Practical session IX
ABINIT I
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Introduction

We will learn in this first lesson how to use ABINIT, in order to get and analyze some physical properties of a solid: the total energy, the lattice constant, the density of states, and the Kohn-Sham bandstructure. The Kohn-Sham eigenvalues and eigenstates are actually the ingredients that the program DP needs to calculate the optical spectra.

ABINIT is a pseudopotential plane wave package which computes the total energy, the charge density, and the electronic structure of periodic systems composed of electrons and nuclei. The program is based on density functional theory (DFT) in the Kohn-Sham scheme. All information about the ABINIT package can be found in the ABINIT's Homepage (http://www.abinit.org). The fundamentals of DFT can be found elsewhere (see DFT paper by Ulf Von Barth). DFT reduces the initial interacting many-particle problem to an *exact* non-interacting single-particle problem. The conceptual advantage is evident. Approximations occur later. Here we point out some approximations used while studying solids with DFT:

- **The choice of the k-point mesh.** An ideal crystal is invariant under translations by any of the vectors defining the direct Bravais lattice. If periodic boundary conditions are applied to the unit cell, remembering the Bloch's theorem, the quantum numbers which label the eigenstates are the wavevector **k** belonging to the first Brillouin zone (BZ) and the band index n. The bandstructure, i.e. the dispersion of the energy levels in **k**-space, is usually depicted for different n's along some high symmetry **k**-lines in the BZ. The number of allowed **k**-points is equal to the number of cells composing the crystal. In the limit of an infinite crystal, this gives a infinite set of points. Thus, when dealing with sums over the **k** points – as in the calculation of a key-quantity like the charge density n – the sum is turned into an integral over the BZ:

$$n(\mathbf{r}) = \frac{\Omega_{\text{cell}}}{(2\pi)^3} \sum_{n}^{\text{occ}} \int_{\text{BZ}} d^3k \, |\phi_{n,\mathbf{k}}(\mathbf{r})|^2 \,, \tag{1}$$

where $\phi_{n,\mathbf{k}}(\mathbf{r})$ are the Kohn-Sham orbitals and Ω_{cell} is the volume of the primitive cell. In practice, to perform a numerical calculation, the integral must be discretized over a set of $N_{\mathbf{k}}$ weighted **k**-points:

$$n(\mathbf{r}) = \sum_{n}^{\text{occ}} \sum_{i=1}^{N_{\mathbf{k}}} w_i \, |\phi_{n,\mathbf{k}_i}(\mathbf{r})|^2 \,, \tag{2}$$

where the (lattice dependent) weights w_i and points $\mathbf{k}_i$ are chosen to reproduce the integral as accurately as possible, by using the smallest number of points. If the function to be integrated is periodic and symmetric in the reciprocal coordinates, the so-called *special points* can be chosen by exploiting the symmetry properties of the crystal. The introduction of the concept of special points is due to Baldereschi in 1973. This idea was further elaborated by Chadi and Cohen and, later, by Monkhorst and Pack. Their methods are now widely used. A Monkhorst-Pack (MP) set consists in points equally spaced in the BZ, that are not related to each other by any symmetry operation. In comparison with an arbitrary grid of points, which does not reflect the symmetries of

the BZ, the MP set reduces drastically the number of points necessary to attain a specific precision in calculating integrals. We will see in the following examples that to solve the integrals occurring in the calculations of optical properties, it is more convenient to use a shifted Monkhorst-Pack grid. Convergence with respect to the **k**-point set must be checked carefully, both for the total energy and for the optical spectra.

- **The cutoff of the plane wave basis.** When studying an infinite system composed of a repeated periodic unit, the most natural choice for the expansion of the one-particle wavefunction $\phi_i = \phi_{n,\mathbf{k}_i}$ is a plane wave basis. In fact, with the help of the Bloch's theorem we can write:

$$\phi_{n,\mathbf{k}_i}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_{\text{cell}}}} e^{i\mathbf{k}_i \cdot \mathbf{r}} \sum_{\mathbf{G}} c_{n,\mathbf{k}_i}(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}} = e^{i\mathbf{k}_i \cdot \mathbf{r}} u_{n,\mathbf{k}_i}(\mathbf{r}),\qquad(3)$$

where $u_{n,\mathbf{k}_i}(\mathbf{r})$ has the same periodicity of the crystal lattice and $\mathbf{G}$ is a reciprocal lattice vector. The choice of a plane wave basis presents some advantages:

