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

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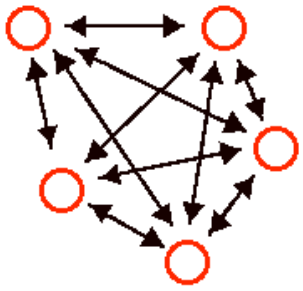
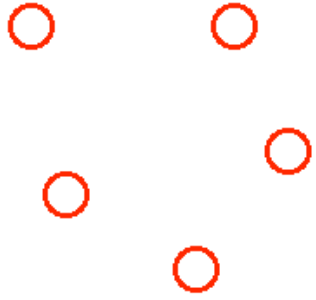
Time-dependent current-density-functional theory

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



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

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 $\vec{j}(\vec{r},t)$.



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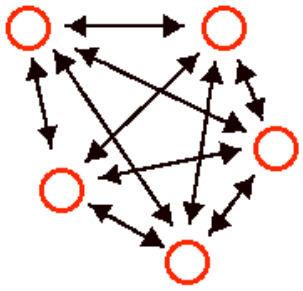

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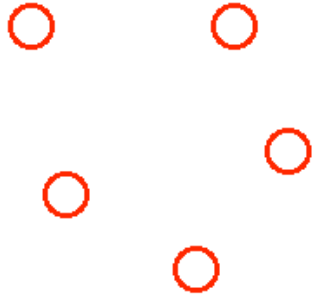

Linear response:

$$\delta\vec{j}(\vec{r},\omega) = \int d\vec{r}\,' \overleftrightarrow{\chi}^{\vec{j}\vec{j}}(\vec{r},\vec{r}\,',\omega)\cdot\vec{A}(\vec{r}\,',\omega)$$

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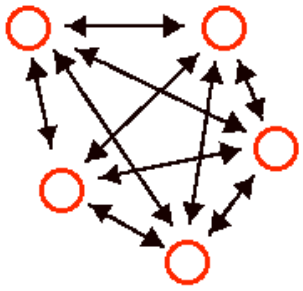

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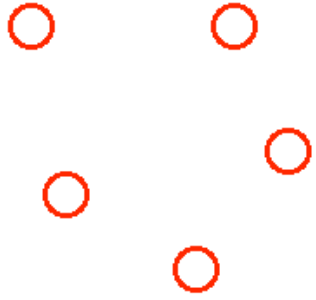

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TDCDFT Kohn-Sham:

$$\delta\vec{j}(\vec{r},\omega) = \int d\vec{r}\,' \overleftrightarrow{\chi}^{\vec{j}\vec{j}}_{KS}(\vec{r},\vec{r}\,',\omega)\cdot\vec{A}_{KS}(\vec{r}\,',\omega)$$

$$A_{KS}(\vec{r},\omega) = A(\vec{r},\omega) + A_H(\vec{r},\omega) + A_{xc}(\vec{r},\omega)$$

Response properties as explicit functional of the current

Many properties can be calculated directly from knowledge of the current:

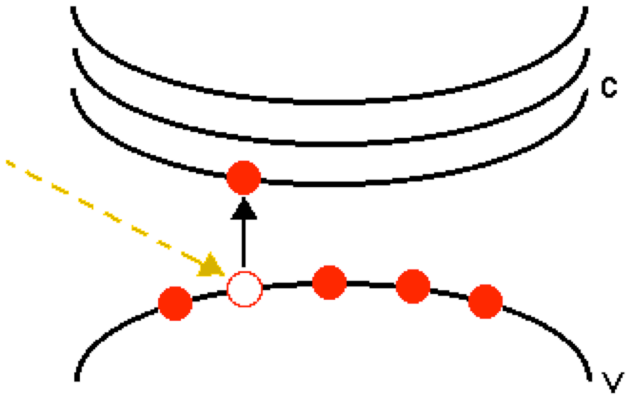
- polarizability $\alpha = \left[\int \delta\vec{j}\right] / E$
- magnetizability $\xi = \left[\int \vec{r} \times \delta\vec{j}\right] / B$
- circular dichroism $G = \left[\int \delta\vec{j}\right] / B$
- optical absorption $\epsilon_M = 1 + 4\pi \left[\frac{1}{V_{unit}} \int_{V_{unit}} \delta\vec{j}\right] / E_{mac}$

No explicit knowledge needed of

- response functions (TD(C)DFT Dyson equation is not solved)
- excitation energies (Casida's equation is not solved)
- etc.

