Hands-On DP I

From ABINIT to DP

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Introduction

In this preliminary short lesson we will revise how to generate a KSS file using ABINIT. You are supposed to be already familiar with the use of ABINIT 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. For more information see the third lesson of the ABINIT tutorial at http://www.abinit.org/documentation/helpfiles/for-v5.7/tutorial/lesson_3.html. The Kohn-Sham eigenvalues and eigenstates are actually the principal ingredients needed by the program DP and they can be stored in the KSS file. A description of the procedure to create a KSS file can be also found in the tutorial GW of ABINIT at http://www.abinit.org/documentation/helpfiles/for-v5.7/tutorial/lesson_gw1.html Before starting we propose a summary of the main approximations used to study solids within ABINIT+DP:

- **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 $\mathbf{k}$ belonging to the first Brillouin zone (BZ) and the band index n. The bandstructure, i.e. the dispersion of the energy levels in $\mathbf{k}$-space, is usually depicted for different n's along some high symmetry $\mathbf{k}$-lines in the BZ. The number of allowed $\mathbf{k}$-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 $\mathbf{k}$ points – as in the calculation of a key-quantity like the charge density n – the sum is turned into an integral over the BZ:

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

  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 $\mathbf{k}$-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:

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

  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:

$$\frac{1}{2} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cutoff}} \,, \tag{4}$$

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

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

    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 slightly smaller cutoff compared to the one necessary for converged total energy calculations.

- **The pseudopotential approximation.** We are interested in valence electrons, 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 essentially 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). Concerning the theory of pseudopotentials, we refer the reader to the rich literature on the subject. In the present tutorial calculations, we use LDA norm-conserving pseudopotentials (both of Hamann and Trouiller-Martins type), which were generated with the fhi98PP package. Many pseudopotentials of different kind, ready to be used, are available at the page http://www.abinit.org/downloads/psp-links.

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:

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

  where $\epsilon_{\rm xc}$ 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 few years ago 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 finally ready to start the practical class on the use of ABINIT to prepare a KSS file. We will assume that all the convergence tests (energy cutoff, k-points grid) and the optimization of the lattice parameters have already been performed (see the third lesson of the ABINIT tutorial). As a first, simple, example we will work with bulk silicon. For the calculation of optical spectra, it can be estimated that the pseudopotential approximation gives an error of the order of 0.1 eV ($\simeq$ 0.004 Hartree). Therefore a cutoff of 8 Hartree is enough for our purposes, as it allows the energy differences to be converged more than an order of magnitude better than this error.

Objectives

- Prepare an input file for ABINIT, defining all the necessary parameters.
- Create the "∗_KSS" file containing complete information on the Kohn-Sham bandstructure and pseudopotentials used.

Tasks

1. **Creation of the "∗_KSS" file**. You can have a fast look at the input file (if you are familiar with the calculation of a bandstructure you will not find many differences). For more details on the input variables you can check the section 1.b "Generating the Kohn-Sham band structure: the KSS file" of the Tutorial GW of ABINIT. Using the charge density calculated in first dataset (stored in the file "si_DS1_o_DEN"), in the second dataset a non-self consistent calculation is performed to 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 any spectra.

Comments

Hands-On DP II

DP I

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Introduction

We are ready to use time-dependent density functional theory (TDDFT) to calculate the absorption spectra of solids. Any property which depends only on the density (in this case the time-dependent 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). Linear response leads to some useful simplifications. In the following we remind the key concepts of the theory.

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

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

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

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 $V_{\mathrm{ext}}(\mathbf{r},t)$ on the system. In the linear approximation the induced charge density is related to the external potential

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

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

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

via

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

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

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

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

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

or, more explicitly,

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

The quantity

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

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 appearance 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 $f_{\rm xc}$ is taken as the (ω-independent, i.e. adiabatic) functional derivative of the static LDA exchange-correlation potential

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

The approximation chosen for the static potential $V_{\rm xc}$ 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 (For a detailed description and references we refer to the theoretical classes!) 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). More sophisticated approaches derived from Many-Body Perturbation Theory (MBPT) have been also able to reproduce bound excitons, or the hydrogen-like excitonic series in the photoemission gap of a rare gas solid (See Practical Session V).