- – It simplifies the evaluation of derivatives and integrals, making it easy to calculate the matrix elements of the Hamiltonian.
- – Fast Fourier transforms (FFT) can be used to move rapidly from the direct to the reciprocal space and vice-versa.
- – Plane waves form a complete and orthonormal set, independent of the atomic positions.
- – The truncation of the infinite basis set is given by a cutoff in energy:

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \le E_{\text{cutoff}},\qquad(4)$$

which is linked to the number of plane waves N_{PW} in the basis by the relation

$$N_{\text{PW}} \propto \Omega_{\text{cell}} \left(E_{\text{cutoff}}\right)^{3/2}.\qquad(5)$$

Convergence of the total energy can be controlled without ambiguity by increasing the cutoff. In applications to spectroscopy, the absolute convergence of the total energy is not very important, the most important quantities being instead energy differences. Energy differences converge more rapidly than the energy itself, so it is possible to achieve convergence – in our case to about a few meV – with a relatively low cutoff compared to total energy converged calculations.

- **The pseudopotential approximation.** In the solids we are interested in, core electrons are rather frozen in their atomic configuration, and do not take part in the chemical bond. The idea of the pseudopotential method is to mimic the effect of core electrons on valence electrons by means of an effective (pseudo) potential, which reproduces the same valence eigenvalues and scattering properties of the real atom. The pseudopotential technique has the double advantage of decreasing the cutoff energy (the pseudowavefunctions are much softer in the core region) and to include a reduced number of electrons (only valence electrons). A plane wave basis set is then particularly suitable to develop the soft pseudowavefunction. Concerning the theory of pseudopotentials, we refer the reader to the rich literature on the subject. In the present tutorial calculations, we use Hamann and Trouiller-Martins norm-conserving pseudopotentials, which were generated with the fhi98PP package.

To conclude, we remind another important approximation in ground state DFT calculations:

- **the choice of the exchange-correlation potential**. In the following, we will use the local density approximation (LDA), which consists in expressing the functional dependence of the exchange-correlation energy on the density with a simple dependence on the local value of the density. It is defined by:

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r})\,\varepsilon_{xc}(n(\mathbf{r}))\,d\mathbf{r}, \tag{6}$$

where ε_{xc} is the exchange-correlation energy for a particle in an interacting homogeneous electron gas, known with a very high precision from Monte Carlo simulations. LDA gives good results in semiconductors.

For curiosity, the steadily growing importance of DFT is witnessed by an interesting paper appeared recently in the e-Print archive cond-mat0407137. This paper presents a quantitative analysis of citations for all publications in Physical Review journals from July 1893 to June 2003. The two most cited articles are the Kohn & Sham (1st) and Hohenberg & Kohn (2nd) papers about DFT. Many other papers related to our previous discussion (pseudopotentials, **k**-points sets, LDA, …) can be found in the top 100.

We are ready to start the practical class on the use of ABINIT to determine the bandstructure of crystalline solids. As a first, simple, example we will work with bulk silicon.

Objectives

- Prepare an input file for ABINIT, defining all the necessary parameters.

- Study the convergence of the ground state energy with respect to the cutoff energy.

- Determine the relaxed lattice constant.

- Output and plot the bandstructure and the density of states (DOS).

- Create the "∗_KSS" file containing complete information on the Kohn-Sham bandstructure and pseudopotentials used.

Tasks

1. **Convergence of the total energy with respect to the cutoff energy**.

   Move to the directory ∼/solids/ground_state/. There you will find the file "gs.files". The different lines have the meaning:

   - the name of the main input file (silicon-gs.in),

   - the name of the main output file (silicon-gs.out),

   - the root names for the other input files (si_i),

   - for the other output files (si_o),

   - and for the temporary files (si_t),

   - the names of the pseudopotential files (si_h.cpi).

   Edit the main input file "silicon-gs.in" and give a look at the input variables and their explanations. Additional information on the input variables are available at
   http://www.abinit.org/ABINIT/Infos_v4.1/keyhr.htm.

You are going to run a convergence study with respect to the planewave cutoff energy. In a real calculation, we should also check the convergence with respect to the **k**-point grid. In this case, the selected **k**-point grid assures an error on the total energy smaller than a few meV, that is sufficient for our purposes. To start the run type:

```
>abinis < gs.files > gs.log
```

This run should last a few minutes.

