Dimensionality-Dependent Self-Energy Corrections and Exchange-Correlation Potential in Semiconductor Nanostructures

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We study the quasiparticle gap in semiconductor nanostructures versus dimensionality and compare it to the value obtained in the local density approximation. We first develop general arguments based on the *GW* approach which we then substantiate numerically by a tight binding version of this theory. We show that the gap correction is dominated by a macroscopic surface self-polarization term and point out its nonmonotonic behavior versus dimensionality.

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The quasiparticle spectrum of semiconductor nanostructures such as quantum dots (zero-dimensional systems, 0D), wires (1D), or wells (2D) is different from its bulk counterpart. In particular, quantum confinement leads to a large increase of the quasiparticle gap ε_g^{qp} when the size or the dimensionality of the system are reduced (ε_g^{qp} is the difference between the separate electron and hole quasiparticle energies). Until now, most calculations have dealt with the eigenvalue gap ε_g^0 determined from the differences in one-particle eigenvalues for the neutral system. ε_g^0 has been obtained from empirical techniques (tight binding [1], pseudopotentials [2]) or from *ab initio* calculations in the local density approximation (LDA) [3] and differs from ε_g^{qp} by large amounts $\delta\Sigma$ corresponding mainly to self-energy corrections. These can be estimated via the *GW* method [4] derived from many-body perturbation theory. However, such computations are very time consuming and can be applied only to small systems [5–7]. Therefore simpler methods such as one-particle calculations are highly desirable but their accuracy is a matter of controversy [8–10]. In principle, the quasiparticle gap ε_g^{qp} can be calculated exactly in density functional theory (DFT) as

$$\varepsilon_g^{qp} = E(n+1) + E(n-1) - 2E(n), \qquad (1)$$

where $E(n)$ is the total energy of the n-electrons neutral system obtained by solving the one-particle Kohn-Sham equations [11] which are written in terms of an effective exchange-correlation potential V_{xc}. In LDA, $V_{xc}(\mathbf{r})$ is approximated locally by the corresponding expression of the homogeneous gas of the same electron density $n(\mathbf{r})$. We discuss in the following why the quasiparticle gap $(\varepsilon_g^{qp})_{\mathrm{LDA}}$ obtained from Eq. (1) in LDA differs from the true ε_g^{qp} and, in finite systems, from the LDA eigenvalue gap $(\varepsilon_g^0)_{\mathrm{LDA}}$. We write

$$\varepsilon_g^{qp} = (\varepsilon_g^{qp})_{\mathrm{LDA}} + \Delta = (\varepsilon_g^0)_{\mathrm{LDA}} + \delta\Sigma. \qquad (2)$$

Here we want to clarify the dependence of $\delta\Sigma$ and Δ upon the dimensionality of the nanostructure. This is important since Δ reflects a discontinuity of the exact V_{xc} of DFT (not contained in LDA) upon addition of one-electron or hole to the neutral system [12]. We find that $\delta\Sigma$ exhibits a smooth decreasing behavior with increasing dimensionality. On the contrary, Δ presents a peak between 0D and 3D, demonstrating the highly nonlocal nature of V_{xc} [13]. We first explain this behavior in terms of general arguments based on the *GW* approximation in which we isolate a surface long range (macroscopic) contribution to the self-energy. We then substantiate these arguments extending our recent work on spherical nanocrystals [14] via a tight binding *GW* calculation, well adapted to quantitatively treat this macroscopic part. We finally discuss the consequences of our results for quantitative predictions of the gap, their extension to metallic systems, and their relation to the Coulomb gap observed for the tunneling current in nanostructures.