Motivation

Spectroscopy: optical absorption of solids



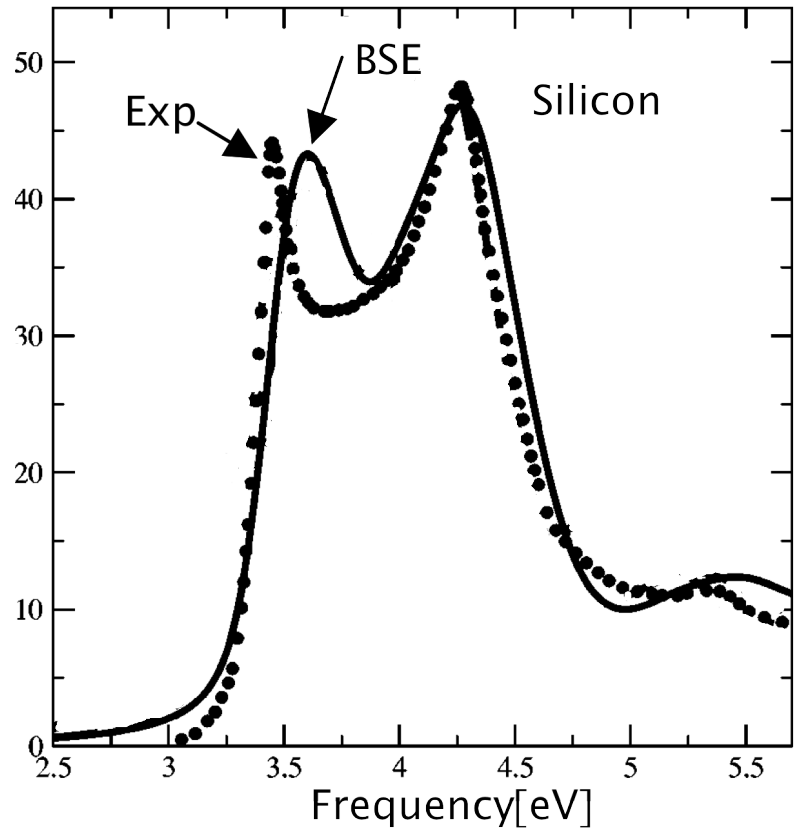


Figure: Adapted from RMP 74, 601 (2002)

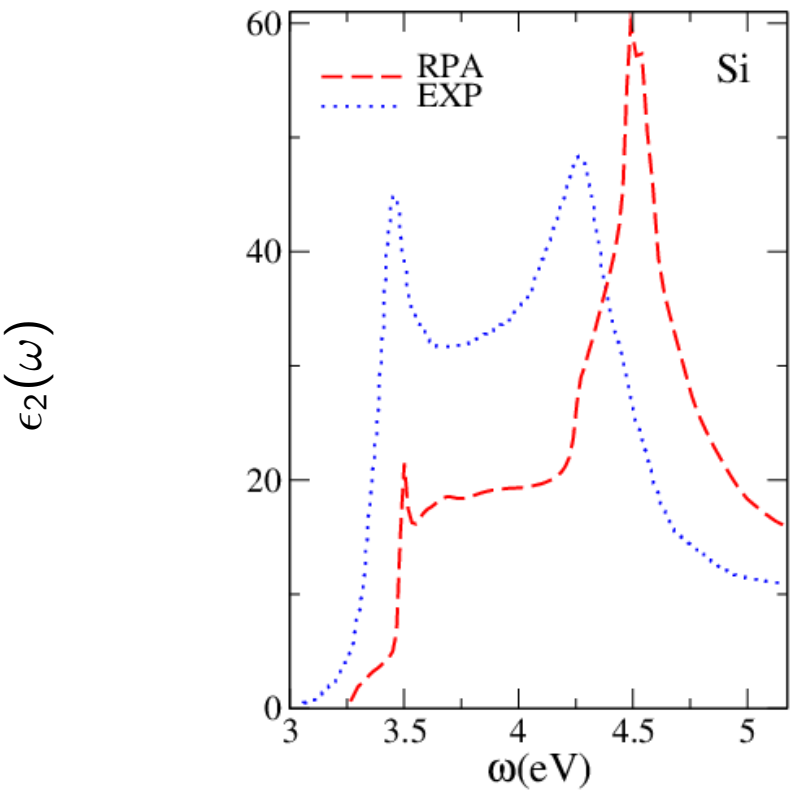
-State of the art: Bethe-Salpeter equation but numerically expensive $[O(N^6)]$

