Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplementary Information for "Quantum-Size Effects in Visible Defect Photoluminescence of Colloidal ZnO Quantum Dots: A Theoretical Analysis."

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Abstract

Within this Electronic Supporting Information we present full derivations of the calculations of overlap integrals and matrix elements.

A. Overlap integrals

The overlap integrals between the conduction band and hole states of eqs. (12) and (14) respectively, as a function of the position of the hole $\mathbf{a}$ are defined as

$$S_{h,(lnm)}(\mathbf{a}) = \frac{\alpha_h^{3/2}}{\sqrt{\pi}} N_{ln} \int_0^R dr\, r^2 \int d\Omega_{\mathbf{r}} e^{-\alpha_h|\mathbf{r}-\mathbf{a}|} j_l\left(\rho_{ln}\frac{r}{R}\right) Y_l^m(\Omega_{\mathbf{r}}), \tag{S1}$$

where the symbol $\Omega_{\mathbf{r}}$ appearing as the argument of the spherical harmonic is a short notation for the arguments (θ, φ). In eq. (S1), $|\mathbf{r} - \mathbf{a}|$ depends on angles through the cosine of the angle γ formed by the vectors $\mathbf{a}$ and $\mathbf{r}$. We use the radius R to normalize variables $x = \frac{r}{R}$ and $a_0 = \frac{a}{R}$ and change $\cos\gamma = t$, and expand $e^{-\alpha_h|\mathbf{r}-\mathbf{a}|}$ in a series of the Legendre polynomials $P_j(t)$ as

$$e^{-\alpha_h|\mathbf{r}-\mathbf{a}|} = e^{-\rho_h\sqrt{a_0^2+x^2-2a_0xt}} = \sum_{j=0}^{\infty} f_j(a_0, x) P_j(t), \tag{S2}$$

with $\rho_h = R\alpha_h$. The coefficients $f_j(a_0, x)$ in eq. (S2) are given by

$$f_j(a_0, x) = \frac{2j+1}{2} \int_{-1}^{+1} dt\, e^{-\rho_h\sqrt{a_0^2+x^2-2a_0xt}} P_j(t). \tag{S3}$$

Expression (S3) can be evaluated analytically. Next, we substitute the last identity of eq. (S2) into eq. (S1), make use of the addition theorem for spherical harmonics:

$$P_j(\cos\gamma) = \frac{4\pi}{2j+1} \sum_{j'=-j}^{j'=j} Y_j^{j'*}(\Omega_{\mathbf{r}}) Y_j^{j'}(\Omega_{\mathbf{a}}), \tag{S4}$$

and obtain

$$S_{h,(lnm)}(\mathbf{a}) = Y_l^m(\Omega_{\mathbf{a}}) \frac{\alpha_h^{3/2}}{\sqrt{\pi}} N_{ln} R^3 \frac{4\pi}{2l+1} \int_0^1 dx\, x^2 f_l(a_0, x) j_l(\rho_{ln} x). \tag{S5}$$

For the state nS, $Y_0^0(\Omega_{\mathbf{a}}) = \frac{1}{\sqrt{4\pi}}$, the corresponding value of $S_{h,1S}$ is plotted in Figure 1.

For comparative purposes, the angular average $[\frac{1}{4\pi}\int d\Omega_{\mathbf{a}} S_{h,(lnm)}(\mathbf{a}) S^*_{h,(lnm)}(\mathbf{a})]^{1/2}$ is plotted in Figure 1 for states with $l \neq 0$. This average goes over the correct value of $S_{h,nS}$ for $l = 0$.

For $a = 0$, $S_{h,nS}$ has the analytical expression

$$S_{h,nS}(\mathbf{a}=0) = \frac{(2\rho_h)^{3/2}}{|j_1(\rho_{0n})|}\int_0^1 dx\, x^2 e^{-\rho_h x} j_0(\rho_{0n}x) \approx$$

$$\approx \frac{(2\rho_h)^{3/2}}{|j_1(\rho_{0n})|}\int_0^\infty dx\, x^2 e^{-\rho_h x} j_0(\rho_{0n}x) = \frac{2^3}{|j_1(\rho_{0n})|}\frac{\rho_h^{5/2}}{(\rho_h^2+\rho_{0n}^2)^2}, \quad \text{(S6)}$$

which, for large values of R, behaves like $S_{h,nS} \approx \frac{1}{R^{3/2}}$.

