Advanced Solid State Theory

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0. Literatur


1. Density functional theory

1.1 Introduction

In the first part of this lecture, we have discussed the Hartree-Fock approximation as an approximate solution to the problem of interacting electrons. It constitutes an effective simple particle theory

\[ H_{\text{eff}}^\alpha \varphi_{k\alpha}(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}^{k\alpha,\sigma}(\vec{r}) \varphi_{k\alpha}^\sigma(\vec{r}) = \varepsilon_{k\alpha}^\sigma \varphi_{k\alpha}^\sigma(\vec{r}) \]  

(1.1)

with an effective potential that depends on the state \( \varphi_{k\alpha}^\sigma(\vec{r}) \), i.e. on the orbital indices \( k_\alpha \):

\[ V_{\text{eff}}^{k\alpha,\sigma}(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_{\text{Hartree}}(\vec{r}) + V_{x}^{k\alpha,\sigma}(\vec{r}) \]  

(1.2)

Here, the “external” potential is that of the ionic cores

\[ V_{\text{ext}}(\vec{r}) = \sum_n V(|\vec{r} - \vec{R}_n|) = \sum_n \frac{Z_n e^2}{|\vec{r} - \vec{R}_n|}, \]  

(1.3)

the Hartree potential arises from the Coulomb interaction of an electron with the electrostatic potential generated by all the other electrons

\[ V_{\text{Hartree}}(\vec{r}) = \frac{e^2}{4\pi\varepsilon_0} \int d^3 r' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \]  

(1.4)

with

\[ n(\vec{r}) = \left\langle \Phi \right| \sum_{\alpha=1}^{N_e} \delta(\vec{r} - \vec{r}_\alpha) \left| \Phi \right\rangle = \sum_{\alpha=1}^{N_e} |\varphi_{k\alpha}^\sigma(\vec{r})|^2 \]  

(1.5)

The exchange operator \( V_{x}^{k\alpha,\sigma}(\vec{r}) \) is given by

\[ V_{x}^{k\alpha,\sigma}(\vec{r}) = -\frac{e^2}{4\pi\varepsilon_0} \sum_\beta \int d^3 r' \varphi_{k\beta}^\sigma(\vec{r}') \varphi_{k\alpha}^\sigma(\vec{r}') \frac{1}{|\vec{r} - \vec{r}'|} \frac{\varphi_{k\beta}^\sigma(\vec{r})}{\varphi_{k\alpha}^\sigma(\vec{r})}; \]  

(1.6)
It is also useful to define the normalized pair distribution and thus the product of probabilities, so that the measure of correlation is for normalized Ψ

\[ \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') = n(\vec{r}, \sigma; \vec{r}', \sigma') - n(\vec{r}, \sigma)n(\vec{r}', \sigma') \]  

and thus

\[ n(\vec{r}, \sigma, \vec{r}', \sigma') = n(\vec{r}, \sigma)n(\vec{r}', \sigma') + \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') \]  

Exchange and correlation

The key problem of electronic structure is that the electrons form an interacting many-body system with a wave function \( \Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \). Since the interactions involve always pairs of electrons, two-body correlation functions are sufficient to determine many properties like for example the total energy \( E = \langle \langle \Psi | H | \Psi \rangle \rangle = \langle H \rangle \). Explicitly, the joint probability of finding electrons of spin \( \sigma \) at \( \vec{r} \) and of spin \( \sigma' \) at \( \vec{r}' \) is given by

\[ n(\vec{r}, \sigma, \vec{r}', \sigma') = \left\langle \sum_{\alpha=\beta} \delta(\vec{r} - \vec{r}_{\alpha})\delta(\sigma - \sigma_{\alpha})\delta(\vec{r}' - \vec{r}_{\beta})\delta(\sigma' - \sigma_{\beta}) \right\rangle 
\]

\[ = N(N-1) \sum_{\sigma_3, \sigma_4, \cdots} \int d^3r_3 \cdots d^3r_N \left| \Psi(\vec{r}, \sigma_1; \vec{r}', \sigma'; \vec{r}_3, \sigma_3; \cdots; \vec{r}_N, \sigma_N) \right|^2 \]

(1.7)

for normalized \( \Psi \). For uncorrelated particles, the joint probability is just the product of probabilities, so that the measure of correlation is

\[ \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') = n(\vec{r}, \sigma; \vec{r}', \sigma') - n(\vec{r}, \sigma)n(\vec{r}', \sigma') \]  

and thus

\[ n(\vec{r}, \sigma, \vec{r}', \sigma') = n(\vec{r}, \sigma)n(\vec{r}', \sigma') + \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') \]  

(1.8)

(1.9)

It is also useful to define the normalized pair distribution

\[ g(\vec{r}, \sigma; \vec{r}', \sigma') = \frac{n(\vec{r}, \sigma; \vec{r}', \sigma')}{n(\vec{r}, \sigma)n(\vec{r}', \sigma')} = 1 + \frac{\Delta n(\vec{r}, \sigma; \vec{r}', \sigma')}{n(\vec{r}, \sigma)n(\vec{r}', \sigma')} \]  

(1.10)

This is 1 for uncorrelated particles; correlation is measured by \( g(\vec{r}, \sigma; \vec{r}', \sigma') - 1 \). All long range correlation is included in the average terms so that the remaining terms \( \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') \) and \( g(\vec{r}, \sigma; \vec{r}', \sigma') - 1 \) are short range and
vanish at large $|\vec{r} - \vec{r}'|$. The Hartree-Fock approximation (HFA) consists of neglecting all correlations except those required by the Pauli exclusion principle. The exchange term in the HFA contains the Pauli exclusion and the self interaction correction, i.e. it cancels a spurious self interaction contained in the Hartree term. Both effects lower the energy which can be interpreted as the interaction of each electron with a positive exchange hole surrounding it. The exchange hole $\Delta n_x(\vec{r}, \sigma; \vec{r}', \sigma')$ is given by $\Delta n(\vec{r}, \sigma; \vec{r}', \sigma')$ in the HFA, were $\Psi$ is approximated by the single determinant wave function $\phi$; one finds

$$
\Delta n_{\text{HFA}}(\vec{r}, \sigma; \vec{r}', \sigma') = \Delta n_x(\vec{r}, \sigma; \vec{r}', \sigma') = -\delta_{\sigma\sigma'} \left| \sum_i \varphi^*_{\kappa x}(\vec{r}) \varphi_{\kappa x}(\vec{r}') \right|^2
$$

(1.11)

It is immediately clear that the exchange hole involves only electrons of the same spin and that the probability for finding two electrons of the same spin at the same point $\vec{r} = \vec{r}'$ vanishes (see eq. (1.9)). There are stringent conditions for the exchange hole: 1) it can never be positive, $\Delta n_x(\vec{r}, \sigma; \vec{r}', \sigma') \leq 0$ (i.e. $\delta_x(\vec{r}, \sigma; \vec{r}', \sigma') \leq 1$) and 2) the integral of the exchange hole density $\Delta n_x(\vec{r}, \sigma; \vec{r}', \sigma')$ over all $\vec{r}'$ is exactly one missing electron per electron at point $\vec{r}$ (if one electron is at $\vec{r}$, then the same electron cannot be at $\vec{r}'$).

The exchange energy can be interpreted as the lowering of the energy due to each electron interacting with its positive exchange hole,

$$
E_x = \left[ \langle V_{\text{int}} \rangle - E_{\text{Hartree}}(n) \right]_{\text{HFA}} = \frac{1}{2} \sum_{\sigma} \int d^3r \, n(\vec{r}) \int d^3r' \frac{\Delta n_x(\vec{r}, \sigma; \vec{r}', \sigma')}{|\vec{r} - \vec{r}'|}
$$

(1.12)

**Correlation:** The energy of a state of many electrons in the Hartree Fock approximation is the best possible wave function made from a single determinant. Improvement of the wave function to include correlation introduces extra degrees of freedom in the wave function and therefore always lowers the energy for any state, ground or excited; this lowering of the energy is called the correlation energy $E_c$. (This definition is not the only possible as a different reference state could be chosen, but it is the one leading to the smallest possible magnitude of $E_c$). The effects of correlation can be cast in terms of the remaining part of the
pair correlation beyond exchange:

\[ \Delta n(\vec{r}, \sigma; \vec{r}', \sigma') \equiv n_{xc}(\vec{r}, \sigma; \vec{r}', \sigma') = n_x(\vec{r}, \sigma; \vec{r}', \sigma') + n_c(\vec{r}, \sigma; \vec{r}', \sigma') \] (1.13)

As the entire exchange-correlation hole obeys the sum rule that it integrates to 1, the correlation hole \( n_c(\vec{r}, \sigma; \vec{r}', \sigma') \) must integrate to zero, i.e. it merely redistributes the density of the hole. In general, correlation is most important for electrons of opposite spin as electrons of the same spin are automatically kept apart by the exclusion principle.

Abbildung 1.1:
Exchange hole \( g_x(\vec{r}) \) in the homogeneous electron gas.

1.2 Foundations of density functional theory

Density functional theory has become the primary tool for calculation of electronic structure in condensed matter, and is increasingly important for quantitative studies of molecules and other finite systems. In a famous 1964 paper\(^1\), P. Hohenberg and W. Kohn showed that a special role can be assigned to the density of particles in the ground state of a quantum manybody system; the density can be considered as a basic variable, i.e. all properties of the system can be considered to be unique functionals of the ground state density. Hohenberg and Kohn formulated density functional theory as an exact theory of manybody systems of interacting particles in

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an external potential $V_{\text{ext}}(\mathbf{r})$ including any problem of electrons and fixed nuclei, where the Hamiltonian can be written

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_\alpha \nabla^2_\alpha + \sum_\alpha V_{\text{ext}}(\mathbf{r}_\alpha) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|}$$  \hspace{1cm} (1.14)$$

Density functional theory is based upon the following two theorems first proved by Hohenberg and Kohn:  

\textit{Theorem 1}: For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

\textit{Corollary 1}: Since the Hamiltonian is thus fully determined except for a constant shift of the energy, it follows that the manybody wave functions for all stated (ground and excited) are determined. Therefore, all properties of the system are completely determined given only the ground state density $n_0(\mathbf{r})$.

\textit{Theorem 2}: A universal functional for the energy $E[n]$ in terms of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{\text{ext}}(\mathbf{r})$. For any particular $V_{\text{ext}}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value for this functional, and the density $n(\mathbf{r})$ that minimizes the functional is the exact ground state state density $n_0(\mathbf{r})$.

\textit{Corollary 2}: The functional $E[n]$ alone is sufficient to determine the exact ground state energy and density. In general, excited states of the electrons must be determined by other means.

Schematic representation of the Hohenberg-Kohn theorem:

$$V_{\text{ext}}(\mathbf{r}) \xrightarrow{\text{HK}} n_0(\mathbf{r})$$

$$\Downarrow \hspace{1cm} \uparrow$$

$$\Psi_i(\mathbf{r}) \Rightarrow \Psi_0(\mathbf{r})$$  \hspace{1cm} (1.15)$$

Small arrows indicate the usual solution of the Schödinger equation where the potential $V_{\text{ext}}(\mathbf{r})$ determines all states of the system $\Psi_i(\mathbf{r})$ including the ground state $\Psi_0(\mathbf{r})$ and ground state density $n_0(\mathbf{r})$. The large arrow indicates the Hohenberg-Kohn theorem which completes the circle.

\textbf{Proof of theorem 1: density as a basic variable}

We use the expressions:

$$n(\mathbf{r}) = \frac{\langle \Psi | n(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = N \int d^3r_1 d^3r_2 \cdots d^3r_N \sum_\sigma |\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)|^2$$

$$\rho(\mathbf{r}) = \frac{\langle \Psi | \rho(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$\rho(\mathbf{r}) = \frac{\langle \Psi | n(\mathbf{r}) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = N \int d^3r_1 d^3r_2 \cdots d^3r_N |\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_N)|^2$$  \hspace{1cm} (1.16)$$

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for the density of particles, with the density operator
\[ \vec{n}(\vec{r}) = \sum_{\alpha=1}^{N} \delta(\vec{r} - \vec{r}_\alpha) \]  
(1.17)

and
\[ E = \frac{\langle \Psi| \hat{H} |\Psi \rangle}{\langle \Psi| \Psi \rangle} = \langle \hat{T} \rangle + \langle \hat{V}_{\text{int}} \rangle + \int d^3r \; V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{\Pi} \]  
(1.18)

for the total energy, where expectation value of the external potential has been written explicitly as a simple integral over the density function. \( E_{\Pi} \) is the electrostatic nucleus-nucleus interaction. Now we prove theorem 1 by *reductio ad absurdum*. Suppose that there were two different external potentials \( V_{\text{ext}}^{(1)}(\vec{r}) \) and \( V_{\text{ext}}^{(2)}(\vec{r}) \) which differ by more than a constant and which lead to the same ground state density \( n(\vec{r}) \). The two external potentials lead to two different Hamiltonians \( \hat{H}^{(1)} \) and \( \hat{H}^{(2)} \) which have different ground state wave functions \( \Psi^{(1)} \) and \( \Psi^{(2)} \) which are hypothesized to have the same ground state density \( n_0(\vec{r}) \). Since \( \Psi^{(2)} \) is not the ground state of \( \hat{H}^{(1)} \), it follows that
\[ E^{(1)} = \langle \Psi^{(1)}| \hat{H}^{(1)} |\Psi^{(1)} \rangle < \langle \Psi^{(2)}| \hat{H}^{(1)} |\Psi^{(2)} \rangle \]  
(1.19)

Here a nondegenerate ground state is assumed which simplifies the proof but is not essential. The last term can be written as
\[ \langle \Psi^{(2)}| \hat{H}^{(1)} |\Psi^{(2)} \rangle = \langle \Psi^{(2)}| \hat{H}^{(2)} |\Psi^{(2)} \rangle + \langle \Psi^{(2)}| \hat{H}^{(1)} - \hat{H}^{(2)} |\Psi^{(2)} \rangle \]
\[ = E^{(2)} + \int d^3r \; [V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r})] n_0(\vec{r}) \]  
(1.20)

so that
\[ E^{(1)} < E^{(2)} + \int d^3r \; [V_{\text{ext}}^{(1)}(\vec{r}) - V_{\text{ext}}^{(2)}(\vec{r})] n_0(\vec{r}) \]  
(1.21)

On the other hand, if we consider \( E^{(2)} \) in exactly the same way, we find the same equation with superscripts 1 and 2 interchanged:
\[ E^{(2)} < E^{(1)} + \int d^3r \; [V_{\text{ext}}^{(2)}(\vec{r}) - V_{\text{ext}}^{(1)}(\vec{r})] n_0(\vec{r}) \]  
(1.22)

If we add Eqs. (1.21) and (1.22), we arrive at the contradictory inequality
\[ E^{(1)} + E^{(2)} < E^{(1)} + E^{(2)} \]  
Thus, there cannot be two different external
potentials differing by more than a constant which give rise to the same nondegenerate ground state density; the density uniquely determines the external potential to within a constant.
The corollary 1 follows since the Hamiltonian is uniquely determined (except for a constant) by the ground state density. Then, in principle, the wave function of any state is determined by solving the Schrödinger equation with this Hamiltonian. Among all solutions consistent with the given density, the unique ground state wave function is the one that has the lowest energy. Of course, no prescription has yet been given to solve the problem. Still, the manybody problem in the presence of $V_{\text{ext}}(\vec{r})$ needs to be solved. For example, for electrons in materials where the external potential is the Coulomb potential due to the nuclei, the theorem only requires that the electron density uniquely determines the positions and types of nuclei.

