Nanocrystal Excitation Energy

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I. The Exciton Hamiltonian

As shown in the lab manual in §6.2.2, the Hamiltonian for the exciton (i.e., the electron/hole pair) is given by

$$\hat{H} = -\frac{\hbar^2}{2m_\mathrm{e}}\nabla_\mathrm{e}^2 - \frac{\hbar^2}{2m_\mathrm{h}}\nabla_\mathrm{h}^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe}\left|\mathbf{s}_\mathrm{e} - \mathbf{s}_\mathrm{h}\right|} + \frac{e^2}{2}\sum_{k=1}^{\infty}\alpha_k\frac{s_\mathrm{e}^{2k} + s_\mathrm{h}^{2k}}{R^{2k+1}}$$

where ∇_e^2 is the Laplacian with respect to the coordinates of the electron: $s_\mathrm{e}, \theta_\mathrm{e}$, and ϕ_e; ∇_h^2 is the Laplacian with respect to the coordinates of the hole: $s_\mathrm{h}, \theta_\mathrm{h}$, and ϕ_h; $\mathbf{s}_\mathrm{e}$ and $\mathbf{s}_\mathrm{h}$ are position vectors that locate the electron and hole, respectively; s_e is the length of $\mathbf{s}_\mathrm{e}$ and s_h is the length of $\mathbf{s}_\mathrm{h}$; finally, R is the radius of the nanoparticle that contains the exciton. Other symbols are defined in the lab manual.

II. The Exciton Wave Function

As a first approximation, we can say that the wave function for the exciton is the product of the wave functions for the electron-in-a-sphere and the hole-in-a-sphere. The Hamiltonian for a particle-in-a-sphere is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$$

where m is the mass of the particle. When this is used to construct Schrödinger's equation and solved, one finds that

$$\hat{H}\psi_n(r) = E_n\psi_n(r)$$

where

$$E_n = \frac{n^2h^2}{8mR^2}$$

and the normalized wave function is

$$\psi_n(r) = \frac{1}{r\sqrt{2\pi R}}\sin\left(\frac{n\pi r}{R}\right)$$

In the above equations, $n = 1, 2, 3, \ldots$, and r is the distance of the particle from the center of the sphere, and R is the radius of the sphere. Here, we will use the ground (i.e., $n = 1$) state for both the electron and the hole to write the exciton wave function:

$$\begin{aligned}\Phi_{\rm ex}(\mathbf{s}_{\rm e}, \mathbf{s}_{\rm h}) &= \psi_1(s_{\rm e})\psi_1(s_{\rm h}) \\ &= \left[\frac{1}{s_{\rm e}\sqrt{2\pi R}}\sin\left(\frac{\pi s_{\rm e}}{R}\right)\right]\left[\frac{1}{s_{\rm h}\sqrt{2\pi R}}\sin\left(\frac{\pi s_{\rm h}}{R}\right)\right]\end{aligned}$$

Note that the wave function only depends on the distance of the electron or hole from the center of the nanoparticle (i.e., $s_{\rm e}$ or $s_{\rm h}$).

III. The Exciton Energy

To find the energy of the exciton when both the electron and hole are in their ground particle-in-a-sphere quantum state, we use the familiar formula for a quantum expectation value:

$$E_{\rm ex} = \int \Phi_{\rm ex}^* \hat{H} \Phi_{\rm ex}\, d\tau$$

Plugging in the above Hamiltonian, this becomes

$$E_{\rm ex} = \int \Phi_{\rm ex}^* \left(-\frac{\hbar^2}{2m_{\rm e}}\nabla_{\rm e}^2 - \frac{\hbar^2}{2m_{\rm h}}\nabla_{\rm h}^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_{\rm CdSe}\,|\mathbf{s}_{\rm e} - \mathbf{s}_{\rm h}|} + \frac{e^2}{2}\sum_{k=1}^{\infty}\alpha_k \frac{s_{\rm e}^{2k} + s_{\rm h}^{2k}}{R^{2k+1}} \right) \Phi_{\rm ex}\, d\tau$$

Consider the first term:

$$\begin{aligned}E_{\rm ex,1} = \int \Phi_{\rm ex}^* \left(-\frac{\hbar^2}{2m_{\rm e}}\nabla_{\rm e}^2\right)\Phi_{\rm ex}\, d\tau &\equiv \int \Phi_{\rm ex}^* \hat{H}_{\rm e} \Phi_{\rm ex}\, d\tau \\ &= \iint \psi_1(s_{\rm e})\psi_1(s_{\rm h})\hat{H}_{\rm e}\psi_1(s_{\rm e})\psi_1(s_{\rm h})\, d\tau_{\rm e} d\tau_{\rm h}\end{aligned}$$

where we have noted that the quantity in parenthesis is none other than the Hamiltonian for an electron-in-a-sphere, $\hat{H}_{\rm e}$. In the above, $d\tau_{\rm e}$ is the volume element corresponding to the coordinates of the electron, and $d\tau_{\rm h}$ is the volume element corresponding to the coordinates of the hole. This Hamiltonian only depends on the coordinates of the electron, so everything that depends on the coordinates of the hole can be pulled out:

$$E_{\rm ex,1} = \int \psi_1(s_{\rm h})\psi_1(s_{\rm h})\, d\tau_{\rm h} \int \psi_1(s_{\rm e})\hat{H}_{\rm e}\psi_1(s_{\rm e})\, d\tau_{\rm e}$$

