MASTER THESIS

Linear response functions of solids within time-dependent density functional theory (TDDFT)

by

Navid Abedi Khaledi

Supervisor:
Prof. Angel Rubio

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Chapter 1

Introduction

Many properties of materials can be defined in terms of response of the system to a perturbation. When in spectroscopic experiments an external field $F(r, \omega)$ is applied to a sample, the functional dependency of a physical property $\mathcal{P}[F]$ in terms of the perturbation is in general complex. If we assume that the perturbation is sufficiently weak, the response can be expanded as a power series of the applied field and we can define as “linear response” the first order term of this series. We call “linear response function” $\chi^{(1)}_{\mathcal{P} \rightarrow F}$ a function mapping the perturbation $F(r, \omega)$ and the physical property $\mathcal{P}$ in the linear response regime [1]:

$$\delta \mathcal{P}^{(1)}(r, \omega) = \chi^{(1)}_{\mathcal{P} \rightarrow F}(r, r', \omega) \delta F(r', \omega) \tag{1.1}$$

Due to the great number of applications in Physics and Engineering, a lot of linear response functions has been renamed like the polarizability $\alpha$, that connect the variation of the dipole moment of a finite systems to the application of an external dipole electric field, or the magnetic susceptibility, the first-order response of the magnetic moment of a system to the variation of a homogeneous magnetic field.

In this work we will start from a Density Functional Theory (DFT) calculation for a periodic system and then we will present an algorithm to calculate the linear response of periodic systems within Time-Dependent Density Functional Theory (TDDFT), using a real space representation of the electron wave functions and calculating the dynamics in real time. We will focus on the calculation in the Adiabatic Local Density Approximation of the dielectric function (and its inverse) in the long wave length limit.

From the dielectric function is possible to determine all the optical constants of the system that are valuable in a lot of applications, like the photoabsorption coefficient, that is measurable directly with optical absorption experiments in transmission, or other relevant physical quantities like the photon scattering amplitude per atom, the inelastic mean-free paths, or the Hamaker constants, useful to determine the distance sample-tip in tunnelling.
microscopy [2]. Although in literature methods based on Kohn Sham equations and LDA functional have given bad band gaps and bad results for the calculation of optical constants for solids, the purpose of realizing this calculation goes beyond the present results and is aimed at exploiting in the future its main interesting feature: this method indeed allows the entire frequency-dependent dielectric function to be calculated at once without needing the exchange correlation kernel, that will make this method very advantageous for beyond-GGAs orbital dependent functionals, like Meta-GGAs, that are supposed to improve the former mentioned TDDFT-ALDA results.

In the first part we will define the main theoretical framework of DFT and TDDFT, then we will introduce the linear response method that we used (the time propagation) for finite systems, and lastly we will introduce the adaptation of this method to solids, presenting the results for one very well known system, the C (diamond).
Chapter 2

Theory

2.1 Density Functional Theory (DFT)

Density functional theory (DFT) is a quantum mechanical modelling method used in Physics and Chemistry to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases. An analytical solution of the many-electron Schrödinger equation is not available, and a numerical solution, while perfectly possible in theory, is effectively impossible in practice for more than a handful of electrons due to the finite speed and memory of computers. In this section we will introduce density functional theory (DFT) as a mean of circumventing solution of the many-electron Schrödinger equation, since the properties of a many-electron system can be determined by using just functionals of the electronic density.

In this section we will use this references [3][4][5][6][7][8].

2.1.1 The Schrödinger equation

The ultimate goal of most approaches in solid state Physics and quantum Chemistry is the solution of the time-independent, non-relativistic Schrödinger equation

\[
\hat{H} \Psi_i(x_1, x_2, ..., x_N, R_1, R_2, ..., R_M) = E_i \Psi_i(x_1, x_2, ..., x_N, R_1, R_2, ..., R_M)
\]  
(2.1)

\(\hat{H}\) is the Hamiltonian for a system consisting of \(M\) nuclei and \(N\) electrons.

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 - \frac{1}{2} \sum_{A=1}^{M} \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}}
\]  
(2.2)
Here, $A$ and $B$ run over the $M$ nuclei while $i$ and $j$ denote the $N$ electrons in the system. The first two terms describe the kinetic energy of the electrons and nuclei. The other three terms represent the attractive electrostatic interaction between the nuclei and the electrons and repulsive potential due to the electron-electron and nucleus-nucleus interactions. (Note: throughout this section atomic units are used.)

### 2.1.2 Born-Oppenheimer approximation

Due to their masses the nuclei move much slower than the electrons so we can consider the electrons as moving in the field of fixed nuclei therefore the nuclear kinetic energy is zero and their potential energy is merely a constant. Thus, the electronic Hamiltonian reduces to

$$
\hat{H}_{\text{elec}} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_{i}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} = \hat{T} + \hat{V}_{\text{Ne}} + \hat{V}_{\text{ee}} \quad (2.3)
$$

The solution of the Schrödinger equation with $\hat{H}_{\text{elec}}$ is the electronic wave function $\Psi_{\text{elec}}$ and the electronic energy $E_{\text{elec}}$. The total energy $E_{\text{tot}}$ is then the sum of $E_{\text{elec}}$ and the constant nuclear repulsion term $E_{\text{nuc}}$

$$
\hat{H}_{\text{elec}} \Psi_{\text{elec}} = E_{\text{elec}} \Psi_{\text{elec}} \quad (2.4)
$$

$$
E_{\text{tot}} = E_{\text{elec}} + E_{\text{nuc}} \quad (2.5)
$$

where $E_{\text{nuc}} = \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$.

### 2.1.3 The variational principle for the ground state

When a system is in the state $\Psi$, the expectation value of the energy is given by

$$
E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.6)
$$

where $\langle \Psi | \hat{H} | \Psi \rangle = \int \Psi^{*} \hat{H} \Psi dX$.

The variational principle states that the energy computed from a guessed $\Psi$ is an upper bound to the true ground-state energy $E_{0}$. Full minimization of the functional $E[\Psi]$ with respect to all allowed $N$-electrons wave functions will give the true ground state $\Psi_{0}$ and energy $E[\Psi_{0}] = E_{0}$; that is

$$
E_{0} = \min_{\Psi \rightarrow N} E[\Psi] = \min_{\Psi \rightarrow N} \left\{ \Psi | \hat{T} + \hat{V}_{\text{Ne}} + \hat{V}_{\text{ee}} | \Psi \right\} \quad (2.7)
$$
2.1. DENSITY FUNCTIONAL THEORY (DFT)

For a system of \( N \) electrons and given nuclear potential \( V_{\text{ext}} \), the variational principle defines a procedure to determine the ground-state wave function \( \Psi_0 \), the ground-state energy \( E_0[N, V_{\text{ext}}] \), and other properties of interest. In other words, the ground state energy is a functional of the number of electrons \( N \) and the nuclear potential \( V_{\text{ext}} \):

\[
E_0 = E[N, V_{\text{ext}}] \tag{2.8}
\]

