Derivations and Brief Sketch

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Introduction

In semiconductor materials, the band-gap, the energy to create a non-interacting electron(e^-) and hole(h^+), is a characteristic property. When an electron and a hole approaches each other, they may form a bound-state(exciton) due to a attractive Coulomb potential. The Hamiltonian for this system is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\varepsilon\left|\overline{S_1}-\overline{S_2}\right|} - \qquad \text{(Wannier Hamiltonian)} \qquad \text{(i)}$$

This simple model for interaction works only for large enough crystal sizes(>>60 Angstroms). The length scale is set by the diameter of the lowest-energy(1S) exciton of CdS. As the crystallite size reduces, this model starts to fail, as the contribution to the Hamiltonian due to crystallite surface polarization needs to be accounted for. These surface effects are realized experimentally from spectral data. The motivation for Brus' paper is to develop using classical electrostatics an expression for the potential energy required to assemble an electron-hole system inside a dielectric crystallite so as to construct a semi-classical Hamiltonian that accounts for the crystallite surface polarization effects.

Derivation of Hamiltonian w/ Surface Term

First, consider an electric charge q localized at point $\overline{s}$ inside a small dielectric sphere of dielectric constant ε_2 and radius R, inside an infinite medium of dielectric constant ε_1. The electrostatic potential due to this configuration can be calculated according to the following method : First, the regions inside and outside the sphere should be identified distinctly. For the outside region, it suffices to just solve Laplace's equation, while for the region inside the sphere, the potential is a superposition of the potential inside the interior of an empty sphere with the potential of the charge q at $\overline{s}$. Finally, boundary conditions for the two regions should be considered.

Starting with the potential due to a charge q located at at $\overline{s}$:

$$\frac{q}{\varepsilon_2\sqrt{\bar{s}^2+r^2+2\bar{s}r\cos\theta}}$$

For $\bar{s}\leq r\leq R$,

$$=\frac{q}{\varepsilon_2 r\sqrt{\left(\frac{\bar{s}}{r}\right)^2+1+2\left(\frac{\bar{s}}{r}\right)\cos\theta}}=\frac{q}{\varepsilon_2 r}\sum_{n=0}^{\infty}\left(\frac{\bar{s}}{r}\right)^n P_n(\cos\theta)$$

For $r\leq\bar{s}$

$$=\frac{q}{\varepsilon_2\bar{s}\sqrt{\left(\frac{r}{\bar{s}}\right)^2+1+2\left(\frac{r}{\bar{s}}\right)\cos\theta}}=\frac{q}{\varepsilon_2 r}\sum_{n=0}^{\infty}\left(\frac{r}{\bar{s}}\right)^n P_n(\cos\theta) \qquad \text{(ii)}$$

With the potential of the dielectric sphere, we then have, by solving Laplace's equation and superposition, the potential due to the configuration given by

$$\phi(r,\bar{s})=$$

$$\begin{cases} r\geq R \\ \displaystyle\sum_{n=0}^{\infty}\left(\frac{A_n}{r^{n+1}}\right)P_n(\cos\theta) \\ \bar{s}\leq r\leq R \\ \displaystyle\sum_{n=0}^{\infty}\left(\frac{q}{\varepsilon_2 r}\left(\frac{\bar{s}}{r}\right)^n+B_n r^n\right)P_n(\cos\theta) \\ r\leq\bar{s} \\ \displaystyle\sum_{n=0}^{\infty}\left(\frac{q}{\varepsilon_2\bar{s}}\left(\frac{r}{\bar{s}}\right)^n+B_n r^n\right)P_n(\cos\theta) \end{cases} \qquad \text{(iii)}$$

By considering boundary conditions on the surface of the sphere:

$$\phi_{in}(R,\bar{s})=\phi_{out}(R,\bar{s})$$

$$\varepsilon_2\left.\frac{\partial\phi_{in}(r,\bar{s})}{\partial r}\right|_{r=R}=\varepsilon_2\left.\frac{\partial\phi_{out}(r,\bar{s})}{\partial r}\right|_{r=R} \qquad \text{(iv)}$$

We find

$$B_n = q\left[\frac{(\varepsilon-1)(n+1)}{\varepsilon_2(n\varepsilon+n+1)}\frac{\overline{s}^{-n}}{R^{2n+1}}\right] \qquad \text{(v)}$$

and

$$\phi(r,\overline{s}) = \sum_{n=0}^{\infty} q\left[\frac{(\varepsilon-1)(n+1)}{\varepsilon_2(n\varepsilon+n+1)}\frac{\overline{s}^{-n}r^n}{R^{2n+1}}\right]P_n(\cos\theta) + \frac{q}{\varepsilon_2\left|\vec{r}-\vec{s}\right|} \qquad \text{(vi)}$$

$$\text{where } \frac{\varepsilon_2}{\varepsilon_1} = \varepsilon$$

This is the same expression derived by Botcher. Now, to calculate the potential energy required to assemble this charge distribution, we first imagine bringing a charge dq from infinity to a finite separation $\overline{s}+\delta$. The work done due to this is $\phi(\overline{s},\overline{s}+\delta)dq$. Thus to find the potential energy for a total charge e, we integrate from q=0 to e to get

$$V(\overline{s}) = \int_0^e \phi(\overline{s},\overline{s}+\delta)dq \approx \int_0^e\left[\phi(\overline{s},\overline{s}) + \frac{q}{\varepsilon_2|\delta|}\right]dq = \sum_{n=0}^{\infty}\frac{(\varepsilon-1)(n+1)}{2\varepsilon_2(n\varepsilon+n+1)}\frac{e^2\overline{s}^{-2n}}{R^{2n+1}} + \frac{e^2}{2\varepsilon_2|\delta|}...(\text{w/}\overline{s}=r) \text{ (vii)}$$

