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2 A Many-body Approach to the Electronic and Optical Properties of Copper and Silver

Andrea Marini

2.1 Introduction

Quasiparticles, plasmons and excitons are the fundamental quantities used to interpret the electronic and optical properties of solids. More important than their isolated description is the comprehension of their mutual interaction. However, due to the high complexity and large computational requirements of many-body calculations the experimental band-structures, optical absorption and electron-energy-loss spectra are often compared with the results of (simpler) calculations performed within density functional theory (DFT). The consequences of this approach must however be considered with great care. DFT is based on the idea that the ground state spatial density of a system of interacting particles can be exactly described by a non-interacting gas of fictitious independent particles, moving under the action of an effective potential. Thus DFT, as a ground state theory, makes the comparison with experiments inadequate, in particular for the description of excited states properties. An alternative approach is time-dependent DFT (TDDFT) where all neutral excitations are, in principle, exactly described [1]. However only very recently an efficient approximation for the exchange-correlation kernel of TDDFT has been proposed [2], mainly focused on semiconductors and insulators. The shortcomings of DFT are particularly evident in noble metals where the electronic and optical properties are only qualitatively described: (a) compared with experiment, the usual local density (LDA) approximation to the exchange-correlation potential yields an overestimated d-band width and a too small binding energy for the d-bands top; (b) the experimental electron–energy loss spectrum of silver is dominated by a sharp plasmon peak at 3.83 eV, underestimated in position and almost completely damped when calculated within the DFT-LDA random-phase approximation (RPA); (c) the experimental optical spectra intensity of copper and silver are overall overestimated by ~30% when calculated within RPA.

In the following sections I will show how these deficiencies of DFT can be successfully corrected using many-body perturbation theory (MBPT). In Section 2.2 I will present the quasiparticle band structure of copper. The effect of the quasiparticle corrections on the optical absorption and EELS of silver will be described in Section 2.3 while in Section 2.4 I will review the most recent results concerning excitonic effects on the optical spectra of metals.
2.2 Quasiparticle Electronic Structure of Copper

The electronic properties of solids are routinely calculated within DFT in the LDA, by expanding the Kohn-Sham orbitals in plane waves, see e.g. Ref. [3]. This is made possible by the use of modern norm-conserving pseudopotentials, which allow one to obtain highly accurate valence and conduction band energies without explicitly including the core electrons in the calculation. “Freezing” the core electrons is crucial when a plane-wave basis is used: the number of basis functions needed to describe the 1s of the Si atom is, in fact, 1000 times larger than in the case of the valence shell. The study of noble metals like copper using first-principles methods based on plane-waves and ab-initio pseudopotentials (PPs) presents some peculiar complication with respect to the case of simple metals or semiconductors. In fact, in addition to metallicity, which implies the use of an accurate sampling of the Brillouin zone in order to describe properly the Fermi surface, one must also take into account the contribution of d-electrons to the bonding and to the valence bandstructure. This means that, within the PP scheme, d states cannot be frozen into the core part, but must be explicitly included in the valence, yielding a large total number of valence electrons (11 for bulk copper) [4]. Using soft Martins–Troullier [5] PPs it is possible to work at full convergence with a reasonable kinetic energy cutoff (60 Ry if the 3s and 3p atomic states are frozen into the core, 160 Ry when they are explicitly included) [4]. In Figure 2.1 the DFT band-structure (dashed line) of bulk copper is compared with the experimental data (circles). In contrast to the case of semiconductors, the disagreement between theory and experiment is far from being limited to a rigid shift of the Kohn–Sham occupied eigenvalues with respect to the empty ones. In particular, the comparison clearly shows substantial differences with respect to the experiment for both the d-band width (3.70 instead of 3.17 eV) and position (more than 0.5 eV up-shifted in the DFT), in agreement with previous works [6, 7]. The reason for these important deviations of the DFT band-structure is the approximate inclusion of exchange and correlation effects in the LDA single-particle Kohn–Sham (KS) potential. Moreover, in DFT, KS eigenvalues cannot be identified with electron addition or removal energies, since there is no equivalent of Koopman’s theorem. MBPT represents an exact method to correct the DFT single particle levels, as the band energies can be obtained in a rigorous way, i.e. as the poles of the one-particle Green’s function \( G(r, r'; \omega) \) [8]. The latter are determined by an equation of the form:

\[
\left[ \frac{\hbar^2}{2m} \Delta_r + V_{\text{external}}(r) + V_{\text{Hartree}}(r) \right] \psi_{nk}(r, \omega) + \int d r' \, \Sigma(r, r'; \omega) \psi_{nk}(r', \omega) = E_{nk}(\omega) \psi_{nk}(r, \omega),
\]

