Time-dependent density functional theory for periodic systems
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Chapter 7

A polarization dependent functional


7.1 Abstract

We present a new approach to calculate optical spectra, which for the first time uses a polarization dependent functional within current density functional theory (CDFT), which was proposed by Vignale and Kohn [108]. This polarization dependent functional includes exchange-correlation (xc) contributions in the effective macroscopic electric field. This functional is used to calculate the optical absorption spectrum of several common semiconductors. We achieved in all cases good agreement with experiment.

7.2 Introduction

Time-dependent density functional theory (TDDFT), as formulated by Runge and Gross [4], makes it in principle possible to study the dynamical properties of interacting many-particle systems. The formulation of a local dynamical approximation for the xc potential turns out to be extremely difficult, because such an xc potential in TDDFT is an intrinsically nonlocal functional of the density (i.e., there does not exist a gradient expansion for the frequency-dependent xc potential in terms of the density alone). Vignale and Kohn [108] were the first who formulated a local gradient expansion in terms of the current density. In a time-dependent current density functional approach to linear response theory, they derived an expression for the linearized xc vector potential $a_{xc}(r, \omega)$ for a system of slowly varying density, subject to a spatially slowly varying external potential at a finite frequency $\omega$. 
7.3 Theory

Let us first recall our definitions for the macroscopic electric field and polarization, before we derive an expression in which the macroscopic xc potential contributions of Vignale and Kohn [108] are incorporated. If we apply a time-dependent electric field of frequency \( \omega \), we will induce a macroscopic polarization \( \mathbf{P}_{\text{mac}}(\omega) \) which will be proportional to the macroscopic field \( \mathbf{E}_{\text{mac}}(\omega) \), i.e., the applied field plus the average electric field caused by induced charges in the solid. The constant of proportionality is known as the electric susceptibility and is a material property,

\[
\mathbf{P}_{\text{mac}}(\omega) = \chi(\omega) \cdot \mathbf{E}_{\text{mac}}(\omega). \tag{7.1}
\]

The macroscopic polarization is defined by the induced current density,

\[
\mathbf{P}_{\text{mac}}(\omega) = \frac{i}{\omega V} \int_V \delta \mathbf{j}(\mathbf{r}, \omega) d\mathbf{r}. \tag{7.2}
\]

We see that if we want to calculate the susceptibility and the related dielectric function we need to calculate the induced current. The induced current \( \delta \mathbf{j} \) and induced density \( \delta \rho \) can, in principle, be calculated from the current-current and density-current response functions of the solid in the following way, where we use a shortened notation which implies integration over spatial coordinates [63]:

\[
\delta \mathbf{j} = \frac{i}{\omega} \chi_{jj} \cdot \mathbf{E}_{\text{mac}}, \tag{7.3}
\]

\[
\delta \rho = \frac{i}{\omega} \chi_{\rho j} \cdot \mathbf{E}_{\text{mac}}. \tag{7.4}
\]

This requires, however, knowledge of the exact response functions of the system. Within a Kohn-Sham formulation the exact density and current response are calculated as the response of an auxiliary noninteracting system to an effective electric field and potential,

\[
\delta \mathbf{j} = \frac{i}{\omega} \chi_{jj}^s \cdot \mathbf{E}_{\text{eff}} + \chi_{j\rho}^s \delta v_{\text{eff}}, \tag{7.5}
\]

\[
\delta \rho = \frac{i}{\omega} \chi_{\rho j}^s \cdot \mathbf{E}_{\text{eff}} + \chi_{\rho\rho}^s \delta v_{\text{eff}}, \tag{7.6}
\]

where the superscript \( s \) indicates that we are dealing with the response functions of the noninteracting Kohn-Sham system. The equations above are our basic equations of time-dependent current-density functional theory (TDCDFT). The effective fields have the property that they produce the exact density and current when applied to the Kohn-Sham system. Hence they are functionals of \( \delta \mathbf{j} \) and \( \delta \rho \), and have to be obtained self-consistently. If we neglect the microscopic contributions to the transverse components, we can split up these fields as follows

\[
\mathbf{E}_{\text{eff}}(\omega) = \mathbf{E}_{\text{mac}}(\omega) + \mathbf{E}_{\text{xc,mac}}(\omega), \tag{7.7}
\]

\[
\delta v_{\text{eff}}(\mathbf{r}, \omega) = \delta v_{\text{mic}}(\mathbf{r}, \omega) + \delta v_{\text{xc,mic}}(\mathbf{r}, \omega), \tag{7.8}
\]
where \( v_{\text{mic}} \) is the microscopic part of the Hartree potential and \( v_{\text{xc,mic}} \) is the microscopic part of the exchange-correlation potential. The term \( E_{\text{xc,mac}} \) denotes the macroscopic xc-electric field. The gauge is chosen in such a way that the microscopic parts of the external field are included in the scalar potential and the macroscopic part of the fields are included in the vector potential. Our goal is to derive an expression for \( E_{\text{xc,mac}} \). Let us first look at the consequences of such a term. With Kohn-Sham theory the macroscopic polarizability is proportional to the effective field \( E_{\text{eff}} \). This defines a Kohn-Sham susceptibility \( \tilde{\chi} \) by the equation,

\[
P_{\text{mac}}(\omega) = \tilde{\chi}(\omega) \cdot E_{\text{eff}}(\omega).
\]

We are, however, interested in the actual susceptibility \( \chi \). With the Eqs. 7.1, 7.7, and 7.9 we obtain

\[
(\chi^{-1}(\omega) - \chi^{-1}(\omega)) \cdot P_{\text{mac}}(\omega) = E_{\text{xc,mac}}(\omega).
\]

We see that we can calculate the susceptibility \( \chi \) once we know how to calculate \( E_{\text{xc,mac}} \). In previous calculations [63, 94], \( E_{\text{xc,mac}} \) was simply put to zero, which yields the approximation \( \chi = \tilde{\chi} \). Here we want to improve upon this approximation and derive an explicit expression for \( E_{\text{xc,mac}} \). The starting point is the current-density functional derived by Vignale and Kohn [108, 109] which we write in the compact form derived by Vignale, Ullrich and Conti [ \( E_{\text{xc}}(r, \omega) \equiv \frac{\mu}{e} a_{\text{xc}}(r, \omega) \) ] [110],

\[
-E_{\text{xc},i}(r, \omega) = -\partial_i v_{\text{xc}}^{\text{ALDA}} + \frac{1}{\rho_0(r)} \sum_j \partial_j \sigma_{\text{xc},ij}(r, \omega). \tag{7.11}
\]

Here \( E_{\text{xc},i} \) is the induced xc-electric field in linear response and \( v_{\text{xc}}^{\text{ALDA}} \) is the first order change in the xc-potential in the adiabatic local density approximation (ALDA). The last term contains the ground state density \( \rho_0 \) of the system and the viscoelastic stress tensor,

\[
\sigma_{\text{xc},ij} = \tilde{\eta}_{\text{xc}} \left( \partial_j u_i + \partial_i u_j - \frac{2}{3} \delta_{ij} (\sum_k \partial_k u_k) \right) + \tilde{\zeta}_{\text{xc}} \delta_{ij} (\sum_k \partial_k u_k). \tag{7.12}
\]