### 2.1.4 The Hartree-Fock approximation

Suppose that \( \Psi_0 \) (the ground state wave function) is approximated as an antisymmetrized product of \( N \) orthonormal spin orbitals \( \psi_i(x) \), each a product of a spatial orbital \( \phi_k(r) \) and a spin function \( \sigma(s) = \alpha(s) \), the Slater determinant

\[
\Psi_0 \approx \Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\psi_1(x_1) & \psi_2(x_1) & \cdots & \psi_N(x_1) \\
\psi_1(x_2) & \psi_2(x_2) & \cdots & \psi_N(x_2) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_1(x_N) & \psi_2(x_N) & \cdots & \psi_N(x_N)
\end{vmatrix} \tag{2.9}
\]

The Hartree-Fock approximation is the method whereby the orthogonal orbitals \( \psi_i \) are found that minimize the energy for this determinant form of \( \Psi_0 \):

\[
E_{HF} = \min_{\Psi_{HF} \rightarrow N} E[\Psi_{HF}] \tag{2.10}
\]

The expectation value of the Hamiltonian operator with \( \Psi_{HF} \) in given by

\[
E_{HF} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i,j=1}^{N} (J_{ij} - K_{ij}) \tag{2.11}
\]

\[
H_i = \int \psi_i^*(x) \left[ -\frac{1}{2} \nabla^2 - V_{\text{ext}}(x) \right] \psi_i(x) dx \tag{2.12}
\]

defines the contribution due to the kinetic energy and the electron-nucleus attraction and

\[
J_{ij} = \int \int \psi_i(x_1) \psi_j^*(x_1) \frac{1}{r_{1,2}} \psi_i^*(x_2) \psi_j(x_2) dx_1 dx_2 \tag{2.13}
\]

\[
K_{ij} = \int \int \psi_i^*(x_1) \psi_j(x_1) \frac{1}{r_{1,2}} \psi_i(x_2) \psi_j^*(x_2) dx_1 dx_2 \tag{2.14}
\]

de the integrals are all real, and \( J_{ij} \geq K_{ij} \geq 0 \). The \( J_{ij} \) are called Coulomb integrals, the \( K_{ij} \) are called exchange integrals. We have the property \( J_{ij} = K_{ij} \).

The variational freedom in the expression of the energy [Eq. (2.11)] is in the
choice of the orbitals. The minimization of the energy functional with the normalization conditions \( \int \psi_i^*(x)\psi_j(x)dx = \delta_{ij} \) leads to the Hartree-Fock differential equations:

\[
\hat{f}\psi_i = \epsilon_i \psi_i, \quad i = 1, 2, 3, ..., N
\]  

(2.15)

These N equations have the appearance of eigenvalue equations, where the Lagrangian multipliers \( \epsilon_i \) are the eigenvalues of the operator \( \hat{f} \). The Fock operator \( \hat{f} \) is an effective one-electron operator defined as

\[
\hat{f} = -\frac{1}{2} \nabla_i^2 - \sum_A Z_A \frac{1}{r_{iA}} + V_{HF}(i)
\]  

(2.16)

The first two terms are the kinetic energy and the potential energy due to the electron-nucleus attraction. \( V_{HF}(i) \) is the Hartree-Fock potential, the average repulsive potential experience by the i'th electron due to the remaining \( N - 1 \) electrons, and it is given by

\[
V_{HF}(x_1) = \sum_j^N (\hat{J}_j(x_1) - \hat{K}_j(x_1))
\]  

(2.17)

\[
\hat{J}_j(x_1) = \int |\psi_j(x_2)|^2 \frac{1}{r_{1,2}} dx_2
\]  

(2.18)

The Coulomb operator \( \hat{J} \) represents the potential that an electron at position \( x_1 \) experiences due to the average charge distribution of another electron in spin orbital \( \psi_j \). The second term in Eq. (2.17) is the exchange contribution to the HF potential. It has no classical analog and it is defined through its effect when operating on a spin orbital:

\[
\hat{K}_j(x_1)\psi_i(x_1) = \int \psi_j^*(x_2) \frac{1}{r_{1,2}} \psi_i(x_2) dx_2 \psi_j(x_1)
\]  

(2.19)

The HF potential is non-local and it depends on the spin orbitals. Thus, the HF equations must be solved self-consistently.

The Koopman’s theorem (1934) provides a physical interpretation of the orbital energies: it states that the orbital energy \( \epsilon_i \) is an approximation of minus the ionization energy associated with the removal of an electron from the orbital \( \psi_i \), i.e. \( \epsilon_i \approx E_N - E_{N-1} = -IE(i) \).

### 2.1.5 The electron density

The electron density is the central quantity in DFT. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables \( (x \equiv r, s) \)

\[
\rho(r) = N \int ... \int |\Psi(x_1, x_2, ..., x_N)|^2 ds_1 dx_2 ... dx_N
\]  

(2.20)
2.1. DENSITY FUNCTIONAL THEORY (DFT)

\( \rho(\mathbf{r}) \) determines the probability of finding any of the \( N \) electrons within a volume element \( d\mathbf{r} \).

**Some properties of the electron density:**

**(I)** \( \rho(\mathbf{r}) \) is a non-negative function of only the three spatial variables which vanishes at infinity and integrates to the total number of electrons:

\[
\rho(\mathbf{r} \rightarrow \infty) = 0 \quad \int \rho(\mathbf{r}) d\mathbf{r} = N
\]  

**(II)** \( \rho(\mathbf{r}) \) is an observable and can be measured experimentally, e.g. by X-ray diffraction.

**(III)** At any position of an atom, the gradient of \( \rho(\mathbf{r}) \) has a discontinuity and a cusp results:

\[
\lim_{r_i,A \rightarrow 0} [\nabla \rho(\mathbf{r}) + 2Z_A \bar{\rho}(\mathbf{r})] = 0
\]  

where \( Z \) is the nuclear charge and \( \bar{\rho}(\mathbf{r}) \) is the spherical average of \( \rho(\mathbf{r}) \).

**(IV)** The asymptotic exponential decay for large distances from all nuclei:

\[
\rho(\mathbf{r}) \sim \exp[-2\sqrt{2I}|\mathbf{r}|]
\]  

where \( I \) is the exact ionization energy.

### 2.1.6 The Thomas-Fermi model

The conventional approaches use the wave function \( \Psi \) as the central quantity, since \( \Psi \) contains the full information of a system. However, \( \Psi \) is a very complicated quantity that cannot be probed experimentally and that depends on \( 4N \) variables, \( N \) being the number of electrons. The Thomas-Fermi model is the first density functional theory (1927). Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

\[
T_{TF}[\rho(\mathbf{r})] = \frac{3}{10} \frac{(3\pi^2)^{2/3}}{2} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r}.
\]  

(2.24)

The energy of an atom is finally obtained using the classical expression for the nuclear-nuclear potential and the electron-electron potential:

\[
E_{TF}[\rho(\mathbf{r})] = \frac{3}{10} \frac{(3\pi^2)^{2/3}}{2} \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} - Z \int \frac{\rho(\mathbf{r})}{r} d\mathbf{r} + \frac{1}{2} \int \int \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{1,2}} d\mathbf{r}_1 d\mathbf{r}_2.
\]  

(2.25)

The energy is given completely in terms of the electron density! In order to determine the correct density to be included in Eq. (2.25), they employed a variational principle. They assumed that the ground state of the system is connected to the \( \rho(\mathbf{r}) \) for which the energy is minimized under the constraint of \( \int \rho(\mathbf{r}) d\mathbf{r} = N \).
2.1.7 The first Hohenberg-Kohn theorem

The first Hohenberg-Kohn theorem demonstrates that the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system.

