

Linear-response excitations from finite to extended systems

Silvana Botti

¹LSI, CNRS-CEA-École Polytechnique, Palaiseau, France

²LPMCN, CNRS-Université Lyon 1, France

³European Theoretical Spectroscopy Facility

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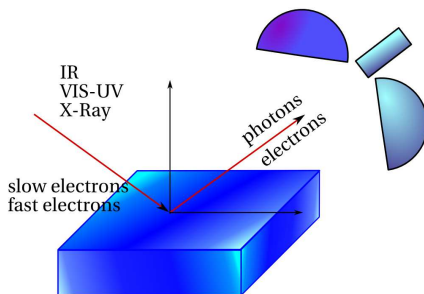
Outline

- 1 Electronic excitations within linear response
- 2 From KS equations to band structures
- 3 Optical absorption: different computational schemes
- 4 More on extended systems

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Spectroscopy



Electronic excitations:

- Optical absorption
- Electron energy loss
- Inelastic X-ray scattering
- Photoemission
- Inverse photoemission
- ...

Linear response

- For a sufficiently **small perturbation**, the response of the system can be expanded into a Taylor series with respect to the perturbation.
- The linear coefficient linking the response to the perturbation is called **response function**. It is independent of the perturbation and depends only on the system.
- We will consider only the first order (**linear**) response.
- We will **not consider strong field interaction** (e.g. intense lasers).
- We will consider **non-magnetic materials**.

Example

Density-density response function: $\delta\rho(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \chi_{\rho\rho}(\mathbf{r}, t, \mathbf{r}', t') v_{\text{ext}}(\mathbf{r}', t')$

Dielectric tensor: $\mathbf{D}(\mathbf{r}, t) = \int dt' \int d\mathbf{r}' \epsilon(\mathbf{r}, t, \mathbf{r}', t') \mathbf{E}(\mathbf{r}', t')$

Microscopic dielectric Function

Question

How can we calculate the **microscopic** dielectric functions?

Answer

They are determined by the elementary excitations of the medium: **interband** and **intraband** transitions, as well as **collective excitations**.

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Kohn-Sham equations

$$\left[-\frac{\nabla^2}{2} + v_{\text{KS}}(\mathbf{r}) \right] \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_i^N |\varphi_i(\mathbf{r})|^2 = \text{electron density}$$

ε_i = KS eigenvalues, $\varphi_i(\mathbf{r})$ = KS single-particle orbitals

Hartree potential

$$v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})$$

unknown exchange-correlation (xc) potential

Can we calculate spectra within static DFT?

- DFT allows calculations of electronic **GROUND STATE** properties in an **accurate** (usually within 1-2%) and **efficient** way:
 - total energy, phase stability,
 - atomic structure, lattice parameters (X-ray diffraction),
 - electronic density (Scanning tunneling microscopy),
 - elastic constants,
 - phonon frequencies (IR, Raman, Neutron scattering).
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 - band gap (photoemission gap and optical gap),
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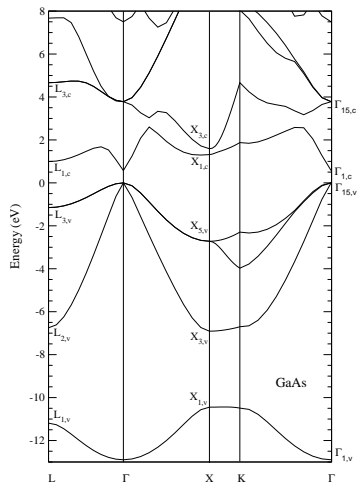
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Kohn-Sham one-electron band structure

The one-electron band structure is the dispersion of the energy levels as a function of \mathbf{k} in the Brillouin zone.

- The Kohn-Sham eigenvalues and eigenstates are **not** one-electron energy states for the electron in the solid.
- However, it is common to interpret the solutions of Kohn-Sham equations as one-electron states: the result is often a **good representation**, especially concerning **band dispersion**.
- **Gap problem**: the KS band structure underestimates systematically the band gap (often by more than 50%).

