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## On the treatment of many-body correlation in finite and extended systems

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### Abstract

*This article gives an overview on recent achievements in the theoretical description of electronic excitations in correlated many-body finite and extended systems. Using the random phase approximation we provide quantitative results for the electron-removal probability from fullerenes and small metal clusters. For extended systems, like solids and surfaces, it is shown how the random phase approximation can be implemented in ab-initio schemes for the calculation of the electronic and optical properties of materials.*

### I. Introduction

In his fundamental work on normal Fermi liquids, Landau<sup>1</sup> underlined the crucial role played by the quasi-particle (qp) and the quasi-hole (qh) excitations. In an interacting system these excitations are closely

related to excitations around the Fermi level of a non-interacting system with one particle more or less. The qp and qh can be considered as the remnants of bare (non-interacting) particles. This relation brings about considerable simplifications and a clear understanding of the physics of low-lying excitations in correlated many-fermion systems. For example, qp and qh excitations are the basis for the description of collective modes, like zero-sound in liquid  $^3\text{He}$ , the plasmon modes in the interacting electron gas and the giant resonances in nuclei and clusters. The universality and the power of Landau's theory is, however, limited by the need for introducing certain (phenomenological) parameters that determine the character of the interaction between the quasi-particles. The extension of Landau's theory to the treatment of finite Fermi systems has been put forward by Migdal<sup>2</sup>. In addition to the restriction of the Landau's theory for extended systems, in a finite system further assumptions has to be made, such as the density dependence of the qp interaction.

For normal Fermi liquids with a sharp Fermi surface, a qp excitation is a well-defined excitation with momentum  $k_F$  and is characterized by a strength parameter  $z_{k_F}$ , the so-called the strength at the qp poles. This strength parameter can be interpreted as the probability for the addition to or for the removal from the correlated ground state a bare particle with momentum  $k_F$ , while ending up in the ground state of the system with one particle more or less. Both these states are characterized by the Fermi energy  $E_F$  for infinite particle number. In this limit the quasi-particle and the quasi-hole have a well-defined energy ( $E_F$ ) and therefore correspond to excitations with an infinite lifetime. This qp picture is expected to be less viable for momenta far from  $k_F$ , where the peak in the sp strength distribution develops a width that increases with large deviations of the sp momentum  $k$  from  $k_F$ . Therefore, for these momenta  $k$ , the qp and qh excitations have in general a finite lifetime describing thus damped excitations.

In finite systems with shell structure, such as spherical metal clusters treated in the next section, the relevant sp quantum numbers for the qp excitations, correspond to those of sp shell model states with energies close to the Fermi energy. These quantum numbers play a role equivalent to that of the sp momentum in the infinite Fermi liquid which equals  $k_F$  for the qp excitations.

Recent progress in the electron addition and removal spectroscopies, such as single photoemission and fully resolved inelastic electron knock-out collisions (also called the (e,2e) process, one electron in two electron out) produced reliable information on the momentum distributions of qh excitations. In particular the (e,2e) experiments yield the values of the removal probabilities providing thus the strength of the qh excitations. Furthermore, these experiments offer a possibility to investigate excitations which carry a very large fraction of sp removal strength concentrated at a single energy (sharply defined quasi-holes) in contrast to strength distributions displaying strong fragmentation in energy (strongly damped excitations).

This work deals with the realistic (parameter free) calculations of the various quantities needed for the description of excitation processes in finite and extended Fermi systems. In particular, we calculate the electron removal probabilities from spherical metal clusters and from the  $C_{60}$  molecule. The calculations are based on self-consistent Hartree-Fock approximation for the single-particle orbitals and on the random-phase approximation (RPA) for the treatment of the particle-hole excitations. In the second part of this work we address the treatment of electronic excitations in extended systems using

the Green's function theory. More precisely we employ the Hedin equations within the GW-approximation and show how the quasi-particle properties can be evaluated in a tractable and parameter free manner.

## II. Excitations of clusters: The random-phase approximation

In a series of experiments<sup>36, 37</sup> the probability for the removal of one electron from the valence band of the carbon fullerenes ( $C_{60}$ ) has been measured. The excitation of this valence electron has been induced by an approaching projectile electron. Density functional calculations with the local density approximation as well as Hartree-Fock calculations failed to reproduce the excitation probability as function of the excitation energy<sup>38-40</sup>. As shown below the reason for this shortcoming of the effective single particle theory is the neglect of collective effects build out of particle-hole de(excitations).

Let us consider the dynamics of the electrons in a cluster of atoms under the influence of an external time-dependent perturbation  $\delta U(\mathbf{r}, t)$ . The perturbation may be induced by an impinging electron (that acts as a test charge) or by an electromagnetic pulse. The response of the system is measured in terms of electron removal probabilities from the valence shell.

In presence of the external source the dynamic of the electrons in the cluster is determined by the Hamiltonian

$$\widehat{H}(\mathbf{r}, t) = \widehat{H}_0(\mathbf{r}) + \delta U(\mathbf{r}, t), \quad (1)$$

where  $\widehat{H}_0$  is the self-consistent mean field Hamiltonian in absence of the perturbation. To determine the solution of the time-dependent Schrödinger equation (atomic units are used throughout)

$$[i\partial_t + \widehat{H}(\mathbf{r}, t)] \Psi(\mathbf{r}, t) = 0$$

we write the total wave function as an antisymmetrized product of single-electron wave functions, i.e.

$$\Psi(\mathbf{r}, t) = e^{-iE_0 t} \det \|\psi_i(\mathbf{r}, t)\|, \quad (2)$$

where  $E_0$  is the Hartree-Fock energy of the system's ground state and is determined as the following expectation value

$$E_0 = \sum_i \langle i | -\frac{\nabla}{2} - V_{ions} | i \rangle + \frac{1}{2} \sum_{i,k} \langle ik | u | ik - ki \rangle.$$

The bare (Coulomb) interaction between the electrons is  $u \equiv \frac{1}{|\mathbf{r}-\mathbf{r}'|}$ .

Each of the time dependent single particle orbitals  $\psi_i(\mathbf{r}, t)$  can be expanded over a set of time-independent Hartree-Fock orbitals

$$\psi_i(\mathbf{r}, t) = A_i \left[ \phi_i(\mathbf{r}) + \sum_m C_{mi}(t) \phi_m(\mathbf{r}) \right]. \quad (3)$$

Here  $m$  denotes states above Fermi level  $E_F$  (particle states) whereas  $i$  labels the states below  $E_F$  (hole states). The factor  $A$  is a normalization coefficient. From the meaning of the indices  $i$  and  $m$  one concludes that the expansion coefficients  $C_{mi}(t)$  are the probability amplitudes for the creation of the  $m$ - $i$  electron-hole pair. The sum in Eq.(3) implies a summation of the discrete states and an integration of the continuum (particle) states. The admixture of particle-hole excitation amplitudes  $C_{mi}(t)$  are determined by inserting Eq.(3) into Eq.(2) and requiring

$$\langle \Psi(\mathbf{r}, t) | \hat{H} - i \frac{\partial}{\partial t} | \Psi(\mathbf{r}, t) \rangle \equiv 0. \quad (4)$$

Expanding in terms of the coefficients  $C_{mi}(t) \neq 0$  and accounting for the first non-vanishing terms one obtains the relation

$$i \sum_{i \leq \epsilon_F < m} C_{mi}^*(t) \frac{\partial}{\partial t} C_{mi}(t) = \sum_{i \leq \epsilon_F < m} \left\{ (\epsilon_m - \epsilon_i) |C_{mi}(t)|^2 + C_{mi}(t) \langle i | \delta U | m \rangle + C_{mi}^*(t) \langle m | \delta U | i \rangle + \right. \\ \left. + \sum_{j \leq \epsilon_F < k} \left[ \frac{1}{2} C_{mi}^*(t) C_{kj}^*(t) \langle mk | u | ij - ji \rangle + \frac{1}{2} C_{mi}(t) C_{kj}(t) \langle ij | u | mk - km \rangle + C_{mi}^*(t) C_{kj}(t) \langle mi | u | kj - kj \rangle \right] \right\}$$

The variation with respect to  $C_{mi}^*(t)$  gives

$$i \frac{\partial}{\partial t} C_{mi}(t) = (\epsilon_m - \epsilon_i) C_{mi}(t) + \langle m | \delta U | i \rangle + \sum_{j \leq \epsilon_F < k} [C_{kj}(t) \langle mk | u | ij - ij \rangle + C_{kj}(t) \langle mj | u | ik - ki \rangle]. \quad (5)$$

The solution of the equation has the form

$$C_{mi}(t) = X_{mi} e^{-i\epsilon_0 t} + Y_{mi}^* e^{i\epsilon_0 t}. \quad (6)$$