This first theorem states that the external potential $V_{\text{ext}}(r)$ is (to within a constant) a unique functional of $\rho(r)$: since, in turn $V_{\text{ext}}(r)$ fixes $H$ we see that the full many particle ground state is a unique functional of $\rho(r)$.

and so that there cannot be two different $V_{\text{ext}}(r)$ that give the same $\rho(r)$ for their ground state. Thus, $\rho(r)$ determines $N$ and $V_{\text{ext}}(r)$ and hence all the properties of the ground state, for example the kinetic energy $T[\rho]$, the potential energy $V[\rho]$, and the total energy $E[\rho]$. Now, we can write the total energy as

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(r)V_{Ne}(r)d\mathbf{r} + F_{HK}[\rho], \quad (2.26)$$

$$F_{HK}[\rho] = T[\rho] + E_{ee} \quad (2.27)$$

This functional $F_{HK}[\rho]$ is the holy grail of density functional theory. If it were known we would have solved the Schrödinger equation exactly. And, since it is an universal functional completely independent of the system at hand, it applies equally well to the hydrogen atom as to gigantic molecules. $F_{HK}[\rho]$ contains the functional for the kinetic energy $T[\rho]$ and that for the electron-electron interaction, $E_{ee}[\rho]$. The explicit form of both these functional lies completely in the dark. However, from the latter we can extract at least the classical part $J[\rho]$,

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{r_{1,2}}d\mathbf{r}_1 d\mathbf{r}_2 + E_{ncl} = J[\rho] + E_{ncl}[\rho]. \quad (2.28)$$

$E_{ncl}$ is the non-classical contribution to the electron-electron interaction: self-interaction correction, exchange and Coulomb correlation. The explicit form of the functionals $T[\rho]$ and $E_{ncl}[\rho]$ is the major challenge of DFT.

2.1.8 The second Hohenberg-Kohn theorem

The second H-K theorem states that $F_{HK}[\rho]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density. This is nothing but the variational principle:

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \quad (2.29)$$

In other words this means that for any trial density $\tilde{\rho}(r)$, which satisfies the necessary boundary conditions such as $\tilde{\rho}(r) \geq 0$, $\int \tilde{\rho}(r)d\mathbf{r} = N$, and which is associated with some external potential $\tilde{V}_{\text{ext}}$, the energy obtained from
2.1. DENSITY FUNCTIONAL THEORY (DFT)

the functional of Eq. (2.26) represents an upper bound to the true ground state energy \( E_0 \). \( E_0 \) results if and only if the exact ground state density is inserted in Eq. (2.24).

### 2.1.9 The Kohn-Sham equations

We have seen that the ground state energy of a system can be written as

\[
E_0 = \min_{\rho \rightarrow N} \left( F[\rho] + \int \rho(r) V_N e dr \right)
\]

where the universal functional \( F[\rho] \) contains the contributions of the kinetic energy, the classical Coulomb interaction and the non-classical portion:

\[
F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho]
\]

Of these, only \( J[\rho] \) is known. The main problem is to find the expressions for \( T[\rho] \) and \( E_{ncl}[\rho] \). The Thomas-Fermi model provides an example of density functional theory. However, its performance is really bad due to the poor approximation of the kinetic energy. To solve this problem Kohn and Sham proposed in 1965 the approach described below [4]. They suggested to calculate the exact kinetic energy of a non-interacting reference system with the same density as the real, interacting one

\[
T_S = -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle \quad \rho_S(r) = \sum_i \sum_s |\psi_i(r,s)|^2 = \rho(r)
\]

where the \( \psi_i \) are the orbitals of the non-interacting system. Of course, \( T_S \) is not equal to the true kinetic energy of the system. Kohn and Sham accounted for that by introducing the following separation of the functional \( F[\rho] \)

\[
F[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho],
\]

where \( E_{XC} \), the so-called exchange-correlation energy is defined through Eq. (2.33) as

\[
E_{XC}[\rho] \equiv (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]).
\]

The exchange and correlation energy \( E_{XC} \) is the functional that contains everything that is unknown.

Now the question is: how can we uniquely determine the orbitals in our non-interacting reference system? In other words, how can we define a potential \( V_S \) such that it provides us with a Slater determinant which is characterized by the same density as our real system? To solve this problem, we write
down the expression for the energy of the interacting system in terms of the separation described in Eq. (2.33)

\[ E[\rho] = T_S[\rho] + J[\rho] + E_{XC}[\rho] + E_{Ne}[\rho] \]  

(2.35)

\[ E[\rho] = T_S[\rho] + \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{r_{1,2}} dr_1 dr_2 + \int V_{Ne}(r) dr = \]

\[ -\frac{1}{2} \sum_i \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \sum_i \sum_j \int \int |\psi_i(r_1)|^2 \frac{1}{r_{1,2}} |\psi_j(r_2)|^2 dr_1 dr_2 + E_{XC}[\rho] - \]

\[ - \sum_i \int \sum_A Z_A r_{1,A} |\psi_i(r_1)|^2 dr_1. \]  

(2.36)

The only term for which no explicit form can be given is $E_{XC}$. We now apply the variational principle and ask: what condition must the orbitals $\{\psi_i\}$ fulfill in order to minimize this energy expression under the usual constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The resulting equations are the Kohn- Sham equations:

\[ \left( -\frac{1}{2} \nabla^2 + \left[ \int \frac{\rho(r_2)}{r_{1,2}} + V_{XC}(r_1) - \sum_A Z_A r_{1,A} \right] \right) \psi_i = \left( -\frac{1}{2} \nabla^2 + V_S(r_1) \right) \psi_i = \epsilon_i \psi_i \]  

(2.37)

\[ V_S(r_1) = \int \frac{\rho(r_2)}{r_{1,2}} dr_2 + V_{XC}(r_1) - \sum_A Z_A r_{1,A} \]  

(2.38)

### 2.1.10 The local density approximation (LDA)

The local density approximation (LDA) is the basis of all approximate exchange-correlation functionals. At the center of this model is the idea of an uniform electron gas. This is a system in which electrons move on a positive background charge distribution such that the total ensemble is neutral.