containing the non-local, non-hermitian and frequency dependent self-energy operator \( \Sigma \). The poles of \( G \) are the QP energies \( \epsilon_{nk}^{\text{QP}} \), the solutions of \( \epsilon_{nk}^{\text{QP}} = E_{nk}(\omega) \). The corresponding quasiparticle wavefunctions are \( \phi_{nk}(r) = \psi_{nk}(r, \epsilon_{nk}^{\text{QP}}) \). The off-diagonal matrix elements of the self-energy operator \( \langle nk | \Sigma | n'k' \rangle \) are usually much smaller than the diagonal elements. Thus the quasiparticle and the KS wavefunctions are identical and Eq. (2.1) can
be rewritten as a scalar equation for \( \epsilon_{nk}^{\text{QP}} \):

\[
\epsilon_{nk}^{\text{QP}} = \epsilon_{nk}^{\text{DFT}} + M_{nk} \left( \epsilon_{nk}^{\text{QP}} \right) + \Sigma_{x}^{nk} - \Sigma_{z}^{nk}.
\]  

(2.2)

Following Ref. [9], we have separated the static, bare-exchange part \( \Sigma_{x}(r, r'; \omega) \) from \( M(r, r'; \omega) \), the energy-dependent correlation contribution, or mass-operator. \( \Sigma_{x}^{\text{QP}} \) is given by:

\[
\langle \Sigma_{x}^{nk} \rangle = \sum_{n_{1}} \int_{\text{BZ}} \frac{dq}{(2\pi)^{3}} \int_{n_{1}(k-q)} d\omega' \int d\omega \int_{-\infty}^{\infty} d\omega' \frac{\Gamma_{nn_{1}}^{\text{c}}(k, q, \omega')}{\omega - \omega' - \epsilon_{n_{1}(k-q)}^{\text{DFT}} + i\delta} + \frac{\Gamma_{nn_{1}}^{\text{v}}(k, q, \omega')}{\omega - \omega' - \epsilon_{n_{1}(k-q)}^{\text{DFT}} - i\delta}. \]

(2.3)

where \( \omega \) is the bare Coulomb interaction and \( 0 \leq f_{n}(k) \leq 1 \) represents the occupation number. \( M \) is usually evaluated according to the so-called \( GW \) approximation, derived by Hedin in 1965 [8, 10], which is based on an expansion in terms of the dynamically screened Coulomb interaction \( W(r, r'; \omega) \):

\[
M_{nk}(\omega) = \langle nk| M(r_{1}, r_{2}, \omega) |nk \rangle = \sum_{n_{1}} \int_{\text{BZ}} \frac{dq}{(2\pi)^{3}} \int_{-\infty}^{\infty} d\omega \int \frac{\Gamma_{nn_{1}}^{\text{v}}(k, q, \omega')}{\omega - \omega' - \epsilon_{n_{1}(k-q)}^{\text{DFT}} - i\delta}. \]

(2.4)

\( \Gamma_{\text{c}}^{\text{c}} \) and \( \Gamma_{\text{c}}^{\text{v}} \) are the conduction, valence contributions to the self-energy spectral function:

\[
\Gamma_{nn_{1}}^{\text{c}}(k, q, \omega) = 2 \left( 1 - f_{n_{1}(k-q)} \right) \int dr dr' \phi_{nk}'(r) \phi_{n_{1}(k-q)}(r) W^{\delta}(r, r'; \omega) \theta(\omega - \epsilon_{n_{1}(k-q)}^{\text{DFT}}) \phi_{nk}(r').
\]

(2.5)

\[
\Gamma_{nn_{1}}^{\text{v}}(k, q, \omega) = 2 f_{n_{1}(k-q)} \int dr dr' \phi_{nk}'(r) \phi_{n_{1}(k-q)}(r) W^{\delta}(r, r'; \omega) \theta(\omega - \epsilon_{n_{1}(k-q)}^{\text{DFT}}) \phi_{nk}(r').
\]

(2.6)

Here \( W^{\delta} \) is the delta-like part of the Lehman representation of the screened Coulomb interaction function. \( W \) is expressed in terms of the microscopical inverse dielectric function, \( W(r, r'; \omega) = v(r, r') + \int dr'' v(r, r'') e^{-1}(r''', r'''; \omega) \).

Most \( GW \) calculations on semiconductor systems use a plasmon-pole approximation (PPA) for \( W(\omega) \) [11], based on the observation that the Fourier components of the inverse dielectric function are generally peaked functions of \( \omega \), and can be approximated by a single pole. Since the evaluation of \( M \) involves an integration over the energy, the fine details of the \( \omega \)-dependence are not critical, and the PPA turns out to work reasonably well for most applications. However, in the case of copper, the use of a PPA becomes more critical. The presence
of flat d-bands 2 eV below the Fermi level implies strong transitions in the inverse dielectric function spread over a large energy range. These transitions are not at all well described as a single-pole function, leading to instabilities when determining the plasmon-pole parameters. Instead, the screened electron–hole interaction must be explicitly computed over a grid of about 200 frequencies from zero to ~130 eV, and the energy integral performed numerically.

