorem implies the equation of motion for G. Conversely, as the equation of motion theory implies the factorization of the free $2n$-point functions, the perturbative expansion for G can be gained back from the equation of motion hierarchy by iteration. In other words, equation of motion theory and perturbation theory are equivalent. If we now want to calculate the first order contributions to the Green function, we have

$$G = G_0 + G_0 \Sigma^1 G_0 \tag{4.98}$$

where $\Sigma^1 = \Sigma^1[G_0]$ is the sum of the Hartree and the Fock term. Without introducing further diagrams, we can go beyond this simple level of perturbation theory by turning this simple explicit equation into a self-consistent equation

$$G = G_0 + G_0 \tilde{\Sigma}^1[G_0] G \tag{4.99}$$

or even

$$G = G_0 + G_0 \tilde{\Sigma}^1[G] G. \tag{4.100}$$

By iteration, one shows that the first of these equations corresponds to an infinite summation of Hartree and Fock terms linked by propagator lines whereas the second equation even corresponds to an infinite summation of graphs in which Hartree and Fock terms can be inserted into each other up to arbitrary order. One shows easily that there are only 2 (out of 10) second order graphs which are not included in this summation. In other words, self-consistent perturbation theory is highly superior to standard perturbation theory because it corresponds to an infinite summation of graphs of a certain type. The drawback of these self-consistent methods is that the determining equation for G is not explicit because G enters in both sides. One therefore usually works with the corresponding quasiparticle equation

$$\left(-\frac{\hbar^2}{2m}\Delta + v_{\text{ext}}(\mathbf{x}) \right) f_s^\pm(\mathbf{x}) + \int \mathrm{d}\mathbf{x}' \; \tilde{\Sigma}(\mathbf{x},\mathbf{x}',\pm\varepsilon_s^\pm) f_s^\pm(\mathbf{x}') = \pm\varepsilon_s^\pm f_s^\pm(\mathbf{x}).$$

If we want to find a self-consistent equation for the f_s we have to substitute $\tilde{\Sigma}^1[G]$ for $\tilde{\Sigma}$ and write the result in terms of the f_s themselves (substituting the Lehmann representation for G into the expressions for the diagrams). Obviously, the Hartree and the Fock term read in terms of Lehmann amplitudes

$$\int \mathrm{d}\mathbf{x}'' \sum_r v(\mathbf{x}',\mathbf{x}'') f_r^-(\mathbf{x}'') f_r^{-*}(\mathbf{x}'') \tag{4.101}$$

and

$$\sum_r f_r^-(\mathbf{x}) v(\mathbf{x},\mathbf{x}') f_r^{-*}(\mathbf{x}'). \tag{4.102}$$

The resulting equations for the Lehmann amplitudes are indeed the Hartree-Fock equations. Note that within this approximation, the self-energy depends only on the occupied orbitals. Due to the instantaneous potential v, the first-order self-energy Σ^1 has no dependence on time/frequency. Finally, notice that contrary to conventional textbook wisdom, the Hartree-Fock orbitals and energies clearly do have a physical interpretation, namely they are approximate Lehmann amplitudes and quasiparticle energies. For later purposes, we now prove what we will call the *self-energy splitting formula*.

Lemma 4.1.10 *Let*

$$\tilde{\Sigma} = \tilde{\Sigma}_1 + \tilde{\Sigma}_2 \tag{4.103}$$

be an arbitrary decomposition of the self-energy and define

$$G_1 = G_0 + G_0\tilde{\Sigma}_1 G_1. \tag{4.104}$$

Then

$$G = G_1 + G_1\tilde{\Sigma}_2 G. \tag{4.105}$$

Proof This follows from the Dyson equation rewritten in the form

$$\tilde{\Sigma}_1(\omega) + \tilde{\Sigma}_2(\omega) = \tilde{\Sigma}(\omega) = G_0^{-1}(\omega) - G^{-1}(\omega) = G_0^{-1}(\omega) - G_1^{-1}(\omega) + G_1^{-1}(\omega) - G^{-1}(\omega). \tag{4.106}$$

$$\square$$

We now apply this result to the above Hartree-Fock solution. The lemma then says: If we take the Hartree-Fock propagator $:= G_1$ as the non-interacting reference Green function in the Dyson equation $G = G_1 + G_1\Sigma_2 G$ then the remaining self-energy Σ_2 corresponds to the (infinite) sum of all skeleton diagrams expressed in terms of G_1. In particular, Σ_2 does not contain any first order diagrams (these would be the Hartree and the Hartree Fock diagram already summed up in G_1) and only 2 second order diagrams which correspond to the first vertex correction and the first bubble diagram.[7]

---

[7]This is the reason why [93] p.390 states that perturbative expansion of the self-energy starts only with second-order terms.

4.1.3. Four-Point Propagator, Polarizability and Bethe-Salpeter Equation

Introduction of the Four-Point Propagator The four-point propagator is defined by

$$(i\hbar)^2 G^4(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_3, \mathbf{x}_4 t_4) = \langle \Psi_0 | \mathcal{T}\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}(\mathbf{x}_2 t_2)\hat{\psi}^\dagger(\mathbf{x}_4 t_4)\hat{\psi}^\dagger(\mathbf{x}_3 t_3)|\Psi_0\rangle. \qquad (4.107)$$

Precisely as in the case of the two-point propagator, for $(i\hbar)^2 G^4(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_3, \mathbf{x}_4 t_4)$ we get the perturbative expansion

$$= \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \frac{g^n}{n!} \int_{-\infty}^{\infty} dt_1 \ldots dt_n \, \langle \mathcal{T}\hat{H}_I(t_1)\ldots\hat{H}_I(t_n)\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}(\mathbf{x}_2 t_2)\hat{\psi}^\dagger(\mathbf{x}_4 t_4)\hat{\psi}^\dagger(\mathbf{x}_3 t_3)\rangle_c$$

where the subscript "c" indicates that the summation is restricted to connected graphs. By the Wick theorem, the free four-point propagator fulfills

$$G_0^4(1,2,3,4) = \frac{1}{(i\hbar)^2}\langle \Phi_0 | \mathcal{T}\hat{\psi}(1)\hat{\psi}(2)\hat{\psi}^\dagger(4)\hat{\psi}^\dagger(3)|\Phi_0\rangle = G_0(1,3)G_0(2,4) - G_0(1,4)G_0(2,3). \tag{4.108}$$

For the full (=interacting) propagator, this suggests the ansatz

$$\begin{aligned} G^4(1,2,3,4) &= G(1,3)G(2,4) - G(1,4)G(2,3) \\ &\quad -i\hbar \int d(5,6,7,8) \, G(1,5)G(2,6)\Gamma(5,6,7,8)G(7,3)G(8,4). \end{aligned}$$

A comparison with the perturbative expansion shows that the *scattering amplitude* Γ has the meaning of a sum over all amputated skeleton graphs which can be put between two electron-hole pairs. If we define a subsum I of Γ which corresponds to all graphs in Γ which are irreducible in the electron-hole channel, then we necessarily have

$$\Gamma = I + i\hbar IGGI + (i\hbar)^2 IGGIGGI + \ldots,$$

i.e.

$$\begin{aligned} \Gamma(1,2,3,4) &= I(1,2,3,4) + \\ &\quad i\hbar \int d(5,6,7,8) \, I(1,5,3,6)G(6,7)G(8,5)\Gamma(7,2,8,4). \end{aligned}$$

This is the well-known *Bethe-Salpeter equation*.[8]

---

[8]The Bethe-Salpeter equation is the direct analog of the Bethe-Salpeter equation in high-energy physics; cf. e.g. [47] p.482.

Density Response Function The reducible, time-ordered density-density response function at temperature $T = 0$ in the non-degenerate N-particle ground-state $\Psi_0^N := \Psi_0$ is defined as

$$\chi(\mathbf{x}t, \mathbf{x}'t') = -\frac{\mathrm{i}}{\hbar} \langle \Psi_0 | \mathcal{T} \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) \hat{\psi}^\dagger(\mathbf{x}'t') \hat{\psi}(\mathbf{x}'t') | \Psi_0 \rangle. \tag{4.109}$$

Precisely as in the case of the Lehmann representation of the Green function, by inserting complete sets $\{\Psi_s^N \equiv \Psi_s\}$ of N-particle energy eigenstates with energies $E_s^N := E_s$ and Fourier transforming with respect to $t - t'$, we get the spectral representation:

$$
\begin{aligned}
\mathrm{i}\hbar\chi(\mathbf{x}t, \mathbf{x}'t') &= \theta(t - t') \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) \hat{\psi}^\dagger(\mathbf{x}'t') \hat{\psi}(\mathbf{x}'t') | \Psi_0 \rangle + \\
&\quad \theta(t' - t) \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}'t') \hat{\psi}(\mathbf{x}'t') \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) | \Psi_0 \rangle \\
&= \theta(t - t') \sum_s \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) | \Psi_s \rangle \langle \Psi_s | \hat{\psi}^\dagger(\mathbf{x}'t') \hat{\psi}(\mathbf{x}'t') | \Psi_0 \rangle + \\
&\quad \theta(t' - t) \sum_s \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}'t') \hat{\psi}(\mathbf{x}'t') | \Psi_s \rangle \langle \Psi_s | \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) | \Psi_0 \rangle \\
&= \sum_s \theta(t - t') \mathrm{e}^{-\mathrm{i}/\hbar(E_s - E_0)(t - t')} \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) | \Psi_s \rangle \langle \Psi_s | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') | \Psi_0 \rangle + \\
&\quad \sum_s \theta(t' - t) \mathrm{e}^{-\mathrm{i}/\hbar(E_s - E_0)(t' - t)} \langle \Psi_0 | \hat{\psi}^\dagger(\mathbf{x}') \hat{\psi}(\mathbf{x}') | \Psi_s \rangle \langle \Psi_s | \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x}) | \Psi_0 \rangle \\
&= \sum_s \theta(t - t') \mathrm{e}^{-\mathrm{i}/\hbar(E_s - E_0)(t - t')} \langle \Psi_0 | \hat{n}(\mathbf{x}) | \Psi_s \rangle \langle \Psi_s | \hat{n}(\mathbf{x}') | \Psi_0 \rangle + \\
&\quad \sum_s \theta(t' - t) \mathrm{e}^{+\mathrm{i}/\hbar(E_s - E_0)(t - t')} \langle \Psi_0 | \hat{n}(\mathbf{x}') | \Psi_s \rangle \langle \Psi_s | \hat{n}(\mathbf{x}) | \Psi_0 \rangle
\end{aligned}
$$

with the density operator $\hat{n}(\mathbf{x}) = \hat{\psi}^\dagger(\mathbf{x}) \hat{\psi}(\mathbf{x})$. In the frequency domain, this yields

$$\chi(\mathbf{x}, \mathbf{x}'; \omega) = \sum_s \left(\frac{\langle \Psi_0 | \hat{n}(\mathbf{x}) | \Psi_s \rangle \langle \Psi_s | \hat{n}(\mathbf{x}') | \Psi_0 \rangle}{\hbar\omega - (E_s - E_0) + \mathrm{i}\eta} - \frac{\langle \Psi_0 | \hat{n}(\mathbf{x}') | \Psi_s \rangle \langle \Psi_s | \hat{n}(\mathbf{x}) | \Psi_0 \rangle}{\hbar\omega + (E_s - E_0) - \mathrm{i}\eta} \right). \tag{4.110}$$

For later purposes, we need in particular the density fluctuation-response function

$$P(\mathbf{x}t, \mathbf{x}'t') = -\frac{\mathrm{i}}{\hbar} \langle \Psi_0 | \mathcal{T} \delta\hat{n}(\mathbf{x}t) \delta\hat{n}(\mathbf{x}'t') | \Psi_0 \rangle \tag{4.111}$$

with

$$\delta\hat{n}(\mathbf{x}t) = \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) - \langle \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) \rangle = \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) - n(\mathbf{x}t) = \hat{\psi}^\dagger(\mathbf{x}t) \hat{\psi}(\mathbf{x}t) - n(\mathbf{x}). \tag{4.112}$$

In the literature, the density fluctuation-response function is usually called *polarizability*. From equation (4.110), we read off that the replacement $\hat{n}(\mathbf{x}t) \mapsto \delta\hat{n}(\mathbf{x}t)$ has the simple effect of cancelling the term

$$\frac{\langle \Psi_0 | \hat{n}(\mathbf{x}) | \Psi_0 \rangle \langle \Psi_0 | \hat{n}(\mathbf{x}') | \Psi_0 \rangle}{\hbar\omega + \mathrm{i}\eta} - \frac{\langle \Psi_0 | \hat{n}(\mathbf{x}') | \Psi_0 \rangle \langle \Psi_0 | \hat{n}(\mathbf{x}') | \Psi_0 \rangle}{\hbar\omega - \mathrm{i}\eta} \tag{4.113}$$

because $\langle\Psi_0|\delta\hat{n}(\mathbf{x})|\Psi_s\rangle = \langle\Psi_0|\hat{n}(\mathbf{x})-n(\mathbf{x})|\Psi_s\rangle = \langle\Psi_0|\hat{n}(\mathbf{x})|\Psi_s\rangle - n(\mathbf{x})\langle\Psi_0|\Psi_s\rangle = \langle\Psi_0|\hat{n}(\mathbf{x})|\Psi_s\rangle$ for $s \neq 0$ and $\langle\Psi_0|\delta\hat{n}(\mathbf{x})|\Psi_{s=0}\rangle = 0$.

Four-Point Propagator and Density Response Function One shows easily that

$$\chi(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) = \mathrm{i}\hbar \lim_{t_3 \to t_1^+} \lim_{t_4 \to t_2^+} G^4(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_1 t_3, \mathbf{x}_2 t_4) \qquad (4.114)$$

or more compactly

$$\chi(1,2) = \mathrm{i}\hbar G^4(1, 2, 1^+, 2^+). \qquad (4.115)$$

Similarly, one shows the important relation (see next subsection)

$$P(1,2) = \mathrm{i}\hbar L(1, 2, 1^+, 2^+) \qquad (4.116)$$

where $L(1, 2, 3, 4) = G^4(1, 2, 3, 4) - G(1, 3)G(2, 4)$ is called *connected four-point propagator*. That means, the transition from the density to the density fluctuation response corresponds to the transition from G^4 to L on the level of the Green functions. The last formula together with the Wick theorem and the Lehmann representation shows that that a non-interacting polarizability can be expressed in terms of the orbtials of the ground-state as

$$P(\mathbf{x}, \mathbf{x}'; \omega) = \sum_{a\,\mathrm{unocc}} \sum_{i\,\mathrm{occ}} \left(\frac{\varphi_i^*(\mathbf{x})\varphi_a(\mathbf{x})\varphi_a^*(\mathbf{x}')\varphi_i(\mathbf{x}')}{\hbar\omega - (\varepsilon_a - \varepsilon_i) + \mathrm{i}\eta} - \frac{\varphi_i^*(\mathbf{x}')\varphi_a(\mathbf{x}')\varphi_a^*(\mathbf{x})\varphi_i(\mathbf{x})}{\hbar\omega + (\varepsilon_a - \varepsilon_i) - \mathrm{i}\eta} \right). \quad (4.117)$$

The cancellation of the term $s = 0$ is here already implemented through the condition that a sums over unoccupied and i over occupied states.

4.1.4. Self-Consistent Set of Equations

Introduction We have seen in the last subsection that infinite subclasses of all Feynman diagrams contributing to the full Green function G can be summed up by going over from a sum of diagrams in ordinary perturbation theory $G = G_0 + G_0\Sigma[G_0, V]G_0$ to the corresponding self-consistent equation $G = G_0 + G_0\tilde{\Sigma}[G, V]G$. In principle, $\tilde{\Sigma}[G, V]$ is the infinite sum over all one-particle, irreducible graphs. Consequently, it is impossible to write down a closed expression for $\tilde{\Sigma}$ in terms of G and V. It is therefore desirable to find a set of self-consistent equations depending on some perturbative quantity I which automatically generates the hierarchy of infinite summations if I is suitably expanded. Furthermore, we require this set of equations to be written in terms of (formal) matrix products, which has the advantage that the equations do not depend on the usage of the space-time domain (i.e. carry over directly to an orbital basis and to the frequency domain). It will turn out that this can be

achieved by suitably combining the Bethe-Salpeter equation with the equation of motion theory. Hence, I will turn out to be the (particle-hole-channel) irreducible scattering amplitude.

Conventions We introduce the following matrix products of four-point quantities

$$(AB)(1,2,3,4) \stackrel{\text{def}}{=} \int \mathrm{d}(5,6) \; A(1,5,3,6)B(6,2,5,4) \tag{4.118}$$

$$(A \cdot B)(1,2) \stackrel{\text{def}}{=} \int \mathrm{d}(3,4,5) \; A(1,4,5,3)B(3,5,4,2). \tag{4.119}$$

Products of two-point functions are defined in the standard way:

$$(AB)(1,2) = \int \mathrm{d}3 \; A(1,3)B(3,2). \tag{4.120}$$

Furthermore, we define a left and a right Dirac distribution via

$$\delta^{\pm}[f] = \int \mathrm{d}t \; f(t)\delta(t^{\pm}) = \lim_{t \to 0^{\pm}} f(t). \tag{4.121}$$

We can think of $\delta^{\pm}$ as acting on an extended space of test functions which are continuous up to countably many jumps. We introduce a four-point Coulomb kernel by

$$V(1,2,3,4) = v(1,4^{+})\delta(4,2^{+})\delta(3,1^{+}). \tag{4.122}$$

with $\delta(1,2^{+}) = \delta(\mathbf{x}_1 - \mathbf{x}_2)\delta(t_1 - t_2^{+})$ and $v(1^{+}) = v(\mathbf{x})\delta(t^{+})$. On top of that, we introduce the four-point quantity

$$L(1,2,3,4) = G^{4}(1,2,3,4) - G(1,3)G(2,4). \tag{4.123}$$

and the new reference propagator $G_0(1,2)$ defined through

$$(\mathrm{i}\hbar\partial_t - \hat{H}_0(1) - v_{\mathrm{H}}(1))G_0(1,2) = \delta(1,2) \tag{4.124}$$

where $v_{\mathrm{H}}(1)$ is a Hartree-type potential with a density $n(1)$ to be specified later.

Theorem 4.1.11 *We have the following closed, exact set of equations:*

$$G = G_0 - \mathrm{i}\hbar G_0 V \cdot L \tag{4.125}$$

$$L = L_0 + \mathrm{i}\hbar L_0 I L \tag{4.126}$$

$$W = V + \mathrm{i}\hbar V L V \tag{4.127}$$

where $L_0(1,2,3,4) = -G(1,4)G(2,3)$.

Remarks

1. *Exactitude*: "Exact" here refers to the fact that formally the self-consistent equations sum up to arbitrary order. Only the first and the third equation are exact in the mathematical sense, the third being a definition. The second equation will be proven from the Bethe-Salpeter equation for the scattering amplitude and therefore ultimately hinges on the use of perturbation theory.

2. *Closure*: The self-consistent set of equations is closed in the sense that for any desired level of accuracy one can choose an expression for I in terms of Feynman graphs which in turn can be expressed through V, W, G and L. I itself is a formal infinite series over such graphs and therefore a closed (= finite algebraic) expression for I in terms of V, W, G and L cannot be written down. The expansion of I will be treated in section 4.2.

3. *Self-Consistency*: The equation for W is a definition.[9] As to the self-consistency, W is actually superfluous. It is only introduced for the purpose of having concise expressions for I. On the other hand, strictly speaking, G_0 is a functional of the full propagator $G_0 = G_0[G]$ because – as the proof will show – the density entering in the definition of G_0 is the self-consistent density of the full propagator G.

Proof Only the first and the second equation have to be proven. In the beginning, the derivations will be formal, i.e. in order not to overload the notation, the left- and right Dirac deltas will be replaced with ordinary deltas. The time-order will be checked afterwards.

1. Recall the equation of motion for the Green function

$$(\mathrm{i}\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_\mathbf{x} - v_{\mathrm{ext}}(\mathbf{x}))G(\mathbf{x}t, \mathbf{x}'t') \quad = \quad \delta(t-t')\delta(\mathbf{x}-\mathbf{x}') + \frac{1}{\mathrm{i}\hbar}\langle\mathcal{T}[\hat{\psi}(\mathbf{x}t), \hat{V}]\hat{\psi}^\dagger(\mathbf{x}'t')\rangle$$

which by the help of

$$\hat{V} \equiv \hat{V}(t) \quad = \quad \mathrm{e}^{\mathrm{i}\frac{\hat{H}}{\hbar}t}\int\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\ v(\mathbf{x}-\mathbf{x}')\hat{\psi}^\dagger(\mathbf{x})\hat{\psi}^\dagger(\mathbf{x}')\hat{\psi}(\mathbf{x}')\hat{\psi}(\mathbf{x})\mathrm{e}^{-\mathrm{i}\frac{\hat{H}}{\hbar}t}$$

$$= \quad \int\mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\ v(\mathbf{x}-\mathbf{x}')\hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t)\hat{\psi}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}t)$$

and

$$[\hat{\psi}(\mathbf{x}t), \hat{V}] = \int\mathrm{d}\mathbf{x}'\ v(x-x')\hat{\psi}^\dagger(\mathbf{x}'t)\hat{\psi}(\mathbf{x}'t)\hat{\psi}(\mathbf{x}t) \tag{4.128}$$

---

[9]Note, however, that W is the condensed matter analog of the full electromagnetic propagator. From this perspective, $W = V + VLV$ is not a definition.

leads to

$$(i\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}} - v_{\text{ext}}(\mathbf{x}))G(\mathbf{x}t, \mathbf{x}'t') = \delta(t-t')\delta(\mathbf{x}-\mathbf{x}') - i\hbar\int \mathrm{d}x''\, v(x-x'')G^4(x'', x, x'', x').$$

where $x = (\mathbf{x}t)$ and $v(x - x') = v(\mathbf{x} - \mathbf{x}')\delta(t - t')$. The last term can be rewritten as

$$
\begin{aligned}
\int \mathrm{d}x''\, v(x-x'')G^4(x'', x, x'', x') &= \int \mathrm{d}4\, v(1,4)G^4(4,1,4,2) \\
&= \int \mathrm{d}(3,4,5)\, v(5,4)\delta(1,5)\delta(3,4)G^4(3,5,4,2) \\
&= \int \mathrm{d}(3,4,5)\, V(1,4,5,3)G^4(3,5,4,2)
\end{aligned}
$$

with

$$V(1,2,3,4) = \delta(2,4)\delta(1,3)v(3,2) = \delta(2,4)\delta(1,3)v(1,4). \tag{4.129}$$

Now, recall that

$$L(1,2,3,4) = G^4(1,2,3,4) - G(1,3)G(2,4). \tag{4.130}$$

Consequently,

$$
\begin{aligned}
\int \mathrm{d}(3,4,5)\, V(1,4,5,3)G^4(3,5,4,2) &= \int \mathrm{d}(3,4,5)\, V(1,4,5,3)L^4(3,5,4,2) \\
&+ \int \mathrm{d}(3,4,5)\, V(1,4,5,3)G(3,4)G(5,2).
\end{aligned}
$$

But with

$$
\begin{aligned}
\int \mathrm{d}(3,4,5)\, V(1,4,5,3)G(3,4)G(5,2) &= \int \mathrm{d}(3,4,5)\, v(1,3)\delta(1,5)\delta(3,4)G(3,4)G(5,2) \\
&\int \mathrm{d}3\, v(1,3)G(1,2)G(3,3)
\end{aligned}
$$

and

$$i\hbar G(\mathbf{x}t, \mathbf{x}t) \equiv i\hbar G(\mathbf{x}t, \mathbf{x}t^+) = -n(\mathbf{x}) \tag{4.131}$$

we see that

$$-i\hbar\int \mathrm{d}(3,4,5)\, V(1,5,3,4)G(3,2)G(4,5) = v_{\text{H}}(1)G(1,2) \tag{4.132}$$

and therefore

$$(i\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}} - v_{\text{ext}}(\mathbf{x}) - v_{\text{H}}(\mathbf{x}))G(\mathbf{x}t, \mathbf{x}'t') = \delta(t-t')\delta(\mathbf{x}-\mathbf{x}') - i\hbar\int \mathrm{d}x''\, v(x-x'')L(x'', x, x'', x').$$

Redefining G_0 as the inverse of $(i\hbar\partial_t + \frac{\hbar^2}{2m}\Delta_{\mathbf{x}} - v_{\text{ext}}(\mathbf{x}) - v_{\text{H}}(\mathbf{x}))$, this equation can be written more abstractly as

$$G(1,2) = G_0(1,2) - i\hbar\int \mathrm{d}(3,4,5,6)\, G_0(1,6)V(6,4,5,3)L(3,5,4,2) \tag{4.133}$$

Finally, we check the time-order. The redefinition of the Coulomb potential leads to

$$
\begin{aligned}
&\int \mathrm{d}(3,4,5)\ V(1,4,5,3)G^4(3,5,4,2) \\
&= \int \mathrm{d}(3,4,5)\ v(1,3^+)\delta(3,4^+)\delta(5,1^+)G^4(3,5,4,2) \\
&= \lim_{t_5 \to t_1^-} \lim_{t_3 \to t_1^+} \lim_{t_4 \to t_3^+} \int \mathrm{d}\mathbf{x}_3\ v(1,3^+)G^4(\mathbf{x}_3 t_3, \mathbf{x}_1 t_5, \mathbf{x}_3 t_4, \mathbf{x}_2 t_2) \\
&= -(\mathrm{i}\hbar)^2 \int \mathrm{d}\mathbf{x}_3\ v(\mathbf{x}_1 - \mathbf{x}_3)\langle \mathcal{T}\hat{\psi}^\dagger(\mathbf{x}_3 t_1)\hat{\psi}(\mathbf{x}_3 t_1)\hat{\psi}(\mathbf{x}_1 t_1)\hat{\psi}^\dagger(\mathbf{x}_2 t_2)\rangle
\end{aligned}
$$

where it has been used that the left- and right- Dirac delta imply the limit to be taken such that $t_5 \le t_1 \le t_3 \le t_4$. We thus obtain precisely the expression which one gets from the equation of motion theory.

2. We now show that L obeys a Bethe-Salpeter-like equation. The starting point is the well-known Bethe Salpeter equation $\Gamma = I + IGG\Gamma$ for the scattering amplitude Γ which reads

$$
\Gamma(1,2,3,4) = I(1,2,3,4) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ I(1,5,3,6)G(6,7)G(8,5)\Gamma(7,2,8,4).
$$
(4.134)

The connection between the four-point propagator and the scattering amplitude is given by

$$
\begin{aligned}
G^4(1,2,3,4) =\ & G(1,3)G(2,4) - G(1,4)G(2,3) \\
& -\mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ G(1,5)G(2,6)\Gamma(5,6,7,8)G(7,3)G(8,4).
\end{aligned}
$$

or

$$
L(1,2,3,4) = -G(1,4)G(2,3)-\mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ G(1,5)G(2,6)\Gamma(5,6,7,8)G(7,3)G(8,4).
$$

Plugging in the Bethe-Salpeter equation for Γ, we get for $-L(1,2,3,4)$ the self-consistent

expression

$$
\begin{aligned}
=\quad & G(1,4)G(2,3) + i\hbar \int d(5,6,7,8)\ G(1,5)G(2,6)I(5,6,7,8)G(7,3)G(8,4) + \\
& (i\hbar)^2 \int d(5,6,7,8,9,10,11,12) \times \\
& G(1,5)G(2,6)I(5,9,7,10)G(10,11)G(12,9)\Gamma(11,6,12,8)G(7,3)G(8,4) \\
\overset{\substack{6\leftrightarrow9\\8\leftrightarrow10}}{=}\quad & G(1,4)G(2,3) + i\hbar \int d(5,6,7,8)\ G(1,5)G(2,6)I(5,6,7,8)G(7,3)G(8,4) + \\
& (i\hbar)^2 \int d(5,6,7,8,9,10,11,12) \times \\
& G(1,5)G(2,9)I(5,6,7,8)G(8,11)G(12,6)\Gamma(11,9,12,10)G(7,3)G(10,4) \\
=\quad & G(1,4)G(2,3) + i\hbar \int d(5,6,7,8)\ G(1,5)G(7,3)I(5,6,7,8) \times \\
& (G(2,6)G(8,4) + i\hbar \int d(9,10,11,12)\ G(2,9)G(12,6)\Gamma(11,9,12,10)G(8,11)G(10,4)) \\
=\quad & G(1,4)G(2,3) - i\hbar \int d(5,6,7,8)\ G(1,5)G(7,3)I(5,6,7,8)L(8,2,6,4)
\end{aligned}
$$

or

$$
L(1,2,3,4) = L_0(1,2,3,4) + i\hbar \int d(5,6,7,8)\ L_0(1,5,3,6)I(6,7,5,8)L(8,2,7,4)
\tag{4.135}
$$

with $L_0(1,2,3,4) = -G(1,4)G(2,3)$. The equation (4.135) coincides with equation (43) in the seminal paper of Kadanoff and Baym[8] derived by the method of functional derivatives.

