Time-dependent current-density-functional theory for metals
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Performance of the Vignale-Kohn Functional in the Linear Response of Metals

We include the Vignale-Kohn current functional in the formulation of the linear response of metallic solids given in chapter 3. Within this approximation the exchange-correlation kernel \( f_{xc}(r, r', \omega) \) is \( \omega \)-dependent, thus relaxation effects due to electron-electron scattering can now be taken into account and some deficiencies of the adiabatic local density approximation, as the absence of the low-frequency Drude-like absorption, can be cured. The self-consistent equations for the inter- and intraband contributions to the induced density and current-density, which are completely decoupled within the ALDA and in the long-wavelength limit, become now coupled. We treat the dominant scalar relativistic effects using the zeroth-order regular approximation in the ground-state density-functional theory calculations, as well as in the time-dependent response calculations. We present our results calculated for the optical properties of the noble metals Cu, Ag, and Au, and we compare them with measurements found in literature.

7.1 Introduction

In treating the linear response of metals to a macroscopic electric field one has to consider both the interband contribution to the response, involving transitions from
(partially) occupied to (partially) unoccupied bands as in nonmetals, and the intraband contribution due to transitions within the same partially occupied bands, more specifically, from just below the Fermi level to just above this level. In chapter 3 we have considered the linear response of the system to a general \( q \) - and \( \omega \)-dependent perturbation. We have found that inter- and intraband processes behave differently for small \( q \) and that the self-consistent-field equations for the inter- and intraband contributions to the response decouple in the optical limit (vanishing \( q \) but finite \( \omega \)) when we make use of the adiabatic local density approximation (ALDA). In this approximation the exchange-correlation scalar potential \( v_{xc}(r, t) \) is just a local functional of the density. Within the ALDA this method yields good results for the dielectric and the electron energy-loss functions of several transition metals. However the adiabatic approximation fails in describing the low-frequency Drude-like absorption, which is missing in all the calculated absorption spectra. This absorption is due to relaxation processes such as electron-electron and electron-phonon scattering. The description of the electron-phonon interaction requires the use of a multicomponent-density functional approach. The electron-electron scattering can be described within our method by using more advanced exchange-correlation functionals where a frequency-dependent xc-kernel \( f_{xc}(r, r', \omega) \) is used.

In this chapter we go beyond the ALDA and we employ an exchange-correlation vector potential, \( A_{xc}(r, t) \), which we approximate as a local functional of the current-density using the expression derived by Vignale and Kohn [21,24]. The evaluation of the VK expression requires knowledge of some properties of the homogeneous electron gas, i.e., the exchange-correlation energy \( e_{xc}(\rho_0) \), and the longitudinal and transverse exchange-correlation kernels, \( f_{xcL}(\rho_0, \omega) \) and \( f_{xcT}(\rho_0, \omega) \), respectively, where \( \rho_0 \) is the electron density of the electron gas. Knowledge of the first is already required in the ALDA and can be obtained from the accurate results of Monte Carlo calculations [65,129]. The xc kernels, on the other hand, are not known accurately. There are two works in which parametrizations are given for both \( f_{xcL}(\rho_0, \omega) \) and \( f_{xcT}(\rho_0, \omega) \). One work is by Conti, Nifosi, and Tosi (CNT) [131], and the other is by Qian and Vignale (QV) [130]. An important difference between the parametrizations of CNT and QV occurs in the \( \omega \to 0 \) limit of \( f_{xcT}(\rho_0, \omega) \). Whereas \( f_{xcT}(\rho_0, \omega) \) of CNT vanishes in that limit, the QV parametrization does not, i.e., it has a small but finite value. The fact that \( f_{xcT}(\rho_0, \omega) \) vanishes in the \( \omega \to 0 \) limit in the case of the CNT parametrization has the important consequence that the VK expression for \( \delta A_{xc}(r, \omega) \) reduces to that of the ALDA in that limit. The value of \( f_{xcT}(\rho_0, 0) \) is related to \( \mu_{xc} \), the exchange-correlation part of the shear modulus, a quantity that is known only approximately. In previous work it has been shown that this difference in behavior of the two parametrizations in the zero-frequency limit leads to very
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diverse absorption spectra of bulk semiconductors [69]. Whereas spectra obtained with the CNT parametrization are relatively close to spectra obtained within the ALDA, spectra obtained with the QV parametrization are very different from the ALDA results and from the experiments. Since Qian and Vignale give an expression for their parametrization in which $f_{xcL,T}(\rho_0,0)$ enter, the QV parametrization can easily be adapted for the case $f_{xc,T}(\rho_0,0)=0$. By using the resulting parametrization the absorption spectra for silicon are again close to the spectra obtained with the CNT parametrization and those obtained within the ALDA [69,132]. In view of the obtained results mentioned above and the fact that we are mainly interested in the $\omega$-dependence of the VK functional in order to describe relaxation effects due to electron-electron scattering, we choose to set $f_{xc,T}(\rho_0,0)=0$ also in the QV parametrization. In Sec. II we describe the theory we use. We introduce the self-consistent set of equations which describes the linear response of metallic crystals and how to include the Vignale-Kohn functional. In the end of the section we give the main equations we use to treat the dominant scalar relativistic effects within the zeroth order regular approximation (ZORA). The ZORA formalism will be used to treat the scalar relativistic effects in the linear response of Au. The main aspects of the implementation are presented in Sec. III. Finally, we show our results for the dielectric and energy-loss functions of the crystals of Cu, Ag, and Au, and we compare them with the best available experimental data [49–51,70,133–135].

