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19 Solids from Time-Dependent Current DFT

P.L. de Boeij

19.1 Introduction

The description of the ground state of crystalline systems within density functional theory, and of their response to external fields within the time-dependent version of this theory, relies heavily on the use of periodic boundary conditions. As a model for the bulk part of the system one considers a large region containing N elementary unit cells. Then, while imposing constraints that ensure the single-valuedness and periodicity of the wave function at the boundary, one considers the limit of infinite N to derive properties for the macroscopic samples. In this treatment, one implicitly assumes that the Hohenberg-Kohn theorem [Hohenberg 1964] and the Kohn-Sham approach [Kohn 1965], and their time-dependent equivalents derived by Runge and Gross [Runge 1984], apply separately to the bulk part of the system. This implies that effects caused by density changes at the outer surface, which are artificially removed in this periodic boundary approach, can be neglected. However, this can not be justified as these effects are real. For example, when a real system is perturbed by an external electric field, there will be a macroscopic response: a current density will (momentarily) be induced in the bulk with a nonzero average. By virtue of the continuity relation, this uniform component corresponds to a density change at the outer surface, but not to a density change inside the bulk. The density change at the surface gives rise to a macroscopic screening field, which can not be described as a functional of the bulk density alone [Gonze 1995b, Gonze 1997b]. Implicit in the periodic boundary treatment of the density functional approach is therefore that the system remains macroscopically unpolarized: charges at the surfaces should be compensated and no uniform external field may be present. While these conditions can be met for the ground-state description, similar assumptions may become problematic in the time-dependent case, where charge may be exchanged between surface and bulk regions, and where the bulk may become polarized. For isotropic systems some of these difficulties can be circumvented within the density functional approach by making use of the relation between the density-density response function and the trace of the current-current response function [Onida 2002, Kim 2002b, Kim 2002a, Nozières 1999]. However, for anisotropic materials this relation does not provide enough information to extract all components of the screening field. The induced polarization

can of course be described as functional of the current density in the bulk. This is the first reason to consider the use of the periodic boundary approach within the framework of time-dependent current density functional theory (TDCDFT). In this approach, the particle density is replaced by the particle current density as the fundamental quantity [Vignale 1996, Gross 1996] (see Chap. 5), which is allowed based on the observation by Ghosh and Dhara [Dhara 1987, Ghosh 1988] that the Runge-Gross theorems can be extended to systems subjected to general time-dependent electromagnetic fields. An additional bonus is that, within this more general treatment, we can look at the response to transverse fields. In the traditional density formulation, only the response to longitudinal fields can be considered, since only purely longitudinal fields can be described by the scalar potentials entering this theory.

There is a second important reason to consider using the current formulation for extended systems. While TDDFT is mostly used within the adiabatic local density approximation (ALDA), it has become clear that in extended systems nonlocal exchange-correlation effects can be very important [Kim 2002b, Kim 2002a, Sottile 2003, Adragna 2003]. In TDCDFT an approach to go beyond the ALDA is possible if one includes such long range exchange-correlation effects in the effective vector potential $\mathbf{A}_{xc}(\mathbf{r}, t)$. Vignale and Kohn [Vignale 1996, Vignale 1998] derived such a form by studying the dynamic response of a weakly inhomogeneous electron gas. They showed that in first order a dynamical exchange-correlation functional can be formulated in terms of the current density that is nonlocal in time but still local in space. Van Faassen et al. [van Faassen 2002, van Faassen 2003a] indeed showed that the inclusion of the Vignale-Kohn functional in TDCDFT calculations gives greatly improved polarizabilities for π -conjugated polymers in which similar surface effects occur [van Gisbergen 1999b].

In this chapter we show how intrinsic, i.e., material properties, can be obtained and how extrinsic, i.e., size and shape dependent effects, can effectively be removed from the computational scheme. The result of this analysis is that a macroscopic component of the current-density appears as an extra degree of freedom, which is not uniquely fixed by the lattice periodic density. A natural way to treat the periodic systems is now obtained by changing the basic dynamical variable from the time-dependent density to the induced current-density. Observable quantities, like for instance the induced macroscopic polarization, can then be given in closed form as current functionals. The response to both longitudinal and transverse fields is treated in this unified approach. We will give the linear response formulation for the resulting time-dependent Kohn-Sham system, and show how (non)-adiabatic density and current-density dependent exchange-correlation functionals can be included.

