



## Optical properties of solids

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The *ab-initio* calculation of optical absorption spectra of nano-structures and solids is a formidable task. The current state-of-the-art is based on many-body perturbation theory: one solves the Bethe-Salpeter equation (BSE) using the one-body Green's function obtained from the *GW* approximation. Resonances, corresponding to bound electron-hole pairs called excitons, which have energies inside the gap, can then appear in the spectrum. This procedure is a well-established method for yielding macroscopic dielectric tensors which are generally in good agreement with experiment. Unfortunately, solving the BSE involves diagonalizing a large matrix making this method computationally very expensive.

Time-dependent density functional theory (TDDFT) [1], which extends density functional theory into the time domain, is another method able, to determine neutral excitations of a system. Although formally exact, the predictions of TDDFT are only as good as the approximation of the exchange-correlation (xc) kernel:  $f_{xc}(\mathbf{r}, \mathbf{r}', t - t') \equiv \delta v_{xc}(\mathbf{r}, t) / \delta \rho(\mathbf{r}', t')$ , where  $v_{xc}$  is the TD exchange-correlation potential and  $\rho$  is the TD density. There are several such approximate kernels in existence, the earliest of which is the adiabatic local density approximation (ALDA) [2]. However in the dielectric function calculated using ALDA the physics of the bound electron-hole pair is totally missing. There have been previous attempts to solve this problem, and there exist kernels which correctly reproduce the peaks in the optical spectrum associated with bound excitons. The nano-quanta kernel [3], derived from the four-point Bethe-Salpeter kernel, is very accurate but has the drawback of being nearly as computationally demanding as solving the BSE itself. The long-range correction (LRC) kernel has a particularly simple form,  $f_{xc} = -\alpha/q^2$ , which limits its computational cost. This kernel produces the desired excitonic peak, but depends on the choice of the parameter  $\alpha$ , which turns out to be strongly material-dependent, thereby limiting the predictiveness of this approximation. In our latest work [4, 5] we propose a new parameter-free approximation for  $f_{xc}$ , and demonstrate that this kernel is nearly as accurate as BSE with a computational cost of ALDA.

The exact relationship between the dielectric function  $\varepsilon$  and the kernel  $f_{xc}$  for a periodic solid can be written as

$$\varepsilon^{-1}(\mathbf{q}, \omega) = 1 + \frac{v(\mathbf{q})\chi_0(\mathbf{q}, \omega)}{1 - [v(\mathbf{q}) + f_{xc}(\mathbf{q}, \omega)]\chi_0(\mathbf{q}, \omega)}, \quad (1)$$

where  $v$  is the bare Coulomb potential,  $\chi$  is the full response function, and  $\chi_0$  is the response function of the non-interacting Kohn-Sham system. All these quantities are matrices in the basis of reciprocal lattice vectors  $\mathbf{G}$ . The bootstrap kernel is a frequency-independent approximation given by:

$$f_{xc}(\mathbf{q}, \omega) = \frac{\varepsilon^{-1}(\mathbf{q}, \omega = 0)}{\chi_0(\mathbf{q}, \omega = 0)} \quad (2)$$

where  $\varepsilon^{-1}(\mathbf{q}, \omega = 0)$  is determined *self-consistently* with Eq. (1). We note that although Eq. (1) is exact, it is useful only when either  $f_{xc}$  or  $\varepsilon$  is given; if neither are available then obviously it cannot be used as a generating equation for both quantities. With the addition of the approximation given by Eq. (2) however, both  $f_{xc}$  and  $\varepsilon$  can be determined from knowledge of  $\chi_0$  exclusively. The advantages of this form for the kernel is that 1. it has the correct  $1/q^2$  behavior; 2. as  $\varepsilon$  improves from cycle to cycle so does  $f_{xc}$ ; 3. the computation cost is minimal and 4. most importantly, no system-dependent external parameter is required. Using the method the optical spectra for various extended systems have been calculated using the ELK code [6].

Presented in Fig. 1 are the results for some small (Ge  $\sim 0.67$  eV) to medium (diamond  $\sim 5.47$  eV) bandgap semiconductors. For comparison, experimental data as well as the RPA spectra are also plotted. The experimental data clearly show that all these materials have weakly bound excitons leading to a small shifting of the spectral weight to lower energies compared to RPA. The results from TDDFT with the new kernel exactly follow this trend and are in excellent overall agreement with experiment.