GaAs band structure



Experimental gap: 1.53 eV
 DFT-LDA gap: 0.57 eV

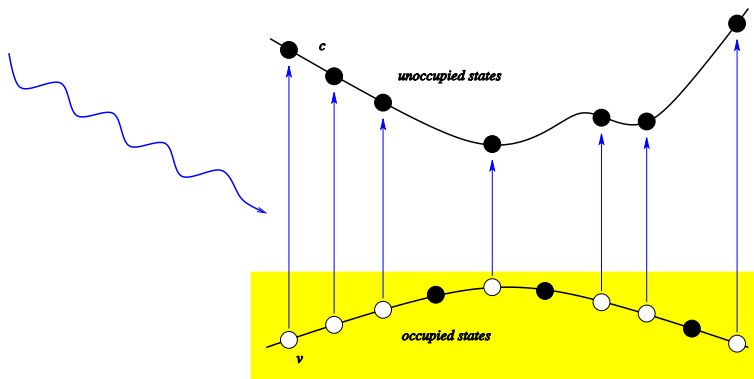
Applying a **scissor operator** (0.8 eV) we can correct the band structure.

See the lectures of Rex Godby!

Outline

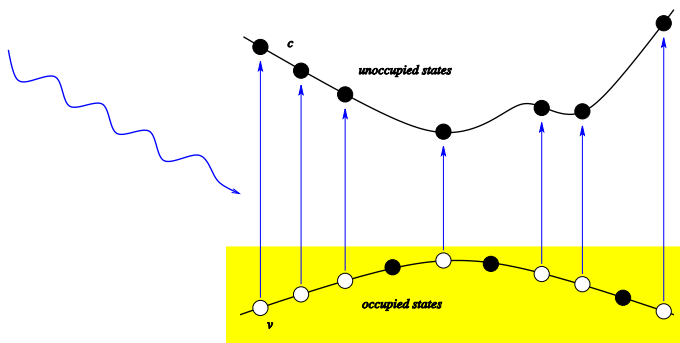
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An intuitive Picture: Absorption



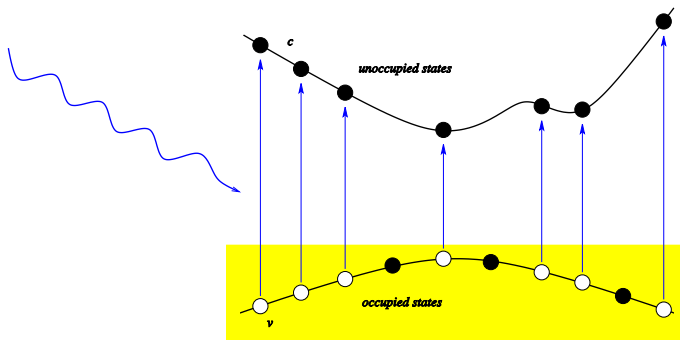
Independent particle KS picture using $\varepsilon_i^{\text{KS}}$ and φ_i^{KS}

The simplest way: independent-particle transitions



Fermi's golden rule: $\chi_{\text{KS}} \sim \sum_{v,c} |\langle c|D|v\rangle|^2 \delta(\epsilon_c - \epsilon_v - \omega)$

The simplest way



$$\epsilon_2(\omega) = 2 \frac{4\pi^2}{\Omega N_{\mathbf{k}} \omega^2} \lim_{q \rightarrow 0} \frac{1}{\mathbf{q}^2} \sum_{v,c,\mathbf{k}} |m_{v,c,\mathbf{k}}|^2 \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

$$m_{v,c,\mathbf{k}} = \langle c | \mathbf{q} \cdot \mathbf{v} | v \rangle \text{ velocity matrix elements}$$

Joint density of states

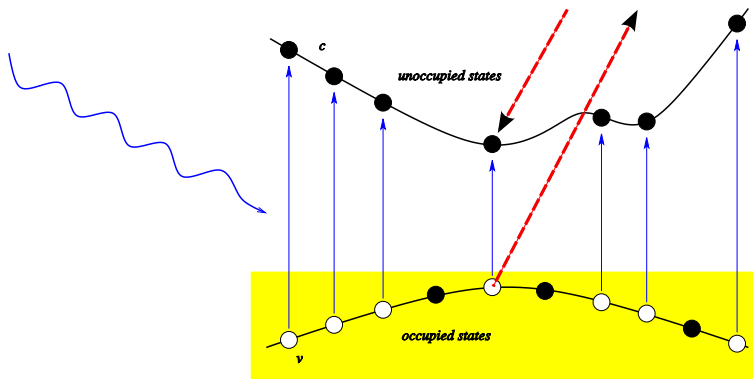
In the independent-particle approximation the dielectric function is determined by two contributions: **optical matrix elements** and **energy levels**.

