
Nanocrystal Excitation Energy

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I. The Exciton Hamiltonian

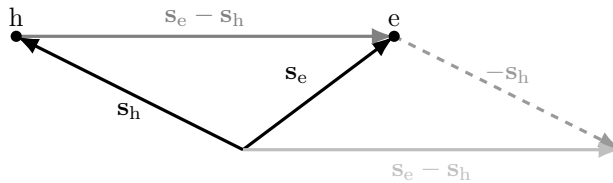
An exciton is formed when an electron is promoted from the valence band of a material to the conduction band. When this happens in a spherical nanoparticle, we can imagine the creation of two ‘particles’, an electron and a hole, that are trapped inside the nanoparticle. This is illustrated in Fig. 1.

As you know, the Hamiltonian is the total energy operator for a system, so to construct the Hamiltonian for an exciton, we need to identify all the contributions to the energy of the system. There are four: the kinetic energies of the electron and hole, the Coulombic potential energy between the negatively charged electron and the positively charged hole, and the polarization potential energy that results from having a dipole within the nanocrystal. These four terms, in the order mentioned above, are:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}}|\mathbf{s}_e - \mathbf{s}_h|} + \frac{e^2}{2}\sum_{k=1}^{\infty}\alpha_k\frac{s_e^{2k} + s_h^{2k}}{R^{2k+1}}$$

where ∇_e^2 is the Laplacian with respect to the spherical coordinates of the electron, viz., s_e, θ_e , and ϕ_e (as shown in Fig. 1); ∇_h^2 is the Laplacian with respect to the coordinates of the hole, viz., s_h, θ_h , and ϕ_h ; \mathbf{s}_e and \mathbf{s}_h are the position vectors that locate the electron and hole, respectively; s_e is the length of \mathbf{s}_e and s_h is the length of \mathbf{s}_h .

From your physics and math courses, you’ll recall that $\mathbf{s}_e - \mathbf{s}_h$ is the vector that points from the hole to the electron, which you can see if you subtract the vectors using the head-to-tail method:



Therefore the length of this vector, $|\mathbf{s}_e - \mathbf{s}_h|$, is simply the distance between the

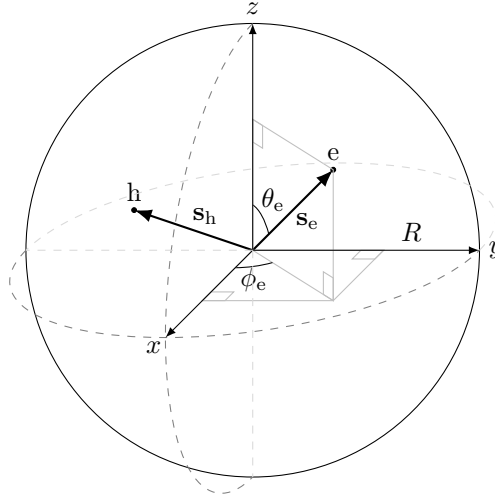


Figure 1. The position vectors for the electron (e) and the hole (h) in the nanocrystal. The spherical coordinates of the electron are also shown. Note that the radius of the nanocrystal is R .

hole and the electron. This scalar can be found using a dot product:

$$\begin{aligned} |\mathbf{s}_e - \mathbf{s}_h| &= \sqrt{(\mathbf{s}_e - \mathbf{s}_h) \cdot (\mathbf{s}_e - \mathbf{s}_h)} = \sqrt{(\mathbf{s}_e \cdot \mathbf{s}_e) + (\mathbf{s}_h \cdot \mathbf{s}_h) - 2(\mathbf{s}_e \cdot \mathbf{s}_h)} \\ &= \sqrt{s_e^2 + s_h^2 - 2s_e s_h \cos \alpha} \end{aligned}$$

where α is the angle between the vectors \mathbf{s}_e and \mathbf{s}_h . (You might also recognize this as the cosine law from trigonometry.) Finally, R is the radius of the nanoparticle that contains the exciton.