Proof of theorem 2

The proof of theorem 2 requires proper definition of the meaning of a functional of the density and restricting the space of densities. We restrict to densities that are V-representable, i.e. densities $n(\vec{r})$ that are ground state densities of the electron Hamiltonian with some external potential $V_{\text{ext}}$. Within this space of densities, we construct functionals of the density. Since all properties such as the kinetic energy, etc. are uniquely determined if $n(\vec{r})$ is specified, each such property can be viewed as a functional of $n(\vec{r})$, including the total energy functional

$$E_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] + \int d^3r V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{\text{II}}$$

$$= F_{\text{HK}}[n] + \int d^3r V_{\text{ext}}(\vec{r})n(\vec{r}) + E_{\text{II}}$$

(1.23)

where $E_{\text{II}}$ is the interaction energy of the nuclei. The functional $F_{\text{HK}}[n]$ thus defined includes all internal energies, kinetic and potential of the interacting electron system

$$F_{\text{HK}}[n] = T[n] + E_{\text{int}}[n]$$

(1.24)

which must be universal by construction since the kinetic energy and interaction energy of the particles are functionals only of the density. Now consider a system with a ground state density $n^{(1)}(\vec{r})$ corresponding to the external potential $V_{\text{ext}}^{(1)}(\vec{r})$. the Hohenberg-Kohn functional is equal to the
expectation value of the Hamiltonian in the unique ground state which has the wavefunction $\Psi^{(1)}$

$$E^{(1)} = E_{HK}[n^{(1)}] = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle$$  \hspace{1cm} (1.25)

Now consider a different density $n^{(2)}(\vec{r})$ which necessarily corresponds to a different wave function $\Psi^{(2)}$. It follows immediately that the energy $E^{(2)}$ of this state is greater than $E^{(1)}$ since

$$E^{(1)} = \langle \Psi^{(1)} | \hat{H}^{(1)} | \Psi^{(1)} \rangle < \langle \Psi^{(2)} | \hat{H}^{(1)} | \Psi^{(2)} \rangle = E^{(2)}$$  \hspace{1cm} (1.26)

Thus the energy given by (1.23) in terms of the Hohenberg-Kohn functional evaluated for the correct ground state density $n_0(\vec{r})$ is indeed lower than the value of this expression for any other density $n(\vec{r})$. This means that if the functional $F_{HK}[n]$ were known, then by minimizing the total energy of the system (1.23) with respect to variations in the density $n(\vec{r})$ one would find the exact ground state density and energy. This establishes corollary 2.

1.3 The Kohn-Sham ansatz

The Kohn-Sham approach is to replace the difficult interacting many-body system with a different auxiliary system that can be solved more easily - it is an ansatz because there is no unique prescription of how to choose the simpler auxiliary system. The ansatz assumes that the ground state density of the original interacting system is equal to that of some chosen non-interacting system. This leads to independent particle equations for the non-interacting system that can be considered exactly solvable with all the difficult many-body terms incorporated into an exchange-correlation functional of the density. By solving the equations one finds the ground state density and energy of the original interacting system with the accuracy limited only by the approximations in the exchange-correlation functional. These approximations, the most important of which are the local density approximation (LDA) and generalized gradient approximation (GGA) functionals will be discussed below. The Kohn-Sham ansatz for the ground state rests on two assumptions:

1) The exact ground state density can be represented by the ground state density of the auxiliary system of noninteracting particles. This is called **non-interacting-V-representability** (see scheme below)
2) The auxiliary Hamiltonian is chosen to have the usual kinetic energy
operator and an effective local potential $V_{\text{eff}}^\sigma(\vec{r})$ acting on an electron of spin $\sigma$ at point $\vec{r}$.

Schematic representation of the Kohn-Sham ansatz:

$$
V_{\text{ext}}(\vec{r}) \overset{\text{HK}}{\leftrightarrow} n_0(\vec{r}) \overset{\text{KS}}{\leftrightarrow} n_0(\vec{r}) \overset{\text{HK}_0}{\rightarrow} V_{\text{KS}}(\vec{r})
$$

$$
\Psi_i(\vec{r}) \Rightarrow \Psi_0(\vec{r}) \quad \psi_{i=1, \ldots, N_e}(\vec{r}) \Leftarrow \psi_i(\vec{r})
$$

$\text{HK}_0$ means Hohenberg-Kohn theorem applied to the noninteracting problem. The KS arrow indicates connection in both directions between the manybody and independent particle systems.

The actual calculations are performed on the auxiliary independent particle system defined by the auxiliary Hamiltonian

$$
H^\sigma_{\text{aux}} = - \frac{1}{2} \nabla^2 + V^\sigma(\vec{r})
$$

$V^\sigma(\vec{r})$ will be specified later. For independent electrons, the ground state has one electron in each of the $N^\sigma(\sigma = \uparrow, \downarrow)$ orbitals $\psi_i^\sigma(\vec{r})$ with the lowest eigenvalues $\varepsilon_i^\sigma$ of the Hamiltonian (1.28). The density of the auxiliary system is given by

$$
n(\vec{r}) = \sum_\sigma n(\vec{r}, \sigma) = \sum_\sigma \sum_{i=1}^{N^\sigma} |\psi_i^\sigma(\vec{r})|^2,
$$

the independent particle kinetic energy $T_s$ is given by

$$
T_s = - \frac{1}{2} \sum_\sigma \sum_{i=1}^{N^\sigma} \langle \psi_i^\sigma | \nabla^2 | \psi_i^\sigma \rangle = \frac{1}{2} \sum_\sigma \sum_{i=1}^{N^\sigma} \int d^3r | \nabla \psi_i^\sigma(\vec{r}) |^2
$$

and we define the classical Coulomb interaction energy of the electron density $n(\vec{r})$ interacting with itself as

$$
E_{\text{Hartree}}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}
$$

The Kohn-Sham approach to the full interacting manybody problem is to rewrite the Hohenberg-Kohn expression for the ground state energy functional (1.23) as

$$
E_{\text{KS}} = T_s[n] + \int d^3r V_{\text{ext}}(\vec{r}) n(\vec{r}) + E_{\text{Hartree}}[n] + E_{\text{II}} + E_{\text{xc}}[n]
$$
Here $V_{\text{ext}}(\mathbf{r})$ is the external potential due to the nuclei and any other external fields (assumed to be independent of spin). All manybody effects of exchange and correlation are grouped into the exchange-correlation energy $E_{\text{xc}}$. Comparing the Hohenberg-Kohn (1.23) and the Kohn-Sham (1.32) expressions for the total energy shows that $E_{\text{xc}}$ can be written as

$$E_{\text{xc}}[n] = F_{\text{HK}}[n] - (T_s[n] + E_{\text{Hartree}}[n])$$  \hspace{1cm} (1.33)

or

$$E_{\text{xc}}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{\text{int}} \rangle - E_{\text{Hartree}}[n]$$  \hspace{1cm} (1.34)

This shows that $E_{\text{xc}}[n]$ is just the difference of the kinetic and internal interaction energies of the interacting manybody system from those of the fictitious independent-particle system with electron-electron interactions replaced by the Hartree energy. As the universal functional $E_{\text{xc}}[n]$ of (1.32) is unknown, approximate forms for $E_{\text{xc}}[n]$ make the Kohn-Sham method a valuable approach for the ground state properties of the manybody electron system.

**The Kohn-Sham variational equations**

The solution of the Kohn-Sham auxiliary system for the ground state can be viewed as a problem of minimization with respect to either the density $n(\mathbf{r}, \sigma)$ or the effective potential $V_{\text{eff}}^\sigma(\mathbf{r})$. As $T_s$ is expressed as a functional of the orbitals but all other terms are considered to be functionals of the density, one can vary the wave functions and use the chain rule to derive the variational equation

$$\frac{\delta E_{\text{KS}}}{\delta \psi^{\sigma*}_i(\mathbf{r})} = \frac{\delta T_s}{\delta \psi^{\sigma*}_i(\mathbf{r})} + \left[ \frac{\delta E_{\text{ext}}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{\text{Hartree}}}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{\text{xc}}}{\delta n(\mathbf{r}, \sigma)} \right] \frac{\delta n(\mathbf{r}, \sigma)}{\delta \psi^{\sigma*}_i(\mathbf{r})} = 0$$  \hspace{1cm} (1.35)

subject to normalization conditions

$$\langle \psi^\sigma_i | \psi^\sigma_j \rangle = \delta_{ij} \delta_{\sigma\sigma'}$$  \hspace{1cm} (1.36)

We use the expressions (1.29) and (1.30) for $n^\sigma(\mathbf{r})$ and $T_s$ which give

$$\frac{\delta T_s}{\delta \psi^{\sigma*}_i(\mathbf{r})} = -\frac{1}{2} \nabla^2 \psi^\sigma_i(\mathbf{r}); \quad \frac{\delta n^\sigma(\mathbf{r})}{\delta \psi^{\sigma*}_i(\mathbf{r})} = \psi^\sigma_i(\mathbf{r})$$  \hspace{1cm} (1.37)
and the method of Lagrange multipliers to handle the constraints:

$$\frac{\delta}{\delta \psi_i^*} \left\{ E_{KS} - \sum_{\sigma} \sum_{j=1}^{N_\sigma} \epsilon_j^\sigma \left( \int d^3r \left| \psi_j^\sigma(\vec{r}) \right|^2 - 1 \right) \right\} = 0$$  \hspace{1cm} (1.38)

This variation leads to the Schrödinger-like **Kohn-Sham equations**

$$(H_{KS}^\sigma - \epsilon_i^\sigma) \psi_i^\sigma(\vec{r}) = 0$$  \hspace{1cm} (1.39)

where $\epsilon_i^\sigma$ are eigenvalues and $H_{KS}$ is the effective Hamiltonian (in Hartree atomics units)

$$H_{KS}^\sigma(\vec{r}) = -\frac{1}{2} \nabla^2 + V_{KS}^\sigma(\vec{r})$$  \hspace{1cm} (1.40)

with

$$V_{KS}^\sigma(\vec{r}) = V_{ext}(\vec{r}) + \frac{\delta E_{Hartree}}{\delta n(\vec{r}, \sigma)} + \frac{\delta E_{xc}}{\delta n(\vec{r}, \sigma)}$$

$$= V_{ext}(\vec{r}) + V_{Hartree}(\vec{r}) + V_{xc}^\sigma(\vec{r})$$  \hspace{1cm} (1.41)

These are the well-known Kohn-Sham equations\(^2\); they have the form of independent particle equations with a potential that must be found self-consistently with the resulting density. The equations are independent of any approximation to the functional $E_{xc}[n]$, and would lead to the exact ground state density and energy for the interacting system if the exact functional $E_{xc}[n]$ were known. Furthermore, the Hohenberg-Kohn theorems guarantee that the ground state density uniquely determines the potential at the minimum, so that there is a unique Kohn-Sham potential $V_{eff}^\sigma(\vec{r})_{min} \equiv V_{KS}^\sigma(\vec{r})$ associated with any given interacting electron system.

$E_{xc}$, $V_{xc}$ and the exchange-correlation hole

The genius of the Kohn-Sham approach is that by explicitly separating out the independent-particle kinetic energy and the long-range Hartree terms, the remaining exchange-correlation functional $E_{xc}[n]$ can reasonably be approximated as a local or nearly local functional of the density. This means that the energy $E_{xc}$ can be expressed in the form

$$E_{xc}[n] = \int d^3r \ n(\vec{r}) \epsilon_{xc}([n], \vec{r})$$  \hspace{1cm} (1.42)

where \( \varepsilon_{xc}(n, \vec{r}) \) is an energy per electron at point \( \vec{r} \) that depends only on the density \( n(\vec{r}, \sigma) \) in some neighborhood of point \( \vec{r} \). The exchange and correlation energy density can be related to the exchange correlation hole using the coupling constant integration. In general, the derivative of the energy with respect to any parameter \( \lambda \) in the Hamiltonian can be calculated using the variational property of the wave function:

\[
\frac{\partial E}{\partial \lambda} = \langle \Psi_\lambda | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_\lambda \rangle \tag{1.43}
\]

and from this, an integral expression can be obtained for calculating energy differences between any two states connected by a continuous variation of the Hamiltonian:

\[
\Delta E = \int_{\lambda_1}^{\lambda_2} d\lambda \frac{\partial E}{\partial \lambda} = \int_{\lambda_1}^{\lambda_2} d\lambda \langle \Psi_\lambda | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_\lambda \rangle \tag{1.44}
\]

Here, we are interested in varying the Hamiltonian continuously between the non-interacting and the fully interacting limits. For this we can use the parameter \( e^2 \) in the interaction energy, scale it by \( e^2 \to e^2\lambda \) where \( \lambda \) is varied from 0 to 1. This we do only to the electron-electron interaction term (nuclear term is treated separately as external potential), and we find for the change in energy

\[
\Delta E = \int_0^1 d\lambda \langle \Psi_\lambda | V_{\text{int}} | \Psi_\lambda \rangle \tag{1.45}
\]

If we do this with the added constraints that the density must be kept constant during this variation, all other terms remain constant and the exchange correlation energy is given by

\[
E_{xc}[n] = \int_0^{e^2} d\lambda \langle \Psi_\lambda | \frac{dV_{\text{int}}}{d\lambda} | \Psi_\lambda \rangle - E_{\text{Hartree}}[n] = \frac{1}{2} \int d^3r \ n(\vec{r}) \int d^3r' \ \bar{n}_{xc}(\vec{r}, \vec{r}') \frac{n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \tag{1.46}
\]

where \( \bar{n}_{xc}(\vec{r}, \vec{r}') \) is the coupling constant averaged hole

\[
\bar{n}_{xc}(\vec{r}, \vec{r}') = \int_0^1 d\lambda \ n_{xc}^\lambda(\vec{r}, \vec{r}') \tag{1.47}
\]

\( n_{xc}(\vec{r}, \vec{r}') \) is the exchange correlation hole summed over parallel (\( \sigma = \sigma' \)) and antiparallel (\( \sigma \neq \sigma' \)) spins. Thus, the exchange correlation density
\( \varepsilon_{xc}([n], \vec{r}) \) can be written as

\[
\varepsilon_{xc}([n], \vec{r}) = \frac{1}{2} \int d^3 \vec{r}' \frac{\bar{n}_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}
\]

(1.48)

This result shows that the exact exchange correlation energy can be understood in terms of the potential energy due to the exchange-correlation hole averaged over the interaction from \( e^2 = 0 \) to \( e^2 = 1 \). For \( e^2 = 0 \) the wave function is just the independent-particle Kohn-Sham wave function so that \( n_{xc}^0(\vec{r}, \sigma; \vec{r}', \sigma') = n(\vec{r}, \sigma; \vec{r}', \sigma') \) where the exchange hole is known from Eq. (1.11). Since the density everywhere is required to remain constant as \( \lambda \) is varied, \( \varepsilon_{xc}([n], \vec{r}) \) is implicitly a functional of the density in all space. Thus \( E_{xc}[n] \) can be considered as an interpolation between the exchange-only and the full correlated energies at the given density \( n(\vec{r}, \sigma) \).

Analysis of the averaged hole \( \bar{n}_{xc}(\vec{r}, \vec{r}') \) is one of the primary approaches for developing improved approximations for \( E_{xc}[n] \).