The set of Eqs. (2.1)–(2.6) constitutes a well-defined and successful scheme to calculate quasiparticle band structure in many different materials [8]. Normally (e.g., in GW calculations for semiconductors), the calculation of $G$ and $W$ to correct the DFT valence band-structure can be performed by including only valence states, and fully neglecting the core states which have been frozen in the pseudopotential approach. Among transition metals, full quasiparticle calculations have been carried out only for Ni [13]. In the case of Ni, $GW$ yields a good description of photoemission data, except for the 6 eV satellite, which is due to strong short-range correlations within the partially filled d-shell. For copper, we would expect band-theory to work better than for transition metals, since d-shells are completely filled. Instead, as showed in Ref. [12], when $\Sigma$ is computed neglecting the 3s and 3p atomic core states (which in the solid create two flat bands, at about 112 and 70 eV, respectively, below
2.3 The Plasmon Resonance of Silver

the Fermi level), the resulting QP corrections on the d-bands are clearly unphysical: $GW$ corrections move the highest occupied d-bands above the DFT-LDA Fermi level. On the other hand, the situation for s/p states (e.g. for the state $L_2$) is much more reasonable, with correlation and exchange parts of the self-energy which largely cancel each other (as in the case of semiconductors), and negative QP corrections of the order of eV. The solution of this puzzling situation is provided by the role of the above-mentioned 3s and 3p states, which, despite being well separated in energy from the 3d ones, have a large spatial overlap with the latter. As a consequence, non-negligible contributions to the self-energy are expected from the exchange contributions between 3d and 3s/3p states as clearly shown in the inset of Figure 2.1, where the difference $\langle \Sigma^{n} - V^{n}_{xc} \rangle$ is strongly affected by the presence of core levels in the $n_1$ summation of Eq. (2.4). The role of core levels in the calculation of the bare exchange contributions (whose importance has already been addressed for transition metals by Aryasetiawan and Gunnarsson [8], but estimated to be of the order of 1 eV) is hence crucial in the case of copper. Moreover their effect is unexpected on the basis of DFT-LDA calculations, where the band structure does not change appreciably even if the 3s/3p orbitals are fully included in the valence [4].

In Figure 2.1 the full $GW$ theoretical band structure [12] is compared with experimental data: the agreement is remarkably good and the fact that the $GW$ corrections cannot be reproduced by any rigid shift of the LDA bands clearly appears. Hence, the $GW$ method, originally devised to describe the long-range charge oscillations [10], is hence shown to yield a good description also of copper, a system characterized by localized orbitals and short-range correlation effects.

2.3 The Plasmon Resonance of Silver

In the previous section we have seen how to correct the DFT single particle levels using MBPT obtaining an excellent agreement with the experimental results. However in a fully interacting electronic system quasiparticles coexist with collective excitations, i.e. plasmons. Plasmons occur at energies for which the real part of the dielectric function vanishes with a corresponding small imaginary part; they can be observed experimentally as sharp peaks in electron energy loss spectra (EELS). A well established technique to calculate EELS uses the independent particles or random phase approximation (RPA) for the polarization function, obtained in terms of ab-initio single-particle energy bands. In the case of silicon, Olevano and Reining [14] showed that using the quasiparticle energies without going beyond the RPA, including excitonic effects (as we will discuss in the next section), the shape of the plasmon peak worsens with respect to the experiment. Inclusion of self-energy corrections and excitonic effects yields a spectrum very similar to the DFT-LDA one and to the experiment. Ku and Eguiluz [15] obtained a correct positive dispersion of the plasmon width in K using the single particle approximation, with no many-body corrections beyond DFT-LDA. In these cases many-body effects (quasiparticle corrections and/or excitonic effects) are not required to describe correctly the experimental data. These results agree with the general feeling that excitonic effects partially cancel self-energy corrections (we will discuss in detail this cancellation in the next section). A similar result has been found for copper [4, 16], where the RPA
response function calculated without many-body corrections yields good agreement with the experimental EEL and optical spectra.

In this framework the case of silver is rather surprising: the experimental EELS (circles in Figure 2.2) is dominated by a sharp plasmon peak at 3.83 eV [17], whose position and width are badly reproduced in DFT-LDA RPA [18] (dashed line in Figure 2.2). In particular, a width of about 0.5 eV is obtained within this approach, to be contrasted with a much narrower experimental width (∼100 meV). A similar discrepancy occurs in the reflectance spectrum (see Figure 2.3), where a very narrow dip at 3.92 eV is hardly reproduced by DFT-LDA calculations.