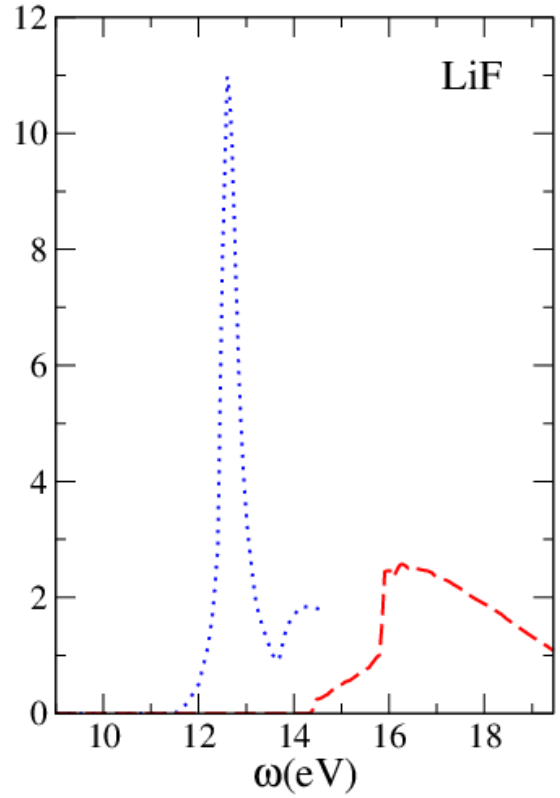
-We would like a density-functional approach giving similar results: $[O(N^3)]$

Standard functionals

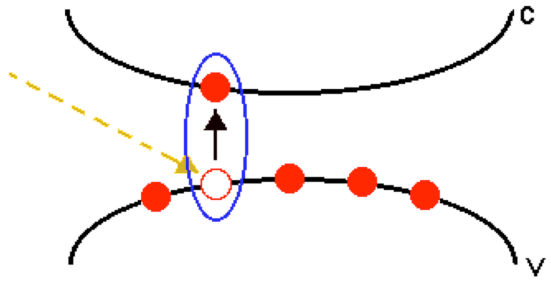
Underestimation of continuum excitons and absence of bound excitons