General arguments.—We start from the *GW* expression of the self-energy [4,15]:

$$\Sigma(\mathbf{r},\mathbf{r}',\omega) = -\sum_k u_k(\mathbf{r})u_k^*(\mathbf{r}')\left[n_k v(\mathbf{r},\mathbf{r}') - \frac{1}{\pi}\int_0^\infty d\omega'\left(\frac{n_k}{\varepsilon_k - \omega - \omega'} - \frac{1-n_k}{\omega - \varepsilon_k - \omega'}\right)\mathrm{Im}\,W(\mathbf{r},\mathbf{r}',\omega')\right], \qquad (3)$$

where the u_k are the quasiparticle wave functions of energy ε_k, n_k their occupation numbers in the neutral system, v and W are, respectively, the bare and dynamically screened electron-electron interactions, and ω' has a small imaginary part $-i\delta$. In bulk metallic systems, W is the potential created by the electron surrounded by a full screening hole with a

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size of the order of the Thomas-Fermi wavelength. In a bulk dielectric system, the long range screened potential is $1/\epsilon_0|\mathbf{r} - \mathbf{r}'|$, where ϵ_0 is the long wavelength dielectric constant. This now corresponds to a screening hole of magnitude $(1 - 1/\epsilon_0)$ around the electron, the corresponding screening charge $-(1 - 1/\epsilon_0)$ being repelled at infinity. However, in finite systems, there is a contribution W_s to W coming from the fact that this screening charge is repelled on the surfaces. This corresponds to the macroscopic surface polarization charge in dielectrics and will give an additional important contribution $\delta\Sigma_s$ to the self-energy correction. Thus, for finite systems the total $\delta\Sigma$ is equal to $\delta\Sigma_b + \delta\Sigma_s$, where $\delta\Sigma_b$ is the bulk correction to the energy gap. In simple cases such as spherical dots, thin layers or cylindrical wires $\delta\Sigma_s$ can be readily estimated by simple classical arguments.

An interesting feature of W_s is that it varies slowly within the nanostructure and can now be treated as a macroscopic potential. The corresponding contribution Σ_s to the self-energy is given by

$$\Sigma_s(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{\pi}\sum_k u_k(\mathbf{r})u_k^*(\mathbf{r}') \times \int_0^\infty d\omega'\left(\frac{n_k}{\varepsilon_k - \omega - \omega'} - \frac{1 - n_k}{\omega - \varepsilon_k - \omega'}\right) \times \operatorname{Im} W_s(\mathbf{r}, \mathbf{r}', \omega'). \tag{4}$$

Let us now consider $\langle u_c|\Sigma_s(\varepsilon_c)|u_c\rangle$ for the LUMO (lowest unoccupied) state. The macroscopic potential W_s will only mix u_c with states u_k extremely close in energy and local behavior, i.e., the nearby empty states for which $|\varepsilon_c - \varepsilon_k| \ll \omega' \approx \omega_p$ the plasmon energies. We can thus safely use static screening to obtain

$$\langle u_c|\Sigma_s(\varepsilon_c)|u_c\rangle = \frac{1}{2}\sum_{c'}\langle u_c u_{c'}|W_s(\omega = 0)|u_{c'} u_c\rangle, \tag{5}$$

where the sum is over empty states $u_{c'}$. We now perform a unitary transformation from the delocalized $u_{c'}$ states to localized Wannier functions c_j and get

$$\langle u_c|\Sigma_s(\varepsilon_c)|u_c\rangle = \frac{1}{2}\sum_j |\langle u_c|c_j\rangle|^2\langle c_j c_j|W_s(\omega = 0)|c_j c_j\rangle. \tag{6}$$

A similar expression holds true with the opposite sign for a hole in the HOMO (highest occupied) state in terms of the Wannier functions of the valence band. $\delta\Sigma_s$ is then obtained as the difference between these two quantities which should practically be equal to averages of the classical image potential over the quantum state of interest.