$$\epsilon_2(\omega) = 2 \frac{4\pi^2}{\Omega N_{\mathbf{k}} \omega^2} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{v,c,\mathbf{k}} |m_{v,c,\mathbf{k}}|^2 \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

If $m_{v,c,\mathbf{k}}$ can be considered constant then the spectrum is essentially given by the **joint density of states**:

$$\epsilon_2 \propto JDOS/\omega^2 = \frac{1}{N_{\mathbf{k}} \omega^2} \sum_{v,c,\mathbf{k}} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)$$

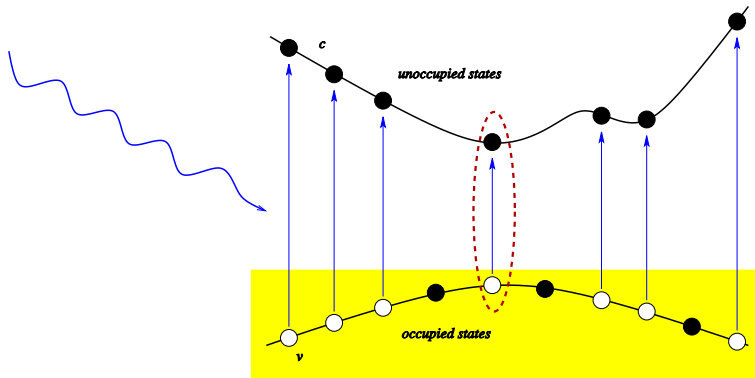
An intuitive Picture: Absorption



Photoemission process

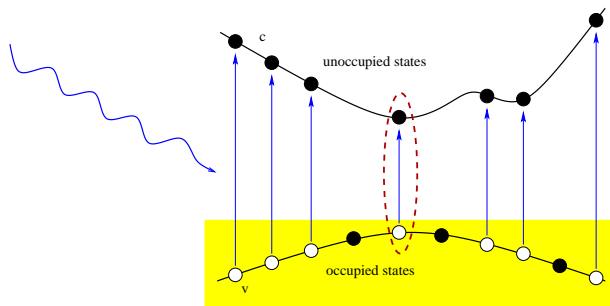
$$h\nu - (E_{\text{kin}} + \phi) = E_{N-1,v} - E_{N,0} = -\varepsilon_v$$

An intuitive Picture: Absorption



Electron-hole interaction: **Excitons!**

Beyond independent-particle picture – one way

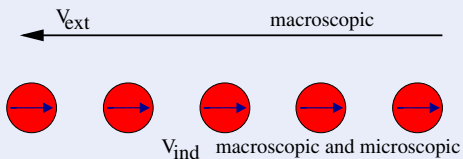


Link to other lectures!

- GW correction to energy levels ([Rex Godby](#))
- Excitons from Bethe-Salpeter equation ([Matteo Gatti](#))

Beyond independent-particle picture – another way

TDDFT and linear response (Hardy Gross)



$$\uparrow$$

$$\delta n = \chi V_{\text{ext}}$$

$$\chi = \chi_{\text{KS}} + \chi_{\text{KS}} (\nu + f_{\text{xc}}) \chi$$

ν = Coulomb potential, related to local field effects

f_{xc} = quantum exchange-correlation effects

Dealing with excitations: absorption

Here we consider **TDDFT within linear response**.

We want to calculate the **absorption cross-section** (or equivalently for a solid the dielectric function),

$$\sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \{ \alpha(\omega) \} \quad (1)$$

where $\alpha(\omega)$ is the **dynamical polarizability**. We have seen that all we need is the **density-density response function**:

$$\alpha(\omega) = - \int d^3r \int d^3r' z \chi(\mathbf{r}, \mathbf{r}', \omega) z'$$

χ measures how the density changes when we perturb the potential

$$\delta n(\mathbf{r}, \omega) = \int d^3r' \chi(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{ext}}(\mathbf{r}', \omega)$$

Changing the perturbation

Different perturbations \Rightarrow different terms but **similar equations!**

- **Electric**

$$V(\mathbf{r}) = \mathbf{r}_i$$

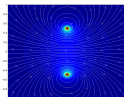
(e.g., polarizabilities, absorption, luminescence ...)