Definition The irreducible counterparts $\tilde{L}$ and $\tilde{I}$ of L and I are defined via

$$
\begin{aligned}
I &= \tilde{I} + V \tag{4.136} \\
\tilde{L} &= L_0 + i\hbar L_0 \tilde{I}\tilde{L}. \tag{4.137}
\end{aligned}
$$

Lemma 4.1.12 *We have the formal identities*

$$
\begin{aligned}
L &= \tilde{L} + i\hbar \tilde{L} V L \tag{4.138} \\
LV &= \tilde{L} W. \tag{4.139}
\end{aligned}
$$

Proof

1. This follows from rewriting equation $L = L_0 + i\hbar L_0 I L$ as

$$
L_0^{-1} - L^{-1} = i\hbar I
\tag{4.140}
$$

and hence

$$L_0^{-1} - \tilde{L}^{-1} + \tilde{L}^{-1} - L^{-1} = i\hbar \tilde{I} + i\hbar V. \qquad (4.141)$$

In this argument, we implicitly assumed that L can be inverted. From the definition of L we read off that L can certainly be inverted if L_0 can because in that case $L_0^{-1} - i\hbar I$ is the inverse of L. $L_0(1,2,3,4) = -G(1,4)G(2,3)$ in turn can be inverted if G can be inverted. Thus, the invertibility of the full Green function is crucial. This, however, is a standard assumption in any approach. To the best of my knowledge it has never been proved.

2. By the help of the first identity, this follows from

$$\begin{aligned} \tilde{L}W &= \tilde{L}V + i\hbar\tilde{L}VLV \\ &= (\tilde{L} + i\hbar\tilde{L}VL)V \\ &= LV. \end{aligned}$$

Theorem 4.1.13 *The self-consistent equations are equivalent to the following "irreducible" set of equations:*

$$\begin{aligned} G &= G_0 - i\hbar G_0 W \cdot \tilde{L} &\qquad (4.142) \\ \tilde{L} &= \tilde{L}_0 + i\hbar\tilde{L}_0\tilde{I}\tilde{L} &\qquad (4.143) \\ W &= V + i\hbar V\tilde{L}W &\qquad (4.144) \end{aligned}$$

where $\tilde{L}_0 = L_0$.

Proof The second equation is a definition. We prove the first and the third equation.

1. We introduce the transpose of a four-point quantity by

$$A^{\mathrm{T}}(1,2,3,4) = A(2,1,4,3). \qquad (4.145)$$

A^{T} is the algebraic transpose in the sense of the four-point product

$$\int \mathrm{d}(5,6)\, A(1,5,3,6)B(6,2,5,4). \qquad (4.146)$$

With

$$\begin{aligned} L(1,2,3,4) &= L(2,1,4,3) \\ \tilde{L}(1,2,3,4) &= \tilde{L}(2,1,4,3) \end{aligned}$$

we concluce that

$$W^{\mathrm{T}} = V^{\mathrm{T}} + i\hbar V^{\mathrm{T}} L V^{\mathrm{T}} \tag{4.147}$$

and therefore

$$\tilde{L}W = LV \tag{4.148}$$

implies

$$\tilde{L}W^{\mathrm{T}} = LV^{\mathrm{T}}. \tag{4.149}$$

Now consider

$$\int d(3,4,5)\ V(1,4,5,3)L(3,5,4,2). \tag{4.150}$$

This can be written as

$$\int d5 \int d(3,4)\ V(1,4,5,3)L(3,5,4,2) = \int d5\ (VL)(1,5,5,2)$$
$$= \int d(5,6)\ \delta(5,6)(VL)(1,5,6,2).$$

Using $(VL)(1,2,3,4) = (LV^{\mathrm{T}})(2,1,4,3)$, we get

$$\int d(5,6)\ \delta(5,6)(VL)(1,5,6,2) = \int d(5,6)\ \delta(5,6)(LV^{\mathrm{T}})(5,1,2,6)$$
$$= \int d(5,6)\ \delta(5,6)(\tilde{L}W^{\mathrm{T}})(5,1,2,6)$$
$$= \int d(5,6)\ \delta(5,6) \int d(3,4)\ \tilde{L}(5,3,2,4)W^{\mathrm{T}}(4,1,3,6)$$
$$= \int d(5,6)\ \delta(5,6) \int d(3,4)\ \tilde{L}(3,5,4,2)W(1,4,6,3)$$
$$= \int d(5,6)\ \delta(5,6) \int d(3,4)\ W(1,4,6,3)\tilde{L}(3,5,4,2)$$
$$= \int d(5,6)\ \delta(5,6)(W\tilde{L})(1,5,6,2),$$

i.e. $V \cdot L = W \cdot \tilde{L}$.

2. Follows from

$$
\begin{aligned}
W &= V + i\hbar VLV \\
&= V + i\hbar V\tilde{L}V + (i\hbar)^2 V\tilde{L}VLV \\
&= V + i\hbar V\tilde{L}(V + i\hbar VLV) \\
&= V + i\hbar V\tilde{L}W.
\end{aligned}
$$

Green Functions and Density Functional Theory Consider the self-energy operator $\tilde{\Sigma}$ as a sum over graphs. By inspection, we see that $\tilde{\Sigma}$ can be written as a sum of an operator, which is local in both space and time, of an only temporally local operator and a non-local operator (simply if we classify the Feynman graphs according to the criterion whether they given rise to a local function or not):

$$
\begin{aligned}
\tilde{\Sigma}(\mathbf{x}t, \mathbf{x}'t') &= \tilde{\Sigma}_1(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')\delta(t - t') + \tilde{\Sigma}_2(\mathbf{x}, \mathbf{x}')\delta(t - t') + \tilde{\Sigma}_3(\mathbf{x}t, \mathbf{x}'t') \\
&= \tilde{\Sigma}_1(\mathbf{x})\delta(\mathbf{x} - \mathbf{x}')\delta(t - t') + \tilde{\Sigma}_{\mathrm{xc}}(\mathbf{x}, \mathbf{x}'; t - t').
\end{aligned}
$$

An analysis of the Feynman graphical expansion now shows that $\tilde{\Sigma}_1$ is the sum over all graphs which result from the first-order Hartree graph $-\int \mathrm{d}2\, v(1,2)\mathrm{i}\hbar G_0(2, 2^+)$ by inserting arbitrarily many interaction lines. This, however, has simply the effect of turning G_0 into the exact propagator G. On the other hand, for the exact propagator, the quantity $-\mathrm{i}\hbar G(2, 2^+)$ equals the exact ground-state density. In other words, the local self-energy contribution is the exact Hartree potential: $\tilde{\Sigma}_1(\mathbf{x}) = v_{\mathrm{H}}(\mathbf{x})$. Per constructionem, the exact ground-state density equals the density of the Kohn-Sham auxiliary system. It therefore seems reasonable to break the self-consistency condition involving G_0 and replace the self-consistent, non-interacting reference propagator with a fixed reference propagator which is the inverse of a Hartree Hamiltonian where the density stems from the Kohn-Sham equations. This fixed reference propagator then has the effect of implicitly summing the total local contribution to $\tilde{\Sigma}$.

Auxiliary Vertex Function We introduce the auxiliary quantities

$$
\Xi(1, 2, 3, 4) = \delta(1, 4)\delta(2, 3) + \mathrm{i}\hbar \int \mathrm{d}(5, 6)\ \Gamma(1, 5, 3, 6)G(6, 4)G(2, 5) \tag{4.151}
$$

$$
\tilde{\Xi}(1, 2, 3, 4) = \delta(1, 4)\delta(2, 3) + \mathrm{i}\hbar \int \mathrm{d}(5, 6)\ \tilde{\Gamma}(1, 5, 3, 6)G(6, 4)G(2, 5) \tag{4.152}
$$

where we define

$$
\tilde{\Gamma}(1, 2, 3, 4) = \tilde{I}(1, 2, 3, 4) + \int \mathrm{d}(5, 6, 7, 8)\ \tilde{I}(1, 5, 3, 6)G(6, 7)G(8, 5)\tilde{\Gamma}(7, 2, 8, 4). \tag{4.153}
$$

In particular in the space-time domain we can write

$$
\Lambda(1, 2; 3) = \tilde{\Lambda}_0(1, 2; 3) + \mathrm{i}\hbar \int \mathrm{d}(4, 5)\ \Gamma(1, 5, 2, 6)G(6, 3)G(3, 5)
$$

$$
\tilde{\Lambda}(1, 2; 3) = \tilde{\Lambda}_0(1, 2; 3) + \mathrm{i}\hbar \int \mathrm{d}(4, 5)\ \tilde{\Gamma}(1, 5, 2, 6)G(6, 3)G(3, 5)
$$

such that

$$
\Lambda(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2; \mathbf{x}_3 t_3) = \Xi(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_3, \mathbf{x}_2 t_2) \tag{4.154}
$$

$$
\tilde{\Lambda}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2; \mathbf{x}_3 t_3) = \tilde{\Xi}(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2, \mathbf{x}_3 t_3, \mathbf{x}_2 t_2). \tag{4.155}
$$

The four-point quantity Ξ will be called *auxiliray vertex function*. Λ is called *vertex corrections*. The auxiliary vertex function also obeys a Bethe-Salpeter like equation. Plugging the Bethe-Salpeter equation into the defining equation for the intermediate vertex function, we get

$$
\begin{aligned}
\tilde{\Xi}(1,2,3,4) &= \delta(1,4)\delta(2,3) + i\hbar \int d(5,6)\ \tilde{\Gamma}(1,5,3,6)G(6,4)G(2,5) \\
&= \delta(1,4)\delta(2,3) + i\hbar \int d(5,6)\ \tilde{I}(1,5,3,6)G(6,4)G(2,5) \\
&\quad + (i\hbar)^2 \int d(5,6,7,8,9,10)\ \tilde{I}(1,7,3,8)G(8,9)G(10,7)\tilde{\Gamma}(9,5,10,6)G(6,4)G(2,5) \\
&\overset{\substack{5\leftrightarrow 7 \\ 6\Leftrightarrow 8}}{=} \delta(1,4)\delta(2,3) + i\hbar \int d(5,6)\ \tilde{I}(1,5,3,6)G(6,4)G(2,5) \\
&\quad + (i\hbar)^2 \int d(5,6,7,8,9,10)\ \tilde{I}(1,5,3,6)G(6,9)G(10,5)\tilde{\Gamma}(9,7,10,8)G(8,4)G(2,7) \\
&= \delta(1,4)\delta(2,3) + i\hbar \int d(5,6,9,10)\ \tilde{I}(1,5,3,6)G(6,9)G(10,5) \times \\
&\quad (\delta(9,4)\delta(2,10) + i\hbar \int d(7,8)\ \tilde{\Gamma}(9,7,10,8)G(8,4)G(2,7)) \\
&= \delta(1,4)\delta(2,3) + i\hbar \int d(5,6,9,10)\ \tilde{I}(1,5,3,6)G(6,9)G(10,5)\tilde{\Xi}(9,2,10,4)
\end{aligned}
$$

i.e.

$$
\tilde{\Xi}(1,2,3,4) = \delta(1,4)\delta(2,3) + i\hbar \int d(5,6,7,8)\ \tilde{I}(1,5,3,6)G(6,7)G(8,5)\tilde{\Xi}(7,2,8,4). \quad (4.156)
$$

Similarly, one shows

$$
\Xi(1,2,3,4) = \delta(1,4)\delta(2,3) + i\hbar \int d(5,6,7,8)\ I(1,5,3,6)G(6,7)G(8,5)\Xi(7,2,8,4). \quad (4.157)
$$

Equating $2 = 4$ and relabeling $4 \mapsto 3$ yields equations

$$
\tilde{\Lambda}(1,2;3) = \delta(1,2)\delta(2,3) + i\hbar \int d(5,6,7,8)\ \tilde{I}(1,5,2,6)G(6,7)G(8,5)\tilde{\Lambda}(7,8;3). \quad (4.158)
$$

which is also sometimes called Bethe-Salpeter equation. Equivalently, one has

$$
\Lambda(1,2;3) = \delta(1,2)\delta(2,3) + i\hbar \int d(5,6,7,8)\ I(1,5,2,6)G(6,7)G(8,5)\Lambda(7,8;3). \quad (4.159)
$$

In the electronic structure community, this last equation is usually referred to as the Bethe-Salpeter equation. This shows that there are a number of different but equivalent Bethe-Salpeter equations which we summarize in the following table.

Quantity	BSE	Comment
Scattering Amplitude	$\Gamma = I + IGG\Gamma$	original BSE; equation (4.134)
irr Scattering Amplitude	$\tilde{\Gamma} = \tilde{I} + \tilde{I}GG\tilde{\Gamma}$	irr part of BSE; equation (4.153)
intermediate Vertex Fct	$\Xi = 1 + IGG\Xi$	equation (4.157)
irr intermediate Vertex Fct	$\tilde{\Xi} = 1 + \tilde{I}GG\tilde{\Xi}$	equation (4.156)
conn Four-Point Prop	$L = L_0 + L_0 IL$	equation (4.135)
irr conn Four-Point Prop	$\tilde{L} = L_0 + L_0 \tilde{I}\tilde{L}$	equation (4.136)
Vertex Corrections	$\Lambda = 1 + IGG\Lambda$	only in real-space; equation (4.159)
irr Vertex Corrections	$\tilde{\Lambda} = 1 + \tilde{I}GG\tilde{\Lambda}$	only in real-space; equation (4.158)

Table 4.1.: Bethe-Salpeter Equations

Derivation of Hedin's Equations We now derive from the self-consistent set of equations a set of equations called *Hedin's equations*, which were first derived by Lars Hedin (cf. [41, 42]) and which are the common starting point of Electronic Structure Theory. We start from

$$\tilde{L}(1,2,3,4) = L_0(1,2,3,4) + i\hbar \int d(5,6,7,8)\, L_0(1,5,3,6)\tilde{I}(6,7,5,8)\tilde{L}(8,2,7,4)$$

$$\tilde{\Xi}(1,2,3,4) = \delta(1,4)\delta(2,3) + i\hbar \int d(5,6,7,8)\, \tilde{I}(1,5,3,6)G(6,7)G(8,5)\tilde{\Xi}(7,2,8,4).$$

The last equation is the fifth Hedin equation. We read off that the connection between $\tilde{L}$ and $\tilde{\Xi}$ is given by

$$\tilde{L}(1,2,3,4) = \int d(5,6)\, L_0(1,5,3,6)\tilde{\Xi}(6,2,5,4)$$

$$= -\int d(5,6)\, G(1,6)G(5,3)\tilde{\Xi}(6,2,5,4).$$

This is the second Hedin equation. The third Hedin equation is $W = V + i\hbar V\tilde{L}W$. We now have to bring the self-energy into play. We use

$$(W \cdot \tilde{L})(1,2) = \int d(3,4,5)\, W(1,4,5,3)\tilde{L}(3,5,4,2) \qquad (4.160)$$

and

$$\tilde{L}(1,2,3,4) = -G(1,4)G(2,3) - i\hbar \int d(5,6,7,8)\, G(1,5)G(2,6)\tilde{\Gamma}(5,6,7,8)G(7,3)G(8,4).$$

Therefore,

$$
\begin{aligned}
(W \cdot \tilde{L})(1,2) &= \int \mathrm{d}(3,4,5) \, W(1,4,5,3)\tilde{L}(3,5,4,2) \\
&= -\int \mathrm{d}(3,4,5) \, W(1,4,5,3)(G(3,2)G(5,4) \\
&\quad +\mathrm{i}\hbar \int \mathrm{d}(9,6,7,8) \, G(3,9)G(5,6)\tilde{\Gamma}(9,6,7,8)G(7,4)G(8,2)) \\
&= -\int \mathrm{d}(3,8,4,5) \, W(1,4,5,3)(\delta(3,8)G(8,2)G(5,4) \\
&\quad +\mathrm{i}\hbar \int \mathrm{d}(9,6,7) \, G(3,9)G(5,6)\tilde{\Gamma}(9,6,7,8)G(7,4)G(8,2)).
\end{aligned}
$$

Introducing now the exchange correlation self-energy $\tilde{\Sigma}_{\mathrm{xc}}$ by

$$
\begin{aligned}
(\mathrm{i}\hbar)^{-1}\tilde{\Sigma}_{\mathrm{xc}}(1,8) &\overset{\text{def}}{=} \int \mathrm{d}(3,4,5) \, W(1,4,5,3)(G(5,4)\delta(3,8) \\
&\quad +\mathrm{i}\hbar \int \mathrm{d}(9,6,7) \, G(3,9)G(5,6)\tilde{\Gamma}(9,6,7,8)G(7,4)) \\
&= \int \mathrm{d}(3,4,5) \, W(1,4,5,3) \times \\
&\quad (G(5,4)\delta(3,8) + \mathrm{i}\hbar \int \mathrm{d}6 \, G(5,6) \int \mathrm{d}(9,7) \, \tilde{\Gamma}(6,9,8,7)G(3,9)G(7,4)) \\
&= \int \mathrm{d}(5,6) \, G(5,6) \int \mathrm{d}(3,4) \, W(1,4,5,3) \times \\
&\quad (\delta(6,4)\delta(3,8) + \mathrm{i}\hbar \int \mathrm{d}(9,7) \, \tilde{\Gamma}(6,9,8,7)G(3,9)G(7,4))) \\
&= \int \mathrm{d}(5,6) \, G(5,6) \int \mathrm{d}(3,4) \, W(1,4,5,3)\tilde{\tilde{\Xi}}(6,3,8,4) \\
&= \int \mathrm{d}(3,4,5,6) \, G(5,6)W(1,4,5,3)\tilde{\tilde{\Xi}}(6,3,8,4).
\end{aligned}
$$

we get

$$
-(W \cdot \tilde{L})(1,2) = (\mathrm{i}\hbar)^{-1} \int \mathrm{d}3 \, \tilde{\Sigma}_{\mathrm{xc}}(1,3)G(3,2). \tag{4.161}
$$

Hedin's equations now read

$$
\begin{aligned}
G(1,2) &= G_0(1,2) + \int \mathrm{d}(3,4)\ G_0(1,3)\tilde{\Sigma}_{\mathrm{xc}}(3,4)G(4,2) \\
\tilde{\Sigma}_{\mathrm{xc}}(1,2) &= \mathrm{i}\hbar \int \mathrm{d}(3,4,5,6)\ G(5,6)W(1,4,5,3)\tilde{\tilde{\Xi}}(3,6,4,2) \\
\tilde{L}(1,2,3,4) &= -\int \mathrm{d}(5,6)\ G(1,6)G(5,3)\tilde{\tilde{\Xi}}(6,2,5,4) \\
W(1,2,3,4) &= V(1,2,3,4) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ V(1,7,3,5)\tilde{L}(5,6,7,8)W(8,2,6,4) \\
\tilde{\tilde{\Xi}}(1,2,3,4) &= \delta(1,4)\delta(2,3) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ \tilde{I}(1,5,3,6)G(6,7)G(8,5)\tilde{\tilde{\Xi}}(7,2,8,4).
\end{aligned}
$$

Usually, Hedin's equations are not written down in this form. Instead, the above set of equations is the "unitarily covariant form" of Hedin's equations. Here, the term "unitarily covariant" means that the equations are form-invariant under unitary transformations in the one-particle Hilbert space. This can be seen by reinterpreting the space-time indices $1 = (\mathbf{x}_1, t_1)$ as referring to orbitals and frequencies and noting that the unitarily covariant Hedin equations are defined in terms of operator products.

Standard Form of Hedin's Equations results from the above set by reinstalling all deltas in V and W and introducing $\tilde{P}(1,2) = \mathrm{i}\hbar\tilde{L}(1,2,1^+,2^+)$, $\tilde{\Lambda}(1,2;3) = \tilde{\tilde{\Xi}}(1,3,2,3)$. Indeed from

$$
W(1,7,8,2) = V(1,7,8,2) + \mathrm{i}\hbar \int \mathrm{d}(3,4,5,6)\ V(1,5,8,3)L(3,4,5,6)V(6,7,4,2)
$$

we find

$$
w(1,2) = v(1,2) + \int \mathrm{d}(3,4)\ v(1,3)P(3,4)v(4,2)
$$

where the right time order is automatically produced through the redefinition of the Coulomb potential and $W(1,2,3,4) = w(1,4)\delta(4,2)\delta(3,1)$. Hedin's equations then ultimately boil down to

$$
\begin{aligned}
G(1,2) &= G_0(1,2) + \int \mathrm{d}(3,4)\ G_0(1,3)\tilde{\Sigma}_{\mathrm{xc}}(3,4)G(4,2) \\
\tilde{\Sigma}_{\mathrm{xc}}(1,2) &= \mathrm{i}\hbar \int \mathrm{d}(3,4)\ G(1,4)W(1,3)\tilde{\Lambda}(4,2;3) \\
\tilde{P}(1,2) &= -\mathrm{i}\hbar \int \mathrm{d}(5,6)\ G(1,6)G(5,1^+)\tilde{\Lambda}(6,5;2) \\
w(1,2) &= v(1,2) + \int \mathrm{d}(3,4)\ v(1,3)\tilde{P}(3,4)v(4,2) \\
\tilde{\Lambda}(1,3;2) &= \delta(1,2)\delta(2,3) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ \tilde{I}(1,5,3,6)G(6,7)G(8,5)\tilde{\Lambda}(7,8;2).
\end{aligned}
$$

In their standard form, Hedin's equations are the direct condensed matter analog[10] of the Schwinger-Dyson equations (cf. e.g. [47] p.475f) in high-energy physics. The unitary covariance is broken by equal-point limits and point-wise products.

Convential Derivation of Hedin's Equations Originally, Hedin's equations have been found through arguments using functional derivatives. For the convenience of the reader we briefly review these arguments without going into details. We follow closely [14, 41, 42]. One starts with a Gell-Mann and Low perturbative expression for the two-point propagator where the perturbation is given by the auxiliary, second-quantized "potential".

$$\hat{U}(t) = \int d\mathbf{x}_1 \mathbf{x}_2 \, u(\mathbf{x}_1 t_1, \mathbf{x}_2 t_2) \hat{\psi}^\dagger(\mathbf{x}_2) \hat{\psi}(\mathbf{x}_1). \tag{4.162}$$

The aim of this construction is to calculate functional derivatives with respect to this potential and then to set $U := 0$. In particular, with the Gell-Mann and Low formula one shows

$$\frac{\delta G(1,2)}{\delta u(3,4)} = -G^4(1,4,2,3) + G(1,2)G(4,3). \tag{4.163}$$

As this formula expresses the four-point propagator in terms of a functional derivative of the two-point-propagator, this can now be plugged into the equation of motion for G and the insertion of an identity in the form $\mathbb{1} = G^{-1}G$ then shows that

$$\tilde{\Sigma}_{\mathrm{xc}}(1,2) = i\hbar \int d(3,4,5) \, v(1^+,3) \frac{\delta G(1,4)}{\delta u(3)} G^{-1}(4,2) \tag{4.164}$$

or

$$\tilde{\Sigma}_{\mathrm{xc}}(1,2) = -i\hbar \int d(3,4,5) \, v(1^+,3) G(1,4) \frac{\delta G^{-1}(4,2)}{\delta u(3)} \tag{4.165}$$

where $u(3,4) := u(3)\delta(3,4)$. The second equation for Σ follows from the first be taking the funtional derivative with respect to u of the equation $\mathbb{1} = G^{-1}G$ using the Leibniz rule. (Note that here, as always, one has to assume that G is an invertible integral operator.) Now, recall classical electrodynamics where we defined

$$\varphi_{\mathrm{tot}} = \varphi_{\mathrm{ext}} + \varphi_{\mathrm{int}}.$$

---

[10]The Green function G, the vertex function $\tilde{\Lambda}$ and the self-energy $\tilde{\Sigma}$ have a direct high-energy counterpart. The high-energy counterpart of the so-called screened potential W is the exact photon propagator and the analog of the polarizability is the photon self-energy. Hedin's equations can then be identified with equations (19.2, 19.5, 19.9, 19.10, 19.12) in the standard reference [12] on relativistic quantum Field Theory. See also `http://de.wikipedia.org/wiki/Dyson-Schwinger-Gleichungen` (June 25, 2012). The equations given there correspond to the first, third and fifth Hedin equation in Fourier space.

In the context of quantum many-body theory, we interpret the induced potential as the Hartree type potential in the external field u. Therefore, one introduces

$$v(1) = u(1) - \mathrm{i}\hbar \int \mathrm{d}2 \; v(1,2)G(2,2^+). \tag{4.166}$$

One now replaces derivatives $\frac{\delta}{\delta u}$ by the chain rule with derivatives $\frac{\delta}{\delta v}$ and gets

$$\tilde{\Sigma}_{\mathrm{xc}}(1,2) = -\mathrm{i}\hbar \int \mathrm{d}(3,4,5) \; v(1^+,3)\frac{\delta G^{-1}(1,4)}{\delta v(5)}\frac{\delta v(5)}{\delta u(3)}G(4,2). \tag{4.167}$$

In accordance with classical electrodynamics, one defines

$$\varepsilon^{-1}(1,2) = \frac{\delta v(1)}{\delta u(2)}. \tag{4.168}$$

Furthermore, we set

$$
\begin{aligned}
w(1,2) &= \int \mathrm{d}3 \; v(1,3)\varepsilon^{-1}(3,2) \\
\tilde{\Lambda}(1,2;3) &= -\frac{\delta G^{-1}(1,2)}{\delta v(3)}
\end{aligned}
$$

and hence

$$\tilde{\Sigma}_{\mathrm{xc}}(1,2) = \mathrm{i}\hbar \int \mathrm{d}(3,4) \; G(1,4)w(3,1^+)\tilde{\Lambda}(4,2;3). \tag{4.169}$$

In order to get an equation for the irreducible vertex function, one uses $G^{-1} = G_0^{-1} - v - \tilde{\Sigma}_{\mathrm{xc}}$ calculates

$$
\begin{aligned}
\tilde{\Lambda}(1,2;3) &= \delta(1,2)\delta(1,3) + \frac{\delta\tilde{\Sigma}_{\mathrm{xc}}(1,2)}{\delta v(3)} \\
&= \delta(1,2)\delta(1,3) + \int \mathrm{d}(4,5) \; \frac{\delta\tilde{\Sigma}_{\mathrm{xc}}(1,2)}{\delta G(4,5)}\frac{\delta G(4,5)}{\delta v(3)} \\
&= \delta(1,2)\delta(1,3) + \int \mathrm{d}(4,5,6,7) \; \frac{\delta\tilde{\Sigma}_{\mathrm{xc}}(1,2)}{\delta G(4,5)}G(4,6)G(7,5)\tilde{\Lambda}(6,7;3)
\end{aligned}
$$

where in the last line we inserted $G^{-1}G$, used again the trick $G\delta_v G^{-1} + \delta_v G G^{-1} = 0$ and inserted the definition of $\tilde{\Lambda}$. Finally, by the definition of ε and v we find

$$\varepsilon^{-1}(1,2) = \delta(1,2) + \int \mathrm{d}3 \; v(1,3)P(3,2) \tag{4.170}$$

where

$$P(1,2) = -\mathrm{i}\hbar\frac{\delta G(1,1^+)}{\delta u(2)}. \tag{4.171}$$

As $-\mathrm{i}\hbar G(1, 1^+) = n(1)$ this is in accordance with the classical relation $\chi = \delta\rho_{\text{int}}/\delta\varphi_{\text{ext}}$. In analogy to the classical relation $\tilde{\chi} = \delta\rho_{\text{ind}}/\delta\varphi_{\text{tot}}$ we define

$$\tilde{P}(1, 2) = -\mathrm{i}\hbar\frac{\delta G(1, 1^+)}{\delta v(2)} \tag{4.172}$$

and by an application of the chain rule we retrieve

$$P(1, 2) = \tilde{P}(1, 2) + \int \mathrm{d}(3, 4)\ \tilde{P}(1, 3)v(3, 4)P(4, 2) \tag{4.173}$$

precisely as in classical electrodynamics. By again inserting $G^{-1}G$ into the defining equation for $\tilde{P}$ and switching the derivative from G to G^{-1} we finally find

$$\tilde{P}(1, 2) = -\mathrm{i}\hbar \int \mathrm{d}(3, 4)\ G(1, 3)G(4, 1)\tilde{\Lambda}(3, 4; 2). \tag{4.174}$$

This concludes the conventional derivation of Hedin's equations.