7.2 Theory

7.2.1 Linear response

To derive the linear response of metals to a macroscopic field (see chapter 3) we consider a general $q$- and $\omega$-dependent perturbation,

$$\delta \hat{h}(\mathbf{q},\omega) = \frac{-i}{2c} \left( e^{i\mathbf{q} \cdot \mathbf{r}} \nabla - \nabla^\dagger e^{i\mathbf{q} \cdot \mathbf{r}} \right) \cdot \delta \mathbf{A}_{q,\text{eff}}(\mathbf{r},\omega) + e^{i\mathbf{q} \cdot \mathbf{r}} \delta v_{q,\text{eff}}(\mathbf{r},\omega). \quad (7.1)$$

In the following we will use the notation $\hat{\rho}_q = e^{-i\mathbf{q} \cdot \mathbf{r}}$ and $\hat{\mathbf{j}}_q = -i(e^{-i\mathbf{q} \cdot \mathbf{r}} \nabla -\nabla^\dagger e^{-i\mathbf{q} \cdot \mathbf{r}})/2$. The perturbing potentials $\delta v_{\text{eff}}(\mathbf{r},\omega) = e^{i\mathbf{q} \cdot \mathbf{r}} \delta v_{q,\text{eff}}(\mathbf{r},\omega)$ and $\delta \mathbf{A}_{\text{eff}}(\mathbf{r},\omega) = e^{i\mathbf{q} \cdot \mathbf{r}} \delta \mathbf{A}_{q,\text{eff}}(\mathbf{r},\omega)$, with $\delta v_{q,\text{eff}}(\mathbf{r},\omega)$ and $\delta \mathbf{A}_{q,\text{eff}}(\mathbf{r},\omega)$ lattice periodic [84], are defined in the microscopic Coulomb gauge of Kootstra et al. [29] as

$$\delta v_{\text{eff}}(\mathbf{r},\omega) = \delta v_{H,\text{mic}}(\mathbf{r},\omega) + \delta v_{xc}(\mathbf{r},\omega), \quad (7.2)$$

$$\delta \mathbf{A}_{\text{eff}}(\mathbf{r},\omega) = \delta \mathbf{A}_{\text{mac}}(\mathbf{r},\omega) + \delta \mathbf{A}_{xc}(\mathbf{r},\omega). \quad (7.3)$$

Here $\delta v_{H,\text{mic}}(\mathbf{r},t)$ and $\delta v_{xc}(\mathbf{r},t)$ are the microscopic component of the Hartree and exchange-correlation potentials, respectively, $\delta \mathbf{A}_{\text{mac}}(\mathbf{r},\omega) = -ic/\omega \mathbf{E}_{\text{mac}}(\mathbf{r},\omega)$, with
\( E_{\text{mac}}(r, \omega) \) the fixed macroscopic electric field, comprising both the external and the induced macroscopic components, and \( \delta A_{xc}(r, \omega) \) is the exchange-correlation vector potential. The linear response of the system is then obtained for vanishing \( q \) but finite \( \omega \), which is the regime describing optical properties. An essential point of the formulation is that inter- and intraband processes behave differently for small \( q \). At finite \( q \) the equations for the induced density \( \delta \rho(r, \omega) = e^{iqr} \delta \rho_q(r, \omega) \) and current-density \( \delta j(r, \omega) = e^{iqr} \delta j_q(r, \omega) \), with \( \delta \rho_q(r, \omega) \) and \( \delta j_q(r, \omega) \) lattice periodic, can be written in the following concise form,

\[
\begin{pmatrix}
\delta \rho_{\text{inter}}^q \\
-i \delta j_{\text{inter}}^q / \omega
\end{pmatrix} = \begin{pmatrix}
\chi_{\text{inter}}^{\rho q} & -i \chi_{\text{inter}}^{\rho q} / \omega \\
-i \chi_{\text{inter}}^{\rho q} / \omega & \chi_{\text{inter}}^{\rho q} - \chi_{\text{inter}}^{\rho, q, 0} / \omega^2
\end{pmatrix} \begin{pmatrix}
\delta v_{\text{q, eff}} \\
i \omega \delta A_{\text{q, eff}} / c
\end{pmatrix},
\]

for the interband contributions, and

\[
i \omega \left( \frac{\omega / q \delta \rho_{\text{intra}}^q}{\delta j_{\text{intra}}^q} \right) = \begin{pmatrix}
\omega^2 / q^2 \chi_{\text{intra}}^{\rho q} & \omega / q \chi_{\text{intra}}^{\rho q} \\
\omega / q \chi_{\text{intra}}^{\rho q} & \chi_{\text{intra}}^{\rho q} - \chi_{\text{intra}, 0}^q / \omega
\end{pmatrix} \begin{pmatrix}
i q \delta v_{\text{q, eff}} \\
i \omega \delta A_{\text{q, eff}} / c
\end{pmatrix},
\]

