Quantum mechanics in 3D

Classical kinematics and dynamics

→ moving from numbers $(x, v_x, a_x, \text{etc.})$ to 3D vectors $(\vec{r}, \vec{v}, \vec{a}, \text{etc})$

We still break the vectors into components, and solve individually for each component

$$m\vec{a} = \Sigma \vec{F} \Rightarrow ma_x = \Sigma F_x \, ; \, ma_y = \Sigma F_y ; \, ma_z = \Sigma F_z$$

$$\downarrow x(t) \qquad \downarrow y(t) \qquad \downarrow z(t)$$

We will use similar approach for quantum description

<u>3D Schrodinger equation</u>

$$\frac{\partial^2 \psi}{\partial x^2} \rightarrow \underbrace{\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}}_{\nabla^2 \psi}$$

Math notation: 3D differentiation vector $\vec{\nabla}$ (del)

$$\nabla = \vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$\boxed{i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r},t) + U(\vec{r}) \Psi(\vec{r},t)}$$

Stationary Schrodinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{r}) + U(\vec{r}) \psi(\vec{r}) = E \psi(\vec{r})$$

$$\Psi(\vec{r},t) = \psi(\vec{r}) e^{-iEt/\hbar} \qquad \text{(same as in 1D case)}$$

In general, we need to solve the above equation to find how the wavefunction depends on x, y, z (or another set of 3 variables (r, θ, φ) or (ρ, φ, z), for example)

However, sometimes we can simplify the situation and separate the wavefunction in an independent pieces: if $U(\vec{r}) = U_1(x) \cdot U_2(y) \cdot U_3(z)$

Then $\psi(\vec{r}) = \psi(x,y,z) = \psi_1(x)\, \psi_2(y)\, \psi_3(z)$

Separation of variables

$$\frac{\partial^2 \psi(\vec{r})}{\partial x^2} = \psi_1'' \cdot \psi_2 \psi_3 \quad \text{etc}$$

$$\nabla^2 \psi = \psi_1'' \psi_2 \psi_3 + \psi_1 \psi_2'' \psi_3 + \psi_1 \psi_2 \psi_3''$$

Simplest quantum system: 3D infinite ~~square~~ ractangular box
a particle is localized between solid walls at $(x=0, x=a)$; $(y=0, y=b)$; $(z=0, z=c)$

Stationary Schrodinger equation

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

$$\{\psi_1'' \psi_2 \psi_3 + \psi_1 \psi_2'' \psi_3 + \psi_1 \psi_2 \psi_3'' + \frac{2mE}{\hbar^2} \psi_1 \psi_2 \psi_3 = 0$$

divide by $\psi_1 \psi_2 \psi_3$

$$\underbrace{\frac{\psi_1''(x)}{\psi_1(x)}}_{f(x)} + \underbrace{\frac{\psi_2''(y)}{\psi_2(y)}}_{f(y)} + \underbrace{\frac{\psi_3''(z)}{\psi_3(z)}}_{f(z)} + \underbrace{\frac{2mE}{\hbar^2}}_{\text{constant}} = 0$$

This equation must be valid for any x, y, z so the only way to ensure this is to make the first three term constant

$$\frac{\psi_1''(x)}{\psi_1(x)} = \frac{2mE_1}{\hbar^2} \qquad \frac{\psi_2''(y)}{\psi_2(y)} = \frac{2mE_2}{\hbar^2} \qquad \frac{\psi_3''(z)}{\psi_3(z)} = \frac{2mE_3}{\hbar^2}$$

Total energy $E = E_1 + E_2 + E_3$

(similar to $E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$)

So instead of solving one equation with 3 variables, we now need to solve three independent equations for each variable.

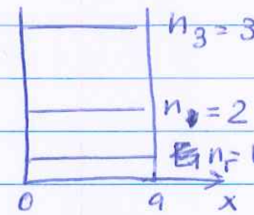
$$\psi_1''(x) + k_x^2 \psi(x) = 0 \qquad k_x^2 = \frac{2mE_1}{\hbar^2}$$

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

$$\psi_1(x) = \sqrt{\frac{2}{a}} \sin \frac{\pi n_1 x}{a} \qquad E_{1n_1} = \frac{\pi^2 \hbar^2 n_1^2}{2ma^2}$$

$$k_x = \frac{\pi n_1}{a}$$

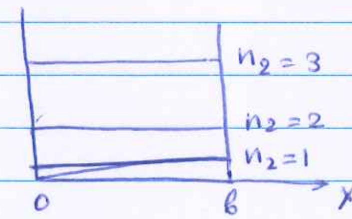
n_1 – quantization index along x



Identical process for y and z

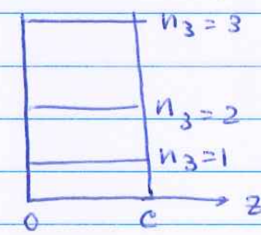
$$\psi_2(y) = \sqrt{\frac{2}{b}} \sin \frac{\pi n_2 y}{b}$$

$$E_{2n_2} = \frac{\pi^2 \hbar^2 n_2^2}{2mb^2}$$



$$\psi_3(z) = \sqrt{\frac{2}{c}} \sin \frac{\pi n_3 z}{c}$$

$$E_{3n_3} = \frac{\pi^2 \hbar^2 n_3^2}{2mc^2}$$



Now we have <u>three</u> quantum numbers to define <u>one</u> energy level

$$E = E_1 + E_2 + E_3 = \frac{\pi^2 \hbar^2}{2m} \left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right)$$

$$\psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{\pi n_1 x}{a} \sin \frac{\pi n_2 y}{b} \sin \frac{\pi n_3 z}{c}$$

