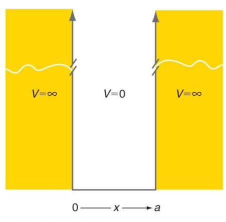
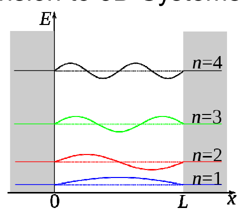
Quantum Confinement Effects in Materials Chemistry

Reading: Engel and Reid "Physical Chemistry",
Chapters 15 and 16 (on reserve)
L. Brus Review (on web)
M. Bawendi JACS article (on web)

Outline:

Solving the SE
Wavefunctions and Energies
Extension to 3D Systems





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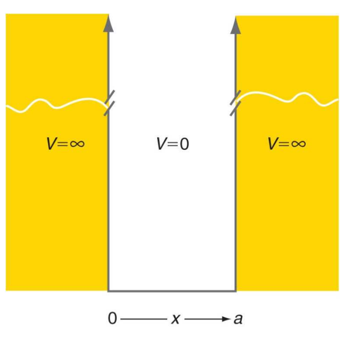
Particle in a Box

Quantum confinement arises when the location of a particle (for example, and electron) is confined to a region of space.

This is the idea behind the "Particle in a Box" system:



$$V(x) = \infty \qquad x < 0, x > a$$

$$V(x) = 0 \qquad 0 \le x \le a$$

Potential energy constrains particle to $0 \le x \le a$.

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Particle in a Box (cont.)

Set up the SE and look for solutions:

$$\hat{H}\psi(x) = E\psi(x)$$
$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x)$$
$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = \left(E - V(x)\right)\psi(x)$$
$$\frac{d^2}{dx^2}\psi(x) = \frac{2m}{\hbar^2}\left(V(x) - E\right)\psi(x)$$

What happens when V(x) = ∞? To ensure that the wave function is well behaved in this region:

$$\psi(0) = \psi(a) = 0$$

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Wave functions

What are the solutions to the SE inside the box?

Here *V(x)* = 0 such that we refer to this problem as "the free particle":

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right)\psi(x) = E\psi(x)$$
$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x)$$

Solutions to this differential equation are of the form:

$$\psi(x) = A\sin kx + B\cos kx$$

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Wave functions (cont.)

Next, we apply the the boundary condition that:

$$\psi(0) = \psi(a) = 0$$

Apply this condition to solutions inside the box and remembering sin(0) = 0, cos(0) = 1:

$$\psi(0) = A\sin k(0) + B\cos k(0) = B$$

At x = 0 boundary condition only satisfied if B = 0.

$$\psi(x) = A\sin kx$$

At x = a boundary condition only satisfied if $ka = n\pi$ such that:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad n = 1, 2, 3, \ldots$$

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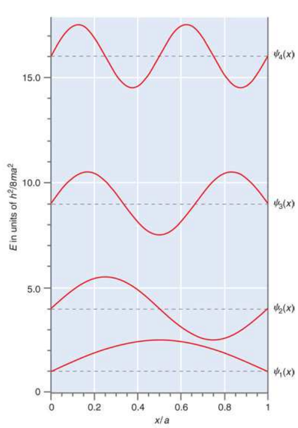
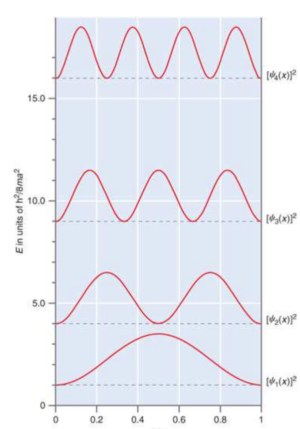
Wave Functions (cont.)





Wave functions have n - 1 “nodes”.