for the intraband part. Here the matrix-vector products also include an integration over a real space coordinate. All matrix elements in these expressions are finite in the limits \( q, \omega \to 0 \). The various interband contributions to the response functions have the following \( \omega \)-dependence,

\[
\chi_{\text{inter}}^{\rho q} \propto 1, \quad \chi_{\text{inter}}^{\rho j q}, \chi_{\text{inter}}^{\rho, j q} \propto \omega, \\
(\chi_{\text{inter}}^{\rho j q} - \chi_{\text{inter}, 0}^{\rho j q}) \propto \omega^2,
\]

whereas the intraband response functions show the following \( \omega \) and \( q \)-dependence at small \( q \) but finite \( \omega \),

\[
\chi_{\rho q}^{\text{intra}} \propto q^2 / \omega^2, \quad \chi_{\rho q}^{\text{intra}}, \chi_{j q}^{\text{intra}} \propto q / \omega, \\
(\chi_{\text{intra}}^{\rho j q} - \chi_{\text{intra}, 0}^{\rho j q}) \propto 1.
\]

Inspection of (7.5) makes immediately clear that in the long-wavelength limit the effective scalar potential does not contribute to the intraband induced density and current-density. In chapter 3 we have used \( \delta v_{xc}^{\text{ALDA}}(r, t) \) for the exchange-correlation scalar potential and we have neglected the exchange-correlation vector potential. In this case the effective vector potential is completely defined by the macroscopic electric field which is kept fixed. We then need to solve only the equation for the interband
induced density self-consistently, and afterwards the inter- and intraband contributions to the induced current can be calculated. Approximations beyond the ALDA imply a self-consistent solution for both the inter- and intraband induced density and induced current-density equations, which will be coupled.

7.2.2 The Vignale-Kohn functional

The general expression for the exchange-correlation vector potential is to first order

\[ \delta A_{xc}(r, \omega) = \int f_{xc}(r, r', \omega) \cdot \delta j(r', \omega) dr'. \]  

(7.7)

This expression defines the tensor kernel \( f_{xc}(r, r', \omega) \). By studying a weakly perturbed electron gas with wavevector \( \mathbf{k} \) under the influence of an external perturbation with wavevector \( \mathbf{q}' \), Vignale and Kohn derived an approximation for \( \delta A_{xc}(r, \omega) \) [21, 24]. By construction the VK functional obeys several exact constraints. The VK functional satisfies the zero-force and zero-torque constraints, which state that the exchange-correlation potentials cannot exert a net force or a net torque on the system. Furthermore, it obeys the requirement of generalized translational invariance, which states that a rigid translation of the current-density implies a rigid translation of the exchange-correlation potentials. Finally, it satisfies the Onsager symmetry relation, which restricts the form of exchange-correlation kernel \( f_{xc}(r, r', \omega) \). Vignale, Ullrich, and Conti showed that the complicated VK-expression for \( \delta A_{xc}(r, \omega) \) could be written in the following physically transparent form [136],

\[ \frac{i\omega}{c} \delta A_{xc,i}(r, \omega) = \nabla \delta v_{xc}^{ALDA}(r, \omega) - \frac{1}{\rho_0(r)} \sum_j \partial_j \sigma_{xc,ij}(r, \omega), \]  

(7.8)

where the first term on the right-hand side is just the linearization of the ALDA xc scalar potential. Using a gauge transformation this longitudinal part of \( \delta A_{xc}(r, \omega) \) can be included in the scalar potential. The second term is the divergence of a tensor field \( \sigma_{xc}(r, \omega) \), which has the structure of a symmetric viscoelastic stress tensor,

\[ \sigma_{xc,ij} = \tilde{n}_{xc} \left( \partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} \sum_k \partial_k u_k \right) + \tilde{\zeta} \delta_{ij} \sum_k \partial_k u_k, \]  

(7.9)

where the velocity field \( \mathbf{u}(r, \omega) \) is given by

\[ \mathbf{u}(r, \omega) = \frac{\delta j(r, \omega)}{\rho_0(r)}. \]  

(7.10)
The coefficients \( \tilde{\eta}_{xc}(\mathbf{r}, \omega) \) and \( \tilde{\zeta}_{xc}(\mathbf{r}, \omega) \) are determined by the longitudinal and transverse response coefficients \( f_{xcL}(\rho_0(\mathbf{r}), \omega) \) and \( f_{xcT}(\rho_0(\mathbf{r}), \omega) \) of the homogeneous electron gas evaluated at the density \( \rho_0(\mathbf{r}) \),

\[
\tilde{\eta}_{xc}(\mathbf{r}, \omega) = \frac{i}{\omega} \rho_0^2(\mathbf{r}) f_{xcT}(\rho_0(\mathbf{r}), \omega),
\]

and

\[
\tilde{\zeta}_{xc}(\mathbf{r}, \omega) = \frac{i}{\omega} \rho_0^2(\mathbf{r}) \left( f_{xcL}(\rho_0(\mathbf{r}), \omega) - \frac{4}{3} f_{xcT}(\rho_0(\mathbf{r}), \omega) - \frac{d^2 e_{xc}}{d\rho^2}(\rho_0(\mathbf{r})) \right),
\]

where \( e_{xc}(\rho_0(\mathbf{r})) \) is the exchange-correlation energy per unit volume of the homogeneous electron gas. The quantities \( \tilde{\eta}_{xc}(\mathbf{r}, \omega) \) and \( \tilde{\zeta}_{xc}(\mathbf{r}, \omega) \) can be interpreted as viscoelastic coefficients [136,137]. The coefficients \( f_{xcL,T}(\rho_0(\mathbf{r}), \omega) \) are defined by the identity [21,138]

\[
f_{xcL,T}(\rho_0(\mathbf{r}), \omega) = \lim_{\mathbf{q} \to 0} f_{xcL,T}(\rho, \mathbf{q}', \omega) |_{\rho = \rho_0(\mathbf{r})}.
\]