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



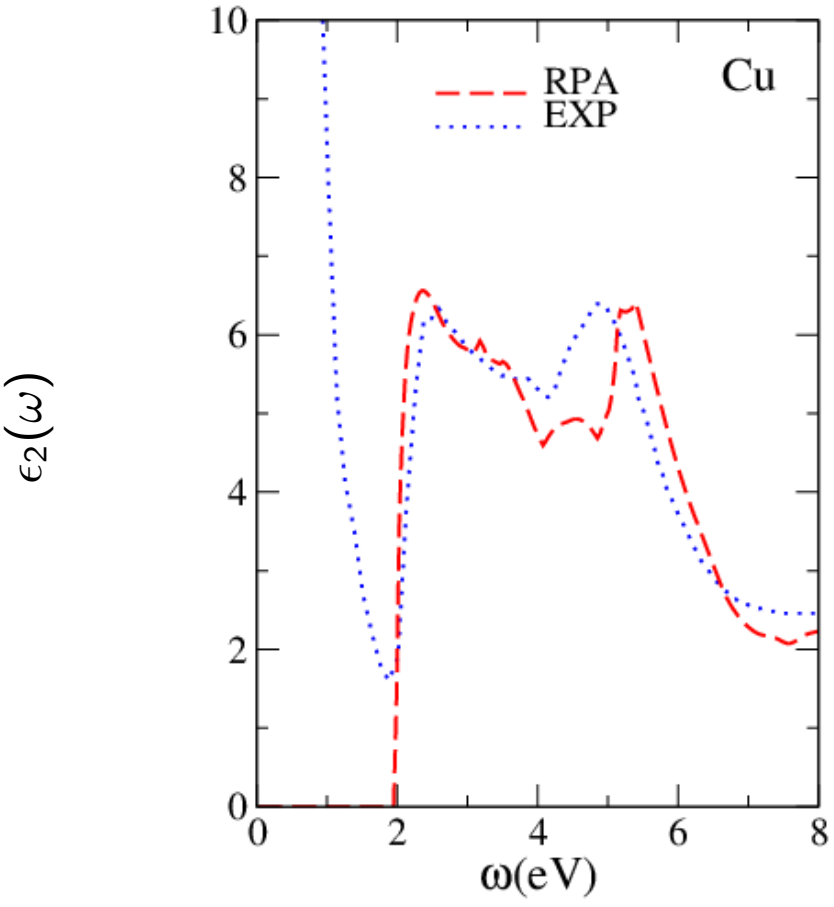


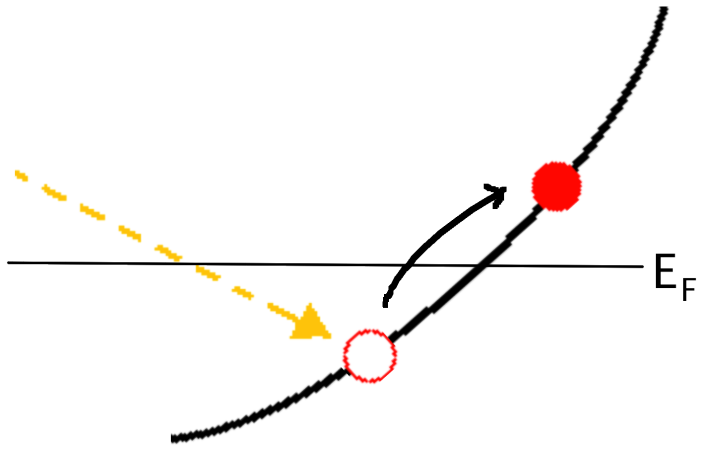
No excitonic effects



Standard functionals

Absence of Drude tails in spectra of metals





Intraband absorption

No relaxation due to scattering effects

Macroscopic xc vector potential

Optical spectra: we can neglect microscopic xc contributions.

$$\delta\vec{j}(\vec{r},\omega) = \int d\vec{r}\,' \overleftrightarrow{\chi}^{\vec{j}\vec{j}}_{KS}(\vec{r},\vec{r}\,',\omega)[\vec{A}_{mac}(\omega) + \vec{A}^{H}(\vec{r}\,',\omega) + \vec{A}^{xc}(\vec{r}\,',\omega)]$$

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

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Polarization functional

$\vec{A}^{xc}_{mac}(\omega)$ can be written as polarization functional:

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

For a given $\overleftrightarrow{\alpha}(\omega)$ we can simply obtain $\overleftrightarrow{\epsilon}_M(\omega)$ from $\overleftrightarrow{\epsilon}^{RPA}_M(\omega)$:

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

Relation to TDCDFT kernel:

$$\overleftrightarrow{\alpha}(\omega) = \frac{1}{V} \int_V d\vec{r} \int d\vec{r}\,' \overleftrightarrow{f}_{xc}(\vec{r}, \vec{r}\,', \omega)$$

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

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Summary:

1. Perform self-consistent RPA ($\overleftrightarrow{\alpha} = 0$) calculation
2. Apply $\overleftrightarrow{\alpha}(\omega)$ to obtain $\overleftrightarrow{\epsilon}_M(\omega)$ (post-SCF)

A static polarization functional

The condition to obtain a bound exciton at $\omega = \omega_{be}$ is
(F. Sottile, *et al.* PRB 68, 205112 (2003))

$$\mathrm{Re}[\alpha(\omega_{be})] = 1/\chi_e^{RPA}(\omega_{be}) \qquad \mathrm{Im}[\alpha(\omega_{be}) \simeq 0]$$

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We Taylor expand $\chi_e^{RPA}(\omega_{be})$ around $\omega = 0$ for a Lorentz model with $\epsilon_M(0) \approx 1$:

$$\chi_e^{RPA}(\omega_{be}) \approx \chi_e^{RPA}(\omega = 0)\epsilon_M^{RPA}(\omega = 0)$$

We obtain

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

AB, Phys. Rev. Lett. 115, 137402 (2015)

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Shortcomings:

1. Static $\rightarrow$ no lifetime for bound excitons
2. No effect on metals: $[\epsilon_M^{RPA}(\omega = 0)]^{-1} \rightarrow 0$: no Drude tails

