$$
\varepsilon_g - E_{\text{Co 1}}^{eh}, \qquad (1)
$$

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

$$
\varepsilon_g^{\rm op} = \varepsilon_g^{\rm qp} - E_{\rm Co~1}^{eh} - E_{\rm pol}^{eh} \tag{2}
$$

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: $\varepsilon_g^{\text{qp}} =$ $[E(n-1) - E(n)] - [E(n) - E(n+1)].$ In fact, the quasiparticle gap can be rigorously written as $\varepsilon_g^{\text{qp}} =$ ε_{g} + Σ_{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

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

where ϵ_{in} is the size-dependent dielectric constant of the nanocrystal, ϵ_0 is the dielectric constant of the barrier

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 $\varepsilon_g^{\text{qp}}$, they neglected them in the calculation of the optical gap $\varepsilon_g^{\text{op}}$. Indeed, the total electron-

hole interaction energy is $E_{\text{Co 1}}^{eh} + E_{\text{pol}}^{eh}$, where $E_{\text{pol}}^{eh} \approx$ $(e^2/R)(1/\epsilon_0 - 1/\epsilon_{\text{in}})$ 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

We calculated the constant ϵ _{in} of ϵ ¹ ϵ ¹ ϵ ₂ (as shown) ϵ ₁ ϵ ₂ (as shown) ϵ ₂ (as shown) ϵ ₂ (as shown) ϵ ₁ as shown ϵ ₂ (as shown) ϵ ₁ and ϵ ₁ (as shown) ϵ ₁ and ϵ