Note that \( f_{xcL}(\rho, \mathbf{q}', \omega) \) is defined in such a way that coincides with \( f_{xc}(\rho, \mathbf{q}', \omega) \) from scalar TDDFT. These exchange-correlation kernels have been extensively studied and some exact features are well known [130,131,137,139,140]. In particular Conti and Vignale [137] obtained the following identities for the three-dimensional electron gas,

\[
\lim_{\omega \to 0} \lim_{\mathbf{q}' \to 0} f_{xcL}(\mathbf{q}', \omega) = \frac{1}{\rho_0^2} \left( K_{xc} + \frac{4}{3} \mu_{xc} \right),
\]

\[
\lim_{\omega \to 0} \lim_{\mathbf{q}' \to 0} f_{xcT}(\mathbf{q}', \omega) = \frac{\mu_{xc}}{\rho_0},
\]

where \( K_{xc} \) and \( \mu_{xc} \) are the real-valued exchange-correlation parts of the bulk and shear moduli, respectively. Since \( K_{xc} = \rho_0^2(2 e_{xc}(\rho_0)/d\rho^2) \), from Eqs. (7.14) and (7.15) one obtains that [136,137]

\[
\lim_{\omega \to 0} \frac{-i\omega \tilde{\zeta}_{xc}(\mathbf{r}, \omega)}{\rho_0^2} = 0,
\]

\[
\lim_{\omega \to 0} \frac{-i\omega \tilde{\eta}_{xc}(\mathbf{r}, \omega)}{\rho_0^2} = f_{xc,T}(\rho_0, 0).
\]

Note that only if \( \mu_{xc} = 0 \) the VK expression (7.8) reduces to the ALDA in the limit \( \omega \to 0 \), otherwise it does not.

Conti, Nifosì, and Tosi (CNT) calculated \( f_{xcL,T}(\rho_0, \omega) \) within a mode coupling approximation scheme [131]. Furthermore, CNT introduced parametrizations for \( \text{Im}f_{xcL,T}(\omega) \) that reproduce their numerical results. The real parts of \( f_{xcL,T}(\rho_0, \omega) \)
can then be obtained from the standard Kramers-Kronig symmetry relations. Their results reduce to the exact values in the limit $\omega \rightarrow \infty$, the high-frequency limit of $f_{\text{xcL}}(\rho_0, \omega)$ being that of Glick and Long [141]. However, they do not reduce to the exact values in the limit $\omega \rightarrow 0$ because they invoke the compressibility sum rule for $f_{\text{xcL}}$,

$$\lim_{\omega \rightarrow 0} \lim_{q' \rightarrow 0} f_{\text{xcL}}(q', \omega) = \frac{K_{\text{xc}}}{\rho_0^2}, \quad (7.18)$$

thereby interchanging the order of the limits with respect to the exact result (7.14). This is equivalent to the approximation $\mu_{\text{xc}} = 0$. Because of the uncertainty in the precise values of $\mu_{\text{xc}}$, the fact that it is small compared to $K_{\text{xc}}$ and the appeal of a theory that reduces to the ALDA in the limit $\omega \rightarrow 0$, they prefer to enforce equality of the order of limits [131].

Qian and Vignale [130] introduced interpolation formulae for $\text{Im} f_{\text{xcL},T}(\omega)$ in which the coefficients were determined by exact constraints in the high- and low-frequency limits. The real parts of $f_{\text{xcL},T}(\rho_0, \omega)$ can again been obtained from the Kramers-Kronig relations. Their results for $f_{\text{xcL},T}(\omega)$ reduce to the correct high-frequency limits as well as to the correct low-frequency limits (7.14) and (7.15). Furthermore, their results for $\text{Im} f_{\text{xcL},T}(\omega)$ also have the correct slope in the limit $\omega \rightarrow 0$, unlike the CNT results. Since QV give an expression for their parametrization in which $f_{\text{xcL},T}(\rho_0, 0)$ enter, their parametrization can easily be adapted for the case $f_{\text{xcL}}(\rho_0, 0) = 0$. For reasons mentioned in the Introduction we, like CNT, prefer to use a theory that reduces to the ALDA in the limit $\omega \rightarrow 0$. This means that we will use the QV parametrization only with $\mu_{\text{xc}} = f_{\text{xcT}}(\rho_0, 0) = 0$.