19.2 Surface and Macroscopic Bulk Effects

First we examine the time-dependent Hartree potential, defined for a finite system as

$$v_{\text{H}}(\mathbf{r}, t) = \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (19.1)$$

For extended crystalline systems we want to separate the surface and sample-shape dependent contributions to this potential from the bulk intrinsic parts. This separation is however not so trivial. We start by writing the contributions from the surface (S) and the bulk regions ($B = \cup_i \mathcal{V}_i$) separately,

$$v_{\text{H}}(\mathbf{r}, t) = \int_S d\sigma' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + \sum_i \int_{\mathcal{V}_i} d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (19.2)$$

Ideally we would like to consider only the bulk part for an infinite periodic lattice, by extending the sum over unit cells (\mathcal{V}_i) to infinity, while effectively removing the surface part. However, the result of this procedure is not uniquely defined. This is easily understood by using a multipole expansion for the contribution of each cell. While the potential of an order- n multipole decays asymptotically at a distance R as $1/R^{n+1}$, the number of such contributions in the lattice sum grows as R^2 . As result, the lattice sum diverges for the monopole moment, and a sample-shape dependence arises due to the truncation at the boundary between bulk and surface of the conditionally convergent lattice sums for the dipole and quadrupole moments. Only for higher order moments the lattice sums do converge uniquely. Fortunately, the shape dependent terms can be isolated and removed if we proceed in the following way. First we write the density in the bulk region as a Fourier integral,

$$n(\mathbf{r}, t) = \int d^3q n_{\mathbf{q}}(\mathbf{r}, t) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (19.3)$$

where the functions $n_{\mathbf{q}}(\mathbf{r}, t)$ are lattice periodic, and the vector \mathbf{q} is restricted to the first Brillouin zone. We will now treat each \mathbf{q} -component of the density individually, and introduce the following excess quantity,

$$\Delta v(\mathbf{r}, t) = \sum_i \int d^3q \Delta v_{\mathbf{q},i}(\mathbf{r}, t) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (19.4)$$

which represents the potential of a background formed by plain monopole, dipole, and quadrupole density waves,

$$\Delta v_{\mathbf{q},i}(\mathbf{r}, t) = \int_{\mathcal{V}_i} d^3r' e^{i\mathbf{q} \cdot (\mathbf{r}' - \mathbf{r})} \times \left[\mu_{\mathbf{q}}(t) + \sum_{\alpha} \mu_{\mathbf{q},\alpha}(t) \frac{\partial}{\partial r'_{\alpha}} + \frac{1}{2} \sum_{\alpha\beta} \mu_{\mathbf{q},\alpha\beta}(t) \frac{\partial^2}{\partial r'_{\alpha} \partial r'_{\beta}} \right] \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (19.5)$$

Here we worked out the full contraction of the rank- n tensors $\mu_{\mathbf{q},(n)}(t)$ and the order- n derivative $\partial^n/\partial\mathbf{r}'^n$. The uniform densities $\mu_{\mathbf{q},(n)}(t)$ have now to give for each cell the same three lowest order terms in the multipole expansion as the corresponding \mathbf{q} -component of the real density. This ensures that the shape dependence of the potential of the excess densities is identical to that of the real density. Combining the contributions of all bulk cells and integrating by parts using Green's integral theorem, the resulting contribution to the excess potential (19.4) can also be represented using a plain monopole density wave in the bulk in combination with a charge and dipole layer at the boundary between bulk and surface. We can now remove the shape dependence and get a model-independent bulk potential by subtracting the excess potential from the bulk contribution,

$$v_{\text{H, mic}}(\mathbf{r}, t) = \int_B d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - \Delta v(\mathbf{r}, t). \quad (19.6)$$

This potential gives the microscopic variation in the bulk and is completely determined by the bulk density. It is well-defined and model independent: the value obtained does not depend on the particular choice for the unit cell of the periodic system or for the origin. The remaining contribution of the bulk is combined with the surface part of the potential and hence contains all shape-dependent parts,

$$v_{\text{H, mac}}(\mathbf{r}, t) = \int_S d\sigma' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + \Delta v(\mathbf{r}, t), \quad (19.7)$$

This macroscopic part of the Hartree potential has to be added to the true external potential, and acts as an “externally” determined perturbing potential for the bulk system. The bulk part of the system may now be treated using the periodic boundary approach if only the microscopic part of the Hartree term, as given in (19.6) is retained. In addition, it will be convenient, and for $\mathbf{q} = 0$ even necessary, to represent the macroscopic potential in the bulk using a macroscopic longitudinal electric field,

$$\mathbf{E}_{\text{mac}}(\mathbf{r}, t) = \nabla v_{\text{ext}}(\mathbf{r}, t) + \nabla v_{\text{H, mac}}(\mathbf{r}, t). \quad (19.8)$$

This field can be chosen to satisfy the same periodic boundary conditions, even though the corresponding macroscopic potential will then violate these. The construction of the microscopic and macroscopic contributions is depicted in Fig. 19.1.