B. Matrix elements between orthogonal orbitals

To evaluate the matrix elements $\tilde{M}_{h,\alpha}$ $(\alpha \neq h)$ between orthogonal orbitals, we make use of eq. (15) of the main text to express them in terms of the matrix elements between non-orthogonal orbitals as

$$\tilde{M}_{h,\alpha} = \sum_{\gamma,\beta} (\mathbf{S^{-1/2}})_{\mathbf{h},\gamma} \mathbf{M}^{\mathbf{n-o}}_{\gamma,\beta} (\mathbf{S^{-1/2}})_{\beta,\alpha}. \quad \text{(S7)}$$

To obtain an approximate expression for eq. (S7), we introduce eq. (16) of the main text into eq. (S7) yielding, up to order $\mathcal{O}S^2_{\alpha,\beta}$,

$$\tilde{M}_{h,\alpha} = M^{n-o}_{h,\alpha} - \frac{1}{2}\sum_\beta M^{n-o}_{h,\beta} S_{\beta,\alpha} - \frac{1}{2}\sum_\gamma S_{h,\gamma} M^{n-o}_{\gamma,\alpha} \quad \text{(S8)}$$

The second term on the right hand side of eq. (S8) is identically zero because, for $\alpha \neq h$, $S_{\beta,\alpha} \neq 0$ only if $\beta = h$ but $M^{n-o}_{h,h} = 0$. This leads to eq. (17) of the main text.

C. Matrix elements between non-orthogonal orbitals

The matrix elements $M^{n-o}_{h,(lnm)}(\mathbf{a})$, given by eq. (6) of the main text, between the conduction band and hole states of eqs. (12) and (14), respectively, depend on the electric field expressed by eq. (8). Notice that eq. (8) implies $\vec{\nabla}\cdot\mathbf{E}=0$. We write down the term $\mathbf{E}\cdot\vec{\nabla}\phi_{lnm}$ as

$$\mathbf{E}\cdot\vec{\nabla}\phi_{lnm}=\left(1-\frac{\alpha(\omega,R)}{R^3}\right)N_{ln}\left[\frac{\partial j_l(\rho_{ln}\frac{r}{R})}{\partial r}\sin\theta\cos\varphi Y_l^m(\theta,\varphi)+\right.$$
$$\left.+\frac{j_l(\rho_{ln}\frac{r}{R})}{r}\left(\cos\theta\cos\varphi\frac{\partial Y_l^m(\theta,\varphi)}{\partial\theta}-\frac{\sin\varphi}{\sin\theta}\frac{\partial Y_l^m(\theta,\varphi)}{\partial\varphi}\right)\right]. \quad \text{(S9)}$$

The two different terms depending on the angles (θ,φ) appearing on the right hand side of eq. (S9) can be expressed in terms of spherical harmonics with $l'=l\pm1$ and $m'=m\pm1$ as

$$\sin\theta\cos\varphi Y_l^m(\theta,\varphi)=\frac{1}{2}\left[C_{l+1}^{m-1}Y_{l+1}^{m-1}(\Omega_\mathbf{r})-C_{l-1}^{m-1}Y_{l-1}^{m-1}(\Omega_\mathbf{r})-\right.$$
$$\left.C_{l+1}^{m+1}Y_{l+1}^{m+1}(\Omega_\mathbf{r})+C_{l+1}^{m+1}Y_{l-1}^{m+1}(\Omega_\mathbf{r})\right], \quad \text{(S10a)}$$

$$\cos\theta\cos\varphi\frac{\partial Y_l^m(\theta,\varphi)}{\partial\theta}-\frac{\sin\varphi}{\sin\theta}\frac{\partial Y_l^m(\theta,\varphi)}{\partial\varphi}=\frac{1}{2}\left[-lC_{l+1}^{m-1}Y_{l+1}^{m-1}(\Omega_\mathbf{r})-\right.$$
$$\left.(l+1)C_{l-1}^{m-1}Y_{l-1}^{m-1}(\Omega_\mathbf{r})+lC_{l+1}^{m+1}Y_{l+1}^{m+1}(\Omega_\mathbf{r})+(l+1)C_{l-1}^{m+1}Y_{l-1}^{m+1}(\Omega_\mathbf{r})\right], \quad \text{(S10b)}$$

where we have used the short notation $\Omega_\mathbf{r}$ for the angular variables (θ,φ), and with the coefficients given by

$$C_{l+1}^{m+1}=\sqrt{\frac{(l+m+1)(l+m+2)}{(2l+1)(2l+3)}} \quad \text{(S11a)} \qquad C_{l-1}^{m+1}=\sqrt{\frac{(l-m-1)(l-m)}{(2l-1)(2l+1)}} \quad \text{(S11c)}$$

$$C_{l+1}^{m-1}=\sqrt{\frac{(l-m+1)(l-m+2)}{(2l+1)(2l+3)}} \quad \text{(S11b)} \qquad C_{l-1}^{m-1}=\sqrt{\frac{(l+m-1)(l+m)}{(2l-1)(2l+1)}} \quad \text{(S11d)}$$