Here  $\epsilon_0$  is the energy carried by the external perturbation (the incoming projectile). With the ansatz (6) we obtain from Eq.(5) two coupled equations for the determination of the coefficients  $X_{mi}$  and  $Y_{mi}^*$ , namely

$$(\epsilon_m - \epsilon_i - \epsilon_0) X_{mi} + \langle m | \delta U | i \rangle + \sum_{j \leq \epsilon_F < k} [\langle mj | u | ki - ik \rangle X_{kj} + \langle mk | u | ji - ij \rangle Y_{kj}] = 0, \quad (7)$$

$$(\epsilon_m - \epsilon_i + \epsilon_0) Y_{mi} + \langle i | \delta U | m \rangle + \sum_{j \leq \epsilon_F < k} [\langle ij | u | km - mk \rangle X_{kj} + \langle ik | u | jm - mj \rangle Y_{kj}] = 0. \quad (8)$$

Introducing the notation

$$-(\varepsilon_m - \varepsilon_i - \varepsilon_0)X_{mi} =: \langle m | F_{eff} | i \rangle, \quad (9)$$

$$-(\varepsilon_m - \varepsilon_i + \varepsilon_0)Y_{mi} =: \langle i | F_{eff} | m \rangle, \quad (10)$$

where  $F_{eff}$  stands for the *effective* external perturbation we conclude from Eqs. (7, 8) the central equation that determines the excitation amplitude of the system in response to an external perturbation (the exchange effects)

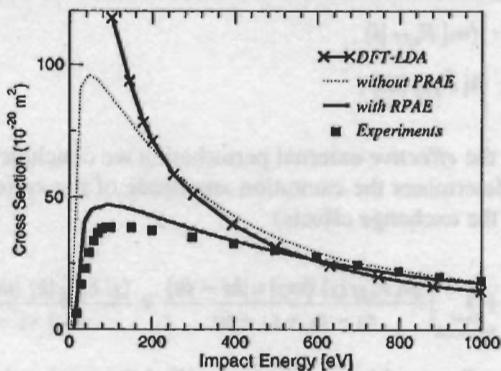
$$\langle m | F_{eff} | i \rangle = \langle m | \delta U | i \rangle + \sum_{j \leq \varepsilon_F < k} \left[ \frac{\langle k | F_{eff} | j \rangle \langle m j | u | k i - i k \rangle}{\varepsilon_0 - \varepsilon_k + \varepsilon_j + i\nu} + \frac{\langle j | F_{eff} | k \rangle \langle m k | u | j i - i j \rangle}{\varepsilon_0 + \varepsilon_k - \varepsilon_j - i\nu} \right]. \quad (11)$$

The approximations leading to this equation are called the random-phase approximation with exchange. Relation (11) implies that excitations in the clusters due to an external perturbation are determined not only by the nature of  $\delta U$  but also by the all behaviour of the system. The latter is constructed as a coherent superposition of excitation and de-excitation amplitudes between hole to particle states and vice versa. The collective behaviour of the system can be viewed as a dressing of the external perturbation to result in the effective interaction  $F_{eff}$ . In the above considerations we employed a test charge (the approaching projectile electron) to assess the correlation in the system. The same above arguments apply as well to the two-particle Coulomb interaction  $u$  present in the system. Similarly to Eq. (11) the interaction  $u$  is modified by the surrounding medium. As in Eq. (11) the modied (screened) interaction  $w$  can be expressed in the algebraic operator form

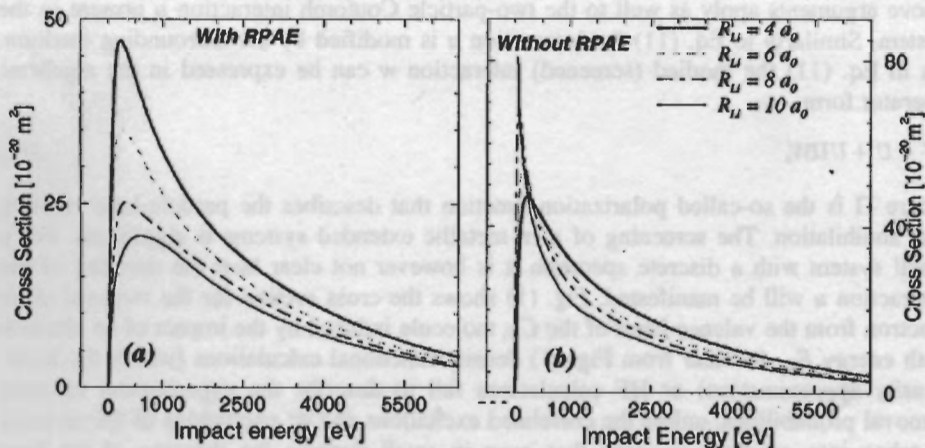
$$W = U + U\Pi W, \quad (12)$$

where  $\Pi$  is the so-called polarization function that describes the particle-hole creation and annihilation. The screening of  $u$  in metallic extended systems is significant. For a small system with a discrete spectrum it is however not clear how the dressing of the interaction  $u$  will be manifested. Fig. (1) shows the cross section for the removal of an electron from the valence band of the  $C_{60}$  molecule induced by the impact of an electron with energy  $E_0$ . As clear from Fig. (1) density-functional calculations (within the local-density approximation) or HF calculations fail to describe the experimental electron removal probabilities, unless the correlated excitations and de-excitations of the ph-pairs is taken into account, meaning that even in small systems the dressing of the bare interaction plays a decisive role.

The importance of the charge-density fluctuations on the excitation processes in  $C_{60}$  raises the question of the system size dependence of the excitation and the de-excitation amplitudes. To address this question we considered within the spherical jellium model the electron-removal amplitudes from  $Li$  clusters with varying sizes. For a judicious conclusions we normalized the cross sections to the number of electrons in the various clusters. The influence of the ph-excitation amplitudes is elucidated by comparing the results within the RPAE and without any account for the ph-excitations (cf. Figs. (2)). As clear from Figs. (2), for small clusters there is hardly an influence of the ph-(de)excitations. On the other hand, with increasing system size one observes a striking influence of charge density fluctuation on the cross section in particular at low energies.



**Figure 1.** The absolute total cross section for the removal of one electron from  $C_{60}$  upon the inelastic collision of electrons with the impact energy displayed on the axis. The experimental data (full squares) are taken from Refs.<sup>36,37</sup>. The solid curve with crosses is the result of DFT calculations<sup>38</sup> whereas the dotted curve shows the present theory without RPAE. Theoretical results based on RPEA are shown by the solid curve.



**Figure 2.** The electron-impact total ionization cross section for spherical  $L_i$  clusters with varying radius size  $R_{L_i}$ . (a) shows the RPAE calculations. (b) shows the results when the particle-hole (de)excitation is neglected.

### III. Green's function method

#### A. General consideration

The Green's function method is a powerful tool for studying ground state and excited state properties of condensed matter materials. The basic idea of the Green's function has its origin in the theory of differential equations. Any inhomogeneous

differential equation with a Hermitian differential operator  $\hat{H}$ , complex parameter  $z$ , and a given source function  $u(\mathbf{r})$  of the form

$$[z - \hat{H}] \psi(\mathbf{r}) = u(\mathbf{r}) \quad (13)$$

can be represented as an integral equation

$$\psi(\mathbf{r}) = \varphi(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}'; z) u(\mathbf{r}'). \quad (14)$$

Here the so-called Green's function  $G(\mathbf{r}, \mathbf{r}'; z)$  is a coordinate representation of the resolvent of the differential operator  $\hat{H}$ , obeying the differential equation

$$[z - H(\mathbf{r})] G(\mathbf{r}, \mathbf{r}'; z) = \delta(\mathbf{r} - \mathbf{r}'), \quad (15)$$

and the function  $\varphi(\mathbf{r})$  is a general solution of the homogeneous equation associated with Eq. (13). This method is in many cases very convenient and widely used in many-body physics. In this review we shall consider the formalism of the Green's function method in condensed matter physics at the absolute zero temperature. This case can be generalised to finite temperatures but will not be considered here.