**Exchange-correlation potential** \( V_{xc} \)

The exchange-correlation potential \( V_{xc}(\vec{r}) \) is the functional derivative of \( E_{xc} \) and can be written as

\[
V_{xc}(\vec{r}) = \varepsilon_{xc}([n], \vec{r}) + n(\vec{r}) \frac{\partial \varepsilon_{xc}([n], \vec{r})}{\partial n(\vec{r}, \sigma)}
\]

(1.49)

where \( \varepsilon_{xc}([n], \vec{r}) \) is defined in (1.42) and is a functional of the density \( n(\vec{r}', \sigma') \). \( V_{xc} \) is not a potential that can be identified with interactions between particles and it behaves in ways that seem paradoxical. The second term in (1.49), sometimes called response potential, is due to the change in the exchange correlation hole with density. In an insulator, this derivative is discontinuous at a band gap where the nature of the state changes discontinuously as a function of \( n \). This leads to a derivative discontinuity where the Kohn-Sham potential for all the electrons in a crystal changes by a constant amount when a single electron is added. This can be understood by examining the kinetic energy. The great advance of the Kohn-Sham approach over the Thomas-Fermi approximation is the incorporation of orbitals to define the kinetic energy. In terms of orbitals, it is easy to see that the kinetic energy \( T_s \) for independent particles changes discontinuously in going from an occupied to an empty band since the \( \psi_i^\sigma(\vec{r}) \) are different for different bands. In terms of the density, this means that the formal density functional \( T_s[n] \) has discontinuous derivatives at
densities that correspond to filled bands. This is a direct consequence of quantum mechanics and is difficult to incorporate into an explicit density functional; also the true exchange-correlation potential must change discontinuously. These properties are not incorporated into any of the simple explicit functionals of the density, such as local density or generalized gradient approximations, but they occur naturally in orbital dependent formulations like the optimized effective potential (OEP).

**Meaning of the Kohn-Sham eigenvalues**

The Kohn-Sham eigenvalues, introduced as Lagrange multipliers, have no direct physical meaning, at least not that of the energies to add or subtract electrons from the interacting manybody system (in analogy to Koopmas theorem for Hartree Fock). The exception is the highest eigenvalue in a finite system which is minus the ionization energy. Nevertheless, the eigenvalues have a well defined meaning within the theory and can be used to construct physically meaningful quantities. For example, they can be used to develop perturbation expressions for excitation energies, either in the form of a functional or in the form of explicit manybody calculations that use the Kohn-Sham eigenfunctions and eigenvalues as an input.

Within the Kohn-Sham formalism, the meaning of the eigenvalues, known as Janak theorem, is that the eigenvalue is the derivative of the total energy with respect to occupation of a state:

\[ \varepsilon_i = \frac{dE_{\text{total}}}{dn_i} = \int d^3r \frac{dE_{\text{total}}}{dn(\vec{r})} dn_i. \]  

(1.50)

1.4 Functionals for exchange and correlation

Even though the exact functional \( E_{\text{xc}}[n] \) must be very complex, the great success of DFT is due to remarkably simple approximations.

**The local spin density approximation (LSDA)**

This approximation is based on the observation that solids can often be considered close to the limit of the homogeneous electron gas. In that limit, the effects of exchange and correlation are local in character. Thus, the local density approximation (LDA), which was already proposed by Kohn and Sham, takes the exchange-correlation energy as an integral over all space, with the exchange-correlation energy density at each point assumed to be
the same as in a homogeneous electron gas with that density:

$$E_{xc}^{\text{LSDA}}[n^\uparrow, n^\downarrow] = \int d^3r \ n(r) \varepsilon_{xc}^{\text{hom}}(n^\uparrow(\mathbf{r}), n^\downarrow(\mathbf{r}))$$

The axis of quantization of the spin is assumed to be the same at all points in space, but this can be generalized to a non-collinear spin case. The LSDA can be formulated either in the two spin densities $n^\uparrow(\mathbf{r})$ and $n^\downarrow(\mathbf{r})$, or in the total density $n(\mathbf{r})$ and the fractional spin polarization

$$\zeta(\mathbf{r}) = \frac{n^\uparrow(\mathbf{r}) - n^\downarrow(\mathbf{r})}{n(\mathbf{r})}. \quad (1.52)$$

Solving the Hartree-Fock equations for the homogeneous electron gas can be done analytically; one finds a dispersion (in atomic units)

$$\varepsilon_k = \frac{k^2}{2} + \frac{k_F}{\pi} f(x) \quad \text{with} \quad x = \frac{k}{k_F} \quad (1.53)$$

and

$$f(x) = - \left(1 + \frac{1-x^2}{2x} \ln \left| \frac{1+x}{1-x} \right| \right) \quad (1.54)$$

where the second term is the matrix element for the exchange operator.

For a polarized system, exchange has the form

$$\varepsilon_x(n, \zeta) = \varepsilon_x(n, 0) + \left[ \varepsilon_x(n, 1) - \varepsilon_x(n, 0) \right] f_x(\zeta) \quad (1.55)$$

with

$$f_x(\zeta) = \frac{1}{2} \frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2}{2^{4/3} - 1} \quad (1.56)$$

For unpolarized systems, the LDA is found by setting $n^\uparrow(\mathbf{r}) = n^\downarrow(\mathbf{r}) = n(\mathbf{r})/2$. The correlation energy of the inhomogeneous electron gas cannot be calculated analytically; it is calculated with manybody methods (RPA) or numerically with Quantum Monte Carlo. It has been parameterized using analytic forms, for example one that is the same as (1.55), as proposed by Perdew and Zunger.

**Generalized gradient approximations (GGAs)**

The first step beyond the local approximation is a functional of the gradient of the density $|\nabla n^\sigma|$ as well as its value $n$ at each point. But a
straightforward expansion can run into problems due to the violation of sum rules. The problem is that gradients in real materials are so large that the expansion breaks down. The term generalized gradient approximation denotes a variety of ways proposed for functions that modify the behavior at large gradients in such a way as to preserve the desired properties. The functional can be defined as a generalized form of (1.51)

$$E_{xc}^{GGA}[n^\uparrow, n^\downarrow] = \int d^3 r n(\vec{r}) \varepsilon_{xc}(n^\uparrow, n^\downarrow, |\nabla n|^\uparrow, |\nabla n|^\downarrow, \cdots)$$

$$\equiv \int d^3 r n(\vec{r}) \varepsilon_{xc}^{hom}(n) F_{xc}(n^\uparrow, n^\downarrow, |\nabla n|^\uparrow, |\nabla n|^\downarrow, \cdots) \quad (1.57)$$

where $F_{xc}$ is dimensionless and $\varepsilon_{xc}^{hom}(n)$ is the exchange energy of the unpolarized gas. For exchange, there is a spin scaling relation

$$E_x[n^\uparrow, n^\downarrow] = \frac{1}{2} [E_x[2n^\uparrow] + E_x[2n^\downarrow]] \quad (1.58)$$

where $E_x[n]$ is the exchange energy for an unpolarized system. Thus, for exchange we need to consider only the spin-unpolarized $F_x(n, |\nabla n|)$. It is natural to work in terms of dimensionless reduced density gradients of $m$th order that can be defined by

$$s_m \equiv \frac{\nabla^m n}{(2k_F)^m n} = \frac{\nabla^m n}{2^m (3\pi^2)^{m/3} n^{1+ m/3}} \quad (1.59)$$

Since $k_F = 3(\frac{2\pi}{3})^{1/3} \frac{1}{r_s}$, $s_m$ is proportional to the $m$th order fractional variation in density normalized to the average distance between electrons $r_s$, for example

$$s_1 \equiv s = \frac{|\nabla n|}{(2k_F)n} = \frac{|\nabla r_s|}{2(\frac{2\pi}{3})^{1/3}r_s} \quad (1.60)$$

The lowest order terms for $F_x$ have been calculated analytically

$$F_x = 1 + \frac{10}{81} s_1^2 + \frac{146}{2025} s_2^2 + \cdots \quad (1.61)$$

Numerous forms $F_x(n, s)$ have been proposed; these can be illustrated (see Fig. 1.2) by the widely used forms of Becke (B88)$^3$, Perdew and Wang

---

(PW99)$^4$ and Perdew, Burke and Ernzerhof (PBE)$^5$. In the region that is most relevant for physical applications, $s < 3$, the three forms have similar shapes and lead to similar results. For the large $s$ region, relatively little is known.


2. Greens function formalism

2.1 Introduction

Greens functions appear naturally as response functions, i.e. as answers to the function how a quantum mechanical system responds to an external perturbation, like for example electrical or magnetic fields; the corresponding response functions would then describe the electrical conductivity or the magnetic susceptibility of a system. Here we will be concerned with small perturbations and thus only the linear response of the system. We describe the system by a Hamiltonian

$$H = H_0 + V_t$$  \hspace{1cm} (2.1)

where $V_t$ represents the interaction with an external field. $H_0$ describes the system with the external field switched off; due to interactions $H_0$ is not necessarily exactly solvable. The external field $F_t$ couples to the observable $\hat{B}$ of the system:

$$V_t = \hat{B}F_t$$  \hspace{1cm} (2.2)

Here, $\hat{B}$ is an operator and $F_t$ is a complex number. We now consider an observable $\hat{A}$ of the system that is not explicitly time dependent and ask how the dynamic expectation value $\langle \hat{A} \rangle$ reacts to the perturbation $V_t$. Without field we have

$$\langle \hat{A} \rangle_0 = \text{Tr}(\rho_0 \hat{A})$$  \hspace{1cm} (2.3)

where $\rho_0$ is the density matrix of the system without external fields:

$$\rho_0 = \frac{e^{-\beta H}}{\text{Tr}e^{-\beta H}}$$  \hspace{1cm} (2.4)

in the grand canonical ensemble $\mathcal{H} = H - \mu \hat{N}$ (with chemical potential $\mu$, particle number operator $\hat{N}$). The density matrix will change if we switch on the field:

$$\rho_0 \to \rho_t$$  \hspace{1cm} (2.5)
This means for the expectation value of $\hat{A}$

$$\langle \hat{A} \rangle_t = \text{Tr}(\rho_t \hat{A})$$  \hspace{1cm} (2.6)

In the Schrödinger picture, the equation of motion of the density matrix (the statistical operator) is determined by the von Neumann equation

$$i\hbar \frac{\partial \rho_t}{\partial t} = [\mathcal{H} + V_t, \rho_t]$$  \hspace{1cm} (2.7)

We consider a perturbation that is switched on at some time so that the boundary condition for our first order differential equation is an unperturbed system for $t \to -\infty$

$$\lim_{t \to -\infty} \rho_t = \rho_0.$$  \hspace{1cm} (2.8)

We now switch to the Dirac picture where we have

$$\rho_t^D(t) = e^{\frac{i}{\hbar} \mathcal{H}_0 t} \rho_t e^{-\frac{i}{\hbar} \mathcal{H}_0 t}$$  \hspace{1cm} (2.9)

with the equation of motion

$$\rho_t^D(t) = \frac{i}{\hbar} [\rho_t^D, V_t^D](t).$$  \hspace{1cm} (2.10)

Integrating with the boundary condition

$$\lim_{t \to -\infty} \rho_t^D(t) = \rho_0$$  \hspace{1cm} (2.11)

leads to

$$\rho_t^D(t) = \rho_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \rho_t^D(t'), \rho_t^D(t')$$  \hspace{1cm} (2.12)

This equation can be solved by iteration (by substituting $\rho_t^D(t)$ repeatedly on the right hand side):

$$\rho_t^D(t) = \rho_0 + \sum_{n=1}^{\infty} \rho_t^{D(n)}(t)$$  \hspace{1cm} with

$$\rho_t^{D(n)}(t) = \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n$$

$$\times [V_{t_1}^D(t_1), [V_{t_2}^D(t_2), \cdots [V_{t_n}^D(t_n), \rho_0]]_\cdot]_\cdot$$  \hspace{1cm} (2.13)
While this formula is exact, it is not practical. For sufficiently small external perturbations, we can restrict to linear terms in the perturbation $V_t$ which is called linear response:

$$\rho_t \approx \rho_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' e^{-\frac{i}{\hbar} \mathcal{H}_0 t} [V^D_t(t'), \rho_0] e^{\frac{i}{\hbar} \mathcal{H}_0 t}$$  \hspace{1cm} (2.14)$$

Here, we have returned to the Schrödinger representation for the density matrix. We can use this result to determine the perturbed expectation value of (2.6):

$$\langle \hat{A} \rangle_t = \text{Tr}(\rho_t \hat{A}) = \langle \hat{A} \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' \text{Tr}\left\{e^{-\frac{i}{\hbar} \mathcal{H}_0 t} [V^D_t(t'), \rho_0] e^{\frac{i}{\hbar} \mathcal{H}_0 t} \hat{A}\right\}$$

$$= \langle \hat{A} \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \text{Tr}\left\{[\hat{B}^D(t'), \rho_0] \hat{A}^D(t)\right\}$$

$$= \langle \hat{A} \rangle_0 - \frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \text{Tr}\left\{\rho_0 [\hat{A}^D(t), \hat{B}^D(t')]\right\}$$  \hspace{1cm} (2.15)$$

Here, cyclic invariance of the trace was exploited. This shows how the system reacts to the external perturbation, as measured from the observable $\hat{A}$:

$$\Delta A_t = \langle \hat{A} \rangle_t - \langle \hat{A} \rangle_0 = -\frac{i}{\hbar} \int_{-\infty}^{t} dt' F_{t'} \langle [\hat{A}^D(t), \hat{B}^D(t')] \rangle_0$$  \hspace{1cm} (2.16)$$

This response is determined by an expectation value of the unperturbed system. The Dirac representation of the operators $\hat{A}^D(t)$, $\hat{B}^D(t')$ corresponds to the Heisenberg representation when the field is switched off.

Now we define the retarded two-time greens function

$$G^r_{AB}(t, t') = \langle\langle A(t); B(t')\rangle\rangle = -i \Theta(t, t') \langle [A(t), B(t')] \rangle_0$$  \hspace{1cm} (2.17)$$

The operators are to be taken in Heisenberg representation of the field free system. The retarded Greens function describes the response of a system as manifested in observable $\hat{A}$ when the perturbation couples to observable $\hat{B}$:

$$\Delta A_t = -\frac{1}{\hbar} \int_{-\infty}^{\infty} dt' F_{t'} G^r_{AB}(t, t')$$  \hspace{1cm} (2.18)$$
It is called retarded because due to the Heaviside function, only perturbations for \( t < t' \) contribute.

With the Fourier transform \( F(\omega) \) of the perturbation

\[
F_t = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, F(\omega) e^{-i(\omega+i\delta)t} \quad (2.19)
\]

where \( \delta > 0 \) is infinitesimally small and using the later result that with a Hamiltonian that is not explicitly time dependent the Greens function depends only on time differences \( t - t' \), we can rewrite (2.18) in the form of the **Kubo formula**

\[
\Delta A_t = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} d\omega \, F(\omega) G^r_{AB}(\omega + i\delta) e^{-i(\omega+i\delta)t} \quad (2.20)
\]

The \( \delta > 0 \) in the exponent enforces the boundary condition (2.8).

We will now look into two applications of response functions.

**Magnetic Susceptibility**

The perturbation is a spatially homogeneous magnetic field that oscillates in time:

\[
B_t = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, B(\omega) e^{-i(\omega+i\delta)t}, \quad (2.21)
\]

which couples to the magnetic moment

\[
\vec{m} = \sum_i m_i = \frac{g\mu_B}{\hbar} \sum_i \vec{S}_i . \quad (2.22)
\]

Thus, the perturbing potential term in the Hamiltonian becomes

\[
V_t = -\vec{m} \cdot \vec{B}_t = -\frac{1}{2\pi} \sum_\alpha \int_{-\infty}^{\infty} d\omega \, m^\alpha B^\alpha(\omega) e^{-i(\omega+i\delta)t} \quad (2.23)
\]

where \( \alpha = x, y, z \) are Cartesian directions. An interesting quantity is now the magnetization in response to the applied field. As it is

\[
\vec{M} = \frac{1}{V} \langle \vec{m} \rangle = \frac{g\mu_B}{\hbar V} \sum_i \langle \vec{S}_i \rangle , \quad (2.24)
\]

we have to choose the magnetic momentum operator for both \( \hat{A} \) and \( \hat{B} \) operators in the Kubo formula:

\[
M^\beta_t - M^\beta_0 = -\frac{1}{V} \sum_\alpha \int_{-\infty}^{\infty} dt' B^\alpha_t \langle \langle m^\beta(t) ; m^\alpha(t') \rangle \rangle . \quad (2.25)
\]
Only in a ferromagnet there is a finite magnetization $M_0$ without a field. Eq. (2.25) defines the magnetic susceptibility tensor

$$
\chi_{ij}^{\beta \alpha}(t, t') = -\frac{\mu_0 g \mu_B^2}{V \hbar^2} \langle S_i^\beta(t); S_j^\alpha(t') \rangle
$$

(2.26)
as a retarded Greens function. Thus

$$
\Delta M_\beta^t = \frac{1}{\mu_0} \sum_{ij} \int_{-\infty}^{\infty} dt' B_\alpha^t \chi_{ij}^{\beta \alpha}(t, t')
$$

(2.27)
or in terms of frequency

$$
\Delta M_\beta^t = \frac{1}{2\pi \mu_0} \sum_{ij} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega e^{-i(\omega + i\delta) t} \chi_{ij}^{\beta \alpha}(\omega) B_\alpha^t(\omega)
$$

(2.28)

We have implicitly assumed that the system we consider has permanent localized moments.