Here \( \mathbf{u}(r, \omega) = \delta \mathbf{j}(r, \omega)/\rho_0(r) \) is the induced velocity field and the constants \( \tilde{\eta}_{\text{xc}}(\rho_0, \omega) \) and \( \tilde{\zeta}_{\text{xc}}(\rho_0, \omega) \) are coefficients, which can be expressed in terms of the transverse and longitudinal xc-kernels of the electron gas [110]. In order to isolate the macroscopic component of the xc-electric field we take the average over a unit cell of the solid and obtain

\[
E_{\text{xc,mac}}(\omega) = \frac{i}{\omega} \sum_k \frac{1}{\Omega} \int_{\Omega} \mathbf{y}_{ik}(r, \omega) \delta \mathbf{j}_k(r, \omega), \tag{7.13}
\]

where \( \Omega \) denotes the unit cell volume and we defined the matrix

\[
\mathbf{y}_{ik}(r, \omega) = -\delta_{ik} \nabla \cdot (f_{\text{xc}T} \nabla \rho_0) \rho_0 - \frac{\partial_k (h_{\text{xc}} \partial_i \rho_0)}{\rho_0}. \tag{7.14}
\]

Here \( f_{\text{xc}T}(\rho_0, \omega) \) is the transverse xc-kernel of the electron gas and \( h_{\text{xc}}(\rho_0, \omega) \) is given as

\[
h_{\text{xc}}(\rho_0, \omega) = f_{\text{xc}L}(\rho_0, \omega) - f_{\text{xc}T}(\rho_0, \omega) - \frac{d^2 e_{\text{xc}}}{d\rho_0^2}. \tag{7.15}
\]
Here \( f_{xcL}(\rho_0, \omega) \) is the longitudinal part of the electron gas xc-kernel and \( e_{xc} \) the xc-energy per volume unit of the electron gas. The equation for the macroscopic part of the xc-electric field can be simplified if we replace \( \delta j \) by its macroscopic value, i.e., its average over the unit cell. In that case we obtain

\[
E_{xc,mac}(\omega) = \frac{i}{\omega} Y([\rho_0], \omega) \cdot \delta j(\omega) = Y([\rho_0], \omega) \cdot P_{mac}(\omega). \tag{7.16}
\]

Here the tensor \( Y \) is given by

\[
Y([\rho_0], \omega) = \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \left( \frac{\nabla \rho_0}{\rho_0^2} f_{xcT}(\rho_0, \omega) + \frac{1}{\Omega} \int_{\Omega} d\mathbf{r} \frac{\nabla \rho_0 \otimes \nabla \rho_0}{\rho_0^2} h_{xc}(\rho_0, \omega) \right). \tag{7.17}
\]

Equation (7.16) represents the first explicit example of the often discussed density-polarization functional \([27, 111, 112]\). With this functional and the Eqs. 7.1, 7.7, and 7.9, we see that the susceptibility becomes equal to

\[
\chi(\omega) = (1 - \tilde{\chi}(\omega) Y([\rho_0], \omega))^{-1} \tilde{\chi}(\omega). \tag{7.18}
\]

This equation clearly displays the influence of the macroscopic xc-electric field on the susceptibility. It remains to find an appropriate approximation for the functions \( f_{xcT} \) and \( f_{xcL} \). These functions have been investigated in detail for the electron gas \([113, 114, 115, 116]\). In these works it has been shown that they are smooth functions of the frequency, except at twice the plasma frequency. For the optical spectra we are, however, interested in much smaller frequencies. In the limit \( \omega \to 0 \) the function \( h_{xc}(\rho_0, \omega) \) becomes equal to \( f_{xcT}(\rho_0, 0)/3 \) \([110]\). In that limit the tensor \( Y([\rho_0], 0) \) is completely determined by \( f_{xcT}(\rho_0, 0) \).

### 7.4 Calculations

We have tested this new functional for silicon as an example of a group IV semiconductor in the diamond structure. We used Eq. 19 (and the values of \( \mu_{xc} \) in Table I) of Ref. \([115]\), to obtain values for \( f_{xcT}(\rho_0, 0) \) at arbitrary \( \rho_0 \), thereby using a cubic spline interpolation in the range 0-5 for the \( r_s \) values, in which we take into account the exactly known small \( r_s \) behavior \([116]\). The macroscopic dielectric function \( \epsilon(\omega) \) can be obtained directly from the electric susceptibility \( \chi(\omega) \) through \( \epsilon(\omega) = 1 + 4\pi \chi(\omega) \). The optical absorption spectrum \( \epsilon_2 \) for Si, shows two major peaks in the range from 3-6 eV \([45, 46]\). The first peak \( (E_1) \) is attributed to an \( M_0 \) or \( M_1 \)-type critical point transition, and the second \( (E_2) \) one to an \( M_2 \) type \([56, 93]\). All previous "one-electron" approximations, ranging from the early pseudopotential approaches in the 1970s \([118, 119]\), to the \textit{ab initio} DFT-LDA of the end 1990s \([120]\), showed the same features for \( \epsilon_2 \). However, the \( E_1 \) peak is usually underestimated, and appears just as a shoulder, whereas the \( E_2 \) is overestimated and appears at too high energies compared to experiment \([45, 46]\). The underestimation of the \( E_1 \) peak was attributed to excitonic effects (the attractive interaction between the
virtual hole and the excited electron). In the recent calculations [121], these excitations are explicitly taken into account by solving the Bethe-Salpeter equation (BSE) for the coupled electron-hole excitations, and in these spectra the $E_1$ peak is clearly resolved and in good agreement with experiment [45, 46]. The ratio of the $E_1$-$E_2$ peak heights in the $\epsilon_2$ of Si proved to be rather sensitive to the numerical value of $\mathbf{Y}(\rho_0,0)$. However, it turned out that the theoretical value that we list in Table 7.1, is too high by about a factor of 2. In view of the uncertainty in the published values of $f_{xcT}(\rho_0,0)$ [116], we introduce a prefactor of 0.4 in front of the matrix $\mathbf{Y}(\rho_0,0)$ in Eq. 7.18, which was determined in order to get an optimal agreement with experiment for the ratio of the $E_1$-$E_2$ peak heights. This prefactor is used in all the subsequent cases.

### 7.5 Results

#### 7.5.1 Silicon

In Fig. 7.1, we show the effect of this polarization functional on the $\epsilon(\omega)$ of Si in comparison with experiment [45, 46]. In order to facilitate the comparison with experiment, the spectra have been shifted to higher energies, see Table 7.1.

Table 7.1: The calculated values for $\mathbf{Y}(\rho_0,0)$, and the applied energy shifts to the dielectric functions, for the crystals in the Figs. 7.1 - 7.5.

<table>
<thead>
<tr>
<th>Solid</th>
<th>$\mathbf{Y}(\rho_0,0)$ (a.u.)</th>
<th>Without $\mathbf{Y}(\rho_0,0)$</th>
<th>With $\mathbf{Y}(\rho_0,0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.367</td>
<td>0.60</td>
<td>0.70</td>
</tr>
<tr>
<td>Si</td>
<td>0.355</td>
<td>0.40</td>
<td>0.58</td>
</tr>
<tr>
<td>GaP</td>
<td>0.409</td>
<td>0.50</td>
<td>0.60</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.416</td>
<td>0.45</td>
<td>0.50</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.489</td>
<td>0.90</td>
<td>0.90</td>
</tr>
</tbody>
</table>

*Spectra have been shifted such that the calculated and experimental zero-crossings of $\epsilon_1$ coincide.