The central idea of LDA is the assumption that we can write $E_{xc}$ in the following form

\[ E^{LDA}_{XC}[\rho] = \int \rho(r) \epsilon_{XC}(\rho(r)) dr \]  

(2.39)

Here, $\epsilon_{XC}(\rho(r))$ is the exchange-correlation energy per particle of an uniform electron gas of density $\rho(r)$. This energy per particle is weighted with the probability $\rho(r)$ that there is an electron at this position. The quantity $\epsilon_{XC}(\rho(r))$ can be further split into exchange and correlation contributions,

\[ \epsilon_{XC}(\rho(r)) = \epsilon_X(\rho(r)) + \epsilon_C(\rho(r)). \]  

(2.40)
The exchange part, \( \epsilon_X \), which represents the exchange energy of an electron in a uniform electron gas of a particular density, was originally derived by Bloch and Dirac in the late 1920’s

\[
\epsilon_X = -\frac{3}{4} \left( \frac{3\rho(r)}{\pi} \right)^{1/3}.
\]  

(2.41)

### 2.2 Time Dependent Density Functional Theory

With DFT we can calculate the ground-state properties of a system, but when we apply the time-dependent external potential to the system we need a theory to simulate the properties of this system. Runge and Gross, whose are establishing time-dependent density functional theory (TDDFT) and generalized the Hohenburg-Kohn theorem to the time-dependent densities and potential [9].

For doing calculation in this case we need to solve time-dependent Schrödinger equation

\[
i\frac{\partial}{\partial t} \Psi(r_1, r_2, ..., r_N, t) = H(r_1, r_2, ..., r_N, t) \Psi(r_1, r_2, ..., r_N, t) 
\]  

(2.42)

in this Hamiltonian we have time-dependent external potential \( v_{\text{ext}}(r, t) \).

For solving this equation we need the initial value of wave function \( \Psi(r, t_0) \), so we use the ground-state.

#### 2.2.1 The Runge-Gross theorem

In this theorem, two densities \( \rho(r, t) \) and \( \rho'(r', t') \) evolving from a common initial state \( \Psi(r_1, r_2, ..., r_N, t_0) \) under the influence of two potentials \( v(r, t) \) and \( v'(r, t) \), both taylor-expandable about the initial time \( t_0 \), eventually differ if the potentials differ by more than a purely time-dependent function, \( v(r, t) - v'(r, t) \neq c(t) \) [9].

#### 2.2.2 Time-dependent Kohn-Sham equation

Fictitious system of non-interacting electrons moving in an effective time-dependent potential \( v_{KS}(r, t) \) with the same density \( \rho(r, t) \) as the interacting system

\[
i \frac{\partial \varphi_j(r, t)}{\partial t} = \left[ -\frac{\nabla^2}{2} + v_{KS}(r, t) \right] \varphi_j(r, t) 
\]  

(2.43)

and the density is \( \rho(r, t) = \sum_{j=1}^{N} |\varphi_j(r, t)|^2 \).

The Kohn-Sham potential is conventionally separated in the following way

\[
v_{KS}(r, t) = v_{\text{ext}}(r, t) + v_H(r, t) + v_{xc}(r, t)
\]  

(2.44)
where \( v_H(\mathbf{r}, t) = \int d^3r' \rho(\mathbf{r}', t) \) is Hartree potential. \( v_{xc} \) is not given as the functional derivative of some other quantity, is not equal to static DFT.

The time-dependent Kohn-Sham equation are first order differential equations, i.e. they can only be solved for a given initial state \( \Phi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t_0) \), a slater determinant constructed out of N Kohn-Sham orbital at \( t = t_0 \). The \( xc \) potential \( v_{xc} \) is a functional of the entire history of \( \rho(\mathbf{r}, t) \), the initial interacting wave function \( \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t_0) \), and the initial Kohn-Sham wave function \( \Phi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t_0) \).

The Runge-Gross theorem ensures that \( v_{KS}(\mathbf{r}, t) \) is unique but not that it exists [10].

2.2.3 Adiabatic Approximations

We need to approximate \( v_{xc}(\mathbf{r}, t) \) which is a functional of the density at all times \( t' \) with \( t_0 \leq t' \leq t \), the initial many-body state and the initial Kohn-Sham state, i.e. \( \rho, \Psi_0, \Phi_0 \). Even if we start in the many-body and Kohn-Sham ground-states, \( v_{xc} \) remembers the density’s past and we say it has memory. This makes finding good approximations much more difficult than in DFT.

Adiabatic approximation neglect the dependence on the past and approximate \( v_{xc}(\mathbf{r}, t) \) to only depend on the density at time \( t \). Use \( \rho^{adi}_{xc}[\rho](\mathbf{r}) \) evaluated at \( \rho = \rho(\mathbf{r}, t) \) to obtain \( \rho^{adi}_{xc}(\mathbf{r}, t) \). The adiabatic approximation is valid if the time-dependent potential changes very slowly. The electrons remain in their instantaneous ground-state, i.e. at each time \( t \) they are in the ground-state corresponding to the potential at that time.

Using the adiabatic approximation any DFT functional can be used in TDDFT.

2.2.4 Comparison between DFT and TDDFT

(I) The both establish a one-to-one correspondence between densities and external potentials. And the most important variable in both is density.

(II) In DFT, the static Schrödinger equation is a second order differential equation in the space coordinates. It can be formulated as an eigenvalue problem

\[
H_{KS}(\mathbf{r}) \Phi_{KS}^i(\mathbf{r}) = \varepsilon_{KS}^i \Phi_{KS}^i(\mathbf{r}).
\]  

(2.45)

In contrast, in TDDFT, the time-dependent Schrödinger equation is a first-order differential equation in the time coordinate. The wave-function (or the density) thus depends on the initial state, which implies that the Runge-Gross theorem can only hold for a fixed initial state (and that the \( xc \) potential depends on that state) [11][12].

(III) In DFT, the ground-state of the system can be determined through
the minimization of the total energy functional

$$\langle \Phi | \hat{H} | \Phi \rangle = E[\rho]. \quad (2.46)$$

In TDDFT, there is no variational principle on the basis of the total energy for it is not a conserved quantity. There exists the quantum mechanical action

$$\int_{t_0}^{t_1} dt \langle \Phi(t) | i \partial_t - \hat{H}(t) | \Phi(t) \rangle = A[\rho]. \quad (2.47)$$

Equating the functional derivative of Eq. (2.47) in terms of $\rho(\mathbf{r}, t)$ to zero we arrive at the time-dependent Schrödinger equation. We can therefore solve the time-dependent problem by calculating the stationary point of the functional $A[\rho]$. In DFT, equating the functional derivative of Eq. (2.46) in terms of $\rho(\mathbf{r})$ to zero we arrive the minimum of $E[\rho]$. In TDDFT, is no minimum principle, but only a stationary principle.

(IV) In DFT, the density just depends on the space coordinate, but In TDDFT, the density depends on the time and space coordinates. The same difference holds for the potentials.
Chapter 3

Applications

3.1 Response method in TDDFT

3.1.1 Response function

In this section, we will show what is response function and, how it links an external perturbation to a physical observable. When we apply an external field $F(r,t)$ to the fully interacting many-body system, we can describe the response in terms of some physical observable $P$:

$$\Delta P = \Delta P_F[F].$$ (3.1)

If the field that we apply to the system is weak enough, we can expand the response as a power series with respect to the field strength. The first-order term of that series is called the linear response of the observable:

$$\delta P^{(1)}(r; t) = \int dt' \int d^3r' \chi^{(1)}_{P \leftarrow F}(r, r'; t - t') \delta F^{(1)}(r'; t').$$ (3.2)

where $\delta F^{(1)}(r'; t')$ is the first order of the field strength and $\chi^{(1)}_{P \leftarrow F}(r, r'; t-t')$ is the linear response function. We can simplify this convolution by moving to the frequency space:

$$\delta P^{(1)}(r; \omega) = \chi^{(1)}_{P \leftarrow F}(r, r'; \omega) \delta F^{(1)}(r'; \omega).$$ (3.3)

The linear response function $\chi^{(1)}_{P \leftarrow F}(r, r'; \omega)$ only depends on a single frequency $\omega$.

