Fully parameter-free calculation of optical spectra for insulators, semiconductors and metals from a simple polarization functional

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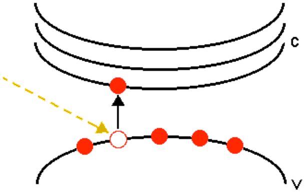
Outline

- Motivation: optical absorption of solids
- Shortcomings of standard DFT approaches
- A simple polarization functional
- Results for optical spectra
- Conclusions

Motivation

Spectroscopy: optical absorption of solids



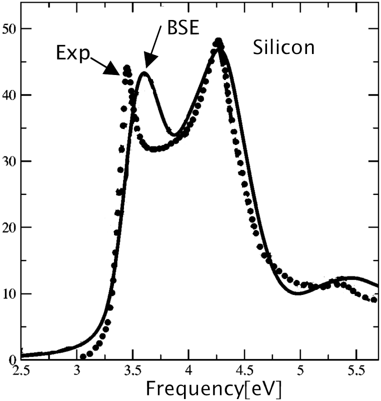


Figure: Adapted from RMP 74, 601 (2002)

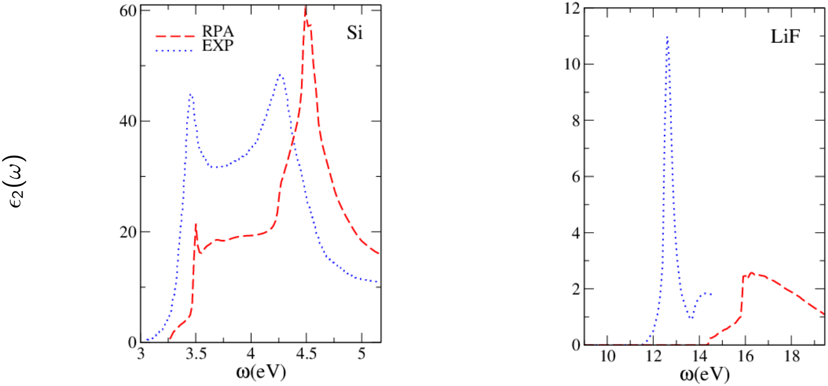
-State of the art: Bethe-Salpeter equation but numerically expensive $[O(N^6)]$

-We would like a density-functional approach giving similar results: $[O(N^3)]$

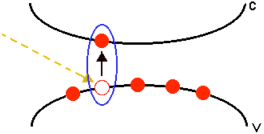
Standard approaches

Underestimation of continuum excitons and absence of bound excitons

RPA = no xc effects in induced potentials (we use a *GW* corrected band gap.)

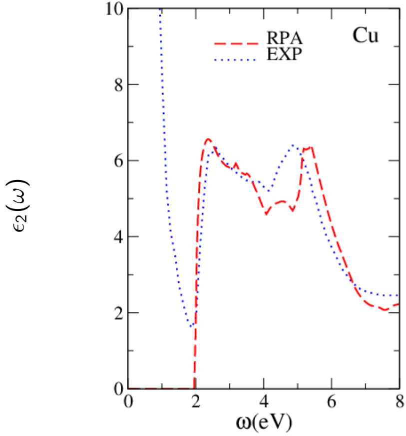


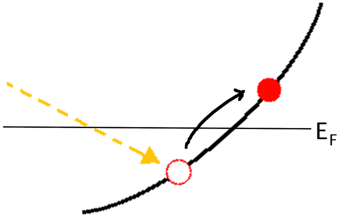
No excitonic effects



Standard approaches

Absence of Drude tails in spectra of metals





Intraband absorption

No relaxation due to scattering effects

Current approaches

Many developments since $\sim$ 2000

Recent approaches: bootstrap method [PRL 107, 186401], functional derived from a meta-GGA [PRL 107, 216402], functional based on jellium-with-gap model [PRB 87, 205143]; guided iteration [PRL 114, 146402 (2015)].