It is clear that without the $\mathbf{E}_{xc,mac}$ contributions, the $E_1$ peak appears as a shoulder and is underestimated in amplitude, the $E_2$ peak is too sharp, and therefore overestimated in magnitude. When including the macroscopic xc-contributions, the $E_1$ peak is now clearly resolved. As can be seen in Fig. 7.1, for both the real and imaginary part of $\epsilon(\omega)$, the whole dielectric function is improved considerably. Therefore it should be concluded that it is necessary to include the $\mathbf{E}_{xc,mac}$ contributions to get the $E_1$ peak in the $\epsilon_2$ of Si in good agreement with experiment [45, 46]. In addition, we have calculated the optical absorption spectra $\epsilon_2$ for C, also a group IV element, GaP and GaAs (III-V), and ZnS (II-VI) using the same polarization functional. We checked that the used prefactor led to uniformly improved spectra, and hence we have obtained a new polarization functional that in all cases improves our previous ALDA results [94].
Figure 7.1: The dielectric function for Silicon (Si), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [45, 46]. The applied energy shifts to the TDDFT calculated dielectric function were 0.60 eV without, and 0.70 eV with the inclusion of $Y([\rho_0], 0)$. 
7.5. RESULTS

7.5.2 Diamond

The experimental [46] absorption spectrum $\epsilon_2$ for diamond shows an $E_2$ peak around 12 eV. In all previous calculations of $\epsilon_2$ for C this $E_2$ peak is overestimated, just like in our recently performed time-dependent DFT calculations [63, 94], as well as in the BSE calculations [117], which include in detail the electron-hole interactions. In Fig. 7.2 we show the effect of including the polarization functional on the $\epsilon_2$ of diamond, in comparison with experiment [46]. Clearly there is a very small effect on $\epsilon_2$ when using the polarization functional. Therefore it can be concluded that the xc-contributions to the effective macroscopic electric field in diamond are negligible.

Figure 7.2: The optical absorption spectrum for Diamond (C), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [46]. The applied energy shifts to the TDDFT calculated dielectric function were 0.40 eV without, and 0.58 eV with the inclusion of $Y(\rho_0, 0)$. 
CHAPTER 7. A POLARIZATION DEPENDENT FUNCTIONAL

7.5.3 Gallium phosphide

The experimental [46] absorption spectrum $\epsilon_2$ of GaP in the zincblende structure, also shows a double peak structure in the range from 3 to 6 eV, just like Si. In Fig. 7.3, the effect of the polarization functional on the $\epsilon_2$ of GaP is shown and compared with experiment [46]. Upon inclusion of the scaled $Y([\rho_0], 0)$ term, the originally underestimated $E_1$ peak is now found in full agreement with experiment [46], but the $E_2$ peak is still overestimated and too sharp.

Figure 7.3: The optical absorption spectrum for Gallium Phosphide (GaP), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [46]. The applied energy shifts to the TDDFT calculated dielectric function were 0.50 eV without, and 0.60 eV with the inclusion of $Y([\rho_0], 0)$. 
7.5. RESULTS

7.5.4 Gallium arsenide

The experimental absorption spectrum for GaAs (Ref. [46]) shows the same features as for GaP. In Fig. 7.4 the effect of the polarization functional is shown on the $\epsilon_2$ of GaAs. Including $Y([\rho_0], 0)$ gives an increase in the oscillator strength for the $E_1$ peak, just like in GaP, and it is now also in good agreement with experiment [46].

![The optical absorption spectrum for Gallium Arsenide (GaAs), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [46].](image)

Figure 7.4: The optical absorption spectrum for Gallium Arsenide (GaAs), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [46]. The applied energy shifts to the TDDFT calculated dielectric function were 0.45 eV without, and 0.50 eV with the inclusion of $Y([\rho_0], 0)$. 

7.5.5 Zinc sulfide

In the II-VI semiconductor ZnS the $E_1$ peak is also underestimated in our previous calculations [94], compared to experiment [90]. In Fig. 7.5, it can be seen that also for ZnS the osillator strength for the $E_1$ peak increases after inclusion of the $Y([\rho_0], 0)$ term, and is now in better agreement with experiment [90].

![Figure 7.5: The optical absorption spectrum for Zinc Sulfide (ZnS), with and without the inclusion of the polarization dependent functional, in comparison with the experimental data [90]. The applied energy shifts to the TDDFT calculated dielectric function were 0.90 eV without and with the inclusion of $Y([\rho_0], 0)$.](image)

7.6 Conclusions

In conclusion, we presented the first successful computational approach of a polarization dependent functional within current density functional theory, as it was suggested in 1996 by Vignale and Kohn [108]. The calculated optical absorption spectra of several semiconductors clearly improved considerably with the inclusion of the exchange-correlation contributions to the effective macroscopic electric field.
Chapter 8

Excitons in crystalline insulators, described by TDDFT


8.1 Abstract

In this chapter we demonstrate that time-dependent density-functional theory (TDDFT), within the adiabatic local density approximation (ALDA), describes the excitonic effects for the insulators CaF$_2$, SiO$_2$, and GaN correctly. Results for the electronic band structure, the density of states (DOS) and the optical spectra ($\epsilon_2$) are reported for these wide band gap insulators. The optical spectra calculated by TDDFT are compared directly with experimental measurements, and with the $\epsilon_2$’s as calculated by a Green’s function approach (DFT/GW/BSE). In DFT/GW/BSE, these excitons are explicitly taken into account by evaluating the two-body Green’s function $G_2$. The features in the optical absorption spectra, that are attributed to excitonic effects according to the DFT/GW/BSE results, are also found in the TDDFT calculations. This contradicts the common assumption that TDDFT is not able to describe these excitonic effects properly.

8.2 Introduction

When a solid in its ground state is perturbed by an electromagnetic field, an electron can be promoted from the valence band to the conduction band, thereby leaving a hole behind. In the case of a Coulombic interaction between this excited electron and the remaining hole, a bound state is formed. Such bound states of electron-hole pairs are called excitons [8]. The optical excitations, e.g., in semiconductors, can be described in terms of very weakly bound electron-hole pairs. On average, the electron-hole distance is large in comparison with the lattice constant of the corresponding semiconductor. Such excitons are called Mott-Wannier excitons. Excitons are called Frenkel excitons, when the correlation between the electron and the hole is strong. In these excitons, the electrons
are always found very close to the holes. Recently, in several groups [122, 123, 124, 125], it has been claimed that the description of optical electron-hole excitations requires an effective two-body approach, which goes beyond the single-particle picture. In the rest of this chapter the single-particle Green’s function approach will be abbreviated as the GW approach\(^1\), in which \(G\) stands for the one-particle Green’s function \(G^1\) and the \(W\) for the screened Coulomb interaction. In the past, the GW approach has been shown to be highly successful for the prediction of quasiparticle spectra [25, 133]. In the effective two-body approach\(^2\) the coupled electron-hole excitations are calculated by solving the Bethe-Salpeter equation (BSE), which enables the evaluation of the optical absorption spectra. The effect of such a two-body approach becomes directly clear when comparing the corresponding optical spectra, 'GW' vs. 'BSE'. The differences between these spectra are defined, in the DFT/GW/BSE theory, as features of excitonic nature. The explicit inclusion of these electron-hole excitations can be quite substantial, e.g., a large influence is observed in the optical absorption of \(\alpha\)-quartz. The question arises to what extent excitonic effects are also included in time-dependent density-functional theory. Therefore it is interesting to investigate if these excitonic features in the optical absorption spectra are also found in a TDDFT calculation.