Two types of susceptibilities are interesting: The longitudinal susceptibility

$$
\chi_{ij}^{zz}(\omega) = \frac{\mu_0 g \mu_B^2}{V \hbar^2} \langle S_i^z; S_j^z \rangle \omega
$$

(2.29)
where the index indicates the Fourier transform of the retarded Greens function. This can be used to obtain information about the stability of magnetic orderings. For the paramagnetic phase, one calculates the spatial Fourier transform

$$
\chi_{q}^{zz}(\omega) = \frac{1}{N} \sum_{ij} \chi_{ij}^{zz}(\omega) e^{i\vec{q} \cdot (\vec{R}_i - \vec{R}_j)}
$$

(2.30)

At the singularities of this response function, an infinitesimally small field is sufficient to create a finite magnetization, i.e. a spontaneous ordering of the moments. For that purpose, the conditions under which

$$
\left\{ \lim_{(\vec{q}, \omega) \to \infty} \chi_{q}^{zz}(\omega) \right\}^{-1} = 0
$$

(2.31)
are studied; they indicate the paramagnetic ↔ ferromagnetic transition.

The other interesting case is the transversal susceptibility

$$
\chi_{ij}^{+-}(\omega) = -\frac{\mu_0 g \mu_B^2}{V \hbar^2} \langle S_i^+; S_j^- \rangle \omega \quad \text{where} \quad S_i^\pm = S_i^x \pm iS_i^y
$$

(2.32)
Poles of this susceptibility correspond to spin wave (magnon) energies:
\[
\left\{ \chi_{q}^{\pm-}(\omega) \right\}^{-1} = 0 \iff \omega = \omega(\mathbf{q}).
\]

(2.33)

The examples show that linear response theory not only treats weak external perturbations but also yields information about the unperturbed system.

**Electrical conductivity**

Now we consider a spatially homogeneous electrical field that oscillates in time:
\[
\tilde{E}_t = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \tilde{E}(\omega)e^{-i(\omega+i\delta)t}.
\]

(2.34)

The electrical field couples to the electrical dipole moment \( \mathbf{P} \)
\[
\mathbf{P} = \int d^3r \mathbf{r} n(\mathbf{r}).
\]

(2.35)

We consider \( N \) point changes \( q_i \) at positions \( \mathbf{r}_i(t) \); the charge density is
\[
n(\mathbf{r}) = \sum_{i=1}^{N} q_i \delta(\mathbf{r} - \mathbf{r}_i).
\]

(2.36)

This gives a dipole moment operator
\[
\mathbf{P} = \sum_{i=1}^{N} q_i \mathbf{r}_i.
\]

(2.37)

The electrical field causes the additional external potential term in the Hamiltonian
\[
V_t = -\mathbf{P} \cdot \tilde{E}_t = -\frac{1}{2\pi} \sum_{\alpha} \int_{-\infty}^{\infty} d\omega \mathbf{P}^{\alpha} E^{\alpha}(\omega)e^{-i(\omega+i\delta)t}.
\]

(2.38)

An interesting quantity is the response of the current density to the external field:
\[
\mathbf{j} = \frac{1}{V} \sum_{i=1}^{N} q_i \mathbf{r}_i = \frac{1}{V} \mathbf{P}.
\]

(2.39)
Its expectation value without field disappears:
\[
\langle \vec{j} \rangle_0 = 0 .
\] (2.40)

After switching the field on, we have
\[
\langle j^\beta \rangle_t = -\frac{1}{\hbar} \sum_\alpha \int_{-\infty}^{\infty} dt' E^\alpha_t \langle j^\beta(t); P^\alpha(t') \rangle .
\] (2.41)

In terms of the Fourier transforms this becomes
\[
\langle j^\beta \rangle_t = \frac{1}{2\pi} \sum_\alpha \int_{-\infty}^{\infty} d\omega e^{-i(\omega+i\delta)t} \sigma^{\beta\alpha}(\omega) E^\alpha(\omega)
\] (2.42)

This is Ohms law, defining the electrical conductivity tensor
\[
\sigma^{\beta\alpha}(\omega) \equiv -\langle j^\beta; P^\alpha \rangle(\omega)
\] (2.43)

that has retarded Greens functions as components. This can be rewritten as
\[
\sigma^{\beta\alpha}(\omega) = \frac{iN}{\sqrt{m(\omega+i\delta)}} \delta_{\alpha\beta} + \frac{i}{\hbar \omega + i\delta} \langle j^\beta; j^\alpha \rangle
\] (2.44)

The first term represents the conductivity of a noninteracting electron system as given by classical Drude theory, and the second one involving a retarded current-current Greens function represents the interaction between the particles.

### 2.2 Two time Greens functions

The full Greens function formalism has two more Greens functions besides the retarded Greens function:

**Retarded Greens function**
\[
G^r_{AB}(t, t') \equiv \langle[A(t); B(t')]^r = -i\Theta(t - t') \langle [A(t), B(t')] \rangle
\] (2.45)

**Advanced Greens function**
\[
G^a_{AB}(t, t') \equiv \langle[A(t); B(t')]^a = i\Theta(t' - t) \langle [A(t), B(t')] \rangle
\] (2.46)

**Causal Greens function**
\[
G^c_{AB}(t, t') \equiv \langle[A(t); B(t')]^c = -i\langle T_\epsilon (A(t)B(t')) \rangle
\] (2.47)
Again, we have for the operators in Heisenberg representation
\[ X(t) = e^{i\beta \hat{H}t} X e^{-i\beta \hat{H}t}, \hat{H} = H - \mu \hat{N}, \langle X \rangle = \frac{\text{Tr}(e^{-\beta \hat{H}} X)}{\text{Tr}e^{-\beta \hat{H}}}, \beta = \frac{1}{k_B T} \] (2.48)

where we omit the index 0 of \( \hat{H} \) and \( H \) as we are not dealing with external perturbations in this chapter. \( \epsilon \) has the value \( \epsilon = - \) for Fermi operators, \( \epsilon = + \) for Bose operators:
\[
[A[t], B(t')]_{-\epsilon} = A(t)B(t') - \epsilon B(t')A(t)
\] (2.49)

\( \epsilon = - \) yields the anticommutator, \( \epsilon = + \) the commutator.

The **Wick time ordering operator** \( T_\epsilon \) sorts operators in a product according to their time arguments:
\[
T_\epsilon(A(t)B(t')) = \Theta(t - t')A(t)B(t') + \epsilon \Theta(t' - t)B(t')A(t)
\] (2.50)

The \( \epsilon \) makes it distinct from the Dirac time ordering operator.

The **spectral density** is another very important function of manybody theory:
\[
S_{AB}(t, t') = \frac{1}{2\pi} \langle [A(t), B(t')]_{-\epsilon} \rangle
\] (2.51)

It contains the same information as the Greens function.

We now prove the fact that Greens function and spectral density are homogeneous in time if the Hamiltonian is not explicitly time dependent:
\[
\frac{\partial \hat{H}}{\partial t} = 0 \rightarrow G_{AB}^\alpha(t, t') = G_{AB}^\alpha(t - t'), \quad (\alpha = r, a, c)
\]
\[
S_{AB}(t, t') = S_{AB}(t - t')
\] (2.52)

We only need to prove that for the so called **correlation functions**
\[
\langle A(t), B(t') \rangle, \quad \langle B(t'), A(t) \rangle
\] (2.53)

The proof is based on cyclic invariance of the trace:
\[
\text{Tr}\{e^{-\beta \hat{H}}A(t), B(t')\} = \text{Tr}\{e^{-\beta \hat{H}}e^{i\beta \hat{H}t} A e^{-i\beta \hat{H}(t-t')} B e^{-i\beta \hat{H}t'}\} = \text{Tr}\{e^{-\beta \hat{H}}e^{i\beta \hat{H}(t-t')} A e^{-i\beta \hat{H}(t-t')} B\} = \text{Tr}\{e^{-\beta \hat{H}}A(t - t')B(0)\}
\] (2.54)

Thus,
\[
\langle A(t), B(t') \rangle = \langle A(t - t'), B(0) \rangle
\] (2.55)
and analogously
\[
\langle B(t'), A(t) \rangle = \langle B(0), A(t-t') \rangle.
\] (2.56)

Actually calculating the Greens function can be done via the general equation of motion for Heisenberg operators
\[
i \hbar \frac{d}{dt} A_H(t) = [A_H, H_H](t) + i \hbar \frac{\partial A_H}{\partial t}
\] (2.57)

We also have
\[
\frac{d}{dt} \Theta(t-t') = \delta(t-t') = -\frac{d}{dt'} \Theta(t-t')
\] (2.58)

Then, all three Greens functions formally have the same equation of motion:
\[
i \hbar \frac{\partial}{\partial t} G_{\alpha AB}(t,t') = \hbar \delta(t-t')\langle [A,B]_{-\epsilon} \rangle + \langle \langle [A, H]_{-\epsilon}(t); B(t') \rangle \rangle^\alpha
\] (2.59)

But the solutions have to obey different boundary conditions:
\[
G_{AB}^r(t,t') = 0 \quad \text{for} \quad t < t'
\]
\[
G_{AB}^a(t,t') = 0 \quad \text{for} \quad t > t'
\]
\[
G_{AB}^c(t,t') = \begin{cases} -i \langle A(t-t'), B(0) \rangle & \text{for} \quad t > t' \\ -i \epsilon \langle B(0), A(t-t') \rangle & \text{for} \quad t < t' \end{cases}
\] (2.60)

On the right hand side of (2.59) a new Greens functions appears as \([A, H]_{-\epsilon}\) is again an operator. Usually this leads to a higher order Greens function, \textit{i.e.} one that contains more operators than the original \(G_{AB}^\alpha(t,t')\). For this higher order Greens function, another equation of motion of type (2.59) can be written. This leads to an infinite chain of equations of motion. The system of equations can only be solved if the chain is stopped at some point by decoupling, \textit{i.e.} by making physically motivated approximations to some higher order Greens functions.

Often it is more practical to work in the frequency domain rather than in the time domain:
\[
G_{AB}^\alpha(\omega) \equiv \langle \langle A; B \rangle \rangle^\alpha_{\omega} = \int_{-\infty}^{\infty} d(t-t') G_{AB}^\alpha(t-t') e^{i\omega(t-t')}
\]
\[
G_{AB}^\alpha(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \ G_{AB}^\alpha(\omega) e^{-i\omega(t-t')}
\] (2.61)
The spectral density transforms in the same way. If we also use the Fourier representation of the Delta function

\[
\delta(\omega - \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' \, d(t - t') \, e^{-i(\omega - \omega')(t-t')}
\]

\[
\delta(t - t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \, e^{i\omega(t-t')}
\]

the equation of motion (2.59) becomes

\[
\omega \langle \langle A; B \rangle \rangle_\omega = \langle [A, B]_\omega \rangle + \frac{\hbar}{\Omega} \langle \langle [A, H]_\omega ; B \rangle \rangle_\omega
\]

(2.63)

This is now an algebraic equation, not a differential equation any more. Meanwhile, the difficulty that an infinite chain of such equations is produced remains.

**Spectral representation**

Spectral representations of the Greens functions are important in order to find boundary conditions for the Eq. (2.63).

We take \( E_n \) and \|E_n\rangle to be eigenenergies and eigenvectors of the Hamiltonian \( \mathcal{H} \) of the system we consider:

\[
\mathcal{H}\langle E_n \rangle = E_n\langle E_n \rangle
\]

(2.64)

We assume the states \|E_n\rangle to form a complete orthonormal system

\[
\sum_n \langle E_n | E_m \rangle = \delta_{nm}
\]

(2.65)

First we consider the correlation functions \( \langle A(t)B(t') \rangle \) and \( \langle B(t'), A(t) \rangle \) (\( \Omega = \text{Tr} e^{-\beta \mathcal{H}} \)):

\[
\Omega \langle A(t)B(t') \rangle = \text{Tr} \{ e^{-\beta \mathcal{H}} A(t)B(t') \} = \sum_n \langle E_n | e^{-\beta \mathcal{H}} A(t)B(t') | E_n \rangle
\]

\[
= \sum_{n,m} \langle E_n | A(t) | E_m \rangle \langle E_m | B(t') | E_n \rangle e^{-\beta E_n}
\]

\[
= \sum_{n,m} \langle E_n | A | E_m \rangle \langle E_m | B | E_n \rangle e^{-\beta E_n} e^{\frac{i}{\hbar}(E_n-E_m)(t-t')}
\]

\[
= \sum_{n,m} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} e^{-\beta(E_m-E_n)} e^{\frac{i}{\hbar}(E_n-E_m)(t-t')}
\]

(81)
Introducing a unit operator $\mathcal{1}$ has significantly simplified the time dependence of the Heisenberg operators. In the last step we have exchanged $n$ and $m$ indices. Analogously we find for the other correlation function

$$\Omega \langle B(t') A(t) \rangle = \sum_{n,m} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} e^{-\frac{1}{\hbar} (E_n - E_m) (t-t')} \quad (2.67)$$

If we now substitute (2.66) and (2.67) into the definition of the spectral density (2.51) or rather its Fourier transform

$$S_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d(t-t') S_{AB}(t-t') e^{i\omega(t-t')}$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d(t-t') e^{i\omega(t-t')} \left( \langle A(t) B(t') \rangle - \varepsilon \langle B(t'), A(t) \rangle \right)$$

$$= \frac{1}{\Omega} \frac{1}{2\pi} \int_{-\infty}^{\infty} d(t-t') e^{i(t-t')} \left( \omega \frac{E_n - E_m}{\hbar} \right) e^{-\beta E_n} (e^{-\beta (E_n - E_m)} - \varepsilon) \times$$

$$\times \sum_{nm} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle$$

$$\quad (2.68)$$

and with the definition of the delta function (2.62)

$$S_{AB}(\omega) = \frac{1}{\Omega} \sum_{nm} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle (e^{\beta \hbar \omega} - \varepsilon) \delta \left( \omega - \frac{E_n - E_m}{\hbar} \right) \quad (2.69)$$

The argument of the delta function contains the possible excitation energies of the system. Now we will express the Greens functions with the help of the spectral density. We use the following representation of the step function:

$$\Theta(t-t') = \frac{i}{2\pi} \int_{-\infty}^{\infty} dx \frac{e^{ix(t-t')}}{x + i0^+} \quad (2.70)$$

This can be proven using the residue theorem (see below). Using this rela-
tion, we can transform the retarded Greens function

\[ G^r_{AB}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega(t-t')} (2\pi S_{AB}(t-t')) (2.71) \]

This leads to the **spectral representation of the retarded Greens function**

\[ G^r_{AB}(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{S_{AB}(\omega')}{\omega - \omega' + i0^+} \quad (2.72) \]

Analogous treatment of the advanced Greens function yields the **spectral representation of the advanced Greens function**

\[ G^a_{AB}(\omega) = \int_{-\infty}^{\infty} d\omega' \frac{S_{AB}(\omega')}{\omega - \omega' - i0^+} \quad (2.73) \]

The only (but significant) difference between \( G^r_{AB} \) and \( G^a_{AB} \) is the sign of \( i0^+ \); it determines the analytic properties of retarded and advanced functions, \( G^r_{AB} \) can be continued analytically into the upper, \( G^a_{AB} \) into the lower complex plane. Neither is true for the causal function \( G^c_{AB} \). Substituting the spectral representation (2.69) of the spectral density into (2.72) and (2.73) yields the important expression

\[ G^a_{AB} = \frac{1}{\Omega} \sum_{nm} \langle E_n|B|E_m\rangle \langle E_m|A|E_n\rangle e^{-\beta E_n} e^{\beta (E_n-E_m) - \varepsilon} \omega - \frac{|E_n-E_m|}{\hbar} \pm i0^+ \quad (2.74) \]

Both functions are meromorphic in the complex plane (holomorphic except for a set of isolated points) with singularities at the exact excitation energies of the interacting system. As retarded and advanced Greens functions have the same physical content, they are sometimes joined into one function \( G_{AB}(\omega) \); \( G^r_{AB} \) and \( G^a_{AB} \) are considered the two branches of a single function in the complex \( \omega \) plane (obtained by considering \( \omega + i\eta \) or \( \omega - i\eta \))
a complex variable and calling it again \( \omega \):

\[
G_{AB}(\omega) = \int_{-\infty}^{\infty} d\omega' S_{AB}(\omega') \frac{1}{\omega - \omega'} = \begin{cases} 
G_{AB}^r(\omega) & \text{if } \text{Im } \omega > 0 \\
G_{AB}^a(\omega) & \text{if } \text{Im } \omega < 0 
\end{cases} \tag{2.75}
\]

The singularities are on the real axis. In textbooks, \( r \) and \( a \) indices are often omitted, and interpretation of Greens functions written like in Eq. (2.75) in terms of retarded or advanced Greens functions is left to the reader.