Remarks A comparison with the derivation of the minimal set from the self-consistent equations shows in particular that

$$\mathrm{i}\hbar\tilde{I}(1, 2, 3, 4) = \frac{\delta\tilde{\Sigma}_{\text{xc}}(1, 3)}{\delta G(2, 4)} \tag{4.175}$$

$$\mathrm{i}\hbar I(1, 2, 3, 4) = \frac{\delta\tilde{\Sigma}(1, 3)}{\delta G(2, 4)}. \tag{4.176}$$

with $\tilde{\Sigma} = \tilde{\Sigma}_{\text{loc}} + \tilde{\Sigma}_{\text{xc}} = v_{\text{H}} + \tilde{\Sigma}_{\text{xc}}$. Finally, we also conclude that the so-called screened potential W does not describe an "effective" (i.e. screened) interaction between the electrons. Such a picture would be wrong on various grounds: (i) the electrons cannot screen their own interaction because screening means to take out certain degrees of freedom and to compensate for this by an effective interaction, (ii) the time-ordered response function is not the physical response function, (iii) a Schrödinger equation where the screened potential enters instead of the Coulomb potential would lead to wrong results, (vi) the role of W is to subsum a certain class of diagrams. It is, however, possible to interpret W as the screened Coulomb interaction of the nuclei as will be explained later.

Reducible Version of Hedin's Equations? It is tempting to write down a reducible counterpart of Hedin's equations as

$$G(1,2) \;=\; G_0(1,2) + \int \mathrm{d}(3,4)\; G_0(1,3)\Sigma_{\mathrm{xc}}(3,4)G_0(4,2)$$

$$\Sigma_{\mathrm{xc}}(1,2) \;=\; \mathrm{i}\hbar \int \mathrm{d}(3,4,5,6)\; G(5,6)W(1,4,5,3)\Xi(3,6,4,2)$$

$$L(1,2,3,4) \;=\; -\int \mathrm{d}(5,6)\; G(1,6)G(5,3)\Xi(6,2,5,4)$$

$$W(1,2,3,4) \;=\; V(1,2,3,4) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\; V(1,7,3,5)L(5,6,7,8)W(8,2,6,4)$$

$$\Xi(1,2,3,4) \;=\; \delta(1,4)\delta(2,3) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\; I(1,5,3,6)G(6,7)G(8,5)\Xi(7,2,8,4).$$

This, however, is wrong on various grounds: (i) in the derivation of Σ_{xc} from VL one cannot factor out G_0 instead of G, (ii) the connection between Σ_{xc} and $\tilde{\Sigma}_{\mathrm{xc}}$ is given by $\Sigma_{\mathrm{xc}} = \tilde{\Sigma}_{\mathrm{xc}} + \tilde{\Sigma}_{\mathrm{xc}}G_0\Sigma_{\mathrm{xc}}$ which is inconsistent with the connection between Ξ and $\tilde{\Xi}$. This is also the reason why Hedin's equations only come in as an irreducible set of equations. In other words, as opposed to the self-consistent set, Hedin's equations exist only for the irreducible quantities.

4.2. Standard Approximations to the Self-Consistent Equations

4.2.1. Definition of Standard Approximations

Introduction One of the most intriguing features of the self-consistent sets of equations

$$G = G_0 - i\hbar G_0 V \cdot L \qquad \text{or} \quad G = G_0 - i\hbar G_0 W \cdot \tilde{L} \qquad (4.177)$$

$$L = L_0 + i\hbar L_0 I L \qquad \text{or} \quad \tilde{L} = \tilde{L}_0 + i\hbar \tilde{L}_0 \tilde{I} \tilde{L} \qquad (4.178)$$

$$W = V + i\hbar V I V \qquad \text{or} \quad W = V + i\hbar V \tilde{I} W \qquad (4.179)$$

is that all standard approximations naturally fit into a hierarchy of approximations for the four-point propagator or – equivalently – for L. In this hierarchy, the accuracy grows along two different directions: inclusions of further graphs and self-consistency. Self-consistency means that the approximative expression for L or $\tilde{L}$ is given in terms of the full propagator G whereas in the corresponding non-self-consistent approximation the same expression is given in terms of G_0. Therefore, every approximation comes in two different guises: in a self-consistent in a non-self-consistent version. The self-consistent version of first-order perturbation theory (in terms of the Hartree propagator) is the Hartree-Fock approximation, the self-consistent version of the Random Phase approximation (RPA)[11] is the GW-approximation and the self-consistent version of the ladder approximation is the W-approximation. Concretely, we have the following definitions:[12]

---

[11]Both of these approximations have it that the four-point propagator factorizes. This is analogous to the factorization of the two-particle correlation function in the classical theory of kinetics. Therefore, the RPA is a quantum version of Boltzmann's famous *Stoßzahlenansatz*. [45]

[12]where GG means $G(1,4)G(2,3)$ and $\bar{W}(1,2,3,4) = W(2,1,3,4)$.

Approximation	L	$\tilde{L}$	L_0	I	$\tilde{I}$
Hartree	0	0	0	0	0
1st order PT	$\tilde{L}$	L_0	$-G_0 G_0$	0	0
Hartree-Fock	$\tilde{L}$	L_0	$-GG$	0	0
RP Approximation	$L = \tilde{L} + \mathrm{i}\hbar \tilde{L} V L$	L_0	$-G_0 G_0$	V	0
GW Approximation	$L = \tilde{L} + \mathrm{i}\hbar \tilde{L} V L$	L_0	$-GG$	V	0
Ladder Approximation	$L = \tilde{L} + \mathrm{i}\hbar \tilde{L} V L$	$\tilde{L} = \tilde{L}_0 + \mathrm{i}\hbar \tilde{L}_0 \tilde{I} \tilde{L}$	$-G_0 G_0$	$V + \tilde{I}$	$-\bar{V}$
W Approximation	$L = \tilde{L} + \mathrm{i}\hbar \tilde{L} V L$	$\tilde{L} = \tilde{L}_0 + \mathrm{i}\hbar \tilde{L}_0 \tilde{I} \tilde{L}$	$-GG$	$V + \tilde{I}$	$-\bar{W}$
Beyond	$L = \tilde{L} + \mathrm{i}\hbar \tilde{L} V L$	$\tilde{L} = \tilde{L}_0 + \mathrm{i}\hbar \tilde{L}_0 \tilde{I} \tilde{L}$	$-GG$	$V + \tilde{I}$	$\tilde{I}[G, V, W]$

Table 4.2.: Selfconsistent Set and Standard Approximations

Finally, note that the Green function perturbation theory carries over to the temperature $T > 0$ case in the sense that the Feynman rules still hold with the proviso that the non-interacting reference Green functions are to be replaced with their temperature counterparts. ([35], appendix A.3.4) Furthermore, the equation of motion theory also carries over to $T > 0$ directly because it is based on operator identities and otherwise makes only use of the fact the Green function is a linear functional of the field operators. Therefore, the self-consistent set of equations also holds for temperature Green functions and the above approximation scheme generalizes immediately to $T > 0$. As this thesis is about Electronic Structure Theory, we do not investigate this case.

4.2.2. Hartree-Fock Approximation

Self-Energy in the Hartree-Fock Approximation To calculate the self-energy, we start from

$$-(W \cdot \tilde{L})(1, 2) \equiv -(V \cdot L)(1, 2) = (\mathrm{i}\hbar)^{-1} \int \mathrm{d}3 \, \tilde{\Sigma}_{\mathrm{xc}}(1, 3) G(3, 2). \qquad (4.180)$$

Concretely, for the Hartree-Fock approximation we find

$$
\begin{aligned}
(V \cdot L)(1, 2) &= \int \mathrm{d}(3, 4, 5) \, V(1, 4, 5, 3) L(3, 5, 4, 2) \\
&= -\int \mathrm{d}(3, 4, 5) \, V(1, 4, 5, 3) G(3, 2) G(5, 4) \\
&= -\int \mathrm{d}(3, 4, 5) \, v(1, 3^+) \delta(1, 5) \delta(4, 3) G(3, 2) G(5, 4) \\
&= -\int \mathrm{d}3 \, v(1, 3^+) G(1, 3) G(3, 2)
\end{aligned}
$$

and hence

$$\tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(1,2) = \mathrm{i}\hbar v(1,2^+)G(1,2). \tag{4.181}$$

Finally, we calculate the corresponding expression in the frequency domain. Introducing the time-difference variable $\tau = t_1 - t_2$ we have

$$\tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2;\tau) = v(\mathbf{x}_1,\mathbf{x}_2)\delta^-(\tau)\mathrm{i}\hbar G(\mathbf{x}_1,\mathbf{x}_2;\tau) \tag{4.182}$$

and hence

$$\tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2;\omega) = v(\mathbf{x}_1,\mathbf{x}_2)\int \frac{\mathrm{d}\omega'}{2\pi}\,(\mathcal{F}\delta^-)(\omega')\mathrm{i}\hbar G(\mathbf{x}_1,\mathbf{x}_2;\omega - \omega'). \tag{4.183}$$

In order to calculate the Fourier transform of $\delta^\pm$, we apply it to a test-function and find (cf. [69], p.70)

$$
\begin{aligned}
(\mathcal{F}^{-1}\delta^\pm)[\tilde{f}] &\overset{\mathrm{def}}{=} \delta^\pm[\mathcal{F}^{-1}\tilde{f}] \\
&= \delta^\pm\left(\int \frac{\mathrm{d}\omega}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega t}\tilde{f}(\omega)\right) \\
&= \lim_{t\to 0^\pm}\int \frac{\mathrm{d}\omega}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega t}\tilde{f}(\omega) \\
&\overset{!}{=} \int \frac{\mathrm{d}\omega}{2\pi}\,(\mathcal{F}\delta^\pm)(-\omega)\tilde{f}(\omega).
\end{aligned}
$$

From this, we read off that

$$(\mathcal{F}\delta^\pm)(\omega) = \lim_{t\to 0^\pm}\mathrm{e}^{\mathrm{i}\omega t} =: \mathrm{e}^{\pm\mathrm{i}\omega\delta} \tag{4.184}$$

where δ is a positive infinitesimal in the distributional sense (i.e. integrate first and then perform the limit $\delta \to 0$). This implies for the frequency domain

$$
\begin{aligned}
\tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2;\omega) &= v(\mathbf{x}_1,\mathbf{x}_2)\int \frac{\mathrm{d}\omega'}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega'\delta}\,\mathrm{i}\hbar G(\mathbf{x}_1,\mathbf{x}_2;\omega - \omega') & (4.185)\\
&= v(\mathbf{x}_1,\mathbf{x}_2)\int \frac{\mathrm{d}\omega'}{2\pi}\,\mathrm{e}^{-\mathrm{i}(\omega-\omega')\delta}\,\mathrm{i}\hbar G(\mathbf{x}_1,\mathbf{x}_2;\omega') & (4.186)\\
&= v(\mathbf{x}_1,\mathbf{x}_2)\int \frac{\mathrm{d}\omega'}{2\pi}\,\mathrm{e}^{\mathrm{i}\omega'\delta}\,\mathrm{i}\hbar G(\mathbf{x}_1,\mathbf{x}_2;\omega') & (4.187)
\end{aligned}
$$

i.e. $\tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2;\omega) := \tilde{\Sigma}_{\mathrm{xc}}^{\mathrm{HF}}(\mathbf{x}_1,\mathbf{x}_2)$ is effectively independent of ω (through a shift in the integration variable – the resulting prefactor $\mathrm{e}^{\mathrm{i}\omega\delta}$ does not feel the integration and becomes unity after performing the limit $\delta \to 0$). In order to perform the frequency integral, we use the residue theorem (the applicability of which is guaranteed by the convergence factor $\mathrm{e}^{\mathrm{i}\omega'\delta}$ stemming from the Fourier transform of the instantaneous Coulomb potential) and close the

contour in the upper half-plane. This leads to the inclusion of the poles corresponding to the occupied states. For these, the Green function reverts to the reduced density matrix and therefore

$$\tilde{\Sigma}^{\mathrm{HF}}_{\mathrm{xc}}(\mathbf{x}_1, \mathbf{x}_2) = -v(\mathbf{x}_1, \mathbf{x}_2) n_2(\mathbf{x}_2, \mathbf{x}_1). \tag{4.188}$$

The prefactor -1 comes in as follows: $\hbar$ is absorbed in the integration measure $\mathrm{d}\hbar\omega$ (G has poles at $e_s = \hbar\omega_s$) and the contour integral contributes $2\pi\mathrm{i}$ times the residues. We conclude that the Hartree-Fock approximation can also be interpreted as an approximation for the hierarchy of reduced density matrices such that

$$n_2(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4) = n_1(\mathbf{x}_1, \mathbf{x}_3) n_1(\mathbf{x}_2, \mathbf{x}_4) - n_1(\mathbf{x}_1, \mathbf{x}_4) n_1(\mathbf{x}_2, \mathbf{x}_3). \tag{4.189}$$

Hartree-Fock and Green Functions We have already shown that the quasiparticle equation for the Lehmann amplitudes corresponding to the Hartree-Fock approximation for $\tilde{\Sigma}_{\mathrm{xc}}$ coincides with the Hartree-Fock equations. This induces a reinterpretation of the Hartree-Fock approximation. In the conventional approach (which we shortly review below), the Hartree-Fock approximation is a ground-state method. There, the Hartree-Fock eigenvectors and eigenvalues do not have a natural interpretation. Their role consists exclusively in the production of an approximate ground-state energy through their Slater determinant. Within the Green function approach, we see that the Hartree-Fock orbitals and eigenvalues are to be interpreted as quasiparticle wave-functions (Lehmann amplitudes) and quasiparticle energies. The corresponding Hartree-Fock propagator implies a self-consistent summation of first-order graphs.

Hartree-Fock Approximation as a Variational Method Variational methods are based on the well-known *Rayleigh-Ritz principle* which we formulate as

Theorem 4.2.1 *The functional* $E : \mathcal{H} \to \mathbb{R}$ *given by*

$$\Psi \mapsto E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{4.190}$$

with the self-adjoint operator $\hat{H}$ *is stationary at* $\Phi = \Psi$ *if and only if* Ψ *is an eigenvector of* $\hat{H}$. *The corresponding eigenvalue of* $\hat{H}$ *is given by* $E[\Psi]$. *Moreover,* $E[\Psi]$ *takes its absolute minimum at the ground-state* Ψ_0 *of* $\hat{H}$.

The Rayleigh-Ritz principle motivates the idea of approximating the ground-state by minimizing the Rayleigh-Ritz functional for a certain class of wave-functions. Within the Hartree-Fock Method, Ψ is supposed to be an antisymmetrized product of one-particle wavefunctions, i.e. a Slater determinant $\Psi = \varphi_1 \wedge \ldots \wedge \varphi_N$ and the orbitals φ_i are chosen such

that the corresponding Slater determinant minimizes the Rayleigh-Ritz functional in the set of Slater determinants. The stationarity of the energy expectation value against first-order variations (under the boundary condition of fixed norm) translates into a non-linear eigenvalue equation for the Hartree-Fock orbitals with the resulting one-particle, auxiliary Hamiltonian being given by

$$\hat{H}_{\mathrm{HF}} = -\frac{\hbar^2}{2m}\Delta + \hat{V}_{\mathrm{ext}} + \hat{V}_{\mathrm{H}} - \hat{V}_{\mathrm{F}} \tag{4.191}$$

where

$$\hat{V}_{\mathrm{H}} = \int \mathrm{d}\mathbf{x}\, v_{\mathrm{H}}(\mathbf{x})\hat{\psi}^{\dagger}(\mathbf{x})\hat{\psi}(\mathbf{x}) \tag{4.192}$$

$$\hat{V}_{\mathrm{F}} = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \hat{\psi}^{\dagger}(\mathbf{x}')v_{\mathrm{F}}(\mathbf{x}',\mathbf{x})\hat{\psi}(\mathbf{x}) \tag{4.193}$$

with

$$v_{\mathrm{H}}(\mathbf{x}) = \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{N}\int \mathrm{d}\mathbf{x}'\, \frac{\varphi_i^*(\mathbf{x}')\varphi_i(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \tag{4.194}$$

$$v_{\mathrm{F}}(\mathbf{x},\mathbf{x}') = \frac{e^2}{4\pi\varepsilon_0}\sum_{i=1}^{N}\frac{\varphi_i(\mathbf{x})\varphi_i^*(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|}. \tag{4.195}$$

Explicitly, the orbitals φ_i are determined by the non-linear eigenvalues problem

$$\hat{H}_{\mathrm{HF}}[\{\varphi_j\}_{j=1,\ldots,N}]\varphi_i = \varepsilon_i\varphi_i \tag{4.196}$$

with the proviso that the corresponding N eigenfunctions minimize the energy expectation value. The Hartree-Fock solution Ψ_{HF}^N is then given by $\mathrm{SLATER}(\varphi_1,\ldots,\varphi_N)$ where the φ_i are the solutions of the non-linear Hartree-Fock equations. For the expectation values in the self-consistent solution $\Psi_{\mathrm{HF}}^N = \varphi_1 \wedge \ldots \wedge \varphi_N$ we find

$$\langle\hat{V}_{\mathrm{H}}\rangle = \frac{e^2}{4\pi\varepsilon_0}\sum_{i,j=1}^{N}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \frac{\varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_j(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \tag{4.197}$$

$$\langle\hat{V}_{\mathrm{F}}\rangle = \frac{e^2}{4\pi\varepsilon_0}\sum_{i,j=1}^{N}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \frac{\varphi_i^*(\mathbf{x})\varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}')\varphi_i(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \tag{4.198}$$

or

$$\langle\hat{V}_{\mathrm{H}}\rangle = \frac{e^2}{4\pi\varepsilon_0}\sum_{i,j=1}^{N}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \frac{\rho^i{}_i(\mathbf{x})\rho^j{}_j(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \tag{4.199}$$

$$\langle\hat{V}_{\mathrm{F}}\rangle = \frac{e^2}{4\pi\varepsilon_0}\sum_{i,j=1}^{N}\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\, \frac{\rho^i{}_j(\mathbf{x})\rho^j{}_i(\mathbf{x}')}{|\mathbf{x}-\mathbf{x}'|} \tag{4.200}$$

with $\rho^i{}_j(\mathbf{x}) = \langle \varphi_i | \hat{\rho}(\mathbf{x}) | \varphi_j \rangle$. The first term, the so-called Hartree energy, can be understood in purely classical terms: it corresponds to the Coulomb interaction of the charge densities of two particles in state φ_i and φ_j respectively. The second term, the so-called exchange interaction, has no classical counterpart. Notice that the self-interaction contributions to the above integrals $(i = j)$ cancel between the Hartree and the exchange term. For the Hartree-Fock ground-state energy, we find

$$E_{\text{HF}}^N \equiv \langle \hat{H} \rangle_{\Psi_{\text{HF}}^N} = \langle \hat{H}_0 \rangle_{\Psi_{\text{HF}}^N} + \langle \hat{V}_{\text{Coul}} \rangle_{\Psi_{\text{HF}}^N} = \langle \hat{H}_0 \rangle_{\Psi_{\text{HF}}^N} + \frac{1}{2} \langle \hat{V}_{\text{H}} \rangle_{\Psi_{\text{HF}}^N} - \frac{1}{2} \langle \hat{V}_{\text{F}} \rangle_{\Psi_{\text{HF}}^N} \qquad (4.201)$$

whereas the evaluation of the Hartree-Fock Hamiltonian yields

$$\langle \hat{H}_{\text{HF}} \rangle_{\Psi_{\text{HF}}^N} = \sum_{i=1}^{N} \varepsilon_i = \langle \hat{H}_0 \rangle_{\Psi_{\text{HF}}^N} + \langle \hat{V}_{\text{H}} \rangle_{\Psi_{\text{HF}}^N} - \langle \hat{V}_{\text{F}} \rangle_{\Psi_{\text{HF}}^N} = \langle \hat{H}_0 \rangle_{\Psi_{\text{HF}}^N} + 2 \langle \hat{V}_{\text{Coul}} \rangle_{\Psi_{\text{HF}}^N}. \qquad (4.202)$$

Hartree-Fock Approximation as Self-Consistent Mean-Field Theory In general, we define a mean-field operator $\hat{H}_{\text{MF}}^{\Psi}$ corresponding to

$$\hat{H} = \hat{A}\hat{B} \qquad (4.203)$$

as

$$\hat{H}_{\text{MF}}^{\Psi} = \hat{A} \langle \hat{B} \rangle_{\Psi} + \langle \hat{A} \rangle_{\Psi} \hat{B} - \langle \hat{A} \rangle_{\Psi} \langle \hat{B} \rangle_{\Psi}. \qquad (4.204)$$

Following this philosophy, we now want to define a mean-field Coulomb potential. First, we write the Coulomb potential in an orbital basis as

$$\hat{V}_{\text{Coul}} = \frac{1}{2} \sum_{ijkl} V^{ij}{}_{lk} a_i^\dagger a_j^\dagger a_k a_l. \qquad (4.205)$$

Essentially, we have to define mean-field operators corresponding to the operator products $a_i^\dagger a_j^\dagger a_l a_k$. We define the corresponding mean field operator as the sum over all products of the form $\langle a_1^{(\dagger)} a_2^{(\dagger)} \rangle_{\Phi_0} a_3^{(\dagger)} a_4^{(\dagger)}$ minus all products of the form $\langle a_1^{(\dagger)} a_2^{(\dagger)} \rangle_{\Phi_0} \langle a_3^{(\dagger)} a_4^{(\dagger)} \rangle_{\Phi_0}$ where Φ_0 is assumed to be a Slater determinant over a complete set of orthonormal orbitals, the Coulomb potential is expanded in the same set of orbitals and the averaged operators have to be commuted into a nearest neighbor position before being contracted. We then get

$$\begin{aligned}
\hat{V}_{\text{MF}}^{\Phi_0} &= \frac{1}{2} \sum_{ijkl} V^{ij}{}_{lk} (\langle a_j^\dagger a_k \rangle_{\Phi_0} a_i^\dagger a_l + \langle a_i^\dagger a_l \rangle_{\Phi_0} a_j^\dagger a_k - \langle a_j^\dagger a_l \rangle_{\Phi_0} a_i^\dagger a_k - \langle a_i^\dagger a_k \rangle_{\Phi_0} a_j^\dagger a_l) \\
&\quad - \frac{1}{2} \sum_{ijkl} V^{ij}{}_{lk} (\langle a_j^\dagger a_k \rangle_{\Phi_0} \langle a_i^\dagger a_l \rangle_{\Phi_0} - \langle a_j^\dagger a_l \rangle_{\Phi_0} \langle a_i^\dagger a_k \rangle_{\Phi_0}) \\
&= \sum_{ijkl} V^{ij}{}_{lk} (\langle a_j^\dagger a_k \rangle_{\Phi_0} a_i^\dagger a_l - \langle a_j^\dagger a_l \rangle_{\Phi_0} a_i^\dagger a_k) - \langle \hat{V}_{\text{Coul}} \rangle_{\Phi_0} \mathbb{1}_{\mathcal{F}} \\
&=: \hat{V}_{\text{HF}}^{\Phi_0} - \langle \hat{V}_{\text{Coul}} \rangle_{\Phi_0} \mathbb{1}_{\mathcal{F}}.
\end{aligned}$$

We then have $\langle a_i^\dagger a_k \rangle_{\Phi_0} = \delta_{ik} n_i$. This implies that $\hat{V}_{\mathrm{HF}}^{\Phi_0}$ is the formal Hartree-Fock potential corresponding to the Slater determinant Φ_0. The Hartree-Fock equations can then be characterized as

$$\hat{H}_{\mathrm{HF}}^{\Phi_0} \Phi_0 \equiv (\hat{H}_{\mathrm{MF}}^{\Phi_0} + \langle \hat{V}_{\mathrm{Coul}} \rangle_{\Phi_0} \mathbb{1}) \Phi_0 = E_0 \Phi_0. \tag{4.206}$$

That means: the Hartree-Fock solution Φ_0 is a self-consistent mean-field ground-state. If the mean-field Hamiltonian $\hat{H}_{\mathrm{MF}}^{\Psi}$ is computed with the solution Φ_0 of the Hartree-Fock equations, we regain precisely the mean-field Hamiltonian which was used to calculate the Hartree-Fock solution. Note, however, that it has to be checked that the Hartree-Fock solutions actually yield a minimum and not only an extremum of the Hartree-Fock functional.

4.2.3. Beyond Hartree-Fock

GW **Approximation for the Four-Point Green Function** The *GW* approximation is algebraically equivalent to the Hartree-Fock equation, but replaces L with $\tilde{L}$. That means, within the *GW* approximation, $\tilde{L}$ (instead of L) is given by

$$\tilde{L}(1,2,3,4) = -G(1,4)G(2,3). \tag{4.207}$$

This makes it evident that the *GW* approximation is highly superior to the Hartree-Fock approximation. The price we have to pay is that the corresponding quasiparticle equation is much more complicated: (i) the self-energy gets frequency dependent and the quasiparticle energies therefore have to fulfill the quasiparticle condition $e_s(\omega_s) = \hbar \omega_s$, (ii) the self-energy depends on all Lehman amplitudes (and not only on the occupied Lehmann amplitudes as in the Hartree-Fock case), (iii) the expression for the self-energy operator in terms of the Lehmann amplitudes is much more complicated than in the Hartree-Fock case, (iv) even for fixed Lehman amplitudes, the self-energy operator is not symmetric. Precisely as in the case of the Hartree-Fock approximation, one shows that the *GW* self-energy is given by

$$\tilde{\Sigma}_{\mathrm{xc}}^{GW}(1,2) = \mathrm{i}\hbar w(1,2^+)G(1,2) \tag{4.208}$$

motivating the name *GW* approximation.

W-**Approximation** We say that an approximation contains *vertex corrections*, whenever $\tilde{\Xi}(1,2,3,4) \neq \delta(1,4)\delta(2,3)$. Analogously, we can say that $\tilde{I} \neq 0$ or by the 5$^{\mathrm{th}}$ Hedin equation

$$\tilde{\Xi}(1,2,3,4) = \delta(1,4)\delta(2,3) + \mathrm{i}\hbar \int \mathrm{d}(5,6,7,8)\ \tilde{I}(1,5,3,6)G(6,7)G(8,5)\tilde{\Xi}(7,2,8,4).$$

The W-approximation is given by

$$\tilde{I}(1,2,3,4) = -\bar{W}(1,2,3,4) = -W(1,2,4,3). \tag{4.209}$$

In the space-time domain, this yields the particularly simple equation

$$\tilde{\Lambda}(1,2;3) = \delta(1,3)\delta(3,2) - i\hbar w(1,2^+) \int d(4,5)\ G(1,4)G(5,2)\tilde{\Lambda}(4,5;3). \tag{4.210}$$

Interpretation The W-approximation can be easily interpreted graphically. First, consider the bare vertex[13]

$$\tilde{\Lambda}_0(1,2;3) = \delta(1,3)\delta(3,2) \tag{4.211}$$

The first vertex correction to the bare vertex is given by

$$\int d(4,5)\ \mathrm{Ver}(4,1,2,5)\tilde{\Lambda}_0(4,5;3) = -G(1,3)w(1,2)G(3,2) \tag{4.212}$$

where

$$\mathrm{Ver}(1,2,3,4) = -i\hbar G(2,1)w(2,3)G(4,3). \tag{4.213}$$

One sees easily that this induces iteratively an infinite subclass of vertex corrections (the loop corrections) via

$$\tilde{\Lambda}_n(1,2;3) = -\tilde{\Lambda}_0(1,2;3) - \int d(4,5)\ \mathrm{Ver}(4,1,2,5)\tilde{\Lambda}_{n-1}(4,5;3) \tag{4.214}$$

such that the summation of that infinite subclass of loop corrections corresponds to the fixed point equation

$$\tilde{\Lambda}(1,2;3) = \tilde{\Lambda}_0(1,2;3) - i\hbar w(1,2) \int d(4,5)\ G(1,4)G(5,2)\tilde{\Lambda}(4,5;3). \tag{4.215}$$

It is noteworthy that the decisive equation (4.215) already appears in an appendix to Hedin's classical paper ([41], equation A33). Hedin arrived at this equation by a completely different way, namely by taking the partial derivative (i.e. neglect implicit G-dependence of W) of Σ in the GW-approximation, $\frac{\delta\Sigma(1,2)}{\delta G(3,4)} = i\hbar w(1,2)\delta(3,4)$, and replugging this result in the self-consistent equation for the vertex function.

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[13]Strictly speaking, such expressions are ill-defined because they involve point-wise products of the Dirac distribution. This is avoided in the four-point formalism.