In this chapter we investigate three wide band gap insulators: CaF\(_2\), SiO\(_2\), and GaN. In these insulators, the optical spectra were all substantially improved upon the inclusion of the electron-hole excitations (i.e., after solving the Bethe-Salpeter equation). In those calculations, the spectra are found in excellent agreement with the experimentally measured spectra. The rest of this chapter is arranged in the following way. In the theory section, we briefly outline the DFT/GW/BSE theory, and we show the similarity between the DFT/GW/BSE equations and the TDDFT equations. In the subsequent section we give the results and analyses for the three wide band gap insulators.

### 8.3 Theory

#### 8.3.1 Green’s function approach

The following outline of the Green’s function approach is based upon the Refs. [125, 126]. The key concept of the Green’s function approach is to describe the excitations of the electronic system by the corresponding one- and two-particle Green’s function. The formalism is fully described and discussed in the Refs. [127, 128, 129, 130, 131, 132]. In practice three computational techniques are combined: (1) The ground state of the electronic system is described by density-functional theory (DFT) within the local density approximation (LDA), (2) The quasiparticle (QP) excitation spectrum of the electrons and holes is obtained within the GW approximation to the electron self-energy operator, (3) The coupled electron-hole excitations are calculated by solving the Bethe-Salpeter equation (BSE), to evaluate the optical spectrum.

\(^1\)‘GW’ in the Figures
\(^2\)‘BSE’ in the Figures
8.3. THEORY

Quasiparticle excitation spectrum

The process of removing and adding an electron to the \(N\)-particle system is described by the one-electron Green’s function

\[
G_1(1, 2) = -i\langle N, 0 | T[\psi(1)\psi^\dagger(2)] | N, 0 \rangle, \tag{8.1}
\]

in which we have used the abbreviated notation \((i) = (r_i, t_i)\). The ground state configuration of the \(N\) electron system is given by \(|N, 0\rangle\), and in second quantization notation, \(\psi^\dagger(i)\) and \(\psi(i)\) are the creation and annihilation operators. In Eq. 8.1, \(T\) is Wick’s time-ordering operator, which is given by:

\[
T[\psi(1)\psi^\dagger(2)] = \begin{cases} 
\psi(1)\psi^\dagger(2) & \text{if } t_1 > t_2, \\
-\psi^\dagger(2)\psi(1) & \text{if } t_1 < t_2.
\end{cases} \tag{8.2}
\]

For an interacting \(N\)-electron system the Hamiltonian is given by,

\[
\hat{H} = \hat{T} + \hat{V} + \hat{U}, \tag{8.3}
\]

in which \(\hat{T}\) is the kinetic term, \(\hat{V}\) the interaction with the external field, and \(\hat{U}\) the Coulomb interaction between the electrons: \(1/|r - r'|\). Similarly, for a fictitious non-interacting system the Hamiltonian is given by,

\[
\hat{H}_0 = \hat{T} + \hat{V}_0, \tag{8.4}
\]

in which \(\hat{V}_0\) is an external potential, which, in addition to the interaction with the external field, also takes into account the electron-electron interaction in an effective way. Therefore this \(\hat{V}_0\) is often denoted by \(\hat{V}_{\text{eff}}\), which includes in addition to the external potential \(\hat{V}\) also the electrostatic electron-electron interaction and the exchange-correlation potential.

The equation of motion for the one-particle Green’s function \(G(1, 2)\) can be derived by using the following commutation rules in second quantization

\[
\begin{align*}
\left[\psi^\dagger(r, t), \psi^\dagger(r', t)\right]_+ &= \left[\psi(r, t), \psi(r', t)\right]_+ = 0, \tag{8.5} \\
\left[\psi(r, t), \psi^\dagger(r', t)\right]_+ &= \delta(r - r'), \tag{8.6}
\end{align*}
\]

and the Heisenberg equations of motion

\[
\begin{align*}
i \frac{\partial \psi(r, t)}{\partial t} &= \left[\psi(r, t), \hat{H}\right], \tag{8.7} \\
-i \frac{\partial \psi^\dagger(r, t)}{\partial t} &= \left[\psi^\dagger(r, t), \hat{H}\right]. \tag{8.8}
\end{align*}
\]

For the non-interacting system this results in:

\[
\left[ i \frac{\partial}{\partial t_1} + \frac{1}{2} \nabla_1^2 - V_{\text{eff}}(1) \right] G_0(1, 2) = \delta(1, 2). \tag{8.9}
\]
In a similar way, for the interacting $N$-electron system, one can derive the equation of motion for interacting Green’s function $G(1, 2)$

$$\left[ i \frac{\partial}{\partial t} + \frac{1}{2} \nabla_1^2 - V_{\text{eff}}(1) \right] G(1, 2) - \int d3 \Sigma(1, 3) G(3, 2) = \delta(1, 2) ,$$

(8.10)

which defines the self-energy operator $\Sigma(1, 3)$ by

$$\int d3 \Sigma(1, 3) G(3, 2) = \langle N, 0 | T \left[ [\psi^\dagger(1), \hat{U} + \hat{V} - \hat{V}_{\text{eff}}] \psi^\dagger(2) \right] | N, 0 \rangle .$$

(8.11)

One now arrives at the Dyson’s equation by combining the Eqs. 8.9 and 8.10

$$G(1, 2) = G_0(1, 2) + \int d3d4 G_0(1, 3) \Sigma(3, 4) G(4, 2) ,$$

(8.12)

which can be written symbolically as: $G = G_0 + G_0 \Sigma G$.

In principle the self-energy operator $\Sigma$ should be calculated self-consistently. This is most easily done by solving the Hedin equations [127] using linear response theory. The Hedin equations are a set of four coupled integral equations, for the self-energy $\Sigma$, the screened interaction $W$, the polarizability $P$, and the vertex function $\Gamma$.

In the GW approximation the vertex function $\Gamma(1, 2, 3)$ is approximated by $\delta(1, 2) \delta(1, 3)$, leading to the following reduced set of equations:

$$P(1, 2) = -2i G(1, 2) G(2, 1^+) ,$$

(8.13)

$$W(1, 2) = v(1, 2) + \int d3d4 v(1^+, 3) P(3, 4) W(4, 2) ,$$

(8.14)

$$\Sigma(1, 2) = i G(1, 2) W(1^+, 2) .$$

(8.15)

Starting from the zeroth-order approximation: $\Sigma = 0$ and $G = G_0$, where $G_0$ can be calculated using DFT-LDA, one first obtains the polarizability $P$ as the response of the system to a change in the effective potential. From $P$, the interaction between the quasiparticles $W$ is calculated, and finally the self-energy operator $\Sigma$ is obtained.

The quasiparticle energies are then calculated by inserting this self-energy operator $\Sigma$ in the quasiparticle equation (i.e., the Dyson’s equation 8.12 in disguise)

$$\left[ -\frac{\nabla^2}{2} + V_{\text{eff}}(\mathbf{r}) \right] \phi_{nk}(\mathbf{r}) + \int d\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', E_{nk}) \phi_{nk}(\mathbf{r}') = E_{nk} \phi_{nk}(\mathbf{r}) .$$

(8.16)

In practice, only one GW iteration is performed to update the DFT-LDA eigenvalues. In this way many band structures and electronic spectra have been calculated within the GW approximation [127, 128]. The GW spectrum, of the individual electron and hole states, serves as input for the Bethe-Salpeter equation, which results in the coupled electron-hole
excitations and the optical absorption spectrum, $\epsilon_2(\omega)$ (Eq. 8.25).