Following the same $GW$ scheme used for copper in the previous section the quasiparticle band structure of silver [19] at high-symmetry points is compared with DFT-LDA results in Table 2.1. While the deeper energy levels remain mostly unchanged, a downward shift of about 1.3 eV of the top d bands leads to a decrease of the bandwidth, and hence to an excellent agreement with experiment.

### Table 2.1: Theoretical band widths and band energies for silver [19], at high-symmetry points. $GW$ energies are relative to the QP Fermi Level. The striking agreement with the experimental results shows that the silver band-structure is very well described at the $GW$ level. The values in the last column are taken from Ref. [20] where spin–orbit splittings have been removed by making degeneracy-weighted averages.

<table>
<thead>
<tr>
<th>Positions of d-bands</th>
<th>DFT-LDA</th>
<th>$GW$</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{12}$</td>
<td>-3.57</td>
<td>-4.81</td>
<td>-4.95</td>
</tr>
<tr>
<td>$X_{5}$</td>
<td>-2.49</td>
<td>-3.72</td>
<td>-3.97</td>
</tr>
<tr>
<td>$L_{3}(2)$</td>
<td>-2.71</td>
<td>-3.94</td>
<td>-4.15</td>
</tr>
<tr>
<td>$I_{12} - I_{25'}$</td>
<td>1.09</td>
<td>0.94</td>
<td>1.11</td>
</tr>
<tr>
<td>$X_{5} - X_{3}$</td>
<td>3.74</td>
<td>3.39</td>
<td>3.35</td>
</tr>
<tr>
<td>$X_{5} - X_{1}$</td>
<td>3.89</td>
<td>3.51</td>
<td>3.40</td>
</tr>
<tr>
<td>$L_{3}(2) - L_{3}(1)$</td>
<td>1.98</td>
<td>1.85</td>
<td>1.99</td>
</tr>
<tr>
<td>$L_{3} - L_{1}$</td>
<td>3.64</td>
<td>3.17</td>
<td>2.94</td>
</tr>
<tr>
<td>$X_{5} - X_{2}$</td>
<td>0.27</td>
<td>0.29</td>
<td>0.38</td>
</tr>
</tbody>
</table>

To calculate the EEL spectra, the most simple expression for the dielectric function is obtained within RPA, where the electron and holes excited by the external perturbation are assumed to move independently. The EELS is given by the imaginary part of the inverse dielectric function $\epsilon^{-1}(\omega)$:

$$\epsilon^{-1}(\omega) = \left[ \epsilon_{ib}(\omega) - \frac{\omega_D^2}{\omega(\omega + i\eta)} \right]^{-1},$$

(2.7)

where $\epsilon_{ib}(\omega)$ is the interband contribution and $\omega_D = 9.48$ eV is the Drude plasma frequency, both calculated ab-initio following the procedure described in Ref. [4]. The interband RPA
2.3 The Plasmon Resonance of Silver

dielectric function is given by

\[ \epsilon_{ib}(\omega) = 1 - 4\pi \lim_{q \to 0} \int_{BZ} \frac{d^3k}{(2\pi)^3} \sum_{n \neq n'} \frac{|\langle n'k - q|e^{-i\mathbf{q} \cdot \mathbf{r}}|nk \rangle|^2}{|q|^2} \left( \frac{f_{n',k-q} - f_{n,k}}{\omega + E_{n,k} - E_{n',k-q} + i\eta} \right), \]

(2.8)

where \( \langle n'k - q|e^{-i\mathbf{q} \cdot \mathbf{r}}|nk \rangle = \int d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} \phi_{n',k-q}^* (\mathbf{r}) \phi_{nk} (\mathbf{r}) \). The \( q \to 0 \) limit of Eq. (2.8) has been done including the effects of the pseudopotential non-locality, as described in Ref. [4]. Using as single-particle energies \( E_{nk} \) the KS levels we obtain the DFT-LDA RPA dielectric function, showed in the inset of Figure 2.2 (dashed line). Because of the under-estimation of the d-bands top position (see Table 2.1) the interband onset is too low compared to the experiment (circles) [21]. Therefore the corresponding plasmon peak is strongly damped and its energy underestimated (dashed line in the main frame of Figure 2.2). When the quasiparticle single-particle energies are used in Eq. (2.8) instead of the DFT-LDA ones, the plasmon peak, underestimated in intensity and position in DFT-LDA, is shifted toward higher energies and strongly enhanced by \( \text{GW} \) corrections, in striking agreement with experiment. This resonance can be interpreted as a collective (Drude-like) motion of electrons in the partially filled band. However, its energy \( \omega_p \) does not coincide with the bare Drude frequency \( \omega_D \), the difference arising from the screening of the electron–electron interaction by virtual interband transitions. The plasmon resonance, although blue shifted with respect to DFT-LDA, remains below the main interband threshold, but overlaps the weak low-energy tail of interband transitions acquiring a small, yet finite, width.