One of the properties of interest is the induced macroscopic polarization, which is defined as the time-integral of the induced macroscopic current density $\mathbf{j}_{\text{mac}}(\mathbf{r}, t)$,

$$\mathbf{P}_{\text{mac}}(\mathbf{r}, t) = - \int_{t_0}^t dt' \mathbf{j}_{\text{mac}}(\mathbf{r}, t'). \quad (19.9)$$

For an isotropic system in a longitudinal external field the induced current will be longitudinal as well. For a finite system, the longitudinal part of the

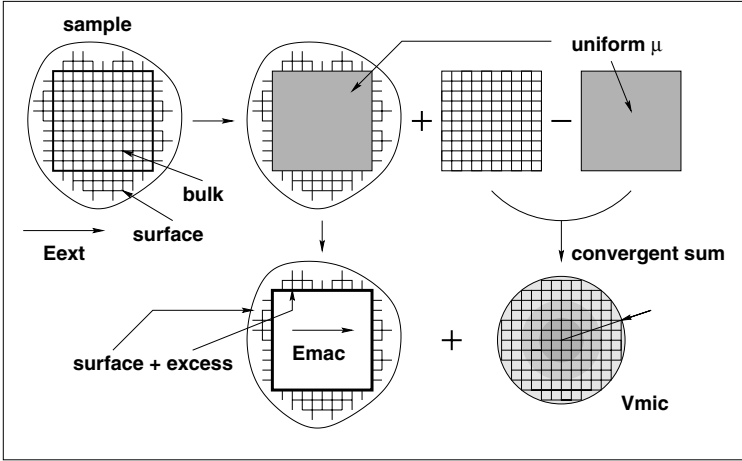


Fig. 19.1. The construction of the microscopic and macroscopic contributions to the Hartree potential

current density can be obtained by integrating the continuity equation,

$$\nabla \cdot \mathbf{j}_L(\mathbf{r}, t) + \frac{\partial}{\partial t} n(\mathbf{r}, t) = 0, \quad \text{with } \mathbf{j}_L(\infty, t) = 0. \quad (19.10)$$

This gives the following density functional for the finite systems,

$$\mathbf{j}_L(\mathbf{r}, t) = \frac{1}{4\pi} \nabla \frac{\partial}{\partial t} \int d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (19.11)$$

If we want to identify surface and shape-dependent contributions we will encounter the same problems as with the Hartree potential. We again need to introduce an excess contribution,

$$\Delta \mathbf{j}_L(\mathbf{r}, t) = \frac{1}{4\pi} \nabla \frac{\partial}{\partial t} \Delta v(\mathbf{r}, t), \quad (19.12)$$

with $\Delta v(\mathbf{r}, t)$ given by (19.4), which allows us to unambiguously define a microscopic longitudinal current density in the bulk,

$$\mathbf{j}_{L, \text{mic}}(\mathbf{r}, t) = \frac{1}{4\pi} \nabla \frac{\partial}{\partial t} \left\{ \int_B d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} - \Delta v(\mathbf{r}, t) \right\}. \quad (19.13)$$

This part contains exactly the same information as the microscopic part of the time-dependent density. The remaining macroscopic part of the current density contains all shape dependent and surface contributions to the longitudinal current in the bulk,

$$\mathbf{j}_{L, \text{mac}}(\mathbf{r}, t) = \frac{1}{4\pi} \nabla \frac{\partial}{\partial t} \left\{ \int_S d^3 r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + \Delta v(\mathbf{r}, t) \right\}. \quad (19.14)$$

The macroscopic longitudinal current density is therefore a measure for the combination of the macroscopic density changes in the bulk with the density changes in the surface region, and it is therefore complementary to the microscopic bulk density. Inserting the above expression in (19.9) gives in combination with (19.7) and (19.8) the well known relation

$$\mathbf{E}_{\text{ext}}(\mathbf{r}, t) = \mathbf{E}_{\text{mac}}(\mathbf{r}, t) + 4\pi\mathbf{P}_{\text{mac}}(\mathbf{r}, t). \quad (19.15)$$

In the linear response regime, the macroscopic polarization of the bulk is related to the macroscopic electric field rather than to the externally applied field, via what is called the constitutive equation,

$$\mathbf{P}_{\text{mac}}(\mathbf{r}, t) = \int_{t_0}^t dt' \int d^3r' \chi(\mathbf{r} - \mathbf{r}', t - t') \cdot \mathbf{E}_{\text{mac}}(\mathbf{r}', t'). \quad (19.16)$$

This equation defines the material property called the electric susceptibility $\chi(\mathbf{r} - \mathbf{r}', t - t')$. As the constitutive equation takes the form of a convolution it is more convenient to work with the Fourier transform $\chi(\mathbf{q}, \omega)$ from which also the macroscopic dielectric function can be derived,

$$\epsilon(\mathbf{q}, \omega) = 1 + 4\pi\chi(\mathbf{q}, \omega). \quad (19.17)$$

In general $\chi(\mathbf{q}, \omega)$ and $\epsilon(\mathbf{q}, \omega)$ are tensors, which transform as scalars in isotropic systems. One of the aims of the application of TDCDFT to the solids is to calculate these response properties.