From the GW spectrum one can also directly calculate the optical absorption spectrum ('one-electron' spectrum, $\epsilon_2^{(0)}(\omega)$). This spectrum does not include the electron-hole interaction, and in this case the excitations are calculated by the vertical transitions between the independent electron and hole states, according to

$$\epsilon_2^{(0)}(\omega) = \frac{16\pi^2}{\omega^2} \sum_{cvk} |\langle ck|\hat{j} \cdot \hat{v}k\rangle|^2 \delta(\omega - (E_{ck} - E_{vk})) \ , \quad (8.17)$$

in which $\hat{j}$ and $\hat{v}$ are the current operator and the polarization unit vector of the electric field respectively.

**Electron-hole excitations**

The two-particle Green’s function can be defined, in analogy with the one-electron Green’s function of Eq. 8.1, as

$$G_2(1, 2, 1', 2') = -\langle N, 0|T[\psi(1)\psi(2)\psi^\dagger(2')\psi^\dagger(1')]|N, 0 \rangle \ . \quad (8.18)$$

The two-particle correlation function is introduced as

$$L(1, 2, 1', 2') = G_1(1, 2')G_1(2, 1') - G_2(1, 2, 1', 2') \ ,
= L_0(1, 2, 2', 1') - G_2(1, 2, 1', 2') \ , \quad (8.19)$$

in which $L_0$ is the propagator for the free electron-hole pair.

The Bethe-Salpeter equation is found as the equation of motion for $L(1, 2, 1', 2')$. The derivation is similar to the one for the Dyson’s equation 8.12, as the equation of motion for $G(1, 2)$.

$$L(1, 2, 1', 2') = L_0(1, 2, 2', 1') + \int d3d4d5d6L_0(1, 4, 1', 3)K(3, 5, 4, 6)L(6, 2, 5, 2') \ , \quad (8.20)$$

where the effective two-particle interaction kernel $K$ is given by

$$K(3, 5, 4, 6) = \frac{\delta\Sigma(3, 4)}{\delta G_{1}(6, 5)} \ . \quad (8.21)$$

If again the GW approximation is used for the self-energy operator $\Sigma$, and if we further neglect the derivative of the screened interaction $W$ with respect to the one-particle Green function $G_1$, one obtains:

$$K(3, 5, 4, 6) = -i\delta(3, 4)\delta(5, 6)v(3, 6) + i\delta(3, 6)\delta(4, 5)W(3, 4) \,
= K^e(3, 5, 4, 6) + K^d(3, 5, 4, 6) \ . \quad (8.22)$$

The term $K^e$ contains the bare Coulomb interaction $v$, and is called the *exchange* term, while $K^d$ results from the screened Coulomb interaction $W$, and has the form of a so-called
direct term. It is the $K^x$ term which is responsible for the attractive nature of the electron-hole interaction and the formation of bound electron-hole states.

The BSE (Eq. 8.20) can be transformed into a generalized eigenvalue problem, if we expand $L_0$ and $L$ in the quasiparticle functions and energies. This results in

$$
(E_{ck} - E_{vk})A_{cve}^S + \sum_{c'v'k'} K_{cve}^{c'v'k'}(\Omega_S)A_{c'v'k'}^S = \Omega_S A_{cve}^S .
$$

(8.23)

The indices $c$, $v$ and $k$ denote the conduction bands, valence bands and the $k$-vectors of the quasiparticle states. The electron-hole amplitudes $A_{cve}^S$, contain information about the electron-hole correlation and the spatial nature of the excited states $|S\rangle$, having excitation energies $\Omega_S$. $K_{cve}^{c'v'k'}(\Omega_S)$ is the electron-hole interaction kernel. The evaluation of $K_{cve}^{c'v'k'}(\Omega_S)$ forms the bottleneck in the BSE calculation, because the screened interaction part $K^d$ contains an energy convolution, depending on the excitation energy $\Omega_S$.

After solving the Bethe-Salpeter equation (Eq. 8.23), the electron-hole amplitudes $A_{cve}^S$ and the coupled electron-hole excitation energies $\Omega_S$ can be used to calculate the excitonic wave functions $\Psi_S(\mathbf{r}_e, \mathbf{r}_h)$, belonging to the excitations $|S\rangle$.

$$
\Psi_S(\mathbf{r}_e, \mathbf{r}_h) = \sum_{cvek} A_{cve}^S \phi_{c}^e(\mathbf{r}_e) \phi_{v}^v(\mathbf{r}_h) .
$$

(8.24)

The optical absorption spectrum $\epsilon_2(\omega)$ now follows from:

$$
\epsilon_2(\omega) = \frac{16\pi^2}{\omega^2} \sum_S \left| \sum_{cvek} A_{cve}^S \langle \mathbf{c}\mathbf{k} | \hat{j} \cdot \hat{e} | \mathbf{v}\mathbf{k} \rangle \right|^2 \delta(\omega - \Omega_S) .
$$

(8.25)

### 8.3.2 TDDFT approach

In this section we focus on the similarity between the DFT/GW/BSE equations of the previous section and the corresponding TDDFT equations. A full description of this real-space formulation to time-dependent density-functional theory can be found in Ref. [63], and results for the dielectric function for a large number of nonmetallic crystals in Ref. [94, 102, 136].

For simplicity we will only consider isotropic systems. The key quantity is the induced density

$$
\delta \rho(\mathbf{r}, \omega) = 2 \sum_{cvek} \psi_{c}^e(\mathbf{r}) \psi_{v}^v(\mathbf{r}) \int_V d\mathbf{r}' \psi_{c}^e(\mathbf{r}') \left( \mathbf{j} \cdot \hat{e} + \delta \nu_{\text{eff}}(\mathbf{r}', \omega) \right) \psi_{v}^v(\mathbf{r}') \left( \epsilon_{c}^e - \epsilon_{v}^v \right) + \omega + i\eta + c.c.(-\omega) ,
$$

(8.26)

in which $\hat{e}$ is the direction of the electric field, $\mathbf{E}(\omega) = -i\omega \cdot \hat{e}$, the summation is over the conduction ($c$) and valence ($v$) states, the (paramagnetic) current operator is given by $\mathbf{j} = -i(\nabla - \nabla^\dagger)/2$, and the effective potential $\delta \nu_{\text{eff}}(\mathbf{r}', \omega)$ is the result of the microscopic
Coulomb potential and the exchange-correlation contribution.

The similarity between the DFT/GW/BSE and TDDFT equations becomes evident if we introduce the density matrix \( P_{cvk}(\omega) \) and write the induced density \( \delta \rho(\mathbf{r}, \omega) \) in Eq. 8.26 as

\[
\delta \rho(\mathbf{r}, \omega) = 2 \sum_{cvk} \psi_{cvk}^*(\mathbf{r}) \psi_{ck}(\mathbf{r}) P_{cvk}(\omega) + \text{c.c.}(\omega) .
\]  

(8.27)

From the Eqs. 8.26 and 8.27, we see that \( P_{cvk}(\omega) \) has to satisfy the following inhomogeneous eigenvalue equation

\[
\left[ (\epsilon_{ck} - \epsilon_{vk}) - \omega \right] P_{cvk}(\omega) + \sum_{c'v'k'} K_{cvk,c'v'k'}^{cvk}(\omega) P_{c'v'k'}(\omega) = -2 \int_V d\mathbf{r} \left( \psi_{cvk}^*(\mathbf{r}) \left[ \hat{j} \cdot \hat{e} \right] \psi_{ck}(\mathbf{r}) \right) ,
\]  