Now, since the wave function for the hole is normalized, the first integral is unity; therefore, we are left with

$$E_{\rm ex,1} = \int \psi_1(s_{\rm e})\hat{H}_{\rm e}\psi_1(s_{\rm e})\, d\tau_{\rm e}$$

To solve the remaining integral we can use the Schrödinger equation for an electron-in-a-sphere: $\hat{H}\psi_1(s_\mathrm{e}) = E_1\psi_1(s_\mathrm{e})$:

$$E_{\mathrm{ex},1} = \int \psi_1(s_\mathrm{e}) \frac{h^2}{8m_\mathrm{e}R^2}\psi_1(s_\mathrm{e})\, d\tau_\mathrm{e} = \frac{h^2}{8m_\mathrm{e}R^2}\int \psi_1(s_\mathrm{e})\psi_1(s_\mathrm{e})\, d\tau_\mathrm{e} = \frac{h^2}{8m_\mathrm{e}R^2}$$

where we have used the fact that ψ_1 is normalized.

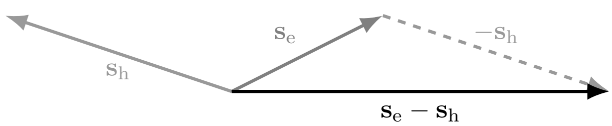
By a similar argument, we may show that the second term in the exciton energy is

$$E_{\mathrm{ex},2} = \int \Phi^*_\mathrm{ex}\left(-\frac{\hbar^2}{2m_\mathrm{h}}\nabla^2_\mathrm{h}\right)\Phi_\mathrm{ex}\, d\tau = \frac{h^2}{8m_\mathrm{h}R^2}$$

The third term in the exciton energy is

$$\begin{aligned} E_{\mathrm{ex},3} &= \int \Phi^*_\mathrm{ex}\left(-\frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe}\left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right|}\right)\Phi_\mathrm{ex}\, d\tau \\ &= -\frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe}}\int \frac{\Phi^*_\mathrm{ex}\Phi_\mathrm{ex}}{\left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right|}d\tau \\ &= -\frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe}}\iint \frac{\left[\psi_1(s_\mathrm{e})\psi_1(s_\mathrm{h})\right]^2}{\left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right|}d\tau_\mathrm{e}d\tau_\mathrm{h} \end{aligned}$$

From your physics and math courses, you'll recall that $\mathbf{s}_\mathrm{e} - \mathbf{s}_\mathrm{h}$ is the vector that points from the hole to the electron:



Therefore, $|\mathbf{s}_\mathrm{e} - \mathbf{s}_\mathrm{h}|$ is simply the distance between the hole and the electron. This can be found using

$$\begin{aligned} \left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right| = \sqrt{(\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h})\cdot(\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h})} &= \sqrt{(\mathbf{s}_\mathrm{e}\cdot\mathbf{s}_\mathrm{e}) + (\mathbf{s}_\mathrm{h}\cdot\mathbf{s}_\mathrm{h}) - 2\mathbf{s}_\mathrm{e}\mathbf{s}_\mathrm{h}} \\ &= \sqrt{s_\mathrm{e}^2 + s_\mathrm{h}^2 - 2s_\mathrm{e}s_\mathrm{h}\cos\alpha} \end{aligned}$$

where α is the angle between the vectors $\mathbf{s}_\mathrm{e}$ and $\mathbf{s}_\mathrm{h}$. (You might also recognize this as the cosine law from trigonometry; this is where it comes from.) So, really, the integral we're dealing with,

$$\iint \frac{\left[\psi_1(s_\mathrm{e})\psi_1(s_\mathrm{h})\right]^2}{\left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right|}d\tau_\mathrm{e}d\tau_\mathrm{h}$$

is the quantum average inverse distance between the electron and the hole. If we write out the full integral, we have

$$\frac{1}{4\pi^2R^2}\iiiint\!\!\iint \frac{1}{\left|\mathbf{s}_\mathrm{e}-\mathbf{s}_\mathrm{h}\right|}\left[\frac{1}{s_\mathrm{e}s_\mathrm{h}}\sin\left(\frac{\pi s_\mathrm{e}}{R}\right)\sin\left(\frac{\pi s_\mathrm{h}}{R}\right)\right]^2 \\ \times s_\mathrm{e}^2\sin\theta_\mathrm{e}ds_\mathrm{e}d\theta_\mathrm{e}d\phi_\mathrm{e}s_\mathrm{h}^2\sin\theta_\mathrm{h}ds_\mathrm{h}d\theta_\mathrm{h}d\phi_\mathrm{h}$$