A dynamical polarization functional

We add a complementary part: the long-range part of the dynamical Vignale-Kohn functional (G. Vignale and W. Kohn, PRL 77, 2037 (1996))

$$\overleftrightarrow{Y}_{VK}(\omega) = \frac{1}{V}\int_V d\vec{r}\left(\frac{\nabla\rho_0(\vec{r})\cdot\nabla\rho_0(\vec{r})}{\rho_0^2(\vec{r})} f_{xcT}(\bar{\rho},\omega)\overleftrightarrow{\mathrm{I}}\right.$$
$$\left. + \frac{\nabla\rho_0(\vec{r})\otimes\nabla\rho_0(\vec{r})}{\rho_0^2(\vec{r})}\left[f_{xcL}(\bar{\rho},\omega) - f_{xcT}(\bar{\rho},\omega) - \frac{d^2 e_{xc}}{d\bar{\rho}^2}\right]\right),$$

- Exact for an inhomogeneous electron gas.
- VK leads to excellent spectra for metals
  AB, P. Romaniello, R. van Leeuwen, P.L. de Boeij, JCP 74, 245117 (2006)
- Only small effect on spectra of semiconductors w.r.t. RPA/ALDA
  AB, P.L. de Boeij, R. van Leeuwen, JCP 75, 035116 (2007)

Summary

We propose:

$$\overleftrightarrow{\alpha}(\omega) = \underbrace{[\overleftrightarrow{\epsilon}^{RPA}_{M}(0)]^{-1}[\overleftrightarrow{\chi}^{RPA}_{e}(0)]^{-1}}_{\textit{Static: Excitons}} + \underbrace{\overleftrightarrow{Y}_{VK}(\omega)}_{\textit{Dynamical: Scattering}}$$

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Static part: excitons

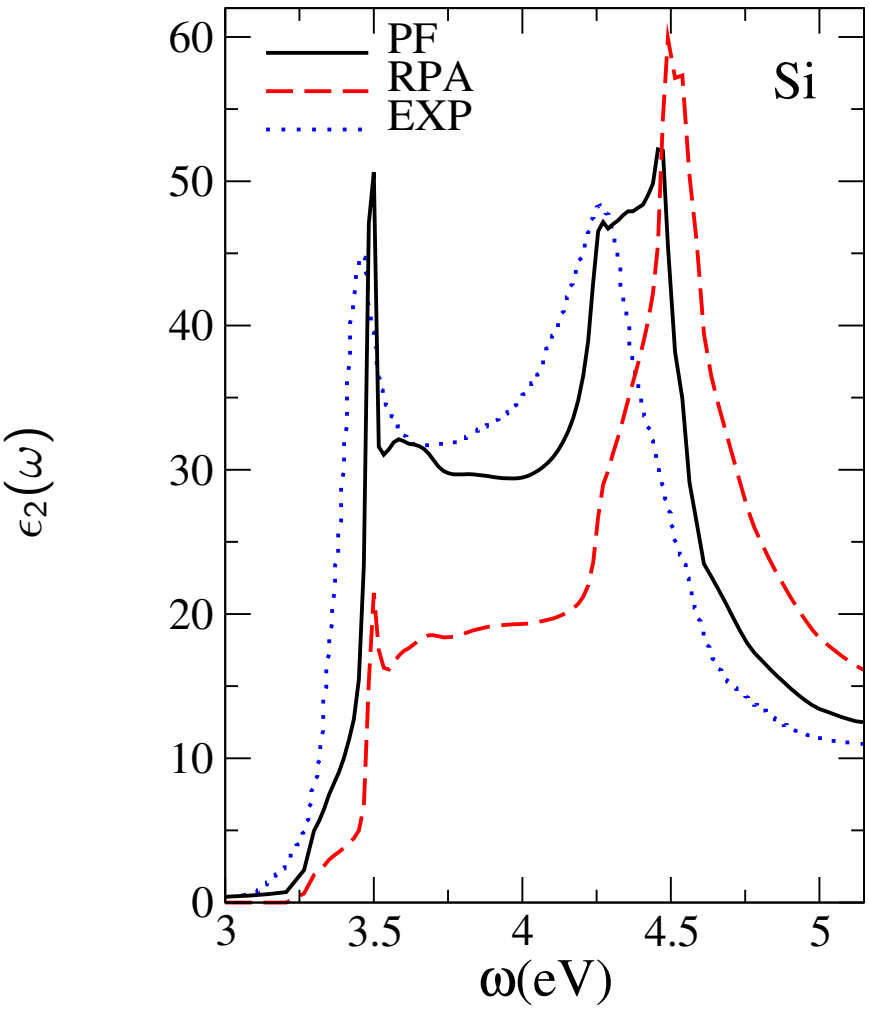
- continuum excitons
- position of bound excitons