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

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

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

where the one-particle states are Bloch wave functions, labeled by wave vector $\mathbf{k}$ and band index $v(c)$.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. The polarization matrices $\tilde{\rho}_{vc\mathbf{k}}(\mathbf{q},\mathbf{G}) = \left\langle v,\mathbf{k}|\mathrm{e}^{-\mathrm{i}(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|c,\mathbf{k}+\mathbf{q}\right\rangle$ 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

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

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

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 $v n_{\mathrm{ind}}$, but also an induced exchange-correlation potential $V_{\mathrm{xc}} = f_{\mathrm{xc}} n_{\mathrm{ind}}$. Therefore

$$\epsilon^{-1}_{\mathrm{TP}} = 1 + v\,\chi \tag{17}$$

$$\epsilon^{-1}_{\mathrm{TE}} = 1 + v\,\chi + f_{\mathrm{xc}}\chi \tag{18}$$

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

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

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

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 $\mathbf{D}$:

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

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

$$\mathbf{D}_{\rm M}(\omega) = \epsilon_{\rm M}(\omega)\mathbf{E}_{\rm M}(\omega)\,. \tag{21}$$

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

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

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 $\epsilon(\mathbf{r},\mathbf{r}')$ 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

$$\epsilon_{\rm M} = \lim_{q\to 0} \epsilon_{\mathbf{G}=0,\mathbf{G}'=0}\,, \tag{23}$$

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:

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

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

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

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

   Approximations involved: None.

Before concluding this paragraph, two remarks are necessary.

1st observation: In the case of solids the crucial step of the previous summary is the third one. In fact, most of the times a simple LDA ground state calculation is able to give satisfying results. In Eq. (12) two terms have to be included. The first – and known – term is the Coulomb potential. The second term – the *unknown* $f_{\rm xc}$ – 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 $f_{xc}^{\rm RPA} = 0$).

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 $V_{\rm ext}(\mathbf{r}, t)$, maintaining the self-consistency between $n(\mathbf{r})$ and $V_{\rm ext}(\mathbf{r}, t)$, 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 $f_{\rm xc} = \frac{\partial V_{\rm xc}}{\partial n}$. Here this "inconsistency" can constitute an advantage because one can calculate the ground state using a reasonable $V_{\rm xc}$, e.g. the LDA one and worry only about finding good approximations for $f_{\rm xc}$.

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 ∼/Tutorial_dp/input/response/Si/. Together with this tutorial you can find the file list_of_variables. 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∗.mdf". Can you answer the following questions?

  Q1. What is the difference between the variables npwmat and matsh? And the variables npwwfn and wfnsh?

Q2. 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?

Q3. Is a scissor operator used?

Q4. Which xc kernel is used?

Q5. How many **k**-points are used?

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

Q6. 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 in: ∼/Tutorial_dp/input/response/Si/graphs-results-to-compare). Try to change the artificial broadening of the spectrum using the utility "broad":
>`broad outlf.mdf`
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/wfnsh, then check the convergence of the local fields, by changing the dimension of the dielectric matrix through npwmat/matsh.

  Q7. Were the variables in "dp-start.in" large enough to obtain a converged absorption spectrum?

  In the directories ∼/Tutorial_dp/input/response/"other material" input files for other simple semiconductors are available. In the directory ∼/Tutorial_dp/input/create-extra-kss input files to create kss files for other simple semiconductors are also available. Choose another material and calculate its RPA optical spectra.

Comments

Hands-On DP III

DP II

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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 EEL spectrum.

Tasks

- **Calculation of a simple TDLDA spectrum**.
  Move to the directory ∼/Tutorial_dp/input/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 make the dielectric matrix larger to get a converged spectrum ?