5. Beyond the Standard Model of Electronic Structure Theory

5.1. Classical Effective Field Theory

5.1.1. Classical Electrodynamics

Classical Lagrangean The action for the electromagnetic field[1] $A^\mu = (\varphi/c, \mathbf{A})$ in the presence of an external current $j^\mu = (c\rho, \mathbf{j})$ is given by

$$S = \int \mathrm{d}^4 x \left(-\frac{1}{4\mu_0} F^{\mu\nu}(x) F_{\mu\nu}(x) - A^\mu(x) j_\mu(x) \right) + S_{\mathrm{el}}[\psi] \tag{5.1}$$

where

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu. \tag{5.2}$$

The last term $S_{\mathrm{el}}[\psi]$ in equation (5.1) denotes the free part of the action referring to the "matter" (typically electronic) degrees of freedom. The Euler-Lagrange equations

$$\frac{\delta S}{\delta A^\mu(x)} = \frac{\partial \mathcal{L}}{\partial A^\mu(x)} - \partial_\nu \frac{\partial \mathcal{L}}{\partial(\partial_\nu A^\mu(x))} = 0 \tag{5.3}$$

lead to the Maxwell equations[2]

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \tag{5.4}$$

$$\nabla \times \mathbf{E} = -\partial_t \mathbf{B} \tag{5.5}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{5.6}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{j} + \varepsilon_0 \mu_0 \partial_t \mathbf{E} \tag{5.7}$$

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[1]The action for the electromagnetic field is of course highly non-unique. The present form is canonical for classical physics because it is of the standard Yang-Mills form $S_{\mathrm{Yang-Mills}} = 1/4 \int_{\mathcal{M}} \mathrm{Tr}\, F \wedge *F$ where $*$ denotes the Hodge operator [5, 71, 84]. However, it turns out that for this action, not all components of the 4-potential are dynamical which makes the Coulomb gauge quantization almost imperative for this action. Therefore, in order to quantize e.g. in the Lorentz gauge, one has to modify the action. For details, we refer to the standard quantum field theoretical literature, as e.g. [40, 46, 47, 63]

[2]Strictly speaking, the action leads to the inhomogeneous Maxwell equations in the form $\partial_\nu F^{\nu\mu} = \mu_0 j^\mu$. The homogeneous Maxwell equations are automatically fulfilled due to the definition of the fields in terms of the potentials.

where the electromagnetic field $(\mathbf{E}, \mathbf{B})$ is given in terms of the potential as

$$\mathbf{E}(\mathbf{x}t) = -\nabla\varphi(\mathbf{x}t) - \partial_t\mathbf{A}(\mathbf{x}t) \tag{5.8}$$

$$\mathbf{B}(\mathbf{x}t) = \nabla \times \mathbf{A}(\mathbf{x}t). \tag{5.9}$$

The Maxwell equations have non-trivial solutions even in the absence of soures j^μ (vacuum solutions). As the general solution to the inhomogeneous equations is given by a particular solution of the inhomogeneous problem plus the general solution of the homogeneous problem, this implies that the electromagnetic field is not determined by the sources. In other words, the electromagnetic field carries independent degrees of freedom which have to be fixed by appropriate boundary and initial value conditions.

Coulomb Gauge The action of the free electromagnetic field is invariant under the gauge transformation

$$A^\mu \mapsto A^\mu - \partial^\mu f. \tag{5.10}$$

This transformation also leaves the fields $(\mathbf{E}, \mathbf{B})$ invariant. Therefore, there is a certain freedom in the choice of the fields A^μ. This freedom can be used to impose conditions on A^μ. Within the realm of non-relativistic Quantum Field Theory, a convenient choice is

$$\nabla \cdot \mathbf{A} = 0 \tag{5.11}$$

or

$$\mathbf{A} = \mathbf{A}_\mathrm{T} = P_\mathrm{T}\mathbf{A} \tag{5.12}$$

$$\mathbf{A}_\mathrm{L} = \mathbf{0}. \tag{5.13}$$

This condition is obviously not Lorentz covariant (but invariant under rotations and translations). This fact alone does not contradict the Lorentz symmetry of the electromagnetic theory. It simply means that equation (5.11) – contrary to e.g. the Maxwell equations – cannot hold in all inertial frames. Our convention therefore is: equation (5.11) holds where the solid is at rest. From equations (5.8, 5.9) and the Maxwell equations, one finds the general equations of motion for the potentials

$$-\Delta\varphi - \partial_t(\nabla \cdot \mathbf{A}) = \frac{\rho}{\varepsilon_0} \tag{5.14}$$

$$\frac{1}{c^2}\partial_t^2\mathbf{A} - \Delta\mathbf{A} + \nabla\left(\nabla \cdot \mathbf{A} + \frac{1}{c^2}\partial_t\varphi\right) = \mu_0\mathbf{j}. \tag{5.15}$$

In the Coulomb gauge this simplifies as

$$\Delta\varphi = -\frac{\rho}{\varepsilon_0} \tag{5.16}$$

$$\left(\frac{1}{c^2}\partial_t^2 - \Delta\right)\mathbf{A} = \mu_0\mathbf{j} - \frac{1}{c^2}\partial_t\nabla\varphi. \tag{5.17}$$

From

$$\partial_t \rho + \nabla \cdot \mathbf{j} = 0 \tag{5.18}$$

it then follows that

$$\nabla \cdot \left(\mu_0 \mathbf{j} - \frac{1}{c^2} \partial_t \nabla \varphi \right) = 0. \tag{5.19}$$

Therefore, the equation of motion for $\mathbf{A}$ can be rewritten as

$$\left(\frac{1}{c^2} \partial_t^2 - \Delta \right) \mathbf{A} = \mu_0 \mathbf{j}_{\mathrm{T}}. \tag{5.20}$$

In order to find the general solution to this equation, we introduce the Coulomb propagator D^{ij} by

$$\left(\frac{1}{c^2} \partial_t^2 - \Delta \right) D_{\mathrm{T}}^{ij}(x, x') = \delta_{\mathrm{T}}^{ij}(x - x') \tag{5.21}$$

where $\delta_T^{ij}(x - x')$ denotes the integral kernel of P_{T}.

Fourier Decomposition The general Fourier decomposition with respect to $\mathbf{x}$ of an arbitrary vector field $\mathbf{F} \in \mathcal{H}_{\mathrm{V}}$ reads

$$\mathbf{F}(\mathbf{x}) = \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{i=1}^{3} \mathbf{e}_i f_i(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}}. \tag{5.22}$$

As we deal with a linear superposition, we are free to choose a different basis $\mathbf{e}_i(\mathbf{k})$ for every Fourier mode. Concretely, we fix the $\mathbf{e}_i(\mathbf{k})$ such that for every $\mathbf{k}$ they form an orthogonal system and $\mathbf{e}_1(\mathbf{k}) = \mathbf{k}/|\mathbf{k}|$. We then have

$$\mathbf{F}(\mathbf{x}) = \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{i=1}^{3} \mathbf{e}_i(\mathbf{k}) f_i(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}} \tag{5.23}$$

$$\nabla \cdot \mathbf{F}(\mathbf{x}) = \int \frac{d\mathbf{k}}{(2\pi)^3} i\mathbf{k} \cdot \mathbf{e}_1(\mathbf{k}) f_1(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}} \tag{5.24}$$

$$\nabla \times \mathbf{F}(\mathbf{x}) = \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{i=2}^{3} i\mathbf{k} \times \mathbf{e}_i(\mathbf{k}) f_i(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}}. \tag{5.25}$$

We read off that for every mode $e^{i\mathbf{k}\cdot\mathbf{x}}$, $|\mathbf{e}_2(\mathbf{k})\rangle\langle\mathbf{e}_2(\mathbf{k})| + |\mathbf{e}_3(\mathbf{k})\rangle\langle\mathbf{e}_3(\mathbf{k})|$ is the projector on $\mathcal{H}_{\mathrm{T}}$. Taking matrix elements of

$$\sum_{i=1}^{3} |\mathbf{e}_i\rangle\langle\mathbf{e}_i| = \mathbb{1}_{3\times 3} \tag{5.26}$$

we see that the integral kernel of P_{T} is given by

$$\delta_{\mathrm{T}}^{ij}(\mathbf{x} - \mathbf{x}') = \int \frac{d\mathbf{k}}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} \left(\delta^{ij} - \frac{k^i k^j}{|\mathbf{k}|^2} \right). \tag{5.27}$$

As $[\Box, P_{\mathrm{T}}] = 0$, we get

$$D_{\mathrm{T}} = DP_{\mathrm{T}} \tag{5.28}$$

where

$$\left(\frac{1}{c^2}\partial_t^2 - \Delta\right) D(x, x') = \delta(x - x')\mathbb{1}_{3\times 3}. \tag{5.29}$$

The latter can be easily solved in the Fourier domain. This yields for the Coulomb propagator

$$D_{\mathrm{T}}^{ij}(x - x') = -\int \frac{\mathrm{d}^4 k}{(2\pi)^4} \frac{\mathrm{e}^{-\mathrm{i}k(x-x')}}{k^2} \left(\delta^{ij} - \frac{k^i k^j}{|\mathbf{k}|^2}\right) \tag{5.30}$$

with $kx = \omega t - \mathbf{k}\cdot\mathbf{x}$ and $k^2 = \omega^2/c^2 - |\mathbf{k}|^2$. The full electromagnetic propagator $D^{\mu\nu}(k)$ is then given by[3]

$$D(k) = \begin{pmatrix} 1/|\mathbf{k}|^2 & 0 \\ 0 & D_{\mathrm{T}}^{ij}(k) \end{pmatrix}. \tag{5.31}$$

Under coordinate transformations, $D^{\mu\nu}$ behaves like a second rank tensor. Therefore, in general $D^{\mu\nu}(k)$ does not preserve its form. Instead, equation (5.31) holds where the Coulomb gauge condition holds.

Quantization of the Electromagnetic Field in Vacuo In the Coulomb gauge, the conjugate momentum to A_0 vanishes. Therefore, only $\mathbf{A}$ is considered a dynamical variable. Explicitly, one has

$$\pi_i = \frac{\partial \mathcal{L}}{\partial(\partial_t A^i)} = -E_i = \partial_t A_i. \tag{5.32}$$

The transition to the corresponding Quantum Field Theory is implemented through the equal-time commutation relation

$$[\hat{E}^i(\mathbf{x}t), \hat{A}^j(\mathbf{x}'t)] = \mathrm{i}\hbar\delta_{\mathrm{T}}^{ij}(\mathbf{x} - \mathbf{x}'). \tag{5.33}$$

This is consistent with $\nabla\cdot\mathbf{E} = 0$. The (non-trivial part of the) Feynman propagator in the Columb gauge is defined by

$$-\mathrm{i}\hbar D_{\mathrm{F}}^{ij}(x - x') = \langle 0|\mathcal{T}\hat{A}^i(x)\hat{A}^j(x')|0\rangle. \tag{5.34}$$

Using $(c^{-2}\partial_t^2 - \Delta)\hat{A}^i = 0$ and $\partial_t\theta(t - t') = \delta(t - t')$ one shows easily that the propagator is a classical Green function and therefore in the Fourier domain given by

$$D_{\mathrm{F}}^{ij}(x - x') = -\int \frac{\mathrm{d}^4 k}{(2\pi)^4} \frac{\mathrm{e}^{-\mathrm{i}k\cdot(x-x')}}{k^2 + \mathrm{i}\eta} \sum_{l=2}^{3} (\mathbf{e}_l(\mathbf{k}) \otimes \mathbf{e}_l(\mathbf{k}))^{ij}. \tag{5.35}$$

Apart from the regularization prescription, this coincides with (5.30).

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[3]In fact, this follows strictly from the facts that (i) the propagator is quantum field theoretically defined as $\propto \langle\mathcal{T}\hat{A}_\mu(x)\hat{A}_\nu(x')\rangle$, (ii) A_0 is non-dynamical and therefore a c-number and (iii) $\langle\hat{A}_i(x)\rangle = 0$ in the ground-state.

5.1.2. Effective Electronic Field Theory

Functional Integral Approach In Quantum Field Theory, one assumes a functional integral representation for the Green functions of the general form [80]

$$\langle 0|\mathcal{T}\hat{\phi}(x_1)\dots\hat{\phi}(x_n)|0\rangle = \frac{1}{Z}\int \mathcal{D}\phi\;\phi(x_1)\dots\phi(x_n)\mathrm{e}^{\mathrm{i}S[\phi]/\hbar} \tag{5.36}$$

where the normalization factor Z is given by $\int \mathcal{D}\phi\;\mathrm{e}^{\mathrm{i}S[\phi]/\hbar}$. (for details, see e.g. [75] Chapter 9, equation (9.18)) In principle, this carries over to the case of Quantum Electrodynamics, where the action $S = S[\psi, A^\mu]$ is given by equation (5.1).[4] Here we are dealing with two fields, the electromagnetic field $\hat{A}^\mu(x)$ and the electronic field $\hat{\psi}(x)$ (Pauli-Schrödinger or Dirac). Suppose now we are only interested in the electronic Green functions[5]

$$\langle 0|\mathcal{T}\hat{\psi}(x_1)\dots\hat{\psi}^\dagger(x_n)|0\rangle = \frac{1}{Z}\int \mathcal{D}\psi\mathcal{D}\bar{\psi}\mathcal{D}A^\mu\;\psi(x_1)\dots\bar{\psi}(x_n)\mathrm{e}^{\mathrm{i}S[\psi, A^\mu]/\hbar} \tag{5.37}$$

where the bar denotes the conjugate Grassmann variable. This suggests to define an effective action through

$$\mathrm{e}^{\mathrm{i}S_{\mathrm{eff}}[\psi]/\hbar} = \int \mathcal{D}A^\mu\;\mathrm{e}^{\mathrm{i}S[\psi, A^\mu]/\hbar} \tag{5.38}$$

such that

$$\langle 0|\mathcal{T}\hat{\psi}(x_1)\dots\hat{\psi}^\dagger(x_n)|0\rangle = \frac{1}{Z}\int \mathcal{D}\psi\mathcal{D}\bar{\psi}\;\psi(x_1)\dots\bar{\psi}(x_n)\mathrm{e}^{\mathrm{i}S_{\mathrm{eff}}[\psi]/\hbar}. \tag{5.39}$$

The effective action can be calculated analytically in terms of Gaussian integrals yielding in terms of photon propagator $D^{\mu\nu}(x - x')$ the well-known result (see e.g. [59] p.225)

$$S_{\mathrm{eff}}[\psi] = S_{\mathrm{el}}[\psi] - \frac{1}{2}\int \mathrm{d}x\mathrm{d}x'\;j_\mu(x)D^{\mu\nu}(x - x')j_\nu(x'). \tag{5.40}$$

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[4]For fermionic variables, the corresponding fields in the path integral formalism become anticommuting and the functional integral becomes a Grassmann integral.

[5]This path integral is actually ill-defined due to the gauge freedom or – equivalently – the non-existence of a propagator which fulfills $-\frac{1}{4}F^{\mu\nu}F_{\mu\nu} = \frac{1}{2}A^\mu(D^{-1})_{\mu\nu}A^\nu$. (cf. e.g. [11, 75, 85]) In fact, in the functional integral, one integrates over infinitely many gauge equivalent field configurations. The kernel of "D^{-1}"= $\eta_{\mu\nu}\Box - \partial_\mu\partial_\nu$ just consists of the pure gauges $\partial_\mu\Lambda$. On the other hand, such a propagator is necessary, in order to solve the path integral in terms of Gaussian integrations. This is a standard problem in gauge theory which is cured by an insertion of 1 in the form $1 = \int \mathcal{D}\Lambda\;\Delta_{\Phi\Pi}[A^\mu]\delta(F[A^\mu_\Lambda])$ where $\Delta_{\Phi\Pi}$ denotes the Fadeev-Popov determinant, $F[\cdot]$ is a gauge-fixing condition and the integral goes over all gauge transforms. $\mathcal{D}\Lambda = \Pi_x\mathrm{d}\Lambda(x)$ and $\mathrm{d}\Lambda(x)$ denotes the Haar-measure on the gauge group U(1). This integration over the "gauge-orbit" can then be separated out and cancels with the normalization factor. All in all, this leads to a redefinition of the generating functional as $\int \mathcal{D}A^\mu\;\Delta_{\Phi\Pi}[A^\mu]\delta(F[A^\mu])\mathrm{e}^{\mathrm{i}S[A^\mu]/\hbar}$. The Fadeev-Popov ghosts come in when the Fadeev-Popov determinant is represented as a Grassmann-Gaussian integral over fermionic ghost fields. Inter alia, this leads to a modification of the action $\mathcal{L} \mapsto \mathcal{L} - 1/\xi(\partial_\mu A^\mu)^2$ (the gauge fixing term) where ξ is a real parameter. (In the Lorentz gauge this term is just zero.) In the following, we do not touch upon these problems because we use the path-integral only as a heuristic method.

Interpretation The effective action can be understood as describing "effectively" a subset of the fundamental degrees of freedom by averaging or integrating out the other degrees of freedom. Typically, this idea is used in quantum Field Theory when one wants to integrate out the high-energy degrees of freedom. In the above example, the partition of the degrees of freedom is canonically given: there are the electronic degrees of freedom for which one wants to have an effective action and the electromagnetic or photonic degrees of freedom which one wants to integrate out. (cf. e.g. [86]) In the case of high energy and low energy degrees of freedom, the situation is not so simple but can nonetheless be interpreted similarly. Consider e.g. a quantum Field Theory with the Fock-space $\mathcal{F}$ over the one-particle Hilbert space $\mathcal{H}$ which we take as $\mathcal{L}^2(\mathbb{R}, \mathbb{C}, \mathrm{d}k)$ (one particle wave-functions in momentum space). We can split $\mathbb{R}$ into $\mathbb{A} := [-k_c, k_c]$ and $\mathbb{B} := \mathbb{R} - [-k_c, k_c]$, i.e. into high and low energy degrees of freedom. The one-particle Hilbert space decomposes accordingly into $\mathcal{L}^2(\mathbb{A}) \oplus \mathcal{L}^2(\mathbb{B})$. For the corresponding Fock space we have $\mathcal{F}(\mathcal{L}^2(\mathbb{A}) \oplus \mathcal{L}^2(\mathbb{B})) = \mathcal{F}(\mathcal{L}^2(\mathbb{A})) \otimes \mathcal{F}(\mathcal{L}^2(\mathbb{B}))$. Suppose now the Hamiltonian $\hat{H}$ of the system is given by the kinetic energy $\hat{H}_0$ plus the Coulomb interaction $\hat{V}$. The free field operator corresponding to $\hat{H}_0$ naturally decomposes into a low and a high frequency part,

$$\hat{\psi}(x) = \sum_{|k| \leq k_c} \mathrm{e}^{\mathrm{i}kx} a_k + \sum_{|k| > k_c} \mathrm{e}^{\mathrm{i}kx} a_k = \hat{\psi}^<(x) + \hat{\psi}^>(x). \tag{5.41}$$

The free Hamiltonian $\hat{H}_0$ can then be brought into the form

$$\hat{H}_0 = \hat{H}_0^< \otimes \mathbb{1}_{\mathcal{F}(\mathcal{L}^2(\mathbb{B}))} + \mathbb{1}_{\mathcal{F}(\mathcal{L}^2(\mathbb{A}))} \otimes \hat{H}_0^>, \tag{5.42}$$

but the Coulomb interaction involves mixed terms with products like $\hat{\psi}^>(x)\hat{\psi}^<(x)$. This shows that with the partition of the system into high and low energy degrees of freedom, the Hamiltonian can be brought into the form of two interacting systems. Integrating out the high (or low) energy degrees of freedom then follows the same logic as in the derivation of the effective electronic action from the fundamental electromagnetic Lagrangean.[6]

The effective interaction also has a simple classical interpretation: it results from the fundamental action by eliminating the electromagnetic field by solving the equation of motion for A^μ in terms of j^ν using the electromagnetic Green function.[7] Put differently, the propagator provides an effective interaction – this should be borne in mind as a paradigm. In this context, it is crucial that the quantum field theoretical propagator is indeed a classical

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[6]In this form, the effective action approach has been pursued e.g. by [75], section 12.1. in the path-integral framework.

[7]The prefactor 1/2 comes in because the free term contributes $F^{\mu\nu}F_{\mu\nu} = -2A_\mu(D^{-1})^{\mu\nu}A_\nu$ which upon elimination $A^\mu = D^{\mu\nu}j_\nu$ yields $-1/2$ the contribution of the interaction term.

Green function for the corresponding field equation of motion.[8] Fundamentally, however, such a procedure leads to various problems which are ultimately due to the fact that the electromagnetic fields carries independent degrees of freedom, i.e. independent initial conditions on the electromagnetic field have to be fixed. This fact makes itself felt in the effective action approach through the problem of choosing the "right" Green function $D^{\mu\nu}(x - x')$. In other words, the effective action is literally ill-defined: there are infinitely many effective actions because there are infinitely many Green functions to the electromagnetic field which differ by free field solutions.[9] In the Fourier domain, this means that there are different regularization procedures for the formal solution $1/k^2$. Two different regularizations always differ by a free solution. Choosing a Green functions corresponds to fixing initial conditions on the electromagnetic field.

A further specialty of the effective action consists in its non-locality. As discussed in the next paragraph, such a non-local action can be treated within the usual formalism as long as its underlying Lagrangean – now being a function of two variables – is symmetric. For this it is necessary that the electromagnetic propagator is symmetric. This is indeed the case for the Feynman propagator, but not for the more physical retarded propagator. On the other hand, the Feynman propagator is in general not real-valued which would render the effective interaction uninterpretable. Fortunately, this is no problem when the effective action is quantized as will be discussed below.

Finally, note that the effective interaction is a field-theoretical version of Feynman-Wheeler electrodynamics.[10] [25] A further analogy to the work of Feynman can be drawn, since the effective action is by no means a Field Theory specific approach. In fact, it can already be used in classical mechanics. The arch example for this approach is provided by a system of two (otherwise free) particles linearly interacting through a harmonic oscillator. The problem of deriving an effective action for the particles by eliminating the oscillator degree of freedom has been studied by Feynman in his dissertation. [23] Feynman's results could be easily reproduced by the method of Green functions (which Feynman does not use in this context). The effective electromagnetic interaction is ultimately equivalent to this when one identi-

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[8]Here, we disregard of course the fact that the Feynman propagator is general neither retarded nor real-valued which one would require in classical physics.

[9]Below, we will rederive the effective action through the Gell-Mann and Low theorem and in that context it will turn out that the usage of the Feynman propagator is imperative.

[10]Indeed, Feynman and Wheeler also wanted the "effective action" (they actually did not consider a Field Theory but charged particles) to be symmetric and therefore chose to take half the sum of the retarded and the advanced Green function.

fies the interaction oscillator with the harmonic oscillators of the electromagnetic field modes.

Non-Local Field Theory Within the realm of local Field Theory, the action S is given in terms of a Lagrangean density $\mathcal{L}(x)$ as $S = \int \mathrm{d}^4x\ \mathcal{L}(x)$. The Lagrangean density in turn is given as a local expression in terms of the fields and its derivatives, i.e. (in the case of only one field) $\mathcal{L}(x)$ is an ordinary function – not a funtional – of the field values $\psi(x)$ and $\partial_\mu\psi(x)$: $\mathcal{L}(x) = \mathcal{L}[\psi, \partial_\mu\psi] = \mathcal{L}(\psi(x), \partial_\mu\psi(x))$. The functional derivative $\delta_{\psi(x)}S$ of the action with respect to the field at x can then be expressed through partial derivatives – not functional derivatives – of $\mathcal{L}(x)$ with respect to $\psi(x)$ (and possibly $\partial_\mu\psi(x)$). The simplest case of a non-local Field Theory is given by an action

$$S = \int \mathrm{d}^4x\mathrm{d}^4y\ \mathcal{L}(x, y) \qquad (5.43)$$

where $\mathcal{L}(x, y)$ is a function of ψ, $\partial_\mu\psi$ evaluated at x and y. This is still in accord with the principle of relativity if the non-local contributions are zero as long as $x - y$ is space-like. Indeed, even local Field Theory can be thought of as being non-local with a Lagrangean $\mathcal{L}(y)\delta(x - y)$. Here, the Dirac delta enforces $x = y$ which is a special case of $x - y$ not being space-like. We now want to express the stationarity condition $\delta_{\psi(x)}S = 0$ as an equation for $\mathcal{L}(y, y')$. Explicitly, we have

$$
\begin{aligned}
\delta_{\psi(x)}S &= \delta_{\psi(x)} \int \mathrm{d}^4y\mathrm{d}^4y'\ \mathcal{L}(y, y') \\
&= \lim_{\eta\to 0} \frac{1}{\eta} \int \mathrm{d}^4y\mathrm{d}^4y'\ (\mathcal{L}[\psi(y) + \eta\delta(y - x), \psi(y') + \eta\delta(y' - x)] - \mathcal{L}[\psi(y), \psi(y')]) \\
&= \lim_{\eta\to 0} \frac{1}{\eta} \int \mathrm{d}^4y\mathrm{d}^4y'\ (\mathcal{L}[\psi(y) + \eta\delta(y - x), \psi(y') + \eta\delta(y' - x)] - \mathcal{L}[\psi(y) + \eta\delta(x - y), \psi(y')] \\
&\quad + \mathcal{L}[\psi(y) + \eta\delta(x - y), \psi(y')] - \mathcal{L}[\psi(y), \psi(y')])
\end{aligned}
$$

Here, the functional dependence $\mathcal{L}[\psi(y), \psi(y')]$ is shorthand for $\mathcal{L}[\psi(y), \partial_\mu\psi(y); \psi(y'), \partial_\nu\psi(y')]$. Introducing an auxiliary field $\varphi(x)$ such that

$$\mathcal{L}(x, y) = \mathcal{L}[\psi(x), \varphi(y)] \qquad (5.44)$$

we can rewrite $\delta_{\psi(x)}S$ as

$$\int \mathrm{d}y\mathrm{d}y'\ \left(\delta_{\psi(x)}\mathcal{L}[\psi, \varphi]|_{\psi=\varphi} + \delta_{\psi(x)}\mathcal{L}[\varphi, \psi]|_{\psi=\varphi} \right). \qquad (5.45)$$

Precisely as in the case of the Euler-Lagrange equations, this leads to

$$\int \mathrm{d}y' \left(\frac{\partial\mathcal{L}(x, y')}{\partial\psi(x)} - \partial_\mu \frac{\partial\mathcal{L}(x, y')}{\partial\psi_\mu(x)} \right) + \int \mathrm{d}y \left(\frac{\partial\mathcal{L}(y, x)}{\partial\psi(x)} - \partial_\mu \frac{\partial\mathcal{L}(y, x)}{\partial\psi_\mu(x)} \right) = 0. \qquad (5.46)$$

If $\mathcal{L}$ is symmetric, this simplifies further as

$$\delta_{\psi(x)}S = 2\int dy \left(\frac{\partial\mathcal{L}(x,y)}{\partial\psi(x)} - \partial_\mu\frac{\partial\mathcal{L}(x,y)}{\partial\psi_\mu(x)}\right) = 0. \tag{5.47}$$

We call (5.46) the *non-local Euler-Lagrange equations*. In the case of an essentially local functional $\mathcal{L}(x,y) = \mathcal{L}(y)\delta(x-y)$, they reproduce the ordinary Euler-Lagrange equations. In the following, we will assume that the non-local Lagrangean density is symmetric[11] and has a free part which is local. In other words, $\mathcal{L}$ is of the form

$$\mathcal{L}(x,y) = \frac{1}{2}(\mathcal{L}_0(x)\delta(x-y) + \mathcal{L}_0(y)\delta(x-y)) + \mathcal{L}_{\text{int}}(x,y). \tag{5.48}$$

Furthermore, we assume that $\mathcal{L}$ depends on $\partial_t\psi$ only through the local part as is indeed the case for the effective electromagnetic action. This implies that the non-locality does not alter the definition of the conjugate momentum. In this case, we can pretend to deal formally with a local Lagrangean with a parametric y-dependence which is integrated out. Therefore, all results of classical Field Theory automatically carry over. In particular, as in the case of local Field Theory, the invariance of the action (or equivalently the invariance of the Lagrangean up to a total divergence) gives rise to a conserved current. In particular, if the Lagrangean is not explicitly dependent on the space-time, we have an energy-momentum tensor

$$T^{\mu\nu}(x) = \int dy \left(\frac{\partial\mathcal{L}(x,y)}{\partial\psi_\mu(x)}\partial^\nu\psi(x) - \eta^{\mu\nu}\mathcal{L}(x,y)\right) \tag{5.49}$$

and a Hamiltonian density

$$T^{00}(x) = \mathcal{H}(x) = \pi(x)\dot{\psi}(x) - \int dy\, \mathcal{L}(x,y) \tag{5.50}$$

with

$$\pi(x) = \int dy\, \frac{\partial\mathcal{L}(x,y)}{\partial\dot{\psi}(x)}. \tag{5.51}$$

The field equations of motion can now be written as

$$\partial_t\psi(x) = \{\psi(x), H(t)\} = \frac{\delta H}{\delta\pi(x)} \tag{5.52}$$

$$\partial_t\pi(x) = \{\pi(x), H(t)\} = -\frac{\delta H}{\delta\psi(x)} \tag{5.53}$$

with the Hamiltonian

$$H(t) = \int d\mathbf{x}\, \mathcal{H}(\mathbf{x}t) \tag{5.54}$$

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[11]We stress again that this is the case if one uses the Feynman propagator in the effective electron-interaction, but not if one uses the retarded or advanced propagator.

and the functional Poisson bracket

$$\{A, B\} = \int d\mathbf{x} \left(\frac{\delta A}{\delta \psi(\mathbf{x}t)} \frac{\delta B}{\delta \pi(\mathbf{x}t)} - \frac{\delta B}{\delta \psi(\mathbf{x}t)} \frac{\delta A}{\delta \pi(\mathbf{x}t)} \right). \tag{5.55}$$

Explicitly, we now find

$$\begin{aligned}
\frac{\delta \mathcal{H}(x)}{\delta \pi(x)} &= \dot{\psi}(x) + \pi(x) \frac{\delta \dot{\psi}(x)}{\delta \pi(x)} - \frac{\delta}{\delta \pi(x)} \int dy\ \mathcal{L}(x, y) \\
&= \dot{\psi}(x) + \pi(x) \frac{\delta \dot{\psi}(x)}{\delta \pi(x)} - \int dy\ \frac{\partial \mathcal{L}(x, y)}{\partial \dot{\psi}(x)} \frac{\delta \dot{\psi}(x)}{\delta \pi(x)} \\
&= \dot{\psi}(x)
\end{aligned} \tag{5.56}$$

and

$$\begin{aligned}
-\frac{\delta \mathcal{H}(x)}{\delta \psi(x)} &= -\frac{\delta \pi(x)}{\delta \psi(x)} \dot{\psi}(x) - \pi(x) \frac{\delta \dot{\psi}(x)}{\delta \psi(x)} + \frac{\delta}{\delta \psi(x)} \int dy\ \mathcal{L}(x, y) \\
&= -0 - \pi(x) \frac{\delta \dot{\psi}(x)}{\delta \psi(x)} + \int dy\ \left(\frac{\partial \mathcal{L}(x, y)}{\partial \dot{\psi}(x)} \frac{\delta \dot{\psi}(x)}{\delta \psi(x)} + \frac{\partial \mathcal{L}(x, y)}{\partial \partial_i \psi(x)} \frac{\delta \partial_i \psi(x)}{\delta \psi(x)} + \frac{\partial \mathcal{L}(x, y)}{\partial \psi(x)} \right) \\
&= \int dy\ \left(\frac{\partial \mathcal{L}(x, y)}{\partial \psi(x)} - \partial_i \frac{\partial \mathcal{L}(x, y)}{\partial \partial_i \psi(x)} \right) \\
&= \dot{\pi}(x).
\end{aligned} \tag{5.57}$$

Here, we have used the fact that in the Hamiltonian formalism, all quantities are to be considered as functionals of $\pi(x), \partial_i \psi(x)$ and $\psi(x)$, i.e. $\dot{\psi}(x)$ is to be eliminated in favor of $\pi(x)$. Finally, we read off the important formula

$$H_{\text{int}}(t) = -\int d\mathbf{x} dy\ \mathcal{L}_{\text{int}}(\mathbf{x}t, y). \tag{5.58}$$

for the interaction Hamiltonian.