Substituting eqs. (S10) into eq. (S9), the terms depending on the radial coordinate r that are proportional to each of the spherical harmonics with $l' = l + 1$ and $m' = m \pm 1$ rearrange to yield a term proportional to the spherical Bessel function $j_{l+1}(\rho_{ln}\frac{r}{R})$ and these proportional to the spherical harmonics with $l' = l - 1$ and $m' = m \pm 1$ rearrange to yield a term proportional to the spherical Bessel function $j_{l-1}(\rho_{ln}\frac{r}{R})$. This allows us to express $M^{n-o}_{h,(lnm)}(\mathbf{a})$ as

$$M^{n-o}_{h,(lnm)}(\mathbf{a}) = \frac{\alpha_h^{3/2}}{\sqrt{\pi}} N_{ln} \left(1 - \frac{\alpha(\omega, R)}{R^3}\right) \frac{\rho_{ln}}{R} \int\limits_0^R dr\; r^2 \int d\Omega_{\mathbf{r}}\; e^{-\alpha_h|\mathbf{r}-\mathbf{a}|} \times \\ \times \left[j_{l+1}\left(\rho_{ln}\frac{r}{R}\right) \left(C^{m+1}_{l+1} Y^{m+1}_{l+1}(\Omega_{\mathbf{r}}) - C^{m-1}_{l+1} Y^{m-1}_{l+1}(\Omega_{\mathbf{r}})\right) + \right. \\ \left. + j_{l-1}\left(\rho_{ln}\frac{r}{R}\right) \left(C^{m+1}_{l-1} Y^{m+1}_{l-1}(\Omega_{\mathbf{r}}) - C^{m-1}_{l-1} Y^{m-1}_{l-1}(\Omega_{\mathbf{r}})\right) \right]. \quad \text{(S12)}$$

Substituting eq. (S2) into eq. (S12) yields the final expression for $M^{n-o}_{h,(lnm)}(\mathbf{a})$ as

$$M^{n-o}_{h,(lnm)}(\mathbf{a}) = \frac{\alpha_h^{3/2}}{\sqrt{\pi}} N_{ln} \left(1 - \frac{\alpha(\omega, R)}{R^3}\right) \frac{\rho_{ln}}{R}\; 4\pi R^3 \times \\ \times \left[\left(C^{m+1}_{l+1} Y^{m+1}_{l+1}(\Omega_{\mathbf{a}}) - C^{m-1}_{l+1} Y^{m-1}_{l+1}(\Omega_{\mathbf{a}})\right) \frac{1}{2l+3} \int\limits_0^1 dx\; x^2 f_{l+1}(a_0, x) j_{l+1}(\rho_{ln}x) + \right. \\ \left. + \left(C^{m+1}_{l-1} Y^{m+1}_{l-1}(\Omega_{\mathbf{a}}) - C^{m-1}_{l-1} Y^{m-1}_{l-1}(\Omega_{\mathbf{a}})\right) \frac{1}{2l-1} \int\limits_0^1 dx\; x^2 f_{l-1}(a_0, x) j_{l-1}(\rho_{ln}x) \right]. \quad \text{(S13)}$$

Following an identical procedure, the matrix elements $M^{n-o}_{(l'n'm'),(lnm)}$ between orbitals (lnm) and $(l'n'm')$ are found to be

$$M^{n-o}_{(l'n'm'),(lnm)} = N_{ln} N_{l'n'} \left(1 - \frac{\alpha(\omega, R)}{R^3}\right) \frac{\rho_{ln}}{R} R^3 \times \\ \times \left[\delta_{l',l+1} \left(C^{m+1}_{l+1} \delta_{m',m+1} - C^{m-1}_{l+1} \delta_{m',m-1}\right) \int\limits_0^1 dx\; x^2 j_{l+1}(\rho_{l'n'}x) j_{l+1}(\rho_{ln}x) + \right. \\ \left. + \delta_{l',l-1} \left(C^{m+1}_{l-1} \delta_{m',m+1} - C^{m-1}_{l-1} \delta_{m',m-1}\right) \int\limits_0^1 dx\; x^2 j_{l-1}(\rho_{l'n'}x) j_{l-1}(\rho_{ln}x) \right]. \quad \text{(S14)}$$

Substituting eqs. (S13), (S14) and (S5) into eq. (17) of the main text, one obtains $\tilde{M}_{h,(lnm)}(\mathbf{a})$ as a sum of four terms each one being proportional to one of the products $C_{l\pm1}^{m\pm1} Y_{l\pm1}^{m\pm1}(\Omega_{\mathbf{a}})$. The angular average $\frac{1}{4\pi}\int d\Omega_{\mathbf{a}} |\tilde{M}_{h,(lnm)}|^2$ is then used in the calculation of the emission spectra and the corresponding values of τ_{ph}.