3.1.2 Linear density response

In TDDFT the most important response function is the linear density response function $\chi^{(1)}_{\rho \leftarrow \upsilon_{\text{ext}}}(r, r', t-t')$, that gives us the linear density response $\delta \rho^{(1)}(r, t)$ to an external scalar potential $\delta \upsilon^{(1)}_{\text{ext}}(r', t')$:

$$\delta \rho(r, t) = \int dt' \int d^3r' \chi^{(1)}_{\rho \leftarrow \upsilon_{\text{ext}}}(r, r', t - t') \delta \upsilon_{\text{ext}}(r', t').$$ (3.4)
If we know exactly the density response function \( \chi^{(1)}_{\mu=\nu,\text{ext}}(\mathbf{r}, \mathbf{r}', t - t') \), then we can calculate the first order response of all properties derivable from the density with respect to any scalar field.

If we have a Kohn-Sham system subjected to an external potential, it means that we can write the density changes in terms of the variation of the Kohn-Sham potential \( v_{KS}(\mathbf{r}, t) \):

\[
\delta \rho(\mathbf{r}, t) = \int dt' \int d^3r' \chi_{KS}(\mathbf{r}, \mathbf{r}', t - t') \delta v_{KS}(\mathbf{r}', t').
\]

(3.5)

where \( \chi_{KS}(\mathbf{r}, \mathbf{r}', t - t') \) is the Kohn-Sham linear density response function. The external potential \( v_{ext}(\mathbf{r}, t) \) and the effective Kohn-Sham potential \( v_{KS}(\mathbf{r}, t) \) are related to the Hartree and the exchange-correlation potentials:

\[
\delta v_{KS}(\mathbf{r}', t') = \delta v_{\text{ext}}(\mathbf{r}', t') + \delta v_H [\rho](\mathbf{r}', t') + \delta v_{\text{xc}} [\rho](\mathbf{r}', t'),
\]

(3.6)

where

\[
\delta v_H [\rho](\mathbf{r}', t') = \int dt'' \int d^3r'' \frac{\delta (t'' - t')}{|\mathbf{r}' - \mathbf{r}''|} \delta \rho(\mathbf{r}'', t'').
\]

(3.7)

And for the exchange-correlation potential variation we have:

\[
\delta v_{\text{xc}} [\rho](\mathbf{r}', t') = \int d^3 r'' \int t'' f_{\text{xc}} [\rho_{GS}](\mathbf{r}', \mathbf{r}'', t - t') \delta \rho(\mathbf{r}'', t'')
\]

(3.8)

where \( f_{\text{xc}} [\rho_{GS}](\mathbf{r}', \mathbf{r}'', t - t') \) is the exchange-correlation kernel defined as:

\[
f_{\text{xc}} [\rho_{GS}](\mathbf{r}', \mathbf{r}'', t - t') = \left. \frac{\delta v_{\text{xc}} [\rho](\mathbf{r}', t')}{\delta \rho(\mathbf{r}'', t'')} \right|_{\rho = \rho_{GS}}.
\]

(3.9)

The remarkable thing is that the exchange-correlation kernel \( f_{\text{xc}} [\rho_{GS}](\mathbf{r}', \mathbf{r}'', t - t') \) is a functional of only the ground-state density and can be evaluated before response calculation.

If we have the same external potential \( v_{\text{ext}}(\mathbf{r}, t) \), then the fully interacting density response should be equal to the Kohn-Sham density response. So, we can write:

\[
\int dt' \int d^3r' \chi(\mathbf{r}, \mathbf{r}', t - t') \delta v_{\text{ext}}(\mathbf{r}', t') = \int dt' \int d^3r' \chi_{KS}(\mathbf{r}, \mathbf{r}', t - t') \delta v_{\text{ext}}(\mathbf{r}', t') + \int dt' \int d^3r' \chi_{KS}(\mathbf{r}, \mathbf{r}', t - t') \times \int dt'' \int d^3r'' \frac{\delta (t'' - t')}{|\mathbf{r}' - \mathbf{r}''|} + f_{\text{xc}} [n_{GS}](\mathbf{r}', \mathbf{r}'', t - t'') \times \int dt''' \int d^3r''' \chi(\mathbf{r}'', \mathbf{r}'''', t''' - t'') \delta v_{\text{ext}}(\mathbf{r}'''', t '''').
\]

(3.10)
3.1. RESPONSE METHOD IN TDDFT

So, transforming from time to frequency we have:

\[
\chi(r, r', \omega) = \chi_{\text{KS}}(r, r', \omega) + \int d^{3}r'' \int d^{3}r''' \chi_{\text{KS}}(r, r'', \omega) \times \left[ \frac{1}{r'' - r'''} + f_{xc}[\rho_{\text{GS}}] (r'', r''', \omega) \right] \chi(r''', r', \omega).
\]

(3.11)

If frequency \(\omega\) is equal to a transition frequency of our system the change in the density is dramatic and \(\chi\) has a pole. \(\chi_{\text{KS}}\) has same poles at the transition frequencies of the Kohn-Sham system, that can be calculated from the knowledge of the occupied KS orbitals \(\varphi_{i}(r)\), the unoccupied KS orbitals \(\varphi_{a}(r)\) and the correspondent KS eigenvalues \(\varepsilon_{i}\) and \(\varepsilon_{a}\):

\[
\chi_{\text{KS}}(r, r', \omega) = \lim_{\eta \to 0} \sum_{a,i} (\rho_{i} - \rho_{a}) [\frac{\varphi_{i}^{\ast}(r) \varphi_{a}(r) \varphi_{i}(r') \varphi_{a}^{\ast}(r')}{\omega - (\varepsilon_{a} - \varepsilon_{i}) + i\eta} - \frac{\varphi_{i}(r) \varphi_{a}^{\ast}(r) \varphi_{a}(r') \varphi_{i}^{\ast}(r')}{\omega - (\varepsilon_{i} - \varepsilon_{a}) + i\eta}] .
\]

(3.12)

We can write the equation of the response in this way:

\[
\chi = (1 - \chi_{\text{KS}}f_{xc})^{-1} \chi_{\text{KS}},
\]

(3.13)

i.d. this equation can be used directly to calculate the fully interacting density response function from eigenvalues and eigenfunctions are the correspondent Kohn-Sham system [13].