  Compare the TDLDA absorption spectrum with the RPA one.
  - Q2. What can you conclude about the effect of the TDLDA xc kernel for the spectrum of silicon?
  - 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 EEL spectrum**. EELS and absorption are closely related spectra, both carrying information about the electronic response of the system. EEL 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 $1/\omega^2 \sum_{v,c} |\langle\psi_v|\mathbf{v}|\psi_c\rangle|^2 \delta(\epsilon_c - \epsilon_v - \omega)$, 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 $-\mathrm{Im}\{1/\epsilon_\mathrm{M}\} = \mathrm{Im}\{\epsilon_\mathrm{M}\}/(\mathrm{Re}\{\epsilon_\mathrm{M}\}^2 + \mathrm{Im}\{\epsilon_\mathrm{M}\}^2)$, 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 ∼/Tutorial_dp/input/response/Si/EELS/. The input file "dp-eels.in" is already there. The convergence parameters 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. Perform both a RPA and a TDLDA calculation. All the information necessary to calculate the EELS is inside the macroscopic dielectric function. To transform the dielectric function contained in "outlf.mdf" to the EEL function use the utility "mdf2eel":
>`mdf2eel outlf.mdf`
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 EEL spectra compare to the experiment?

Comments

Hands-On DP IV

DP III

Prepared by: Silvana Botti

May 26, 2009 ■ 14h30m-17h30m

Objectives

- Calculate optical spectra with the α/q^2 xc-kernel.
- Observe the effects of a change of α on the absorption spectrum.

Tasks

- **Calculation of a simple optical spectrum with the α/q^2 xc-kernel**. Move to the directory ∼/Tutorial_dp/input/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 [1]. Note that the convergence parameters which give a converged RPA spectrum are good also for this calculation. Calculate various 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 the 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 ∼/Tutorial_dp/input/create-extra-kss input files to create kss files for other simple semiconductors are available. You can play with other materials by calculating the values of α which gives the best agreement with experiments. Using the table of dielectric constants below, it is possible to establish the dependence of α on the dielectric constant.

Table 1: Dielectric constant of some semiconductors.

Si	GaAs	AlAs	Diamond	SiC
11.4	10.6	8.2	5.65	6.5

  - Q4. What is the relation between α and the dielectric constant?

Comments

We want to thank Francesco Sottile for parts of these tutorial taken from his Ph. D. thesis. For more information: http://etsf.polytechnique.fr/People/Permanent Researchers/francesco.

[1] For Silicon soenergy must be set to 0.65 eV, for GaAs 0.8 eV, for AlAs 0.9 eV, for SiC the file "sic.gw" containing GW corrections is given.

Hands-On DP V

DP IV

Prepared by: Francesco Sottile

May 29, 2009 ■ 14h30m-17h30m

Objectives

- Calculate spectra with the MT xc-kernel (NANOQUANTA kernel).

Tasks

- **Calculation of a simple spectrum with the MT xc-kernel**. Move to the directory ∼/Tutorial_dp/input/response/Si/MT/. Create an input file to run the calculation of the optical response using the MT xc-kernel. Giving the cumbersome character of such calculations, it is better to start testing a model system, like Si with only 2 k-points.

  You can use as an example the input file for the RPA[2] calculation. Remind that the quasiparticle eigenenergies are needed, or use a scissor operator energy. Once the model calculation has been accomplished, let's calculate the optical spectrum of Si: use for this a converged set of k-points (256 shifted are ok).

  The first task here is to compare MT results with BSE results. Another important point is to verify if the converged parameters for the RPA spectrum are also good for this calculation.

  – Q1. What are the converged parameters ?
  – Q2. How's the comparison with respect to BSE (once averaged)?

  Do not forget that in the directory ∼/Tutorial_dp/input/create-extra-kss input files to create kss files for other simple semiconductors are available. You can play with other materials by previously calculating the kss and scr files (no need to calculate the gw corrections).

  – Q3. Can you obtain (within MT) the same accuracy as in Si, for all the other materials?

[2] Remember that for a MT calculation only one polarization direction can be given.