### 7.2.3 Relativistic corrections

Scalar-relativistic effects can be treated in our formulation by using the zeroth-order regular approximation (ZORA) [79,80,113] as described in chapter 4. In particular the nonrelativistic operator $\hat{j}_q$ will become

$$\hat{j}^{\text{ZORA}}_q = -\frac{i}{2} \left( e^{-iq \cdot r} K(r) \nabla - \nabla K(r) e^{-iq \cdot r} \right), \quad (7.19)$$

in scalar ZORA calculations. Here $K(r) = (1 - v_{\text{eff},0}(r)/2c^2)^{-1}$, with $c$ the velocity of light and $v_{\text{eff},0}(r)$ the ground-state self-consistent effective potential. Furthermore, as we will show in the next section, in the implementation of the VK functional we will need the curl of the induced current-density $\delta \mathbf{m}(r, \omega) = \nabla \times \delta \mathbf{j}(r, \omega)$. An expression for $\delta \mathbf{m}(r, \omega) = e^{-iq \cdot r} \delta \mathbf{m}_q(r, \omega)$ can be obtained by taking the curl of the induced current-density given in Eqs. (7.4) and (7.5). This amounts to the substitution of the
operator \( \mathbf{m}_q = -i(\nabla^\dagger \times e^{-i\mathbf{q} \cdot \mathbf{r}}) \) for \( \mathbf{j}_q \) in the corresponding Kohn-Sham response functions. The scalar ZORA expression for the operator \( \mathbf{m}_q \) results to be

\[
\mathbf{m}_q^{ZORA} = -i(\nabla^\dagger \times e^{-i\mathbf{q} \cdot \mathbf{r}} K(\mathbf{r}))
- \frac{i}{2} (e^{-i\mathbf{q} \cdot \mathbf{r}} \nabla K(\mathbf{r}) \times \nabla + \nabla^\dagger \times e^{-i\mathbf{q} \cdot \mathbf{r}} \nabla K(\mathbf{r})).
\]

(7.20)

Since for the systems studied in this chapter \( K(\mathbf{r}) \approx 1 \) and \( v_{eff,0}(\mathbf{r}) \) is a smooth function of \( \mathbf{r} \) (thus \( \nabla v_{eff,0}(\mathbf{r}) \ll 2c^2 \)), we have that \( \nabla K(\mathbf{r}) = K^2(\mathbf{r}) \nabla v_{eff,0}(\mathbf{r})/2c^2 \ll 1 \), and hence we will neglect the second term of the right-hand side of (7.20).

### 7.3 Implementation

Berger et al. [69] have shown that the exchange-correlation vector potentials \( \delta \mathbf{A}_{xc}(\mathbf{r}, \omega) \) as expressed in Eqs (7.8)-(7.10) can be written in the following more convenient way,

\[
\delta \mathbf{A}_{xc}(\mathbf{r}, \omega) = -\frac{ic}{\omega} \nabla \delta u_{xc}(\mathbf{r}, \omega) + \delta \mathbf{a}_{xc}(\mathbf{r}, \omega) + \nabla \times \delta \mathbf{b}_{xc}(\mathbf{r}, \omega).
\]

(7.21)

Here \( \delta u_{xc}(\mathbf{r}, \omega) \) is a scalar field, \( \delta \mathbf{a}_{xc}(\mathbf{r}, \omega) \) is a polar vector field, and \( \delta \mathbf{b}_{xc}(\mathbf{r}, \omega) \) is an axial vector field. These contributions can be chosen to have a form that involves only the local values of \( \delta \mathbf{j}(\mathbf{r}, \omega) \), \( \nabla \cdot \delta \mathbf{j}(\mathbf{r}, \omega) = i\omega \delta \rho(\mathbf{r}, \omega) \), and \( \nabla \times \delta \mathbf{j}(\mathbf{r}, \omega) = \delta \mathbf{m}(\mathbf{r}, \omega) \).

In this case one can write the following compact matrix vector product,

\[
\begin{pmatrix}
\delta u_{xc} \\
i\omega \delta \mathbf{a}_{xc}/c \\
i\omega \delta \mathbf{b}_{xc}/c
\end{pmatrix} =
\begin{pmatrix}
y_{pp} & y_{pj} & 0 \\
y_{jp} & y_{jj} & y_{jm} \\
0 & y_{mj} & y_{mm}
\end{pmatrix} \cdot
\begin{pmatrix}
\delta \rho \\
i\delta \mathbf{j}/\omega \\
i\delta \mathbf{m}/\omega
\end{pmatrix},
\]

(7.22)

where matrix entries are given as

\[
y_{pp} = -i\omega \frac{4\tilde{\eta}_{xc} + \tilde{\zeta}_{xc}}{\rho_0^2},
\]

(7.23)

\[
y_{pj} = y_{jp}^T = -i\omega \left( \frac{4\tilde{\eta}_{xc} + \tilde{\zeta}_{xc}}{\rho_0^2} \right) \frac{\nabla \rho_0}{\rho_0},
\]

(7.24)

\[
y_{jj} = -i\omega \left( \frac{4\tilde{\eta}_{xc} + \tilde{\zeta}_{xc}}{\rho_0^2} - 4\tilde{\eta}_{xc} \nabla \rho_0 + 2\tilde{\eta}_{xc} \nabla \frac{\rho_0 \times \nabla \rho_0}{\rho_0^2} \right) - i\omega \left( \frac{2\tilde{\eta}_{xc} \nabla \nabla \rho_0}{\rho_0} + \tilde{\eta}_{xc} \frac{\rho_0^2}{\rho_0^2} \nabla \rho_0 \right)
\]

\[
- i\omega \left( \frac{2\tilde{\eta}_{xc} \nabla \nabla \rho_0}{\rho_0} + \tilde{\eta}_{xc} \frac{\rho_0^2}{\rho_0^2} \nabla \rho_0 \right)
\]

