In a recent Letter [1], Öğüt, Chelikowsky, and Louie (OCL) calculated the optical gap of Si nanocrystals as

\[ \varepsilon_{g,\text{OCL}}^{\text{qp}} = \varepsilon_g - E_{\text{Coul}}^{\text{e}} \]

where \( \varepsilon_g \) 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 \( E_{\text{pol}}^{\text{e-h}} \). When this term is taken into account, the corrected optical gap

\[ \varepsilon_{g,\text{OCL}}^{\text{opt}} = \varepsilon_{g,\text{OCL}}^{\text{qp}} - E_{\text{Coul}}^{\text{e}} - E_{\text{pol}}^{\text{e-h}} \]

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: \( \varepsilon_g = [E(n-1) - E(n)] - [E(n) - E(n+1)] \). In fact, the quasiparticle gap can be rigorously written as \( \varepsilon_{g,\text{OCL}}^{\text{qp}} = \varepsilon_g + \Sigma_{\text{pol}}, \) where \( \Sigma_{\text{pol}} \) is the surface polarization energy of the charged \( n + 1 \) and \( n - 1 \) clusters. \( \Sigma_{\text{pol}} \) can be approximated [3] as

\[ \Sigma_{\text{pol}} \approx \frac{e^2}{R} \left[ \frac{1}{\varepsilon_{\text{pol}}} - \frac{1}{\varepsilon_{\text{out}}} + \frac{0.94}{\varepsilon_{\text{in}}} \left( \frac{\varepsilon_{\text{in}}}{\varepsilon_{\text{in}} + \varepsilon_{\text{out}}} \right) \right], \]

where \( \varepsilon_{\text{in}} \) is the size-dependent dielectric constant of the nanocrystal, \( \varepsilon_{\text{out}} \) is the dielectric constant of the barrier (i.e., vacuum), and \( R \) is the nanocrystal radius. We have calculated \( \Sigma_{\text{pol}} \) from Eq. (3) using the dielectric constant \( \varepsilon_{\text{in}} \) of OCL. As shown in Fig. 1(a), the self-energy correction \( \Sigma_{\text{OCL}} = \varepsilon_{g,\text{OCL}}^{\text{qp}} - \varepsilon_g \) calculated by OCL via local density approximation (LDA) (diamonds) is almost entirely due to the classical polarization energy \( \Sigma_{\text{pol}} \) (solid line) for the full range of sizes. Consequently, the fact that the quasiparticle gap \( \varepsilon_{g,\text{OCL}}^{\text{qp}} \) is different from the single-particle gap \( \varepsilon_g \) 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 \( \varepsilon_{g,\text{OCL}}^{\text{qp}} \), they neglected them in the calculation of the optical gap \( \varepsilon_{g,\text{OCL}}^{\text{opt}} \). Indeed, the total electron-hole interaction energy is \( E_{\text{Coul}}^{\text{e-h}} + E_{\text{pol}}^{\text{e-h}} \), where \( E_{\text{pol}}^{\text{e-h}} = (e^2/R)(1/\varepsilon_{\text{pol}} - 1/\varepsilon_{\text{in}}) \) 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