$$\varepsilon_g = E_{\rm Co\ 1}^{eh}, \qquad (1)$$

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  $E_{pol}^{eh}$ . When this term is taken into account, the corrected optical gap

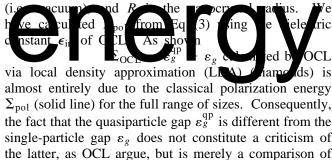
$$\varepsilon_g^{\rm op} = \varepsilon_g^{\rm qp} - E_{\rm Co\ 1}^{eh} - E_{\rm pol}^{eh} \tag{2}$$

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

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

where  $\epsilon_{in}$  is the size-dependent dielectric constant of the nanocrystal,  $\epsilon_{o}$  is the dielectric constant of the barrier



physically distinct quantities. While OCL included surface polarization effects in the calculation of  $\varepsilon_g^{qp}$ , they neglected them in the calculation of the optical gap  $\varepsilon_g^{op}$ . Indeed, the total electronhole 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

## correctio