(7.25)

\[
y_{jm} = y_{mj}^T = -i\omega \frac{\tilde{\eta}_{xc}}{\rho_0^2} \left[ \frac{\nabla \rho_0}{\rho_0} \times \right],
\]

(7.26)

\[
y_{mm} = -i\omega \frac{\tilde{\eta}_{xc}}{\rho_0^2} \mathbf{I}.
\]

(7.27)
Here we define the antisymmetric $3 \times 3$ matrix $[\nabla \rho_0/\rho_0 \times]_{ij} = -\sum_k \epsilon_{ijk}(\partial_k \rho_0)/\rho_0$, and $\tilde{\eta}_{xc}(r, \omega)$ and $\tilde{\eta}''_{xc}(r, \omega)$ are the first and second order derivatives of $\eta_{xc}(r, \omega)$ with respect to the ground-state density. The matrix in Eq. (7.22) is a local function of the ground-state density and its first and second order gradients, and has additional $\omega$-dependence through the coefficients $\tilde{\eta}_{xc}(r, \omega)$ and $\tilde{\zeta}_{xc}(r, \omega)$.

By using Eq. (7.21) the xc contribution to the perturbation (7.1) can be written as

$$
\delta h_{xc}(q, \omega) = \hat{\rho}_{-q} \delta v^\text{ALDA}_{q,xc}(r, \omega) + \hat{\rho}_{-q} \delta u_{q,xc}(r, \omega) + \frac{1}{c} \hat{m}_{-q} \cdot \delta b_{q,xc}(r, t). 
$$

The operators $\hat{j}_q$ and $\hat{m}_q$ have been discussed in Sec. (7.2.3). Using Eq. (7.28) the self-consistent linear-response equations (7.4) and (7.5) can be written in the following form,

$$
\begin{pmatrix}
\delta \rho^\text{inter}_q \\
\delta j^\text{inter}_q/\omega \\
\delta m^\text{inter}_q/\omega
\end{pmatrix} =
\begin{pmatrix}
\chi^\text{inter}_{\rho q} & -i\chi^\text{inter}_\rho j_q/\omega & -i\chi^\text{inter}_\rho m_q/\omega \\
i \chi^\text{inter}_j q/\omega & \Delta \chi^\text{inter}_{jj} / \omega^2 & \Delta \chi^\text{inter}_{jm} / \omega^2 \\
i \chi^\text{inter}_m q/\omega & \Delta \chi^\text{inter}_{mj} / \omega^2 & \Delta \chi^\text{inter}_{mm} / \omega^2 \\
\end{pmatrix}
\begin{pmatrix}
\delta v_{q,H,\text{mic}} + \delta v^\text{ALDA}_{q,xc,\text{mic}} + \delta u_{q,xc} \\
i \omega(\delta A_{q,\text{mic}} + \delta a_{q,xc})/c \\
i \omega \delta b_{q,xc}/c
\end{pmatrix},
$$

for the interband parts, and as

$$
i \omega
\begin{pmatrix}
\omega q \delta \rho^\text{intra}_q \\
\delta j^\text{intra}_q \\
\delta m^\text{intra}_q
\end{pmatrix} =
\begin{pmatrix}
\omega^2 / q^2 \chi^\text{intra}_{\rho q} & \omega / q \chi^\text{intra}_\rho j_q & \omega / q \chi^\text{intra}_\rho m_q \\
\omega / q \chi^\text{intra}_j q & \Delta \chi^\text{intra}_{jj} / \omega^2 & \Delta \chi^\text{intra}_{jm} / \omega^2 \\
\omega / q \chi^\text{intra}_m q & \Delta \chi^\text{intra}_{mj} / \omega^2 & \Delta \chi^\text{intra}_{mm} / \omega^2 \\
\end{pmatrix}
\begin{pmatrix}
i q(\delta v_{q,H,\text{mic}} + \delta v^\text{ALDA}_{q,xc,\text{mic}} + \delta u_{q,xc}) \\
i \omega(\delta A_{q,\text{mic}} + \delta a_{q,xc})/c \\
i \omega \delta b_{q,xc}/c
\end{pmatrix},
$$