3.1.3 Time-propagation method

In the time-propagation method, we propagate the time-dependent Kohn-Sham equation in the real-time, for example, by solving the following non-linear partial differential equation

\[
i \frac{\partial}{\partial t} \varphi_{k}(r, t) = \hat{H}_{\text{KS}}[\rho(r', t)](r, t) \varphi_{k}(r, t),
\]

(3.14)

for starting from initial state we put \(t=0\), then we have \(\psi_{k}(r, t = 0) = \phi^{0}_{k}(r)\), where \(\phi^{0}_{k}(r)\) is the ground-state Kohn-Sham wave function. Here we assume that the Kohn-Sham Hamiltonian \(\hat{H}_{\text{KS}}[\rho(r, t)]\) depends on the density \(\rho(r, t)\) at each instant of time and it is not related to the hole history of density.

When we do not apply any perturbation to our system, the system stays in the ground-state and the time-evaluation of the Kohn-Sham wave function is trivial: \(\psi_{k}(t) = \phi^{0}_{k} e^{-i\varepsilon_{k}^{0} t}\). And when we apply a weak time-dependent external perturbation, that time-evaluation of the Kohn-Sham wave function becomes nontrivial because of the non-linearity of the Kohn-Sham Hamiltonian. A general form of the external field with \(\omega\) frequency is:

\[
u_{\text{ext}}(r, t) = \lambda \nu_{\text{ext}}^{\text{cos}}(r) \cos(\omega t) + \lambda \nu_{\text{ext}}^{\text{sin}}(r) \sin(\omega t)
\]

(3.15)
CHAPTER 3. APPLICATIONS

or, rewriting in terms of the exponential:

\[ \psi_{\text{ext}}(r, t) = \lambda \psi_{\text{ext}}(r)e^{+i\omega t} + \lambda \psi_{\text{ext}}(r)e^{-i\omega t}, \quad (3.16) \]

where \( \lambda \) represents the magnitude of the perturbation. By applying an external potential to the time-dependent Kohn-Sham equation and propagate that in time, we can obtain physical observables from the time dependent expectation values. For example, if we apply a weak external delta pulse of a dipole electric field

\[ \psi_k(r, t = 0^+) = \exp \left\{ -i \int_0^{0^+} dt [H(t) - e r . K_\delta \delta(t)] \right\} \psi_k(r, t = 0^-) = \exp(i e r . K_\delta) \psi_k(r, t = 0^-), \quad (3.18) \]

and propagate the free oscillations in time. Then the time-dependent dipole moment is:

\[ \mu(t) = -e \int d^3 r \rho(r, t) \quad (3.19) \]

can be used to extract the dynamic polarizability tensor \( \alpha(\omega) \). The series expansion of the time-dependent dipole moment in frequency space is:

\[ \mu(\omega) = \mu(0) + \alpha(\omega)K_\delta(\omega) + o(K_\delta) \quad (3.20) \]

where \( \mu(\omega) \) is the Fourier transform of the time-dependent dipole moment along the direction \( \gamma \), and \( \mu(0) \) is the static dipole moment. We obtain

\[ \alpha(\omega) = \frac{1}{K_\delta} \int_0^\infty dt [\mu(\omega) - \mu(0^-)]e^{i\omega t} + o(K_\delta). \quad (3.21) \]

The imaginary part of the diagonal component of the dynamic polarizability \( \Im[\alpha(\omega)] \) is proportional to the absorption spectrum. The above equation includes an integral over infinite time. Obviously, infinite time-propagation is not possible in practice, and we have to add an artificial lifetime to the equation by introducing a decay \( e^{-\eta t} \):

\[ \alpha(\omega) = \frac{1}{K_\delta} \int_0^\infty dt [\mu(\omega) - \mu(0^-)]e^{-i\omega t}e^{-\eta t} + o(K_\delta). \quad (3.22) \]

which corresponds to force all excitations to decay back to the ground state with rate \( \eta \).
3.2 A real time and real space method for periodic systems

It has been proven that real-space methods are useful for calculating the linear response of finite system in time-dependent density functional theory [14][15]. But to use this methods with (infinite) periodic systems, we need to consider some modifications. For example applying a uniform electric field to a finite system is a trivial task: it’s sufficient to specify the certain desired (linear) potential inside the simulation box. But for periodic systems this cannot be done, because that would be incompatible with the periodic boundary conditions. (See picture 3.1)

We will show here that is straightforward to treat periodic systems in the real-time formulation of time dependent density functional theory simply by adding a vector potential within the Lagrangian.

The electromagnetic interaction is divided into a Coulomb field $V(r)$ that satisfies periodic boundary conditions in the unit cell and a vector potential $\hat{z}A(t)$. The vector potential is uniform, in the sense that it does not have any dependence on $r$. The electric field is then given by

$$E(r) = -\nabla V(r) - \hat{z} \frac{dA}{dt}$$

In these formal equations, we use units with $\hbar = c = 1$.

The Lagrangian that we have to write in order to include the dynamics of the vector potential is:

![Figure 3.1: One dimensional example of incompatibility of linear electric potential and Born Von Karman boundary conditions](image)
\[ L = \int d^3r \left( \sum_j \frac{1}{2m} |\nabla \phi_j / i - e A_\phi \phi_j|^2 - \frac{1}{8\pi} \nabla V(r) \cdot \nabla V(r) + \right. \\
\left. + e n(r)V(r) + e n_{ion}(r)V(r) + V_{ion}[(\rho(r,r')) + V_{xc}(r)] - \right. \\
\left. - \frac{\Omega}{2\pi} \left( \frac{dA}{dt} \right)^2 - i \int d^3r \sum_j \phi_j^* \frac{\partial \phi_j}{\partial t} \right) (3.23) \]

Here the \( \phi_j \) are the Bloch wave functions of the electrons, normalized so that \( \rho(r) = \sum_j |\phi_j(r)|^2 \) is the electron density. The volume of the unit cell is \( \Omega \). The pieces of the Lagrangian containing \( A \) are the Kinetic energy term (that with this add is gauge invariant), and the one derived from the static energy of the electromagnetic field

\[ \int d^3r |E|^2 = \int d^3r \left( \nabla V(r) \cdot \nabla V(r) - \left( \frac{d\phi_j}{dt} \right)^2 \right) . \]

The terms \( \int d^3r (en(r)V(r) + en_{ion}(r)V(r) + V_{ion}(r)) \) are the direct Coulomb interaction of the electrons and ionic interaction separated into a long range part that can be associated to an ionic charge density \( \rho_{ion}(r) \) and a short range part \( V_{ion}[\rho(r,r')] \). The latter depends on the full one-electron density matrix \( \rho(r,r') = \sum_j \phi_j^*(r)\phi_j(r') \) so in order to restore the gauge invariance we should apply the gauge operator directly to the density matrix: \( V_{ion,A} = V_{ion}[e^{-iA(z-z')}\rho(r-r')] \). Finally, the \( V_{xc} \) is the usual exchange-correlation energy density of density functional theory.