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Energies

To determine the energy eigenvalues, we substitute the wavefunction back into the SE:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) = E\psi(x) \qquad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$$

$$E_n = \frac{n^2 h^2}{8ma^2} \qquad \{n = 1, 2, 3, ...\}$$

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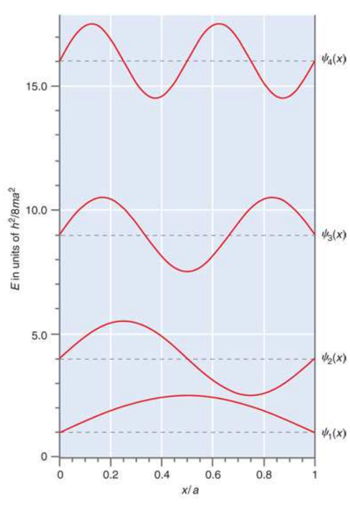
Energies (cont.)



$$E_n = \frac{n^2 h^2}{8ma^2} \qquad \{n = 1, 2, 3, ...\}$$

Energies go as n^2

Spacings between levels increase with *n*

More nodes in wave function…higher energy.

Increase in *a*….decrease in *E*.

Increase in m….decrease in *E*.

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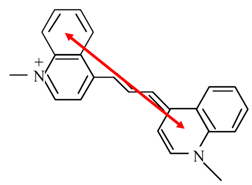
Application of P in B

The electronic energy levels of conjugated molecules can be (roughly) modeled using particle in a box.



L = 8 Å

What wavelength of light corresponds to ΔE from n=1 to n=2?

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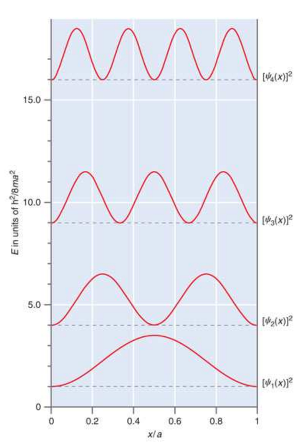
Contrasting with Classical Mechanics



In QM, the “probability density” is structured, with regions of space demonstrating enhanced probability (depending on the wave function).

In classical mechanics (CM), the probability density is constant throughout the box.

Both QM and CM are consistent with no probability of observing the particle outside of the box.

When do the QM and CM pictures converge?

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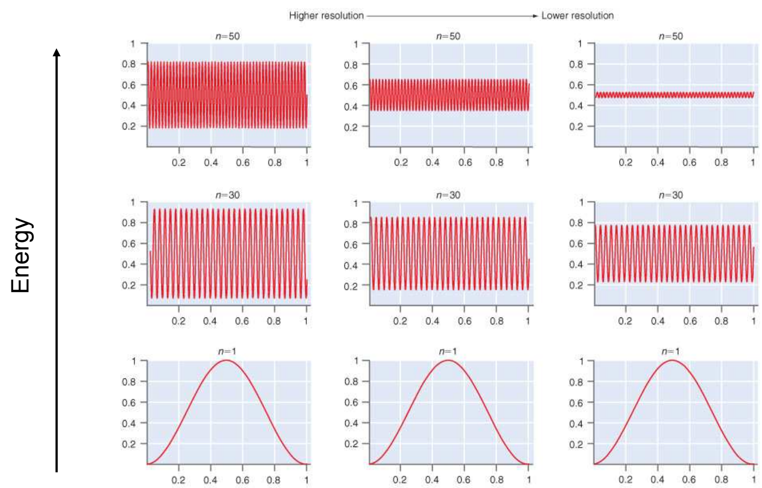
Contrasting with CM (cont.)

When do the QM and CM pictures converge? Ans: At high *E*!



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Contrasting with CM (cont.)

In CM, energies are continuous (not quantized). Does QM converge on this limit as well?

Look at difference between adjacent energy levels versus total energy.

$$\frac{E_{n+1}-E_n}{E_n} =$$

As n approaches infinity, spectrum becomes continuous…convergence with CM!

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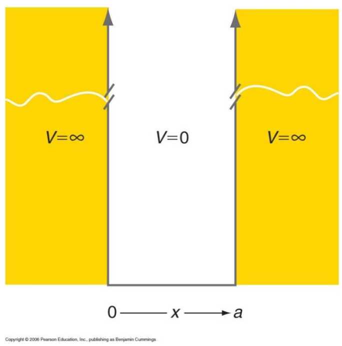
Multidimensional Particle in a Box

The particle in a box system is easily extended to 2 and 3 dimensions:



$$V(x,y,z)=\infty \qquad x<0, x>a$$
$$y<0, y>b$$
$$z<0, z>c$$

$$V(x,y,z)=0 \qquad 0\le x\le a$$
$$0\le y\le b$$
$$0\le z\le c$$

We now have to concern ourselves with three dimensions.