Shortcomings:

1. not parameter free: an *ad hoc* material-dependent broadening parameter is used to compare theory and experiment.
2. static: cannot describe finite width of Drude tails and bound excitons
3. explicit calculation of the KS density response function

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Our approach:

1. parameter free: truly predictive
2. dynamical: memory effects
3. no explicit calculation of response functions

Optical absorption from the current

Knowledge of the current density in the unit cell is sufficient to calculate absorption spectra $[\epsilon_2 = Im(\overleftrightarrow{\epsilon}_M)]$

The macroscopic polarization can be obtained from the induced current density

$$\vec{P}_{mac}(\omega) = \frac{-i}{\omega V} \int_V d\vec{r} \delta\vec{j}(\vec{r}, \omega),$$

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(V= volume of unit cell).

It is proportional to the macroscopic electric field:

$$\vec{P}_{mac}(\omega) = \overleftrightarrow{\chi}_e(\omega) \cdot \vec{E}_{mac}(\omega),$$

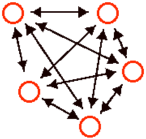
where the electric susceptibility $\overleftrightarrow{\chi}_e(\omega)$ is related to $\overleftrightarrow{\epsilon}_M$:

$$\overleftrightarrow{\epsilon}_M(\omega) = 1 + 4\pi \overleftrightarrow{\chi}_e(\omega).$$

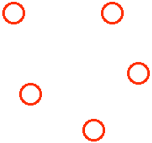
Time-dependent current-density-functional theory

Interacting many-body system in external field described by $\{v(\vec{r},t), \vec{A}(\vec{r},t)\}$

Non-interacting system in an effective field described by $\{v_{KS}(\vec{r},t), \vec{A}_{KS}(\vec{r},t)\}$ with identical $\rho(\vec{r},t)$ and $\vec{j}(\vec{r},t)$.



$\Leftarrow \vec{j}(\vec{r},t) \Rightarrow$



Linear response (F. Kootstra, *et al.* JCP 112, 6517 (2000), P. Romaniello and P.L. de Boeij, PRB 71, 155108 (2005)):

$$\delta\vec{j}(\vec{r},\omega) = -\frac{i}{\omega}\int d\vec{r}'\,\overleftrightarrow{\chi}^{\vec{j}\vec{j}}_{KS}(\vec{r},\vec{r}',\omega)[\vec{E}_{mac}(\omega) + \vec{E}^{xc}(\vec{r},\omega)]$$
$$+ \int d\vec{r}'\,\vec{\chi}^{\vec{j}\rho}_{KS}(\vec{r},\vec{r}',\omega)\delta v^{Hxc}_{mic}(\vec{r}',\omega),$$

Here we will neglect microscopic contributions to the xc potentials ($\delta v^{Hxc}_{mic} \rightarrow \delta v^{H}_{mic}$; $\vec{E}^{xc} \rightarrow \vec{E}^{xc}_{mac}$).

We need an approximation for $E^{xc}_{mac}(\omega)$

Polarization functional

We use a polarization functional:

$$\vec{E}^{xc}_{mac}(\omega) = \overleftrightarrow{\alpha}(\omega) \cdot \vec{P}_{mac}(\omega)$$

Relation to TDCDFT kernel:

$$\overleftrightarrow{\alpha}(\omega) = -\frac{\omega^2}{V} \int_V d\vec{r} \int d\vec{r}' \overleftrightarrow{f}_{xc}(\vec{r}, \vec{r}', \omega)$$

$\overleftrightarrow{\alpha}(\omega)$ relates $\overleftrightarrow{\chi}_e(\omega)$ and $\overleftrightarrow{\chi}_e^{RPA}(\omega)$

$$[\overleftrightarrow{\chi}_e]^{-1}(\omega) = [\overleftrightarrow{\chi}_e^{RPA}]^{-1}(\omega) - \overleftrightarrow{\alpha}(\omega)$$

P.L. de Boeij, F. Kootstra, AB, R. van Leeuwen and J.G. Snijders, JCP 115, 1995 (2001)

Bound exciton

Let us assume that all quantities are isotropic.

$$\chi_e(\omega) = \frac{\chi_e^{RPA}(\omega)}{1 - \chi_e^{RPA}(\omega)\alpha(\omega)}$$