The evolution of an  $N$ -body system can be obtained from the time-dependent Schrödinger equation

$$i\hbar \frac{d\Psi(t)}{dt} = \hat{H}\Psi(t), \quad (16)$$

where  $\Psi(t) \equiv \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t)$  is a wave function of the system and  $\hat{H}$  is the many-body Hamiltonian, which includes the kinetic energy and interactions between particles. Knowing the wave function  $\Psi(t)$ , an average value of any operator  $\hat{A}$  can be obtained from the equation:

$$\mathcal{A}(t) = \langle \Psi^*(t) \hat{A} \Psi(t) \rangle. \quad (17)$$

The many-body wave function can be expanded in a complete set of time-independent single-particle states  $\phi_i(\mathbf{r})$ :

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; t) = \sum_{\{i_1, i_2, \dots, i_N\}} C_{\{i_1, i_2, \dots, i_N\}}(t) \phi_{i_1}(\mathbf{r}_1) \phi_{i_2}(\mathbf{r}_2) \dots \phi_{i_N}(\mathbf{r}_N). \quad (18)$$

The basis set can be arbitrary, but in practice one uses functions which are adequate for the particular problem. For example, the plane wave basis is appropriate for description of

a system with free or nearly free electrons. For systems with localised electrons one usually takes atomic-like functions. For systems with a large number of particles solving Eq. (16) using the basis expansion (18) is very difficult. To describe a system with  $N$ -particles one can use second quantisation, in which instead of giving a complete wave function one specifies the numbers of particles to be found in the states  $\phi_1(\mathbf{r}), \phi_2(\mathbf{r}), \dots, \phi_N(\mathbf{r})$ . As a result the many-body wave function is defined by the occupation numbers and Hamiltonian, and any other operator can be expressed in terms of the so-called creation and annihilation operator  $\hat{c}_i^+$  and  $\hat{c}_i$ , obeying certain commutation or anti-commutation relations according to the statistical properties of particles (fermions or bosons). The creation operator  $\hat{c}_i^+$  increases the number of particles by one, while the annihilation operators  $\hat{c}_i$  decreases the occupation number of particles by one. Any observable can be represented as some combination of those operators. For example, the one-particle operator (17) can be expressed as follows:

$$\hat{A} = \sum_{i,k} A_{ik} \hat{c}_i^+ \hat{c}_k, \quad (19)$$

where  $A_{ik}$  are matrix elements of the operator  $\hat{A}$ . Sometimes it is convenient to use field operators

$$\begin{aligned} \hat{\psi}^+(\mathbf{r}) &= \sum_i \phi_i(\mathbf{r}) \hat{c}_i^+ \\ \hat{\psi}(\mathbf{r}) &= \sum_i \phi_i(\mathbf{r}) \hat{c}_i, \end{aligned} \quad (20)$$

which can be interpreted as creation and annihilation operators of a particle at a given point  $\mathbf{r}$ . In this representation a single particle operator is given as

$$\hat{A}_\psi = \int d\mathbf{r} \hat{\psi}^+(\mathbf{r}) \hat{A} \hat{\psi}(\mathbf{r}). \quad (21)$$

Suppose we have a system with  $N$  particles in the ground state, which is defined by the exact wave function  $\Psi_0$ . If at time  $t_0 = 0$  a particle with momentum  $\mathbf{k}_0$  will be added into the system, this can be described by  $c_{\mathbf{k}_0}^+ |\Psi_0\rangle$ . The evolution of the system in time will now proceed according to  $e^{-i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}_0}^+ |\Psi_0\rangle$ . The probability amplitude for the existence of the added particle in the momentum state  $\mathbf{k}$ , is a scalar product of  $e^{-i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}_0}^+ |\Psi_0\rangle$  with the function describing the ground state at time  $t$  plus a particle added in the state  $\mathbf{k}$  at time  $t$ :  $c_{\mathbf{k}}^+ e^{-i\hat{H}(t-t_0)/\hbar} |\Psi_0\rangle$ . Then the resulting probability amplitude is given by  $\langle \Psi_0 | e^{i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}} e^{-i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}_0}^+ |\Psi_0\rangle$ . Analogously, the existence of an empty state can be described with the function  $\pm \langle \Psi_0 | e^{-i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}_0}^+ e^{i\hat{H}(t-t_0)/\hbar} c_{\mathbf{k}} |\Psi_0\rangle$ , where plus sign applies to Bose statistics and minus sign to Fermi statistics. Both



processes contribute in the following definition of the one-particle causal Green's function:

$$G(\mathbf{k}, t; \mathbf{k}_0, t_0) = -i \langle \Psi_0 | T [\hat{c}_{\mathbf{k}}(t) \hat{c}_{\mathbf{k}_0}^\dagger(t_0)] | \Psi_0 \rangle. \quad (22)$$

Here we have used Heisenberg representation of the operators  $\hat{c}_{\mathbf{k}}$  and  $\hat{c}_{\mathbf{k}}^\dagger$ :

$$\hat{c}_{\mathbf{k}}(t) = e^{i\hat{H}t} c_{\mathbf{k}} e^{-i\hat{H}t}. \quad (23)$$

The symbol  $T$  is Wick's time-ordering operator which rearranges a product of two time-dependent operators so that the operator referring to the later time appears always on the left:

$$T [\hat{c}_{\mathbf{k}}(t) \hat{c}_{\mathbf{k}_0}^\dagger(t_0)] = \begin{cases} \hat{c}_{\mathbf{k}}(t) \hat{c}_{\mathbf{k}_0}^\dagger(t_0) & (t > t_0) \\ \pm \hat{c}_{\mathbf{k}_0}^\dagger(t_0) \hat{c}_{\mathbf{k}}(t) & (t < t_0) \end{cases}. \quad (24)$$

The physical meaning of the Green's function in the momentum space is that for  $t > t_0$   $G(\mathbf{k}_0, t_0; \mathbf{k}, t)$  describes the propagation of a particle in the state  $\mathbf{k}_0$  created at time  $t_0$  and detected in the state  $\mathbf{k}$  at time  $t$ . For  $t < t_0$ , the Green's function describes the propagation of a hole with wave vector  $\mathbf{k}$  emitted at time  $t$  into the state  $\mathbf{k}_0$  at time  $t_0$ . Analogously to the above, one can write down the Green's function in the real-space representation:

$$G(\mathbf{r}_0, t_0; \mathbf{r}, t) = -i \langle \Psi_0 | T [\hat{\psi}(\mathbf{r}_0, t_0) \hat{\psi}^\dagger(\mathbf{r}, t)] | \Psi_0 \rangle, \quad (25)$$

where  $\hat{\psi}(\mathbf{r}, t)$  and  $\hat{\psi}^\dagger(\mathbf{r}, t)$  are particle annihilation and creation operators (23).

The one-particle Green's function has some significant properties which make the use of the Green's function method in condensed matter physics attractive. The main advantage of the Green's function is, that it contains great deal of information about the system in a considered time interval. Knowing the single-particle Green's function, one can calculate the expectation value of any single-particle operator in the ground state:

$$\mathcal{A}(t) = \pm i \int \left[ \lim_{t' \rightarrow t+0} \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \hat{A}(\mathbf{r}) G(\mathbf{r}, t; \mathbf{r}', t') \right] d\mathbf{r}. \quad (26)$$

As a consequence, the charge density and total energy can also be found for any system in the ground state at the absolute zero temperature. Another important property of the Green's function is that it can describe single-particle excitations. In that follows, we shall discuss the latter in more detail.

We start from the definition of the Green's function in the momentum representation (22). For simplicity, we can consider only diagonal elements of the Green's function ( $\mathbf{k} =$

$k_0$ ). The chronological operator  $T$  can be mathematically expressed via Heaviside function  $\theta(z)$ , which leads to the following equation for the Green's function

$$iG_{\mathbf{k}}(t-t') = \theta(t-t') \sum_n e^{-i[E_n^{N+1}-E_0^N](t-t')} |\langle N+1|c_{\mathbf{k}}^+|N\rangle|^2 \pm \theta(t'-t) \sum_n e^{-i[E_0^N-E_n^{N-1}](t-t')} |\langle N-1|c_{\mathbf{k}}|N\rangle|^2. \quad (27)$$

Here  $E_n^{N+1}$  and  $E_n^{N-1}$  are all the exact eigenvalues of the  $N+1$  and  $N-1$  particle systems respectively,  $n$  is all quantum numbers necessary to specify the state completely, and  $E_0^N$  is the exact ground state energy for the system with  $N$  particles ( $n=0$ ). Using the integral formula of the  $\theta(t) = -\lim_{\Gamma \rightarrow 0} \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{e^{-i\omega t}}{\omega+i\Gamma}$  the Green's function of the above form can be easily Fourier transformed into the energy representation:

$$G_{\mathbf{k}}(\omega) = \lim_{\Gamma \rightarrow 0} \left[ \sum_n \frac{|\langle N+1|c_{\mathbf{k}}^+|N\rangle|^2}{\omega - [E_n^{N+1} - E_0^N] + i\Gamma} \mp \sum_n \frac{|\langle N-1|c_{\mathbf{k}}|N\rangle|^2}{\omega - [E_0^N - E_n^{N-1}] - i\Gamma} \right]. \quad (28)$$