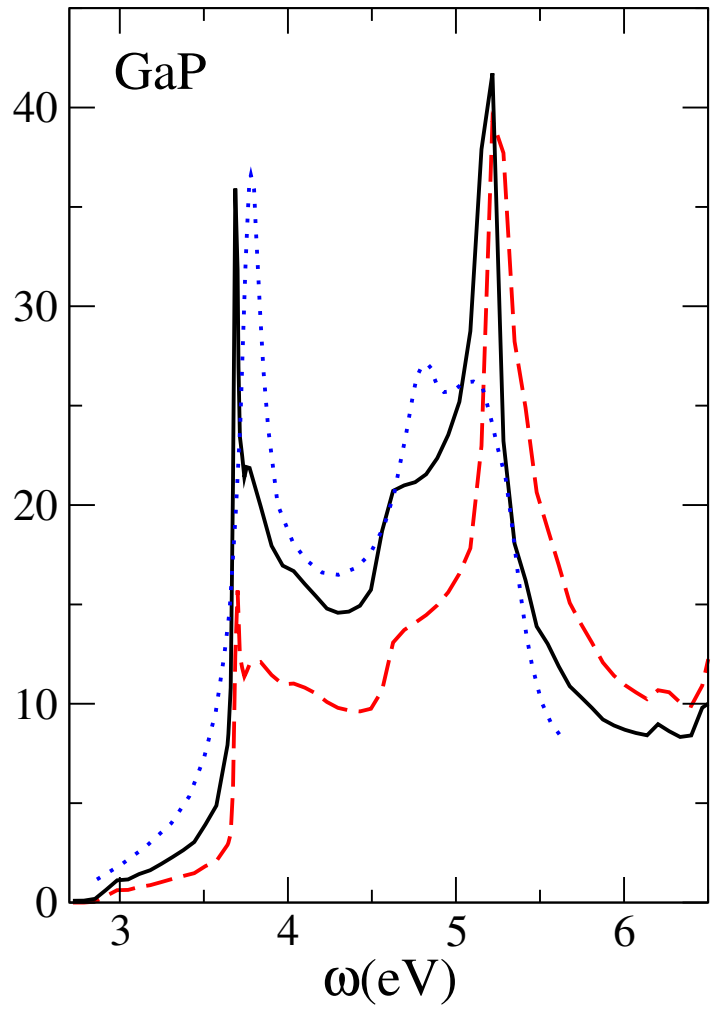
Dynamical part: electron-electron scattering

- Drude tails
- lifetime of bound excitons

AB, Phys. Rev. Lett. 115, 137402 (2015)