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Following F. Sottile *et al.*, PRB 68 205112 (2003):

$$\mathrm{Im}[\chi_e(\omega)] = \frac{(\chi_e^{RPA}(\omega))^2 \mathrm{Im}[\alpha(\omega)]}{(1 - \chi_e^{RPA}(\omega)\mathrm{Re}[\alpha(\omega)])^2 + (\chi_e^{RPA}(\omega)\mathrm{Im}[\alpha(\omega)])^2}$$

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A bound exciton is obtained if for some frequency $\omega_{be} < \omega_{gap}$:

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Unfortunately we do not know ω_{be}

Can we relate it to a quantity we do know? For example $\chi_e^{RPA}(\omega = 0)$

Lorentz model

Limiting case: low-density insulator ($N_e/V =$ small)
RPA spectrum centered around plasmon frequency ω_p.

$$\chi_e^{RPA}(\omega) \approx -\frac{\omega_p}{8\pi}\left[\frac{1}{\omega-\omega_p+i\gamma}-\frac{1}{\omega+\omega_p+i\gamma}\right]$$

Prefactor ensures that the f-sum rule is satisfied.

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ω_p corresponds to the frequency at which $\mathrm{Re}[\epsilon_M(\omega)] = 0$ and $\mathrm{Im}[\epsilon_M(\omega)] \approx 0$

$$\omega_p = \sqrt{2}\omega_{be}$$

Taylor expansion:

$$\chi_e^{RPA}(\omega_{be}) = \chi_e^{RPA}(0) + 4\pi[\chi_e^{RPA}(0)]^2 = \chi_e^{RPA}(0)\epsilon_M^{RPA}(0)$$

A simple polarization functional

Summary:

1. $\mathrm{Re}[\alpha(\omega_{be})] = 1/\chi_e^{RPA}(\omega_{be})$ with $\mathrm{Im}[\alpha(\omega)] << 1$
2. $\chi_e^{RPA}(\omega_{be}) \approx \chi_e^{RPA}(0)\epsilon_M^{RPA}(0)$

We obtain for α

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Shortcoming:

Static → no memory effects → unable to account for the finite width of bound excitons and Drude tails.

A simple polarization functional

We add $\overleftrightarrow{Y}_{VK}(\omega)$, the long-range part of the dynamical Vignale-Kohn functional (exact for an inhomogeneous electron gas) [G. Vignale and W. Kohn, PRL 77, 2037 (1996)]

$$\overleftrightarrow{Y}_{VK}(\omega) = \frac{1}{V}\int_V d\vec{r}\Bigg(\frac{\nabla\rho_0(\vec{r})\cdot\nabla\rho_0(\vec{r})}{\rho_0^2(\vec{r})} f_{xcT}(\bar{\rho},\omega)\overleftrightarrow{\mathrm{I}}$$

$$+\frac{\nabla\rho_0(\vec{r})\otimes\nabla\rho_0(\vec{r})}{\rho_0^2(\vec{r})}\left[f_{xcL}(\bar{\rho},\omega) - f_{xcT}(\bar{\rho},\omega) - \frac{d^2 e_{xc}}{d\bar{\rho}^2}\right]\Bigg),$$

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Final result:

$$\overleftrightarrow{\alpha}(\omega) = [\overleftrightarrow{\epsilon}_M^{RPA}(0)]^{-1}[\overleftrightarrow{\chi}_e^{RPA}(0)]^{-1} + \overleftrightarrow{Y}_{VK}(\omega)$$