(8.28)

in which the couplings matrix \( K_{cvk,c'v'k'}^{cvk}(\omega) \) is given by

\[
K_{cvk,c'v'k'}^{cvk}(\omega) = 2 \int_V d\mathbf{r} \int_V d\mathbf{r}' \times \left( \psi_{cvk}^*(\mathbf{r}) \psi_{cvk}(\mathbf{r}) \left[ \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}(\mathbf{r}, \mathbf{r}', \omega) \right] \psi_{c'v'k'}^*(\mathbf{r}') \psi_{c'v'k'}(\mathbf{r}') \right) .
\]  

(8.29)

Let us first look for the eigenvalues \( \Omega_S \) and eigenstates \( P_{cvk}^S(\omega) \) of the following eigenvalue equation, i.e., the homogeneous part of Eq. 8.28:

\[
\left[ (\epsilon_{cvk} - \epsilon_{vk}) \right] P_{cvk}^S(\omega) + \sum_{c'v'k'} K_{cvk,c'v'k'}^{cvk}(\omega) P_{c'v'k'}^S(\omega) = \Omega_S P_{cvk}^S .
\]  

(8.30)

The solution of the inhomogeneous equation (Eq. 8.28) can be expressed in terms of these eigenvalues and eigenstates, in the following way

\[
P_{cvk}(\omega) = -2 \sum_S \frac{P_{cvk}^S \langle \psi_{ck} | \hat{j} \cdot \hat{e} | \psi_{cvk}^* \rangle}{\Omega_S - \omega - i\eta} P_{cvk}^S .
\]  

(8.31)

We can now get the induced macroscopic current according to the expressions in the Eqs. 4.58 ff., which is very similar to the induced density of Eq. 8.27

\[
\delta \mathbf{j}(\omega) \cdot \hat{e} = 2 \sum_{cvk} \langle \psi_{vk} | \hat{j} \cdot \hat{e} | \psi_{cvk} \rangle P_{cvk}(\omega) + \text{c.c.}(\omega) .
\]  

(8.32)

For isotropic systems, we now get the imaginary part of the electric susceptibility and dielectric function, \( \epsilon_2(\omega) \), according to

\[
\epsilon_2(\omega) = 4\pi \text{Im} \chi_e(\omega) = \frac{16\pi^2}{\omega^2} \sum_S \sum_{cvk} P_{cvk}^S \langle \psi_{vk} | \hat{j} \cdot \hat{e} | \psi_{cvk} \rangle^2 \delta(\omega - \Omega_S) .
\]  

(8.33)
When we neglect the Coulomb and exchange-correlation interactions in the TDDFT calculations, by setting the couplings matrix $K_{cvk}^{c^\prime v^\prime k}(\omega)$ to zero, it immediately becomes clear from Eq. 8.30, that the $\Omega_S$ reduce to the Kohn-Sham energy differences ($\Omega_S = \epsilon_{c^k} - \epsilon_{v^k}$), and that the $P_{cvk}^S$ become the unit vectors. The optical absorption spectrum is then obtained according to

$$\epsilon_2^{(0)}(\omega) = \frac{16\pi^2}{\omega^2} \sum_{cvk} \left| \langle \psi_{c^k} | \hat{j} \cdot \hat{e} | \psi_{v^k} \rangle \right|^2 \delta(\omega - (\epsilon_{c^k} - \epsilon_{v^k})) .$$

(8.34)

This is completely equivalent to Eq. 8.17, with the obvious difference that there the $\Omega_S$ are the quasiparticle energy differences ($\Omega_S = E_{c^k} - E_{v^k}$).

Now the similarities have become evident. If we identify the density matrix elements $P_{cvk}^S$ with the electron-hole amplitudes $A_{cvk}^S$, then Eq. 8.30 can be interpreted as the Bethe-Salpeter equation (Eq. 8.23), with the quasiparticle eigenvalues replaced by the Kohn-Sham eigenvalues (and a different coupling matrix, in which the self-energy operator, $\Sigma$ has been replaced by the exchange-correlation kernel, $f_{xc}$). With the same identification, the resulting expression for the electric susceptibility (Eq. 8.33) yields exactly the same expression for the optical absorption spectrum $\epsilon_2(\omega)$ as was obtained in the BSE derivation (Eq. 8.25).

8.4 Calculations on insulators

8.4.1 Calcium fluoride

CaF$_2$ is a highly ionic (wide band gap) insulator, which has been examined extensively for many years as well experimentally [83, 84, 137, 138, 139, 140] as theoretically [64, 70, 122, 141, 142]. The CaF$_2$ crystal has the fluoride structure with a lattice constant a=5.46 Å [64].

Bandstructure

The calculated band structure for CaF$_2$ is shown in Fig. 8.1. The bottom of the conduction-band (CB) is found at $\Gamma$, whereas the top of the valence-band (VB) is found at $X$. Therefore we get an indirect band gap of 6.93 eV, which is an underestimation by LDA of 43% compared to the experimental value of 12.1 eV found by Rubloff [139]. Other theoretical bandstructures are given in the Refs. [70, 141, 142]. Albert [141] used the tight-binding method for the VB and a pseudopotential method for the CB. The experimental band gap was reproduced by using a Slater exchange parameter of $\alpha=0.795$ in their overlapping-atomic-potential model. Heaton [142] used the self-consistent linear combination of atomic orbitals (LCAO) method, for as well the CB as the VB, and found, when using the full exchange parameter ($\alpha=1$), an indirect band gap of 9.8 eV in their overlapping-atomic-charge model. Gan [70] found an indirect band gap of 6.53 eV,
when using their self-consistent orthogonalised LCAO method in the LDA approximation. Looking at the complete bandstructures of Refs. [70, 141, 142], we see a clear resemblance of our structure and that of Albert [141], which is, however, different (for example at the point \( L \) in the Brillouin zone) from the structures found by Gan [70] and Heaton [142].

**Density of states**

The Density of States (DOS) for CaF\(_2\), as calculated from the bandstructure, is also depicted in Fig. 8.1. We find for the upper VB two peaks at -5.35 and -3.80 eV respectively (zero energy is centered between VB and CB). The same two peak structure in the DOS for the VB was found by others [70, 142]. The total width of this upper VB is 2.84 eV, which is in good agreement with the experimental value of 3.0 eV by Pool [140]. Others calculated the width of the VB to be 3.1 [70], 2.7 [141], and 2.0 eV [142] respectively. The DOS for the CB is rather complicated, and shows peaks at 6.25, 8.90, 9.75, 12.35, 13.10, 13.55, 13.95 and 15.58 eV (as indicated in Fig. 8.1.). A very similar structure for the DOS for the CB was found by Gan [70], which was rather different from the one found by Heaton [142].

**Optical spectrum**

The earliest experimental reflectance and optical spectra of CaF\(_2\) [84, 137, 138, 139, 140] showed interesting and substantial differences from the most recent one by Barth [83]. The early measurements (photographic photometry, ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS)) all revealed the presence of an exciton peak around 11 eV. In the most recent spectroscopic ellipsometric synchrotron measurements of \( \epsilon_1 \) and \( \epsilon_2 \) however, this exciton could not be resolved clearly, because the peak is in the energy range that is contaminated by second-order diffracted light. Furthermore, the intensity of the \( \epsilon_2 \) of the early measurements [84, 137, 138, 139, 140] differed by a factor of 2 from the one measured by Barth [83]. Despite the fact that Barth claimed to be convinced that their spectroscopic ellipsometry measurements are significantly more accurate than all the previous ones [84, 137, 138, 139, 140], from a simple Kramers-Kronig (KK)
transformation of their directly measured $\epsilon_1$ and $\epsilon_2$, it can be seen that these components do not form a KK-couple.