Ground state: $n_1 = n_2 = n_3 = 1$

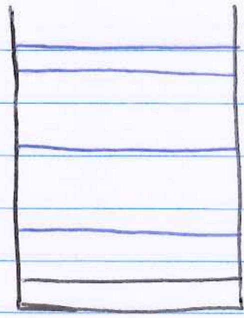
$$E_0 = \frac{\pi^2 \hbar^2}{2m} \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right)$$

Assume that $a = b = c$ (for simplicity)

First excited state $n_1 = 2,\ n_2 = n_3 = 1$, or $n_1 = n_3 = 1\ n_2 = 2$ or $n_1 = n_2 = 1\ \ n_3 = 2$

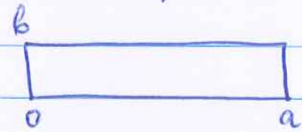
$$E_1 = \frac{\pi^2 \hbar^2}{2m} \left(\frac{4}{a^2} + \frac{1}{a^2} + \frac{1}{a^2} \right) = \frac{3\pi^2 \hbar^2}{ma^2} \qquad \left(E_0 = \frac{3}{2} \frac{\pi^2 \hbar^2}{ma^2} \right)$$

this state is triple-degenerate, since there are three distinct quantum state of the same energy



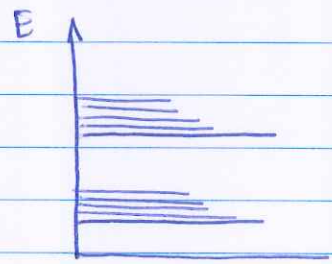
$E_4 = 6 \frac{\pi^2 \hbar^2}{ma^2}$	single	(2,2,2)
$E_3 = \frac{11}{2} \frac{\pi^2 \hbar^2}{ma^2}$	triple	(3,1,1)
$E_2 = \frac{9}{2} \frac{\pi^2 \hbar^2}{ma^2}$	triple	(2,2,1)
$E_1 = 3 \frac{\pi^2 \hbar^2}{ma^2}$	triple	(2,1,1)
$E_0 = \frac{3}{2} \frac{\pi^2 \hbar^2}{ma^2}$	single	~~[illegible]~~ (1,1,1)

Non-symmetric well (we'll do 2D for ~~sym~~ simpicity)



$a >> b \qquad \frac{\pi^2 \hbar^2}{ma^2} << \frac{\pi^2 \hbar^2}{mb^2}$

$$E_{n_1 n_2} = \frac{\pi^2 \hbar^2}{m} \left(\frac{n_1^2}{a^2} + \underbrace{\frac{n_2^2}{b^2}}_{\text{dominating}} \right)$$