The polarization of the “medium” where the plasmon oscillates (the d electrons) is hence important to determine its energy and width. This polarization is absent in the homogeneous electron gas because there are no localized d orbitals and no interband transitions; it is weak in semiconductors (like Si), because interband transitions occur at energies far from that of the plasma resonance. The same polarization effect is present, but destructive in copper due to the lower onset of interband transitions. EELS peaks occur above this onset and are therefore strongly broadened. In conclusion, the delicate interplay of plasmon-frequency renormalization with the shift of the interband-transition onset, both due to QP corrections, may yield (in silver) or may not yield (in copper) a sharp plasmon resonance.

Another important quantity is the reflectance, \( R(\omega) = (|N(\omega) - 1| / |N(\omega) + 1|)^2 \), where \( N \) is the complex refraction index defined by \( |N(\omega)|^2 = \epsilon(\omega) \). In Figure 2.3 we compare the \( \text{GW} \) \( R(\omega) \) with the DFT-LDA one, and with experimental results [22]. The latter shows a very narrow dip at 3.92 eV, close to the plasmon frequency, arising from the zero-reflectance point \( \omega_0 \), defined as \( \epsilon(\omega_0) = 1 \). Again, the width and depth of this reflectance dip are related to the imaginary part of \( \epsilon(\omega) \). \( \text{GW} \) corrections make \( \omega_0 \) occur below the main onset of interband transitions, and hence produce a very narrow and deep reflectance minimum. Here the agreement between \( \text{GW} \) results and experiments for the intensity and width of the dip at 3.92 eV is even more striking than in the EELS.
A Many-body Approach to the Electronic and Optical Properties of Copper and Silver

Figure 2.2: Electron energy loss spectrum (EELS) of silver from Ref. [19]. Solid line: $GW$. Dashed line: DFT-LDA. Circles: experiment [22]. The non trivial quasiparticle $GW$ corrections improve considerably the DFT-LDA plasmon peak, yielding a striking agreement with the experiment. Inset: optical absorption of silver within RPA. Solid line: $GW$ energy levels are used in Eq. (2.8). Dashed line: DFT-LDA energy levels are used. Circles: experiment [22].

Figure 2.3: Reflectivity spectrum of silver from Ref. [19]. Solid line: $GW$. Dashed line: DFT-LDA. Boxes: experiment [22]. The experimental sharp dip at 3.92 eV is correctly reproduced by $GW$, with a substantial improvement on the DFT-LDA spectrum.
2.4 Dynamical Excitonic Effects in Metals

In the inset of Figure 2.2 we observe a strong overestimation of the absorption spectrum intensity with respect to the experiment (similar to that found in copper [4]). However this residual discrepancy cannot be traced back to the standard phenomenology observed in semiconductors and insulators where the observed light-absorption spectra largely deviate from independent-particle, RPA calculations [1]. These deviations are corrected by including the electron–hole interaction [23]. The strength of these modifications increases as the inverse of the dielectric constant of the system. In insulators, where the electron–hole interaction is only weakly screened, sharp peaks with energy below the optical gap (bound excitons) can be observed in the experimental spectra [24]. If this description is extrapolated to the metallic case the natural conclusion is that the electron–hole interaction has a negligible effect on the optical spectra of metals as the static electron–hole interaction is completely screened by the long–range part of the dielectric function. This simple argument has been considered definitive to assert that there are no excitonic effects in metals. However the standard approach to account for the electron–hole interaction in the optical spectra involves approximations whose validity is assumed a priori, and not sustained by theoretical motivations. These approximations are the key to understanding the apparently inexplicable overestimation observed in the RPA optical spectra of silver and copper.

To introduce the theoretical framework commonly used to calculated optical properties beyond the RPA we have to rewrite the dielectric function as

\[ \varepsilon(\omega) \equiv 1 - \frac{8\pi}{\Lambda} P(\omega) \Lambda, \]

where \( P(\omega) \) is the matrix representation of the polarization function in the non-interacting electron–hole basis and \( \Lambda \) is a vector embodying the corresponding optical oscillators \( \langle n'k - q|e^{-iqr}|nk \rangle \) already introduced in Eq. (2.8). The polarization function is obtained by solving the Bethe–Salpeter equation (BSE), an integral equation for the four point electron–hole Green’s function \( L(t_1, t_2; t_3, t_4) \) [1, 23, 25]. As we are interested in the polarization function \( P(t) \equiv -iL(t, 0; t, 0) \), the BSE can be rewritten as:

\[
P(t) = P(0)(t) - \int dt_1 P(0)(t - t_1) V P(t_1) + \int dt_1 dt_2 L(0)(t, t_2; t, t_1) \widetilde{W}(t_1 - t_2) L(t_1, 0; t_2, 0). \tag{2.9}
\]