19.3 The Time-Dependent Current Density Functional Approach

For finite systems, and for a given initial state, the Runge-Gross theorem [Runge 1984] ensures a one-to-one mapping between the time-dependent density and the time-dependent external potential. As first step in the original proof of this theorem, invertibility is established for the mapping from external potentials to v -representable currents. This is done by using the equation of motion for the current density, without having to refer explicitly to the boundary of the system. To arrive at a one-to-one relation with the time-dependent density, however, one needs to invoke explicitly the finiteness of the system. This second step becomes problematic for the periodic boundary approach [Maitra 2003a].

We have to conclude that, in the periodic-boundary formulation, the microscopic bulk density and microscopic bulk potential are not sufficient, and that the complementary information about the surface region that is contained in $\mathbf{j}_{L, \text{mac}}(\mathbf{r}, t)$ and $\mathbf{E}_{L, \text{mac}}(\mathbf{r}, t)$ has to be included in the description. The justification of the application of the Runge-Gross theorem in the periodic-boundary approach will depend on the existence of a similar exact

mapping between on one hand the accessible densities in the bulk region, in this case the microscopic density in combination with the macroscopic longitudinal current density, and on the other hand the external potentials for this region, i.e., the combination of the microscopic external potential with the macroscopic longitudinal electric field,

$$\{n_{\text{mic}}(\mathbf{r}, t), \mathbf{j}_{\text{L, mac}}(\mathbf{r}, t)\}_{\text{bulk}} \leftrightarrow \{v_{\text{ext, mic}}(\mathbf{r}, t), \mathbf{E}_{\text{L, mac}}(\mathbf{r}, t)\}_{\text{bulk}} . \quad (19.18)$$

Equivalently, one could work with the full longitudinal current density $\mathbf{j}_{\text{L}}(\mathbf{r}, t)$ and the total external longitudinal field $\mathbf{E}_{\text{L}}(\mathbf{r}, t)$. An alternative route is formed by obtaining the current density within the current density functional framework [Dhara 1987, Ghosh 1988, Vignale 1996, Gross 1996]. In this framework, one allows for both longitudinal and transverse external fields, and as basic variable one uses the total current density rather than just the density. We will allow for the more general case of anisotropic systems and/or transverse fields, for which we will assume the existence of an exact mapping between the current density and the total external electric field for the bulk region, similar to the Ghosh-Dhara theorem for finite systems. For the static limit [Gonze 1995b, Gonze 1997b, Martin 1997a], and for a one-dimensional circular geometry, this can indeed be established [Maitra 2003a], but no proof exists for the validity of these theorems in the general periodic boundary case. We will assume these theorems to hold true in the remainder.

In the corresponding time-dependent Kohn-Sham scheme, the true density and current density of the interacting system are reproduced in a non-interacting system with effective scalar and vector potentials, via

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2 , \quad (19.19)$$

and,

$$\mathbf{j}(\mathbf{r}, t) = \sum_{j=1}^N \Re\{-i\varphi_j^*(\mathbf{r}, t)\nabla\varphi_j(\mathbf{r}, t)\} + \frac{1}{c}n(\mathbf{r}, t)\mathbf{A}_{\text{KS}}(\mathbf{r}, t) . \quad (19.20)$$

The first and second term on the right-hand side are the paramagnetic and diamagnetic currents respectively. Here we merely need to assume that the density and current density are non-interacting \mathbf{A} -representable, which is a much weaker condition than the non-interacting v -representability, which is indeed problematic for the current density [D'Agosta 2005a]. The orbitals are solutions of the time-dependent Kohn-Sham equations,

$$i\frac{\partial\varphi_j(\mathbf{r}, t)}{\partial t} = \left\{ \frac{1}{2} \left| -i\nabla + \frac{1}{c}\mathbf{A}_{\text{KS}}(\mathbf{r}, t) \right|^2 + v_{\text{KS, mic}}(\mathbf{r}, t) \right\} \varphi_j(\mathbf{r}, t) , \quad (19.21)$$

where periodic boundary constraints are imposed on the orbitals and on the effective potentials, i.e., the gauge is chosen to be compatible with the

periodic boundary assumption [Kootstra 2000a, Kootstra 2000b]. At t_0 we assume that $\mathbf{j}(\mathbf{r}, t_0) = 0$ and $\mathbf{A}_{\text{KS}}(\mathbf{r}, t_0) = 0$, and that $v_{\text{KS, mic}}(\mathbf{r}, t_0)$ is the effective scalar potential giving the initial density $n(\mathbf{r}, t_0)$, which we choose to be the lattice periodic ground state density $n_{\text{GS}}(\mathbf{r})$. The initial potential is then uniquely determined by virtue of the Hohenberg-Kohn. This potential will be lattice periodic, and we can choose the orbitals to be initially of Bloch form. For $t > t_0$ the effective time-dependent potentials are uniquely determined, apart from an arbitrary gauge transform, by the exact time-dependent density and current density as result of the Ghosh-Dhara theorem. To comply with the periodic boundary constraints, the gauge is chosen such that only microscopic Hartree and exchange-correlation contributions are included in the time-dependent scalar potential,

$$v_{\text{KS, mic}}(\mathbf{r}, t) = v_{\text{ext, mic}}(\mathbf{r}, t) + v_{\text{Hxc, mic}}[n, \mathbf{j}](\mathbf{r}, t), \quad (19.22)$$

while all macroscopic terms are included in the effective vector potential,

$$\mathbf{A}_{\text{KS}}(\mathbf{r}, t) = -c \int_{t_0}^t dt' \mathbf{E}_{\text{mac}}(\mathbf{r}, t') + \mathbf{A}_{\text{xc}}[n, \mathbf{j}](\mathbf{r}, t). \quad (19.23)$$