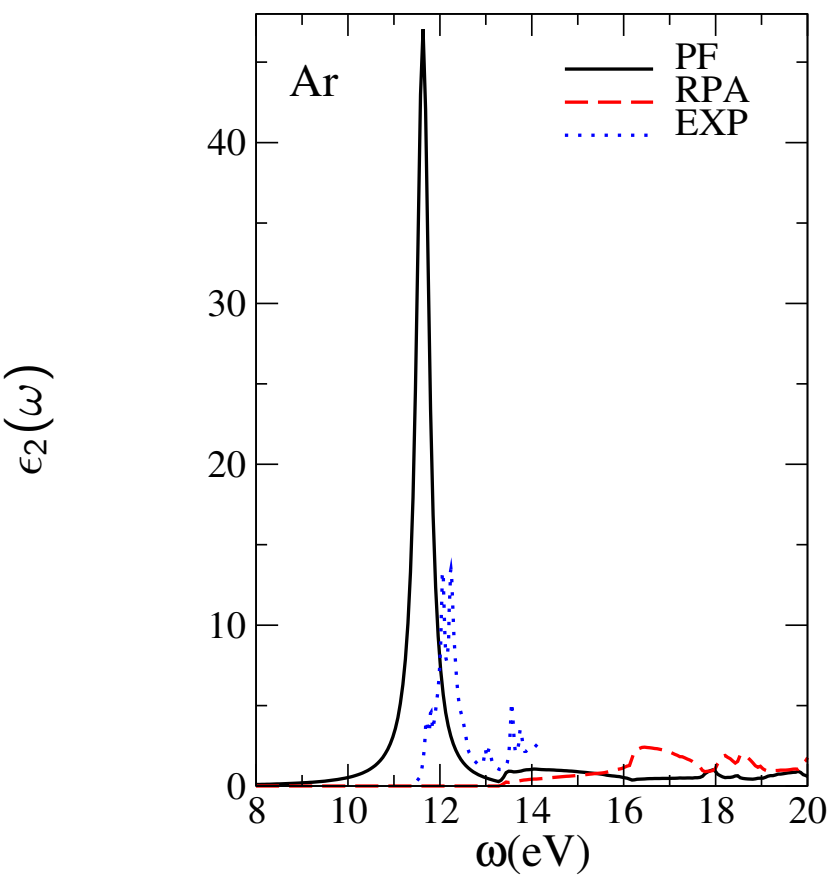
Results: Silicon and GaP

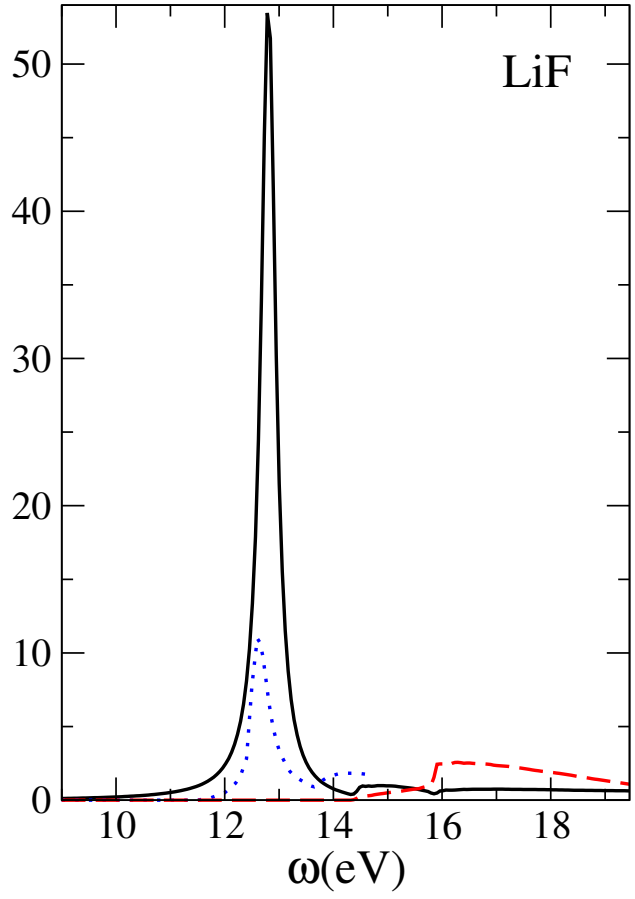




Continuum excitons.