It is to be noted that the second term is independent of crystal radius,R, so it merely scales the potential energy. So the term can be dropped. Thus the potential energy of the system just becomes

$$V(\overline{s}) \doteq \sum_{n=0}^{\infty}\frac{(\varepsilon-1)(n+1)}{2\varepsilon_2(n\varepsilon+n+1)}\frac{e^2\overline{s}^{-2n}}{R^{2n+1}} = P(\overline{S}) \qquad \text{(viii)}$$

The same arguments are now applied to an electron(at position $\overline{S}_1$) and hole(at position $\overline{S}_2$) inside a dielectric sphere of dielectric constant ε_2 surrounded by an infinite medium of dielectric constant ε_1. The potential energy required to assemble this distribution is

$$V(\overline{S}_1,\overline{S}_2) = P(\overline{S}_1) + P(\overline{S}_2) - P(\overline{S}_1,\overline{S}_2) - \frac{e^2}{\varepsilon_2\left|\overline{S}_1-\overline{S}_2\right|} \qquad \text{(ix)}$$

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Where

$$P(\overline{S_1}, \overline{S_2}) = \sum_{n=0}^{\infty} \frac{(\varepsilon - 1)(n+1)}{\varepsilon_2 (n\varepsilon + n + 1)} \frac{e^2 \overline{S_1}^n \overline{S_2}^n}{R^{2n+1}} P_n(\cos\theta) \qquad \text{(x)}$$

Where θ is the angle between $\overline{S_1}$ and $\overline{S_2}$. $P(\overline{S_1}, \overline{S_2})$ here should be identified as the surface polarization term(due to $\overline{S_1}$ on $\overline{S_2}$, and vice-versa) Limiting ourselves to s-wave electron-hole wavefunctions(i.e. only n=0) for the surface interaction term, there is considerable simplification in the potential energy:

$$V(r) = -\frac{e^2}{\varepsilon_2 |\overline{S_1} - \overline{S_2}|} + \sum_{n=1}^{\infty} \frac{(\varepsilon - 1)(n+1)}{\varepsilon_2 (n\varepsilon + n + 1)} \frac{\overline{S_1}^{2n} + \overline{S_2}^{2n}}{R^{2n+1}} \frac{e^2}{2} \qquad \text{(xi)}$$

Thus, under these approximations, the Hamiltonian of the system is given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\varepsilon |\overline{S_e} - \overline{S_h}|} - \sum_{n=1}^{\infty} \frac{(\varepsilon - 1)(n+1)}{\varepsilon_2 (n\varepsilon + n + 1)} \frac{\overline{S_e}^{2n} + \overline{S_h}^{2n}}{R^{2n+1}} \frac{e^2}{2} \qquad \text{(xii)}$$

Lowest-Excited State

For small enough crystals, carrier-confinement effects dominate, that is the electron and hole, individually, behave as particles trapped in a three-dimensional sphere of radius R. Also, for not too small(>>12 nm) crystals, coupling effects of the conduction band electron and valence band hole can be neglected. Under this approximation, the uncorrelated electron-hole ground-state wavefunction can be written as products of just electron and hole wavefunctions, ie:

$$\psi_{0,e-h} = \psi_{0,e}\psi_{0,h} \qquad \text{(xiii)}$$

Thus the ground state energy can be calculated by dealing with the Coulomb interaction and the surface term using first order perturbation theory to yield

$$E_0 = \frac{\hbar^2 \pi^2}{2R^2}\left[\frac{1}{m_e} + \frac{1}{m_h}\right] - \frac{1.8e^2}{\varepsilon_2 R} + \left\langle \psi_{0,e-h} \left| \sum_{n=1}^{\infty} \frac{(\varepsilon - 1)(n+1)}{\varepsilon_2 (n\varepsilon + n + 1)} \frac{\overline{S_e}^{2n} + \overline{S_h}^{2n}}{R^{2n+1}} \frac{e^2}{2} \right| \psi_{0,e-h} \right\rangle$$

Or simply. $E_0 = \dfrac{\hbar^2 \pi^2}{2R^2}\left[\dfrac{1}{m_e} + \dfrac{1}{m_h}\right] - \dfrac{1.8e^2}{\varepsilon_2 R} + \left\langle \psi_{0,e-h} \left| \displaystyle\sum_{n=1}^{\infty} \dfrac{(\varepsilon - 1)(n+1)}{\varepsilon_2 (n\varepsilon + n + 1)} \dfrac{\overline{S}^{2n} e^2}{R^{2n+1}} \right| \psi_{0,e-h} \right\rangle$ \qquad (xiv)

Limitations

Recent spectral data has shown that the effective mass approximation breaks down for crystallite sizes approaching 12 nm. A more sophisticated treatment has to be adopted to take spin-orbit coupling of the valence band electron and conduction band hole. The Luttinger-Kohn Hamiltonian, a topic for a future presentation, takes into account degeneracy of quantum electron-hole states and spin-orbit coupling to make better predictions about the absorption spectra for small crystallite radii. But the importance of this classical work cannot be neglected. A lot of the formalism adapted here will carry forward to the more current methods for QSL calculations.