The equation (28) provides an insight into the analytical properties of the single-particle Green's function. The frequency  $\omega$  appears only in the denominator of the sum of the above equation. The Green's function is a meromorphic function of a complex variable  $\omega$  and all its singularities are simple poles, which are infinitesimally shifted into the upper half-plane of  $\omega$  when  $\omega > 0$  and into the lower one if  $\omega < 0$ . Each pole corresponds to an excitation energy. If we set now

$$E_n^{N+1} - E_0^N = (E_n^{N+1} - E_0^{N+1}) + (E_0^{N+1} - E_0^N) = \omega_n - \mu \\ E_n^{N-1} - E_0^N = (E_n^{N-1} - E_0^{N-1}) + (E_0^{N-1} - E_0^N) = \omega'_n - \mu', \quad (29)$$

then  $\omega_n$  and  $\omega'_n$  denote excitation energies in the  $(N+1)$ - and  $(N-1)$ -particle systems respectively and  $\mu$  and  $\mu'$ , known as the chemical potentials, are changes of the ground state energy when a particle is added to the  $N$ -particle system or otherwise is removed from the  $N$ -particle system. In the thermodynamic limit ( $N \rightarrow \infty, V \rightarrow \infty, N/V = \text{const}$ ) one can assume, with an error  $N^{-1}$ , that

$$\omega_n \approx \omega'_n, \quad \mu \approx \mu',$$

where  $\mu$  is now the chemical potential of the  $N$ -particle system. Another simple property of the Green's function that follows from the Eq. (28) is that for  $|\omega|$  very large:

$$G_{\mathbf{k}}(\omega) \sim \frac{1}{\omega}. \quad (30)$$

It is convenient to introduce the spectral densities:

$$A_{\mathbf{k}}^+(\omega) = \sum_n \langle N+1 | c_{\mathbf{k}}^+ | N \rangle|^2 \delta(\omega - \omega_n)$$

$$A_{\mathbf{k}}^-(\omega) = \sum_n \langle N-1 | c_{\mathbf{k}} | N \rangle|^2 \delta(\omega - \omega_n),$$

which are real and positive functions, and whose physical interpretation is simple. The spectral density function  $A_{\mathbf{k}}^+(\omega)$  gives the probability that the original  $N$ -particle, system and a particle added into the state  $\mathbf{k}$  will be found in an exact eigenstate of the  $(N+1)$ -particle system. The spectral function  $A_{\mathbf{k}}^+(\omega)$  counts the number of states with excitation energy  $\omega$  and momentum  $\mathbf{k}$  which are connected to the ground state through the addition of an extra particle. In a system with non-interacting particles,  $A_{\mathbf{k}}^+(\omega)$  is just the density of states, which shows that a particle with momentum  $\mathbf{k}$  definitely has the energy  $\omega$ . Similarly, the function  $A_{\mathbf{k}}^-(\omega)$  is the probability that the original  $N$ -particle system and a hole will be found at an exact eigenstate of the  $(N-1)$ -particle system. Using the spectral density functions (31), we may write the causal Green's function (28) in the Lehmann representation:

$$G_{\mathbf{k}}(\omega) = \lim_{\Gamma_{\mathbf{k}} \rightarrow 0} \int_0^{\infty} \left[ \frac{A_{\mathbf{k}}^+(\omega)}{\omega - (\omega_n + \mu) + i\Gamma_{\mathbf{k}}} \mp \sum_n \frac{A_{\mathbf{k}}^-(\omega)}{\omega + \omega_n - \mu - i\Gamma_{\mathbf{k}}} \right]. \quad (31)$$

In addition, the spectral density functions (31) may be expressed via the causal Green's function (28):

$$A_{\mathbf{k}}^+(\omega - \mu) = -\frac{1}{\pi} \text{Im} G_{\mathbf{k}}(\omega), \quad \omega > \mu$$

$$A_{\mathbf{k}}^-(\omega - \mu) = \pm \frac{1}{\pi} \text{Im} G_{\mathbf{k}}(\omega), \quad \omega < \mu.$$

## B. Quasi-particles

From the Lehmann representation of the Green's function (31), it is easy to see that the special features of the Green's function come from the denominator whose zeros can be interpreted as single-particle excitations. If the Green's function has a pole  $\omega_{\mathbf{k}}$  in the momentum state  $\mathbf{k}$ , then the spectral function  $A_{\mathbf{k}}^+(\omega)$  will have a strong maximum at this energy  $\omega_{\mathbf{k}} = \omega - \mu$ . If the  $c_{\mathbf{k}}^+ | N \rangle$  were an eigenstate, the peak would be a  $\delta$ -function. In the presence of an interaction, the  $c_{\mathbf{k}}^+ | N \rangle$  will not be, in general, an eigenstate, because the system will have many other states with the same momentum and energy, and an exact eigenstate will be a linear combination of the respective single-particle states with energies spread out by the interaction. The shape of the function  $A_{\mathbf{k}}^+(\omega)$  will be strongly dependent on the interaction, and the stronger the interaction the greater the spread of energies and so the greater the width of the function  $A_{\mathbf{k}}^+(\omega)$ . One can expect that if a pole is infinitesimally displaced from the real axis, the Green's function can be written as

$$G_{\mathbf{k}}(\omega) = \frac{z_{\mathbf{k}}}{\omega - \omega_{\mathbf{k}} + i\Gamma_{\mathbf{k}}} + \phi_{\mathbf{k}}(\omega), \quad \omega > \mu, \quad (32)$$

where  $z_{\mathbf{k}}$  is the residue of  $G_{\mathbf{k}}(\omega)$  at the pole, and  $\phi_{\mathbf{k}}(\omega)$  is a smooth function. This yields for the spectral function

$$A_{\mathbf{k}}^+(\omega) \sim \left| \frac{\text{Re } z_{\mathbf{k}} + \text{Im } z_{\mathbf{k}}(\omega - \omega_{\mathbf{k}})}{(\omega - \omega_{\mathbf{k}}) + i\Gamma_{\mathbf{k}}} \right|. \quad (33)$$

One can see from the last equation that the shape of  $A_{\mathbf{k}}^+(\omega)$  is determined by the pole in the complex plane, and in the limiting case,  $\text{Im } z_{\mathbf{k}} = 0$ , it has the symmetric Lorentzian form. In general, the spectral function has the asymmetric Breit-Wigner shape as illustrated in Fig. 3. The peak in  $A_{\mathbf{k}}^+(\omega)$  is associated with a quasi-particle state or elementary excitation. The physical meaning of  $\Gamma_{\mathbf{k}}$  is clearly seen from the Fourier transformation of Eq. (32):

$$iG_{\mathbf{k}}(t) \sim z_{\mathbf{k}} e^{-i\omega_{\mathbf{k}}t - \Gamma_{\mathbf{k}}t}, \quad \Gamma_{\mathbf{k}} > 0, \quad t > 0. \quad (34)$$

This shows that  $\Gamma_{\mathbf{k}}$  is the inverse lifetime of the particle. For negative  $\Gamma_{\mathbf{k}}$  there are only contributions from the poles to the Green's function if  $t < 0$ . In this case, the Green's function describes quasi-holes rather than quasi-particles.

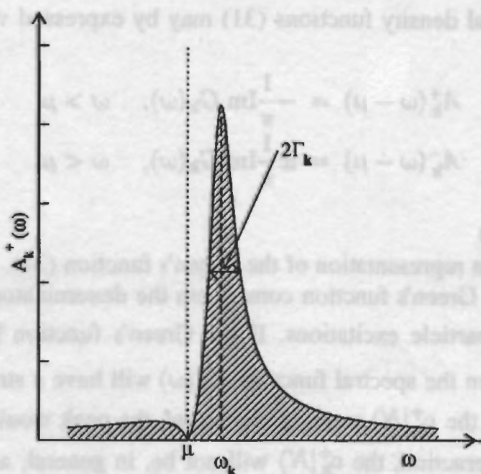


Figure 3. Spectral function  $A_{\mathbf{k}}^+(\omega)$  with a quasi-particle peak of energy  $\omega_{\mathbf{k}} > \mu$  with lifetime  $\Gamma_{\mathbf{k}}^{-1}$ .

