

Excitonic effects in the optical properties of CdSe nanowires

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Using a first-principle approach beyond density functional theory we calculate the electronic and optical properties of small diameter CdSe nanowires. Our results demonstrate how some approximations commonly used in bulk systems fail at this nanoscale level and how indispensable it is to include crystal local fields and excitonic effects to predict the unique optical properties of nanowires. From our results, we then construct a simple model to describe the optical gap as a function of the diameter of the wire, that turns out to be in excellent agreement with experiments for intermediate and large diameters. © 2010 American Institute of Physics. [doi:10.1063/1.3368126]

Nanowires (NWs) exhibit a wide range of unique properties,¹ including tunable band gaps, ballistic transport, optical anisotropy,² and strong excitonic effects.³ It is therefore not surprising that for the past 20 years NWs have emerged as one of the most active fields of research in material science.¹ This growing interest is mainly due to their short term promising applications and is empowered by a strong demand from industries for smaller and more effective devices. To a large extent, the properties of NWs emerge from the lateral confinement of the electrons, leading to the blueshift in the electronic band gap with decreasing diameter.

In this article, we focus on the optical properties of CdSe NWs from a first-principle perspective, based and going beyond standard density functional theory (DFT). Beside analyzing how optical properties evolve with the diameter of the wire, we test some approximations that are commonly used for bulk materials and discuss their applicability to electronic excitations in one-dimensional systems. Several studies of the optical properties of CdSe wires have appeared in the past years.^{4–6} Classical² and semiempirical⁶ methods have been quite useful in describing large-diameter wires but they fail for small and medium diameters. Moreover, none of the articles using first-principle methods present in the literature^{4,5} was capable of capturing the physics of electronic excitations in these confined systems. This was due to the neglect of at least one of the following physical effects that are fundamental for an accurate description of nanoscale objects:

- (a) Crystal local-field effects. When the polarization of the light is perpendicular to the long axis there is an accumulation of charges at the wire surface, which in turn is responsible for the attenuation of the electric field inside the NW. This leads to a strong suppression of the absorption for light polarized perpendicular to the NW axis, increasing dramatically the optical anisotropy of the system.⁷ This huge effect has already been measured² in polarized photoluminescence experiments, but unfortunately some recent theoretical works^{5,8} still neglect it.
- (b) Electron-electron interaction and excitonic effects.

These effects are very pronounced in semiconducting NWs due to the attenuation of the screening. The strong electron-hole binding is responsible for a red-shift in the fundamental absorption frequency. Due to this effect, NWs can be seen as exciton traps, a property that endows them of great technological interest.³

To study the importance of local-field corrections, we calculated the absorption spectra of unpassivated CdSe NWs of five different diameters (0.73, 1.17, 1.59, 1.77, and 2.01 nm) starting from DFT Kohn–Sham states and applying the random-phase approximation (RPA) to obtain the dielectric tensor (for details on this and all the other approximations employed in the following refer to Ref. 9). The neglect of local-field effects is equivalent to applying Fermi's golden rule, i.e., to treat only independent particle transitions and to ignore completely the inhomogeneity in the dielectric response due to the reduced dimensionality of the nano-object.

All CdSe NWs were assumed to be infinitely long with periodic length 7.01 Å and with their axis parallel to the wurtzite (001) axis. Ground state calculations were performed using the DFT code ABINIT, and the core electrons of Cd ([Kr]4d¹⁰) and Se ([Ar]3d¹⁰) were described by Hamann norm conserving pseudopotentials. We chose the Perdew–Burke–Ernzerhof¹⁰ approximation to the exchange–correlation functional. Converged calculations required a cutoff energy of 20 Ha and a 1 × 1 × 8 Monkhorst-Pack sampling of the Brillouin zone. Atomic positions were relaxed starting from the bulk wurtzite structure. The converged spacing between the wires in our supercell approach was at least 7 Å.

The optical spectra of the wire with 0.73 nm, calculated at the RPA level including or neglecting local fields is shown in Fig. 1. Without local fields, there is a small anisotropy between the absorption perpendicular and parallel to the NW axis, comparable to the anisotropy in bulk CdSe. However, and as expected, turning on local-field effects suppresses completely the low energy absorption peaks in the perpendicular direction, rendering the wire almost transparent below 6.5 eV. This optical anisotropy, in agreement with experiments,² clearly decreases with increasing diameter, but it is known to be still relevant for NWs with a diameter of 100 nm.