The effective vector potential will in general contain exchange-correlation contributions to ensure that, apart from the true time-dependent density, also the true current density is reproduced in the Kohn-Sham system.

In order to obtain the dielectric function of the crystal, we will consider the linear response to a given macroscopic electric field $\mathbf{E}_{\text{mac}}(\mathbf{r}, t)$, which is \mathbf{q} - and ω -dependent [Romaniello 2005],

$$\mathbf{E}_{\text{mac}}(\mathbf{r}, t) = \mathbf{E}(\mathbf{q}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} + \text{c.c.} \quad (19.24)$$

The induced density, and similarly the induced current density, can now be given in the following form,

$$\delta n(\mathbf{r}, t) = \delta n_{\mathbf{q}}(\mathbf{r}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} + \text{c.c.}, \quad (19.25)$$

and

$$\delta \mathbf{j}(\mathbf{r}, t) = \delta \mathbf{j}_{\mathbf{q}}(\mathbf{r}, \omega) e^{i(\mathbf{q} \cdot \mathbf{r} - \omega t)} + \text{c.c.}, \quad (19.26)$$

in which $\delta n_{\mathbf{q}}(\mathbf{r}, \omega)$ and $\delta \mathbf{j}_{\mathbf{q}}(\mathbf{r}, \omega)$ are lattice periodic. By using first order perturbation theory, the induced density is readily expressed in terms of the unperturbed Bloch orbitals $\varphi_{i\mathbf{k}}(\mathbf{r})$, orbital energies $\varepsilon_{i\mathbf{k}}$, and occupation numbers $n_{i\mathbf{k}}$. One arrives at,

$$\delta n_{\mathbf{q}}(\mathbf{r}, \omega) = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \sum_{i, j} \varphi_{i\mathbf{k}}^*(\mathbf{r}) \hat{n}_{\mathbf{q}} \varphi_{j\mathbf{k}+\mathbf{q}}(\mathbf{r}) P_{ij\mathbf{k}}(\mathbf{q}, \omega), \quad (19.27)$$

where $\hat{n}_{\mathbf{q}} = e^{-i\mathbf{q} \cdot \mathbf{r}}$, and

$$P_{ij\mathbf{k}}(\mathbf{q}, \omega) = \frac{n_{i\mathbf{k}} - n_{j\mathbf{k}+\mathbf{q}}}{\varepsilon_{i\mathbf{k}} - \varepsilon_{j\mathbf{k}+\mathbf{q}} + \omega + i\eta} \langle \varphi_{j\mathbf{k}+\mathbf{q}} | \delta \hat{h}(\mathbf{q}, \omega) | \varphi_{i\mathbf{k}} \rangle. \quad (19.28)$$

Here the positive infinitesimal η ensures causality. We have introduced the following short-hand notation for the first-order self-consistent perturbation,

$$\delta\hat{h}(\mathbf{q}, \omega) = \frac{-i}{2c} [\delta\mathbf{A}_{\text{KS}}(\mathbf{r}, \omega) \cdot \nabla - \nabla^\dagger \cdot \delta\mathbf{A}_{\text{KS}}(\mathbf{r}, \omega)] + \delta v_{\text{KS, mic}}(\mathbf{r}, \omega), \quad (19.29)$$

where the perturbing effective scalar and vector potentials, $\delta v_{\text{KS, mic}}(\mathbf{r}, \omega)$ and $\delta\mathbf{A}_{\text{KS}}(\mathbf{r}, \omega)$, are linear in the macroscopic field $\mathbf{E}_{\text{mac}}(\mathbf{q}, \omega)$.

For the induced current-density we can derive expressions along the same lines as used for the induced density. We get two contributions to the induced current density, $\delta\mathbf{j}_{\mathbf{q}}(\mathbf{r}, \omega) = \delta\mathbf{j}_{\mathbf{q}}^{\text{p}}(\mathbf{r}, \omega) + \delta\mathbf{j}_{\mathbf{q}}^{\text{d}}(\mathbf{r}, \omega)$. The paramagnetic component can be obtained from,

$$\delta\mathbf{j}_{\mathbf{q}}^{\text{p}}(\mathbf{r}, \omega) = \frac{1}{N_k} \sum_{\mathbf{k}} \sum_{ij} \varphi_{i\mathbf{k}}^*(\mathbf{r}) \hat{\mathbf{j}}_{\mathbf{q}} \varphi_{j\mathbf{k}+\mathbf{q}}(\mathbf{r}) P_{ij\mathbf{k}}(\mathbf{q}, \omega), \quad (19.30)$$