Read thoroughly the output file "silicon-gs.out" to understand how the information is organized. Then print the total energy as a function of the kinetic energy cutoff.

Can you answer the following questions?

Q1. What distinguishes the 10 datasets?

Q2. How many SCF cycles were needed to have the tolerance criterion (toldfe) satisfied?

Q3. How many **k**-points are used for the integration of the charge density over the Brillouin zone?

Q5. Which cutoff energy assures an error for the total energy smaller than 10 meV?

Q4. What can you say about the convergence of the eigenvalue differences at a given k-point?

For the calculation of optical spectra, the pseudopotential approximation gives an error of the order of 0.1 eV ($\simeq$ 0.004 Hartree). Therefore we estimate that a cutoff of 7.5 Hartree is enough as it allows the energy differences to be converged better than this error.

2. **Determination of the relaxed lattice constant**. The equilibrium structural parameters (i.e. the Bravais lattice type and the lattice constants) can be determined *ab initio*, by inspecting the minimum of the total energy. With ABINIT, we can run the automatic optimization of the cell volume. The main input file is "silicon-relax.in". The list of files is in "relax.files".

What are the new variables with respect to the previous run? Check their use on the ABINIT web page. To start the run type:

```
>abinis < relax.files > relax.log
```

This run should last a few minute.

Read the output file.

Q1. What are the residual stresses?

Q2. What is the theoretical lattice constant?

Q3. Which is the percentage error with respect to the experimental lattice constant (5.431 Ångström at 25 degrees Celsius)?

In the following steps we will use the theoretical lattice constant that we have just calculated.

3. **Calculation of the bandstructure and the density of states**. We now run again a total energy calculation at the theoretical lattice constant. The run associated to the first dataset produces two additional output files, the file "'*_DEN" containing the electron density and the file "*_DOS" containing the density of states. In the run associated to the second dataset, we build the KS Hamiltonian using the charge density stored in the file "*_DEN" and we diagonalize it along some high symmetry directions in the BZ.

The main input file is "silicon-bands.in" and the file names are in "bands.files".

Q1. Which parameters are set in the input file to get the additional output files "*_DEN" and "*_DOS" ?

To start the run type:

```
>abinis < bands.files > bands.log
```

Print the density of states. Extract the bandstructure from the file "silicon-bands.out" using the script "abi-bands". Plot the Kohn-Sham bandstructure. It is well known that the Kohn-Sham eigenvalues are not quasiparticle energies. However, in the case of silicon, in spite of the strong underestimation of the band gap (0.65 eV smaller than the quasi-particle gap), the band dispersion and width are in agreement with quasiparticle GW calculations. Thus, quasiparticle bands can be easily reproduced by applying a "scissor operator", i.e. shifting the conduction bands rigidly upwards.

4. **Creation of the "∗_KSS" file**. Using the charge density calculated in the previous run (link the "∗_DEN" file to an input file "si_i_DEN"), produce the "∗_KSS" file, that contains information on the pseudopotentials and the eigenstates at the **k**-points needed for the calculation of the spectra. The input file is "silicon-kss256ks.in". To start the run type:

```
>abinis < kss.files > kss.log
```

Analyze the output file and the file "kss.log":

Q1. What is exactly contained in the "∗_KSS" file?

The KSS file will be our starting point for the calculation of spectra.

Comments

Introduction

In lessons V, VI, and VII, we will use time-dependent density functional theory (TDDFT) to calculate the absorption spectra of solids. Any property which depends only on the density, can be obtained (in principle exactly) by the Kohn-Sham formalism. Here we are interested in excitation energies and polarizabilities within linear response (although TDDFT can, of course, also describe non-linear response), which leads to some simplifications. In the following we remind the key concepts of the theory.

The starting point are the time-dependent Kohn-Sham equations:

$$i\frac{\partial}{\partial t}\varphi_i(\mathbf{r},t) = \left[-\frac{\nabla^2}{2} + v_{KS}(\mathbf{r},t)\right]\varphi_i(\mathbf{r},t); \tag{7}$$

$$n(\mathbf{r},t) = \sum_i^{occ}|\varphi_i(\mathbf{r},t)|^2$$

The solutions of Eq. (7) are the time dependent Kohn-Sham orbitals which yield the true charge density $n(\mathbf{r},t)$.

