Linear-response excitations
from finite to extended systems

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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
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
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: \( \delta \rho(r, t) = \int dt' \int dr' \chi_{\rho \rho}(r, t, r', t') v_{\text{ext}}(r', t') \)
- Dielectric tensor: \( D(r, t) = \int dt' \int dr' \epsilon(r, t, r', t') E(r', t') \)
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.
### 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**
Electronic excitations

Kohn-Sham equations

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

\[
n(\mathbf{r}) = \sum_{i}^{N} |\varphi_i(\mathbf{r})|^2 = \text{electron density}
\]

\[
\varepsilon_i = \text{KS eigenvalues}, \varphi_i(\mathbf{r}) = \text{KS single-particle orbitals}
\]

**Hartree potential**

\[
v_{\text{KS}}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{\text{xc}}(\mathbf{r})
\]

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).

- Ground-state DFT is **not** designed to access **EXCITED STATES**:
  - quasiparticle electronic structures (photoemission spectra),
  - band gap (photoemission gap and optical gap),
  - electronic excitations spectra (absorption, EELS, IXS, etc.).
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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 $k$ 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!
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3. Optical absorption: different computational schemes
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An intuitive Picture: Absorption

Independent particle KS picture using $\varepsilon_i^{KS}$ and $\varphi_i^{KS}$
The simplest way: independent-particle transitions

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

\[ \epsilon_2(\omega) = 2 \frac{4\pi^2}{\Omega N_k \omega^2} \lim_{q \to 0} \frac{1}{q^2} \sum_{\nu, c, k} |m_{\nu, c, k}|^2 \delta(\epsilon_{ck} - \epsilon_{vk} - \omega) \]

\[ m_{\nu, c, k} = \langle c | q \cdot v | \nu \rangle \text{ velocity matrix elements} \]
Joint density of states

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

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

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

\[
\epsilon_2 \propto \text{JDOS}/\omega^2 = \frac{1}{N_k \omega^2} \sum_{v,c,k} \delta(\epsilon_{c\mathbf{k}} - \epsilon_{v\mathbf{k}} - \omega)
\]
An intuitive Picture: Absorption

Photoemission process

\[ h\nu - (E_{\text{kin}} + \phi) = E_{N-1,\nu} - E_{N,0} = -\varepsilon_{\nu} \]
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)*

\[
\delta n = \chi v_{\text{ext}}
\]

\[
\chi = \chi_{\text{KS}} + \chi_{\text{KS}} (v + f_{\text{xc}}) \chi
\]

- \(v = \text{Coulomb potential, related to local field effects}\)
- \(f_{\text{xc}} = \text{quantum exchange-correlation effects}\)
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),

\[ \sigma(\omega) = \frac{4\pi\omega}{c} \text{Im} \{ \alpha(\omega) \} \]  

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

\[ \alpha(\omega) = -\int d^3r \int d^3r' z \chi(r, r', \omega) z' \]

\( \chi \) measures how the density changes when we perturb the potential

\[ \delta n(r, \omega) = \int d^3r' \chi(r, r', \omega) \delta v_{\text{ext}}(r', \omega) \]
Changing the perturbation

Different perturbations ⇒ different terms but similar equations!

- Electric
  \[ V(r) = r_i \]
  (e.g., polarizabilities, absorption, luminescence ...)

- Magnetic
  \[ V(r) = L_i \]
  (e.g., susceptibilities, NMR ...)

- Atomic Displacements
  \[ V(r) = \frac{\partial v(r)}{\partial R_i} \]
  (e.g., phonons ...)

Electric

\[ V(r) = r_i \]

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Electronic excitations

KS band structure

Absorption

Extended systems

Linear-response excitations

Silvana Botti
1) Time propagation of the KS equations

- **Apply a perturbation** of the form \( \delta \nu_{\text{ext}} \sigma(r, t) = -\kappa_0 z \delta(t) \) to the ground state of a finite system.
- At \( t = 0^+ \) the Kohn-Sham orbitals are
  \[
  \varphi_j(r, t = 0^+) = e^{i\kappa_0 z} \tilde{\varphi}_j(r).
  \]
- **Propagate** these occupied KS wave-functions for a (in)finite time.
- The dynamical polarizability can be obtained from
  \[
  \alpha(\omega) = -\frac{1}{\kappa_0} \int d^3 r \ z \ \delta n(r, \omega).
  \]
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 \( \approx 10000 \) time-steps with a time-step of \( \approx 10^{-3} \) fs.
II) The response function: TDDFT equations

The response function yields $\delta n$ upon a infinitesimal change in the potential:

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

By construction of the time-dependent KS system, $\delta n$ can also be calculated from

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

$\chi_{\text{KS}}$ is the density-density response function of the non-interacting KS electrons. In terms of the stationary KS orbitals it reads

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

Using the definition of the KS potential, we have

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

where the \( \text{xc} \) kernel \( f_{\text{xc}} \) is the functional derivative

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

Combining the previous results, we arrive at the Dyson equation

\[ \chi(r, r', \omega) = \chi_{\text{KS}}(r, r', \omega) \]
\[ + \int d^3 x \int d^3 x' \chi(r, x, \omega) \left[ \frac{1}{|x - x'|} + f_{\text{xc}}(x, x', \omega) \right] \chi_{\text{KS}}(x', r', \omega) \]
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**
  \[
  f_{xc}^{ALDA}(\mathbf{r}, \mathbf{r}', \omega) = \delta(\mathbf{r} - \mathbf{r}') \frac{d}{dn} v_{xc}^{HEG}(n(\mathbf{r}))
  \]

- **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:

\[ \chi(\omega) = \chi_{\text{KS}}(\omega) + \chi_{\text{KS}}(\omega) (\nu + f_{\text{xc}}(\omega)) \chi(\omega) \]

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

- 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:

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

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

After some pages of algebra:

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

where we have defined the matrix element

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

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

$$
\omega_{\text{trip}} = \omega_{12} + 2\Re \int d^3r \int d^3r' \varphi_1^*(r)\varphi_2(r) f_{xc}^{(2)}(r, r', \omega) \varphi_1(r')\varphi_2^*(r'),
$$

where

$$
f_{xc}^{(1)} = \left( f_{xc\uparrow\uparrow} + f_{xc\uparrow\downarrow} \right)/2 \quad f_{xc}^{(2)} = \left( f_{xc\uparrow\uparrow} - f_{xc\uparrow\downarrow} \right)/2
$$
Casida’s formulation

Parametrization of the linear change of the density:

\[
\delta n(r, \omega) = \sum_{ia} \left[ \xi_{ia}(\omega) \varphi^*_a(r) \varphi_i(r) + \xi_{ai}(\omega) \varphi_a(r) \varphi^*_i(r) \right],
\]

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

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

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

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 Schrödinger 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 $H_0u_0 = E_0u_0$, and to the first order in $Q$, we obtain

$$(H_0 - E_0)u_1 = -H_1u_0. \quad (4)$$
The Sternheimer equation

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

with

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

and

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

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**:

\[
\langle P_1 | (\omega - \mathcal{L})^{-1} | Q_1 \rangle = \frac{1}{\omega - a_1 + \frac{b_2}{\omega - a_2 + \cdots}}
\]

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

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 H₂, Na₂, 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: $\epsilon_M(\mathbf{q}) = \frac{1}{\epsilon^{-1}_{00}(\mathbf{q})}$

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.

Independent-particle absorption spectrum of silicon

Comparison with Hartree-Fock calculation

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**.