Results: solid argon and LiF



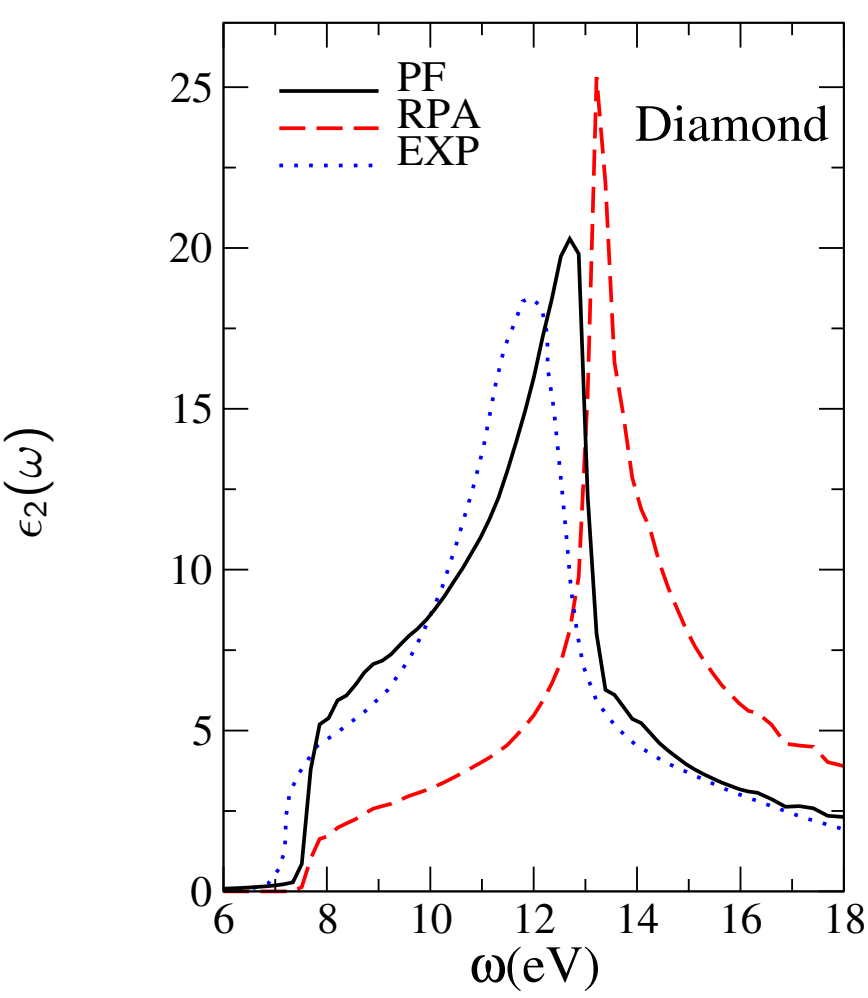


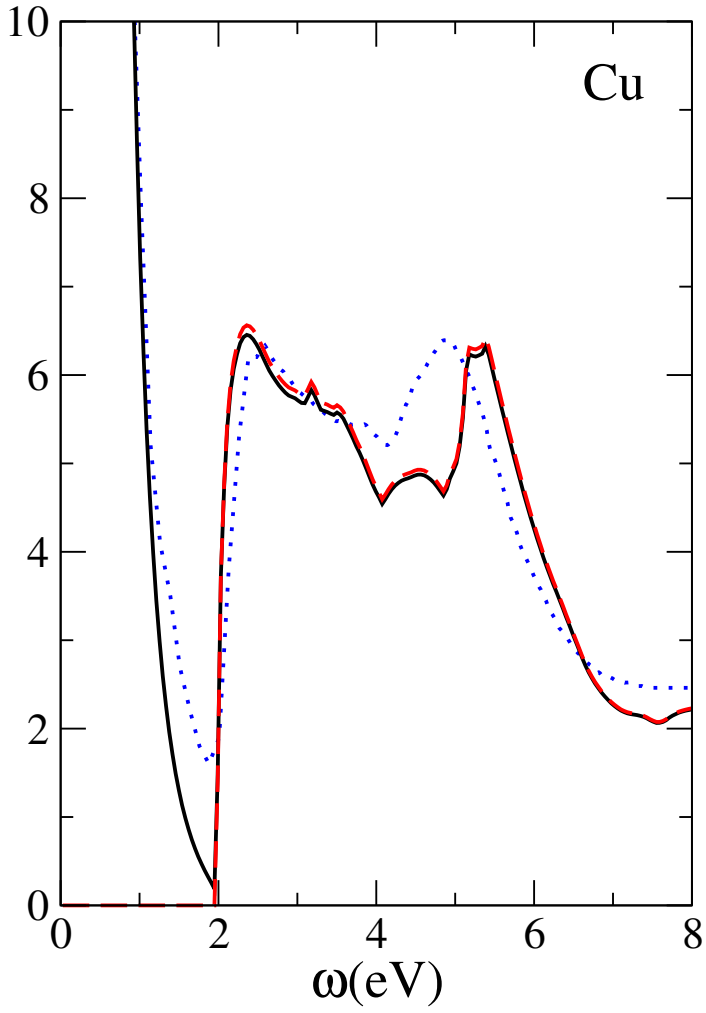
Bound excitons.

Table: Exciton binding energy (eV)

	PF	Exp
Ar	2.3	2.3
LiF	1.6	1.6

Results: diamond and copper





Drude tails.

Conclusions

- We presented a 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.