One can wonder if this surface contribution is contained in a LDA calculation of nanostructures such as the one performed in Ref. [10], i.e., in $(\varepsilon_g^{qp})_{\mathrm{LDA}}$ obtained from Eq. (1). The difference $E(n + 1) - E(n)$ can be calculated to lowest order (equivalent to linear screening) by using Slater's transition state [16] as detailed in Ref. [17], expressing $E(n + 1) - E(n) = \varepsilon_c(n + 1/2)$, the LUMO calculated self-consistently with 1/2 electron occupation. This corresponds to a bare excess electron density $(1/2)|u_c(\mathbf{r})|^2$ which should be screened. For 1D, 2D, and 3D systems where the wave function has infinite extension, this is vanishingly small with no net effect on $\varepsilon_c(n + 1/2) = \varepsilon_c(n)$. This is not true, however, for 0D systems where this density is finite of order $1/\Omega$ (Ω being the quantum dot volume). In that case, a total screening charge of $-(1/2)(1 - 1/\epsilon_0)$ is repelled on the surface giving a contribution analogous to Eq. (6). The same is true for a hole. We thus end up with the conclusion that $\delta\Sigma_s$ is correctly obtained in LDA for 0D systems but not for 1D and 2D systems.

Tight binding GW calculations.—We now want to substantiate these general arguments by a more detailed calculation. However, *ab initio GW* calculations for large nanostructures are presently not possible due to computational limits. This is why we extend the tight binding formulation of Ref. [14] performed for nanocrystals with diameter up to 2.2 nm to single Si quantum wells with (001) surfaces saturated by hydrogen atoms to avoid spurious states in the band gap. The electronic structure is calculated in an atomic basis composed of one s and three p orbitals for each silicon atom and one s orbital for each hydrogen atom. We use the Si parametrization of Ref. [18] which includes interactions up to third-nearest neighbors and three center terms. It gives for bulk silicon a good band structure over a large energy range and a correct dielectric function. Our static dielectric constant (10.63 [14]) is slightly underestimated compared to the experimental value of 11.4 [19] but it does not affect the conclusions of the present work. We have checked that similar results are obtained with other parameters which give a band structure of the same quality [20]. We calculate the self-energy correction $\delta\Sigma - \delta\Sigma_b$ to the one-particle gap in the manner described in Ref. [14].

In Fig. 1, we plot $\delta\Sigma - \delta\Sigma_b = \delta\Sigma_s$ with respect to the width d of the quantum well. As for spherical nanocrystals [14], we find that $\delta\Sigma_s$ is close to the macroscopic value calculated using the image-charge method [21] and assuming an effective mass wave function $\cos(\pi z/d)$ for the electron and the hole:

$$\delta\Sigma_s \approx \frac{2e^2}{\epsilon_0 d}\left[0.219\left(\frac{\epsilon_0 - 1}{\epsilon_0 + 1}\right) - \ln\left(\frac{2}{\epsilon_0 + 1}\right)\right]. \tag{7}$$

Thus, we can write to a good degree of accuracy:

$$\varepsilon_g^{qp} = \varepsilon_g^0 + \delta\Sigma \approx \varepsilon_g^0 + \delta\Sigma_b + \delta\Sigma_s, \tag{8}$$

as was the case for spherical nanocrystals also [14]. This confirms the previous general arguments so that Eq. (8) is valid for any dimensionality. Furthermore, for the same reasons, and as argued in detail in Ref. [14], it applies to any type of one-particle calculations, in particular, to LDA where $\delta\Sigma_b \approx 0.65$ eV [5]. This is supported by

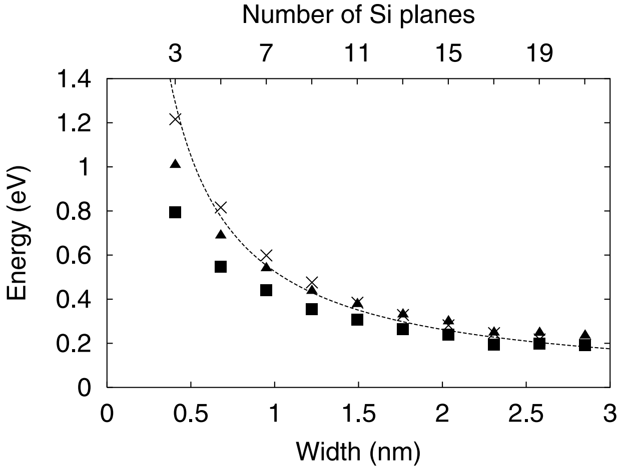

FIG. 1. Variation versus size d of the self-energy correction ($\delta\Sigma - \delta\Sigma_b$) in Si layers (squares: full tight binding; ×: first LDA method; triangles: second LDA method; the three methods are described in Ref. [14]). Line: macroscopic electrostatic energy ($\delta\Sigma_s$) for the separate addition of an electron and a hole, Eq. (7).