### C. Self-energy

The exact explicit expression for the single-particle Green's function or its spectral function is only known for a few systems. In practical applications one usually takes

some approximations for the Green's function, which can be afforded by specific properties of a particular problem. Many approximations start usually from the equation of motion. Without any loss of generality, we shall consider this approach for systems with translationally invariant symmetry, where all equations can be easily manipulated in the momentum space representation, since all entering functions are diagonal in  $k$ -space. One usually starts with the Heisenberg equation of motion for the annihilation field operator  $\hat{\psi}_{\mathbf{k}}(t)$

$$i \frac{\partial \hat{\psi}_{\mathbf{k}}(t)}{\partial t} = [\hat{\psi}_{\mathbf{k}}(t), \hat{H}], \quad (35)$$

and with a similar equation for the creation field operator  $\hat{\psi}_{\mathbf{k}}^{\dagger}(t)$ . The Hamiltonian operator

$$\hat{H} = \hat{H}_0 + \hat{V} \quad (36)$$

can be split into a non-interacting part  $\hat{H}_0$  and an interaction  $\hat{V}$ . The non-interacting part includes the kinetic energy, the Coulomb potential from the nuclei and the Coulomb potential from the electron charge density. The Green's function,  $G_{\mathbf{k}}^0(\omega)$ , of the non-interacting part  $\hat{H}_0$  and the dispersion law  $\omega_{\mathbf{k}}^0$  are known, and by using Eq. (22), the equation of motion for the Green's function can be written as

$$\left[ i \frac{\partial}{\partial t} - \omega_{\mathbf{k}}^0 \right] G_{\mathbf{k}}(t) - \int dt' \Sigma_{\mathbf{k}}(t-t') G_{\mathbf{k}}(t') = \delta(t). \quad (37)$$

Here  $\Sigma_{\mathbf{k}}(t-t')$  is a mass operator which contains all exchange and correlation effects. In the energy representation this equation has more simple form:

$$[\omega - \omega_{\mathbf{k}}^0] G_{\mathbf{k}}(\omega) - \Sigma_{\mathbf{k}}(\omega) G_{\mathbf{k}}(\omega) = 0. \quad (38)$$

If  $G_{\mathbf{k}}^0(\omega)$  is the Green's function corresponding to  $\Sigma_{\mathbf{k}}(\omega) = 0$  then we have the Dyson equation:

$$G_{\mathbf{k}}(\omega) = G_{\mathbf{k}}^0(\omega) + G_{\mathbf{k}}^0(\omega) \Sigma_{\mathbf{k}}(\omega) G_{\mathbf{k}}(\omega) \quad (39)$$

with the formal solution

$$G_{\mathbf{k}}(\omega) = \frac{1}{\omega - \omega_{\mathbf{k}}^0 - \Sigma_{\mathbf{k}}(\omega)}. \quad (40)$$

To solve the Dyson equation we have to evaluate the self-energy, which is completely defined by the interaction  $\hat{V}$  in the Hamiltonian (36). The simplest approach for the self-energy, as can be seen from the equation (36), is the Hartree approximation:

$$\Sigma \equiv \Sigma_H = 0 \quad (41)$$

corresponding to the case of  $\hat{V} = 0$ . The Hartree potential is already included in  $H_0$  of Eq.(36).

Straightforwardly, the self-energy can be evaluated by using Wick's theorem, Feynman diagram technique or by Schwinger functional derivative method. When dynamical interaction effects are taken into account, the self-energy is a functional of the full Green's function and can be expressed as a series expansion in a dynamically screened interaction  $W$ . In turn, the screened Coulomb interaction can be expressed via the polarisation function  $P$  which is also a functional derivative of the full Green's function. One can also show that all functions appearing in the evaluation of the full Green's function and the self-energy, form a set of coupled integral equations which are well known as the Hedin equations. Here we present this set of equations, as it common in literature, in the real-space - time representation (the symbol  $t^+$  means  $\lim_{\eta \rightarrow 0} (t + \eta)$  where  $\eta$  is a positive real number)

$$G(1, 2) = G_0(1, 2) + \int d(3, 4) G_0(1, 3) \Sigma(3, 4) G(4, 2), \quad (42)$$

$$\Sigma(1, 2) = i \int d(3, 4) W(1, 3^+) G(1, 4) \Lambda(3, 2, 4), \quad (43)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4) P(3, 4) W(4, 2), \quad (44)$$

$$P(1, 2) = -i \int d(3, 4) G(1, 3) \Lambda(3, 4, 2) G(4, 1^+), \quad (45)$$

$$\Lambda(1, 2, 3) = \delta(1-2)\delta(2-3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Lambda(6, 7, 3), \quad (46)$$

where we have used an abbreviated notation  $(1) = (\mathbf{r}_1, t_1)$ . Here  $v(1, 2) = v(\mathbf{r}, \mathbf{r}') \delta(t_1 - t_2)$  is the bare Coulomb potential, and  $\Lambda(1, 2, 3)$  is the vertex function containing fluctuations of the charge density. The Hedin set of equations should be solved self-consistently: one sets  $\Sigma = 0$  in the Eq. (46), then one calculates the polarisation function (45) with some starting Green's function, the screened Coulomb function (44), the self-energy (43), and the new Green's function with the Dyson equation (42), which should be used with the self-energy for evaluation of the vertex function (46). This process should be repeated until the resulting Green's function coincides with the starting one. For real materials such calculations are very difficult, mainly because of the complicity of the vertex function (46). In practice one usually approximates one or more functions, appearing in the Hedin set of equations (42)-(46).

Before we turn to practical approaches for the self energy, we shall consider its characteristic features following from quite general considerations<sup>3</sup>. The singularities of the exact Green's function  $G_{\mathbf{k}}(\omega)$ , considered as a function of  $\omega$ , determine both the excitation energies  $\omega_{\mathbf{k}}$  of the system and their damping  $\Gamma_{\mathbf{k}}$ . From the Lehman representation (31) and the Dyson equation (40) it follows that the excitation energy  $\omega_{\mathbf{k}}$  is given by

$$\omega_{\mathbf{k}} = \omega_{\mathbf{k}}^0 + \text{Re } \Sigma_{\mathbf{k}}(\omega_{\mathbf{k}}). \quad (47)$$

Analogously, the damping  $\Gamma_{\mathbf{k}}$  is defined by the imaginary part of the self-energy:

$$\Gamma_{\mathbf{k}} = [1 - \frac{\partial \text{Re } \Sigma_{\mathbf{k}}(\omega_{\mathbf{k}})}{\partial \omega}]^{-1} \text{Im } \Sigma_{\mathbf{k}}(\omega_{\mathbf{k}}). \quad (48)$$

Since from (30) the Green's function for large  $|\omega|$  is

$$[G_{\mathbf{k}}(\omega)]^{-1} = \omega + a_{\mathbf{k}} + b_{\mathbf{k}}/\omega + \dots, \quad (49)$$

it follows from (40) that the self-energy at infinity

$$\Sigma_{\mathbf{k}}(\omega) = -(\omega_{\mathbf{k}}^0 + a_{\mathbf{k}} + b_{\mathbf{k}}/\omega +) \quad (50)$$

is regular function. Further, since the imaginary part of the Green's function never vanishes unless on the real axis, the Green's function  $G_{\mathbf{k}}(\omega)$  has no complex zeros. From the analyticity of  $G_{\mathbf{k}}(\omega)$  it then follows that  $\Sigma_{\mathbf{k}}(\omega)$  is analytic everywhere in the complex plane with the possible exception of the real axis. The self-energy has a spectral representation similar to that of the Green function:

$$\Sigma_{\mathbf{k}}(\omega) \sim \frac{1}{\pi} \int_G \frac{|\text{Im } \Sigma_{\mathbf{k}}(\omega')|}{\omega - \omega'} d\omega' \quad (51)$$

Another important property of the self-energy when  $\omega$  approaches  $\mu^4$ :

$$|\text{Im } \Sigma_{\mathbf{k}}(\omega)| \sim (\omega - \mu)^2. \quad (52)$$

This relation is not valid in general because one of its consequences is the existence of a sharp Fermi surface, which is certainly not present in some systems of fermions with attractive forces between particles.