5.2. Effective Hamiltonians for Electronic Structure Theory

5.2.1. Quantized Effective Electronic Field Theory

Introduction The purpose of the following consists in deriving an effective electronic Hamiltonian which on the one hand accounts for the full electromagnetic interaction,[12] but on the

[12]The idea of quantizing the full electromagnetic interaction but with an effective Lagrangean has been put forward apparently for the first time by Hoyle and Narlikar [44] who quantized Feynman-Wheeler electrodynamics in the path-integral formalism. (see also [18] p.178f and references therein)

other hand is still an ab-initio Hamiltonian. The road to this goal is clear: we quantize the classical Field Theory corresponding to the effective action (5.40) where the free term is given by the free action for the classical Schrödinger field $\psi(x)$ in an external potential $v_{\text{ext}}(\mathbf{x})$ as in equation (2.145). Correspondingly, the electromagnetic 4-current is given by[13]

$$\rho(x) = e\psi^*(x)\psi(x) \tag{5.59}$$

$$\mathbf{j}(x) = \frac{e\hbar}{2m\mathrm{i}}(\psi^*(x)\nabla\psi(x) - (\nabla\psi)^*(x)\psi(x)). \tag{5.60}$$

In particular, this implies that the interaction term of the effective action does not contain time-derivatives and therefore

$$\pi(x) = \frac{\delta S}{\delta\partial_t\psi(x)} = \mathrm{i}\hbar\psi^*(x) \tag{5.61}$$

still holds in the interacting case and the canonical Poisson brackets are unaltered. We therefore simply postulate

$$[\hat{\psi}(\mathbf{x}t), \hat{\psi}^\dagger(\mathbf{x}'t)]_+ = \delta(\mathbf{x} - \mathbf{x}'). \tag{5.62}$$

Consequently, we can quantize naively by replacing $\psi^{(*)}(x) \mapsto \hat{\psi}^{(\dagger)}(x)$ and imposing a suitable normal order prescription on the multilinear terms. We are free to do this because on the classical level, the fields commute and can therefore be brought in whatever order we like.

Interaction Hamiltonian If we use the photon propagator in the Coulomb gauge given by equation (5.31), then the term involving $1/2\int\mathrm{d}x\mathrm{d}x'\,j_0D^{00}j_0$ simply reproduces the Coulomb potential.[14] Therefore, the free action plus this term produce the standard ab-initio Hamiltonian. We now go beyond this level by taking into account the whole propagator. Equation (5.58) suggests to introduce a current-current interaction term via

$$\hat{H}_{\text{int}}(t) = \frac{1}{2}\int\mathrm{d}\mathbf{x}\mathrm{d}x'\,\hat{j}_i(\mathbf{x}t)D^{ij}(x - x')\hat{j}_j(x') \tag{5.63}$$

up to a suitable normal-ordering prescription. It therefore seems plausible to introduce the

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[13]As this subsection is heuristic in nature, in the following, we always work with a "naive" current. The problem of the general expression for the current has been discussed in Chapter 2.

[14]This is actually the derivation of the Coulomb potential. [40, 63, 52] The identification of the Coulomb potential as the 00-component of a current-current interaction naturally leads to the question, what is so special about the Coulomb potential? The answer lies in the fact that A^0 is non-dynamical. Therefore, the 00-component of the photon-propagator does not depend on the underlying quantum state. The Coulomb potential can be fully expressed in terms of the electronic operators. By contrast, D^{ij} depends on the quantum state of the electromagnetic field. Inter alia, this means that the current-current interaction is temperature dependent!

effective ab-initio interaction Hamiltonian $\hat{H}_{\text{int}}(t)$ given by

$$-\frac{e^2\hbar^2}{8m^2}\int \mathrm{d}\mathbf{x}\mathrm{d}x'\, D^{ij}(x-x')(-\partial_j\hat{\psi}^\dagger(x')\hat{\psi}^\dagger(x)\partial_i\hat{\psi}(x)\hat{\psi}(x') + \hat{\psi}^\dagger(x')\hat{\psi}^\dagger(x)\partial_i\hat{\psi}(x)\partial_j\hat{\psi}(x')$$

$$-\hat{\psi}^\dagger(x')\partial_i\hat{\psi}^\dagger(x)\hat{\psi}(x)\partial_j\hat{\psi}(x') + \partial_j\hat{\psi}^\dagger(x')\partial_i\hat{\psi}^\dagger(x)\hat{\psi}(x)\hat{\psi}(x')). \tag{5.64}$$

This operator is obviously symmetric (hermitean) if $D^{\mu\nu}(x-x')$ is real-valued. To fully fix this Hamiltonian we still have to meet two conventions: (i) we have to define the regularization of the photon propagator, (ii) we have to define the time dependence of the operators in the interaction term. Interestingly enough, both problems can be solved by taking recourse to the Gell-Mann and Low theorem:

$$\mathrm{i}\hbar G(\mathbf{x}t, \mathbf{x}'t') = \sum_{n=0}^\infty \left(-\frac{\mathrm{i}}{\hbar}\right)^n \frac{g^n}{n!}\int_{-\infty}^\infty \mathrm{d}t_1\ldots\mathrm{d}t_n\, \langle\Phi_0|\mathcal{T}\hat{H}_I(t_1)\ldots\hat{H}_I(t_n)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|\Phi_0\rangle_c$$

Assume now that the we deal with different kinds of degrees of freedom, say with electromagnetic and electronic degrees of freedom such that the Hilbert space is given by $\mathcal{H}_{\text{el}}\otimes\mathcal{H}_{\text{em}}$. We assume the free Hamiltonian to be of the form

$$\hat{H}_0 = \mathbb{1}_{\text{em}}\otimes\hat{H}_{\text{el}0} + \hat{H}_{\text{em}0}\otimes\mathbb{1}_{\text{el}} \tag{5.65}$$

and the ground-state to factorize $\Phi_{\text{el−em}} = \Phi_0\otimes|0\rangle$. The interaction Hamiltonian $\hat{H}_{\text{int}}$ is supposed to be of the form "electromagnetic field times quadratic expression in the electronic field", say $\int \mathrm{d}^4x\, A^\mu j_\mu$. Consider now a generic n-th order contribution

$$\left(-\frac{\mathrm{i}}{\hbar}\right)^n \frac{g^n}{n!}\int_{-\infty}^\infty \mathrm{d}t_1\ldots\mathrm{d}t_n\, \langle\Phi_{\text{el−em}}|\mathcal{T}\hat{H}_I(t_1)\ldots\hat{H}_I(t_n)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|\Phi_{\text{el−em}}\rangle. \tag{5.66}$$

The interaction Hamiltonians contribute a factor $\hat{A}^\mu(x_1)\ldots\hat{A}^\nu(x_n)$. As the ground-state factorizes, this contribution can be evaluated explicitly as $\langle0|\mathcal{T}\hat{A}^{\mu_1}(x_1)\ldots\hat{A}^{\mu_n}(x_n)|0\rangle$. The Wick theorem decomposes this into products of $\langle0|\mathcal{T}\hat{A}^{\mu_i}(x_i)\hat{A}^{\mu_j}(x_j)|0\rangle$. Furthermore, it follows that the interaction only contributes for even n, i.e. $n = 2m$. Under the integral, we therefore get

$$\langle0|\mathcal{T}\hat{A}^{\mu_1}(x_1)\ldots\hat{A}^{\mu_n}(x_n)|0\rangle\mathcal{T}\hat{j}_{\mu_1}(x_1)\ldots\hat{j}_{\mu_n}(x_n)$$

$$= \sum_{\text{pairings}} \langle0|\mathcal{T}\hat{A}^{\mu_{\sigma(1)}}(x_{\sigma(1)})\hat{A}^{\mu_{\sigma(2)}}(x_{\sigma(2)})|0\rangle\cdot\ldots\cdot\langle0|\mathcal{T}\hat{A}^{\mu_{\sigma(n-1)}}(x_{\sigma(n-1)})\hat{A}^{\mu_{\sigma(n)}}(x_{\sigma(n)})|0\rangle\times$$

$$\mathcal{T}\hat{j}_{\mu_1}(x_1)\ldots\hat{j}_{\mu_n}(x_n)$$

$$= \sum_{\text{pairings}} \langle0|\mathcal{T}\hat{A}^{\mu_{\sigma(1)}}(x_{\sigma(1)})\hat{A}^{\mu_{\sigma(2)}}(x_{\sigma(2)})|0\rangle\cdot\ldots\cdot\langle0|\mathcal{T}\hat{A}^{\mu_{\sigma(n-1)}}(x_{\sigma(n-1)})\hat{A}^{\mu_{\sigma(n)}}(x_{\sigma(n)})|0\rangle\times$$

$$\mathcal{T}\hat{j}_{\mu_{\sigma(1)}}(x_{\sigma(1)})\ldots\hat{j}_{\mu_{\sigma(n)}}(x_{\sigma(n)})$$

$$= (\mathrm{i}\hbar)^m \sum_{\text{pairings}} D^{\mu_{\sigma(1)}\mu_{\sigma(2)}}(x_{\sigma(1)}-x_{\sigma(2)})\cdot\ldots\cdot D^{\mu_{\sigma(n-1)}\mu_{\sigma(n)}}(x_{\sigma(n-1)}-x_{\sigma(n)})\times$$

$$\mathcal{T}\hat{j}_{\mu_{\sigma(1)}}(x_{\sigma(1)})\ldots\hat{j}_{\mu_{\sigma(n)}}(x_{\sigma(n)})$$

where we used that the current operators in the range of the time-ordering commute.[15] $\sum_{\text{pairings}}$ denotes the sum over all splittings of $\{1, \ldots, n\}$ into pairs with $i < j$. Under the integral, all pairings give the same contribution, their total number being $n!/2^m m!$.[16] Therefore, we can introduce the effective four-point (or two-particle) interaction[17]

$$\hat{H}_{\text{eff}}(t) = \frac{1}{2} \int \mathrm{d}\mathbf{x}\mathrm{d}x' \; \hat{j}_\mu(\mathbf{x}t) D^{\mu\nu}(x - x')\hat{j}_\nu(x') \tag{5.67}$$

such that the expression (5.66) equals

$$\left(-\frac{\mathrm{i}}{\hbar}\right)^m \frac{(g^2)^m}{m!} \int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \mathrm{d}t_m \; \langle\Phi_0|\mathcal{T}\hat{H}_{\text{eff}}(t_1) \ldots \hat{H}_{\text{eff}}(t_m)\hat{\psi}(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')|\Phi_0\rangle. \tag{5.68}$$

It is astonishing (if not magic) that the Gell-Mann and Low theorem reproduces exactly the effective action given by the field-theoretical considerations. We conclude that in the effective Hamiltonian (5.64), the time-dependence of the field operators is given in terms of $\hat{H}_{\text{el0}}$ and the electromagnetic Green function is given by the Feynman propagator.[18]

Static Approximation Within the realm of solid state physics, it is plausible to approximate the time-dependent interaction by an instantaneous interaction mediated by the propagator

$$D^{ij}(\mathbf{x} - \mathbf{x}') = \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \frac{e^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{k}|^2} \left(\delta^{ij} - \frac{k^i k^j}{|\mathbf{k}|^2}\right). \tag{5.69}$$

The first term in this integral simply reproduces the Coulomb potential. Using[19]

$$\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \; e^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}} \frac{k^i k^j}{|\mathbf{k}|^4} = \frac{1}{8\pi} \partial_i \partial_j |\mathbf{x} - \mathbf{x}'| \tag{5.70}$$

we get

$$D^{ij}(\mathbf{x} - \mathbf{x}') = \left(\frac{\delta^{ij}}{8\pi|\mathbf{x} - \mathbf{x}'|} + \frac{(\mathbf{x} - \mathbf{x}')^i (\mathbf{x} - \mathbf{x}')^j}{8\pi|\mathbf{x} - \mathbf{x}'|^3}\right). \tag{5.71}$$

---

[15]In general, operators in the range of the time-ordering commute or anticommute. The current operators, in particular, commute because they are bilinear in the field operators.

[16]The number off all pairings times the of permutations of the pairs ($= m!$) times the number of permutations in each pair ($= 2^m$) equals the number of all permutations ($= n!$).

[17]An S-matrix version of this fact has been derived apparently for the first time by Akhiezer and Berestetskii ([1] p.299f) who showed by a different method that the expectation value of $\mathcal{T}\exp(-\mathrm{i}\int \mathrm{d}x \; \hat{j}^\mu(x)\hat{A}_\mu(x))$ in the photonic vacuum equals $\mathcal{T}\exp(\frac{\mathrm{i}}{2}\int \mathrm{d}x\mathrm{d}x' \; \hat{j}^\mu(x)D_{\mu\nu}(x - x')\hat{j}^\nu(x'))$ (see their equation (24.26)).

[18]This solves the aforementioned conundrum of the complex valuedness of the Feynman propagator (or the resulting non-hermiticity of the effective interaction Hamiltonian). Within the context of quantum Field Theory, this does not pose any (conceptual) problems because the role of the effective interaction Hamiltonian consists in the reproduction of the right Green function. Recall in this context that the self-energy is also not hermitean. With the non-hermitean effective interaction, the Schrödinger equation has to be interpreted as a quasiparticle equation from the very outset.

[19]cf. [54], p.765, equation (1.89)

The corresponding classical interaction energy reads

$$\frac{1}{2} \int d\mathbf{x} d\mathbf{x}' dt' \; j_\mu(\mathbf{x}t) D^{\mu\nu}(\mathbf{x} - \mathbf{x}') \delta(t - t') j_\nu(\mathbf{x}'t'). \tag{5.72}$$

In the special case of two charges $j^\mu = j_1^\mu + j_2^\mu$ with

$$(\rho_1(\mathbf{x}), \mathbf{j}_1(\mathbf{x})) = (q_1 \delta(\mathbf{x} - \mathbf{x}_1), q_1 \mathbf{v}_1 \delta(\mathbf{x} - \mathbf{x}_1)) \tag{5.73}$$

$$(\rho_2(\mathbf{x}), \mathbf{j}_2(\mathbf{x})) = (q_2 \delta(\mathbf{x} - \mathbf{x}_2), q_2 \mathbf{v}_2 \delta(\mathbf{x} - \mathbf{x}_2)) \tag{5.74}$$

we get disregarding an infinite self-interaction term and reinstalling all constants

$$\frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{|\mathbf{x} - \mathbf{x}'|} + \frac{1}{8\pi\varepsilon_0} \frac{1}{c^2} \left(q_1 q_2 \frac{\mathbf{v}_1 \cdot \mathbf{v}_2}{|\mathbf{x} - \mathbf{x}'|} + q_1 q_2 \frac{(\mathbf{v}_1 \cdot (\mathbf{x} - \mathbf{x}'))(\mathbf{v}_2 \cdot (\mathbf{x} - \mathbf{x}'))}{|\mathbf{x} - \mathbf{x}'|^3} \right). \tag{5.75}$$

This form of interaction was first obtained by Darwin in 1920 ([48], p.411).

Gauge Independence In the following we want to derive a first approximation to check whether the electromagnetic ab-initio Hamiltonian (5.63) gives reasonable results. The corresponding quantum theory can be interpreted as a non-relativistic Breit Hamiltonian. However, in order to do this, it is not reasonable to start from the complicated Darwin Lagrangean. In the Lorentz gauge, the propagator reads

$$D_{\mu\nu}(k) = -\frac{\eta_{\mu\nu}}{k^2 + i\eta} \tag{5.76}$$

in the Fourier domain and the effective interaction simply yields (compare e.g. [52], p.258, equation (8.45))

$$\frac{1}{2} \int dx \; (\rho(x) v(x, x') \rho(x') + j^\mu(x) v(x, x') j_\mu(x')) \tag{5.77}$$

in the static limit $D_{\mu\nu}(\omega) \mapsto D_{\mu\nu}(\omega = 0)$. This differs from the Darwin Lagrangean. The original effective action is of course independent of the gauge. To see this, we consider the effective action in the Fourier domain where it is given by

$$\frac{1}{2} \int \frac{d^4 k}{(2\pi)^4} \; j^*(k) D(k) j(k). \tag{5.78}$$

For the spatial part, we find using current conservation in the Fourier domain

$$\int \frac{d^4 k}{(2\pi)^4} \; j_i^*(k) \frac{-1}{k^2} \left(\delta^{ij} - \frac{k^i k^j}{|\mathbf{k}|^2} \right) j_j(k) \tag{5.79}$$

$$= \int \frac{d^4 k}{(2\pi)^4} \; \frac{-1}{k^2} \left(j_i^*(k) j^i(k) - \frac{j_i^*(k) k^i k^j j_j(k)}{|\mathbf{k}|^2} \right) \tag{5.80}$$

$$= \int \frac{d^4 k}{(2\pi)^4} \; \left(\frac{-j_i^*(k) j^i(k)}{k^2} + \frac{\omega^2 \rho^*(k) \rho(k)}{k^2 |\mathbf{k}|^2} \right) \tag{5.81}$$

$$= \int \frac{d^4 k}{(2\pi)^4} \; \left(\frac{-j_i^*(k) j^i(k)}{k^2} + \rho^*(k) \rho(k) \left(-\frac{1}{k^2} - \frac{1}{|\mathbf{k}|^2} \right) \right). \tag{5.82}$$

The last contribution just cancels the instantaneous Coulomb potential and the penultimate contribution replaces it with a retarded charge-charge interaction. Therefore, the total effective interaction yields the same result as in the case of the Lorentz gauge. This makes it plausible to take

$$D^{ij}(\mathbf{x} - \mathbf{x}') = \frac{\delta^{ij}}{4\pi\varepsilon_0|\mathbf{x} - \mathbf{x}'|} \tag{5.83}$$

as the instantaneous current-current interaction kernel.

Effective Action in the Four-Point Formalism In order to derive suitable approximations for the corresponding Green function theory, we incorporate this interaction in the four-point formalism. That means we plug it into equation (5.64) and rewrite it as

$$\frac{1}{2}\int \mathrm{d}(1,2,3,4)\, D(1,2,3,4)\hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(4)\hat{\psi}(3) \tag{5.84}$$

where the situation is complicated because the current-current interaction contains terms which involve derivatives of the field operator. These can be pulled back on the level of the integral kernel D by using derivatives of the Dirac delta. For the sake of simplicity, we first treat a one-dimensional system (for which $\delta^{ij} = \delta^{11} = 1$). We introduce the formal expression $\delta(1, 2')$ meaning that

$$\int \mathrm{d}(1,2)\, \varphi^*(1)\delta(1,2')\varphi(2) \;=\; -\int \mathrm{d}1\, \varphi^*(1)\varphi'(1) \tag{5.85}$$

$$=\; \int \mathrm{d}1\, \varphi'^*(1)\varphi(1) \tag{5.86}$$

$$\stackrel{!}{=}\; \int \mathrm{d}1\, \varphi^*(1)\delta(1',2)\varphi(2). \tag{5.87}$$

It follows that $\delta(1, 2') = \delta(1', 2)$ under suitable boundary conditions which we always assume to be given. In the following, we do not want to have temporal derivatives because the current operator contains only spatial derivatives of the field operators. We therefore redefine

$$\delta(1, 2') = \delta(t_1, t_2)\delta(\mathbf{x}_1, \mathbf{x}'_2). \tag{5.88}$$

Furthermore, the following notation will come in handy

$$G(1, 2') \;=\; \partial_2 G(1,2) \tag{5.89}$$

$$G(1, 1') \;=\; \lim_{2\to 1} \partial_2 G(1,2). \tag{5.90}$$

The integral kernel D can now be written as

$$D(1,2,3,4) \;=\; -\frac{e^2\hbar^2}{4m^2}(+v(2,3)\delta(1',3)\delta(2,4') + v(1,4)\delta(1,3')\delta(2',4)$$
$$+v(1,2)\delta(1,3')\delta(2,4') + v(3,4)\delta(1',3)\delta(2',4)). \tag{5.91}$$

With these conventions, we can plug the electromagnetic interaction into the formalism of the self-consistent equations.

Hartree-Fock Approximation To find the self-energy in the Hartree-Fock approximation, we define

$$-D \cdot G^4 = (\mathrm{i}\hbar)^{-1} \Sigma_{\mathrm{magn}} G \tag{5.92}$$

with $G^4(1,2,3,4) = G(1,3)G(2,4) - G(1,4)G(2,3)$. Factoring out G in $D \cdot G^4$ yields after a somewhat lengthy calculation for $\Sigma_{\mathrm{magn}}^{\mathrm{HF}}(1,2)$

$$
\begin{aligned}
= \; & \frac{e^2\hbar^2}{4m^2} \int \mathrm{d}3 \; (v(1,3)\mathrm{i}\hbar(G(3,3') - G(3',3))\delta(1,2') + \delta(1',2)v(3,2)\mathrm{i}\hbar(G(3,3') - G(3',3))) \\
& + \frac{e^2\hbar^2}{4m^2} \int \mathrm{d}3 \; (v(1,3)\mathrm{i}\hbar G(1',3)\delta(3,2') - \delta(1',3)v(3,2)\mathrm{i}\hbar G(3,2')) \\
& + \frac{e^2\hbar^2}{4m^2} v(1,2)\mathrm{i}\hbar G(1',2') - \frac{e^2\hbar^2}{4m^2} \int \mathrm{d}(4,5) \; \delta(1',5)v(5,4)\mathrm{i}\hbar G(5,4)\delta(4,2').
\end{aligned} \tag{5.93}
$$

The equal time limits are to be performed as in the case of Coulomb potential. Indeed, the magnetic interaction has the same structure with respect to the time-order as the Coulomb interaction of which we could have kept track be writing it in terms of left and right Dirac deltas. We did not do this in order not to overload the notation. The 3-dimensional magnetic self-energy can be restored as follows: every term in the magnetic self-energy contains two derivatives like $G(1',2)\delta(3',4)$ etc.; these are to be redefined as $\delta^{ij}\partial_{1i}\partial_{3j}G(1,2)\delta(3,4)$ etc. It is interesting to compute the corresponding energy contribution[20] $1/2 \sum_{a \; \mathrm{occ}} \tilde{\Sigma}^a_{\; a}$ in terms of the Lehmann amplitudes. Using the expression for the current in terms of the Green function shows the first two terms of the magnetic self-energy yield

$$\frac{1}{4\pi\varepsilon_0} \frac{1}{c^2} \sum_{a \; \mathrm{occ}} \sum_{b \; \mathrm{occ}} \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \; \frac{-\mathbf{j}^a_a(\mathbf{x}_1) \cdot \mathbf{j}^b_b(\mathbf{x}_2) + \mathbf{j}^a_b(\mathbf{x}_1) \cdot \mathbf{j}^b_a(\mathbf{x}_2)}{|\mathbf{x}_1 - \mathbf{x}_2|} \tag{5.94}$$

This corresponds to a Hartree-Fock contribution where the density operator has been replaced with the current operator (cf. equation (4.199)). Indeed the standard Hartree-Fock terms and the magnetic Hartree-Fock terms can be summed up in a covariant total Hartree-Fock contribution of the form $\propto ((j^\mu)^a_a(\mathbf{x})(j_\mu)^b_b(\mathbf{x}') - (j^\mu)^a_b(\mathbf{x})(j_\mu)^b_a(\mathbf{x}'))/|\mathbf{x} - \mathbf{x}'|$ because in the magnetic Hartree-Fock theory, the signs of the Hartree and the Fock term are interachanged. Consequently, the first two terms in the magnetic self-energy could have been found by educated guessing from the standard Hatree-Fock self-energy whereas the last two terms go beyond the naive expectation. Note that, usually the total ground-state current vanishes (Theorem of Bloch about ground-state current). Therefore, only the current exchange contributes.

---

[20]cf. the Migdal formula (3.24).