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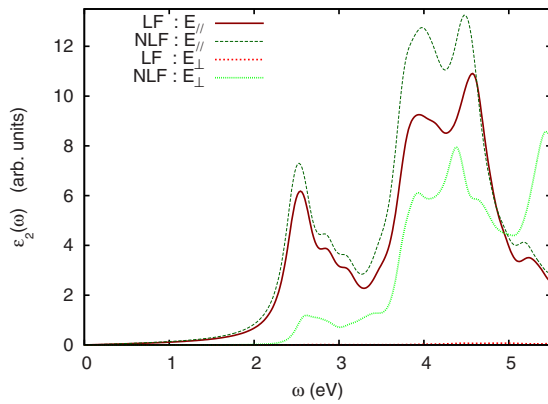


FIG. 1. (Color online) Imaginary part of the dielectric function for the smallest NW ($d=0.73$ nm), calculated in the RPA with local fields (LF) and without (NLF), for light polarized parallel (E_{\parallel}) and perpendicular (E_{\perp}) to the wire axis. Note that the absorption is zero for NLF: E_{\perp} .

To observe how the optical properties vary with the diameter, we plot the RPA spectrum (including local fields) for five small wires in Fig. 2. It is expected that the RPA gives a poor quantitative result due to the inappropriate treatment of electron-electron and electron-hole interactions but it is however possible to extract qualitative trends thanks to the partial cancellation of these two terms (see below). Increasing the diameter, thereby decreasing the confinement effect, leads to a redshift in the spectrum, with the absorption threshold moving toward the RPA bulk value. There is also a redistribution of the oscillator strengths, with the first peak losing intensity.

To go beyond the RPA and to include the relevant missing contributions, we performed calculations solving the Bethe–Salpeter equation (BSE) and using time-dependent DFT⁹—both in the adiabatic local density approximation (ALDA) and with the model long range (LRC) kernels¹¹ derived from the BSE. The BSE approach is the state-of-the-art method for calculations of optical absorption and gives results in excellent agreement with experiments.⁹ For the LRC and BSE calculations, one requires as a starting point the quasiparticle band structure, usually obtained within the GW approximation. Note that the GW approximation predicts accurate band gap energies for CdSe, in contrast with the systematic underestimation of the gap obtained in DFT. Unfortunately, GW calculations are computationally demanding, even for the small wires studied here. We therefore used the

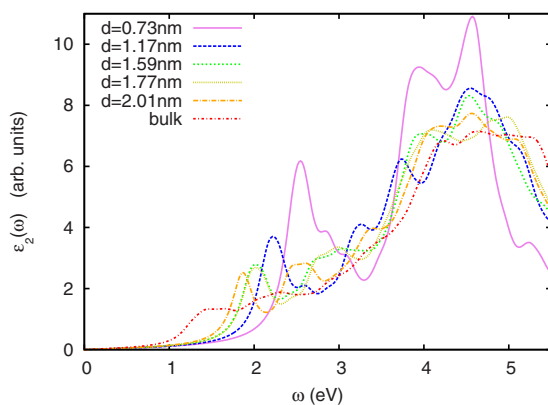


FIG. 2. (Color online) Dependence of the RPA absorption spectrum with the diameter of the NW. For comparison we also show the RPA result for the wurtzite CdSe bulk material.

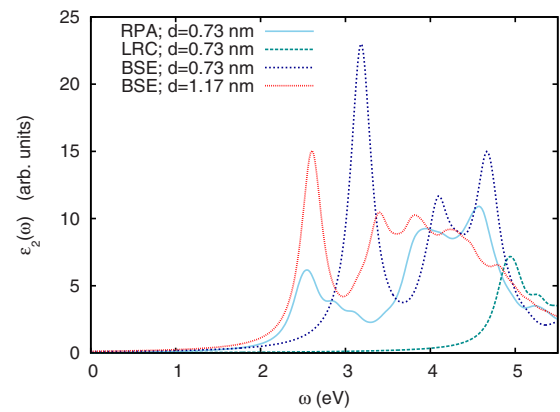


FIG. 3. (Color online) Imaginary part of the dielectric constant in the different approximations: RPA, LRC kernel, and BSE for the $d=0.73$ nm NW. The ALDA results (not shown) are almost identical to the RPA. Also shown are the BSE results for the $d=1.17$ nm NW.

following approach to obtain the quasiparticle corrections: we solved the GW equations for the smallest NW, and then used a simple analytical model¹² that accounts for surface and size effects to interpolate between this result and the GW gap of the bulk.¹³

The GW calculations were performed with ABINIT, applying the standard plasmon-pole approximation. An energy cutoff for the dielectric matrix of 9 Ha and the technique of Ref. 14 to reduce the number of unoccupied states in the sums over states were employed. Despite the use of a cylindrical cutoff for the Coulomb interaction,¹⁵ a distance of 10 Å between the wires was required to converge the GW corrections to the Kohn–Sham band structure. These corrections turned out to be quite insensitive to the \mathbf{k} -point and band index, in agreement with other results for Si and Ge NWs,^{8,16} and in contrast with findings for graphene nanoribbons.¹⁷ The GW gap for the smallest wire was $E_{\text{gap}}^{\text{GW}}=4.84$ eV, and the final form of the model relating the quasiparticle gap with the diameter of the wire (d in nanometer) turned out to be $E_{\text{GWgap}}^{\text{model}}(d)=1.91+2.14/d$ (eV). Note that a simple effective mass approximation, accounting for confinement, would give a $1/d^2$ scaling. However, the $1/d$ law^{12,18} is in better agreement with theoretical and experimental data, even for small NWs.