Linear response theory can be applied to study the effect of a small perturbation $V_{ext}(\mathbf{r},t)$ on the system. In the linear approximation the induced charge density is related to the external potential

$$n_{ind}(\mathbf{r},t) = \int d^3rdt'\chi(\mathbf{r},\mathbf{r}',t-t')V_{ext}(\mathbf{r}',t') \tag{8}$$

via the response function $\chi(\mathbf{r},\mathbf{r}',t-t')$, also called polarizability.

In the (TD)KS-scheme it is also possible to describe the response of the system (i.e. in terms of induced charge density) to an *effective* total potential V_{tot}, given by

$$V_{tot}(\mathbf{r},t) = V_{ext}(\mathbf{r},t) + V_H(\mathbf{r},t) + V_{xc}(\mathbf{r},t), \tag{9}$$

via

$$n_{ind}(\mathbf{r},t) = \int d^3rdt\chi^0(\mathbf{r},\mathbf{r}',t-t')V_{tot}(\mathbf{r}',t') \tag{10}$$

where the independent-particle polarizability χ^0 is the linear response of the fictitious Kohn-Sham system (non-interacting one), and has the well known form

$$\chi^0(\mathbf{r},\mathbf{r}',\omega) = \sum_{vc}\frac{(f_v - f_c)\phi_v^*(\mathbf{r})\phi_c(\mathbf{r})\phi_c^*(\mathbf{r}')\phi_v(\mathbf{r}')}{\omega - (\varepsilon_c - \varepsilon_v) + i\eta}, \tag{11}$$

directly translated in frequency domain. The damping factor η is also used for a Lorentzian broadening of χ^0. Here f_v and f_c are Fermi occupation numbers, ε_c and ε_v are KS eigenvalues, and the sums run over all KS orbitals (continuum states included). The two response functions χ and χ^0 are related by Eq. (9), giving

$$\chi = \frac{\delta n}{\delta V_{ext}} = \frac{\delta n}{\delta V_{tot}}\frac{\delta V_{tot}}{\delta V_{ext}} = \chi^0\left[\frac{\delta V_{ext}}{\delta V_{ext}} + \frac{\delta V_H}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta V_{ext}}\right] =$$

$$= \chi^0\left[1 + \frac{\delta V_H}{\delta n}\frac{\delta n}{\delta V_{ext}} + \frac{\delta V_{xc}}{\delta n}\frac{\delta n}{\delta V_{ext}}\right] = \chi^0 + \chi^0(v + f_{xc})\chi$$

or, more explicitly,

$$\chi(\mathbf{r},\mathbf{r}',\omega) = \chi^0(\mathbf{r},\mathbf{r}',\omega) +$$

$$+ \iint d\mathbf{r}'' d\mathbf{r}''' \left\{ \chi^0(\mathbf{r},\mathbf{r}'',\omega) \left[v(\mathbf{r}'',\mathbf{r}''') + f_{\mathrm{xc}}(\mathbf{r}'',\mathbf{r}''',\omega) \right] \chi(\mathbf{r}''',\mathbf{r}',\omega) \right\}. \quad (12)$$

The quantity

$$f_{\mathrm{xc}}(\mathbf{r},\mathbf{r}',t,t') = \frac{\delta V_{\mathrm{xc}}[n](\mathbf{r},t)}{\delta n(\mathbf{r}',t')}$$

has been introduced. It is called exchange correlation kernel and takes into account all dynamical exchange and correlation effects to linear order in the perturbing potential. The appeareance of the variation of the Hartree and exchange-correlation potentials in the response function comes from the fact that the total perturbation acting on the system is calculated self-consistently.

Of course, the exact time dependent exchange-correlation potential and kernel are unknown and realistic calculations rely on some approximations. A widely used approximation is the adiabatic local density approximation (TDLDA), in which f_{xc} is taken as the (ω-independent, i.e. adiabatic) functional derivative of the static LDA exchange-correlation potential

$$f_{\mathrm{xc}}^{TDLDA}(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \frac{\partial V_{\mathrm{xc}}^{LDA}(n(\mathbf{r}),\mathbf{r})}{\partial n(\mathbf{r})}. \quad (13)$$

The approximation chosen for the static potential V_{xc} determines the ground state, and hence χ^0. In principle the exchange-correlation kernel should always be the functional derivative of the exchange-correlation potential used to calculate the ground state, if one wants the sum rules to be fulfilled.

