Size-dependent Photoionization in Single CdSe/ZnS Nanocrystals

Supporting Information

Kevin T. Early* and David J. Nesbitt

JILA, National Institute of Standards and Technology and University of Colorado,

Department of Chemistry and Biochemistry, University of Colorado

Boulder, CO 80309

Current affiliation: 3M, St. Paul, MN 55144

9/3/2013

Wavefunction calculations

Wavefunctions have been calculated for electron and hole charge carriers in the effective mass approximation according to techniques outlined by Haus, *et al.*,[1] and Schoos, *et al.*[2] Because of the rapid relaxation of the initial excitation into the $1S_e$-$1S_h$ band edge, the spherical harmonics are a constant and the radial wavefunction for the 1S-like states are considered. The radial function must satisfy the following conditions to yield physical results: 1) R_{1S} is finite at $r = 0$ and decays appropriately as r approaches infinity, 2) the first derivatives obey the continuity at the interface,

$$R_{1S,core}(r)\big|_{r=a} = R_{1S,shell}(r)\big|_{r=a},$$

where $R_{1S,core}$ and $R_{1S,shell}$ are the core and shell radial functions with the core/shell interface located at r = a, and 3) the effective-mass weighted first derivatives at r = a are matched according to

$$\frac{1}{m^*_{core}}\frac{dR_{1S,core}(r)}{dr}\bigg|_{r=a} = \frac{1}{m^*_{shell}}\frac{dR_{1S,shell}(r)}{dr}\bigg|_{r=a},$$

where m^*_{core} and m^*_{shell} denote the carrier effective masses in each layer. For this simple two-component system, the core and shell functions are described by spherical Bessel functions, $R_{1S,core}(r) = Aj_0(k_{1S}r)$ and $R_{1S,core}(r) = Bh_0^{(1)}(i\kappa_{1S}r)$ where j_0 and $h_0^{(1)}$ are spherical Bessel and Hankel functions,

$$k_{1S} = \sqrt{2m^*_{core}(E_{1S})/h^2}\,,$$

and

$$\kappa_{1S} = \sqrt{2m^*_{shell}(V - E_{1S})/h^2}\,.$$

(1) Haus, J. W.; Zhou, H. S.; Honma, I.; Komiyama, H. *Phys Rev B* **1993**, *47*, 1359.
(2) Schooss, D.; Mews, A.; Eychmuller, A.; Weller, H. *Phys Rev B* **1994**, *49*, 17072.