We still need the spectral representation of the causal Greens functions. Using the definition (2.47), we have

\[
G_{AB}^c(\omega) = -i \int_{-\infty}^{\infty} d(t-t') e^{-i\omega(t-t')} \{ \Theta(t-t') \langle A(t)B(t') \rangle + \varepsilon \Theta(t'-t) \langle B(t'), A(t) \rangle \}
\]

Using results (2.66), (2.67) and (2.70), we obtain

\[
G_{AB}^c(\omega) = \frac{1}{\Omega} \sum_{nm} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt'' \int_{-\infty}^{\infty} dx \frac{1}{x + i0^+} \\
\left\{ e^{\beta(E_n-E_m)} e^{i(\omega E_n-E_m-x) t''} + \varepsilon e^{i(\omega E_n-E_m+x) t''} \right\}
\]

\[
= \frac{1}{\Omega} \sum_{nm} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} \int_{-\infty}^{\infty} dx \frac{1}{x + i0^+} \\
\left\{ e^{\beta(E_n-E_m)} \delta\left( \omega - \frac{E_n-E_m}{\hbar} - x \right) + \varepsilon \delta\left( \omega - \frac{E_n-E_m}{\hbar} + x \right) \right\}
\]

This yields the spectral representation of the causal Greens function

\[
G_{AB}^c(\omega) = \frac{1}{\Omega} \sum_{nm} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} \left\{ \frac{e^{\beta(E_n-E_m)}}{\omega - \frac{E_n-E_m}{\hbar} + i0^+} - \frac{\varepsilon}{\omega - \frac{E_n-E_m}{\hbar} - i0^+} \right\}
\]

We have expressed the retarded and advanced Greens functions by the spectral density. Using the Dirac identity

\[
\frac{1}{x \pm i0^+} = \text{P} \frac{1}{x} \pm i\pi\delta(x)
\]

(2.79)
that should be interpreted as
\[
\lim_{\delta \to 0^+} \int dx \frac{f(x)}{x \pm i\delta} = P \int dx \frac{f(x)}{x} \pm i\pi f(0)
\] (2.80)
with the Cauchy principal value denoted by P, we can write the spectral density in terms of the Greens functions:
\[
G_{AB}(\omega + i0^+) - G_{AB}(\omega - i0^+)
= \int_{-\infty}^{\infty} d\omega S_{AB}(\omega') \left\{ \frac{1}{\omega - \omega' + i0^+} - \frac{1}{\omega - \omega' - i0^+} \right\}
\]
\[
= \int_{-\infty}^{\infty} d\omega S_{AB}(\omega') \left\{ -2\pi i\delta(\omega - \omega') \right\} = \frac{2\pi}{i} S_{AB}(\omega),
\] (2.81)
and thus
\[
S_{AB}(\omega) = \frac{i}{2\pi} \left\{ G_{AB}(\omega + i0^+) - G_{AB}(\omega - i0^+) \right\}
\] (2.82)
Assuming the spectral density to be real, this means
\[
S_{AB}(\omega) = \mp \text{Im} \ G_{AB}^r(\omega)
\] (2.83)
We now prove the formula
\[
\theta(t) = \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} dx \frac{e^{-ixt}}{x + i\delta}
\] (2.84)
that was essential for arriving at the spectral representation of the Greens functions (2.72) and (2.73). We first consider the case \( t > 0 \). For these \( t \) values we can obtain a closed integration contour by adding a semicircle of radius \( R \) in the lower complex plane for the integral (2.84) (see Fig. 2.1); the factor \( e^{-ixt} \) ensures that in the limit \( R \to \infty \), the contribution of the semicircle to the integral vanishes (Jordan’s lemma). To see that, we consider the argument \(-ixt\) of the exponential function:
\[
-ixt = -i(x' + ix'')t = -ix't + x''t
\] (2.85)
In order to have a vanishing exponential function in the limit \( R = |x| \to \infty \), we need \( x''t \to -\infty \) and thus a contour in the lower complex plane \( x'' < 0 \) for \( t > 0 \). Thus the integral (2.84) can be written as
\[
\lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} dx \frac{e^{-ixt}}{x + i\delta} = \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{C<} dx \frac{e^{-ixt}}{x + i\delta}
\] (2.86)
This can be evaluated with the residue theorem
\[
\oint_{\partial D} dx f(x) = 2\pi i \sum_{x_i \in D} \text{Res} \{f(x_i)\}
\] (2.87)

where \(D\) is a domain in the complex plane with outline \(\partial D\). The contour integration needs to be done in the mathematically positive sense which is counterclockwise. The sum runs over all poles \(x_i\) of \(f(x)\) in \(D\). \(\text{Res}f(x_i)\) is the residue of \(f(x)\) at \(x_i\); if the Laurent series of \(f(x)\) at \(x_i\) has the form
\[
f(x) = \frac{a_{-1}}{x - x_i} + \sum_{n=0}^{\infty} a_n(x - x_i)^n
\] (2.88)

then \(a_{-1} = \text{Res} \{f(x_i)\}\). For a simple pole at \(x_0\) the residue can be calculated as
\[
\text{Res} \{f(x_0)\} = \lim_{x \to x_0} (x - x_0)f(x)
\] (2.89)

Alternatively if \(f(x) = \frac{p(x)}{q(x)}\) and \(q(x)\) has a simple zero at \(x = x_0\)
\[
\text{Res} \{f(x_0)\} = \frac{p(x_0)}{q'(x_0)}
\] (2.90)

For a pole of order \(m > 1\)
\[
\text{Res} \{f(x_0)\} = \frac{1}{(m-1)!} \lim_{x \to x_0} \left\{ \frac{d^{m-1}}{dx^{m-1}} [(x - x_0)^m f(x)] \right\}
\] (2.91)
Here,

\[ a_{-1} = \lim_{x \to -i\delta} \frac{x + i\delta}{x + i\delta} e^{-ixt} = e^{-\delta t} = 1 \quad \text{for} \quad \delta \to 0 \quad (2.92) \]

Thus,

\[ \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{C^-} dx \frac{e^{-ixt}}{x + i\delta} = 2\pi i \frac{i}{2\pi} a_{-1} = 1 \quad (2.93) \]

For the second case, \( t < 0 \), we have to close the integration contour \( C^> \) in the upper half plane (see Fig. 2.2). Then we can write

\[ \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} dx \frac{e^{-ixt}}{x + i\delta} = \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{C^>} dx \frac{e^{-ixt}}{x + i\delta} \quad (2.94) \]

As the contour doesn’t contain a singularity of the integrand the value of the integral is zero according to Cauchy’s integral theorem. Combining the cases for \( t > 0 \) and \( t < 0 \), we find

\[ \lim_{\delta \to 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} dx \frac{e^{-ixt}}{x + i\delta} = \Theta(t) \quad (2.95) \]

Now we can discuss the analytical properties of the Greens functions, \( i.e. \) their analyticity in the complex \( \omega \) plane. First we defined the Greens functions \( G_{AB}^\alpha(\omega) \) via (2.61) only for real frequencies \( \omega \), but the spectral representations (2.72) and (2.73) offer an analytic continuation in the complex
\( \omega \) plane. Meanwhile, Eq. (2.78) for the causal Greens function indicates that analytic continuation is not possible as \( G^c_{AB}(\omega) \) has singularities in the upper and in the lower complex plane. For retarded and advanced Greens functions one can show that the continuation doesn’t only exist but is analytic – for the retarded Greens function in the upper complex plane and for the advanced function in the lower complex plane. To see that we reconsider the definition

\[
G^\alpha_{AB}(\omega) = \int dt \, G^\alpha_{AB}(t) e^{i\omega t} \quad (2.96)
\]

and separate real and imaginary parts of \( \omega \):

\[
\omega = \omega' + i\omega'' \quad (2.97)
\]

Then, because of

\[
e^{i\omega t} = e^{i\omega' t - \omega'' t} \quad (2.98)
\]

an analytic continuation in the complex plane is possible if only positive values of \( t \) are accepted for \( \omega'' > 0 \) and if only negative values of \( t \) are admitted for \( \omega'' < 0 \) because under these conditions \( e^{-\omega'' t} \) guarantees the convergence of the integral (2.96) and its \( \omega \) derivatives for a large class of functions \( G^\alpha_{AB}(\omega) \). As the retarded Greens function is only nonzero for \( t > 0 \) and the advanced function only for \( t < 0 \), the convergence conditions are fulfilled and thus the retarded Greens function is analytic in the upper complex \( \omega \) plane and the advanced function in the lower. The advanced function generally doesn’t permit analytic continuation as \( \omega'' > 0 \) as well as \( \omega'' < 0 \) would lead to divergencies. This makes retarded and advanced functions better suited for many applications.

**Spectral theorem**

We saw that Greens functions and spectral density contain microscopic information about the excitation energies of the considered system. We will now find that also the macroscopic thermodynamic properties are available from suitably defined Greens functions. We start with the correlation function \( \langle B(t'), A(t) \rangle \) because its spectral representation (2.67) is similar to the corresponding representation of the spectral density (2.69). Combining (2.67) and (2.69) yields

\[
\langle B(t'), A(t) \rangle = \int_{-\infty}^{\infty} d\omega \frac{S^{(-)}_{AB}(\omega)}{e^{\beta \hbar \omega} + 1} e^{-i\omega(t-t')} \quad (2.99)
\]
where we have chosen the anticommutator spectral density with $\varepsilon = -1$. When using commutator spectral densities ($\varepsilon = +1$) a constant $D$ needs to be added to this expression

$$\langle B(t'), A(t) \rangle = \int_{-\infty}^{\infty} d\omega \frac{S_{AB}^{(\varepsilon)}(\omega)}{e^{\beta h\omega} - \varepsilon} e^{-i\omega(t-t')} + \frac{1}{2}(1 + \varepsilon)D \quad (2.100)$$

This is due to the fact that the commutator spectral density doesn’t determine the correlation function completely. We can see that by separating diagonal (in $\omega$) and offdiagonal parts of $S_{AB}(\omega)$ (Eq. (2.69))

$$S_{AB}^{(\varepsilon)}(\omega) = \hat{S}_{AB}^{(\varepsilon)}(\omega) + (1 - \varepsilon)D\delta(\omega) \quad (2.101)$$

where

$$\hat{S}_{AB}^{(\varepsilon)}(\omega) = \frac{1}{\Omega} \sum_{n \neq m}^{E_n \neq E_m} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} \left( e^{\beta h\omega} - \varepsilon \right) \delta \left( \omega - \frac{E_n - E_m}{h} \right)$$

$$D = \frac{1}{\Omega} \sum_{n \neq m}^{E_n \neq E_m} \langle E_n | B | E_m \rangle \langle E_m | A | E_n \rangle e^{-\beta E_n} \quad (2.102)$$

The diagonal terms contained in $E$ fall out of the commutator spectral density even though they are needed for determining the correlations. We have

$$\langle B(t'), A(t) \rangle = D + \int_{-\infty}^{\infty} d\omega \frac{\hat{S}_{AB}^{(\varepsilon)}(\omega)}{e^{\beta h\omega} - \varepsilon} e^{-i\omega(t-t')}$$

$$\langle A(t), B(t') \rangle = D + \int_{-\infty}^{\infty} d\omega \frac{S_{AB}^{(\varepsilon)}(\omega)e^{\beta h\omega}}{e^{\beta h\omega} - \varepsilon} e^{-i\omega(t-t')} \quad (2.103)$$

as can be read off from the spectral representations (2.66) and (2.67).

**Exact relations**

There are a number of symmetry relations and sum rules for Greens functions that are useful as soon as approximations for calculating Greens functions need to be developed.

1. $$G_{AB}^{(\varepsilon)}(t, t') = \varepsilon G_{BA}^{(\varepsilon)}(t', t) \quad (2.104)$$
follows from the definitions because
\[
\langle\langle A(t); B(t) \rangle\rangle^r = -i\Theta(t - t') \langle[A(t), B(t')]_{-\epsilon} \rangle
\]
\[
= i\epsilon\Theta(t - t') \langle[B(t'), A(t)]_{-\epsilon} \rangle = \epsilon \langle\langle B(t'); A(t) \rangle\rangle^a
\]
(2.105)

2.

\[G^r_{AB}(\omega) = \epsilon G^g_{BA}(-\omega) \quad \text{for real } \omega\] (2.106)

follows by Fourier transforming Eq. (2.104). From the combined Greens functions for complex \(\omega\) (Eq. (2.81)) we have

\[G_{AB}(\omega) = \epsilon G_{BA}(-\omega) \quad \text{for complex } \omega\] (2.107)

3.

\[(G^r_{AB}(t, t'))^* = \epsilon G^{r,a}_{A^+B^+}(t', t)\] (2.108)

4. Another important relation follows from the equation of motion:

\[
\int_{-\infty}^{\infty} d\omega \left\{ \omega \langle\langle A; B \rangle\rangle^r_{\omega} - \hbar \langle[A, B]_{-\epsilon} \rangle \right\} = \int_{-\infty}^{\infty} d\omega \langle\langle A, \mathcal{H}; B \rangle\rangle_{\omega}^r
\]

\[
= \int_{-\infty}^{\infty} d\omega (-i) \int_{0}^{\infty} dt \langle[A, \mathcal{H}]_{-\epsilon}(t), B(0) \rangle e^{i\omega t}
\]

\[
= \hbar \int_{0}^{\infty} dt \langle[\dot{A}(t), B(0)]_{-\epsilon} \rangle \int_{-\infty}^{\infty} d\omega e^{i\omega t} = 2\pi\hbar \int_{0}^{\infty} dt \langle[\dot{A}(t), B(0)]_{-\epsilon} \rangle \delta(t)
\]

(2.109)

Using \(\int_{0}^{\infty} dx f(x)\delta(x) = \frac{1}{2} f(0)\) we find

\[
\int_{-\infty}^{\infty} d\omega \left\{ \omega G^r_{AB}(\omega) - \hbar \langle[A, B]_{-\epsilon} \rangle \right\} = \pi\hbar \langle[\dot{A}(0), B(0)]_{-\epsilon} \rangle
\]

(2.110)

and analogously for the other two Greens functions

\[
\int_{-\infty}^{\infty} d\omega \left\{ \omega G^a_{AB}(\omega) - \hbar \langle[A, B]_{-\epsilon} \rangle \right\} = -\pi\hbar \langle[\dot{A}(0), B(0)]_{-\epsilon} \rangle
\]

\[
\int_{-\infty}^{\infty} d\omega \left\{ \omega G^c_{AB}(\omega) - \hbar \langle[A, B]_{-\epsilon} \rangle \right\} = \pi\hbar \left\{ \langle\dot{A}(0), B(0) \rangle + \epsilon \langle B(0), \dot{A}(0) \rangle \right\}
\]

(2.111)
The importance for these relations arises from the following argument: The right hand sides, being expectation values of products of operators (observables) are finite; thus, the integrals on the left hand side need to converge. This leads to the requirement for the integrands:

$$\lim_{\omega \to \infty} G_{AB}^\alpha(\omega) = \frac{\hbar}{\omega} \langle [A, B] - \varepsilon \rangle$$

The expectation value on the right can usually be calculated directly so that this relation determined the high frequency behavior of the Greens function; they fall off as $\frac{1}{\omega}$. In case the (anti)commutator on the right hand side of (2.112) vanishes, the Greens function will go to zero with a higher power of $\frac{1}{\omega}$ for $\omega \to \infty$.