5.2.2. Effective Phonon-Mediated Electron-Electron Interaction

Introduction The purpose of this subsection consists in the derivation of an effective electron-electron interaction mediated by phonons quite the same way as the effective electromagnetic electron-electron interaction is mediated by photons. In other words, the effective phonon-mediated electron-electron interaction results from the fundamental model through the elimination of the phononic field.[21]

Interaction Hamiltonian Fundamentally, the classical electron-nuclei Coulomb interaction[22] is given by

$$\hat{H}_{\mathrm{I}} = -\frac{Ze^2}{4\pi\varepsilon_0} \sum_{\mathbf{n}} \int \mathrm{d}\mathbf{x}\, \frac{n(\mathbf{x})}{|\mathbf{x_n} - \mathbf{x}|} \tag{5.95}$$

where $\mathbf{n}$ indexes the nuclear coordinates and $\rho(\mathbf{x}) = en(\mathbf{x})$ denotes the charge density of the electron liquid. In the case of solid state physics, we are entitled to assume the nuclei to be highly localized around the classical equilibrium positions because otherwise the state would not be so solid. This suggests a Taylor expansion of the Coulomb potential around the equilibrium positions the zero order contribution of which corresponds to the external potential of the nuclei in a crystal lattice. The first order contribution reads

$$\hat{H}_{\mathrm{I1}}(t) = \frac{Ze^2}{4\pi\varepsilon_0} \sum_{\mathbf{n}} \hat{\mathbf{u}}(\mathbf{x_{n0}}t)\cdot\int \mathrm{d}\mathbf{x}\, n(\mathbf{x}t)\frac{(\mathbf{x_{n0}} - \mathbf{x})}{|\mathbf{x_{n0}} - \mathbf{x}|^3} =: -\sum_{\mathbf{n}} \int \mathrm{d}\mathbf{x}\, \mathbf{u}(\mathbf{x_{n0}}t)\cdot\mathbf{F}(\mathbf{x_{n0}}, \mathbf{x}; t) \tag{5.96}$$

with

$$\mathbf{F}(\mathbf{x_{n0}}, \mathbf{x}; t) = en(\mathbf{x}t)\mathbf{E}(\mathbf{x_{n0}}, \mathbf{x}) = -en(\mathbf{x}t)(\nabla_{\mathbf{x}}v)(\mathbf{x_{n0}}, \mathbf{x}). \tag{5.97}$$

---

[21]Usually, Fröhlich [33] is credited with the original introduction of effective, phonon-mediated electron-electron interactions (through second-order perturbation theory). Bardeen, Cooper and Schrieffer in their classical paper on superconductivity [7] refer to Bardeen and Pines [6] for the derivation of the effective interaction. Their overall result is equivalent to [4] p.518, equation (26.24). This order of events is also confirmed by [65]. The equivalence of this approach to the Gellmann and Low Theorem approach as in [15] p.316, equation (17.16) is usually demonstrated by considering the total effective interaction in an appropriate approximation, typically the RPA (see [15], Chapter 17, in particular equation (17.39)). Apart from the apparently new derivation itself, the present dissertation goes beyond these results by emphasising the real space approach to the phonon-propagator which allows for the formulation of the general connection between the phonon propagator and the nuclear polarizability. This connection will show that quite generally the inclusion of phononic effects corresponds to the screening of the Coulomb interaction with the nuclear degrees of freedom. It will also allow for a simple derivation of the Yukawa potential and a closed formula for its decay length. Furthermore, the concrete expression for the phonon-mediated interaction as presented in this dissertation turns out to be slightly more general.

[22]In principle, one could also consider the full electromagnetic interaction of electrons and nuclei.

This modifies the classical equation of motion for the displacement field $\mathbf{u}(\mathbf{x_{n0}}t)$ as

$$M\partial_t^2 \mathbf{u}(\mathbf{x_{n0}}t) + \sum_{\mathbf{m}} \mathbf{K}(\mathbf{x_{n0}} - \mathbf{x_{m0}})\mathbf{u}(\mathbf{x_{m0}}t) = \int d\mathbf{x} \ \mathbf{F}(\mathbf{x_{n0}}, \mathbf{x}; t) \qquad (5.98)$$

We solve for $\mathbf{u}(\mathbf{x_{n0}}t)$ through

$$\mathbf{u}(\mathbf{x_{n0}}t) = \sum_{\mathbf{m}} \int d\mathbf{x}' dt' \ \mathbf{D}_{\mathrm{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t')\mathbf{F}(\mathbf{x_{m0}}, \mathbf{x}'; t'). \qquad (5.99)$$

With this formula, we can eliminate the phononic field in the interaction Hamiltonian (5.96) which yields a purely electronic interaction given by

$$H_{\mathrm{el-el}}(t) \ = \ \frac{1}{2} \sum_{\mathbf{n},\mathbf{m}} \int d\mathbf{x} d\mathbf{x}' dt' \ \mathbf{F}(\mathbf{x}, \mathbf{x_{n0}}; t)\mathbf{D}_{\mathrm{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t')\mathbf{F}(\mathbf{x_{m0}}, \mathbf{x}'; t') \quad (5.100)$$

The minus sign comes in because $\mathbf{F}$ is an antisymmetric function. The prefactor 1/2 has been inserted in order to avoid double-counting. (This prefactor is derived rigorously in the next paragraph.) The formal expression $\mathbf{F}\mathbf{D}_{\mathrm{phon}}\mathbf{F}$ is the direct analog of $j^\mu D_{\mu\nu}j^\nu$. Replacing now the electronic charge density by the corresponding operator and imposing a normal order prescription, we get the interaction Hamiltonian operator $H_{\mathrm{el-el}}(t)$ as

$$\frac{Z^2 e^4}{32\pi^2\varepsilon_0^2} \sum_{\mathbf{m},\mathbf{n}} \int d\mathbf{x} d\mathbf{x}' dt' \ v_i(\mathbf{x} - \mathbf{x_{n0}})D_{\mathrm{phon}}^{ij}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t')v_j(\mathbf{x_{m0}} - \mathbf{x}')\hat{\psi}^\dagger(\mathbf{x}t)\hat{\psi}^\dagger(\mathbf{x}'t')\hat{\psi}(\mathbf{x}'t')\hat{\psi}(\mathbf{x}t)$$

$$(5.101)$$

where

$$\mathbf{v}(\mathbf{x}) = -\frac{\mathbf{x}}{|\mathbf{x}|^3}. \qquad (5.102)$$

By recourse to the Gell-Mann and Low theorem, we conclude that the time-dependence of the field operators is given by the free electronic Hamiltonian. In the four-point formalism, the interaction reads

$$\hat{D}_{\mathrm{phon}} = \frac{1}{2} \int d(1, 2, 3, 4) \ D(1, 2, 3, 4)\hat{\psi}^\dagger(1)\hat{\psi}^\dagger(2)\hat{\psi}(4)\hat{\psi}(3) \qquad (5.103)$$

with

$$D(1, 2, 3, 4) \ = \ v_{\mathrm{phon}}(1, 4)\delta(4, 2^+)\delta(3, 1^+) \qquad (5.104)$$

$$v_{\mathrm{phon}}(\mathbf{x}t, \mathbf{x}'t') \ = \ \frac{Z^2 e^4}{16\pi^2\varepsilon_0^2} \sum_{\mathbf{m},\mathbf{n}} \sum_{i,j=1}^{3} v_i(\mathbf{x} - \mathbf{x_{n0}})D_{\mathrm{phon}}^{ij}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t')v_j(\mathbf{x_{m0}} - \mathbf{x}'). \ (5.105)$$

In particular, this means that the phonon-mediated interaction is time-dependent. The discussion of the effective current-current interaction made it clear that the thus obtained

effective, phonon-mediated interaction reproduces the correct ground-state Green functions and therefore could also be obtained from the Gell-Mann and Low theorem.[23] In particular, any calculation of a finite number of Feynman diagrams with the effective interaction yields *exactly* the same result for the electronic Green function as the corresponding diagrams of the fundamental theory with electron-phonon interactions included. The advantage of a purely electronic interaction lies of course in the fact that it can be fed into the standard approximations of the self-consistent equations.

Effective Action Approach The phononic Lagrangean including the interaction term with the electrons reads

$$
\begin{aligned}
L(t) &= -\frac{1}{2} \int \mathrm{d}t' \sum_{\mathbf{n},\mathbf{m}} \langle \mathbf{u}(\mathbf{x_{n0}},t) | \mathbf{D}_{\mathrm{phon}}^{-1}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t') \mathbf{u}(\mathbf{x_{m0}},t') \rangle_{\mathbb{R}^3} \\
&\quad + \sum_{\mathbf{n}} \int \mathrm{d}\mathbf{x} \, \langle \mathbf{F}(\mathbf{x_{n0}},\mathbf{x};t) | \mathbf{u}(\mathbf{x_{n0}}t) \rangle_{\mathbb{R}^3}.
\end{aligned}
\tag{5.106}
$$

The total effective Lagrangean (involving exclusively dynamical variables from the electrons) now follows from eliminating $\mathbf{u}$ in terms of $\mathbf{D}_{\mathrm{phon}}$. One sees that – exactly as in the electromagnetic case – the free term then contributes $-1/2$ the contribution of the interacting term. This explains the prefactor $1/2$ which in the last paragraph has been introduced ad hoc. As in the electromagnetic case, the effective action can also be derived by a path integral approach. As the phonon field is naturally defined on a lattice, this approach now exactly corresponds to solving a Gaussian integral by means of the master formula (cf. e.g. [11, 54, 86])

$$
\frac{1}{(2\pi)^{N/2}} \int \det D^{-1} \mathrm{d}^N u \, \mathrm{e}^{-\frac{1}{2}\langle u|D^{-1}|u\rangle + \langle F|u\rangle} = \mathrm{e}^{\frac{1}{2}\langle F|D|F\rangle}.
\tag{5.107}
$$

Here the scalar product, the determinant etc. correspond to the total linear space of field configurations (which is $\mathbb{R}^3 \otimes \mathcal{L}^2(\Gamma)$ in the phononic case). This confirms for the phonon field that the effective action as defined by the path integral is equivalent to eliminating the phononic degrees of freedom through the Green function.

Refined Effective Hamiltonian In practice, the dynamical matrix $\mathbf{K}$ already contains electronic effects on the nuclei. A second order expansion of the pure mutual Coulomb interaction of the nuclei is not possible because such a system does not allow for stable equi-

---

[23]This way has indeed been used by Bruus/Flensberg [15] p.313f. who deduced their effective interaction from the Gell-Mann and Low Theorem but in reciprocal space. Their final result equation (17.16) essentially agrees with our result although this may not be completely evident because Bruus/Flensberg use the phononic Green function in reciprocal space and neglect its tensorial nature.

libria.[24] We may therefore think of the dynamical matrix as being a second order expansion of the internuclear Coulomb interaction and of the nuclear Coulomb interaction with the external charge density of the electrons. Thereby the latter should be calculated in a suitable reference ground-state. This makes it plausible to replace the density operator $\hat{\rho}_{\mathrm{el}}(\mathbf{x})$ in the above formulas starting from equation (5.96) with the density fluctuation operator $\delta\hat{\rho}_{\mathrm{el}}(\mathbf{x}) = \hat{\rho}_{\mathrm{el}}(\mathbf{x}) - \langle\hat{\rho}_{\mathrm{el}}(\mathbf{x})\rangle_0$. In addition to the above interaction, this replacement creates a Hartree-type potential[25]

$$-\int \mathrm{d}\mathbf{x}'\, v_{\mathrm{phon}}(\mathbf{x},\mathbf{x}';\omega=0)\rho(\mathbf{x}') := -v_{\mathrm{phon}}^{\mathrm{H}}(\mathbf{x}) \tag{5.108}$$

where $v_{\mathrm{phon}}(\mathbf{x},\mathbf{x}';\omega=0)$ denotes that Fourier transform of v_{phon} with respect to $\tau = t - t'$ evaluated at zero frequency. This implies that the Hartree potential $v_{\mathrm{phon}}^{\mathrm{H}}(\mathbf{x})$ corresponding to the effective phonon mediated interaction is time-independent even though the corresponding interaction depends on time. This is due to $\rho(\mathbf{x}t) = \langle\hat{\rho}(\mathbf{x}t)\rangle = \rho(\mathbf{x})$ for a non-interacting reference ground-state in which the density is evaluated. One then gets[26]

$$
\begin{aligned}
v_{\mathrm{phon}}^{\mathrm{H}}(\mathbf{x}t) &= \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\, v_{\mathrm{phon}}(\mathbf{x}t,\mathbf{x}'t')\rho(\mathbf{x}'t') & (5.109)\\
&= \int \mathrm{d}\mathbf{x}'\mathrm{d}t'\, v_{\mathrm{phon}}(\mathbf{x}t,\mathbf{x}'t')\rho(\mathbf{x}') & (5.110)\\
&= \int \mathrm{d}\mathbf{x}'\mathrm{d}\tau\, v_{\mathrm{phon}}(\mathbf{x},\mathbf{x}';\tau)\rho(\mathbf{x}') & (5.111)\\
&= \int \mathrm{d}\mathbf{x}'\, v_{\mathrm{phon}}(\mathbf{x},\mathbf{x}';\omega=0)\rho(\mathbf{x}') & (5.112)\\
&= v_{\mathrm{phon}}^{\mathrm{H}}(\mathbf{x}). & (5.113)
\end{aligned}
$$

This will be discussed below in detail. For the time being, note that the Hartree-type terms are one-particle operators and therefore do not give rise to an effective interaction. Instead, they can be absorbed in a redefinition of the reference Hamiltonian. The following considerations are independent of this replacement because they concern exclusively the interaction kernel.

[24]Suppose it would be possible to arrange classical point charges interacting through the Coulomb potential in a static equilibrium. Then the external field acting on a given particle exerted by all other particles would tend to restore the particle to its equilibrium position for arbitrary elongations. This contradicts $\nabla \cdot \mathbf{E} = 0$ at the equilibrium position.

[25]Note in this context that $\hat{V}_{\mathrm{Coul}} = \hat{V}_{\mathrm{Coul}}^{\mathrm{fluct}} + \hat{V}_{\mathrm{H}}$ where $\hat{V}_{\mathrm{Coul}}^{\mathrm{fluct}}$ denotes the operator which results from the Coulomb operator by replacing the density operators with the density fluctuation operators.

[26]In fact, one gets two contributions which by virtue of the symmetry in the effective phonon-mediated interaction coincide. This then cancels the prefactor $1/2$ of the effective interaction.

Interaction Hamiltonian in the Fourier Domain In order to calculate the phonon-mediated interaction in the Fourier domain we write

$$v_{\text{phon}}(\mathbf{x}t, \mathbf{x}'t') = -\frac{Z^2 e^4}{16\pi^2 \varepsilon_0^2} \sum_{i,j=1}^{3} \partial_i \partial_j' \sum_{\mathbf{m},\mathbf{n}} \frac{1}{|\mathbf{x} - \mathbf{x}_{\mathbf{n}0}|} D_{\text{phon}}^{ij}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \frac{1}{|\mathbf{x}_{\mathbf{m}0} - \mathbf{x}'|}. \tag{5.114}$$

Now, from

$$\frac{1}{4\pi} \int d\mathbf{x} \, \frac{e^{-i\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{x}|} = \frac{1}{|\mathbf{k}|^2} \tag{5.115}$$

it follows that

$$\frac{1}{4\pi} \int d\mathbf{x} \, \frac{e^{-i\mathbf{k}\cdot\mathbf{x}}}{|\mathbf{x} - \mathbf{x}_0|} = \frac{e^{-i\mathbf{k}\cdot\mathbf{x}_0}}{|\mathbf{k}|^2}. \tag{5.116}$$

Therefore,

$$-\int \frac{d\mathbf{x}d\mathbf{x}'}{16\pi^2} e^{-i(\mathbf{k}\cdot\mathbf{x} - \mathbf{k}'\cdot\mathbf{x}')} \sum_{\mathbf{m},\mathbf{n}} \frac{1}{|\mathbf{x} - \mathbf{x}_{\mathbf{n}0}|} D_{\text{phon}}^{ij}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \frac{1}{|\mathbf{x}_{\mathbf{m}0} - \mathbf{x}'|} \tag{5.117}$$

$$= -\frac{1}{|\mathbf{k}|^2 |\mathbf{k}'|^2} \sum_{\mathbf{m},\mathbf{n}} e^{-i(\mathbf{k}\cdot\mathbf{x}_{\mathbf{n}0} - \mathbf{k}'\cdot\mathbf{x}_{\mathbf{m}0})} D_{\text{phon}}^{ij}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \tag{5.118}$$

$$= -\frac{1}{|\mathbf{k}|^2 |\mathbf{k}'|^2} \sum_{\mathbf{m},\mathbf{n}} e^{-i((\mathbf{k}_0+\mathbf{G})\cdot\mathbf{x}_{\mathbf{n}0} - (\mathbf{k}_0'+\mathbf{G})\cdot\mathbf{x}_{\mathbf{m}0})} D_{\text{phon}}^{ij}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \tag{5.119}$$

$$= -\frac{1}{|\mathbf{k}|^2 |\mathbf{k}'|^2} \sum_{\mathbf{m},\mathbf{n}} e^{-i(\mathbf{k}_0\cdot\mathbf{x}_{\mathbf{n}0} - \mathbf{k}_0'\cdot\mathbf{x}_{\mathbf{m}0})} D_{\text{phon}}^{ij}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t') \tag{5.120}$$

$$= -\frac{1}{|\mathbf{k}|^2 |\mathbf{k}'|^2} N D_{\text{phon}}^{ij}(\mathbf{k}_0 t, \mathbf{k}_0' t') \tag{5.121}$$

$$= -\frac{1}{|\mathbf{k}|^2 |\mathbf{k}'|^2} N D_{\text{phon}}^{ij}(\mathbf{k}t, \mathbf{k}'t') \tag{5.122}$$

where $\mathbf{k} = \mathbf{k}_0 + \mathbf{G}$ is the decomposition into a vector in the FBZ and a reciprocal vector. Using $\partial_i \partial_j' \mapsto ik_i(-ik_j)$,[27] the phonon-mediated interaction then reads in the Fourier domain

$$v_{\text{phon}}(\mathbf{k}t, \mathbf{k}'t') = -\frac{N Z^2 e^4}{\varepsilon_0^2} \frac{D_{\text{phon}}^{ij}(\mathbf{k}t, \mathbf{k}'t') k_i k_j'}{|\mathbf{k}|^2 |\mathbf{k}'|^2} = -\frac{N Z^2 e^4}{\varepsilon_0^2} \frac{D_{\text{phon}}^{ij}(\mathbf{k}_0 t, \mathbf{k}_0' t') k_i k_j'}{|\mathbf{k}_0 + \mathbf{G}|^2 |\mathbf{k}_0' + \mathbf{G}'|^2}. \tag{5.123}$$

In general, the phonon-mediated interaction does not preserve the momentum but only the sum of the part of the momenta which lie in the FBZ. This is completely sensible because ultimately the phonon-mediated interaction corresponds to the interaction of the electrons with the external field of the nuclei and in an external field there is no momentum conservation.

---

[27]The Fourier transform for operator kernels reads $\int dx dx' \, e^{-ikx} D(x, x') e^{ik'x'}$.

Static, Homogeneous, Isotropic Continuum Approximation We first consider the crudest approximation to the effective, phonon-mediated interaction which corresponds to a static, isotropic, homogeneous continuum approximation. This means

1. $D^{ij} \propto \delta^{ij}$.

2. $D_{\mathrm{phon}} \mapsto D_{\mathrm{phon}}(\omega = 0)$.

3. $\sum_{\mathbf{k} \in \Gamma^*} \mapsto \frac{V}{(2\pi)^3} \int \mathrm{d}\mathbf{k}$.

The first condition implies $D^{ij} k_i k_j \mapsto D k^2$. The second condition implies the time-dependence of the phonon-mediated interaction to be instantaneous. The third condition implies that

$$\delta_{\mathbf{k}\mathbf{k}'} \mapsto \frac{(2\pi)^3}{V} \delta(\mathbf{k} - \mathbf{k}') \tag{5.124}$$

which ensures $\sum \delta_{\mathbf{k}\mathbf{k}'} \mapsto \int \mathrm{d}\mathbf{k}\ \delta(\mathbf{k} - \mathbf{k}')$. The volume is given by Na^3 where a denotes the lattice constant in real space. Putting all this together and using the phonon-propagator in momentum space yields for the effective interaction the concise expression

$$v_{\mathrm{phon}}(\mathbf{q}) = -\frac{(2\pi)^3 Z^2 e^4}{Ma^3 \varepsilon_0^2} \frac{1}{\omega_{\mathbf{q}}^2 |\mathbf{q}|^2}. \tag{5.125}$$

Furthermore, for small wave-vectors we may assume a simple dispersion relation $\omega_{\mathbf{q}} = v_L |\mathbf{q}|$ and get

$$v_{\mathrm{phon}}(\mathbf{q}) = -\frac{(2\pi)^3 Z^2 e^4}{ma^3 \varepsilon_0^2 v_L^2} \frac{1}{|\mathbf{q}|^4}. \tag{5.126}$$

This is to be compared with the Coulomb interaction

$$v_{\mathrm{Coul}}(\mathbf{q}) = \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2}. \tag{5.127}$$

Effective Phonon-Mediated Interaction and Long-Range Screening of the Coulomb Interaction The total effective interaction of the electrons is given by

$$v_{\mathrm{tot}}(\mathbf{q}) = v_{\mathrm{Coul}}(\mathbf{q}) + v_{\mathrm{phon}}(\mathbf{q}) = \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2} \left(1 - \frac{(2\pi)^3 Z^2 e^2}{ma^3 \varepsilon_0 v_L^2} \frac{1}{|\mathbf{q}|^2}\right). \tag{5.128}$$

As the phonon mediated contribution has the opposite sign, it tends to weaken or screen the Coulomb interaction. Empirically, one often describes this screening of the Coulomb interaction by a Yukawa potential of the form

$$v_{\mathrm{Yuk}}(\mathbf{q}) \quad = \quad \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2 + \mu^2} \tag{5.129}$$

$$= \quad \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2} \frac{1}{1 + \frac{\mu^2}{|\mathbf{q}|^2}} \tag{5.130}$$

$$\approx \quad \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2} \left(1 - \frac{\mu^2}{|\mathbf{q}|^2}\right). \tag{5.131}$$

Identifying equal powers yields

$$\mu^2 \equiv \frac{1}{r_0^2} = \frac{(2\pi)^3 Z^2 e^4}{m a^3 \varepsilon_0 v_L^2} \tag{5.132}$$

where r_0 is the decay length entering in the real-space Yukawa potential as

$$v_{\text{Yuk}}(\mathbf{x}) = \frac{e^2}{4\pi\varepsilon_0} \frac{e^{-r/r_0}}{r} \tag{5.133}$$

with $r = |\mathbf{x}|$. This derivation of the decay length may seem somewhat obscure because our effective phonon-mediated interaction is certainly not of the Yukawa type. This, however, is due to the approximation $\omega_{\mathbf{q}} = v_L|\mathbf{q}|$. We may therefore ask, which dispersion relation $\omega_{\mathbf{q}}$ yields exactly the Yukawa potential? In order to find this, we have to equate

$$\frac{e^2}{\varepsilon_0}\left(\frac{1}{|\mathbf{q}|^2 + \mu^2} - \frac{1}{|\mathbf{q}|^2}\right) \overset{!}{=} -\frac{(2\pi)^3 Z^2 e^4}{M a^3 \varepsilon_0^2} \frac{1}{\omega_{\mathbf{q}}^2 |\mathbf{q}|^2}. \tag{5.134}$$

A short calculation yields

$$\omega_{\mathbf{q}}^2 = \frac{(2\pi)^3 Z^2 e^2}{M a^3 \varepsilon_0 \mu^2}(|\mathbf{q}|^2 + \mu^2) \tag{5.135}$$

which corresponds to the dispersion relation of the Klein-Gordon equation. This is nice because the Yukawa potential is a static solution of the Klein-Gordon equation. The prefactor of $(|\mathbf{q}|^2 + \mu^2)$ has the dimension – and in fact even the meaning – of a squared speed (of sound). Equating this prefactor to v_L^2 yields again equation (5.132). Finally, the dispersion relation (2.164) yields in the continuum limit the expression

$$\omega_{\mathbf{q}}^2 = \frac{\kappa a^2}{M}|\mathbf{q}|^2 + \frac{\lambda}{M}. \tag{5.136}$$

Comparison with equation (5.135) leads to

$$\kappa = (2\pi)^3 \frac{Z^2 e^2}{a^5 \varepsilon_0 \mu^2} \tag{5.137}$$

$$\lambda = (2\pi)^3 \frac{Z^2 e^2}{a^3 \varepsilon_0}. \tag{5.138}$$

This allows for an estimation of the decay length in terms of the nearest neighbor interaction.[28]

---

[28]The Yukawa potential, if not simply postulated, is mostly derived from an *electronic* screening of the Coulomb potential by the Lindhard dielectric function. (cf. e.g. [15] p.251) The paragraph does not say that the phonon effects in the solid state generally lead to a Yukawa type potential, already not because the static, isotropic force law is a very crude approximation as compared to the "true" phonon mediated interaction. Quite to the contrary, the paragraph shows that for a Yukawa potential one needs a very

General Form of Isotropic, Homogeneous Screening Abandoning the static limit $\omega \to 0$, we are immediately led to the frequency dependent interaction

$$v_{\text{phon}}(\mathbf{q}; \omega) = \frac{(2\pi)^3 Z^2 e^4}{Ma^3 \varepsilon_0^2} \frac{1}{|\mathbf{q}|^2} \frac{1}{\omega^2 - \omega_{\mathbf{q}}^2 + \mathrm{i}\eta}. \tag{5.139}$$

This form of interaction coincides with the one derived by Blatter ([13], p.234, equation (11.14)) using a different method. The total interaction now reads

$$v_{\text{tot}}(\mathbf{q}; \omega) = \frac{e^2}{\varepsilon_0} \frac{1}{|\mathbf{q}|^2} \left(1 + \frac{(2\pi)^3 Z^2 e^2}{Ma^3 \varepsilon_0} \frac{1}{\omega^2 - \omega_{\mathbf{q}}^2} \right). \tag{5.140}$$

Writing this in the form $v_{\text{Coul}}/\varepsilon_{\text{nucl}}$ yields for the nuclear dielectric function the expression[29]

$$\varepsilon_{\text{nucl}}^{-1}(\mathbf{q}; \omega) = 1 + \frac{(2\pi)^3 Z^2 e^2}{Ma^3 \varepsilon_0} \frac{1}{\omega^2 - \omega_{\mathbf{q}}^2}. \tag{5.141}$$

This is a very satisfying result because this is a dielectric function of the Lorentz-Drude type (see appendix A.4) with one oscillator for each $\mathbf{q}$-mode but without damping term ($\Gamma \to 0$).[30] The last two paragraphs made it clear that there must be a fundamental connection between effective interactions and screening. This will now be investigated in detail.

---

special dispersion relation, namely of Klein-Gordon type. Such a dispersion relation is rather unphysical because it results from a coupling of all atoms to their equilibrium position in the form $H_{\text{int}} = \lambda/2 \sum u_n^2$. Such a term in the Hamiltonian will lead to a change of energy even if all atoms are displaced by the same amount. However, the Klein-Gordon relation is not completely unphysical either because it could correspond e.g. to a sublattice of atoms. The Klein-Gordon dispersion relation would then describe approximately an optical branch of the whole phonon spectrum. After all, in the Einstein model the potential Hamiltonian even reduces to a term $H_{\text{int}} = \lambda/2 \sum u_n^2$. The solid then consists of N decoupled harmonic oscillators all having the same frequency.

[29] The frequency dependence of this effective, phonon-mediated interactions differs from standard expressions which are of the form $\propto \omega^2/(\omega^2 - \omega_{\mathbf{q}}^2)$ (cf. [15] equation (17.39), [65] equation (1) or [4] equation (26.25)). This is not due to a failure of the present approach. Instead, the standard expressions are recovered from our approach by making a transition from the Coulomb potential (as it couples to the phonon propagator) to a dynamically screened interaction and from the so-called bare phonon frequencies to "screened frequencies". This is demonstrated in [13], section 11.1.3. Note that the standard expression vanishes at zero frequency and therefore do not give rise to an effective, instantaneous interaction.

[30] Note that there is no clash of prefactors between the above equation and equation (A.67) of appendix A.4: the mass M in the above equation refers to the mass of an atom or ion whereas in equation (A.67), the mass m refers to the ("effective") mass of the oscillator. The oscillators in the above formula are not the atoms but the wave modes of the lattice oscillations. By constrast, the units of the prefactors of course coincide. Finally, the absence of the damping term is a necessity because damping is a macroscopic effect.