MultiD Particle in a Box (cont.)

Setting up the SE :

$$\frac{-\hbar^2}{2m}\left(\nabla^2+V(x,y,z)\right)\psi\left(x,y,z\right)=E\psi\left(x,y,z\right)$$
$$\frac{-\hbar^2}{2m}\left(\nabla^2\right)\psi\left(x,y,z\right)=E\psi\left(x,y,z\right)$$
$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi\left(x,y,z\right)=E\psi\left(x,y,z\right)$$

“Del-squared” comes from vector calculus, and is a convenient way to indicate the second-derivatives shown.

MultiD Wave functions

What are the solutions to the SE inside the box?

They will be free particle again, but now we have each dimension to consider. However, notice that the Hamiltonian can be described as a sum of single-variable terms:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi\left(x,y,z\right)=E\psi\left(x,y,z\right)$$

This suggests we can assume "separability" of the wave function:

$$\psi\left(x,y,z\right)=X(x)Y(y)Z(z)$$

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MultiD Wave functions (cont.)

Let's plug our separable wave function into the SE and see what happens:

$$\frac{-\hbar^2}{2m}\left(\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}+\frac{1}{Z(z)}\frac{\partial^2 Z(z)}{\partial z^2}\right)=E$$

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MultiD Wave functions (cont.)

The following expression suggests that E can be viewed as containing contributions associated with the three coordinates:

$$E = E_x + E_y + E_z$$

Using this idea, we can decompose this problem into three differential equations of a single variable. The equation for "x" is:

$$\frac{-\hbar^2}{2m}\frac{\partial^2 X(x)}{\partial x^2} = E_x X(x)$$

Solutions are identical to the 1D particle in a box…just need to construct the product:

$$\psi\left(x, y, z\right) = X(x)Y(y)Z(z) = N\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right)$$

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MultiD Energies

Since the total energy was the sum of energy along each coordinate

$$E = E_x + E_y + E_z$$

Sub the 1D energy expressions into the above, keeping track of the coordinates:

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

The concept of separability is general: *If the energy can be decomposed into different degrees of freedom, the wave function can be decomposed into a product of functions corresponding to each degree of freedom.*

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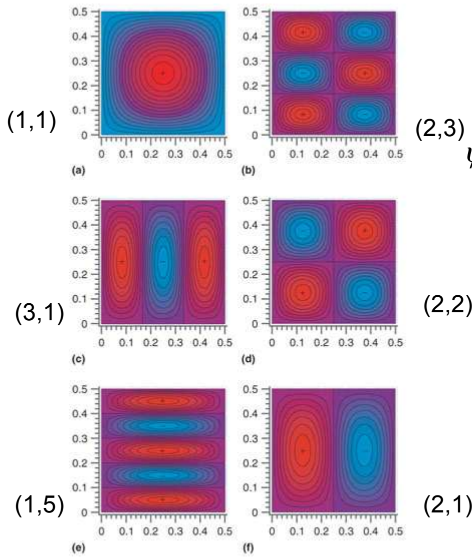
2D Particle in a Box



By analogy, the wave functions and energies for the 2D box are:

$$\psi(x,y) = N \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right)$$

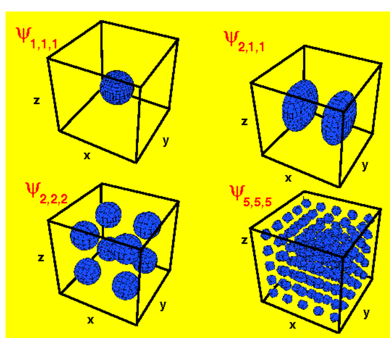
$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

For this system *a* = *b*:

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$$

3D Particle in a Box

The wave functions for the 3D box are very similar to that of the 2D box…just add a dimension:



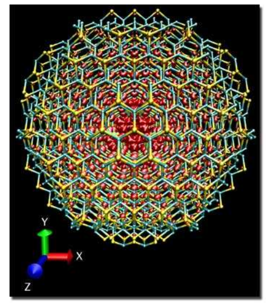
www.chem.ufl.edu/~itl/4412_aa/Gifs/box3_00.gif

These are actually surface plots where the wave function has a defined amplitude….would need to do a 4D plot to do this correctly (and that's hard to do).