The BSE results (see Fig. 3), obtained using the code YAMBO,¹⁹ prove the existence of strong excitonic effects, with the excitonic peaks in the visible energy range. The excitonic binding energy compensates almost entirely the large blueshift coming from the quasiparticle corrections, and leads to a transfer of the oscillator strength from the higher energy absorption peaks to the first peak. On the other hand, the LRC kernels derived from the BSE, that yield results comparable to the solution of the BSE for bulk CdSe,¹¹ fail dramatically for NWs—in fact, as shown in Fig. 3, even the optical gap resulting from DFT+RPA calculation is in better agreement with the BSE result. The attempt to increase the excitonic effect by modulating the empirical parameters of the LRC kernel did not lead to improvements. The reason is that the simple LRC approximations are only valid for delocalized excitons but fail to reproduce the considerable binding energy of the very localized excitons existing in NWs.

The exciton binding energies from BSE calculations, for the NWs with diameters of 0.73 and 1.17 nm are, respec-

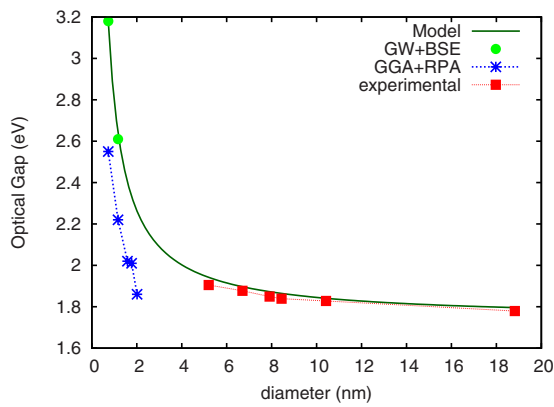


FIG. 4. (Color online) Optical gaps calculated with the RPA and the BSE compared to experiment of Ref. 21. The dotted and dashed lines are a guide to the eye. The solid line is the model interpolation between the smallest NW and the bulk.

tively, 1.6 and 1.13 eV. These values are much larger than the binding energy in bulk CdSe,³ 15 meV, and almost twice as large as the ones found in carbon nanotubes.²⁰ The decrease in the binding energy with the NW diameter, also followed by a transfer of the intensity of the absorption-edge peak to the higher energy ones (see Fig. 3), reflects the weakening of the excitonic effects with the increasing exciton spatial extent. In fact, the exciton radius of bulk CdSe is 5.6 nm.³ A nano-object where one of its dimensions is smaller than this value will have strongly bound excitons, due to a large overlap between electron and hole. Furthermore one expects that the larger the confinement the larger is the excitonic binding energy. In our BSE results we also found spin singlet dark excitons throughout the spectra, with the first one appearing at 3.2 eV for the smallest wire. This dark exciton may play a role in nonradiative decay processes and thus affect the luminescence properties.

Based on our BSE results for the two smallest wires and on the experimental optical gap of the bulk,²¹ we constructed a simple model to interpolate the optical gaps of CdSe NWs. The form is the same as the previous model for the GW gaps, and the formula connecting optical gaps and the diameter of the wire turns out to be $E_{\text{BSEgap}}^{\text{model}}(d \text{ in nm}) = 1.74 + 1.05/d$ (eV). We can see, from Fig. 4, that this model describes extremely well the experimental results²¹ not only for large NWs but also in the intermediate regime. Finally, from Fig. 4 we conclude that although the RPA results are redshifted with respect to the latter they still conserve approximately the correct slope.

In conclusion, the first-principle calculations reported here show how indispensable is the inclusion of local-field and excitonic effect to describe quantitatively the optical re-

sponse of CdSe NWs. In fact, calculations based on the Fermi's golden rule will never be able to catch the physics arising from the low dimensionality of the system, which is at the heart of the properties of NWs. We have then provided a simple model for the dependency of the optical gap with diameter, which is in excellent agreement with available experimental results. Furthermore we have observed the failure of long-range model kernels of time-dependent DFT for these nanoscale systems, in spite of their achievement in the calculation of the optical properties of bulk CdSe.

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