where $\hat{\mathbf{j}}_{\mathbf{q}} = -i(e^{-i\mathbf{q}\cdot\mathbf{r}}\nabla - \nabla^\dagger e^{-i\mathbf{q}\cdot\mathbf{r}})/2$. The diamagnetic contribution to the induced current-density is much simpler and is given by,

$$\delta\mathbf{j}_{\mathbf{q}}^{\text{d}}(\mathbf{r}, \omega) = \frac{1}{c} n(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} \delta\mathbf{A}_{\text{KS}}(\mathbf{r}, \omega). \quad (19.31)$$

In practical calculations it is important to consider the relation between the diamagnetic and paramagnetic contributions, as they tend to cancel one another at small frequency due to the longitudinal conductivity sum rule [Nozières 1999].

Like in the ordinary linear response scheme of TDDFT, we need to obtain the perturbing potentials self-consistently. The contribution of the induced density to the microscopic Hartree potential is evaluated using (19.6), while the macroscopic contribution is by construction already contained in the macroscopic electric field. We can choose to retain only terms linear in the induced density in the microscopic exchange-correlation parts of the first-order scalar potential and gauge transform all other terms to the exchange-correlation vector potential. In this way we keep contact with the traditional TDDFT description. For the first-order exchange-correlation scalar potential we write,

$$\delta v_{\text{xc, mic}}(\mathbf{r}, \omega) = \int d^3r' f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \delta n(\mathbf{r}', \omega), \quad (19.32)$$

in which we explicitly assume that the integration over space is converging, i.e., that the kernel is short-range. Here we use the adiabatic local density approximation for this exchange-correlation kernel,

$$f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \left. \frac{dv_{\text{xc}}^{\text{LDA}}(n)}{dn} \right|_{n=n(\mathbf{r})}. \quad (19.33)$$

All other exchange-correlation effects are included in the exchange-correlation vector potential. As the induced density is a (local) functional of the induced

current-density through the continuity equation, we can formally write this vector potential as a pure functional of the induced current-density,

$$\delta A_{xc, \alpha}(\mathbf{r}, \omega) = \int d^3r' \sum_{\beta} f_{xc, \alpha\beta}(\mathbf{r}, \mathbf{r}', \omega) \cdot \delta \mathbf{j}_{\beta}(\mathbf{r}', \omega). \quad (19.34)$$

It remains to find good approximations for this exchange-correlation contribution. If it is neglected altogether, we retrieve the adiabatic local density approximation. Here we consider a functional proposed by Vignale and Kohn, which takes the form of a viscoelastic field [Vignale 1997] (see Chap. 5),

$$\frac{i\omega}{c} \delta A_{xc, \alpha}(\mathbf{r}, \omega) = -\frac{1}{n_{GS}(\mathbf{r})} \sum_{\beta} \frac{\partial}{\partial r_{\beta}} \sigma_{xc, \alpha\beta}(\mathbf{r}, \omega), \quad (19.35)$$

where $\sigma_{xc}(\mathbf{r}, \omega)$ is a tensor field which has the structure of a symmetric viscoelastic stress tensor,

$$\sigma_{xc, \alpha\beta} = \tilde{\eta}_{xc} \left(\frac{\partial u_{\alpha}}{\partial r_{\beta}} + \frac{\partial u_{\beta}}{\partial r_{\alpha}} - \frac{2}{3} \delta_{\alpha\beta} \nabla \cdot \mathbf{u} \right) + \tilde{\zeta} \delta_{\alpha\beta} \nabla \cdot \mathbf{u}. \quad (19.36)$$

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

$$\mathbf{u}(\mathbf{r}, \omega) = \frac{\delta \mathbf{j}(\mathbf{r}, \omega)}{n_{GS}(\mathbf{r})}. \quad (19.37)$$

The coefficients $\tilde{\eta}_{xc}(\mathbf{r}, \omega)$ and $\tilde{\zeta}_{xc}(\mathbf{r}, \omega)$ are directly related to the transverse and longitudinal response coefficients $f_{xc, T}(n, \omega)$ and $f_{xc, L}(n, \omega)$ of the homogeneous electron gas, which are evaluated at the local density $n(\mathbf{r})$.

19.4 Application to Solids

The lattice-periodicity of $\delta \mathbf{j}_{\mathbf{q}}(\mathbf{r}, \omega)$ allows to calculate the macroscopic induced polarization as,

$$\mathbf{P}_{\text{mac}}(\mathbf{q}, \omega) = \chi(\mathbf{q}, \omega) \cdot \mathbf{E}_{\text{mac}}(\mathbf{q}, \omega) = \frac{-i}{V\omega} \int_V d^3r' \delta \mathbf{j}_{\mathbf{q}}(\mathbf{r}', \omega), \quad (19.38)$$

where the average is taken over the unit cell. This result immediately gives the electric susceptibility $\chi(\mathbf{q}, \omega)$, and hence the dielectric function $\epsilon(\mathbf{q}, \omega)$.