The TDLDA systematically fails in the description of absorption spectra of solids. The problem is the incorrect asymptotic behavior of the adiabatic local density exchange-correlation potential, which decays exponentially instead of having the correct $1/r$ tail. Several attempts have been proposed to overcome these problems. Recently, Reining *et al.* [Phys. Rev. Lett. **88**, 066404 (2002)] have shown that a *static long-range contribution* (LRC) of the form

$$f_{xc}(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = -\delta_{\mathbf{G},\mathbf{G}'}\alpha/|\mathbf{q}+\mathbf{G}|^2 \quad (14)$$

can simulate the strong continuum exciton effect in the absorption spectrum of bulk Si ($\mathbf{q}$ is a vector in the first Brillouin zone (BZ), $\mathbf{G}$ and $\mathbf{G}$' are reciprocal lattice vectors, and α is a material dependent parameter).

In Fourier space, the independent-particle polarizability (11) is written as

$$\chi^0(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{2}{\Omega} \sum_{v,c,\mathbf{k}} (f_{c,\mathbf{k}+\mathbf{q}} - f_{v,\mathbf{k}}) \frac{\langle v,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\rangle \langle c,\mathbf{k}+\mathbf{q}|e^{i(\mathbf{q}+\mathbf{G}')\cdot\mathbf{r}'}|v,\mathbf{k}\rangle}{\omega - (\varepsilon_{c,\mathbf{k}+\mathbf{q}} - \varepsilon_{v,\mathbf{k}}) + i\eta},$$

$$\chi^0(\mathbf{q},\mathbf{G},\mathbf{G}',\omega) = \frac{2}{N_{\mathbf{k}}} \sum_{v,c,\mathbf{k}} \frac{(f_{c,\mathbf{k}+\mathbf{q}} - f_{v,\mathbf{k}}) \tilde{\rho}_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}) \tilde{\rho}_{vc\mathbf{k}}^*(\mathbf{q},\mathbf{G}')}{\omega - (\varepsilon_{c,\mathbf{k}+\mathbf{q}} - \varepsilon_{v,\mathbf{k}}) + i\eta}, \quad (15)$$

where the one-particle states are Bloch wave functions, labeled by wave vector $\mathbf{k}$ and band index $v(c)$.[1] The sum over spins is responsible for the factor 2. The response function is normalized with the volume Ω of the system which reads $\Omega = \Omega_{\mathrm{cell}} \cdot N_{\mathbf{k}}$, i.e. number of k-points times the volume of the unit cell.

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[1] v (or c) stands for valence (or conduction) band index if the system is a semiconductor or an insulator.

The polarization matrices $\tilde{\rho}_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}) = \langle v,\mathbf{k}|e^{-i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\rangle$ have also been introduced to simplify the notation.

In order to connect the macroscopic (measurable) optical quantities and the microscopic electronic structure, we need to define a dielectric function ε. In the linear approximation, the effective potential V_{tot} is related to the external potential V_{ext} via

$$V_{\text{tot}}(\mathbf{r},\omega) = \int d^3 r \varepsilon^{-1}(\mathbf{r},\mathbf{r}',\omega) V_{\text{ext}}(\mathbf{r}',\omega) \tag{16}$$

where the inverse dielectric function ε^{-1} acts as a screening for the external potential. From the previous equation and the Eqs. (9) and (8) one can easily find the connection between the dielectric function and the polarizability. However, the portion of screening that has to be included in ε^{-1}, depends on the probe (different probes will be "screened" by different parts of the response function). We have to read that in two steps:

1 The external perturbation V_{ext} produces an induced charge density in the system $n_{\text{ind}} = \chi V_{\text{ext}}$ with χ as response function. When V_{ext} can be considered to be classical, χV_{ext} depends only on the nature of the system (in our case, a gas of interacting electrons, so $\chi = (1 - \chi^0 v - \chi^0 f_{\text{xc}})^{-1}\chi^0$).

2 The induced charge creates a screening, described by ε^{-1} which depends on the nature of the perturbation to be screened. If the probe is a test-particle, it has no exchange-correlations effects with the responding electron gas. On the contrary an electron (test-electron) "feels" not only an induced classical potential vn_{ind}, but also an induced exchange-correlation potential $V_{\text{xc}} = f_{\text{xc}}n_{\text{ind}}$. Therefore

$$\varepsilon_{\text{TP}}^{-1} = 1 + v\chi \tag{17}$$

$$\varepsilon_{\text{TE}}^{-1} = 1 + v\chi + f_{\text{xc}}\chi \tag{18}$$

for the test-particle and test-electron cases, respectively.