- **Magnetic**

$$V(\mathbf{r}) = \mathbf{L}_i$$

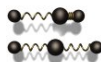
(e.g., susceptibilities, NMR ...)



- **Atomic Displacements**

$$V(\mathbf{r}) = \frac{\partial v(\mathbf{r})}{\partial \mathbf{R}_i}$$

(e.g., phonons ...)



1) Time propagation of the KS equations

- Apply a perturbation of the form $\delta v_{\text{ext } \sigma}(\mathbf{r}, t) = -\kappa_0 z \delta(t)$ to the ground state of a finite system.
- At $t = 0^+$ the Kohn-Sham orbitals are

$$\varphi_j(\mathbf{r}, t = 0^+) = e^{i\kappa_0 z} \tilde{\varphi}_j(\mathbf{r}) .$$

- Propagate these **occupied KS wave-functions** for a (in)finite time.
- The dynamical polarizability can be obtained from

$$\alpha(\omega) = -\frac{1}{\kappa_0} \int d^3 r z \delta n(\mathbf{r}, \omega) .$$

Time propagation of the KS equations

Main advantages:

- Accurate photo-absorption spectrum of several finite systems.
- Can be easily extended to study non-linear response.
- Decreases storage requirements.
- It allows the entire frequency-dependent dielectric function to be calculated at once.
- The scaling with the number of atoms is quite favorable.

Disadvantages:

- The prefactor is fairly large as such calculations typically require ≈ 10000 time-steps with a time-step of $\approx 10^{-3}$ fs.

II) The response function: TDDFT equations

The response function yields δn upon a infinitesimal change in the potential:

$$\delta n(\mathbf{r}, \omega) = \int d^3 r' \chi(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{ext}}(\mathbf{r}', \omega)$$

By construction of the **time-dependent KS system**, δn can also be calculated from

$$\delta n(\mathbf{r}, \omega) = \int d^3 r' \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{KS}}(\mathbf{r}', \omega)$$

χ_{KS} is the density-density response function of the **non-interacting** KS electrons. In terms of the stationary KS orbitals it reads

$$\chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_{jk}^{\infty} (f_k - f_j) \frac{\varphi_j(\mathbf{r}) \varphi_j^*(\mathbf{r}') \varphi_k(\mathbf{r}') \varphi_k^*(\mathbf{r})}{\omega - (\epsilon_j - \epsilon_k) + i\eta}$$

The Dyson equation

Using the definition of the KS potential, we have

$$\delta v_{\text{KS}}(\mathbf{r}, \omega) = \delta v_{\text{ext}}(\mathbf{r}, \omega) + \int d^3 r' \frac{\delta n(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r' f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \delta n(\mathbf{r}', \omega),$$

where the **xc kernel** f_{xc} is the functional derivative

$$f_{\text{xc}}[n](\mathbf{r}, \mathbf{r}', t - t') = \left. \frac{\delta v_{\text{xc}}[n](\mathbf{r}, t)}{\delta n(\mathbf{r}', t')} \right|_{n=n_0}$$

Combining the previous results, we arrive at the **Dyson equation**

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}', \omega) &= \chi_{\text{KS}}(\mathbf{r}, \mathbf{r}', \omega) \\ &+ \int d^3 \mathbf{x} \int d^3 \mathbf{x}' \chi(\mathbf{r}, \mathbf{x}, \omega) \left[\frac{1}{|\mathbf{x} - \mathbf{x}'|} + f_{\text{xc}}(\mathbf{x}, \mathbf{x}', \omega) \right] \chi_{\text{KS}}(\mathbf{x}', \mathbf{r}', \omega) \end{aligned}$$

xc kernels: approximations

The key ingredient of linear-response within TDDFT is the **xc kernel**. This is a very complicated functional of the density that encompasses **all non-trivial many-body effects** of the system.

Example of common approximations:

- Adiabatic LDA

$$f_{xc}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{d}{dn} v_{xc}^{\text{HEG}}(n(\mathbf{r}))$$

- Adiabatic GGAs
- ... (many more kernels in the TDDFT book)

Adiabatic kernels are local in time.