for the intraband contributions, with $\Delta \chi^\text{intra/inter}_{abq} = (\chi^\text{inter/inter}_{abq}(\omega) - \chi^\text{inter/inter}_{ab}(\omega = 0))$. These relations have been written in such a way that all matrix elements are real and finite in the limit $q, \omega \to 0$. The expressions for the response kernels have been given in chapter 3. The new kernels involving the operator $\hat{m}$ have the same form as those involving the operator $\hat{j}$, but with the substitution of $\hat{m}$ for $\hat{j}$. In the limit of vanishing $q$ the set of equations (7.29) reduces to that one used in the case of nonmetallic crystalline systems [69] for which we need to consider only fully occupied bands $i$ and fully unoccupied bands $a$. In this limit the term $iq(\delta v_{q,H,\text{mic}} + \delta v^\text{ALDA}_{q,xc,\text{mic}} + \delta u_{q,xc})$
on the right-hand side of Eqs (7.30) vanishes [84], thus the intraband contributions
to the induced density, current-density, and its curl only depend on the response to
the vector potential in the optical limit \( q \rightarrow 0 \). Once the two sets of Eqs (7.29)
and (7.30) are solved, we can calculate the macroscopic dielectric function from
\[
\epsilon(\omega) = 1 + 4\pi\chi_e(\omega), \quad \text{with } \chi_e(\omega) \text{ the electric susceptibility,}
\]
and the electron energy-loss function as \(-\Im \{ \mathbf{q} \cdot \epsilon(\omega) \cdot \mathbf{q} \}^{-1}\) in the optical limit \( q \rightarrow 0 \) [84]. In chapter 3 we have
shown [84] that within the ALDA and the optical limit the intraband contribution to
the dielectric function is real, thus there is no intraband contribution to the absorp-
tion spectrum within this approximation. By using the Vignale-Kohn functional it is
not possible anymore to separate inter- and intraband contributions to the dielectric
function. Inter and intraband processes are coupled through the exchange-correlation
potentials \( \delta u_{\mathbf{q}xc}, \delta a_{\mathbf{q}xc}, \) and \( \delta b_{\mathbf{q}xc}, \) which are complex vectors and give rise to the
Drude-like tail on the low-frequency side of the absorption spectrum.

### 7.4 Results

We calculated the optical dielectric functions \( \epsilon(\omega) \) and the electron energy-loss func-
tions \(-\Im \{ \epsilon(\omega) \}^{-1}\) in the spectral range 0-10 eV for the isotropic crystals of copper,
silver, and gold in a fcc lattice. We used the experimental lattice constants 3.61 Å for Cu, 4.09 Å for Ag, and 4.08 Å for Au. All calculations were performed using a
modified version of the ADF-BAND program [29,30, 61–63, 84]. We made use of a
hybrid valence basis set consisting of Slater-type orbitals (STOs) in combination with
the numerical solutions of a free-atom Herman-Skillman program [64]. Cores were
kept frozen up to 3\( p \) for Cu, 4\( p \) for Ag, and 4\( f \) for Au. The spatial resolution of
this basis is equivalent to a STO triple-zeta basis set augmented with two polarization
functions. The Herman-Skillman program also provides us with the free-atom effective
potential. The crystal potential was evaluated using an auxiliary basis set of
STO functions to fit the deformation density in the ground-state calculation and the
induced density in the response calculation. For the evaluation of the \( k \)-space inte-
grals we found converged results using a quadratic (linear for the response calculation)
numerical integration scheme based on 175 sample points in the irreducible wedge of
the Brillouin zone, which was constructed by adopting a Lehmann-Taut tetrahedron
scheme [59,60]. In all our ground-state calculations we used the local density approx-
imation (LDA) for the exchange-correlation functional. In the response calculations
we employed the Vignale-Kohn functional. All results shown here were obtained
using the Vosko-Wilk-Nusair parametrization [65] of the LDA exchange-correlation
potential, which was also used to derive the ALDA exchange-correlation kernel, and
both the QV and CNT parametrizations for the longitudinal and transverse kernels
7.4. Results

$f_{xcL}/T(\omega)$ which enter the VK expression. In the QV parametrization we used the extra constraint $f_{xcT}(\omega = 0) = 0$. In Figs 7.1-7.3 the real and imaginary parts of the dielectric functions of Cu, Ag, and Au are reported. The two parametrizations to the VK functional yield similar results, with the main difference in the Drude-like absorption tail where the two results are roughly 0.25 eV apart. For convenience we do not report the ALDA results [84,110], which are very close to the VK results for the real part and for the region in the absorption spectra where the interband contribution is dominant. The low-frequency Drude-like absorption is missing in the ALDA absorption spectra, since ALDA is a functional local in time and, therefore, cannot describe electron-electron scattering, which is in part responsible for this absorption. In App. F we analyze the low-frequency behavior of the dielectric function within our method. There we show that if we use the Vignale-Kohn functional with $\mu_{xc} = 0$, then for frequencies higher than a characteristic frequency $\omega_1$, which we defined in the appendix, the real part of the dielectric function diverges as $\omega^{-2}$, whereas the imaginary part should decay as $\omega^{-3}$. For frequencies below $\omega_1$ the real part of the dielectric function is finite and the imaginary part diverges as $\omega^{-1}$. If on the other hand we use the Vignale-Kohn functional with $\mu_{xc} \neq 0$, we obtain the same low-frequency

![Figure 7.1: The calculated and measured real, $\epsilon_1(\omega)$, and imaginary, $\epsilon_2(\omega)$, parts of the dielectric function of Cu. Experiments are taken from Ref. [51,133,134].](image)
Figure 7.2: The calculated and measured real, $\epsilon_1(\omega)$, and imaginary, $\epsilon_2(\omega)$, parts of the dielectric function of Ag. Experiments are taken from Ref. [50,51,133].