Imposing the Lagrangian to be stationary we can derive the equations of motion for \( \phi_j \) and \( A \) and the Poisson equation for \( V \). The dynamic equation for \( \phi_j \) is the time-dependent Kohn-Sham equation,

\[ -\frac{\nabla^2}{2m} \phi_j - \frac{e^2}{m} A \nabla \phi_j + \frac{e^2}{2m} A^2 \phi_j + \left( e V + \frac{\delta\nu_{ion}}{\delta n} + \frac{\delta\nu_{xc}}{\delta n} \right) \phi_j = i \frac{\partial \phi_j}{\partial t} . (3.24) \]

The equation for \( A \) is

\[ \frac{\Omega}{4\pi} \frac{d^2A}{dt^2} - \frac{e}{m} \sum_j \langle \phi_j | \nabla_z i | \phi_j \rangle + \frac{e^2}{m} A N_e + \frac{\delta}{\delta A} \int \Omega \nu_{ion} d^3r = 0 , (3.25) \]

where \( N_e = \int \Omega d^3r(n(r)) \) is the number of electrons per unit cell.

### 3.3 Procedure for determining the linear response

The procedure for calculating of the dielectric function is very similar to the corresponding calculation of dynamic polarizability of finite systems.
The link between the photo-absorption cross section $\sigma$ and the dynamical polarizability $\alpha$ is indeed given by: $\sigma(\omega) = \frac{4\pi}{c} \text{Im} \alpha(\omega)$. Indeed in solids the imaginary part of the dielectric function $\varepsilon(\omega)$ has the same role of $\alpha(\omega)$ for the calculation of the absorption spectrum. We can define $\varepsilon(\omega)$ in momentum space as the function that connects the total and external fields in linear response:

$$
\varepsilon(\omega) \equiv \lim_{q \to 0} \varepsilon(q, \omega) = \lim_{q \to 0} \frac{V_{\text{ext}}(q, \omega)}{V_{\text{tot}}(q, \omega)} \equiv \frac{V_{\text{ext}}(\omega)}{V_{\text{tot}}(\omega)}
$$

The procedure to calculate $\varepsilon^{-1}$ is the following: first we perform a static calculation with $A = 0$ to get the ground-state electron orbitals and the periodic Coulomb potential $V$. Then a sudden change in $A$ is applied so that $A(t = 0^+) = A_0$ which means applying a delta-duration electric field at $t = 0$, $\varepsilon(t) = -A_0 \delta t$. In the linear response regime, one can then determine the entire frequency dependence response in a single time-dependent calculation, which would not be the case if the system were perturbed in the usual way with an oscillatory external field. From the time-dependent evolution, we find the polarization electric field $\varepsilon(t) = -dA(t)/dt$. Once that the polarization electron field is calculated, from the definition 3.26 of dielectric function we can write the following relationship between the Fourier components of polarization and external electric fields:

$$
\frac{1}{\varepsilon(\omega)} = \frac{V_{\text{tot}}(\omega)}{V_{\text{ext}}(\omega)} = \frac{E_{\text{tot}}(\omega)}{E_{\text{ext}}(\omega)} = 1 + \frac{E_{\text{pol}}(\omega)}{E_{\text{ext}}(\omega)}
$$

So from the previous 3.27 we have in terms of the vector potential:

$$
\frac{1}{\varepsilon(\omega)} - 1 = \frac{1}{A_0} \int_{0^+}^{\infty} e^{i\omega t - \eta t} \frac{dA(t)}{dt} dt
$$

Here $\eta$ is a small quantity to establish the imaginary part of the response.

We will show here that we can derive a sum rule concerning the integral:

$$
\int_{0^+}^{\infty} \omega \text{Im} \varepsilon^{-1}(\omega) d\omega
$$

From the previous equation of the dielectric function $\varepsilon(\omega)$ 3.28 we have

$$
\int_{0^+}^{\infty} \omega \text{Im} \varepsilon^{-1}(\omega) d\omega = \frac{1}{A_0} \int_{0^+}^{\infty} \frac{dA}{dt} \text{Im} \int_{0^+}^{\infty} d\omega \omega e^{i\omega t - \eta t} = \frac{\pi}{2A_0} (\frac{d^2 A}{dt^2})_{t=0^+}.
$$

The second derivative in the last expression can be obtained also from the dynamical equation of the vector potential 3.25. At $t = 0^+$ the wave functions have not yet had time to change so $A(0^+) = A_0$ and $\langle \nabla_z \rangle = 0$. 

3.3. PROCEDURE FOR DETERMINING THE LINEAR RESPONSE
Then if the last term in 3.25 can be neglected,
\[ \frac{d^2 A}{dt^2} = -\frac{4\pi e^2 N_e A_0}{m\Omega}. \] (3.30)

So from eq. 3.29 and 3.30 the linear energy-weighted sum rule follows:
\[ \int_0^\infty \omega \text{Im} \epsilon^{-1}(\omega) d\omega = -\frac{2\pi^2 e^2 N_e}{m\Omega}. \] (3.31)

Note that in the time-dependent treatment this sum rule is satisfied if the last term of the Lagrangian equation 3.30 is zero, i.e. the sum rule is satisfied only for nonlocal pseudopotentials. Let us now see the example of the vector potential treatment in a simple model, namely the homogeneous electron gas. As mentioned before, when the field \( A_0 \) is applied, there is no immediate response to the operator \( \nabla \), since the wave function does not change at the instant \( t = 0 \). But in the Fermi gas the single-particle states are eigenstates of momentum so the response remains \( \langle \nabla \rangle = 0 \) for all time. Putting this in eq. 3.30, and dropping the pseudopotential term, the equation for \( A \) gives us simply the solution of an harmonic equation:
\[ A(t) = A_0 \cos \omega_{pl} t, \] (3.32)
where \( \omega_{pl} \) is the plasmon frequency,
\[ \omega_{pl}^2 = \frac{4\pi e^2 N_e}{m\Omega} = \frac{4\pi e^2 n}{m}. \] (3.33)

The dielectric function may now be calculated from equation 3.28. One obtains the familiar electron gas result
\[ \epsilon(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2}. \] (3.34)

### 3.4 Numerical details

The algorithm used is the one derived from finite systems in nuclear physics [16].

For our calculation we used a real time propagation of the wave functions \( \phi_j \) representing Bloch states on a periodic lattice, using as time propagator the approximated enforced time-reversal symmetry (aetrs) implemented in Octopus code [17].

Bloch’s theorem states that the energy eigenfunctions of Schrödinger equation in presence of a periodic potential may be written as the product of a plane wave envelope function and a periodic function \( u_{nk}(r) \) that has the same periodicity as the potential, so that:
\[ \phi_j \equiv \phi_{nk}(r) = e^{ikr} u_{nk}(r) \] (3.35)
3.5. RESULTS FOR DIAMOND(C)

So setting as boundary conditions for \( u_{nk}(r) \) the periodic boundary conditions (labelled by the Block momenta \( k \)), we have:

\[
\phi_{nk}(r + a) = \exp(iak)\phi_k(r) \quad (3.36)
\]

About the Hamiltonian: the Kohn-Sham operator is approximated by a finite-difference expansion on a real space grid as in [18]:

\[
\frac{\partial^2 \psi}{\partial x^2} = \sum_{n=-N}^{N} C_n \psi(x_i + nh, y_j, z_k) + O(h^{2N+2}) \quad (3.37)
\]

The periodic potential \( V(r) \) is calculated by Fourier transformation of the Poisson equation (this actually gives automatically the required periodicity to \( V(r) \)). In practice, many Bloch states are needed to obtain smooth dielectric functions. However, constructing the states takes much less time than for the same number of electrons in a finite system, because the Bloch states in a given band are automatically orthogonal.