**Kramers Kronig relations**

We have seen that $G_{AB}^r$ and $G_{AB}^a$ are completely defined by the spectral density $S_{AB}$. But $S_{AB}$ can be obtained solely from the imaginary part of these functions. Thus, real and imaginary parts of the Greens functions are not independent. We consider the integral

$$I_c(\omega) = \int_c d(\omega') \frac{G_{AB}^r(\omega')}{\omega - \omega' - i0^+}$$

$G_{AB}^r(\omega)$ is analytic in the complete upper frequency plane. If we take $\omega$

**Abbildung 2.3:**
Integration contour in the complex $\omega'$ plane for the Kramers Kronig relations.
to be real, this is true for the entire integrand; then the integral along the contour \( C \) of Fig. 2.3 becomes

\[
I_c(\omega) = 0
\] (2.114)

Letting the radius \( R \) of the semicircle go to infinity, the part of the contour integral along the semicircle disappears because of (2.112), and using the Dirac identity (2.79) we find

\[
0 = \int_{-\infty}^{\infty} d\omega' \frac{G^r_{AB}(\omega')}{\omega - \omega' + i0^+} = P \int_{-\infty}^{\infty} d\omega' \frac{G^r_{AB}(\omega')}{\omega - \omega'} + i\pi G^r_{AB}(\omega)
\] (2.115)

This gives

\[
G^r_{AB}(\omega) = \frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{G^r_{AB}(\omega')}{\omega - \omega'}
\] (2.116)

Analogously we find for the advanced Greens function if we close the semicircle in the lower complex \( \omega' \) plane where \( G^a_{AB}(\omega') \) is analytic and by replacing \(-i0^+ \) by \(+i0^+ \):

\[
G^a_{AB}(\omega) = -\frac{i}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{G^a_{AB}(\omega')}{\omega - \omega'}
\] (2.117)

This means that we don’t need to know the entire Greens functions; it is enough to know the real or the imaginary part, and the other part is given by the Kramers Kronig relations which we read off from (2.116) and (2.117):

\[
\begin{align*}
\text{Re} G^r_{AB}(\omega) &= \mp \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\text{Im} G^a_{AB}(\omega')}{\omega - \omega'} \\
\text{Im} G^r_{AB}(\omega) &= \pm \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \frac{\text{Re} G^a_{AB}(\omega')}{\omega - \omega'}
\end{align*}
\] (2.118)

Assuming the spectral density to be real, (Eq. (2.83)) is valid and thus

\[
\begin{align*}
\text{Re} G^r_{AB}(\omega) &= \text{Re} G^a_{AB}(\omega) = P \int_{-\infty}^{\infty} d\omega' \frac{S_{AB}(\omega')}{\omega - \omega'} \\
\text{Im} G^r_{AB}(\omega) &= -\text{Im} G^a_{AB}(\omega) = -\pi S_{AB}(\omega)
\end{align*}
\] (2.119)

Eqs. (2.69) and (2.70) provide a connection to the causal Greens function:

\[
\begin{align*}
\text{Im} G^c_{AB}(\omega) &= -\pi S_{AB}(\omega) \frac{e^{\beta \omega} + \epsilon}{e^{\beta \omega} - \epsilon} \\
\text{Re} G^c_{AB}(\omega) &= \text{Re} G^r_{AB}(\omega).
\end{align*}
\] (2.120)
While the Kramers Kronig relations (2.118) are generally valid, the following relations require the spectral density to be real as it often is; in this case, the different types of Greens functions can be converted by these equations; this can be useful as equations of motion methods determine $G_{AB}^{r,a}$ while diagrammatic techniques are used to calculate $G_{AB}^{c}$.

### 2.3 Application to noninteracting electrons

We will get to know the properties of Greens functions for the simple example of noninteracting electrons. The advantage of using the Greens function formalism is not obvious in this case as all results could have been obtained with other methods, but the real strength of the new formalism will become clear in the case of interacting electrons.

We first consider Bloch electrons that don’t interact with another but are subject to the periodic potential of the lattice. The Hamiltonian is

$$
\mathcal{H} = H_0 - \mu \hat{N} , \quad H_0 = \sum_{\vec{k}\sigma} \epsilon(\vec{k}) a_{k\sigma}^\dagger a_{k\sigma} , \quad \hat{N} = \sum_{\vec{k}\sigma} a_{k\sigma}^\dagger a_{k\sigma} \quad (2.121)
$$

All properties we are interested in can be obtained from the so-called one-electron Greens function

$$
G_{k\sigma}^\alpha(\omega) = \langle \langle a_{k\sigma}; a_{k\sigma}^\dagger \rangle \rangle^\alpha_\omega , \quad \alpha = r, a, c ; \quad \epsilon = -1 \quad (2.122)
$$

The choice of $\epsilon = -1$ is plausible as we deal with a purely Fermionic system but it is not necessary. We now proceed in the same way in which more complicated problems would be tackled: The first step is writing and solving the equation of motion:

$$
\omega G_{k\sigma}^\alpha(\omega) = \langle [a_{k\sigma}^-; a_{k\sigma}^\dagger ]_+ \rangle + \langle [a_{k\sigma}^-; \mathcal{H}^-; a_{k\sigma}^\dagger ] \rangle^\alpha_\omega \quad (2.123)
$$

Using the commutation relations

$$
[a_{k\sigma'}^-; a_{k'\sigma'}^-]_+ = [a_{k\sigma}^\dagger; a_{k\sigma}^\dagger]_+ = 0 , \quad [a_{k\sigma}^-; a_{k\sigma}^-]_+ = \delta_{kk'}\delta_{\sigma\sigma'} \quad (2.124)
$$

we find

$$
[a_{k\sigma}; \mathcal{H}_0^-] = \sum_{kk'} (\epsilon(\vec{k'}) - \mu) [a_{k\sigma}^-; a_{k'\sigma'}^\dagger; a_{k'\sigma'}^-]_-
$$

$$
= \sum_{k'\sigma'} (\epsilon(\vec{k'}) - \mu) \delta_{kk'}\delta_{\sigma\sigma'} a_{k'\sigma'}^- = (\epsilon(\vec{k}) - \mu) a_{k\sigma}^- \quad (2.125)
$$
Substituting in (2.123) leads to
\[
\omega G^\alpha_{k\sigma}(\omega) = 1 + (\varepsilon(\vec{k}) - \mu)G^\alpha_{k\sigma}(\omega)
\]
(2.126)
solving for \(G^\alpha_{k\sigma}\) and fulfilling the boundary conditions with \(+i0^+\) or \(-i0^+\) yields
\[
G^r_{k\sigma}(\omega) = \frac{1}{\omega - \varepsilon(\vec{k}) + \mu \pm i0^+}
\]
(2.127)

We will use the convention \(\hbar = 1\) from now on. The singularities of this function correspond to the possible excitation energies of the system. With complex argument \(\omega\) we have the combined function
\[
G^-_{k\sigma}(\omega) = \frac{1}{\omega - \varepsilon(\vec{k}) + \mu}
\]
(2.128)
The one electron spectral density is
\[
S^-_{k\sigma}(\omega) = \delta(\omega - \varepsilon(\vec{k}) + \mu)
\]
(2.129)

From the frequency domain we can now change to the time domain. The retarded Greens function is
\[
G^r_{k\sigma}(t-t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega(t-t')}}{\omega - \varepsilon(\vec{k}) + \mu + i0^+}
\]
(2.130)
Substitution of \(\omega\) by \(\omega' = \omega - \varepsilon(\vec{k}) + \mu\) leads to
\[
G^r_{k\sigma}(t-t') = e^{-i(\varepsilon(\vec{k})-\mu)(t-t')} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' e^{-i\omega'(t-t')} (\omega' + i0^+)
\]
(2.131)
Using Eq. (2.70) gives
\[
G^r_{k\sigma}(t-t') = -i\Theta(t-t')e^{-i(\varepsilon(\vec{k})-\mu)(t-t')}
\]
(2.132)
This shows how indeed the introduction of \(+i0^+\) has fulfilled the boundary condition. Analogously we find for the advanced function:
\[
G^a_{k\sigma}(t-t') = -i\Theta(t'-t)e^{-i(\varepsilon(\vec{k})-\mu)(t-t')}
\]
(2.133)

In the noninteracting system, the time dependent Greens functions show an oscillatory behavior with a frequency that corresponds to an exact excitation energy. We will see later that this remains true for interacting systems,
but they will additionally have a damping factor that corresponds to a finite lifetime of the quasiparticles. The time dependent spectral density is easily found from (2.129):

\[
S_{\vec{k}\sigma}(t - t') = \frac{1}{2\pi} e^{-i(\varepsilon(\vec{k}) - \mu)(t - t')}
\] (2.134)

The average occupation number \( \langle n_{\vec{k}\sigma}^- \rangle \) of the level \((\vec{k}\sigma)\) can be found by substituting (2.129) into the spectral theorem (2.100)

\[
\langle a_{\vec{k}\sigma}^\dagger(t) a_{\vec{k}\sigma}(t) \rangle = \langle n_{\vec{k}\sigma}^- \rangle = \int_{-\infty}^{\infty} d\omega \frac{\delta(\omega - \varepsilon(\vec{k}) - \mu)}{e^{\beta\omega} + 1} = \frac{1}{e^{\beta(\varepsilon(\vec{k}) - \mu)} + 1}
\] (2.135)

This is the result known from quantum statistics, the Fermi function

\[
f_-(\omega) = \frac{1}{e^{\beta(\omega - \mu)} + 1}
\] (2.136)

evaluated for \( \omega = \varepsilon(\vec{k}) \). Using \( \langle n_{\vec{k}\sigma}^- \rangle \) we can fix the total electron number \( N_e \) by summing over wave vector and spin:

\[
N_e = \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} d\omega S_{\vec{k}\sigma}^-(\omega) \frac{1}{e^{\beta\omega} + 1} = \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} d\omega f_-(\omega) S_{\vec{k}\sigma}^-(\omega - \mu)
\] (2.137)

If we denote with \( \rho_\sigma(\omega) \) the density of states per spin for the free Fermion system (for which \( \rho_\sigma(\omega) = \rho_{-\sigma}(\omega) \)), we can write \( N_e \) as

\[
N_e = N \sum_{\sigma} \int_{-\infty}^{\infty} d\omega f_-(\omega) \rho_\sigma(\omega)
\] (2.138)

\( N \) is the number of lattice sites if we consider a one band model; \( \rho_\sigma(\omega) \) is normalized to 1. Comparing (2.137) and (2.138) leads to the definition of quasiparticle density of states

\[
\rho_\sigma(\omega) = \frac{1}{N} \sum_{\vec{k}} S_{\vec{k}\sigma}^-(\omega - \mu)
\] (2.139)

These considerations are not only true for the free system but are generally valid. We will see that (2.139) represents the general definition of
the quasiparticle density of states for any interacting electron system. For noninteracting systems we can enter $S_{\vec{k}\sigma}(\omega)$:

$$\rho_{\sigma}(\omega) = \frac{1}{N} \sum_{\vec{k}} \delta(\omega - \varepsilon(\vec{k})) \quad (2.140)$$

The internal energy $U$ is the thermodynamic expectation value of the Hamiltonian and therefore determined in a simple way by $\langle n_{\vec{k}\sigma}^{-} \rangle$:

$$U = \langle H_0 \rangle = \sum_{\vec{k}\sigma} \varepsilon(\vec{k}) \langle n_{\vec{k}\sigma}^{-} \rangle = \frac{1}{2} \sum_{\vec{k}\sigma} \int_{-\infty}^{\infty} d\omega \left( \omega + \varepsilon(\vec{k}) \right) f_-(\omega) S_{\vec{k}\sigma}^{-}(\omega - \mu) \quad (2.141)$$

The last expression will turn out to be generally valid for interacting systems. From $U$ we obtain the free energy $F$ and thus the entire thermodynamics by considering that

$$F(T, V) = U(T, V) - TS(T, V) = U(T, V) + T \left( \frac{\partial F}{\partial T} \right)_V \quad (2.142)$$

which leads to

$$U(T, V) = -T^2 \left[ \frac{\partial}{\partial T} \left( \frac{1}{T} F(T, V) \right) \right]_V \quad (2.143)$$

Using the third law of thermodynamics

$$\lim_{T \to 0} \left[ \frac{1}{T} (F(T) - F(0)) \right] = \left( \frac{\partial F}{\partial T} \right)_V (T = 0) = -S(T = 0, V) = 0 \quad (2.144)$$

and $F(0, V) = U(0, V)$ we can integrate (2.143) and obtain

$$F(T, V) = U(0, V) - T \int_0^T dT' \frac{U(T', V) - U(0, V)}{T'} \quad (2.145)$$

All other properties of equilibrium thermodynamics can be derived from $F(T, V)$. Here we considered Greens functions $G_{\vec{k}\sigma}^{\alpha} (\omega)$ corresponding to Bloch electrons; we could also have worked in Wannier representation. For the Greens function

$$G_{ij\sigma}^{\alpha}(\omega) = \langle \langle a_i; a_j^{\dagger} \rangle \rangle^{\alpha}_{\omega} \quad (2.146)$$

one finds the equation of motion
\[ \omega G_{ij}^\alpha(\omega) = \delta_{ij} + \sum_m (t_{im} - \mu \delta_{im}) G_{mj}^\alpha(\omega) \] (2.147)

that doesn’t directly decouple but can be solved by Fourier transformation:

\[ G_{ij}^r(\omega) = \frac{1}{N} \sum_k \frac{e^{i \hat{k} (\mathbf{R}_i - \mathbf{R}_j)}}{\omega - (\varepsilon(\hat{k}) - \mu) + i0^+} \] (2.148)