No parameters

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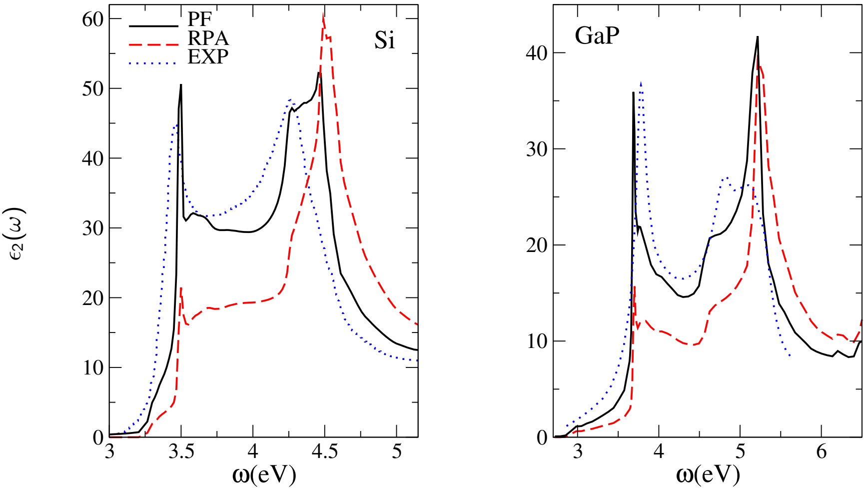
We do not include effects due to electron-phonon coupling.

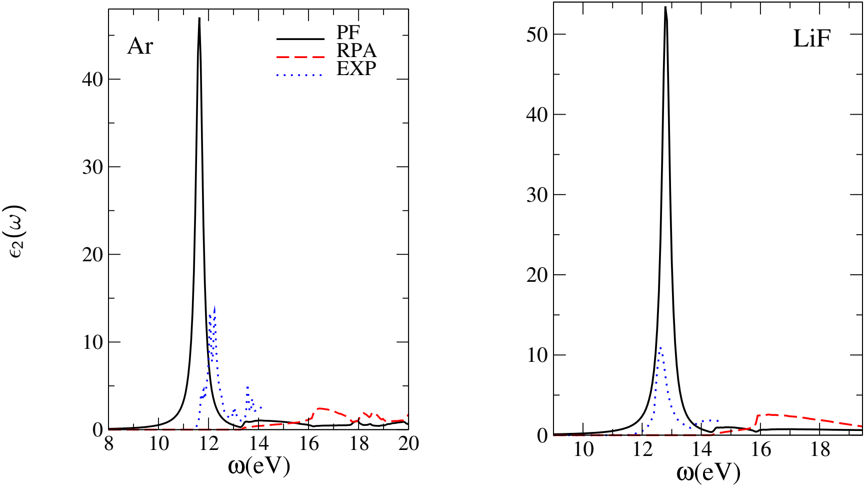
The spectra we obtain are predictions of the optical spectra at low temperature where electron-electron scattering dominates

Results: Silicon and GaP



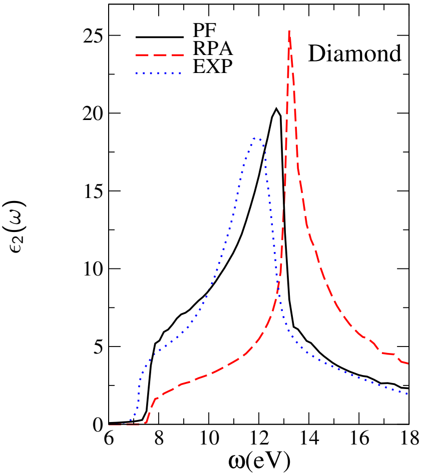
Polarization functional describes continuum excitons.

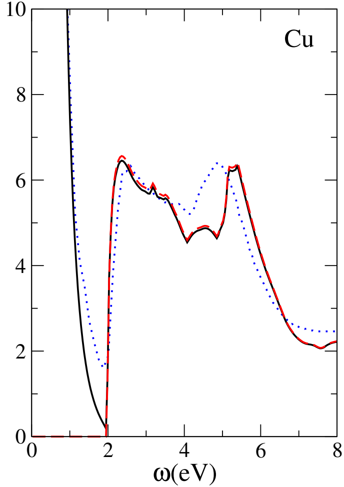
Results: solid argon and LiF



Polarization functional describes bound excitons.

Results: diamond and copper





Polarization functional describes Drude tails.

Conclusions

- We presented the first fully parameter-free density-functional approach that gives accurate optical spectra for insulators, semiconductors and metals alike.
- Our approach is therefore truly predictive and due to its numerical efficiency opens the way for the prediction of optical spectra of large systems.

arXiv:1503.00333

Thanks: Paul de Boeij, Lucia Reining, Pina Romaniello