We have studied the static dielectric constant in the ALDA approximation for several binary compounds [Kootstra 2000a, Kootstra 2000b]. In Figs. 19.2 and 19.3 we have compiled the results for the static dielectric constants ϵ_{∞} for this large set of compounds. The materials have been grouped according to the chemical groups of the constituent elements as well as to their lattice type. For the whole range of materials we see a fairly good agreement of

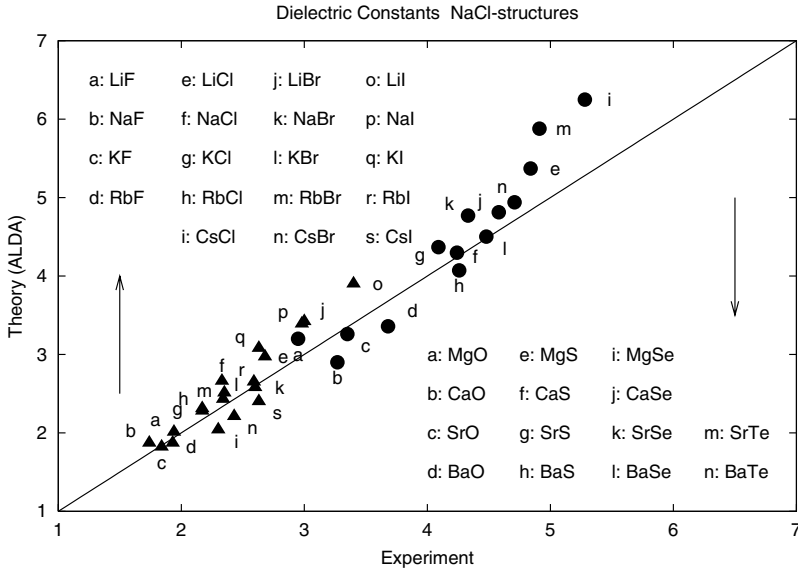


Fig. 19.2. Theoretical (ALDA) versus experimental dielectric constant for binary crystals of the rocksalt lattice type

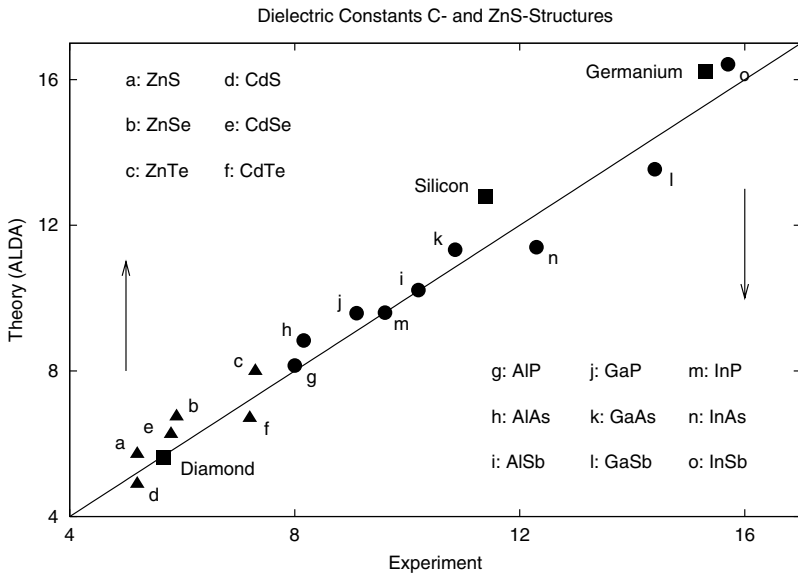


Fig. 19.3. Theoretical (ALDA) versus experimental dielectric constant for the elementary and binary crystals of the diamond and zinc-blend lattice types

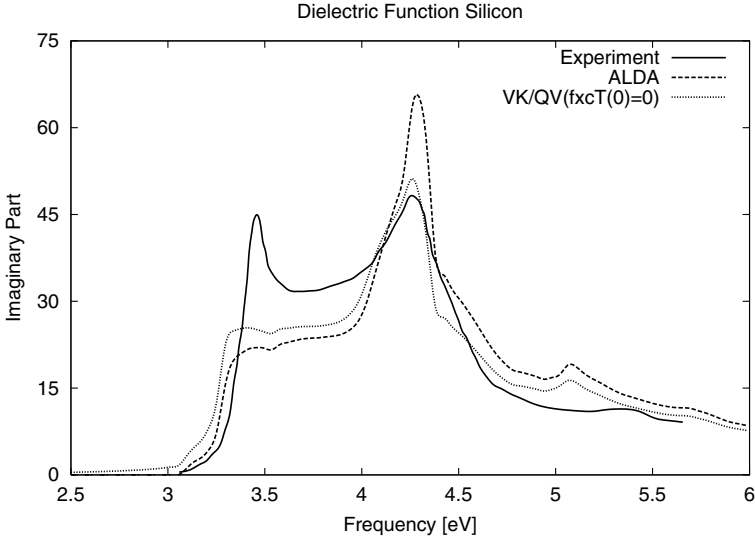


Fig. 19.4. The imaginary part of the calculated dielectric function for silicon using the ALDA and Vignale-Kohn (see text) functionals. The experimental data have been obtained from [Lautenschlager 1987]