## D. Kohn-Sham approximation for the self-energy

In the last section we have discussed the general properties of the Green's function method and how the Green's function is related to quasi-particle excitations. Now we shall consider some practical approaches for the self-energy, with that we can solve the Dyson equation (39) on the first-principle (or *ab-initio*) level. One of the most powerful and widely used *ab-initio* methods is the density functional theory (DFT), based on the Hohenberg and Kohn theorem, which implies, that all ground state properties of an inhomogeneous electron gas can be described by a functional of the electron density. This theorem provides a background to obtain self-consistent equations for the description of ground state properties. Further development of the density functional theory was done by Kohn and Sham<sup>5</sup>, which used the total energy functional to obtain self-consistent equations for the charge density. The total energy, which is a functional of an external potential, yields from

$$E[v^{ext}] = \min_{\rho} \left\{ \int v^{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + \frac{1}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + T[\rho] + E_{xc}[\rho] \right\}. \quad (53)$$

Here the first term is the potential energy of the external field  $v^{ext}(\mathbf{r})$ , the second one is the Hartree energy,  $T[\rho]$  is the kinetic energy, and the exchange-correlation energy  $E_{xc}[\rho]$  entails all interactions, which are not included into the Hartree term. The charge density  $\rho(\mathbf{r})$  can be expressed through the orthonormal functions  $\varphi_i(\mathbf{r})$  as

$$\rho(\mathbf{r}) = \sum_i^{occ.} |\varphi_i(\mathbf{r})|^2. \quad (54)$$

Varying the function  $\varphi_i(\mathbf{r})$  one obtains a set of equations, which has to be solved self-consistently to provide the minimum of the functional (53). This scheme corresponds to the single-particle approach, in which electrons move in an effective potential

$$v^{eff}(\mathbf{r}) = v^{ext}(\mathbf{r}) + v_H(\mathbf{r}) + v_{ex}(\mathbf{r}). \quad (55)$$

Here  $v_H(\mathbf{r})$  is the Hartree potential and  $v_{ex}(\mathbf{r}) = \frac{\delta E_{xc}(\rho(\mathbf{r}))}{\delta(\rho(\mathbf{r}))}$  is the exchange-correlation potential. The one-electron wave function  $\varphi_i(\mathbf{r})$  satisfies the Kohn-Sham equation, which is a single-particle Schrödinger equation

$$\left[ -\frac{\Delta^2}{2} + v^{eff}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}). \quad (56)$$

The functional (53) provides in principle the exact ground state energy if the exchange-correlation energy  $E_{xc}[\rho]$  is known exactly. For real systems this functional is difficult to find and this remains the main problem of the density-functional theory. For applications the exchange-correlation energy  $E_{xc}[\rho]$  is usually approximated by some known functionals obtained for some more simpler systems. One of the most popular



approaches is the local-density approximation (LDA), in which the exchange-correlation energy  $E_{xc}[\rho]$  of an inhomogeneous system is approximated by the exchange-correlation energy of a homogeneous electron gas. Thereby all many-body effects are included in the local exchange-correlation potential, which depends on the electronic density and some parameters obtained from many-body calculations for a the homogeneous electron gas<sup>6-10</sup>. In the case of a slowly varying electronic density the LDA works well and is widely used for many systems in the last three decades (see review by R. O. Jones and O. Gunnarsson<sup>11</sup>). The simplicity of the local density approximation makes possible to solve the Kohn-Sham equation (56) with different basis sets and for different symmetry cases. When the on-site Coulomb interaction dominates the behaviour of electrons (strongly correlated systems), the local-density does not work well, and another approximation of  $E_{xc}[\rho]$  is needed.

As was already mentioned above, the density functional theory is designed for study of ground state properties. It is intuitively reasonable to interpret the eigenvalues  $\epsilon_i$  in the one-particle equation (56) as excitation energies, but as it was pointed out by Sham and Kohn<sup>12</sup>, there is no real justification for such an interpretation. However, according to the Hohenberg-Kohn theorem, also the Green's function and thus the self-energy are functionals of the electronic density. In this way one can use the theorem for a discussion how to calculate the excitation spectrum. For the self-energy one can use the local density approximation<sup>12</sup>:

$$\Sigma(\mathbf{r}, \mathbf{r}'; \omega) \approx \Sigma_0(\mathbf{r} - \mathbf{r}', \omega - V(\mathbf{r})), \quad (57)$$

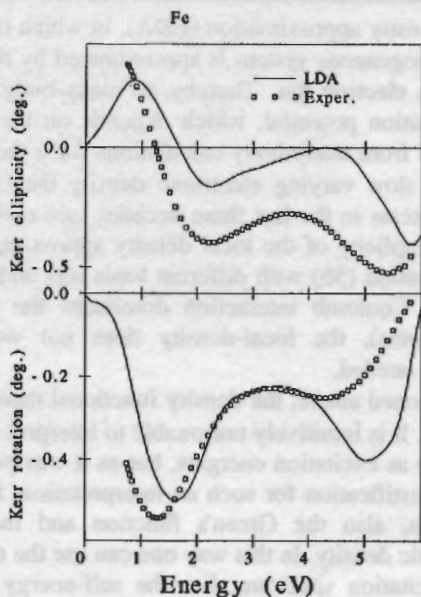
where  $\Sigma_0$  is the electron gas self-energy, evaluated for zero Hartree potential, which explains the appearance of the potential  $V(r)$  in the argument. The potential  $\Sigma_0$  is still not local in the space. When the electronic density is slowly varying, the self-energy can be used in the form

$$\Sigma \approx \Sigma_{0k}(\omega_k), \quad (58)$$

where  $\omega_k$  is the quasi-particle energy. Further approximation can be done when  $\Sigma_{0k}(\omega_k)$  depends weakly on  $\mathbf{k}$ , that corresponds to not too highly excited states ( $\omega \lesssim 2\mu$ ). In this case the self-energy can be replaced by the exchange-correlation potential:

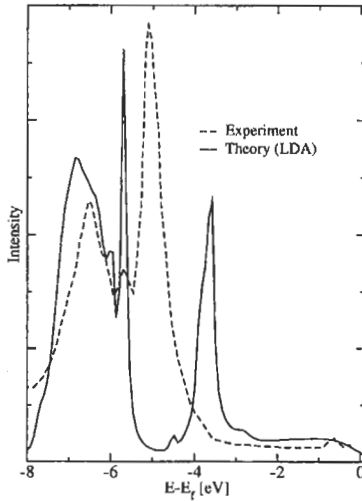
$$\Sigma \longrightarrow v_{xc}. \quad (59)$$

This assumption makes possible using the density functional theory for quasi-particle calculations. The single-particle Green's function, obtained from the Kohn-Sham equation (56), may be used for spectroscopy calculations if energies are not too high. This fact led to the development of variety of methods on the first-principle level, which are successfully applied for many spectroscopy phenomena (see recent reviews in<sup>13,14</sup>). An example, how the density functional theory within the LDA does work, is illustrated in Fig. 4. Here we present calculated by a self-consistent LMTO method<sup>15</sup> and experimental<sup>16</sup> magneto-optical spectra for iron. Because the magneto-optics belongs to



**Figure 4.** Calculated<sup>15</sup> and experimental<sup>16</sup> magneto-optical spectra of Fe

the low-energy spectroscopy, one can expect, that the use of the LDA is reasonable. Indeed, the calculated polar Kerr rotation and Kerr ellipticity agree very well with the experimental curve. The theoretical curve reproduces all main features of the experimental result. With increasing the energy the agreement with experiment is getting worse, that can be explained by deterioration of the LDA approximation for high excited states. The theory could not represent also the magnitude of the experimental curve for whole energy range, and this is related to the damping of the quasi-particle states. The main failure of the LDA in the description of spectroscopic phenomena is inability to reproduce the damping of single-particle excitation, which is defined by the imaginary part of the self-energy (48). This part is not present in the approximation (59). In practice the spectrum is usually smeared by Lorentzian broadening with some constant width  $\Gamma$ , but it is not sufficient approximation, because in reality the damping has more complicated behaviour. An evident case when the LDA does not work is shown in the Fig. 5. Here we present photoemission spectra for silver at a photon energy of 26 eV. The solid line shows a theoretical spectra calculated by authors using a self-consistent Green's function method<sup>17,18</sup> within the LDA. The dashed line reproduces the experiment<sup>19</sup>. The low part of the spectra (up to 5.5 eV below the Fermi level) is adequately represented by theory. At the energy 5.1 eV below the Fermi level the experiment shows a peak corresponding to an  $4d$ -state, which is predicted by theory at 3.6 eV below the Fermi level. The discrepancies are related to the inadequacy of the local approximation of  $v_{xc}(r)$  and to the failure of correlating single-particle eigenvalues with excitation energies in the photoemission experiment. Below we point some serious faults of the DFT and the LDA in the description of ground state and quasi-particle state properties:



**Figure 5.** Photoemission spectra of silver at a photon energy of 26 eV: theory (solid line) and experiment (dashed line)<sup>19</sup>

- Approximation of the exchange-correlation energy is crucial point of DFT calculations. Existing approximations are usually applicable for systems with low varying electronic densities. In presence of strong-correlated electrons the LDA does not provide reasonable results.
- The LDA is not self-interaction free. The unphysical interaction of an electron with itself can be subtracted if the electron is sufficiently localized<sup>9</sup>. This remarkably improves the total energy and other ground state properties, but excited states are still described badly because the Kohn-Sham approximation (59) is not appropriate for strong localized electrons. Applying the SIC method for extended systems is difficult since electron states may be not localized in such systems.
- The band gaps in *sp*-semiconductors like Si, GaAs, Ge, etc. are by 70-100% systematically underestimated.
- The damping of excitation states can not be conceptually described within the density functional theory.

