Comment on "Quantum Confinement and Optical Gaps in Si Nanocrystals"

In a recent Letter [1], Öğüt, Chelikowsky, and Louie (OCL) calculated the optical gap of Si nanocrystals as $\varepsilon_{g,\mathrm{OCL}}^{\mathrm{opt}} = \varepsilon_g^{\mathrm{qp}} - E_{\mathrm{Coul}}^{eh}$, where $\varepsilon_g^{\mathrm{qp}}$ is the *quasiparticle* gap and E_{Coul}^{eh} is the conventional electron-hole Coulomb energy. The authors argued that their method produces different results from previous calculations based on the standard equation

$$\varepsilon_g^{\mathrm{opt}} = \varepsilon_g - E_{\mathrm{Coul}}^{eh}, \tag{1}$$

where ε_g is the *single-particle* gap. We show that the equation for the optical gap used by OCL is in error, as it omits an electron-hole polarization energy E_{pol}^{eh}. When this term is taken into account, the corrected optical gap

$$\bar{\varepsilon}_g^{\mathrm{opt}} = \varepsilon_g^{\mathrm{qp}} - E_{\mathrm{Coul}}^{eh} - E_{\mathrm{pol}}^{eh} \tag{2}$$

is in excellent agreement with the results of the conventional approach [Eq. (1)].

Classical electrostatics [2] provides a useful, simple interpretation of the quasiparticle gap calculated by OCL, defined as the difference between the ionization potential and the electron affinity of an n-electron cluster: $\varepsilon_g^{\mathrm{qp}} = [E(n-1) - E(n)] - [E(n) - E(n+1)]$. In fact, the quasiparticle gap can be rigorously written as $\varepsilon_g^{\mathrm{qp}} = \varepsilon_g + \Sigma_{\mathrm{pol}}$, where Σ_{pol} is the surface polarization energy of the charged $n+1$ and $n-1$ clusters. Σ_{pol} can be approximated [3] as

$$\Sigma_{\mathrm{pol}} \simeq \frac{e^2}{R}\left[\frac{1}{\epsilon_{\mathrm{out}}} - \frac{1}{\epsilon_{\mathrm{in}}} + \frac{0.94}{\epsilon_{\mathrm{in}}}\left(\frac{\epsilon_{\mathrm{in}} - \epsilon_{\mathrm{out}}}{\epsilon_{\mathrm{in}} + \epsilon_{\mathrm{out}}}\right)\right], \tag{3}$$

where ϵ_{in} is the size-dependent dielectric constant of the nanocrystal, ϵ_{out} is the dielectric constant of the barrier (i.e., vacuum), and R is the nanocrystal radius. We have calculated Σ_{pol} from Eq. (3) using the dielectric constant ϵ_{in} of OCL. As shown in Fig. 1(a), the self-energy correction $\Sigma_{\mathrm{OCL}} = \varepsilon_g^{\mathrm{qp}} - \varepsilon_g$ calculated by OCL via local density approximation (LDA) (diamonds) is almost entirely due to the classical polarization energy Σ_{pol} (solid line) for the full range of sizes. Consequently, the fact that the quasiparticle gap $\varepsilon_g^{\mathrm{qp}}$ is different from the single-particle gap ε_g does not constitute a criticism of the latter, as OCL argue, but is merely a comparison of physically distinct quantities.

While OCL included surface polarization effects in the calculation of $\varepsilon_g^{\mathrm{qp}}$, they neglected them in the calculation of the optical gap $\varepsilon_g^{\mathrm{opt}}$. Indeed, the total electron-hole interaction energy is $E_{\mathrm{Coul}}^{eh} + E_{\mathrm{pol}}^{eh}$, where $E_{\mathrm{pol}}^{eh} \simeq (e^2/R)(1/\epsilon_{\mathrm{out}} - 1/\epsilon_{\mathrm{in}})$ describes the interaction between the electron and the surface polarization charge produced by the hole, and between the hole and the surface polarization charge produced by the electron [2,3]. Conventional dielectric functions, such as the one used by OCL, do not build in these surface effects, so they should be added in as an explicit term, as shown in Eq. (2). We see from Fig. 1(a) (dashed line) that the electron-hole polarization energy E_{pol}^{eh}, which was neglected by OCL, is comparable with Σ_{pol}. These two quantities enter Eq. (2) with opposite signs, so in reality they tend to cancel.

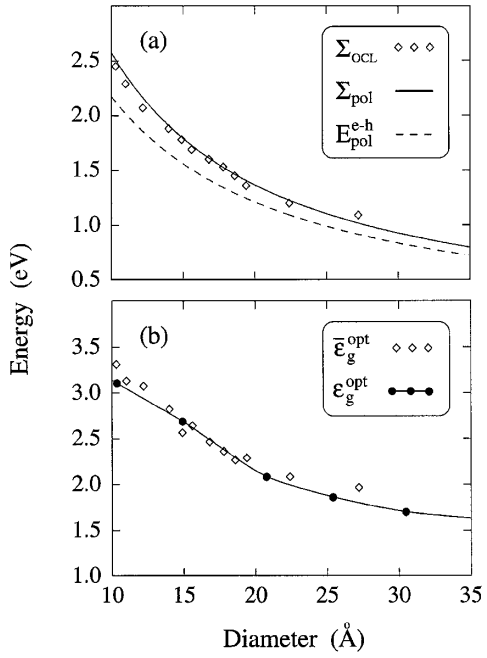

FIG. 1. The symbols are discussed in the text. An LDA correction [5] of 0.68 eV is added to the LDA quasiparticle gap for $D > 10$ Å.

Figure 1(b) compares the corrected optical gap of Eq. (2) with the conventional optical gap of Eq. (1), where the single-particle gap ε_g is obtained from semiempirical pseudopotential calculations [4], and the screened Coulomb energy E_{Coul}^{eh} is borrowed, for consistency of comparison, from OCL's Letter [1]. The optical gap is now slightly lower than the experimental data cited by OCL. The excellent agreement between $\bar{\varepsilon}_g^{\mathrm{opt}}$ and $\varepsilon_g^{\mathrm{opt}}$ suggests that the conventional equation for the optical gap is correct, and that OCL's approach is consistent with this once the omitted terms are introduced.

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