The first calculated optical spectra of CaF$_2$ by Gan et al. [64, 70], were obtained using uncoupled response calculations, i.e., without the inclusion of Coulomb and exchange-correlation contributions in the response calculation. Therefore these spectra can not show the exciton peak, and the overall comparison with the experimental data available [83, 84, 137, 138, 139, 140], was very poor. Recently this exciton peak was calculated by explicitly including the electron-hole interaction in the Green’s function (DFT/GW/BSE) approach by Benedict [122].

![Figure 8.2: Comparison of the calculated $\epsilon_2(\omega)$ for CaF$_2$; DFT-LDA vs. GW (left), and TDDFT vs. BSE (right).](image)

In Fig. 8.2, the GW and BSE results of Benedict [122] are compared with the DFT-LDA and TDDFT results respectively. By comparing the GW vs. BSE results, and the DFT-LDA vs. TDDFT results in Fig. 8.2, it is clear that the electron-hole interaction in CaF$_2$ is very strong. The calculated BSE spectrum, which does include the electron-hole interaction, were obtained by evaluating Eq. 8.25. The GW spectrum, which does not include the electron-hole interaction, were obtained by evaluating Eq. 8.17. In GW the excitations are calculated using only the vertical transitions between the independent hole and electron states. The DFT-LDA spectrum was calculated by setting the couplings matrix $K_{c\nu,k\nu^{'}}(\omega)$ in Eq. 8.28 to zero. Therefore it should give 'in principle’ the same result as the GW spectrum as calculated by Eq. 8.17, apart from a shift to lower energies, which accounts for the differences in energies ($\sim 4$ eV) between the GW and DFT-LDA wavefunctions. This shift between the DFT-LDA and GW spectra is exactly found, as can be seen in Fig. 8.2. The $\epsilon_2^{\text{TDDFT}}$ clearly resembles $\epsilon_2^{\text{BSE}}$ in Fig. 8.2, in particular in the region from 10-15 eV, and thus it should be concluded that the excitonic effects, that are obtained in CaF$_2$ using the BSE, are also properly handled in the TDDFT calculation, already within the ALDA. In the region above 15 eV, $\epsilon_2^{\text{TDDFT}}$ still differs from $\epsilon_2^{\text{BSE}}$, because there the correct description of the higher conduction bands becomes important and depends heavily on the method and accuracy of the calculation.

In Fig. 8.3 the $\epsilon_2^{\text{TDDFT}}$ is compared with several experiments [83, 84, 137]. The double
8.4. Calculations on Insulators

Figure 8.3: Comparison of the TDDFT calculated $\epsilon_2(\omega)$ for CaF$_2$ with experimentally measured $\epsilon_2(\omega)$ by Tousey (Ref. [137]), Stephan (Ref. [84]), and Barth (Ref. [83]).

peak structure around 13-14 eV, which was not found in the $\epsilon_2^{BSE}$, agrees well with the experimental findings of Stephan et al. [84].

8.4.2 $\alpha$-Quartz

$\alpha$-quartz has a hexagonal structure with the lattice constants $a$=4.9134 and $c$=5.4052 Å. The basis functions used in the SiO$_2$ calculation, are a combination of numerical atomic and Slater type orbitals. The 3Z2P NAO/STO basis (basis $V$ in the ADF-BAND program [37, 38]) consists of a triple zeta set augmented with two polarization functions. For the integration in reciprocal space, only 4 symmetry unique $k$ points (kspace 2 in the BAND program) were used, which was sufficient due to the large unit cell size, and consequently the small Irreducible Brillouin Zone (IBZ), and hence very small energy dispersion.

Bandstructure

The bandstructure for $\alpha$-quartz, as obtained in our DFT-LDA calculation, is shown in Fig. 8.4. The indirect band gap, as found in our LDA calculation, is $E_g^{\text{LDA}}$=5.92 eV ($\Gamma \rightarrow \Gamma$). This is considered to be an LDA underestimation, because the GW correction opens up the band gap to $E_g^{\text{GW}}$=10.1 eV [143]. In the current literature available the experimental band gap of SiO$_2$ is reported to be 9.0 eV [145, 146, 147], 8.9 eV [148]. The question of the exact experimental band gap of SiO$_2$ is still an issue which is not fully agreed on. The reason for this is that the optical absorption spectrum ($\epsilon_2$) is still not completely understood for several reasons. First of all, SiO$_2$ is a structurally quite complex material, it appears in many polycrystalline forms under different thermodynamical conditions ($\alpha$-quartz, $\beta$-quartz, $\beta$-tridymite, $\alpha$-cristobalite, $\beta$-cristobalite, keatite, coesite, and stishovite). Therefore it is experimentally hard to grow specific crystals. Secondly, SiO$_2$ has an excitonic resonance peak in the absorption spectrum very close to the absorption edge, which consequently makes the determination of the absorption edge very hard from experimental measurements. The absorption edge of SiO$_2$ is further influenced by
low absorption levels near the absorption threshold originating from direct transitions near $\Gamma$, which are formally symmetry forbidden [144].

Figure 8.4: The bandstructure of SiO$_2$

Density of states

The experimental DOS for the valence bands obtained using ultraviolet-photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS) can be found in the Refs. [147] and [149]. The complete DOS, as measured by x-ray emission spectroscopy, is given in Ref. [150]. The density of states resulting from our DFT calculation (Fig. 8.5) showed a similar structure as was found in the self-consistent pseudopotential calculation of Che-likowsky [151].

Figure 8.5: Density of States (DOS) of SiO$_2$

The features in the region $-0.81 \leftrightarrow -0.72$ a.u. (not shown in the Figs. 8.4 and 8.5) originate from the oxygen ($2s$) nonbonding state. The contributions in the energy region
−0.45 ↔ −0.28 (shown in Fig. 8.4, but not in Fig. 8.5) result from bonding states between the oxygen \((2p)\) and silicon \((3s, 3p)\) atomic orbitals. The nonbonding states on the oxygen \((2p)\) are found in the energy region \(-0.23 ↔ −0.11\) (as shown in the Figs. 8.4 and 8.5). The DOS for the conduction bands [the energy range starting from 0.11 a.u and higher] (as shown in Fig. 8.5) consisted of bonding states between the oxygen and the silicon atomic orbitals. These DFT results for the DOS of \(\alpha\)-quartz were very similar to the self-consistent pseudopotential results as calculated by Chelikowsky [151], and in good agreement with the experimentally found UPS and XPS [147, 149] results.

**Optical spectrum**

The static dielectric constant for electric fields with a polarization direction within the hexagonal plane, is determined in experiment, and found to be \(\epsilon^\text{Exp}\infty = 2.38\) [135]. In our TDDFT calculation we found \(\epsilon^\text{TDDFT}\infty = 2.03\), the same value which was found by Chang et al. [143] in their RPA calculation, where they took local field effects into account. This value of \(\epsilon^\text{RPA}\infty = 2.0\), was greatly enhanced, after taking the electron-hole interactions (the excitons) into account, to \(\epsilon^\text{BSE}\infty = 2.44\). The experimental optical spectrum [146] of \(\alpha\)-quartz shows four peaks, located at 10.3, 11.7, 14.0 and 17.3 eV. The first two are, according to the BSE calculations of Chang [143] clearly excitonic in nature, and are consequently only found in the BSE calculation. The TDDFT \(\epsilon_2\) for \(\alpha\)-quartz is shown in Fig. 8.6 up to \(\sim 10.5\) eV (because of convergence problems in the SCF procedure at higher photon energies), together with the GW and BSE results of Chang [143].