recent results [20,22,23] which consistently show that $(\varepsilon_g^0)_{TB}$ obtained by the best tight binding methods agrees with $(\varepsilon_g^0)_{\rm LDA} + (\delta\Sigma_b)_{\rm LDA}$.

In Fig. 2, we plot the variations of $\delta\Sigma_s$ when going from 0D to 3D [24]. As a gedanken experiment, we can consider a continuous change in the shape of a nanostructure with an ellipsoid surface of equation $x^2/a^2 + y^2/b^2 + z^2/c^2 = 1$, going from a sphere of diameter d ($a = b = c = d/2$), to a cylindrical wire ($a \rightarrow \infty$), to a well ($b \rightarrow \infty$), and to the bulk ($c \rightarrow \infty$). It is important to note that the size of the nanostructure is always increasing, and thus we expect that the influence of the surfaces must decrease. This is verified in Fig. 2, where $\delta\Sigma_s$ is continuously decreasing as must be the case for the self-interaction energy with surface polarization charges.

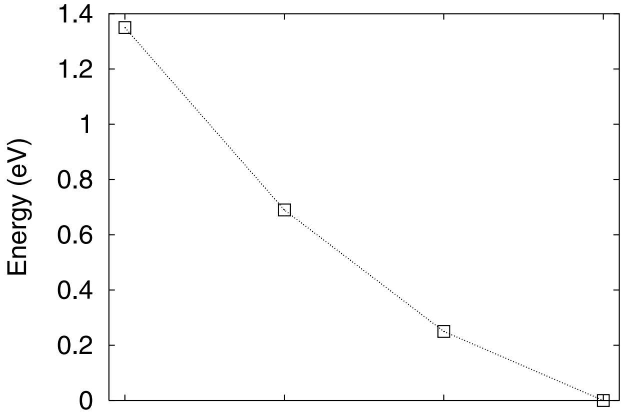

FIG. 2. Variation of $\delta\Sigma - \delta\Sigma_b$ in Si nanostructures of increasing size, going from a sphere (0D) of diameter d ($d = 2$ nm), to a cylindrical wire (1D) of diameter d, to a well (2D) of width d, and then to the bulk. The lines are only guides for the eyes.

We can now deduce the variations of the gap correction $\Delta - \Delta_b$ from those of $\delta\Sigma - \delta\Sigma_b = \delta\Sigma_s$. From Eq. (2) and using the fact that $\Delta_b = \delta\Sigma_b$, we obtain

$$\Delta - \Delta_b = \delta\Sigma_s - [(\varepsilon_g^{qp})_{\rm LDA} - (\varepsilon_g^0)_{\rm LDA}]. \qquad (9)$$

For reasons discussed previously, $(\varepsilon_g^{qp})_{\rm LDA} = (\varepsilon_g^0)_{\rm LDA}$ in extended systems (1D, 2D, 3D), while at 0D the situation is different because $(\varepsilon_g^{qp})_{\rm LDA}$ fully includes the surface contribution $\delta\Sigma_s$. This leads to the curve of Fig. 3, calculated for $d = 2$ nm. Contrary to $\delta\Sigma - \delta\Sigma_b$, the behavior of the gap correction is strongly nonmonotonic with dimensionality.