Only the valence electrons are included explicitly; core electrons are treated by a pseudopotential.

The exchange-correlation energy of the electrons is calculated in the local density approximation following the prescription of Perdew and Zunger [19]. The presence of a vector gauge potential requires a modification in the pseudopotential calculation, as we said before. The \( A \)-dependence of \( \nu_{\text{ion}} \) is correctly treated simply by gauging the density matrix directly,

\[
\nu_{\text{ion, } A}(\rho(r, r')) = \nu_{\text{ion}}(e^{iA(z-z')}\rho(r, r')). \quad (3.38)
\]

The algorithm used, provided the time step is less than the inverse energy span of the Kohn-Sham operator, conserves the energy.

3.5 Results for diamond(C)

The system chosen for the calculation of the dielectric function in the linear response regime is a typical insulator: C (diamond). The diamond lattice is represented in our calculation by the conventional unit cell which contains 8 carbon atoms, as we can see in picture 3.2. The diamond structure indeed can be considered as the ensemble of two overlapping cubic FCC lattices shifted of \((a/4, a/4, a/4)\), where \( a = 6.746322 \) bohr is the lattice constant taken from experiment [20]. We remember that the wave functions of the four valence electrons of each Carbon atom are calculated explicitly while the core electrons are only treated implicitly by the pseudopotential.

For the pseudopotential: the local component of the angular momentum is \( l = 0 \), while the maximum component is \( l = 1 \). We use here a time-step \( \Delta t = 0.002 \) \( \hbar/\text{Ha} \). With a cubical unit cell and 8 Carbon atoms, there are
8 \times 4/2 = 16 \text{ occupied bands. The bands are actually two-fold degenerate because we have not exploited the symmetries that allow a smaller unit cell with two carbons. The convergence procedure that we used for the calculation follows: we converged the band gap and all the differences in the eigenvalues at k-point } \Gamma \text{ with respect to the spacing for a small k-points-grid (} 2 \times 2 \times 2 \text{). For solids we used spacings which are divisor of the lattice constant for preserving the periodic boundary conditions, so in order to converge the eigenvalues at the threshold of 0.1 eV we took a } 18^3 \text{ points lattice in real space which implies a mesh spacing of } \Delta x = a/18 b \approx 0.37 b. \text{ See picture } 3.3.

Then with the spacing found we converged again with respect to the k-points grid the differences in the eigenvalues and the indirect gap at the same threshold of 0.1 eV , finding that the converged grid is the } 8 \times 8 \times 8.\text{ (See picture } 3.4)\text{. The value of band gap found is } 4.25 \text{ eV, a value which is not very good in comparison with the experimental results (5.48 eV), but is quite good in comparison to other LDA calculations in literature (see [21]). For finding the appropriate value of the vector potential field applied we checked that the sum rule } 3.31 \text{ was actually satisfied.}

We can see in picture } 3.6 \text{ the results for the inverse of the dielectric function of diamond(C) calculated by Octopus code [17]. The qualitative behaviour of the Real and Imaginary part of } \varepsilon(\omega)^{-1} \text{ (dimensionless) calculated in picture } 3.6 \text{ are good if compared with experimental results from 0 to 25 eV. Indeed if we derive from this the dielectric function (by matrix inversion) and we compare with experimental results, we can see}
3.5. RESULTS FOR DIAMOND(C)

Figure 3.3: Convergence of the band gap with respect to the spacing for diamond on a small k-points grid (2x2x2)

Figure 3.4: Convergence of the band gap with respect to the k-points grid for C(diamond)
that we can reproduce a maximum of the imaginary part of the dielectric function at 11.35 eV versus experimental data of 11.71 eV (approx. 3.5 % of difference), while the calculated absolute value is equal to 20.10 eV versus an experimental result of 18.46 eV (approx 8.9 % of difference) (see picture 3.7).

For what concerns the pick in the optical region of the Imaginary part of the dielectric function, this seems to be an artefact due to low-energies noise in the optical region of the Inverse dielectric function and we verified that it can be simply eliminated by increasing the number of k-points from 8x8x8 to 12x12x12.

The problem is that we were only able to verify the convergence in time till a total propagation of 100 a.u. as we can in see in picture 3.8, but in the observed interval of time the result seems well converged. Previously calculations performed with bigger time-steps (0.05 \( \hbar/\text{Ha} \)) or bigger applied fields showed a lot of noise for observed interval of time of 500 a.u., so we decided to use these parameters.
Figure 3.5: Sum rule for the second derivative of the applied vector potential $A(t)$ for three different values of the applied field $A_0$: in the three cases the value of $\frac{1}{A_0} \frac{d^2 A(t)}{dt^2}$ is equal for $t \to 0$. 
Figure 3.6: Real and Imaginary part of the inverse of the dielectric function of diamond(C) calculated on a 8x8x8 k-points grid, in comparison to experimental data of Ref.[22]
Figure 3.7: Real and Imaginary part the dielectric function of diamond(C) calculated on a 8x8x8 k-points grid, in comparison to experimental data of Ref.[22]
Figure 3.8: Time convergence of the Imaginary part of the inverse dielectric constant: till the time observed the convergence seems good, being the rms of the distance between each point of the curve at 74.2 and the ones at 100.4 a.u. (after 26.2 a.u.) is approximately 0.016.
Chapter 4

Conclusions

In this thesis we presented a DFT-LDA ground state calculation for the periodic system C(diamond) and the results for a real time-real space method within TDDFT-ALDA for the linear response (dielectric function and its inverse) of the same system. The ground state results are not in good agreement with experiments for the absolute value of the indirect band gap (as expected), but gave results in good agreement with the ones found in literature by LDA calculations. This means that at least for the ground state we have fulfilled an important test to verify that our calculations for periodic systems are correct (and the results showed were also good for small k-points sampling, like 4x4x4 grids).

For what concerns the results of the linear response method in real time and real space within TDDFT proposed, we are satisfied of the qualitative results of both the Imaginary part and the Real part of the Inverse dielectric function since they reproduce results of the same precision of other results presented in literature [2]. However more investigation is needed to optimize the parameters of the calculation, especially for what is related to the time step and the total time interval of observation, since for time-steps bigger than the one chosen in this work we obtained noisy results for the same calculated dielectric function. Being the noise problem connected to the time-step, probably time propagators different from “aetrs” (approximated enforced time reversal symmetry) are needed for this purpose, and surely the implementation of k-points symmetries is crucial to speed up the calculations.

The next step will be studying new systems, before passing to take into account ionic movement and new functionals which showed good results for optical constant in solids (see Tran-Blaha Meta-GGA functional ([21]) ). Moreover, with this method it will be possible to include naturally nonlinear optical corrections generalizing the method for finite systems proposed by Takimoto, Villa and Rehr ([23]).
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