### 2.4 Quasiparticles

We will now investigate how to extract information about interacting electron systems using Greens functions. We consider the Hamiltonian in Bloch representation

\[ H = \sum_{\mathbf{k} \sigma} \varepsilon(\mathbf{k}) a_{\mathbf{k} \sigma}^\dagger a_{\mathbf{k} \sigma} + \frac{1}{2} \sum_{\mathbf{k} \mathbf{p} \mathbf{q} \sigma} v_{\mathbf{k} \mathbf{p}}(\mathbf{q}) a_{\mathbf{k} \mathbf{q} \sigma}^\dagger a_{\mathbf{p} \mathbf{q} \sigma'} a_{\mathbf{p} \mathbf{q} \sigma'} a_{\mathbf{k} \sigma} \] (2.149)

where we consider a one band problem so that we can suppress band indices. The Bloch energies are:

\[ \varepsilon(\mathbf{k}) = \int d^3r \psi^*_\mathbf{k}(\mathbf{r}) \left[ -\frac{\hbar^2}{2m} \Delta + V(\mathbf{r}) \right] \psi_\mathbf{k}(\mathbf{r}) \] (2.150)

where \( \psi^*_\mathbf{k}(\mathbf{r}) \) is a Bloch function and \( V(\mathbf{r}) \) is the periodic lattice potential. The \( \varepsilon(\mathbf{k}) \) are given once the model that we study is specified. The Coulomb matrix element is

\[ v_{\mathbf{k} \mathbf{p}}(\mathbf{q}) = \frac{e^2}{4\pi\varepsilon_0} \int d^3r_1 d^3r_2 \frac{\psi^*_{\mathbf{k} + \mathbf{q}}(\mathbf{r}_1) \psi^*_{\mathbf{p} - \mathbf{q}}(\mathbf{r}_2) \psi_\mathbf{p}(\mathbf{r}_2) \psi_\mathbf{k}(\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \] (2.151)

For a constant lattice potential \( V(\mathbf{r}) = \text{const} \) this becomes

\[ v_{\mathbf{k} \mathbf{p}}(\mathbf{q}) \xrightarrow{V(\mathbf{r})=\text{const}} v_0(\mathbf{q}) = \frac{e^2}{\varepsilon_0 q^2} \] (2.152)

We will also use the Hamiltonian in Wannier representation

\[ H = \sum_{ij\sigma} t_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} v(ij; kl) a^\dagger_{i\sigma} a_{j\sigma'} a_{l\sigma'} a_{k\sigma} \] (2.153)
The hopping integrals $t_{ij}$ are connected to the Bloch energies $\epsilon(\vec{k})$ by Fourier transform. We will now see that the one electron Greens functions

$$G^\alpha_{\vec{k}\sigma}(\omega) \equiv \langle \langle a^-_{\vec{k}\sigma} ; a^+_{\vec{k}\sigma} \rangle \rangle^\alpha_\omega,$$

$$G^\alpha_{ij\sigma}(\omega) \equiv \langle \langle a_{i\sigma} ; a^+_{j\sigma} \rangle \rangle^\alpha_\omega, \quad \alpha = r, a, c; \quad \epsilon = -1 \quad (2.154)$$

and the corresponding one electron spectral density

$$S^-_{\vec{k}\sigma}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d(t - t') e^{-i\omega(t-t')} \langle \langle a^-_{\vec{k}\sigma}(t), a^+_{\vec{k}\sigma}(t') \rangle \rangle^\sigma_\omega$$

$$S^-_{ij\sigma}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d(t - t') e^{-i\omega(t-t')} \langle \langle a_{i\sigma}(t), a^+_{j\sigma}(t') \rangle \rangle^\sigma_\omega \quad (2.155)$$

determine the full equilibrium thermodynamics also for interacting electron systems. To calculate them, we write down the equation of motion of the $\vec{k}$-dependent Greens function, we need the commutator

$$[a^-_{\vec{k}\sigma}, \mathcal{H}] = (\epsilon(\vec{k}) - \mu) a^+_{\vec{k}\sigma} \sum_{\vec{p}\vec{q}\sigma'} v_{\vec{p}\vec{k}+\vec{q}}(\vec{q}) a^-_{\vec{p}\sigma'} a^-_{\vec{k}+\vec{q}\sigma} \quad (2.156)$$

using the higher order Greens function

$$\Gamma^\alpha_{\vec{p}\vec{k};\vec{q}}(\omega) \equiv \langle \langle a^+_{\vec{p}\sigma} a^-_{\vec{q}\sigma'} a^-_{\vec{k}+\vec{q}\sigma} ; a^+_{\vec{k}\sigma} \rangle \rangle^\alpha_\omega \quad (2.157)$$

we have the equation of motion

$$(\omega - \epsilon(\vec{k}) + \mu) G^\alpha_{\vec{k}\sigma}(\omega) = 1 + \sum_{\vec{p}\vec{q}\sigma'} v_{\vec{p}\vec{k}+\vec{q}}(\vec{q}) \Gamma^\alpha_{\vec{p}\vec{k};\vec{q}}(\omega) \quad (2.158)$$

The unknown function $\Gamma$ prevents us from directly solving for $G^\alpha_{\vec{k}\sigma}$. But we postulate that the following decomposition is possible:

$$\langle \langle [a^-_{\vec{k}\sigma}, \mathcal{H} - \mathcal{H}_0]_{\vec{k}} ; a^+_{\vec{k}} \rangle \rangle^\alpha_\omega = \sum_{\vec{p}\vec{q}\sigma'} v_{\vec{p}\vec{k}+\vec{q}}(\vec{q}) \Gamma^\alpha_{\vec{p}\vec{k};\vec{q}}(\omega) \equiv \Sigma^\alpha_{\vec{k}}(k, \omega) G^\alpha_{\vec{k}\sigma}(\omega) \quad (2.159)$$

This equation defines the self energy $\Sigma^\alpha_{\vec{k}}(k, \omega)$. It allows us to solve Eq. (2.158) for $G^\alpha_{\vec{k}\sigma}$:

$$G^\alpha_{\vec{k}\sigma}(\omega) = \frac{1}{\omega - \epsilon(\vec{k}) + \mu - \Sigma^\alpha_{\vec{k}}(k, \omega)} \quad (2.160)$$
Comparison with the corresponding expression for noninteracting electrons shows that the entire effect of the particle interactions is contained in the selfenergy. Usually it is a complex function of \((\vec{k}, \omega)\); the real part determines the energy of the quasiparticles, and the imaginary part their lifetime.

We can rearrange (2.160) a bit; writing \(G_{k\sigma}^{(0)}\) for the one electron Greens function of noninteracting electrons, we have (suppressing the index \(\alpha\))

\[
G_{k\sigma}(\omega) = \frac{1}{\{[G_{k\sigma}^{(0)}(\omega)]^{-1} - \Sigma(\vec{k}, \omega)\}^{-1}} - 1
\]

This gives us the so-called Dyson equation

\[
G_{k\sigma}(\omega) = G_{k\sigma}^{(0)}(\omega) + G_{k\sigma}^{(0)}(\omega)\Sigma(\vec{k}, \omega)G_{k\sigma}(\omega)
\]

(Equation 2.162)

**Electronic self energy**

We will now investigate the general structure of self energy, Greens function and spectral density. The self energy corresponding to Eq. (2.160) is in general a complex quantity.

\[
\Sigma^{\alpha}(\vec{k}, \omega) = R^{\alpha}(\vec{k}, \omega) + iI^{\alpha}(\vec{k}, \omega), \quad \alpha = r, a, c
\]

(Equation 2.163)

Eq. (2.108) for the Greens function implies

\[
(\Sigma^{\alpha}(\vec{k}, \omega))^* = \Sigma^{\alpha}(\vec{k}, \omega)
\]

(Equation 2.164)

This simple relation allows us to concentrate on the retarded Greens functions, and we will omit the \(+i0^+\) if \(I_{\sigma} \neq 0\). We can rewrite Eq. (2.160) as

\[
G_{k\sigma}^{r}(\omega) = \frac{\omega - \varepsilon(\vec{k}) + \mu - R_{\sigma}(\vec{k}, \omega) + iI_{\sigma}(\vec{k}, \omega)}{(\omega - \varepsilon(\vec{k}) + \mu - R_{\sigma}(\vec{k}, \omega))^2 + (I_{\sigma}(\vec{k}, \omega))^2}
\]

(Equation 2.165)

Thus, the spectral density is

\[
S_{k\sigma}^{\sigma}(\omega) = -\frac{1}{\pi} \frac{I_{\sigma}(\vec{k}, \omega)}{(\omega - \varepsilon(\vec{k}) + \mu - R_{\sigma}(\vec{k}, \omega))^2 + (I_{\sigma}(\vec{k}, \omega))^2}
\]

(Equation 2.166)

If we compare this to the spectral representation of the spectral density (2.69)

\[
S_{k\sigma}^{\sigma}(\omega) = \frac{1}{\omega} \sum_{n,m} |\langle E_n | a_{k\sigma}^\dagger | E_m \rangle|^2 e^{-\beta E_n} (e^{\beta \omega} + 1) \delta(\omega - (E_n - E_m))
\]

(Equation 2.167)
which is nonnegative for all \((\vec{k}, \sigma, \omega)\), we find for the imaginary part of the retarded self energy

\[ I_{\sigma}(\vec{k}, \omega) \leq 0. \quad (2.168) \]

We will now investigate (2.166) further. Without explicit knowledge of \(R_{\sigma}(\vec{k}, \omega)\) and \(I_{\sigma}(\vec{k}, \omega)\) we expect more or less pronounced maxima at the resonances

\[ \omega_{i\sigma}(\vec{k}) \equiv \varepsilon(\vec{k}) - \mu + R_{\sigma}(\vec{k}, \omega_{i\sigma}(\vec{k})), \quad i = 1, 2, 3, \ldots \quad (2.169) \]

We have to distinguish two cases:

Case 1: In a certain energy range containing \(\omega_{i\sigma}\),

\[ I_{\sigma}(\vec{k}, \omega) \equiv 0 \quad (2.170) \]

Then we have to consider the limit \(I_{\sigma} \rightarrow -0^+\). Representing the delta function as the limit

\[ \delta(\omega - \omega_0) = \frac{1}{\pi} \lim_{x \rightarrow 0} \frac{x}{(\omega - \omega_0)^2 + x^2} \quad (2.171) \]

we have

\[ S_{\vec{k}\sigma}(\omega) = \delta(\omega - \varepsilon(\vec{k}) + \mu - R_{\sigma}(\vec{k}, \omega)) \quad (2.172) \]

Using

\[ \delta[f(x)] = \sum_i \frac{1}{|f'(x_i)|} \delta(x - x_i); \quad f(x_i) = 0 \quad (2.173) \]

we can write this as

\[ S_{\vec{k}\sigma}(\omega) = \sum_{i=1}^n \alpha_{i\sigma}(\vec{k}) \delta(\omega - \omega_{i\sigma}(\vec{k})) \]

\[ \alpha_{i\sigma}(\vec{k}) = \left| 1 - \frac{\partial}{\partial \omega} R_{\sigma}(\vec{k}, \omega) \right|_{\omega = \omega_{i\sigma}}^{-1} \quad (2.174) \]

The sum runs over the resonances \(\omega_{i\sigma}\) in the energy range for which Eq. (2.170) holds.

Case 2: We consider

\[ I_{\sigma}(\vec{k}, \omega) \neq 0 \quad (2.175) \]
but in a certain energy range around the resonance $\omega_{i\sigma}$

$$|I_{\sigma}(\hat{k}, \omega)| \ll |\epsilon(\hat{k}) - \mu + R_{\sigma}(\hat{k}, \omega)|$$  \hspace{1cm} (2.176)

There we expect a pronounced maximum at $\omega = \omega_{i\sigma}$. To see this, we expand the expression

$$F_{\sigma}(\hat{k}, \omega) = \epsilon(\hat{k}) - \mu + R_{\sigma}(\hat{k}, \omega)$$  \hspace{1cm} (2.177)

close to the resonance up to the linear term:

$$F_{\sigma}(\hat{k}, \omega) = F_{\sigma}(\hat{k}, \omega_{i\sigma}) + (\omega - \omega_{i\sigma}) \frac{\partial F_{\sigma}}{\partial \omega} \bigg|_{\omega = \omega_{i\sigma}} + \cdots$$  \hspace{1cm} (2.178)

This means

$$(\omega - \epsilon(\hat{k}) + \mu - R_{\sigma}(\hat{k}, \omega))^2 \simeq (\omega - \omega_{i\sigma})^2 \left(1 - \frac{\partial R_{\sigma}}{\partial \omega} \bigg|_{\omega = \omega_{i\sigma}} \right)^2$$  \hspace{1cm} (2.179)

We substitute this expression in (2.166), assuming that $I_{\sigma}(\hat{k}, \omega)$ is only weakly dependent on $\omega$ around $\omega_{i\sigma}$ so that

$$I_{\sigma}(\hat{k}, \omega) \approx I_{\sigma}(\hat{k}, \omega_{i\sigma}(\hat{k})) \equiv I_{i\sigma}(\hat{k})$$  \hspace{1cm} (2.180)

and find the following approximation for the spectral density:

$$S^{(i)}_{k\sigma}(\omega) \approx -\frac{1}{\pi} \frac{\alpha_{i\sigma}(\hat{k})^2 I_{i\sigma}(\hat{k})}{(\omega - \omega_{i\sigma}(\hat{k}))^2 + (\alpha_{i\sigma}(\hat{k}) I_{i\sigma}(\hat{k}))^2}$$  \hspace{1cm} (2.181)

Under our assumptions, the spectral density has a Lorentzian shape close to the resonance. These considerations show that the spectral density will typically be a linear combination of weighted Lorentzians and delta peaks. The consequence for the time dependence of the spectral density in Case 1 is like in a noninteracting electron system an undamped oscillation:

$$S^{-}_{k\sigma}(t - t') = \frac{1}{2\pi} \sum_{i=1}^{n} \alpha_{i\sigma}(\hat{k}) e^{-i\omega_{i\sigma}(\hat{k})(t-t')}$$  \hspace{1cm} (2.182)

The resonance frequencies $\omega_{i\sigma}(\hat{k})$ determine the oscillation frequencies. In Case 2, the Lorentzians lead to damped oscillations. To see that we assume
that (2.181) is approximately valid for the entire energy range. Then we can write

\[
S^{(i)}_{\vec{k}\sigma}(t - t') \approx \frac{1}{4\pi^2i} \int_{-\infty}^{\infty} d\omega \ e^{-i\omega(t-t')} \alpha_{i\sigma}(\vec{k}) \times \\
\times \left\{ \frac{1}{\omega - \omega_{i\sigma}(\vec{k}) + i\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})} - \frac{1}{\omega - \omega_{i\sigma}(\vec{k}) - i\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})} \right\}
\]

(2.183)

because

\[
\frac{1}{\omega - \omega_{i\sigma}(\vec{k}) + i\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})} - \frac{1}{\omega - \omega_{i\sigma}(\vec{k}) - i\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})} = \frac{-2i\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})}{(\omega - \omega_{i\sigma}(\vec{k}))^2 + (\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k}))^2}
\]

(2.184)

The integrals can be solved with the residue theorem. The spectral weights \(\alpha_{i\sigma}(\vec{k})\) are positive definite so that because of Eq. (2.168)

\[
\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k}) \leq 0
\]

(2.185)

Thus the first term has a pole in the upper, the second in the lower complex plane. Therefore we choose the integration contours dependent on \(t > t'\) as

\[
\int_{-\infty}^{\infty} d\omega \ldots = \begin{cases} 
\int_{C^<} d\omega \ldots & \text{for } t - t' > 0 \\
\int_{C^>} d\omega \ldots & \text{for } t - t' < 0 
\end{cases}
\]

(2.186)

where \(C^<\) is a contour closed by a semicircle in the lower complex plane, \(C^>\) in the upper complex plane. Then the exponential function in (2.183) suppresses the contribution of the semicircle. This yields (see Eq. (2.87))

\[
S^{(i)}_{\vec{k}\sigma}(t - t') \approx \frac{1}{2\pi} \alpha_{i\sigma}(\vec{k}) e^{-i\omega_{i\sigma}(\vec{k})(t-t')} e^{-|\alpha_{i\sigma}(\vec{k}) I_{i\sigma}(\vec{k})| |t-t'|}
\]

(2.187)

This is indeed a damped oscillation, again with the resonance frequency, but now damped with the damping mostly given by the imaginary part of the self energy. Thus we expect for interacting systems a spectral density \(S_{\vec{k}\sigma}(t - t')\) that is composed of damped and undamped oscillations.