![Figure 8.6: Comparison of the calculated \(\epsilon_2(\omega)\) for SiO\(_2\) within TDDFT (solid line), BSE (dashed line), the GW theory (dotted line) and Experiment (dash-dotted line).](image)

As can be seen from Fig. 8.6, by comparing the GW with the BSE results, the first two peaks in the \(\epsilon_2\) for \(\alpha\)-quartz are excitonic in nature, although they appear to be shifted a little to lower energy when compared to experiment. It is also clear that, looking at the TDDFT results, the first excitonic peak in the absorption spectrum is found exactly at the experimental value of 10.3 eV, although much sharper and overestimated compared to experiment [146].
8.4.3 Gallium nitride

In the last few years also many theoretical [67, 68, 69, 122, 152, 153, 154, 155] and experimental [152, 154, 155, 156, 157] studies have been performed on GaN. This nitride occurs in the wurtzite (WZ) as well as in the zincblende (ZB) structure, and is a very interesting and challenging compound. First of all, it has a high ionicity like CaF$_2$ and short bond lengths. GaN may therefore find application in the blue-light-emitting diodes and lasers which operate in the blue and ultraviolet regime, or in high temperature transistors. Measurements of the optical properties of GaN have always been difficult, in reflectivity measurements, as well as in spectroscopic ellipsometry performed with synchrotron radiation. In the reflectivity measurements [155] there is an ambiguity in the Kramers-Kronig transformation between $\epsilon_1$ and $\epsilon_2$, and in the spectroscopic ellipsometry measurements [156, 157] the synchrotron light is contaminated by second-order radiation in certain energy regions. Furthermore, it is extremely difficult to grow high-quality GaN crystals, and due to the surface roughness the intensity is decreased in reflectivity and ellipsometry measurements. We used the experimental lattice constants in the calculations, which, for the WZ structure are: $a = 3.19$, $c = 5.189$ and $u = 0.375\text{Å}$ [66], while for the ZB structure the parameter is: $a = 4.54\text{Å}$ [159].

Bandstructure

The LDA band structures for GaN are depicted in Fig. 8.7 for in the WZ and the ZB structure. They have direct ($\Gamma_{1v} \rightarrow \Gamma_{1c}$) band gaps of $E_g^{\text{LDA}} = 2.24$ and 1.89 eV respectively, which is an underestimation of the experimental values, respectively $E_g^{\exp}(\text{WZ}) = 3.5$ [49] and $E_g^{\exp}(\text{ZB}) = 3.2$ [158] / 3.3 [159] eV.

![Figure 8.7: The bandstructures of GaN in the ZB (left) and the WZ structure (right).](image)

The bandstructures for both structures resembled those found in other calculations [68, 152, 153, 154, 155] apart from the LDA band gap mismatch.
Density of states

The DOS for GaN in the ZB and WZ structure are depicted in Fig. 8.8. The similarity between both DOS spectra is high.

![Figure 8.8: Density of States for GaN in the ZB (left) and the WZ (right) structure.](image)

Optical spectrum

The static dielectric constants $\epsilon_\infty$ for GaN calculated for both structures have been collected in Table 8.1, together with the lattice constants [66, 159], the experimental values [49, 87, 88] for $\epsilon_\infty$ and other theoretical results [66, 67, 68, 69]. Our result for the $\epsilon_\infty$ of GaN in the wurzite structure is found in better agreement with experiment than other theoretical calculations. For the zincblende structure, our calculated $\epsilon_\infty$ matches exactly the experimental value.

The dielectric function of GaN in the WZ structure can be resolved into two components, with the polarization field either parallel to the $z$ direction (c axis) [E∥c], or perpendicular to the $z$ direction [E⊥c].

![Figure 8.9: Comparison of the calculated $\epsilon_2(\omega)$ for GaN in the WZ structure [E∥c (left) and E⊥c (right)]. TDDFT (solid line), BSE (dashed line) and the GW theory (dotted line).](image)

In Fig. 8.9, the TDDFT results for E∥c are compared to the BSE and GW results of
Table 8.1: Optical dielectric constants for GaN in the wurtzite and the zincblende lattice structure

<table>
<thead>
<tr>
<th>GaN Structure</th>
<th>Lattice (Å)</th>
<th>This work</th>
<th>Exp.</th>
<th>Error</th>
<th>Other theory</th>
<th>Method</th>
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<td>0.30</td>
<td>5.2&lt;sup&gt;h&lt;/sup&gt;</td>
<td>5.7&lt;sup&gt;i&lt;/sup&gt;</td>
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<td>(u=0.375)</td>
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<td>5.5&lt;sup&gt;n&lt;/sup&gt;</td>
<td>0</td>
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<td>4.78&lt;sup&gt;k&lt;/sup&gt;</td>
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<sup>a</sup>In case of the wurtzite structure: $\epsilon_\infty = \bar{\epsilon}_\infty = \frac{1}{3}(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$

<sup>b</sup>$\Delta\epsilon_\infty = \epsilon_{zz} - \frac{1}{2}(\epsilon_{xx} + \epsilon_{yy})$

<sup>c</sup>UR: uncoupled response.

<sup>d</sup>FP: full potential; PP: pseudopotential; ASA: atomic-sphere approximation.

<sup>e</sup>PW: plane wave; LMTO: linearized muffin-tin orbitals; LCAO: linear combination of atomic orbitals.

<sup>f</sup>LF: local-field effects.

<sup>g</sup>Ref. [66]  
<sup>h</sup>Ref. [87]  
<sup>i</sup>Ref. [88]  
<sup>j</sup>Ref. [67]  
<sup>k</sup>Ref. [68]  
<sup>l</sup>Ref. [69]  
<sup>m</sup>Ref. [159]  
<sup>n</sup>Ref. [49]

Benedict [122]. The same comparisons are made in Fig. 8.10 for the $\epsilon_2$ of GaN in the ZB structure. Inspection of the Figs. 8.9 and 8.10 reveals the three major peaks in the absorption spectra for both structures of GaN. It can be seen from the absorption spectra, that the TDDFT results are more similar to the BSE results [122] than the GW results [68, 122, 155]. In particular the intensity and position of the first absorption peak fully agrees with the BSE results for both components ($E_\parallel c$ and $E_\perp c$) of the WZ structure. So, again, we find that the excitonic effects, for both structures of GaN, are also obtained in the TDDFT calculations.

Figure 8.10: Comparison of the calculated $\epsilon_2(\omega)$ for GaN in the ZB structure. TDDFT (solid line), BSE (dashed line) and the GW theory (dotted line).
8.5 Conclusions

In this chapter we investigated to what extent excitonic effects are included in time-dependent density-functional theory (TDDFT) within the adiabatic local density approximation (ALDA). First we briefly outlined the Green’s function approach (DFT/GW/BSE), and we showed the similarity between the Bethe-Salpeter equation and the corresponding TDDFT equations. Three wide band gap insulators, CaF$_2$, SiO$_2$ and GaN, were examined. We compared the calculated TDDFT optical spectra for these insulators with the experimental measurements, and also with the $c_2(\omega)$’s as calculated by DFT/GW/BSE. The optical absorption spectra calculated using TDDFT showed all the excitonic features that were obtained using BSE, and agreed very well with experiment. In conclusion we can say that, contrary to the the general assumption, TDDFT is quite capable of describing these excitonic effects, at least in the systems investigated here.