Discussion and conclusion.—Our main result is that the correction to the exchange-correlation potential is much larger in wires and wells than in spherical dots, whereas the system size is constantly increasing. Thus, $\Delta - \Delta_b$ does not follow a simple scaling law with respect to the size of the nanostructure. These results point out a fundamental difference between finite and infinite systems as regards their description in a Kohn-Sham approach. It is particularly interesting to note that a similar conclusion can be drawn for calculations of optical spectra in time-dependent density functional theory using the adiabatic LDA (TDLDA) for the exchange-correlation kernel f_{xc}. It turns out that, in general, TDLDA yields good results in finite systems [25,26], with spectra considerably improved compared to bare spectra based on time-independent Kohn-Sham LDA eigenvalues (e.g., [27]), but for solids TDLDA results are close to those obtained in a simple random phase approximation [25,28]. Transition energies in finite systems calculated in TDLDA include the time-dependent response to the density variation due the electron-hole excitation, which is infinitesimally small in extended systems [25,29].

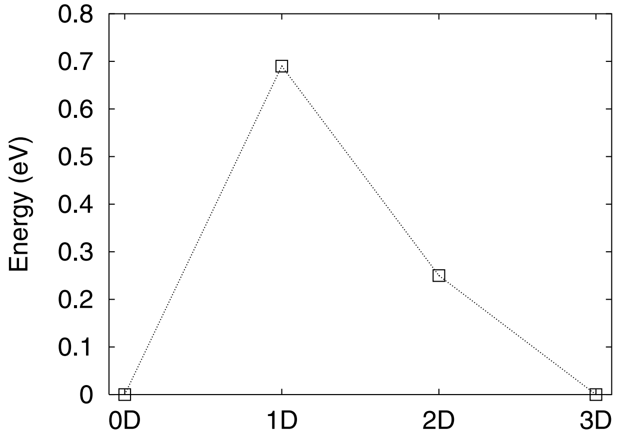

FIG. 3. Variation of $\Delta - \Delta_b$ in Si nanostructures of increasing size, going from a sphere (0D) of diameter d ($d = 2$ nm), to a cylindrical wire (1D) of diameter d, to a well (2D) of width d, and then to the bulk. The lines are only guides for the eyes.

We can now discuss the origin of the evolution of $\Delta - \Delta_b$. Taking into account that the variations of the self-energy correction $\delta\Sigma - \delta\Sigma_b$ have a simple dependence on the system size which can be understood from macroscopic electrostatics, the behavior of $\Delta - \Delta_b$ reflects that the decomposition between the different terms in the Kohn-Sham effective potential is arbitrary [13]. This is particularly clear when going from 0D to 1D (i.e., varying a from d to infinity) since the same physical quantity, the self-polarization energy, which is provided by the Hartree self-consistent term at 0D has to be totally included in the true V_{xc} at 1D. Thus, any attempt to include surface self-polarization terms in the exchange-correlation energy, for example, using a more sophisticated description of the exchange-correlation hole in the vicinity of a surface, would require for V_{xc} an ultra-non-local functional on the electron density.

Our previous considerations show how one might improve current LDA calculations of nanostructures in a simple way. One possibility would be to use a standard LDA calculation for the nanostructure, then add the bulk correction $\delta\Sigma_b$ as a scissor operator, and finally determine the surface correction $\delta\Sigma_s$. To calculate this macroscopic surface polarization term, one could discretize the system into cells (of the order of the atomic cell or more), evaluate the charge in such a cell, calculate self-consistently the corresponding W_s, and determine the average self-energy correction from Eqs. (5) or (6).

As a final point, we would like to emphasize the fact that the macroscopic surface contribution also occurs for metallic nanostructures, even when using a free electron approximation. In that case, the full screening hole is repelled to the surface ($\epsilon_0^{-1} \rightarrow 0$). It is this term which is at the origin of the Coulomb blockade and usually treated in terms of capacitance in association with the electrodes.

In conclusion, we have shown that the self-energy correction to the one-particle gap in Si nanostructures mainly comes from the macroscopic surface polarization term. The exact Kohn-Sham exchange-correlation potential largely differs from its bulk counterpart in extended systems (1D, 2D), whereas it remains close to its bulk value at 0D. One important consequence is that LDA yields comparatively much better results for the quasiparticle gap in 0D systems than in 1D and 2D ones.

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