For the mass of the hole, use $m_h = 0.018 m_e$. This value has been chosen to minimize the error in excitation energy for the size of the nanocrystals you will make in lab. Other symbols in the Hamiltonian 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 an electron-in-a-sphere and a hole-in-a-sphere. By doing this, we are assuming that the electron and hole are independent and do not interact with each other. 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

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

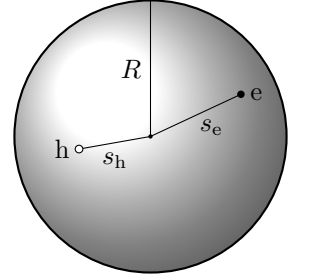
and the normalized wave function is

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

In the above equations, the possible values of the quantum number n are given by $n = 1, 2, 3, \dots$, r is the distance between the particle and 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 approximate exciton wave function as

$$\begin{aligned} \Phi_{\text{ex}}(\mathbf{s}_e, \mathbf{s}_h) &\approx \psi_1(s_e) \psi_1(s_h) \\ &= \left[\frac{1}{s_e \sqrt{2\pi R}} \sin\left(\frac{\pi s_e}{R}\right) \right] \left[\frac{1}{s_h \sqrt{2\pi R}} \sin\left(\frac{\pi s_h}{R}\right) \right] \end{aligned}$$

Note that the wave function is a function of the distances of the electron and hole from the center of the nanoparticle (i.e., s_e or s_h , as shown at right).



The distance variables in a nanocrystal with an exciton.

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 states, we use the familiar formula for a quantum expectation value:

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

Plugging in the above Hamiltonian, this becomes

$$E_{\text{ex}} = \int \Phi_{\text{ex}}^* \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}} |\mathbf{s}_e - \mathbf{s}_h|} + \frac{e^2}{2} \sum_{k=1}^{\infty} \alpha_k \frac{s_e^{2k} + s_h^{2k}}{R^{2k+1}} \right) \Phi_{\text{ex}} d\tau$$

Let us evaluate this expression one term at a time.

A. The Kinetic Energy of the Electron

Consider the first term:

$$\begin{aligned} E_{\text{ex},1} &= \int \Phi_{\text{ex}}^* \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 \right) \Phi_{\text{ex}} d\tau \equiv \int \Phi_{\text{ex}}^* \hat{H}_e \Phi_{\text{ex}} d\tau \\ &= \iint \psi_1(s_e) \psi_1(s_h) \hat{H}_e \psi_1(s_e) \psi_1(s_h) d\tau_e d\tau_h \end{aligned}$$

where we have noted that the quantity in parenthesis is none other than the Hamiltonian for an electron-in-a-sphere, \hat{H}_e . This Hamiltonian only depends on

the coordinates of the electron, so everything that depends on the coordinates of the hole can be pulled out:

$$E_{\text{ex},1} = \int \psi_1(s_h)\psi_1(s_h) d\tau_h \int \psi_1(s_e)\hat{H}_e\psi_1(s_e) d\tau_e$$

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

$$E_{\text{ex},1} = \int \psi_1(s_e)\hat{H}_e\psi_1(s_e) d\tau_e$$

To solve the remaining integral we can use the Schrödinger equation for an electron-in-a-sphere, given above: $\hat{H}\psi_1(s_e) = E_1\psi_1(s_e)$. Substituting this into the last equation and writing out the expression for E_1 , we have

$$E_{\text{ex},1} = \int \psi_1(s_e)\frac{\hbar^2}{8m_eR^2}\psi_1(s_e) d\tau_e = \frac{\hbar^2}{8m_eR^2} \int \psi_1(s_e)\psi_1(s_e) d\tau_e = \frac{\hbar^2}{8m_eR^2}$$

... where we have used the fact that ψ_1 is normalized in the last step.