In this lesson, we deal with the test-particle dielectric matrix, hence in reciprocal space,

$$\varepsilon_{\mathbf{G},\mathbf{G}'}^{-1}(\mathbf{q},\omega) = \delta_{\mathbf{G},\mathbf{G}'} + v_{\mathbf{G}}(\mathbf{q})\chi_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega). \tag{19}$$

It is useful at this point to define the crystal local fields. A solid which possesses lattice-potential symmetry is non-homogeneous on the microscopic scale, even when it is characterized by a cubic symmetry group which yields isotropic optical properties. When an external perturbing field of small wave vector $\mathbf{q}$ and frequency ω is applied to the system, the local field will in general contain "Bragg reflected" terms, i.e. dependent on the wave vector $\mathbf{q}+\mathbf{G}$, where $\mathbf{G}$ is a reciprocal lattice vector. These microscopically varying terms fluctuate on the wavelength of the interatomic spacing. The frequency ω is not affected, as time is homogeneous. The difference between the local and the macroscopic field constitutes the local-field corrections in the electromagnetic response.

Let us consider an electric field $\mathbf{E}$ incoming on a non-homogeneous medium. In the linear approximation polarization effects are described by the electric displacement vector $\mathbf{D}$:

$$\mathbf{D}(\mathbf{q}+\mathbf{G},\omega) = \sum_{\mathbf{G}'}\varepsilon_{\text{mic}}(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}';\omega)\mathbf{E}(\mathbf{q}+\mathbf{G}',\omega). \tag{20}$$

We are interested in a relation which, in the limit of a negligible $\mathbf{q}$, considers only macroscopic quantities:

$$\mathbf{D}_{\text{M}}(\omega) = \varepsilon_{\text{M}}(\omega)\mathbf{E}_{\text{M}}(\omega). \tag{21}$$

The macroscopic dielectric tensor can be related to the inverse of the microscopic dielectric matrix:

$$\varepsilon_M(\omega) = \lim_{\mathbf{q}\to 0} \left.\frac{1}{\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)}\right|_{\mathbf{G}=\mathbf{G}'=0}. \tag{22}$$

The difference between a homogeneous and a non-homogeneous medium lies in the off-diagonal terms. In direct space this means that the microscopic dielectric function $\varepsilon(\mathbf{r},\mathbf{r}')$ depends explicitly on the positions $\mathbf{r}$ and $\mathbf{r}'$, and not simply on the distance $|\mathbf{r}-\mathbf{r}'|$.

If the medium were homogeneous, the macroscopic dielectric function would be

$$\varepsilon_M = \lim_{q\to 0}\varepsilon_{\mathbf{G}=0,\mathbf{G}'=0}, \tag{23}$$

i.e. the spatial average of the microscopic dielectric function. In case of isotropic media, the direction in which the limit of the small $\mathbf{q}$ vector has to be taken is insignificant.

Absorption and electron energy loss spectra (EELS) are related to the macroscopic dielectric function through:

$$\text{Abs} = \Im\{\varepsilon_M\} \qquad ; \qquad \text{EELS} = -\Im\left\{\frac{1}{\varepsilon_M}\right\}.$$

We can now summarize the steps leading to the determination of an optical spectrum when using the DP code.

1) **A ground state calculation** is usually done in the DFT framework, where a reasonable exchange-correlation potential V_{xc} has been chosen, e.g. the V_{xc}^{LDA}. From this first step one obtains the ground state electronic structure in terms of the (ground state) wavefunctions ϕ_i and eigenvalues ε_i.

   Approximations involved: $V_{xc}[n](\mathbf{r}) \approx V_{xc}^{LDA}(n(\mathbf{r}))$ and pseudo-potentials. Moreover, the convergence of the calculations with respect to the **k**-points and the dimension of the plane wave basis must be assured.

2) **The Independent-Particle polarizability** χ^0 can be built using wavefunctions and eigenvalues obtained in the previous step, via Eq. 15.

   Approximations involved: None, except the linear response framework.

3) **The full polarizability** χ can then be obtained from $\chi = (1 - \chi^0 v - \chi^0 f_{xc})^{-1}\chi^0$.