Equation (2.8) is obtained when no electron–hole effects are included in \( P \), i.e. \( P \approx P(0) = -iL(0) \). Like \( P \), also \( V \) and \( \widetilde{W} \) are matrix representations in the non-interacting electron–hole basis. Using generalized indexes \( K := (c,v,k) \); \( c,v,k \) being conduction, valence band and k-point indexes, we can express those quantities as:

\[
\widetilde{W}_{KK'}(t_1 - t_2) = i\langle c'k',vk|W(r,r';t_1 - t_2) - v(r,r')|c'k',v'k' \rangle, \tag{2.10}
\]

\[
V_{KK'}(t_1 - t_2) = i \int drr' \phi_{c'k'}(r) \phi_{vk}(r) v(r,r') \phi_{v'k'}^*(r') \phi_{c'k'}^*(r'). \tag{2.10'}
\]
$L^{(0)}$ is the non-interacting electron–hole Green’s function

$$
L^{(0)}_{k,k'}(t_1,t_2;t_3,t_4) = \delta_{v,v'}\delta_{c,c'}\delta_{k,k'}Z_{c}kZ_{v}k\theta(t_1 - t_4) e^{-iE_{c}k(t_1-t_4)}\theta(t_3 - t_2) e^{iE_{v}k(t_3-t_2)}.
$$

Equation (2.11)

$Z_{n,k}$ (smaller than 1) are the QP energies and renormalization factors, respectively. The latter represent the weights of the QP peak in the many-body single-particle spectral function. The more $Z_{n,k}$ differs from 1, the more the high energy structures in the spectral function (like plasmonic replicas) become important. Those high-energy peaks are not visible in the optical energy range but, nevertheless, subtract intensity from the QP peaks. Very little is known about the role played by the $Z$ factors in optical spectra calculations [26]. In Section 2.3 we had to assume $Z = 1$, because if the $Z$ factors are included in an RPA calculation [27], or even in the BSE (see below), the intensity of the resulting spectra is strongly underestimated, both in metals and in semiconductors. Thus the $Z$ factors are commonly set to 1 by hand in the solution of the BSE or in the calculation of the independent-QP spectra. This is the first approximation needed to reproduce the experimental results, and it is important to note that it lacks sound theoretical justification.

But there is another important approximation needed to solve Eq. (2.9), related to the time dependent term $\tilde{W}(t_1-t_2)$. Indeed, the BSE with a time-dependent interaction is considered hardly solvable (if not “practically unsolvable” [26]) and for computational convenience the electron–hole interaction is assumed to be instantaneous; this is equivalent to approximating $W$ with its static value, $W(r_1,r_2,\omega=0)$. This approximation is verified a posteriori through comparison with experiment and physically corresponds to the assumption that the electron–hole scattering time is much longer than the characteristic screening time of the system (roughly speaking, the inverse of the plasma frequency). Indeed, the static approximation is expected to work well for transition energies much smaller than the plasma frequency [23]. However the most striking examples of systems that do not fulfill this condition are silver and copper. From Figure 2.2 it is evident that the plasmon of silver, which dominates the EELS, is located just above the interband gap ($\sim 3.9$ eV). Similarly, the EELS of copper shows strong, broad peaks in the optical range [4]. When $\tilde{W}(t) \approx \tilde{W}(\omega = 0) \delta(t)$ [1,23]. Equation (2.9) can be formally solved by means of a Fourier transform:

$$
P(\omega) = P^{(0)}(\omega) - P^{(0)}(\omega) \left(V + \tilde{W}\right) P(\omega).
$$

Equation (2.12)

This is the static BSE (SBSE) commonly applied neglecting the renormalization factors in Eq. (2.9), i.e. taking $Z_{n,k} = 1$. It yields optical spectra in good agreement with experiments in semiconductors and insulators [23]. When applied to copper and silver however, the SBSE result (dotted lines in Figure 2.5) is indistinguishable from the independent-QP calculation, without improving the agreement with experiment.