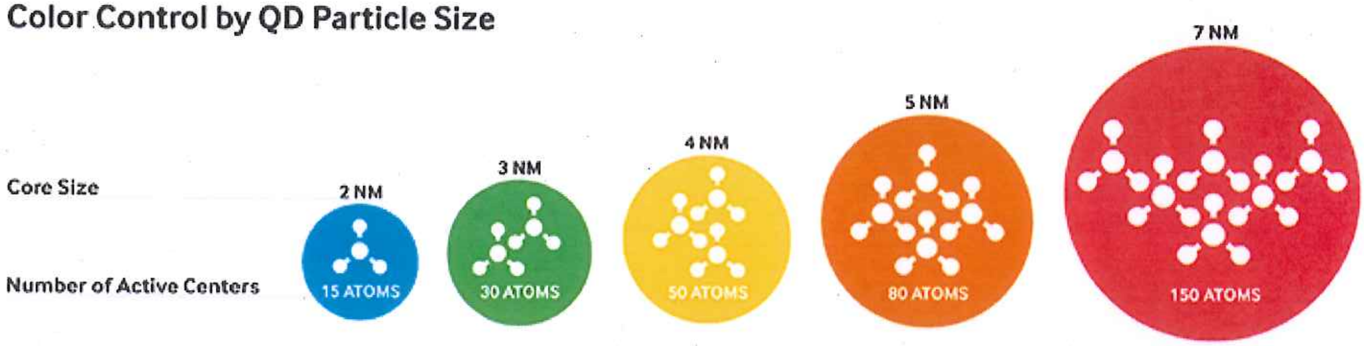


$n_2 = 2, \quad n_1 = 1, 2, 3 \ldots$

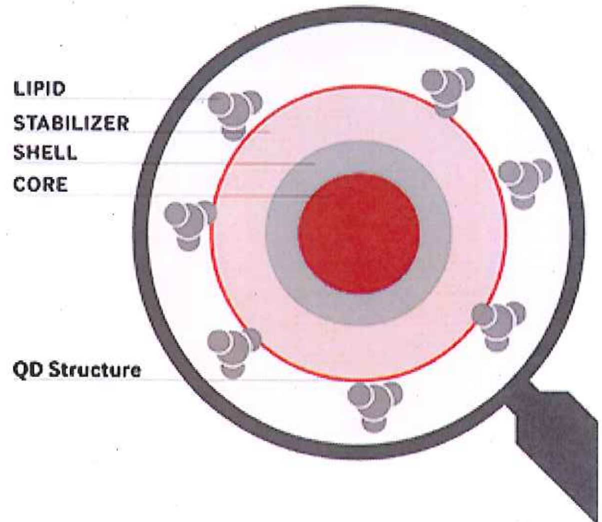
$n_2 = 1, \quad n_1 = 1, 2, 3 \ldots$

hierarchy of energy levels

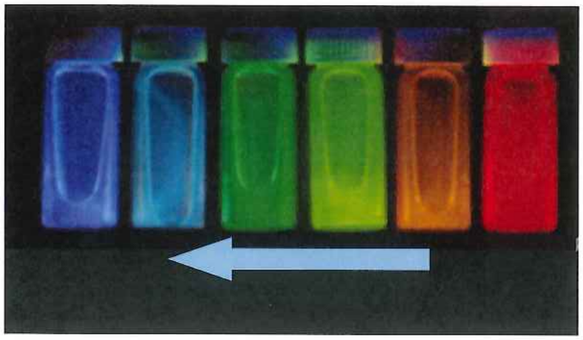
Color Control by QD Particle Size



Depending on size,
quantum dots emit different color light
due to quantum confinement.
Illustrated is the range of QDs with emission
gradually stepping from violet to red.



Quantum dot: particle in 3D box



CdSe quantum dots dispersed in hexane (Bawendi group, MIT

Color from photon absorption

Determined by energ level **spacing**

- Energy level spacing increases as particle size decreases.
- i.e

$$E_{n+1} - E_n = \frac{(n+1)^2 h^2}{8mL^2} - \frac{n^2 h^2}{8mL^2}$$

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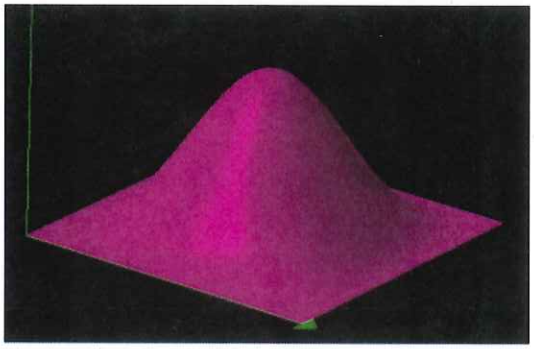
Quantum Wave Functions

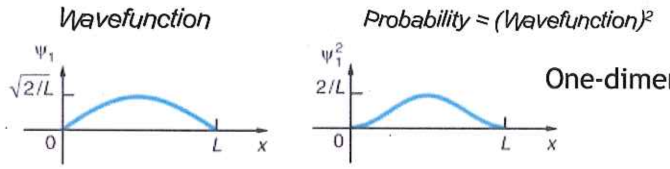


Ground state: same waveleng (longest) in both x and y

Need two quantum #'s,
one for x-motion
one for y-motion

Use a pair (n_x, n_y)

Ground state: (1,1)



One-dimensional (1D) case

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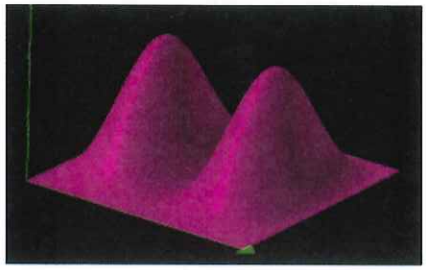
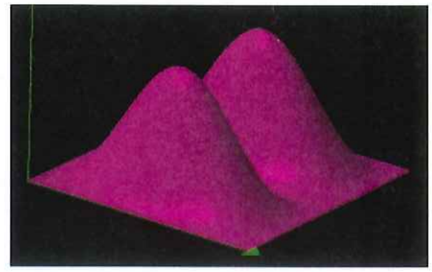
2D excited states



$(n_x, n_y) = (2,1)$



$(n_x, n_y) = (1,2)$

These have exactly the same energy, but the probabilities look different.

The different states correspond to ball bouncing in x or in y direction.

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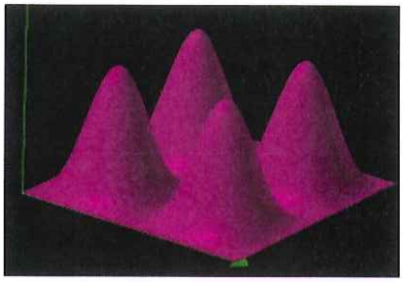
Particle in a box

What quantum state could this be?

√ A. $n_x=2$, $n_y=2$
B. $n_x=3$, $n_y=2$
C. $n_x=1$, $n_y=2$



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