Common implementation for solids

The TDDFT equations in the linear-response regime can be cast in numerous different forms. For solids, in most implementations:

- The Dyson equation is solved routinely by projecting all quantities onto a suitable set of basis functions (planewaves within pseudopotentials, or localized basis for all-electron calculations).
- We get the matrix equation:

$$\chi(\omega) = \chi_{KS}(\omega) + \chi_{KS}(\omega) (v + f_{xc}(\omega)) \chi(\omega)$$

with $\chi(\omega) = \chi_{\mathbf{G},\mathbf{G}'}(\omega)$

- To obtain an absorption spectrum or the loss function at a given momentum transfer only one component of the matrix is required, obtained by solving a linear system of equations, thus avoiding the matrix inversion.

The poles of the response function

Lehmann representation of the density response function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_m \left[\frac{\langle 0 | \hat{n}(\mathbf{r}) | m \rangle \langle m | \hat{n}(\mathbf{r}') | 0 \rangle}{\omega - (E_m - E_0) + i\eta} - \frac{\langle 0 | \hat{n}(\mathbf{r}') | m \rangle \langle m | \hat{n}(\mathbf{r}) | 0 \rangle}{\omega + (E_m - E_0) + i\eta} \right]$$

χ (for a finite system) has **poles** at the **excitation energies**, $\Omega = E_m - E_0$, while χ_{KS} has **poles** at the **KS eigenvalue differences**, $\omega_{jk} = \epsilon_j - \epsilon_k$.

After some pages of algebra:

$$\sum_{j'k'} [\delta_{jj'} \delta_{kk'} \omega_{jk} + (f_{k'} - f_{j'}) K_{jk,j'k'}(\Omega)] \beta_{j'k'} = \Omega \beta_{jk},$$

where we have defined the matrix element

$$K_{jk,j'k'}(\omega) = \int d^3r \int d^3r' \varphi_j^*(\mathbf{r}) \varphi_k(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}(\mathbf{r}, \mathbf{r}', \omega) \right] \varphi_{j'}(\mathbf{r}') \varphi_{k'}^*(\mathbf{r}')$$

Single pole approximation

If the excitation is well described by **one single-particle transition** we can neglect the off-diagonal terms of $K_{jk,j'k'}$:

$$\Omega^{\text{SPA}} = \omega_{12} + 2\Re K_{12,12}.$$

The SPA also describes the **spin-multiplet structure** of otherwise spin-unpolarized ground states through the spin-dependence of f_{xc} :

$$\begin{aligned}\omega_{\text{sing}} &= \omega_{12} + 2\Re \int d^3r \int d^3r' \varphi_1^*(\mathbf{r}) \varphi_2(\mathbf{r}) \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{\text{xc}}^{(1)}(\mathbf{r}, \mathbf{r}', \omega) \right] \varphi_1(\mathbf{r}') \varphi_2^*(\mathbf{r}') \\ \omega_{\text{trip}} &= \omega_{12} + 2\Re \int d^3r \int d^3r' \varphi_1^*(\mathbf{r}) \varphi_2(\mathbf{r}) f_{\text{xc}}^{(2)}(\mathbf{r}, \mathbf{r}', \omega) \varphi_1(\mathbf{r}') \varphi_2^*(\mathbf{r}'),\end{aligned}$$

where

$$f_{\text{xc}}^{(1)} = (f_{\text{xc}\uparrow\uparrow} + f_{\text{xc}\uparrow\downarrow}) / 2 \quad f_{\text{xc}}^{(2)} = (f_{\text{xc}\uparrow\uparrow} - f_{\text{xc}\uparrow\downarrow}) / 2$$

Casida's formulation

Parametrization of the linear change of the density:

$$\delta n(\mathbf{r}, \omega) = \sum_{ia} [\xi_{ia}(\omega) \varphi_a^*(\mathbf{r}) \varphi_i(\mathbf{r}) + \xi_{ai}(\omega) \varphi_a(\mathbf{r}) \varphi_i^*(\mathbf{r})] ,$$

where i denotes an occupied and a a virtual state. After some algebra, one can prove that the excitation energies can be determined as solutions of the **pseudo-eigenvalue problem**

$$\sum_{a'i'} [\delta_{aa'} \delta_{i'i'} (\epsilon_j - \epsilon_k)^2 + 2\sqrt{\epsilon_a - \epsilon_i} K_{ai,a'i'}(\Omega) \sqrt{\epsilon_{a'} - \epsilon_{i'}}] \beta_{a'i'} = \Omega^2 \beta_{ai} .$$

The eigenvalues of this equation are the **square of the excitation energies**, while the eigenvectors can be used to calculate the **oscillator strengths**.