   Approximations involved: f_{xc}. The simplest choice, namely the random phase approximation (RPA), is to put the kernel to zero $f_{xc}^{RPA} = 0$. The TDDLA $f_{xc}^{TDLDA} = \delta(\mathbf{r} - \mathbf{r}')\frac{\partial V_{xc}^{LDA}(n(\mathbf{r}),\mathbf{r})}{\partial n(\mathbf{r})}$ is another possibility. Here we will also see the application of the α/q^2 kernel.

4) **The dielectric function**, calculated as $\varepsilon^{-1} = 1 + v\chi$, permits one to obtain both absorption and EELS via the macroscopic function $\varepsilon_M = 1/\varepsilon_{00}^{-1}$.

   Approximations involved: None.

Before concluding this paragraph, two remarks are necessary.

1st observation: the crucial step of the previous summary is clearly the third one. In Eq. (12) two terms have to be included. The first – and known – term is the Coulomb potential. The second term – the *unknown* f_{xc} – is the key of TDDFT, and its goal is to reproduce all the quasi-particle and excitonic effects, which are not contained in the RPA (which is the starting point, since $f_{xc}^{RPA} = 0$).

2ⁿᵈ observation: the TDDFT scheme we have used here, the most convenient to deal with solids, is based on the linear response framework, it works in the Fourier space and in frequency domain. Another difference with respect to real-space real-time TDDFT, where one lets the density $n(\mathbf{r})$ evolve according to $V_{\text{ext}}(\mathbf{r},t)$, maintaining the self-consistency between $n(\mathbf{r})$ and $V_{\text{ext}}(\mathbf{r},t)$, is that here it is quite natural to decouple the ground state calculation from that one of the response. Mathematically that means that not necessarily $f_{\text{xc}} = \frac{\partial V_{\text{xc}}}{\partial n}$. Here this constitutes an advantage because one can calculate the ground state using a reasonable V_{xc}, e.g. the LDA one.

Objectives

- Prepare an input file for DP, defining all the necessary parameters.

- Output and plot an absorption spectrum.

- Study the convergence of the spectrum with respect to the number of bands, the number of plane waves in the wavefunctions, the dimension of the dielectric matrix, the set of **k**-points.

Tasks

- **Calculation of a simple RPA spectrum.** Move to the directory ~/solids/response/Si/. You will find the file README. In this file you will find all the information you need to create an input file and run the program. Now move in the subdirectory RPA and open the file "dp-start.in" and check if you understand the meaning of all variables. Link the KSS file created by ABINIT to an input file "si.kss". Then run the program:

  ```
  >dp -i dp-start.in -k si.kss > dp.out
  ```

  In the file "dp.out" you can find a summary of the information contained in the "dp.in" and "si.kss" files, and you can check if the different steps of the calculation have been completed correctly. The results are in the files "out*.eps". Can you answer the following questions?

  Q1. What is the dimension of the dielectric matrix? What happens if you run again the program after setting the dimension of the dielectric matrix in the input file to 1?

  Q2. Is a scissor operator used?

  Q3. Which xc kernel is used?

  Q4. How many **k**-points are used?

  Consider the two files "outlf.eps" and "outnlf.eps".

  Q5. Can you understand by reading the legend included at the beginning of the file what they contain?

  Plot the imaginary part and the real part of the dielectric function of silicon and compare with the experimental spectrum (you find the curves in the xmgrace files). Try to change the artificial broadening of the spectrum using the utility "broad":

  ```
  >broad outlf.eps
  ```

  A reasonable broadening is usually about 0.1-0.2 eV.

- **Convergence of a simple RPA spectrum.** The set of shifted **k**-points that we are using have already been tested to assure the convergence of the spectra. Check the convergence with the number of bands and the number of planewaves in the wavefunction starting from the absorption

spectrum without local fields, in the energy range up to 6 eV. Once you have found the converged values for nbands and npwwfn, then check the convergence of the local fields, by changing the dimension of the dielectric matrix npwmat.

Q6. Were the variables in "dp-start.in" large enough to obtain a converged absorption spectrum?

In the directories ~/solids/response/"other material" input and KSS files for other simple semiconductors are available. Choose another material and calculate its RPA optical spectra.

Comments

Objectives

- Compare the spectra obtained within RPA or with a TDLDA xc kernel.

- Understand the origin of the peaks through the comparison with the bandstructure and density of state plots.

- Calculate an EELS spectrum.