As you might guess, this is a tricky integral to solve, especially since $|\mathbf{s}_\mathrm{e} - \mathbf{s}_\mathrm{h}|$ depends on the angles. However, we can make a pretty good guess at its value using dimensional analysis. Notice the units of the full expression above are inverse distance. The only quantity that will remain after integration is R, so we should expect the value to be something on the order of $1/R$. Indeed, Kippeny, *et al.* say the result is simply $1.8/R$.* Therefore, the third term in the exciton energy is

$$E_{\mathrm{ex},3} = \int \Phi_\mathrm{ex}^* \left(-\frac{e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe} |\mathbf{s}_\mathrm{e} - \mathbf{s}_\mathrm{h}|} \right) \Phi_\mathrm{ex}\, d\tau = -\frac{1.8e^2}{4\pi\epsilon_0\epsilon_\mathrm{CdSe} R}$$

The final term in the exciton energy is the polarization energy:

$$E_{\mathrm{ex},4} \equiv E_\mathrm{pol} = \int \Phi_\mathrm{ex}^* \left(\frac{e^2}{2} \sum_{k=1}^{\infty} \alpha_k \frac{s_\mathrm{e}^{2k} + s_\mathrm{h}^{2k}}{R^{2k+1}} \right) \Phi_\mathrm{ex}\, d\tau$$

At this point, a simplifying assumption is made; the positions of the electron and hole are combined:

$$\frac{s_\mathrm{e}^{2k} + s_\mathrm{h}^{2k}}{2} \equiv r^{2k}$$

This also allows us to use a single particle-in-a-sphere wave function for Φ_ex:

$$\Phi'_\mathrm{ex}(r) = \frac{1}{r\sqrt{2\pi R}} \sin\left(\frac{\pi r}{R}\right)$$

With these approximations, our integral becomes

$$\begin{aligned} E_\mathrm{pol} &= \int \Phi_\mathrm{ex}^* \left(\frac{e^2}{R} \sum_{k=1}^{\infty} \alpha_k \frac{r^{2k}}{R^{2k}} \right) \Phi_\mathrm{ex}\, d\tau \\ &= \iiint \frac{1}{r^2\,(2\pi R)} \sin^2\left(\frac{\pi r}{R}\right) \frac{e^2}{R} \sum_{k=1}^{\infty} \alpha_k \left(\frac{r}{R}\right)^{2k} r^2 \sin\theta\, dr\, d\theta\, d\phi \\ &= \frac{e^2}{2\pi R^2} \int_0^R \int_0^\pi \int_0^{2\pi} \sin^2\left(\frac{\pi r}{R}\right) \sum_{k=1}^{\infty} \alpha_k \left(\frac{r}{R}\right)^{2k} \sin\theta\, dr\, d\theta\, d\phi \end{aligned}$$

The integrals over θ and ϕ are 2 and 2π, respectively, so we have

$$E_\mathrm{pol} = \frac{2e^2}{R^2} \sum_{k=1}^{\infty} \alpha_k \int_0^R \sin^2\left(\frac{\pi r}{R}\right) \left(\frac{r}{R}\right)^{2k} dr$$

This is Eq. (11) in the lab manual. Before looking at the solution, we can again get a feel for what this integral will look like using dimensional analysis: note that the integrand is unitless, so the integral must have units of distance. After integration, the only variable with units of distance that will remain is R. In

*Using a simplified version of this integral, I was able to estimate its value to be $1.7/R$, so the result does indeed seem reasonable. Feel free to see me if you'd like to see how I approached this.

addition, the answer will depend on the value of k, since that is not integrated out either. As explained in a bit more detail in the manual, the above integral can be evaluated analytically; the solutions are given by

$$E_{\text{pol}} = \frac{2e^2}{R^2} \sum_{k=1}^{\infty} \alpha_k \left\{ \frac{R}{2+4k} \left[1 - {}_1F_2(\tfrac{1}{2}+k; \tfrac{1}{2}, \tfrac{3}{2}+k; -\pi^2) \right] \right\}$$

Each of the terms in the above sum have been evaluated for you and are listed in Table I on p. 60 of the manual. If you put in the expression for α_k and those terms, you'll end up with the following:

$$E_{\text{pol}} = \frac{e^2\,(\epsilon - 1)}{2\pi\epsilon_{\text{CdSe}}\epsilon_0 R} \left(\frac{0.282673}{2+\epsilon} + \frac{0.171117}{1+2\,(1+\epsilon)} + \frac{0.112337}{1+3\,(1+\epsilon)} + \cdots + \frac{0.0191615}{1+10\,(1+\epsilon)} \right)$$

So, given the constants e, ϵ, ϵ_{CdSe}, ϵ_0, and the measured value of R from your experiment, you can calculate the polarization energy of the exciton, and from there the energy of the exciton, E_{ex}.