The main reason for all those discrepancies of the DFT is a fact, that the density functional theory is not naturally designed for excited states. The approximation (59) is conceptually right only for specific materials and for a limited range of energies.

## E. GW approximation

Here we shall consider more natural way for the self-energy approximation using the Hedin's set of equations (43)-(46). Most difficult part of those equations is the evaluation of the vertex function (46). The vertex function entails correlation effects and is defined implicitly through the Bethe-Salpeter equation, which involves a two-particle Green's function. The functional derivative  $\delta\Sigma/\delta G$  is not trivial to obtain, because the

Green's function is not explicitly contained in  $\Sigma$  but only calculated from it by mean of the Dyson equation (42). If electrons interact not too strongly, this functional derivative is close to zero, and the vertex function is given then by the following simple equation<sup>20-22</sup>:

$$\Lambda(1, 2, 3) \approx \delta(1 - 2)\delta(2 - 3). \quad (60)$$

This yields a simplified version of Hedin's set of equations (in real-space/time representation):

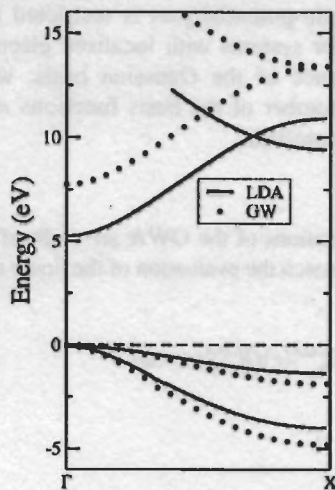
$$\Sigma(1, 2) = iW(1, 2)G(1, 2), \quad (61)$$

$$W(1, 2) = v(1, 2) + \int d(3, 4)W(1, 3)P(3, 4)v(4, 2), \quad (62)$$

$$P(1, 2) = -iG(1, 2)G(2, 1). \quad (63)$$

In this approximation the self-energy is expressed as a product of the self-consistent single-particle propagator  $G$  and the self-consistent dynamically screened interaction  $W$ , that gives the name for the approximation:  $GW$ . The GWA is consistent in the sense that it is a particle- and energy-conserving approximation in the Baym-Kadanoff sense<sup>23,24</sup>. The GWA corresponds to the first iteration of the Hedin's equations and can be interpreted as the first order term of an expansion of the self-energy in terms of the screened interaction. The equations (42), (61)-(63) can be solved self-consistently but in practice, such a determination is computationally very expensive. Moreover, the experience with self-consistent GW implementations (see the review by F. Aryasetiawan and O. Gunnarson<sup>25</sup> and references therein) shows that in many cases the self-consistency even worsen results as non-self-consistent calculations. The main reason for it is the neglecting the vertex correction that to say correlations. Most existing GWA calculations do not attempt self-consistent calculations but determine good approximations for the single-particle propagator  $G$  and the screened interaction separately, i.e., these calculations adopt a "best G, best W" philosophy. The common choice for the single-particle propagator is usually the LDA or Hartree-Fock Green's function. Using this Green's function the linear response function is obtained via the equation (63), and afterward it is used for the calculation of the screened Coulomb interaction (62). The self-energy is then determined without further iteration. Nevertheless, with the first iteration of the  $GW$  approximation encouraging results have been achieved. In Fig. (6) we show a typical result for the energy bands of MgO within the GWA (dotted line) compared to the conventional LDA calculation. As clear from this plot the GWA gap is in much better agreement with the experimental value than the LDA calculations.

Below we consider briefly some existing implementations of the  $GW$  method. More detail can be found in the original papers and in the reviews<sup>25,26</sup>. The integral GWA equations (42),(61)-(63) can be represented in some basis and solved by matrix inversion in the real or reciprocal space. The basis should be appropriate to the symmetry of the particular problem and be able as accurate as possible to represent quite distinctive behavior of the  $GW$  operators.



**Figure 6.** Energy bands of MgO from KKR-LDA (solid) and GWA (dots) calculations. The LDA band gap is found to be 5.2 eV, the GWA band gap is 7.7 eV which is in good agreement with the experimental gap of 7.83 eV.

#### • Plane wave methods

Pseudo-potentials in conjunction with a plane wave basis set are widely used in computational condensed matter theory due to their ease of use and systematic convergence properties. Because of simplicity of the GW equations in the plane wave basis, the implementation of the GWA is easy, and many pseudo-potential codes entail a GW part. Conventionally a pseudo-potential method can be applied for electronic structure study of systems with delocalised *sp*-electrons for which the plane wave basis converges rapidly. But due to recent development of the pseudo-potential technique new ultra-soft pseudo-potential methods can be also applied to materials with localised *d*- and *f*-electrons. Most of existing pseudo-potential programs are well optimised and successfully used not only for bulk-systems but also for surfaces, interfaces, defects, and clusters. A disadvantage of the plane wave basis is bad convergence for systems with localised electrons. For transition metals or *f*-electron systems one needs more thousand plane waves. Also the number of basis functions needed for convergence is increasing with the volume of the system. Typically a plane wave GW calculation scales with  $N^4$ , that makes expensive calculations of extended systems.

#### • The Gaussian basis method

Rohlfing, Krüger, and Pollman<sup>27</sup> have developed a GW method which combines a pseudo-potential basis and localised Gaussian orbitals. In this approach the LDA Green function is obtained by a conventional pseudo-potential method. Afterwards the Green function and all GW equations are represented in the localised Gaussian orbitals. This lets essentially reduce the size of the problem. Typically one needs 40-60 Gaussian functions. Another advantage of the method is that many of integrals can be calculated

analytically. Because the pseudo-potential part is restricted for *sp*-electron compounds, the method can not be used for systems with localised electrons. A serious problem of the approach is the convergence of the Gaussian basis: while a Gaussian basis can systematically converge, the number of the basis functions needed for convergence can be quite various for different materials.

### • The spacetime method

Most of existing implementations of the GWA are realized in the real energy-reciprocal space representation. In this approach the evaluation of the linear response function

$$P_{\mathbf{q}}(\omega) = -\frac{i}{(2\pi)^4} \int_{-\infty}^{\infty} d\varepsilon \int_{\Omega_{BZ}} d\mathbf{k} G_{\mathbf{k}}^{LDA}(\varepsilon) G_{\mathbf{k}-\mathbf{q}}^{LDA}(\varepsilon - \omega) \quad (64)$$

and the self-energy

$$\Sigma_{\mathbf{q}}(\omega) = \frac{i}{(2\pi)^4} \int_{-\infty}^{\infty} d\varepsilon \int_{\Omega_{BZ}} d\mathbf{k} W_{\mathbf{k}}(\varepsilon) G_{\mathbf{k}-\mathbf{q}}^{LDA}(\varepsilon - \omega) \quad (65)$$

involves very expensive convolutions. In the real-space/time representation both functions are simple products (63) and (61), which eliminate two convolutions in reciprocal and energy space. The idea to chose different representations to minimise the computations is realized in the spacetime method<sup>28</sup>. According to this scheme the LDA wave functions  $\Phi_{\mathbf{nk}}(\mathbf{r})$  are calculated with a pseudo-potential method. Then the non-interacting Green's function is analytically continued from real to imaginary energy and Fourier transformed into the imaginary time:

$$G^{LDA}(\mathbf{r}, \mathbf{r}'; i\tau) = \begin{cases} i \sum_{\substack{\mathbf{nk} \\ \text{occ.}}} \Phi_{\mathbf{nk}}(\mathbf{r}) \Phi_{\mathbf{nk}}^*(\mathbf{r}') e^{\varepsilon_{\mathbf{nk}} \tau}, & \tau > 0 \\ -i \sum_{\substack{\mathbf{nk} \\ \text{unocc.}}} \Phi_{\mathbf{nk}}(\mathbf{r}) \Phi_{\mathbf{nk}}^*(\mathbf{r}') e^{\varepsilon_{\mathbf{nk}} \tau}, & \tau < 0 \end{cases} \quad (66)$$

Here  $\mathbf{r}$  denotes a point in the irreducible part of the real space unit cell while  $\mathbf{r}'$  denotes a point in the "interaction cell" outside of which  $G^{LDA}$  is set to zero. The linear response function is calculated in the real-space and for imaginary time with the formula (63) and afterwards Fourier transformed from  $i\tau$  to  $i\omega$  and from real space to reciprocal one. The screened Coulomb interaction is evaluated as in a conventional plane wave method, and, in turn, is transformed into the real-space/imaginary time representation to obtain the self-energy according the equation (61). Further, the self-energy can be transformed into the imaginary energy axis and reciprocal space, and analytically continued to real energies. The spacetime method decreases essentially computational time and makes the calculation of large systems accessible. A main computational problem of the spacetime method is the storage of evaluated functions ( $G$ ,  $P$ ,  $W$ , and  $\Sigma$ ) in both representations that can trouble calculations of large systems.