This is the formula implemented in quantum-chemistry codes.

III) The Sternheimer equation

PHYSICAL REVIEW

VOLUME 84, NUMBER 2

OCTOBER 15, 1951

On Nuclear Quadrupole Moments

R. STERNHEIMER

*Los Alamos Scientific Laboratory, Los Alamos, New Mexico, and Brookhaven National Laboratory, Upton, New York**

(Received June 18, 1951)

units. If E_0 denotes the unperturbed 1s energy, the Schrodinger equation becomes

$$(H_0 + H_1)(u_0 + u_1) = E_0(u_0 + u_1), \quad (3)$$

since the first-order perturbation of the energy is zero for s states. Upon subtracting $H_0 u_0 = E_0 u_0$, and to the first order in Q , we obtain

$$(H_0 - E_0)u_1 = -H_1 u_0. \quad (4)$$

Hartree-Fock: Coupled Hartree-Fock method

DFPT: Density functional perturbation theory



The Sternheimer equation

$$\left\{ H^{(0)} - \epsilon_m \pm \omega + i\eta \right\} \psi_m^{(1)}(\mathbf{r}, \pm\omega) = -P_c H^{(1)}(\pm\omega) \psi_m^{(0)}(\mathbf{r})$$

with

$$H^{(1)}(\omega) = V(\mathbf{r}) + \int d^3 r' \frac{n^{(1)}(\mathbf{r}', \omega)}{|\mathbf{r} - \mathbf{r}'|} + \int d^3 r' f_{xc}(\mathbf{r}, \mathbf{r}') n^{(1)}(\mathbf{r}', \omega)$$

and

$$n^{(1)}(\mathbf{r}, \omega) = \sum_m^{\text{occ.}} \left\{ \left[\psi_m^{(0)}(\mathbf{r}) \right]^* \psi_m^{(1)}(\mathbf{r}, \omega) + \left[\psi_m^{(1)}(\mathbf{r}, -\omega) \right]^* \psi_m^{(0)}(\mathbf{r}) \right\}$$



X. Andrade *et al.*, J. Chem. Phys. **126**, 184106 (2007).

The Sternheimer equation

Main **advantages**:

- (Non-)Linear system of equations solvable by standard methods.
- Only the occupied states enter the equation.
- Scaling is N^2 , where N is the number of atoms.
- Easy to use to extend to hyperpolarizabilities.

Disadvantages:

- It is hard to converge close to a resonance.

IV) Superoperators and Lanczos methods

- The dynamical polarizability is represented by a **matrix continued fraction** whose coefficients can be obtained from a **Lanczos method**:

$$\langle \mathbf{P}_1 | (\omega - \mathcal{L})^{-1} | \mathbf{Q}_1 \rangle = \frac{1}{\omega - \mathbf{a}_1 + \mathbf{b}_2 \frac{1}{\omega - \mathbf{a}_2 + \dots} \mathbf{c}_2}$$

- This method uses **only occupied states**.
- Calculations **scale favorably** with the system size.
- Up to now only test applications.



B. Walker *et al.*, Phys. Rev. Lett. **96**, 113001 (2006).



D. Rocca *et al.*, J. Chem. Phys. **128**, 154105 (2008).

Summary for finite systems

- A large majority of the calculations is done using the **ALDA approximation**.
- In many cases (low Z atoms) **ALDA** gives essentially the same results as **AGGA**.
- The results are quite good, often of the **same quality of more demanding approaches**, like CI using only single-excitations, or BSE.
- In some systems the ALDA **underestimates the onset** of absorption mainly due to the incorrect asymptotics of the LDA potential.
- The ALDA also fails to reproduce the excitations of **stretched** H_2 , Na_2 , etc.

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Absorption spectra

Question

Which level of approximation should I use if I am interested in comparing to experiments?

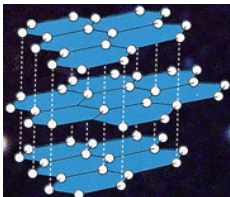
Answer

There is **not** a unique answer.

It **depends** on the system and on the kind of spectroscopy.