the TDCDFT-ALDA calculations and experiments, with deviations in the order of about 5–10%. Even though the LDA yields Kohn-Sham gaps that are smaller than the experimental (fundamental) gap by about 40–50% we do not systematically overestimate the dielectric constant.

We have also obtained the dielectric function $\epsilon(\omega)$ within the ALDA. For the most studied elemental material, silicon, the imaginary part is depicted in Fig. 19.4. Usually two distinct deficiencies are visible in the calculated absorption spectrum. First the spectrum appears to be shifted to lower frequency over about 0.5 eV, and second the first peak appears merely as a shoulder in the calculation, whereas the second peak is too high. The first shortcoming can be understood since the ALDA response calculation is performed starting from the LDA ground state. As most spectral features can be attributed to the van Hove-type singularities in the joint-density of states, this is in keeping with the general trend found in LDA calculations: orbital energies lead to gaps between occupied and virtual states smaller than the observed excitation gaps. The calculated position of the absorption onset coincides with the vertical Kohn-Sham energy gap of 2.6 eV. We thus get a more-or-less uniformly shifted absorption spectrum. This is observed for other materials too. When a uniform shift is applied to the calculated spectra by using a so-called scissors shift, one usually gets a good correspondence between the measured and calculated spectral features [Levine 1989]. By starting from an improved ground state description using an exact-exchange calculation, Kim and Görling [Kim 2002b, Kim 2002a] could indeed correctly describe the

absorption edge for silicon. To get the results in Fig. 19.4 we used a scissors shift.

The incorrect description of the first peak within the ALDA, which arises from excitonic effects [Reining 2002, Rohlfing 1998a, Benedict 1998a, Benedict 1998b], is caused by the local nature of the time-dependent density functional, which cannot describe nonlocal effects like the electron-hole attraction. Improved approximate expressions for the exchange-correlation kernel, for instance using the time-dependent exact exchange kernel [Kim 2002b, Kim 2002a], lead to a considerably improved intensity for the exciton peak in silicon. Similar results can be obtained by using a form based on the Kohn-Sham Green's function obtained from a perturbation expansion to first order in the screened interaction, in combination with Kohn-Sham orbital energy corrections [Sottile 2003, Adragna 2003]. Guided by the form of the Vignale-Kohn functional, and by retaining only macroscopic contributions, a simple polarization dependent exchange-correlation functional [Gonze 1995b, Gonze 1997b, Martin 1997a] could be derived. Using an additional empirical prefactor, the spectra could be improved using such a polarization functional [de Boeij 2001]. However, inclusion of the full Vignale-Kohn functional leads to much worse results unless a much reduced transverse kernel $f_{xc, T}(n, \omega)$ is used to calculate the viscoelastic coefficients [Berger 2006]. In particular, this is true for the static limit of the transverse kernel, which was found to determine to a large extent the strength of the screening field, and hence the absorption spectrum of π -conjugated polyacetylene polymers [Berger 2005]. There a better correspondence with experiment and other calculations were found with reduced values for the static transverse kernel. Figure 19.4 shows the slightly improved result for the case in which the frequency dependence of this kernel is treated [Qian 2002, Qian 2003] but with a vanishing static limit. The static response reduces then again to the ALDA results. We do not observe a correct description of the exciton peak, but the second peak is reduced in strength considerably.

19.5 Conclusion

The description of extended systems using periodic boundary conditions within a density-functional framework is most naturally done using the time-dependent current-density functional approach. In this scheme information about changes of the density in the surface region that may lead to macroscopic screening effects, but that may not show up in the periodic density in the bulk region, is contained in the (macroscopic) current-density in the bulk. Even if the periodic boundary assumption is used within the current functional approach, the exchange-correlation contributions to the potentials may still depend on these surface effects as the potentials are now functionals of the current density. Other than the traditional density formulation, the current functional approach is able to describe the response of not only isotropic

but also anisotropic systems to both transverse and longitudinal fields. At the same time, the nonlocal density dependence that is inherent to the nonadiabatic exchange-correlation functionals in the traditional density functional approach can be formulated using a local current-density dependent contribution to the Kohn-Sham vector potential. The common adiabatic local density approximation yields on average reasonable static dielectric constants for nonmetallic compounds, but the frequency dependent dielectric functions exhibit several deficiencies which can be attributed to the incorrect description of the exchange-correlation effects by the presently available density and current functionals.