Figure 7.3: The calculated and measured real, $\epsilon_1(\omega)$, and imaginary, $\epsilon_2(\omega)$, parts of the dielectric functions of Au. Experiments are taken from Ref. [50,70,135]. The theoretical curves are results of scalar relativistic calculations.
behavior found above with the important difference that for frequencies lower than a characteristic frequency $\omega_0 < \omega_1$, which we defined in the appendix, the imaginary part of the dielectric function will go to zero as $\omega$. Therefore, instead of a Drude-like tail we observe a low-frequency peak around $\omega_1$ in the calculated absorption spectra. The low-frequency behavior obtained by using the Vignale-Kohn functional with $\mu_{xc} = 0$ is compatible with the description of the intraband contribution to the dielectric function within the classical Drude model. Within this simple model the real and imaginary parts of the dielectric functions, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, respectively, are given by

$$
\epsilon_1^D(\omega) = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2},
$$

(7.31)

$$
\epsilon_2^D(\omega) = \frac{\omega_p^2 \tau}{\omega(1 + \omega^2 \tau^2)},
$$

(7.32)

with $\omega_p$ the plasma frequency and the $\tau$ the relaxation time. Here we consider a frequency range in which the $\omega$-dependence of the relaxation time can be neglected [142–145]. In this frequency range, for $\omega\tau \gg 1$ Eqs (7.31) and (7.32) become

$$
\epsilon_1^D(\omega) = 1 - \frac{\omega_p^2}{\omega^2},
$$

(7.33)

$$
\epsilon_2^D(\omega) = \frac{\omega_p^2 \tau}{\omega^3 \tau},
$$

(7.34)

The real part of the dielectric function diverges as $\omega^{-2}$, whereas the imaginary part diverges as $\omega^{-3}$ in agreement with our calculations. For $\omega\tau \ll 1$, the Drude equations reduce to

$$
\epsilon_1^D(\omega) = 1 - \omega_p^2 \tau^2,
$$

(7.35)

$$
\epsilon_2^D(\omega) = \frac{\omega_p^2 \tau}{\omega}.
$$

(7.36)

Again we find a qualitative agreement between the Drude description and our model: a finite real part and an imaginary part which diverges as $\omega^{-1}$. It is important to note that in our calculations we only take into account relaxation processes due to electron-electron scattering, whereas the Drude model also describes relaxation processes due to other phenomena such as electron-phonon scattering. However, the analysis given above does not depend on the precise value of $\tau$. Our results are also in good agreement with the experimental results although the spectra obtained for gold show some discrepancies, especially the first peak in the absorption spectrum is not well described. The Drude-like tail in the absorption spectra seems to be well described for all the three materials. However, since we only consider relaxation
Figure 7.4: Electron energy-loss spectra of copper, silver, and gold. The experimental results are taken from Ref. [49, 50, 70]. The calculated results reported for Au refer to scalar relativistic calculations.

processes due to electron-electron scattering and not those due to electron-phonon scattering, our results should be below the experimental ones. We therefore expect that the results we obtain for the Drude-like tail using the VK functional with the QV parametrization are the closest to the exact Drude-like tail due to electron-electron scattering only.

In Fig. 7.4 we have reported the electron energy-loss spectra (EELS) of the three metals. The EELS of the Cu and Ag are already well described within the ALDA [84], with one notable discrepancy: this approximation fails to reproduce the finite width of the sharp plasmon peak at about 3.8 eV in the electron energy-loss spectrum of silver [49, 70]. This feature is well described by the VK functional with both the QV and CNT parametrizations for $f_{xcL,T}(\omega)$. The appearance of this peak is due to the fact that now there is a small but non vanishing imaginary part in the dielectric function at the frequency where the real part crosses the zero axes. Also for gold the
VK performs very similar to ALDA and with a good agreement with the experiments by using both the parametrizations. For convenience we do not report the ALDA results. Note that for Au we have obtained the experimental electron energy-loss spectra from optical measurements.

7.5 Conclusions

In this chapter we have included the Vignale-Kohn expression for the the exchange-correlation vector potential in our formulation of the linear response of metals within the time-dependent current-density approach. This functional is nonlocal in time and therefore relaxation effects due to electron-electron scattering can be taken into account. The evaluation of the VK functional requires the knowledge of the exchange-correlation kernels of the homogeneous electron gas $f_{xcL,T}(\rho_0,\omega)$ as a function of the density and of the frequency. We have used in this chapter two existing parametrizations of these xc kernels: that one proposed by Qian and Vignale (QV) and the other one by Conti, Nifosi, and Tosi (CNT). In the optical limit $q \to 0$ and by using the VK functional the two sets of equations describing the inter- and intraband contributions to the response are coupled. We have calculated the dielectric and electron energy-loss functions of copper, silver, and gold and we have compared them with measurements reported in literature and with our previous calculations within the adiabatic local density approximation. The VK functional yields results which are in good agreement with the experiments. The real parts of the dielectric functions and the regions in the absorption spectra where the interband processes are dominant are similarly described by the two approximations and are close to previous results obtained within the ALDA. In addition the VK functional reproduces the low-frequency Drude-like tail in the absorption spectra, which was missing in the previous ALDA calculations. The electron energy-loss spectra obtained with the VK functional are close to the spectra obtained within the ALDA with a notable difference in the case of silver: whereas the first sharp plasmon peak found in the experimental EELS was absent in the ALDA spectrum, this feature is well described in the spectrum obtained with the VK functional.
Chapter 7. Performance of the VK functional in the Linear response of Metals