- **The linearised augmented plane waves (LAPW) method**

The LAPW method is one of the most popular methods for the electronic structure study. The basis consists of local functions, obtained from the Schrödinger equation for atomic-like potential in a muffin-tin sphere on some radial mesh, and plane waves, which describe the interstitial region. The local functions are matched on the sphere to plane waves. Such combination of two different kinds of basis functions makes the LAPW method extremely accurate for systems with localised or delocalised electrons. Also the plane waves describe better high energy states, which are usually badly represented by a conventional tight-binding method. All this makes the LAPW method attractive for the GWA implementation. Hamada and coworker developed a GW method with the LAPW<sup>29</sup> and applied it to Si. 45 basis functions per Si atom are needed which corresponds to a reduction by factor of five compared to plane wave calculations. But the computational afford is comparable with the pseudo-potential calculations because of the expensive evaluation of matrix elements. Although a GW-LAPW realization was successfully used also in Ni<sup>30</sup>, the method did not become popular because of this computational problem. With development of computer technology this method may be very promising, as it was showed recently by Usuda and coworkers<sup>31</sup> in the GW-LAPW study in wurtzite ZnO.

- **The linearised muffin-tin orbitals (LMTO) method**

The LMTO is an all-electron method<sup>32,33</sup> in which the wave functions are expanded as follows,

$$\psi_{nk} = \sum_{\mathbf{RL}} \chi_{\mathbf{RL}}(\mathbf{r}; \mathbf{k}) b_{nk}(\mathbf{RL}), \quad (67)$$

where  $\chi$  is the LMTO basis given in the atomic sphere approximation by

$$\chi_{\mathbf{RL}}(\mathbf{r}, \mathbf{k}) = \varphi_{\mathbf{RL}}(\mathbf{r}) + \sum_{\mathbf{R}'L'} \dot{\varphi}_{\mathbf{R}'L'}(\mathbf{r}) H_{\mathbf{RL};\mathbf{R}'L'}(\mathbf{k}). \quad (68)$$

Here  $\varphi_{\mathbf{RL}}(\mathbf{r}) = \phi_{\mathbf{RL}} Y_L(\Omega)$  is a solution to the Schrödinger equation inside a sphere centred on an atom at site  $\mathbf{R}$  for a certain energy  $\epsilon_\nu$ ,  $\dot{\varphi}_{\mathbf{R}'L'}(\mathbf{r})$  is the energy derivative of  $\varphi_{\mathbf{RL}}(\mathbf{r})$  at the energy  $\epsilon_\nu$ , and  $H_{\mathbf{RL};\mathbf{R}'L'}(\mathbf{k})$  are the LMTO structure constants. An advantage of the LMTO is that the basis functions do not depend on k-vector. The LMTO method is characterised by high computational speed, requirement of a minimal basis set (typically 9-16 orbitals per an atom), and good accuracy in the low energy range.

Aryasetiawan and Gunnarsson suggested to use a combination of the LMTO basis functions for solving the GW equations<sup>34</sup>. They showed that a set of products  $\phi\phi$ ,  $\phi\dot{\phi}$ , and  $\dot{\phi}\dot{\phi}$  forms a complete basis for the polarisation function (63) and the self-energy (61). They introduced an optimised basis set which consists of product functions

$$B_{\mathbf{RL}L'} = \phi_{\mathbf{RL}}(\mathbf{r})\phi_{\mathbf{R}'L'}(\mathbf{r}). \quad (69)$$

This scheme allows accurate description of systems with any kinds of electrons typically with 60-100 product functions. A disadvantage of the approach is a bad representation of high energy states in the LMTO method, which are important for calculations of the polarisation function and the self-energy. Recently, Kotani and van Schilfgaarde developed a full-potential version of the LMTO product basis method<sup>35</sup>, which accuracy is substantially better as the conventional GW-LMTO implementation.

## IV. Summary

The aim of this paper is to provide a concise overview on the theoretical description of electronic excitations in finite and extended systems using the random-phase approximation. We discussed how this scheme can be implemented to describe the electron removal probabilities from metal clusters and large molecules and to deal with the electronic structure and optical properties of solids. From the derivation of the random phase approximation it is clear however, that the RPA is the first step (first-order perturbation approximation) towards a systematic treatment of electronic correlation. For strongly correlated systems and/or highly excited states, higher-order terms in the perturbation expansion may well be important.

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## References

1. Landau L D 1956 Zh. Eksp. Teor. Fiz. **30** 1058 (1957 Sov. Phys.-JETP **3** 920); 1957 Zh. Eksp. Teor. Fiz. **32** 59 (1957 Sov. Phys.-JETP **5** 101) - 1958 2 Ehp. Teor. Fiz. **35** 97 (1959 Sou. Phys.-JETP **8** 70)
2. Migdal A B 1967 *Theory of Finite Fermi Systems* (New York Wiley).
3. J. M. Luttinger, Phys.Rev **121**, 942 (1961).
4. J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).
5. W. Kohn and L. J. Sham, Phys. Rev **140**, A1133 (1965).
6. U. von Barth and L. Hedin, J. Phys. C: Sol. State Phys. **5**, 1629 (1972).
7. D. J. Ceperley and L. Alder, Phys. Rev. Lett. **45**, 566 (1980).
8. S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
9. J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
10. J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
11. R. O. Jones and O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).
12. L. J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).
13. H. Ebert and G. Schütz, eds., *Magnetic Dichroism and Spin Polarization in Angle-Resolved Photoemission*, no. 466 in Lecture Notes in Physics (Springer, Berlin, 1996).
14. H. Dreysse, ed., *Electronic Structure and Physical Properties of Solids. The Uses of the LMTO Method* (Springer, Berlin, 2000).
15. V. N. Antonov, A. Y. Perlov, A. P. Shpak, and A. N. Yaresko, JMMM **146**, 205 (1995).
16. G. Krinichik and V. Artem'ev, Zh. Exp. Teor. Fiz. **53**, 1901 (1967).
17. A. Ernst, W. M. Temmerman, Z. Szotek, M. Woods, and P. J. Durham, Phil. Mag. B **78**, 503 (1998).
18. M. Lüders, A. Ernst, W. M. Temmerman, Z. Szotek, and P. J. Durham, J. Phys.: Condens. Matt. **13**, 8587 (2001).



19. M. Milun, P. Pervan, B. Gumhalter, and D. P. Woodruff, *Phys. Rev. B* **59**, 5170 (1999).
20. L. Hedin, *Phys. Rev.* **139**, A796 (1965).
21. L. Hedin, *Ark. Fys.* **30**, 231 (1965).
22. L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (New York: Academic, 1969), vol. 23.
23. G. Baym and L. Kadanoff, *Phys. Rev.* **124**, 287 (1961).
24. G. Baym, *Phys. Rev.* **127**, 1391 (1962).
25. F. Aryasetiawan and O. Gunnarson, *Rep. Prog. Phys.* **61**, 237 (1998).
26. W. G. Aulbur, L. Jönsson, and J. W. Wilkins, in *Solid State Physics*, edited by H. Ehrenreich and F. Spaepen (Academic, San Diego, 2000), vol. 54.
27. P. K. M. Rohlfing and J. Pollmann, *Phys. Rev. B* **48**, 17791 (1993).
28. H. N. Rojas, R. W. Godby, and R. J. Needs, *Phys. Rev. Lett.* **74**, 1827 (1995).
29. N. Hamada, M. Hwang, and A. J. Freeman, *Phys. Rev. B* **41**, 3620 (1990).
30. F. Aryasetiawan, *Phys. Rev. B* **46**, 13051 (1992).
31. M. Usuda, N. Hamada, T. Kotani, and M. van Schilfgarde, *Phys. Rev. B* **66**, 125101 (2002).
32. O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975).
33. O. K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53**, 2571 (1984).
34. F. Aryasetiawan and O. Gunnarsson, *Phys. Rev. B* **49**, 16214 (1994).
35. T. Kotani and M. van Schilfgarde, *Solid State Communications* **121**, 461 (2002).
36. Matt, S. *et al.* 1996, *J. Chem. Phys.*, 105, 1880.
37. Foltin V. *et al.* 1998, *Chem. Phys. Lett.*, 289, 181.
38. Keller, S., Engel, E. 1999, *Chem. Phys. Lett.*, 299, 165.
39. Keller, S. 2001, *Eur. Phys. J. D*, 13, 51.
40. Kidun, O., Berakdar, J. 2001, *Phys. Rev. Lett.*, 87, 263401.