We will learn more about the significance of the spectral density \(S_{\vec{k}\sigma}(t - t')\) by considering the special case \(T = 0, |\vec{k}| > k_F, t > t'\) where \(k_F\) is the Fermi
wave vector; thus, the system is in its ground state $|E_0\rangle$. By addition of a $(\vec{k}, \sigma)$ electron at time $t$ the state

$$|\varphi_0(t)\rangle = \alpha^\dagger_{k\sigma}(t)|E_0\rangle \quad (2.188)$$

is created which is not necessarily an eigenstate of the Hamiltonian. If we now consider the definition

$$S^\leftarrow_{k\sigma}(t-t') = \frac{1}{2\pi} \langle [a^\leftarrow_{k\sigma}(t), a^\dagger_{k\sigma}(t)]_+ \rangle$$

of the spectral density, due to $|\vec{k}| > k_F$ only one term can contribute; thus,

$$2\pi S^\leftarrow_{k\sigma}(t-t') = \langle \varphi_0(t)|\varphi_0(t')\rangle \quad (2.189)$$

This has a simple interpretation: $2\pi S^\leftarrow_{k\sigma}(t-t')$ is the probability that the state $|\varphi_0(t)\rangle$ that was created by addition of a $(\vec{k}, \sigma)$ electron from the state $|E_0\rangle$ at time $t'$ will still exist at $t > t'$; $S^\leftarrow_{k\sigma}(t-t')$ characterizes the time evolution or propagation of an additional $(\vec{k}, \sigma)$ electron in the $N$ particle system. This is why $S^\leftarrow_{k\sigma}$ (and $G^\alpha_{k\sigma}$) are sometimes propagators.

If we had assumed $|\vec{k}| < k_F$, $S^\leftarrow_{k\sigma}(t-t')$ would describe the propagation of a hole.

There are two typical states:

- stationary state: $|\langle \varphi_0(t)|\varphi_0(t')\rangle|^2 = \text{const}$
- state with finite lifetime: $|\langle \varphi_0(t)|\varphi_0(t')\rangle|^2 \longrightarrow 0 \quad (t-t' \rightarrow \infty) \quad (2.190)$

We now apply this consideration first to noninteracting electrons. The Hamiltonian in Bloch formulation is

$$\mathcal{H} = \sum_{\vec{k}\sigma} (\varepsilon(\vec{k}) - \mu) a^\dagger_{k\sigma} a^\leftarrow_{k\sigma} \quad (2.191)$$

Now we can calculate

$$[\mathcal{H}, a^\dagger_{k\sigma}]_- = (\varepsilon(\vec{k}) - \mu) a^\dagger_{k\sigma} \quad (2.192)$$

and

$$\mathcal{H}_0 (a^\dagger_{k\sigma}|E_0\rangle) = a^\dagger_{k\sigma} \mathcal{H}_0 |E_0\rangle + [\mathcal{H}_0 a^\dagger_{k\sigma}]_- |E_0\rangle = (E_0 + \varepsilon(\vec{k}) - \mu) (a^\dagger_{k\sigma}|E_0\rangle) \quad (2.193)$$
In this case, $a_{k\sigma}^\dagger |E_0\rangle$ turns out to be an eigenstate of $\mathcal{H}_0$ again. Further, we find

$$|\varphi_0(t)\rangle = e^{i\xi \cdot \vec{a}_{k\sigma}^\dagger} e^{-iE_0t} |E_0\rangle = e^{-iE_0t} e^{i\xi \cdot \vec{a}_{k\sigma}^\dagger} (a_{k\sigma}^\dagger |E_0\rangle)$$

$$= e^{i\left(\xi \cdot \vec{k} - \mu\right) t} (a_{k\sigma}^\dagger |E_0\rangle)$$

(2.194)

Because of $|\vec{k}| > k_F$ and $\langle E_0|E_0\rangle = 1$ we also have

$$\langle E_0|a_{k\sigma}^- a_{k\sigma}^\dagger |E_0\rangle = \langle E_0|E_0\rangle - \langle E_0|a_{k\sigma}^\dagger a_{k\sigma}^- |E_0\rangle = 1$$

(2.195)

This finally leads to

$$\langle \varphi_0(t)|\varphi_0(t')\rangle = e^{i\left(\xi \cdot \vec{k} - \mu\right)(t-t')}$$

(2.196)

Thus the propagator is an undamped harmonic oscillation with an exact excitation energy of the system $(\xi \cdot \vec{k} - \mu)$. As

$$|\langle \varphi_0(t)|\varphi_0(t')\rangle|^2 = 1$$

(2.197)

it is a stationary state.

Next we consider an interacting system. By inserting a unit operator from a complete set of eigenstates $|E_n\rangle$ we have:

$$2\pi S_{k\sigma} (t - t') = \sum_n \left| \langle E_n|a_{k\sigma}^\dagger |E_0\rangle \right|^2 e^{-i(E_n - E_0)(t-t')}$$

(2.198)

In the free system, $a_{k\sigma}^\dagger |E_0\rangle$ is an eigenstate, and the orthogonality of the eigenstates implies that only one term in the sum is nonzero. In the interacting system, this is no longer the case; in the expansion

$$|\varphi_0(t)\rangle = a_{k\sigma}^\dagger |E_0\rangle = \sum_m c_m |E_m\rangle$$

(2.199)

many, usually infinitely many expansion coefficients will be nonzero. The superposition of oscillations with different frequencies will lead to a sum in (2.198) that is maximal for $t = t'$ and will destructively interfere for $t - t' > 0$ so that

$$|\langle \varphi_0(t)|\varphi_0(t')\rangle|^2 \xrightarrow{t-t' \to \infty} 0$$

(2.200)
Then, the state $|\varphi_0(t')\rangle$ created at time $t'$ has only a finite lifetime. Under certain conditions, however, the irregular time dependence of the propagator can be represented as superposition of damped oscillations with well defined frequency:

$$2\pi S_{k_0}(t - t') = \sum_i \alpha_{i\sigma}(\vec{k}) e^{-in_{i\sigma}(\vec{k})(t-t')} \quad (2.201)$$

This formally has the same form as the corresponding expression (2.196) for the free system, but the new single-particle energies are complex quantities:

$$\eta_{i\sigma}(\vec{k}) = \text{Re} \eta_{i\sigma}(\vec{k}) + i \text{Im} \eta_{i\sigma}(\vec{k}) \quad (2.202)$$

The imaginary part is responsible for the exponential damping of the oscillation. The energies $\eta_{i\sigma}(\vec{k})$ are now ascribed to a fictive particle, the so called quasiparticle. This is motivated by the fact that the particle number $(N+1)$ that is added to the system at time $t'$ propagates as if it decays into several quasiparticles of energy $\text{Re} \eta_{i\sigma}(\vec{k})$ and lifetime $\frac{1}{\text{Im} \eta_{i\sigma}(\vec{k})}$ ($\eta_{i\sigma}$ is again measured in units of $\hbar$, i.e. it is a frequency). Every quasiparticle has a spectral weight $\alpha_{i\sigma}(\vec{k})$ for which the conservation of total particle number means

$$\sum_i \alpha_{i\sigma}(\vec{k}) = 1 \quad (2.203)$$

If we now compare

$$S\overset{(i)}{_{k_0}\sigma}(t - t') = \frac{1}{2\pi} \alpha_{i\sigma}(\vec{k}) e^{-i\text{Re} \eta_{i\sigma}(\vec{k})(t-t')} e^{-|\text{Im} \eta_{i\sigma}(\vec{k})|(t-t')} \quad (2.204)$$

to (2.187) we recognize the relationship between quasiparticle properties and electronic selfenergy:

quasiparticle energy: $\omega_{i\sigma}(\vec{k}) = \epsilon(\vec{k}) - \mu + R_{\sigma}(\vec{k}, \omega = \omega_{i\sigma}(\vec{k}))$

quasiparticle lifetime: $\tau_{i\sigma}(\vec{k}) = \frac{1}{|\alpha_{i\sigma}(\vec{k})I_{i\sigma}(\vec{k})|}$ \quad (2.205)

The spectral weights $\alpha_{i\sigma}$ are determined by the real part of the self energy. Thus, the quasiparticle lifetime is also influenced by the real part of the self energy. Another analogy between quasiparticle and free particle is the effective mass $m^*_{i\sigma}(\vec{k})$ which is also determined by the real part of the self
energy. With the same argumentation as for the Bloch density of states \( \rho_0(\omega) \) we can define a quasiparticle density of states

\[
\rho_\sigma(\omega) = \frac{1}{N} \sum_k S_{k\sigma}(\omega - \mu)
\]  

(2.206)

In contrast to \( \rho_0(\omega) \), this density of states for the interacting system will be temperature dependent; it will also depend on the particle number. As the spectral density represents a weighted superposition of delta functions, in the arguments of which appear the excitation energies that are required to add a \( \langle k\sigma \rangle \) electron to an \( N \) particle system or remove one from it, \( \rho_\sigma(\omega) \) has a direct link to the photoemission experiment.

**Application to interacting systems**

We now apply the formalism to a simple interacting problem, the Hubbard model in the limit of infinitely narrow bands. The Hamiltonian is

\[
H = \sum_{ij\sigma} (t_{ij} - \mu \delta_{ij}) a_{i\sigma}^\dagger a_{j\sigma} + \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i\bar{\sigma}},
\]

(2.207)

where we use the notation \(-\sigma \equiv \bar{\sigma}\). In order to calculate the one electron Greens function, it is convenient to proceed in the Wannier representation

\[
G_{ij\sigma}(\omega) = \langle \langle a_{i\sigma}; a_{j\sigma}^\dagger \rangle \rangle_\omega
\]

(2.208)

For the equation of motion, we need the commutator

\[
[a_{i\sigma}, H]_- = \sum_m (t_{im} - \mu \delta_{im}) a_{m\sigma} + n_{ni\bar{\sigma}} a_{i\sigma}
\]

(2.209)

The second term leads to the higher order Greens function

\[
\Gamma_{iim;j\sigma}(\omega) = \langle \langle a_{i\bar{\sigma}}^\dagger a_{i\sigma} a_{m\bar{\sigma}}; a_{j\sigma}^\dagger \rangle \rangle_\omega
\]

(2.210)

This leads to the equation of motion

\[
(\omega + \mu) G_{ij\sigma}(\omega) = \delta_{ij} + \sum_m t_{im} G_{mij\sigma}(\omega) + U \Gamma_{iim;j\sigma}(\omega)
\]

(2.211)

Due to the higher order Greens function \( \Gamma^\alpha \) we cannot directly solve for \( G^\alpha \). Therefore we determine the equation of motion for \( \Gamma^\alpha \); we need

\[
[a_{i\sigma}, H_0]_- = \sum_m (t_{im} - \mu \delta_{im}) \left\{ n_{i\bar{\sigma}} a_{m\sigma} + a_{i\bar{\sigma}}^\dagger a_{m\bar{\sigma}} a_{i\sigma} - a_{m\bar{\sigma}}^\dagger a_{i\sigma} a_{i\bar{\sigma}} \right\}
\]

\[
[a_{i\sigma}, H_1]_- = U a_{i\sigma} n_{i\bar{\sigma}}
\]

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where the relation $n_{i\sigma}^2 = n_{i\bar{\sigma}}$ was used. This yields

\[
(\omega + \mu - U)\Gamma_{ii;ij\sigma}(\omega) = \delta_{ij}\langle n_{i\sigma} \rangle + \sum_m t_{im} \{\Gamma_{imi;j\sigma}(\omega) + \Gamma_{imi;j\sigma}(\omega) - \Gamma_{mi;ij\sigma}(\omega)\}
\]

(2.213)

Now we will specialize to the limit of infinitely narrow bands (atomic limit)

\[
\varepsilon(\vec{k}) = t_0 \quad \Leftrightarrow \quad t_{ij} = t_0 \delta_{ij}
\]

(2.214)

Then the equation of motion hierarchy decouples and (2.213) simplifies to

\[
(\omega + \mu - U - t_0)\Gamma_{ii;ij\sigma}(\omega) = \delta_{ij}\langle n_{\sigma} \rangle
\]

(2.215)

Translation symmetry implies lattice site independence of the particle number operator: $\langle n_{i\sigma} \rangle = \langle n_{\sigma} \rangle \forall i$. Eq. (2.215) can now be inserted in Eq. (2.211):

\[
(\omega + \mu - t_0)G_{ii\sigma}^\alpha = 1 + \frac{U\langle n_{\sigma} \rangle}{\omega - t_0 + \mu - U}
\]

(2.216)

Then we have for the retarded Greens function

\[
G_{ii\sigma}^r(\omega) = \frac{1 - \langle n_{\sigma} \rangle}{\omega - t_0 + \mu + i0^+} + \frac{\langle n_{\bar{\sigma}} \rangle}{\omega - t_0 - U + \mu + i0^+}
\]

(2.217)

Thus, $G_{ii\sigma}^r(\omega)$ has two poles corresponding to the excitation energies:

\[
\omega_{1\sigma} = t_0 - \mu = \omega_{1\bar{\sigma}}
\]

\[
\omega_{2\sigma} = t_0 + U - \mu = \omega_{2\bar{\sigma}}
\]

(2.218)

The original level at $t_0$ splits, due to the Coulomb repulsion, into two spin independent quasiparticle levels $\omega_{1\sigma}$, $\omega_{2\sigma}$. The spectral density can be easily calculated as $S_{ii\sigma}(\omega) = -\frac{1}{\pi} \text{Im} G_{ii\sigma}^r(\omega)$ to be

\[
S_{ii\sigma}(\omega) = \sum_{j=1}^2 \alpha_{j\sigma} \delta(\omega - \omega_{j\sigma})
\]

(2.219)

The spectral weights

\[
\alpha_{1\sigma} = 1 - \langle n_{\bar{\sigma}} \rangle; \quad \alpha_{2\sigma} = \langle n_{\bar{\sigma}} \rangle
\]

(2.220)
measure the probability that a $\sigma$ electron meets a $\bar{\sigma}$ electron at a site $(\alpha_{2\sigma})$ or that it finds an unoccupied site $(\alpha_{1\sigma})$. In the first case it has to pay the Coulomb interaction $U$. The quasiparticle density of states consists in this limit of two infinitely narrow bands at the energies $t_0$ and $t_0 + U$:

$$\rho_\sigma(\omega) = \frac{1}{N} \sum_i S_{ii\sigma}(\omega - \mu) = S_{ii\sigma}(\omega - \mu)$$

$$= (1 - \langle n_{\bar{\sigma}} \rangle) \delta(\omega - t_0) + \langle n_{\bar{\sigma}} \rangle \delta(\omega - t_0 - U)$$

(2.221)

The lower band contains $(1 - \langle n_{\bar{\sigma}} \rangle)$, the upper $\langle n_{\bar{\sigma}} \rangle$ states per atom. Thus the number of states in the quasiparticle subbands is temperature dependent. Now we have to determine the expectation value $\langle n_{\bar{\sigma}} \rangle$ using the spectral theorem (2.100):

$$\langle n_{\bar{\sigma}} \rangle = \int_{-\infty}^{\infty} d\omega \frac{S_{i\bar{i}\sigma}(\omega)}{e^{\beta\omega} + 1} = (1 - \langle n_{\sigma} \rangle) f_-(t_0) + \langle n_{\sigma} \rangle f_-(t_0 + U)$$

(2.222)

with Fermi function $f_-(\omega)$. Using the corresponding equation for $\langle n_{\bar{\sigma}} \rangle$, we find

$$\langle n_{\bar{\sigma}} \rangle = \frac{f_-(t_0)}{1 + f_-(t_0) - f_-(t_0 + U)}$$

(2.223)

Then the complete solution for $\rho_\sigma(\omega)$ is

$$\rho_\sigma(\omega) = \frac{1}{1 + f_-(t_0) - f_-(t_0 + U)} \left\{ (1 - f_-(t_0 + U)) \delta(\omega - t_0) + f_-(t_0) \delta(\omega - t_0 - U) \right\}$$

(2.224)