- In some cases, the independent-particle approximation already gives results good enough.
- It is often necessary to go beyond the independent particle approximation.
- *See the lectures of Matteo Gatti!*

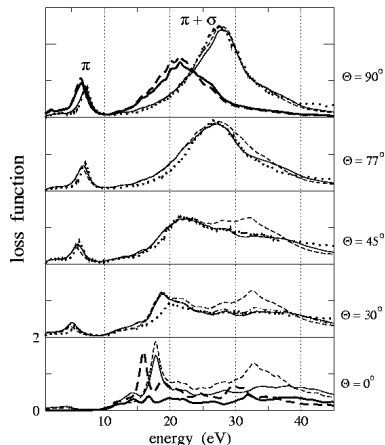
EELS of graphite



For a \mathbf{q} in the plane the independent-particle approximation agrees with experiment.

What happens when $\mathbf{q} \neq 90^\circ$?

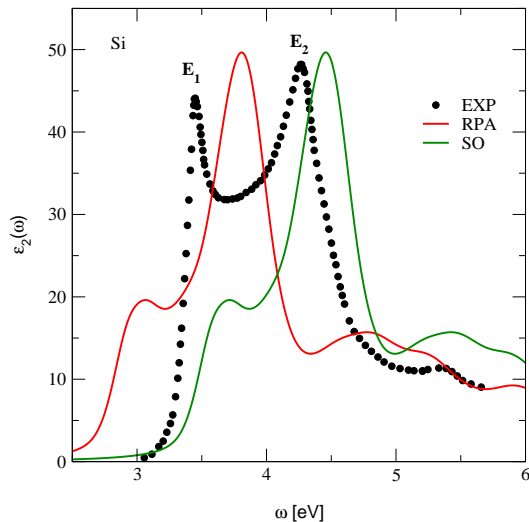
Remind: $\epsilon_M(\mathbf{q}) = \frac{1}{\epsilon_{00}^{-1}(\mathbf{q})}$



A. G. Marinopoulos *et al.*, Phys. Rev. Lett. **89**, 076402 (2002).

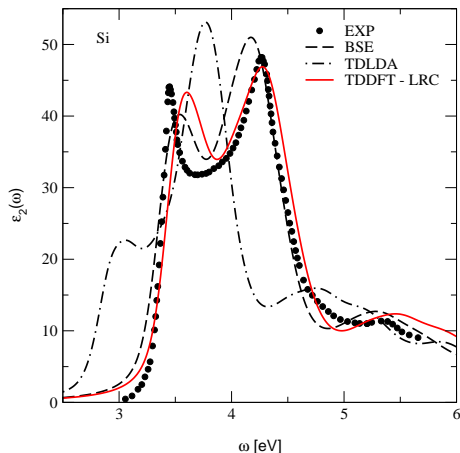


Absorption spectrum of silicon



- E_1 and E_2 peaks are red-shifted.
- excitonic effects on E_1 are missing.
- Scissor operator does not help: blue-shifted peaks.

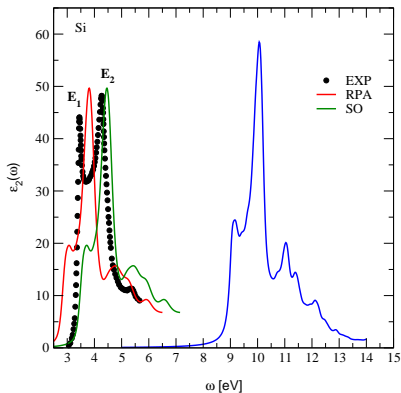
Absorption spectrum of silicon



- Adiabatic LDA for xc kernel does not improve the spectrum.
- BSE gives the correct result.
- BSE-derived kernels give the correct results.

 S. Botti *et al.*, Rep. Prog. Phys. **70**, 357 (2007).

Independent-particle absorption spectrum of silicon



- Comparison with Hartree-Fock calculation



F. Bruneval *et al.*, *J. Chem. Phys.* **124**, 144113 (2006)

For extended systems

- The **ALDA approximation** does not improve the independent-particle absorption spectra.
- In many cases **ALDA** gives essentially the same results as RPA.
- **BSE and BSE-derived xc kernels** + GW energies correct the spectra.
- The main problem of ALDA is the **wrong asymptotic limit**.