In Ref. [28] a solution of Eq. (2.9) is proposed without the two major approximations employed in the SBSE, i.e. keeping the $Z$s smaller than 1 and $W$ frequency dependent. To this end $L^{(0)}\tilde{W}L$ is expanded in powers of $\tilde{W}$. The first order term of this expansion, $P^{(1)}(t)$,
2.4 Dynamical Excitonic Effects in Metals

is given by:

$$
P^{(1)}_{K_1 K_2} (t) = \int dt_1 \int dt_2 \theta (t_1 - t_2)$$

$$\times \left[ W_{K_1 K_2}^{(0)} (t_1 - t_2) L_{K_1}^{(0)} (t_1, 0; t_2, 0)$$

$$+ L_{K_1}^{(0)} (t_1, t_2) W_{K_1 K_2}^{(0)} (t_2 - t_1) L_{K_2}^{(0)} (t_2, 0; t_1, 0) \right]. \quad (2.13)$$

From Eq. (2.10) it is straightforward to see that

$$L_{K_1}^{(0)} (t_1; t_2, t_1) = i \left[ P_{K_1}^{(0)} (t - t_1) e^{iE_{v_1 k_1} (t_1 - t_2) \theta (t_1 - t_2)}$$

$$+ P_{K_1}^{(0)} (t - t_2) e^{-iE_{c_2 k_2} (t_2 - t_1) \theta (t_2 - t_1)} \right], \quad (2.14)$$

$$L_{K_2}^{(0)} (t_1, 0; t_2, 0) = i \left[ P_{K_2}^{(0)} (t_2) e^{-iE_{c_2 k_2} (t_1 - t_2) \theta (t_1 - t_2)}$$

$$+ P_{K_2}^{(0)} (t_1) e^{iE_{v_1 k_1} (t_2 - t_1) \theta (t_2 - t_1)} \right], \quad (2.14')$$

that inserted in Eq. (2.13), casts $P^{(1)} (t)$ as a time convolution of three terms (as shown diagrammatically in Figure 2.4).

![Figure 2.4: Diagrammatic representation of the first order contribution to the polarization function $P (t)$ according to the BSE. Crosses indicate the time points where the incoming and outgoing non-interacting Green’s functions are “cut” according to Eqs. (2.14). The right-hand side represents the first order polarization diagram of the dynamical Bethe–Salpeter as discussed in the text. It can be used to sum all orders of BSE with non overlapping interaction lines.](image)

As a consequence, in the frequency domain $P^{(1)} (\omega)$ has the form:

$$P^{(1)} (\omega) = - P^{(0)} (\omega) \left[ \Pi^{(a)} (\omega) + \Pi^{(b)} (\omega) \right] P^{(0)} (\omega), \quad (2.15)$$

with

$$\Pi^{(a)}_{K_1 K_2} (\omega) = \tilde{W}_{K_1 K_2}^{(+) \omega} (E_{v_1 k_1} - E_{c_2 k_2}), \quad (2.16)$$

and

$$\Pi^{(b)}_{K_1 K_2} (\omega) = \tilde{W}_{K_1 K_2}^{(+) \omega} (E_{v_2 k_2} - E_{c_1 k_1}). \quad (2.16')$$
\( \tilde{W}^{(+)}(\omega) \) being the Laplace transform of \( \tilde{W}(t) \). The two terms denoted by \((a)\) and \((b)\) correspond to the two possible time orderings of the interaction ends \( t_1 > t_2 \) for term \((a)\), shown in Figure 2.4; \( t_2 > t_1 \) for term \((b)\), not shown). Equation (2.15) can be thought of as the first order expansion of \( P(\omega) \) in the frequency–dependent interaction \( \Pi(\omega) = \Pi^{(a)}(\omega) + \Pi^{(b)}(\omega) \), which replaces \( \tilde{W} \) of the SBSE. Thus a partial summation of the BSE can be performed writing:

\[
P(\omega) = P^{(0)}(\omega) - P^{(0)}(\omega)[V + \Pi(\omega)] P(\omega).
\]  

This is the Dynamical Bethe–Salpeter equation (DBSE) [28]. The diagrams summed up in Eq. (2.17) are those containing the ladder series of repeated electron–hole interactions with non overlapping (in time) interaction lines. The poles of \( P(\omega) \), \( \Omega_\lambda \), will be given by the solution of the equation \( \{P^{(0)}(\Omega_\lambda)\}^{−1} + V + \Pi(\Omega_\lambda) = 0 \). In contrast to the kernel of the SBSE, \( \Pi(\Omega_\lambda) \) is not hermitian and, consequently, \( \Omega_\lambda \) is in general complex. Its imaginary part gives the inverse excitonic lifetime. Thus the interacting electron–hole states are actually dressed excitons, or quasiexcitons. This agrees with what has been already found in the core exciton limit [29] and emphasizes the analogy between the DBSE and the Dyson equation. Consequently, as in the single-particle problem, we expect to find similar renormalization effects on the quasiexcitonic Green’s function. To develop further this aspect we expand linearly the smooth function \( \tilde{W}^{(+)}(\omega) \) around the non-interacting electron–hole energies, obtaining \( \Pi_{K_1K_2}(\omega) \approx \Pi_{K_1K_2}^{(st)} + \Theta_{K_1K_2}(\omega − E_{c2k_2} + E_{v2k_2}) \). \( \Pi_{K_1K_2}^{(st)} \approx \Pi_{K_1K_2}(\omega)|_{\omega=E_{c2k_2}−E_{v2k_2}} \) is the static limit of the dynamical Bethe–Salpeter kernel which turns out to be quite similar to the kernel of the SBSE. \( \Theta_{K_1K_2} = \partial \Pi_{K_1K_2}(\omega)/\partial \omega|_{\omega=E_{c2k_2}−E_{v2k_2}} \) are the excitonic dynamical-renormalization factors. Thus Eq. (2.17) can be strongly simplified in the case of copper and silver where the effect of \( \Pi^{(st)} \) + \( V \) is very small. The corresponding polarization function \( P(\omega) \) is approximatively given by:

\[
P_{K_1K_2}(\omega) \approx \frac{(Z_{\chi}^{\text{eh}})^{-1} + \Theta_{K_1K_2}^{-1}}{\omega − E_{c2k_2} + E_{v2k_2} + i 0^+},
\]  

with \( Z_{\chi K_1K_2} = Z_{c1k_1}Z_{v1k_2}\delta_{K_1K_2}. \)

The connection between dynamical excitonic and self-energy effects is now clear. \( Z_{\chi K_1K_2}^{-1} = 1 − \beta_{nk} \), where the negative factor \( \beta_{nk} \), the frequency derivative of the self-energy, is the weight lost by the QP because of the coupling with the excitations of \( W(\omega) \). The excitonic factors \( \Theta \), instead, are due to the modification of such coupling as a consequence of the electron–hole interaction. Those two effects tend to cancel each other but the cancellation is, in general, not complete, as exemplified in Figure 2.5 for copper and silver. The SBSE calculation (dotted line), with \( Z_{nk} = 1 \) and \( \Theta = 0 \), overestimates the experimental intensity (circles), while the inclusion of the \( Z \)s only (dashed line) underestimates it. In the DBSE (full line) the dynamical \( \Theta \) factors partially compensate for the \( Z^{\text{eh}} \) factors yielding a spectral intensity in good agreement with experiment.

Similarly the optical spectra of semiconductors can be obtained with the DBSE in excellent agreement with experiment, as shown in the case of silicon in Ref. [28]. In contrast to the
metallic case, however, the DBSE kernel of silicon must contain second-order contributions in order to reproduce correctly the experimental optical spectrum. The main effect of the first order kernel $\Pi(\omega)$ is indeed to balance the reduction of optical strengths due to self-energy renormalization factors, as suggested by Bechstedt et al. [26]. However, the renormalized QP weights also imply a reduction of the statically screened electron–hole of almost $\sim 30\%$, which is the reason for the wrong relative intensities of the two peaks in the SBSE result. This shortcoming is fixed by the second-order diagrams.

Thus in both the metallic and semiconducting cases the DBSE correctly describes the measured optical spectra without the a priori approximations commonly used in solving the BSE. This result can be interpreted by thinking of the electron–hole pair as a neutral excitation, thus, less efficient than the electron and the hole alone in exciting virtual plasmons, which is the main process leading to QP renormalization. Only when dynamical effects are coherently included both in the self energy and in the electron–hole interaction does this (physically expected) result emerges from the bundle of many-body equations. This confirms the SBSE results but not the separate approximations involved therein.

![Figure 2.5](image.png)
2.5 Conclusions

Several conclusions can be drawn from the presented results. Starting from DFT we have reviewed all the steps needed to correct the observed disagreements between the experiment and the calculated band-structure (Section 2.2), electron energy loss spectrum (Section 2.3) and optical spectra (Section 2.4). We have observed in all cases a key role played by the localized d-orbitals. They contribute to the self-energy with strong exchange effects with the 3s/3p core states, balancing the large correlation part of the mass-operator. Thus core levels cannot be neglected in the quasiparticle calculations of noble metals. Then, in contrast to semiconductors and simple metals, the plasma frequency of silver is renormalized by the interband transitions between d and s/p bands when QP single particle energies are used to calculate the RPA polarization function. This clearly shows that the low-energy peaks in the dielectric function due to the d states affect also the excitations occurring at the Fermi surface where the main contribution to the metallic screening arises. Finally, even if the s/p metallic bands completely screen the electron–hole interaction at zero energy (static contribution), the localized d-orbitals induce a dynamical term in the Bethe–Salpeter kernel that partially cancel the dynamical self-energy effects (renormalization factors). In conclusion single-particle, two-particle excitations, as well as plasmons in copper and silver, can be successfully described within many-body perturbation theory. The role of the localized, d-orbitals must be correctly included in the calculations and, more importantly, in the theory. These unique features of noble and, in general, d metals make them a stringent test for modern ab-initio Many-Body theories.

References