B. The Kinetic Energy of the Hole

By a very similar argument, you can show that the second term in the exciton energy is

$$E_{\text{ex},2} = \int \Phi_{\text{ex}}^* \left(-\frac{\hbar^2}{2m_h} \nabla_h^2 \right) \Phi_{\text{ex}} d\tau = \frac{\hbar^2}{8m_hR^2}$$

C. The Electrostatic Potential Energy

The third term in the exciton energy is

$$\begin{aligned} E_{\text{ex},3} &= \int \Phi_{\text{ex}}^* \left(-\frac{e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}}|\mathbf{s}_e - \mathbf{s}_h|} \right) \Phi_{\text{ex}} d\tau \\ &= -\frac{e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}}} \int \frac{\Phi_{\text{ex}}^* \Phi_{\text{ex}}}{|\mathbf{s}_e - \mathbf{s}_h|} d\tau \\ &= -\frac{e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}}} \iint \frac{[\psi_1(s_e)\psi_1(s_h)]^2}{|\mathbf{s}_e - \mathbf{s}_h|} d\tau_e d\tau_h \end{aligned}$$

In the above, $d\tau_e = s_e^2 \sin\theta_e ds_e d\theta_e d\phi_e$ is the volume element corresponding to the coordinates of the electron, and $d\tau_h = s_h^2 \sin\theta_h ds_h d\theta_h d\phi_h$ is the volume element corresponding to the coordinates of the hole. So the integral we're dealing with,

$$\iint \frac{[\psi_1(s_e)\psi_1(s_h)]^2}{|\mathbf{s}_e - \mathbf{s}_h|} d\tau_e d\tau_h$$

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

$$\begin{aligned} &\iiint \frac{1}{|\mathbf{s}_e - \mathbf{s}_h|} \left[\frac{1}{2\pi R s_e s_h} \sin\left(\frac{\pi s_e}{R}\right) \sin\left(\frac{\pi s_h}{R}\right) \right]^2 \\ &\quad \times s_e^2 \sin\theta_e ds_e d\theta_e d\phi_e s_h^2 \sin\theta_h ds_h d\theta_h d\phi_h \end{aligned}$$

As you might guess, this is a tricky integral to solve, especially since $|\mathbf{s}_e - \mathbf{s}_h|$ depends on the angle between the electron and the hole position vectors. However, we can make a pretty good guess at its value using dimensional analysis. Notice the units of the integral above are inverse distance. The only quantity that will remain after the integrations 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 $1.8/R$.^{*} Therefore, the third term in the exciton energy is

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

D. The Polarization Energy

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

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

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

$$\frac{s_e^{2k} + s_h^{2k}}{2} \equiv r^{2k}$$

This ‘merging’ of the electron and hole into a single particle a distance r from the center of the nanoparticle also allows us to use a single particle-in-a-sphere wave function for Φ_{ex} :

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

With these approximations, our integral becomes

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

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

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

^{*}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.

Before looking at the solution of this integral, we can again get a feel for what it 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 addition, the answer will depend on the value of k , since that is not integrated out either. It turns out that the above integral can be expressed in terms of something called the generalized hypergeometric function, ${}_1F_2$:

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

The values of the hypergeometric function for the first ten terms in the above sum have been evaluated for you and are listed in Table I on p. 58 of the manual. If you put in the expression for α_k and those values, 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} . (A spreadsheet will make this relatively easy.)

Putting all the pieces back together, we have an expression for the energy of the exciton:

$$\begin{aligned} E_{\text{ex}} &= E_{\text{ex},1} + E_{\text{ex},2} + E_{\text{ex},3} + E_{\text{ex},4} \\ &= \frac{h^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_{\text{CdSe}}R} + E_{\text{pol}} \end{aligned}$$

This is the result given in the manual. Note that once the constants are known, the exciton energy is really just a function of the nanocrystal radius, R .