5.2.3. Effective Interactions, Mean Fluctuation Theory and Screening

Effective Interaction and Nuclear Polarizability The effective, phonon-mediated interaction can also be seen from a completely different angle. This different point of view is important in order to elucidate the connection between the phonon-mediated interaction and the contribution of the nuclei to the polarizability. We start with a classical treatment. The interaction energy of the induced electronic charge density $\rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)$ in an external field $\varphi(\mathbf{x})$ is given by

$$H_{\mathrm{int}}(t) = \int \mathrm{d}\mathbf{x} \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)\varphi_{\mathrm{ext}}(\mathbf{x}t). \tag{5.142}$$

Here, "external field" means that the field is external to the electronic degrees of freedom. This applies in particular if the external field is the induced field of the nuclei $\varphi_{\mathrm{nucl}}^{\mathrm{ind}}(x)$, where "induced field" now means that the field is induced by a field which is external to the nuclei. We now have

$$
\begin{aligned}
H_{\mathrm{int}}(t) &= \int \mathrm{d}\mathbf{x} \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)\varphi_{\mathrm{nucl}}^{\mathrm{ind}}(\mathbf{x}t) && (5.143) \\
&= \int \mathrm{d}\mathbf{x}\mathrm{d}x' \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)v(\mathbf{x}t, x')\rho_{\mathrm{nucl}}^{\mathrm{ind}}(x'). && (5.144)
\end{aligned}
$$

On the other hand, we can think of the induced nuclear density as being induced by the electrostatic potential of the electrons themselves, i.e.

$$
\begin{aligned}
H_{\mathrm{int}}(t) &= \int \mathrm{d}\mathbf{x}\mathrm{d}x' \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)v(\mathbf{x}t, x')\rho_{\mathrm{nucl}}^{\mathrm{ind}}(x') && (5.145) \\
&= \int \mathrm{d}\mathbf{x}\mathrm{d}x'\mathrm{d}x'' \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)v(\mathbf{x}t, x')\chi_{\mathrm{nucl}}(x', x'')\varphi_{\mathrm{el}}^{\mathrm{ind}}(x'') && (5.146) \\
&= \int \mathrm{d}\mathbf{x}\mathrm{d}x'\mathrm{d}x''\mathrm{d}x''' \; \rho_{\mathrm{el}}^{\mathrm{ind}}(\mathbf{x}t)v(\mathbf{x}t, x')\chi_{\mathrm{nucl}}(x', x'')v(x'', x''')\rho_{\mathrm{el}}^{\mathrm{ind}}(x''') && (5.147)
\end{aligned}
$$

with the nuclear response function χ_{nucl}. Replacing the classical electronic densities[31] $\rho(x)$ with quantum operators $\hat{\rho}(x) = \hat{\psi}(x)\hat{\psi}(x)$ and imposing the usual normal ordering condition yields (up to Hartree type term) again a two-particle interaction Hamiltonian[32]

$$
\begin{aligned}
\hat{H}_{\mathrm{int}} &= \frac{1}{2}\int \mathrm{d}(1,2,3,4) \; D(1,2,3,4)\hat{\psi}^{\dagger}(1)\hat{\psi}^{\dagger}(2)\hat{\psi}(4)\hat{\psi}(3) && (5.148) \\
D(1,2,3,4) &= D(1,4)\delta(4,2^{+})\delta(3,1^{+}) && (5.149)
\end{aligned}
$$

---

[31]Following the same logic as in the paragraph about the refined effective Hamiltonian, it is also plausible to work with the density fluctuation operators here instead of the density operators themselves.

[32]Again, we insert a prefactor 1/2 in front of the effective Hamiltonian in order to avoid double counting. As before this prefactor can be justified rigorously as will be shown in the next paragraph.

with the interaction kernel being given by

$$D(1,2) = \int \mathrm{d}(3,4)\ v(1,3)\chi_{\mathrm{nucl}}(3,4)v(4,2). \tag{5.150}$$

This effective electron-electron interaction interaction is indeed identical to the above phonon-mediated interaction as will be shown in the following. Recall that the nuclear polarizability can be expressed in terms of the phonon propagator as

$$\chi_{\mathrm{nucl}}(\mathbf{x}t, \mathbf{x}'t') = Z^2 e^2 \sum_{\mathbf{n},\mathbf{m}} \langle (\nabla\delta)(\mathbf{x} - \mathbf{x}_{\mathbf{n}0}) | \mathbf{D}_{\mathrm{phon}}(\mathbf{x}_{\mathbf{n}0}t, \mathbf{x}_{\mathbf{m}0}t')(\nabla\delta)(\mathbf{x}_{\mathbf{m}0} - \mathbf{x}') \rangle_{\mathbb{R}^3}. \tag{5.151}$$

Convoluting this from the and from the right with the Coulomb potential yields precisely the electron-electron interaction we already found above, i.e. $v_{\mathrm{phon}} = v\chi_{\mathrm{nucl}}v$ or

$$v_{\mathrm{phon}}(1,2) = \int \mathrm{d}(3,4)\ v(1,3)\chi_{\mathrm{nucl}}(3,4)v(4,2). \tag{5.152}$$

With this formula, we find still another interpretation of the effective interaction. With the inclusion of the phonon-mediated interaction, the total electron-electron interaction v_{tot} reads

$$v_{\mathrm{tot}} = v + v_{\mathrm{phon}} = v + v\chi_{\mathrm{nucl}}v. \tag{5.153}$$

As $\varepsilon^{-1} = 1 + v\chi$ this implies the total interaction to be given by

$$v_{\mathrm{tot}} = v/\varepsilon_{\mathrm{nucl}}. \tag{5.154}$$

In other words, the transition from a purely Coulombic interaction to a Coulomb interaction modified by an interaction mediated by the nuclear degrees of freedom corresponds to the screening of the original Coulomb interaction with the nuclear permittivity.[33]

Systematic Treatment of the Decoupling of Nuclear and Electronic Degrees of Freedom – Effective Interactions and Mean Field Theory The fundamental interaction Hamiltonian between electrons and nuclei reads[34]

$$\hat{H}_{\mathrm{int}}(t) \;\; = \;\; \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\mathrm{d}t'\ \hat{\rho}_{\mathrm{el}}(\mathbf{x}t)v(\mathbf{x}t, \mathbf{x}'t')\hat{\rho}_{\mathrm{nucl}}(\mathbf{x}t') \tag{5.155}$$

---

[33] As opposed to the so-called screened interaction $W = v/\varepsilon$ in Hedin's equations, the effective interaction v_{tot} really describes a screening effect because it enters in a purely electronic model on which the nuclear degrees of freedom only act through their permittivity. We stress again that Hedin's W cannot be a screened interaction of the electrons because it is calculated with the permittivity of that very degrees of freedom whose interaction it describes. In other words, in that case the electrons would screen their own interaction. It is, however, possible to interpret W as the screened Coulomb interaction of the nuclei.

[34] Note in this context that due to the commutativity of nuclear and electronic operators, the normal ordering prescription is irrelevant here.

which acts on the Hilbert space $\mathcal{H}_{\text{el}} \otimes \mathcal{H}_{\text{nucl}}$ of electrons and nuclei. The free Hamiltonians of electrons and nuclei consist of a kinetic term and an electron-electron or nucleus-nucleus interaction Hamiltonian respectively. The goal of the decoupling procedure consists in replacing the fundamental interaction Hamiltonian with a Hamiltonian which acts exclusively on the electronic or nuclear degrees of freedom respectively.[35] The most obvious way to do this is the mean field approach which in the case of an electronic Hamiltonian replaces $\hat{\rho}_{\text{nucl}}$ with $\rho_{\text{nucl}} = \langle \hat{\rho}_{\text{nucl}} \rangle$ where the evaluation $\langle \cdot \rangle$ is performed in a suitable nuclear state.[36] In the context of solid-state physics, it is plausible that

$$\rho_{\text{nucl}}^0(\mathbf{x}) = Ze \sum_{\Gamma} \delta(\mathbf{x} - \mathbf{x}_{\mathbf{n}0}) \tag{5.156}$$

roughly holds. The resulting effective electronic Hamiltonian is obviously just the so-called external potential $v_{\text{ext}}(\mathbf{x})$ of the nuclei. The standard model of Electronic Structure Theory therefore corresponds to a mean field approach. Note that this naive mean-field approach leads to a one-electron operator and therefore, in this approximation, the nuclei do not induce an effective electron-electron interaction. Instead, effective electron-electron interactions come into play, when we replace the naive mean-Field Theory by a *Mean Fluctuation Field Theory*, i.e. we replace the operator $\hat{\rho}_{\text{nucl}}$ with

$$\rho_{\text{nucl}}^0(\mathbf{x}) + \delta\hat{\rho}_{\text{nucl}}(\mathbf{x}t) \equiv \rho_{\text{nucl}}^0(\mathbf{x}) + \hat{\rho}_{\text{nucl}}^{\text{ind}}(\mathbf{x}t) \tag{5.157}$$

where now the first term corresponds to the ordinary Mean Field Theory. It has been shown in the last paragraph that the second term if treated with Linear Response Theory (where the electrons provide the external potential) leads to the effective phonon-mediated electron-electron interaction. The total mean fluctuation field electronic operator therefore reads

$$\int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\mathrm{d}t' \ \hat{\rho}_{\text{el}}(x)v(x,x')\rho_{\text{nucl}}^0(x') +$$
$$\frac{1}{2} \int \mathrm{d}\mathbf{x}\mathrm{d}x'\mathrm{d}x''\mathrm{d}x''' \ \delta\hat{\rho}_{\text{el}}(x)v(x,x')\chi_{\text{nucl}}(x',x'')v(x'',x''')\delta\hat{\rho}_{\text{el}}(x'''). \tag{5.158}$$

This decoupling procedure will now be investigated from a more abstract point of view.

---

[35]Note that in this context the systems of electrons and nuclei are not decoupled in the sense of partial differential equations because the Hamiltonian of one subsystem still depends on the state of the other subsystem. Decoupling in this context only means that the Hamiltonian of the subsystem does not contain operators acting on the other system. In the same sense, one says that the Hartree approximation decouples the electrons into effective one-particle systems. The corresponding Hamiltonian of a given electron of course depends on the other electrons.

[36]Typically, this will be the ground-state or the thermal ensemble.

Mean Fluctuation Theory Consider a Hamiltonian of the form

$$\hat{H}_{\text{int}} = \hat{A} \otimes \hat{B}. \tag{5.159}$$

Mean Field Theory replaces this by the decoupled Hamiltonian

$$\hat{H}_{\text{int}}^{\text{MF}} = \hat{A}B_0 + A_0\hat{B} - A_0B_0. \tag{5.160}$$

Mean Fluctuation Field Theory goes beyond this. Instead of replacing $\hat{A}$ and $\hat{B}$ with fixed (time-independent) expectation values, it replaces them by a fixed expectation value plus fluctuating terms

$$\hat{A} = A_0 + \delta\hat{A}(t) \tag{5.161}$$
$$\hat{B} = B_0 + \delta\hat{B}(t). \tag{5.162}$$

For the fluctuation operators, mean fluctuation theory then uses a formal Kubo ansatz

$$\delta\hat{A}(t) \mapsto \int \mathrm{d}t' \, \chi_{AA}(t,t')\delta\hat{B}(t') \tag{5.163}$$
$$\delta\hat{B}(t) \mapsto \int \mathrm{d}t' \, \chi_{BB}(t,t')\delta\hat{A}(t'). \tag{5.164}$$

All in all, this leads to the mean fluctuation field Hamiltonian

$$
\begin{aligned}
\hat{H}_{\text{int}} &= \hat{A} \otimes \hat{B} \\
&= A_0B_0 + \delta\hat{A}B_0 + A_0B_0 + A_0\delta\hat{B} - A_0B_0 + \frac{1}{2}\delta\hat{A}\delta\hat{B} + \frac{1}{2}\delta\hat{A}\delta\hat{B} \\
&\mapsto \hat{A}B_0 + \hat{B}A_0 - A_0B_0 + \\
&\quad \frac{1}{2}\int \mathrm{d}t' \, \delta\hat{A}(t)\chi_{BB}(t,t')\delta\hat{A}(t') + \frac{1}{2}\int \mathrm{d}t' \, \delta\hat{B}(t)\chi_{AA}(t,t')\delta\hat{B}(t') \quad (5.165) \\
&=: \hat{H}_{\text{int}}^{\text{MFF}}(t) \tag{5.166}
\end{aligned}
$$

where the time dependence of the operators is given by a suitable reference Hamiltonian, e.g. the total, naive mean field Hamiltonian $(\hat{H}_0 + \hat{H}_{\text{int}}^{\text{MF}})$. Equation (5.165) is the fundamental equation of the Mean Fluctuation Field Theory. It also explains the prefactor $1/2$ which cancelled the double-counting: this prefactor results from the partioning of the interaction Hamiltonian between the subsystems. All in all, this shows that there are 5 equivalent ways to the effective interaction: (i) the path-integral approach (= integrating out unwanted degrees of freedom), (ii) the Gell-Mann and Low approach (= evaluating explicitly the scalar product of the unwanted operators in the Gell-Mann and Low formula), (iii) the classical Green function approach (= eliminating the unwanted degrees of freedom in the classical

Lagrangean or Hamiltonian by means of the classical Green function), (iv) the Mean Fluc-tuation Field approach (= decomposing the unwanted operator into a fixed mean field and a fluctuating part which is eliminated by a formal Kubo formula) and (v) the screening approach (= replacing the fundamental interaction for the total system by an interaction which is screened by the unwanted degrees of freedom).[37]

Conceptual Problems The last paragraph underlined again what has been evident as a problem from the very beginning: in principle, effective Hamiltonians are time-dependent.[38] For time-dependent Hamiltonians, the Green function cannot be defined as a ground-state expectation value. Practically, however, this does not pose any problem because: (i) the Green function formalism is quasi Lorentz-invariant in that it treats space and time on an equal footing (time-dependent interaction Hamiltonians do not change the functional form of the Green function perturbation theory or of the self-consistent set of equations)[39] and (ii) the full, interacting propagator can be defined by the quasiparticle equation which is also indifferent to a possible time-dependence of the interaction Hamiltonian. The thus defined propagator gives indeed rise to *time-independent* "ground-state" expectation values. These expectation values in principle (i.e. if perturbation theory holds) coincide with the expecta-tion values of the full interacting ground-state of the coupled Hamiltonian. This is evident from the discussion of the Gell-mann and Low theorem and its connection to the theory of effective interactions. For the time being, we may therefore conclude that the Green function approach is actually more fundamental than the Schrödinger equation – as is indeed the case in high-energy physics[40] – and that the effective Hamiltonians are nothing but a means to

---

[37]Indeed, classical texts, as e.g. [4] p.518, start with a Coulomb interaction screened by the nuclear degrees of freedom and define the difference between this interaction and the bare Coulomb interaction as mediated by phonons. The resulting expressions for the effective interaction differ of course from the ones given here. This is due to the fact that the nuclear polarizability is not calculated from the phonon-propagator. Ashcroft and Mermin state in their footnote 18 on page 518 that they consider their derivation more as an "indication of plausibility" whereas a "systematic derivation" would require "field theoretic ('Green function') methods". Our approach has made it clear that the "indication of plausibility" as by Ashcroft and Mermin in fact *is* a derivation because the Green function approach is equivalent to the screening of the Coulomb interaction by the nuclear degrees of freedom. In other words, it is *not* a specialty of the RPA and some crude guess for the nuclear polarizability that they meet in the same effective interaction.

[38]A similar problem (with a similar solution) is that the effective interaction Hamiltonian is in general not self-adjoint (at least not if it is calculated from the Feynman propagator).

[39]The Green function perturbation theory even has been developed for a time dependent Hamiltonian (although this time-dependence is the artificial adiabatic switching on).

[40]In fact, it is one of the basic problems for every beginner in relativistic Quantum Field Theory coming from the Quantum Mechanics course (at least it has been for the author of this thesis), that usually one does not calculate state vectors or solve a Schrödinger equation.

define Green function equations. Nonetheless, the author of this thesis is convinced that deeper truths wait for their discovery here.

5.2.4. Self-Consistent Green Function Equations for Electrons and Nuclei

Phononic Hamiltonian and Effective Phonon-Phonon Interaction from Mean Fluctuation Field Theory The above discussion is completely symmetric in $\hat{A}$ and $\hat{B}$. For the concrete case of Electronic Structure Theory, we have seen that mean fluctuation theory replaces the purely electronic Hamiltonian consisting of a kinetic term and an electron-electron interaction (through the Coulomb potential) with a Hamiltonian consisting of the original Hamiltonian plus the external potential of the nuclei (corresponding to the mean field Hamiltonian) and the effective phonon-mediated electron-electron interaction (corresponding to the mean fluctuation field Hamiltonian). By symmetry, the same should apply to the nuclei. In other words, the corresponding Hamiltonian for the nuclei reads

$$\hat{H}_{\text{nucl}}^{\text{MFF}}(t) = -\frac{\hbar^2}{2M}\sum_{i=1}^{N}\Delta_i + \frac{1}{2}\sum_{i,j=1}^{N}v(\mathbf{x}_i,\mathbf{x}_j) + \int \text{d}\mathbf{x}\text{d}\mathbf{x}'\,\rho_{\text{el}}^0(\mathbf{x}')v(\mathbf{x}',\mathbf{x})\hat{\rho}_{\text{nucl}}(\mathbf{x})$$

$$+\frac{1}{2}\int \text{d}\mathbf{x}\text{d}x'\text{d}x''\text{d}x'''\,\delta\hat{\rho}_{\text{nucl}}(\mathbf{x}t)v(x,x')\chi_{\text{el}}(x',x'')v(x'',x''')\delta\hat{\rho}_{\text{nucl}}(x''').\tag{5.167}$$

Here, χ_{el} corresponds to the electronic density response function. The third term of the Hamiltonian is the external potential of the electrons exerted on the nuclei. The fourth term is the effective nucleus-nucleus ("phonon-phonon") interaction mediated by electrons. We will now show that this Hamiltonian in fact reproduces (or even generalizes) the usual phononic Hamiltonian. For this purpose, we recall that in Electronic Structure Theory the phononic Hamiltonian is derived from the second derivatives

$$\frac{\partial^2 E}{\partial\mathbf{u}(\mathbf{x}_{\mathbf{n}0})\partial\mathbf{u}(\mathbf{x}_{m0})}\big|_{\mathbf{u}=0}.\tag{5.168}$$

The inter-nuclear Coulomb potential and the kinetic energy are present in both approaches and therefore do not have to be treated. Hence, we restrict our attention to the case where E is given by the electronic energy in the external potential of the nuclei considered as a functional of these very nuclear position. In other words, we consider the contribution

$$E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle\tag{5.169}$$

with the electronic Hamiltonian

$$\hat{H} = \hat{T}_{\text{kin}} + \hat{V}_{\text{el}-\text{el}} + \hat{V}_{\text{ext}}.\tag{5.170}$$

Now, by the Hellmann-Feynman theorem we have

$$\frac{\partial E_0}{\partial \mathbf{u}(\mathbf{x_{n0}})} = \langle \Psi_0 | \frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{u}(\mathbf{x_{n0}})} | \Psi_0 \rangle. \tag{5.171}$$

Hence, with second order perturbation theory, we find

$$\frac{\partial^2 E_0}{\partial \mathbf{u}(\mathbf{x_{n0}}) \partial \mathbf{u}(\mathbf{x_{m0}})} = \langle \Psi_0 | \frac{\partial^2 \hat{V}_{\text{ext}}}{\partial \mathbf{u}(\mathbf{x_{n0}}) \partial \mathbf{u}(\mathbf{x_{m0}})} | \Psi_0 \rangle + 2\Re\mathfrak{e} \sum_s \frac{\langle \Psi_0 | \frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{x_n}} | \Psi_s \rangle \langle \Psi_s | \frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{x_m}} | \Psi_0 \rangle}{E_0 - E_s}.$$

The first term simply corresonds to the quadrupole moment $\delta_{\mathbf{mn}} \mathbf{Q}(\mathbf{x}, \mathbf{x_{n0}})$ integrated against the electronic ground-state density $\rho(\mathbf{x})$. For the second term, we observe

$$\hat{V}_{\text{ext}} = \int \mathrm{d}\mathbf{x} \; v_{\text{ext}}(\mathbf{x}) \hat{\rho}(\mathbf{x}) \tag{5.172}$$

$$= \int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; \rho_{\text{nucl}}(\mathbf{x}') v(\mathbf{x}', \mathbf{x}) \hat{\rho}(\mathbf{x}) \tag{5.173}$$

$$= \sum_{\mathbf{n}} \int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; (\delta(\mathbf{x}' - \mathbf{x_{n0}}) - \mathbf{u}(\mathbf{x_{n0}}) \cdot (\nabla \delta)(\mathbf{x}' - \mathbf{x_{n0}})) v(\mathbf{x}', \mathbf{x}) \hat{\rho}(\mathbf{x}) \tag{5.174}$$

and hence

$$\frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{x_m}} = -\int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; (\nabla \delta)(\mathbf{x}' - \mathbf{x_{m0}})) v(\mathbf{x}', \mathbf{x}) \hat{\rho}(\mathbf{x}) = \int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; \mathbf{E}(\mathbf{x_{m0}}, \mathbf{x}) \hat{\rho}(\mathbf{x}). \tag{5.175}$$

We then find

$$2\Re\mathfrak{e} \sum_s \frac{\langle \Psi_0 | \frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{x_n}} | \Psi_s \rangle \langle \Psi_s | \frac{\partial \hat{V}_{\text{ext}}}{\partial \mathbf{x_m}} | \Psi_0 \rangle}{E_0 - E_s} \tag{5.176}$$

$$= 2\Re\mathfrak{e} \int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; \mathbf{E}(\mathbf{x_{m0}}, \mathbf{x}) \sum_s \frac{\langle \Psi_0 | \hat{\rho}(\mathbf{x}) | \Psi_s \rangle \langle \Psi_s | \hat{\rho}(\mathbf{x}') | \Psi_0 \rangle}{E_0 - E_s} \mathbf{E}(\mathbf{x_{n0}}, \mathbf{x}') \tag{5.177}$$

$$= -\int \mathrm{d}\mathbf{x} \mathrm{d}\mathbf{x}' \; \mathbf{E}(\mathbf{x_{m0}}, \mathbf{x}) \chi_{\text{el}}(\mathbf{x}, \mathbf{x}'; \omega = 0) \mathbf{E}(\mathbf{x}', \mathbf{x_{n0}}). \tag{5.178}$$

After summation over the nuclear coordinates and multiplication with $1/2\mathbf{u}(\mathbf{x_{n0}})\mathbf{u}(\mathbf{x_{m0}})$ (second order Taylor expansion), this equals

$$\frac{1}{2} \int \mathrm{d}\mathbf{x} \mathrm{d}x' \mathrm{d}x'' \mathrm{d}x''' \; \delta\hat{\rho}_{\text{nucl}}(\mathbf{x}t) v(x, x') \chi_{\text{el}}(x', x'') v(x'', x''') \delta\hat{\rho}_{\text{nucl}}(x''')$$

upon the idenitification $\delta\hat{\rho}_{\text{nucl}}(\mathbf{x}t) = -\sum_{\mathbf{n}} \hat{\mathbf{u}}(\mathbf{x_{n0}}) \cdot (\nabla \delta)(\mathbf{x} - \mathbf{x_{n0}})$. Consequently, the second term of the energy Hessian matrix simply corresponds to the effective phonon-phonon interaction but with the electronic density response function evaluated at frequency $\omega = 0$.

Dyson Equation for Phonon Propagator The last subsection makes it plausible to identify the dynamical matrix $\mathbf{K}$ in the free equation

$$\left(M\partial_t^2 + \mathbf{K}\right)\mathbf{D}^0_{\mathrm{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t') = \delta(t-t')\delta_{\mathbf{nm}}\mathbb{1}_{3\times 3} \tag{5.179}$$

with the second order expansion of the internuclear Coulomb potential plus the quadrupole term $\delta_{\mathbf{mn}}\int \mathrm{d}\mathbf{x}\,\rho_{\mathrm{el}}(\mathbf{x})\mathbf{Q}(\mathbf{x}, \mathbf{x_{n0}})$. The full propagator then fulfills

$$\left(M\partial_t^2 + \mathbf{K} - \mathbf{P}\right)\mathbf{D}_{\mathrm{phon}}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t') = \delta(t-t')\delta_{\mathbf{nm}}\mathbb{1}_{3\times 3} \tag{5.180}$$

where

$$\mathbf{P}(\mathbf{x_{n0}}t, \mathbf{x_{m0}}t') = \int \mathrm{d}\mathbf{x}\mathrm{d}\mathbf{x}'\,\mathbf{E}(\mathbf{x_{n0}}, \mathbf{x})\chi_{\mathrm{el}}(\mathbf{x}t, \mathbf{x}'t')\mathbf{E}(\mathbf{x}', \mathbf{x_{m0}}). \tag{5.181}$$

Here, $\mathbf{P}$ is a 3×3 matrix and $\mathbf{EE}$ is to be understood as the tensor product of the vectors. An elementary reasoning (cf. e.g. subsection $(1.2.2)$)[41] shows that these propagators are related through

$$\mathbf{D}_{\mathrm{phon}} = \mathbf{D}^0_{\mathrm{phon}} + \mathbf{D}^0_{\mathrm{phon}}\mathbf{P}\mathbf{D}_{\mathrm{phon}}. \tag{5.182}$$

This is the Dyson equation for the phonon propagator.[42] $\mathbf{P}$ is the phononic self-energy. Note, however, that as compared to the electronic self-energy, the phononic self-energy is of a completely different nature because $\mathbf{P}$ is not a functional of $\mathbf{D}_{\mathrm{phon}}$ while Σ is a functional of G. Therefore, the Dyson equation for the phonon propagator is actually not a Dyson equation but a mere resolvent identity.

Green Function Equations for Electrons and Nuclei The decisive insight of the last paragraph is that the phononic self-energy is not a functional of the phonon propagator. Therefore, the phononic Green function theory consists of only one equation, namely the phononic Dyson equation, as opposed to three equations in the case of the electronic Green function theory. We are now in a position to combine electronic and phononic Green function theory into a closed, self-consistent set of equations which is the ultimate goal of this thesis. These equations read

$$G = G_0 - \mathrm{i}\hbar G_0 W \cdot \tilde{L} \tag{5.183}$$

$$W = V_{\mathrm{tot}} + \mathrm{i}\hbar V_{\mathrm{tot}}\tilde{L}W \tag{5.184}$$

$$\tilde{L} = L_0 + \mathrm{i}\hbar L_0 \tilde{I}\tilde{L} \tag{5.185}$$

$$V_{\mathrm{tot}} = V_{\mathrm{Coul}} + V_{\mathrm{phon}} \tag{5.186}$$

$$\mathbf{D}_{\mathrm{phon}} = \mathbf{D}^0_{\mathrm{phon}} + \mathbf{D}^0_{\mathrm{phon}}\mathbf{P}\mathbf{D}_{\mathrm{phon}}. \tag{5.187}$$

---

[41]Even more easier, this equation can be shown by multiplying through with $(\mathbf{D}^0_{\mathrm{phon}})^{-1} = M\partial_t^2 + \mathbf{K}$ which yields directly the equation of motion for the full propagator $\mathbf{D}_{\mathrm{phon}}$.

[42]The Dyson equation for the phonon propagator has been derived – apparently for the first time – by Engelsberg and Schrieffer ([19], equation (A.15)) by a completely different method.

The nature of these equations is clear now: the first three equations simply correspond to the electronic, self-consistent propagator equations with the Coulomb potential replaced by the total (electron + phonon-induced) interaction (equation (5.186)). Note in this context that the self-consistent set of equations is independent of the interaction V as long as it is of a two-particle type. Equation (5.187) is the aforementioned Dyson equation for the phonon propagator. These equations have to be supplemented by the following definitions (in symbolic notation):

$$V_{\text{phon}} = v\chi_{\text{nucl}}v \tag{5.188}$$

$$\mathbf{P} = \mathbf{E}\chi_{\text{el}}\mathbf{E} \tag{5.189}$$

$$\chi_{\text{nucl}} = e^2(\nabla\delta)\mathbf{D}_{\text{phon}}(\nabla\delta) \tag{5.190}$$

$$\chi_{\text{el}} = L \tag{5.191}$$

$$L = \tilde{L} + \tilde{L}VL \tag{5.192}$$

$$G_0 = (\text{i}\hbar\partial_t - \hat{H}_0 - v_{\text{H}})^{-1}. \tag{5.193}$$

The phonon induced interaction has been left out of the reference propagator G_0 because – as has been discussed already – it is plausible that the phonon induced interaction is a pure fluctuation interaction and does therefore not contribute a Hartree type term.

The self-consistent Green function equations for electrons and phonons are a result of the interplay between Linear Response Theory, Green function theory and the theory of effective interactions.

A. Appendices

A.1. Complex Tensor Calculus

Definitions We consider $\mathcal{H} = \mathbb{C}^N$ with the standard scalar product $\langle \cdot | \cdot \rangle$ and a 'coordinate transformation', i.e. an invertible, l inear mapping $\hat{U} : \mathbb{C}^N \to \mathbb{C}^N$. We think of $\mathbb{C}^N$ as a discretized Hilbert space and denote the standard basis by φ_i, i.e. $\langle \varphi_i | \varphi_j \rangle = \delta^i{}_j$. All results carry over immediately to a separable Hilbert space $\simeq \ell^2$. By the Riesz theorem, we identify the dual Hilbert space with the complex conjugate vector space via the scalar product

$$\varphi^i := \langle \varphi_i | \cdot \rangle. \tag{A.1}$$

As opposed to the real tensor calculus, we have to differentiate between 4 different transformation behaviours.

1. The basis in $\mathcal{H}$ transforms with

$$U^i{}_j = \langle \varphi_i | \hat{U} | \varphi_j \rangle, \tag{A.2}$$

2. Expansion coefficients a^i of a vector $\varphi \in \mathcal{H}$ with respect to the basis φ_i transform with the contragredient matrix $(U^{\mathrm{T}})^{-1}$.

3. Expansion coefficients a_i of a dual vector transform with the complex conjugate of the contragredient matrix $((U^*)^{\mathrm{T}})^{-1}$.