A stringent test for any approximate xc-kernel is in its ability to treat materials with strongly bound excitons. In these cases a new resonant peak appears in the bandgap itself and represents the bound state of an electron-hole pair. Perhaps the most studied test case for this phenomenon is the ionic solid LiF. Other excitonic materials which have also attracted attention and are considered particularly difficult to treat are the noble gas solids. Plotted in the first column of Fig. 2 are the results for three materials of this class: LiF, solid

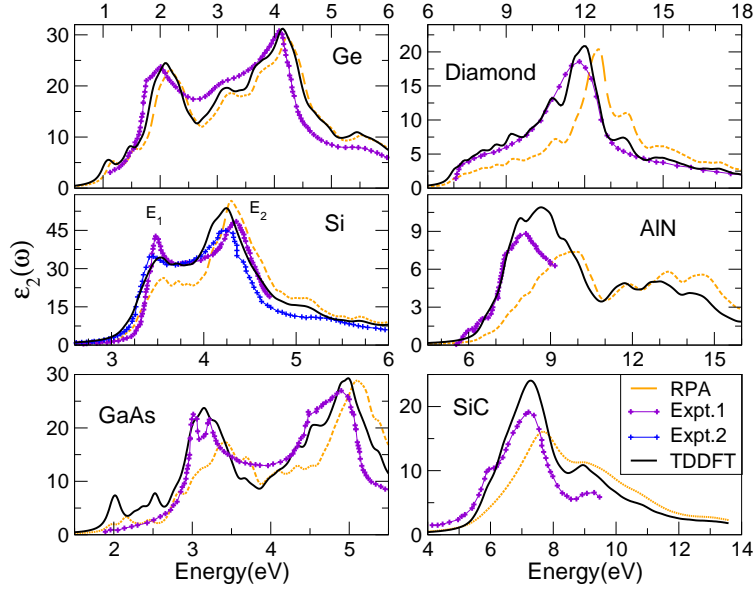


FIG. 1: Imaginary part of the dielectric tensor ( $\varepsilon_2$ ) as function of photon energy (in eV).

Ar and Ne. What is immediately clear is that the bootstrap procedure, which gave only a slight shift of spectral weight for Ge, now gives rise to an entirely new bound excitonic peak inside the gap in all three cases. The location of the peak, which corresponds to the excitonic binding energy, is also very well reproduced for all these materials.

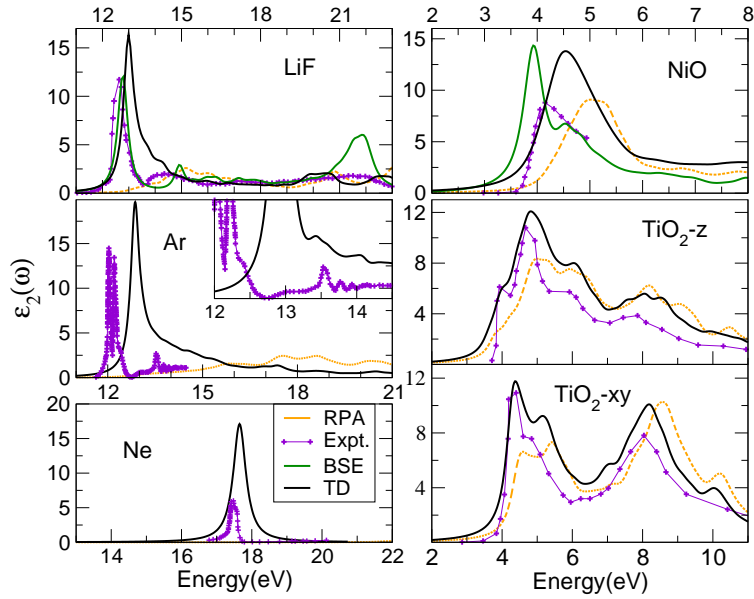


FIG. 2: Imaginary part of the dielectric tensor ( $\varepsilon_2$ ) as function of photon energy (in eV).

The second column of Fig. 2 consists of some special cases – NiO has an anti-ferromagnetic ground state and provides the bootstrap technique with a test of its validity for magnetic

materials. It is clear from Fig. 2 that the bootstrap method leads once again to the correct excitonic binding energy. Results for the anatase phase of  $\text{TiO}_2$  are also presented in Fig. 2.  $\text{TiO}_2$  is a useful test for the bootstrap method due to its non-cubic unit cell, which leads to directional anisotropy in the optical spectrum. As can be seen the bootstrap method captures this anisotropy very well. Even subtle features like the small shoulder at  $\sim 4$  eV in the out-of-plane dielectric function, which is missing in the in-plane case, are well reproduced.

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