Application: Quantum Dots

Quantum dots are semiconducting materials (CdS, CdSe, etc.) with dimension on the nanometer scale.

The optical properties of the quantum dots are highly dependent on the size of the particle.



CdSe quantum dots

As diameter decreases, energy gap between ground and excited state increases.

http://sitemason.vanderbilt.edu/files/ioOfKM/cdse4.jpg

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Quantum Dots (cont.)

Can model quantum dots using “particle in an spherical well” model where the potential energy is zero inside the well. The SE for this system in spherical-polar coordinates is:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\delta}{\delta r}\right)\psi(r,\theta,\phi)+\frac{1}{2mr^2}\hat{L}^2\psi(r,\theta,\phi)=E\psi(x)$$

We’ll see this equation again, but for these systems the ground-excited state energy gap is given by:

$$E = E_{bulk} + \boxed{\frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right)-\frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 a}}$$

Confinement dependence: as *a* (radius) decreases, the gap increases!

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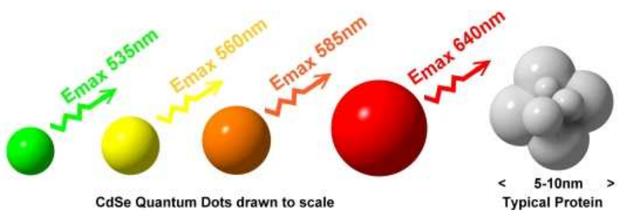
Quantum Dots (cont.)

Current research strategy: Make quantum dots based on different semi-conductors to change spectral coverage.

$$E = E_{bulk} + \frac{\hbar^2 \pi^2}{2a^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 a}$$

Although "nanoscale", it is important to keep in mind the size of these particles relative to other things you may be familiar with:



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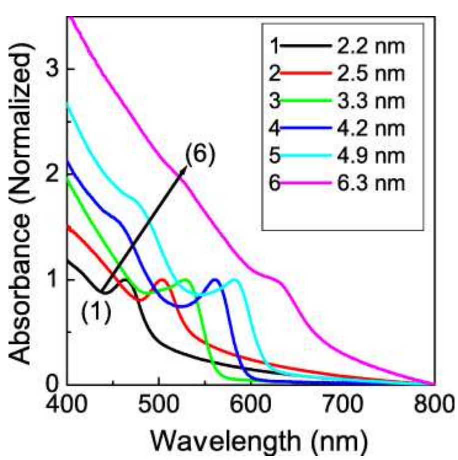
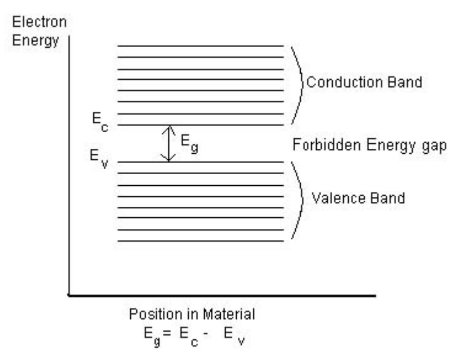
Quantum Dots (cont.)

Specific Example: CdSe Nanocrystals:





$$E_g \propto \frac{1}{r^2}$$

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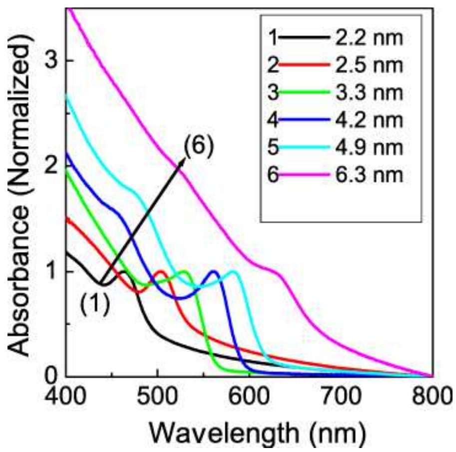
Quantum Dots (cont.)

Eg ("band gap") of bulk CdSe: 1.74 eV



What wavelength corresponds to the band gap of bulk CdSe?

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