4. The dual basis transforms with the complex conjugate matrix U^*.

In principle, this necessitates the introduction of four different kinds of indices (as with the four fundamental representations of the Lorentz group (or rather its covering group $\mathrm{SL}(2, \mathbb{C})$)). In this text, however, we can restrict attention to the transformation properties of vectors and dual vectors. With these, we associate upper and lower indices transforming as

$$b^i = U^i{}_j a^j \tag{A.3}$$
$$b_i = U_i{}^j a_j \tag{A.4}$$

where a summation convention is understood. Now, if a^i are the expansion coefficient of a vector with respect to a certain basis then the corresponding dual vector has expansion coefficients $a_i = (a^i)^*$. Therefore, under a change of basis with a matrix $U^i{}_j$,

$$b_i = (b^i)^* = (U^i{}_j a^j)^* \overset{!}{=} U_i{}^j a_j. \tag{A.5}$$

It follows that indices can be drawn up and down by complex conjugation; in particular

$$U_i{}^j = (U^i{}_j)^*. \tag{A.6}$$

If we further restrict attention to transformations from one complete orthogonal system to another, then $\hat{U}$ is necessarily unitary and the dual basis transforms like the vector coefficients and the basis like the dual vector coefficients. The general tensor calculus can now easily be derived by considering multilinear mappings from the various tensor products of $\mathcal{H}$ and its dual to the complex numbers. Furthermore, note that by the above definition in any basis φ_i the dual basis is given by $\varphi^i = \langle\varphi_i|\cdot\rangle$. Therefore, in general (i.e. in an arbitrary basis) $\varphi^i(\varphi_j) \neq \delta^i{}_j$. This is in contrast to general relativity where the dual basis of a real vector space is defined by $\mathbf{e}^i(\mathbf{e}_j) = \delta^i{}_j$ whereas the dual vector is still defined by $y_\mu = g(y^\mu, \cdot)$ (abstract index notation [98]). More precisely this means[1]: If E is a vector space with metric $g : E \times E \to \mathbb{R}$ and E^* the dual space, then $\forall y \in E$, $g(y, \cdot)$ is a dual vector the components of which with respect to the standard dual basis are given by $y_\nu = g_{\nu\mu} y^\mu$ where $g_{\mu\nu} = g(\mathbf{e}_\mu, \mathbf{e}_\nu)$. The proof reads $\forall x \in E$:

$$g(y, x) = y(x) = (y_\nu \mathbf{e}^\nu)(x^\mu \mathbf{e}_\mu) = y_\nu x^\mu \mathbf{e}^\nu(\mathbf{e}_\mu) = y_\nu x^\nu = g_{\mu\nu} y^\mu x^\nu. \tag{A.7}$$

Now, in our case we can consider the scalar product as a sesqui-linear mapping $\mathcal{H}^* \times \mathcal{H} \to \mathbb{C}$ given by the matrix $\delta_i{}^j$ in the standard basis. Both definitions of the dual basis then coincide as long as the transformation $\hat{U}$ conserves the form of the scalar product. This is just the case for the unitary transformations for which U^* *is* the contragredient matrix.

---

[1]In general relativity, this applies to the tangent space $T_x\mathcal{M}$ where $\mathbf{e}_\mu = \partial_\mu$, $\mathbf{e}^\nu = \mathrm{d}\mathbf{x}^\nu$ etc.

A.2. Fourier Transformation

A.2.1. Definitions and Conventions

Definition For Schwartz functions, the Fourier transform and its inverse are defined by

$$\mathcal{F}[\psi](\mathbf{k}) \equiv \tilde{\psi}(\mathbf{k}) \ = \ \int d\mathbf{x} \ \psi(\mathbf{x}) \exp(-i\mathbf{k}\mathbf{x}) \tag{A.8}$$

$$\psi(\mathbf{x}) = \mathcal{F}^{-1}[\tilde{\psi}](\mathbf{x}) \ = \ \int \frac{d\mathbf{k}}{(2\pi)^3} \ \tilde{\psi}(\mathbf{k}) \exp(i\mathbf{k}\mathbf{x}). \tag{A.9}$$

Remarks

1. The *BLT theorem* says: For a bounded linear transformation T from a normed linear space $(V_1, \|\cdot\|_1)$ to a complete normed linear space $(V_2, \|\cdot\|_2)$, there exists an unique extension $\tilde{T}$ which maps the completion of $(V_1, \|\cdot\|_1)$ to $(V_2, \|\cdot\|_2)$. This extension is again linear and bounded with the same bound: $\|T\| = \|\tilde{T}\|$ where $\|\cdot\|$ denotes the operator norm. The importance of the BLT theorem lies in the following: The existence and isometric character of the Fourier transform for a Schwartz function is easy to verify. As the Schwartz functions are dense in the Hilbert space of square-integrable functions, the Fourier transform can be uniquely extended to $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$.

2. Conventions for Quantum Mechanics: A plane wave is of the form

$$\psi(\mathbf{x}t) = \exp(i\mathbf{k}\mathbf{x} - i\omega t). \tag{A.10}$$

This solves the free Schrödinger equation

$$i\hbar\partial_t\psi(\mathbf{x}t) = -\frac{\hbar^2}{2m}\Delta\psi(\mathbf{x}t) \tag{A.11}$$

iff $\omega = \omega(\mathbf{k}) = \frac{\hbar k^2}{2m}$. The general solution of the free equation then reads:

$$\psi(t, \mathbf{x}) = \int d\mathbf{k} \ f(\mathbf{k}) \exp(i\mathbf{k}\mathbf{x} - i\omega t) = \int d\mathbf{k} \ f(\mathbf{k}, t) \exp(i\mathbf{k}\mathbf{x}). \tag{A.12}$$

This suggests to define

$$\hat{\psi}(\mathbf{k}, \omega) \ = \ \int d\mathbf{x}dt \ \exp\left(-i\mathbf{k}\mathbf{x} + i\omega t\right) \psi(\mathbf{x}t). \tag{A.13}$$

$$\psi(\mathbf{x}t) \ = \ \int \frac{d\mathbf{k}d\omega}{(2\pi)^4} \ \exp\left(i\mathbf{k}\mathbf{x} - i\omega t\right) \tilde{\psi}(\mathbf{k}, \omega). \tag{A.14}$$

The important thing to remember about this equation is that in Quantum Mechanics the Fourier Transform with respect to t corresponds to the inverse Fourier transform. The equations can be written more concisely by introducing a Minkowski space notation $x = (\mathbf{x}t)$, $k = (\omega, \mathbf{k})$ and $kx = \omega t - \mathbf{k}\mathbf{x}$.

A.2.2. Discretization

Definition The linear mapping $\hat{U} : \mathbb{C}^N \to \mathbb{C}^N$ defined by the matrix

$$U_{ij} = \frac{1}{\sqrt{N}} \exp\left(-\mathrm{i}\frac{2\pi}{N}ij\right). \tag{A.15}$$

in the standard basis is called *discrete Fourier transform*.

Lemma A.2.1 $\hat{U}$ *is a unitary transformation.*

Proof The adjoint matrix $\hat{U}^\dagger$ is given by

$$(\hat{U}^\dagger)_{ij} = \frac{1}{\sqrt{N}} \exp\left(\mathrm{i}\frac{2\pi}{N}ji\right). \tag{A.16}$$

Hence, we find

$$
\begin{aligned}
\sum_{k=1}^{N} U_{ik}(U^\dagger)_{kj} &= \frac{1}{N} \sum_{k=1}^{N} \exp\left(-\mathrm{i}\frac{2\pi}{N}(ik - kj)\right) \\
&= \frac{1}{N} \sum_{k=1}^{N} \exp\left(-\mathrm{i}\frac{2\pi}{N}(i - j)k\right) \\
&= \frac{1}{N} \sum_{k=1}^{N} \left(\exp\left(-\mathrm{i}\frac{2\pi}{N}(i - j)\right)\right)^k \\
&= \frac{1}{N} \frac{\exp\left(-\mathrm{i}\frac{2\pi}{N}(i - j)\right) - \exp\left(-\mathrm{i}\frac{2\pi}{N}(N + 1)(i - j)\right)}{1 - \exp\left(-\mathrm{i}\frac{2\pi}{N}(i - j)\right)}
\end{aligned}
$$

This equals 0 for

$$\exp\left(-\mathrm{i}\frac{2\pi}{N}(i - j)\right) \neq 1. \tag{A.17}$$

If this condition is not fulfilled, then $i = j$ and $\sum_{k=1}^{N} \exp\left(-\mathrm{i}\frac{2\pi}{N}(ik - kj)\right) = N$. Therefore

$$\sum_{k=1}^{N} U_{ik}(U^\dagger)_{kj} = \delta_{ij}. \tag{A.18}$$

Remark In particular, the discrete Fourier transform conserves the standard scalar product in $\mathbb{C}^N$ given by

$$\langle f | g \rangle = \sum_{i=1}^{N} f_i^* g_i. \tag{A.19}$$

Reinterpetation as a Space of Functions Consider the group

$$\mathbb{Z}_N = \mathbb{Z}/N\mathbb{Z} = \{1, 2, \ldots, N\} \tag{A.20}$$

as a finite set. A function $f : \mathbb{Z}_N \to \mathbb{C}$ is uniquely defined by its values on each element of its domain. In other words, such a function is given by a vector $(f_1, \ldots, f_N)$ with complex entries. This shows that the vector space $\mathcal{H}$ of functions $f : \mathbb{Z}_N \to \mathbb{C}$ is isomorphic to $\mathbb{C}^N$. We now reinterpret $\mathbb{Z}_N$ as an equally spaced lattice in $[0, L] = \mathbb{R}/L\mathbb{Z}$ with $L = Na$ and lattice points $\{a, 2a, \ldots, Na\}$. We denote this lattice by $\Gamma_{a,N} = a\mathbb{Z}_N$. We rewrite

$$\exp\left(-\mathrm{i}\frac{2\pi}{N}ij\right) = \exp\left(-\mathrm{i}\frac{2\pi j}{aN}ai\right) = \exp\left(-\mathrm{i}kx\right) \tag{A.21}$$

with $x = x_i = ia \in \Gamma_{a,N}$ and $k = k_j = 2\pi j/L$. We define a dual lattice $\Gamma^*_{a,N}$ by

$$\Gamma^*_{a,N} = \frac{2\pi}{L}\mathbb{Z}_N = \Gamma_{\frac{2\pi}{L},N}. \tag{A.22}$$

such that $k \in \Gamma^*_{a,L}$ and $L^* = 2\pi/a$. We define discrete integrations

$$\int_{\Gamma_{a,N}} \mathrm{d}x \, f(x) = a \sum_{i=1}^{N} f(x_i) \tag{A.23}$$

$$\int_{\Gamma^*_{a,N}} \mathrm{d}k \, \tilde{f}(k) = \frac{2\pi}{L} \sum_{i=1}^{N} \tilde{f}(k_i) \tag{A.24}$$

$$\tag{A.25}$$

for functions $f : \Gamma_{a,N} \to \mathbb{C}$ and $\tilde{f} : \Gamma^*_{a,N} \to \mathbb{C}$. Furthermore, we define the respective scalar products as

$$\langle f | f \rangle_{\Gamma} = \int_{\Gamma_{a,N}} \mathrm{d}x \, f^*(x)f(x) = a \sum_{i=1}^{N} f^*(x_i)f(x_i) \tag{A.26}$$

$$\langle \tilde{f} | \tilde{f} \rangle_{\Gamma^*} = \int_{\Gamma^*_{a,N}} \mathrm{d}k \, f^*(k)f(k) = \frac{2\pi}{L} \sum_{i=1}^{N} \tilde{f}^*(k_i)f(k_i). \tag{A.27}$$

We now want to redefine the Fourier transform such that it is unitary with respect to these scalar products. By inspection we see that we have to rescale with a factor

$$\sqrt{\frac{L}{2\pi a}} = \sqrt{\frac{N}{2\pi}} \tag{A.28}$$

leading to matrix elements

$$U_{ij} = \frac{1}{\sqrt{2\pi}} \exp\left(-\mathrm{i}\frac{2\pi}{N}ij\right) = \frac{1}{\sqrt{2\pi}} \exp\left(-\mathrm{i}k_j x_i\right). \tag{A.29}$$

The Fourier transforms for lattice functions now read

$$\tilde{f}(k) = \frac{1}{\sqrt{2\pi}} \int_{\Gamma} \mathrm{d}x \, \mathrm{e}^{-\mathrm{i}kx} f(x) \tag{A.30}$$

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{\Gamma^*} \mathrm{d}k \, \mathrm{e}^{\mathrm{i}kx} \tilde{f}(k). \tag{A.31}$$

$$\tag{A.32}$$

In particular, we find

$$\frac{1}{2\pi} \int_{\Gamma^*} \mathrm{d}k \, \mathrm{e}^{\mathrm{i}k(x-x')} \;\; = \;\; a^{-1}\delta_{ij} \tag{A.33}$$

with $x = x_i = ia$, $x' = x_j = ja$.

A.3. Laplace Transformation, Hilbert Transformation & All That

A.3.1. Fourier Transformation and Complex Analysis

Theorem A.3.1 *(Residue Theorem) Let f be a meromorphic function: $U \to \mathbb{C}$. Let C be a piece-wise continuous, closed path which lies in the open set $U \subset \mathbb{C}$. Let f have the poles $z_1, \ldots, z_m$ inside the region enclosed by C and no poles on C. Then the following equation holds:*

$$\frac{1}{2\pi \mathrm{i}} \int_C f(z)\mathrm{d}z = \sum_{k=1}^{m} \mathrm{Res}_f(z_k) \tag{A.34}$$

where the integration is supposed to go along C in the anticlockwise sense. ([100], p.215)

Theorem A.3.2 *(Cauchy integral formula) Let f be holomorphic on U and C a piece-wise continuous, closed path in U. Then, the following equation holds:*

$$f(z_0) = \frac{1}{2\pi \mathrm{i}} \int_C \mathrm{d}z \, \frac{f(z)}{z - z_0}. \tag{A.35}$$

In particular, $f(z_0)$ is the residue in z_0 of the function $\frac{f(z)}{z-z_0}$.

Application to Fourier Transforms Consider the special case $f(t) = \exp(-\frac{\mathrm{i}}{\hbar}Et)$ with the complex energy $E \in \mathbb{C}$. The Cauchy integral formula then yields

$$\exp\left(-\frac{\mathrm{i}}{\hbar}E_0 t\right) = \frac{1}{2\pi \mathrm{i}} \int_C \mathrm{d}E \, \frac{\exp\left(-\frac{\mathrm{i}}{\hbar}Et\right)}{E - E_0}. \tag{A.36}$$

where the integration path is supposed to be homotopic to a circle around E_0. In the case of a Fourier transform however, one does not integrate along a closed path but along the real line. This can be remedied by using an auxiliary path in the upper or lower half plane, e.g. a half-circle with radius r and shifting the poles by a small amount $\eta \in \mathbb{R}_+$. The integral is then evaluated with the Cauchy formula by choosing a contour in the half-plane in which the exponential decays. In the limit $r \to \infty$, the contribution of the auxiliary path

vanishes and the integration along the real line recovers the original Fourier transform. For the exponential, this can be summarized in the master formula

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}E}{2\pi} \, \frac{\exp(-\mathrm{i}Et/\hbar)}{E \mp (E_0 - \mathrm{i}\eta)} = \mp \mathrm{i}\theta(\pm t) \exp\left(\mp \frac{\mathrm{i}}{\hbar}(E_0 - \mathrm{i}\eta)t\right). \tag{A.37}$$

The $\mp$ sign in front is due to the fact that in one case one encloses the poles clockwise whereas in the other case one encloses the poles anticlockwise. The Heaviside function stems from the fact that the auxiliary contour has to be chosen such that the respective contribution vanishes. It then depends on the sign of t whether one closes the contour in the lower or in the upper half-plane. Only in one case the contour then encloses the poles. In the other case, the contour encloses no poles and the respective integral vanishes. The converse directions can be shown even more easily, e.g.

$$
\begin{aligned}
-\int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{i}\theta(t) \exp\left(\frac{\mathrm{i}}{\hbar}(E - E_0 + \mathrm{i}\eta)t\right) &= -\mathrm{i} \int_0^{\infty} \mathrm{d}t \, \exp\left(-\frac{\mathrm{i}}{\hbar}(-E + E_0 - \mathrm{i}\eta)t\right) \\
&= -\hbar \frac{\exp\left(-\frac{\mathrm{i}}{\hbar}(-E + E_0 - \mathrm{i}\eta)t\right)|_0^{\infty}}{E - E_0 + \mathrm{i}\eta} \\
&= \frac{\hbar}{E - E_0 + \mathrm{i}\eta}.
\end{aligned}
$$

We will now see that we simply redefined a formal ansatz for a Fourier transform as a boundary value of a Laplace transform.

A.3.2. Laplace Transformation

Standard Definition The Laplace Transform $\hat{f}(k)$ of $f(x)$ and its inverse are defined by

$$\mathcal{L}[f(t)] \equiv \hat{f}(p) = \int_0^{\infty} \mathrm{d}t \, \exp(-pt)f(t) \tag{A.38}$$

$$\mathcal{L}^{-1}[\hat{f}(p)] = \frac{1}{2\pi\mathrm{i}} \int_{c-\mathrm{i}\infty}^{c+\mathrm{i}\infty} \mathrm{d}p \, \exp(pt)\hat{f}(p) \tag{A.39}$$

where $p = c + \mathrm{i}d \in \mathbb{C}$. For the sake of Quantum Mechanics it is useful to redefine $p = -\mathrm{i}E$ with $E \in \mathbb{C}$ and

$$\mathcal{L}[f(t)] \equiv \hat{f}(E) = \int_0^{\infty} \mathrm{d}t \, \exp(\mathrm{i}Et)f(t) \tag{A.40}$$

$$\mathcal{L}^{-1}[\hat{f}(E)] = \frac{1}{2\pi} \int_{-\infty+\mathrm{i}\Gamma}^{\infty+\mathrm{i}\Gamma} \mathrm{d}E \, \exp(-\mathrm{i}Et)\hat{f}(E). \tag{A.41}$$

On the real axis – i.e. in the limit $\mathfrak{Im}(E) = \Gamma \to 0$ – the Laplace Transform then reads

$$\mathcal{L}[f(t)] \equiv \hat{f}(E) \;\; = \;\; \int_{-\infty}^{\infty} \mathrm{d}t \; \theta(t) \exp(\mathrm{i}Et) f(t) \tag{A.42}$$

$$\mathcal{L}^{-1}[\hat{f}(E)] \;\; = \;\; \frac{1}{2\pi} \int_{-\infty}^{\infty} \mathrm{d}E \; \exp(-\mathrm{i}Et) \hat{f}(E) = \begin{cases} f(t) & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{cases} \tag{A.43}$$

Remarks

1. Disregarding domains of definition, the Fourier transform of a *retarded* function is the boundary value of a Laplace Transform with $\mathfrak{Im}(E) \to 0$. For $t > 0$ *every* Fourier back transform can be interpreted as the boundary value of a Laplace transform with $\mathfrak{Im}(E) \to 0$. Conversely, the boundary value of a Laplace Transform does not necessarily yield the Fourier Transform of a function. In general, it will yield a distribution.

2. The *Paley-Wiener Theorem* says: For each test function with compact support, the Laplace transform is holomorphic in the complex energy plane and satisfies $\forall N \in \mathbb{N}$:

$$|\hat{f}(E)| \le C_1 \frac{\exp(C_2|\mathfrak{Im}(E)|)}{(1 + |E|)^N}. \tag{A.44}$$

   with appropriate constants C_1, C_2 and vice-versa.

3. The *Schwartz Theorem* says: Each compactly supported distribution has a holomorphic Laplace transform satisfying

$$|G(E)| \le \exp(C_2|\mathfrak{Im}(E)|)(1 + |E|)^N. \tag{A.45}$$

   for some fixed natural N. Conversely, a holomorphic function satisfying the above growth condition is the Laplace transform of a compactly supported distribution.

The general connection between the Laplace transform, the Fourier transform and the Hilbert transform is given by the following theorem which we write in a way that its relation to the retarded response function should be evident.

Theorem A.3.3 *(Titchmarsh Lemma) For a square integrable function $\chi(\omega)$ the following is equivalent*

1. *The Fourier preimage $\chi(\tau)$ satisfies:*

$$\chi(\tau) = 0 \quad (\tau < 0). \tag{A.46}$$

2. $\chi(\omega)$ *is the boundary value for* $\eta \to 0$ *of a holomorphic function* $\chi(\omega + \mathrm{i}\eta)$ *in the upper complex energy plane which is square-integrable along every line parallel to the real axis in the upper half-plane*

3. *The real and the imaginary part of* $\chi(\omega)$ *are interrelated by a Hilbert transform:*

$$\mathfrak{Re}(\chi)(\omega) \;=\; \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \mathrm{d}\omega' \, \frac{\mathfrak{Im}(\chi)(\omega')}{\omega' - \omega} \tag{A.47}$$

$$\mathfrak{Im}(\chi)(\omega) \;=\; -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \mathrm{d}\omega' \, \frac{\mathfrak{Re}(\chi)(\omega')}{\omega' - \omega}. \tag{A.48}$$

These are called Kramers-Kronig relations.

A.3.3. Pole-Shift Formula

An important integral which we used main text is given by the convolution

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\omega' \, \frac{1}{\omega' - \varepsilon_i + \mathrm{i}\eta} \frac{1}{\omega - \omega' - \varepsilon_j + \mathrm{i}\eta}. \tag{A.49}$$

This can be solved in at least four different manners: by a brute force approach through direct integration, by the help of the residue theorem, by the Cauchy formula and and by the Convolution Theorem. The last one is certainly the most elegant method. By the convolution theorem, the Fourier transform of $\tilde{f}(\omega)$ is given by the point-wise product of

$$g(t) = 2\pi \mathrm{i}\theta(t) \exp(-\mathrm{i}\varepsilon_i t) \tag{A.50}$$

and

$$h(t) = 2\pi \mathrm{i}\theta(t) \exp(-\mathrm{i}\varepsilon_j t) \tag{A.51}$$

which yields

$$\tilde{f}(\omega) = \frac{2\pi \mathrm{i}}{\omega - (\varepsilon_i + \varepsilon_j) + \mathrm{i}\eta}. \tag{A.52}$$

Equally important is the integral

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\omega' \, \frac{1}{\omega' - \varepsilon_i + \mathrm{i}\eta} \frac{1}{\omega + \omega' - \varepsilon_j - \mathrm{i}\eta}. \tag{A.53}$$

This can be rewritten as

$$-\int_{-\infty}^{\infty} \mathrm{d}\omega' \, \frac{1}{\omega' - \varepsilon_i + \mathrm{i}\eta} \frac{1}{-\omega - \omega' + \varepsilon_j + \mathrm{i}\eta}. \tag{A.54}$$

Therefore, we now have

$$\tilde{f}(\omega) = \frac{2\pi \mathrm{i}}{\omega - (\varepsilon_j - \varepsilon_i) + \mathrm{i}\eta} = \frac{2\pi \mathrm{i}}{\omega - (\varepsilon_j - \varepsilon_i) + \mathrm{i}\eta}. \tag{A.55}$$

This result will be called *pole-shift formula* because it shows that the convolution of fractions of the form $1/(\omega - \varepsilon_i)$ leaves the functional form invariant but shifts the pole to the difference $\varepsilon_i - \varepsilon_j$.

A.4. Classical Harmonic Oscillator and Linear Response

Green Function Approach Consider the classical, one-dimensional, damped harmonic oscillator

$$m(\ddot{x} + \Gamma\dot{x} + \omega_0^2 x) = 0. \tag{A.56}$$

How does $x(t)$ change upon external perturbation? To answer this question, one has to include a perturbative term $e\delta E(t)$ in the equation of motion

$$m(\ddot{x} + \Gamma\dot{x} + \omega_0^2 x) = e\delta E(t) \tag{A.57}$$

corresponding to an interaction Hamiltonian $H_{\text{int}} = -ex(t)\delta E(t)$. To solve for the perturbed equation of motion, we use the method of Green functions

$$m\left(\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \Gamma\frac{\mathrm{d}}{\mathrm{d}t} + \omega_0^2\right) G(t - t') = \delta(t - t'). \tag{A.58}$$

In the Fourier domain we then get

$$m\left(-\omega^2 - \mathrm{i}\Gamma\omega + \omega_0^2\right) G(\omega) = 1. \tag{A.59}$$

Hence

$$G(t - t') = -\frac{1}{m}\int\frac{\mathrm{d}\omega}{2\pi}\frac{\exp(-\mathrm{i}\omega(t - t'))}{\omega^2 - \omega_0^2 + \mathrm{i}\Gamma\omega} = \theta(t - t')\frac{\sin(\omega_1(t - t'))}{m\omega_1}\exp\left(-\frac{\Gamma}{2}(t - t')\right) \tag{A.60}$$

with $\omega_1 = \sqrt{\omega_0^2 - \Gamma^2/4}$. The solution to the perturbed system then reads

$$x(t) - x_0(t) \equiv \delta x(t) = \int \mathrm{d}t'\, G(t - t')\delta E(t'). \tag{A.61}$$

Electromagnetic Properties The "susceptibility" in this case is defined as minus[2] the derivative of the "polarization" ex with respect to the external field $E \equiv E_{\text{ext}} := D/\varepsilon_0$. In the Fourier domain, we get

$$\chi(\omega) = -\frac{\delta x(\omega)}{\delta D(\omega)} = \frac{e^2}{\varepsilon_0 m}\frac{1}{\omega^2 - \omega_0^2 + \mathrm{i}\Gamma\omega} \tag{A.62}$$

The "conductivity" in turn is defined as the derivative of the "current" $j = e\dot{x}$ with respect to the external field E.

$$\sigma(\omega) = \frac{\delta j(\omega)}{\delta E(\omega)} = \frac{e^2}{m}\frac{\mathrm{i}\omega}{\omega^2 - \omega_0^2 + \mathrm{i}\Gamma\omega} \tag{A.63}$$

---

[2]We include the minus sign in order to make the susceptibility the analog of $\chi = \delta\rho_{\text{ind}}/\delta\varphi_{\text{ext}}$ as in the first part of this work. Standard texts often define $\mathbf{P} = \chi_e\mathbf{E}$. The thus defined susceptibility is the macroscopic counterpart of $-\tilde{\chi}$ (possibly convoluted with the Coulomb kernel).

With $\varepsilon^{-1} = 1 + \chi$ (see below) these relation imply in particular that

$$\varepsilon^{-1} = 1 - \frac{\mathrm{i}}{\varepsilon_0 \omega} \sigma. \tag{A.64}$$

This is of course a standard relation which should be fulfilled for any kind of model. We consider two typical applications.

Lorentz Model of Polarizability Here, one simply considers the medium as being composed of N harmonic oscillators enclosed in the volume V which leads to the susceptibility

$$\chi(\omega) = -\frac{\delta P}{\delta D} = \frac{e^2 N}{m \varepsilon_0 V} \frac{1}{\omega_0^2 - \omega^2 - \mathrm{i}\Gamma\omega} \tag{A.65}$$

for the macroscopic polarization P ("dipole moment per unit volume"). We defined as always $\varepsilon_0 E_{\mathrm{ext}} = D$. This is a standard result. (cf. e.g. [27] p.30f) It implies

$$D = \varepsilon_0 E + P = \varepsilon_0 E - \chi D \tag{A.66}$$

or $(1 + \chi)D = \varepsilon_0 E$. Hence

$$\varepsilon^{-1}(\omega) = 1 + \frac{e^2 N}{m \varepsilon_0 V} \frac{1}{\omega^2 - \omega_0^2 + \mathrm{i}\Gamma\omega}. \tag{A.67}$$

Note that Fox [27] p.31 gets the analogous result for ε (instead of ε^{-1}) because he interprets the perturbation as the total field $\mathbf{E}$ in $\mathbf{D} = \mathbf{E} + \mathbf{P}$. Consequently, the presign of the ω-dependent term is different. This is completely analogous to the microscopic equations $\varepsilon^{-1} = 1 + v\chi$ and $\varepsilon = 1 - v\tilde{\chi}$.

Drude Model of Conductivity Again, we apply the oscillator model to N atoms in the volume V. For the Drude model, we have to set $\omega_0 = 0$ (free valence electrons) and $\Gamma = \frac{1}{\tau}$ leading to

$$\sigma(\omega) = \frac{\delta j(\omega)}{\delta E(\omega)} = \frac{\sigma_0}{1 - \mathrm{i}\omega\tau} \tag{A.68}$$

where

$$\sigma_0 = \frac{N e^2 \tau}{V m} \tag{A.69}$$

is the conductivity of the naive Drude model without damping. Thereby we concede that the term "oscillator model" is something of a misnomer when the restoring force vanishes.

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