Tasks

- **Calculation of a simple TDLDA spectrum**. Move to the directory ∼/solids/response/Si/TDLDA/. Create an input file to run the TDLDA calculation of the optical response. You can use as an example the input file for the RPA calculation. Note that the number of bands and plane waves which give a converged RPA spectrum should also give a converged TDLDA spectrum. Only the convergence with the dimension of the dielectric matrix must be checked.

  - Q1. Is it necessary to take a larger dielectric matrix?

  Compare the TDLDA absorption spectrum with the RPA one.

  - Q2. What can you conclude about the effect of the xc kernel for the spectrum of silicon within TDLDA?

  - Q3. Can you understand which transitions contribute to the peaks, by inspecting the plots of the bandstructure and the density of states?

- **Calculation of a simple EELS spectrum**. EELS and absorption are closely related spectra, both carrying information about the electronic response of the system. EELS is traditionally interpreted as being dominated by collective plasmon excitations, whereas single particle-hole excitations (essentially joint density-of-states) control the absorption spectra. This can be understood easily in the independent particle picture, since the imaginary part of the Fourier transform of Eq. (23) is proportional to $1/\omega^2 \sum_{v,c} |\langle \psi_v | \mathbf{v} | \psi_c \rangle|^2 \delta(\varepsilon_c - \varepsilon_v - \omega)$, where $\mathbf{v}$ is the velocity operator, and the sum runs over occupied (valence) and unoccupied (conduction) states ψ_v, ψ_c with energy ε_v and ε_c, respectively. Instead, since $-\mathrm{Im}\{1/\varepsilon_M\} = \mathrm{Im}\{\varepsilon_M\}/(\mathrm{Re}\{\varepsilon_M\}^2 + \mathrm{Im}\{\varepsilon_M\}^2)$, the structure in EELS is mainly given by regions where both the real and the imaginary part of ε_M are close to zero, that is the classical condition for a collective (plasmon) mode.

  Move to the directory ∼/solids/response/Si/EELS/. The input file "dp-eels.in" is already there. The convergence parameter have been increased with respect to the absorption spectrum calculation. In particular, the number of bands is increased, as the plasmon peak appears at about 17 eV. Run DP as usual. All the information necessary to calculate the EELS is inside the macroscopic dielectric function. To transform the dielectric function in "outlf.eps" in the EELS function, the utility "eps2eels" can be used as follows:

```
>eps2eel outlf.eps
```
The new file "outlf.eel" contains the EELS. You can broaden the curve with the utility "broad" as usual.

- Q1. How do the RPA and TDLDA EELS spectra compare to the experiment?

Comments

Practical session XIII
DP III
LECTURERS: SILVANA BOTTI, VALERIO OLEVANO
September 5, 2004 ■ 14h30m-16h00m

Objectives

- Calculate spectra with the α/q^2 xc-kernel.

- Observe the effects on the spectra due to variations of α.

Tasks

- **Calculation of a simple spectrum with the α/q^2 xc-kernel**. Move to the directory ∼/solids/response/Si/ALPHA/. Create an input file to run the calculation of the optical response using the α/q^2 xc-kernel. You can use as an example the input file for the RPA calculation. Remind that the quasiparticle eigenenergies are needed. For these simple semiconductor materials the application of a scissor operator is usually sufficient [2]. The parameters which give a converged RPA spectrum are good also for this calculation. Calculate spectra for different negative values of α and compare the imaginary part of ε_M to the experimental absorption spectrum.

    - Q1. What can you observe when the absolute value of α increases from 0 to 2?
    - Q2. What is the value which gives the best agreement with experiment?
    - Q3. How does the real part of the dielectric function compare to the experiment for this optimal value of α?

- **Scaling of α with respect to the dielectric constant**. Do not forget that in the directory ∼/solids/response/other_material input files for other simple semiconductors are available. You can play with other materials by calculating the value of α which gives the best agreement with experiment. Using the table of dielectric constants below, it is possible to establish the dependence of α on the dielectric constant.

Tabela 1: Dielectric constant of some semiconductors.

Si	GaAs	AlAs	Diamond	SiC
11.4	10.6	8.2	5.65	6.5

Comments

I want to thank Francesco Sottile for parts of the introduction to lesson V taken from his Ph. D. thesis. For more information, the pdf file of the thesis can be found at http://theory.polytechnique.fr/people/sottile/sottile.html.

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[2] For Silicon soenergy must be set to 0.6 eV, for GaAs 0.8 eV, for AlAs 0.9 eV, for SiC the file 'SiC.gw' containing GW corrections is given.