Stationary States

Consider the special case where all coefficients are zero except for $c_1 = 1$. Then $\Psi(x,y,z,t) = \psi_1(x,y,z)e^{-iE_1t/\hbar}$

The probability density in this special case is

$|\Psi(x,y,z,t)|^2 = |\psi_1(x,y,z)|^2 \rightarrow$ static, stationary

ie no time dependence. Why: $|e^{-iE_nt/\hbar}|^2 = 1$.

Hence the probability density is literally "stationary" or static. In EM theory, a static charge density cannot emit radiation. This suggests that these are the stationary, non-radiating states imagined by Bohr (1913).

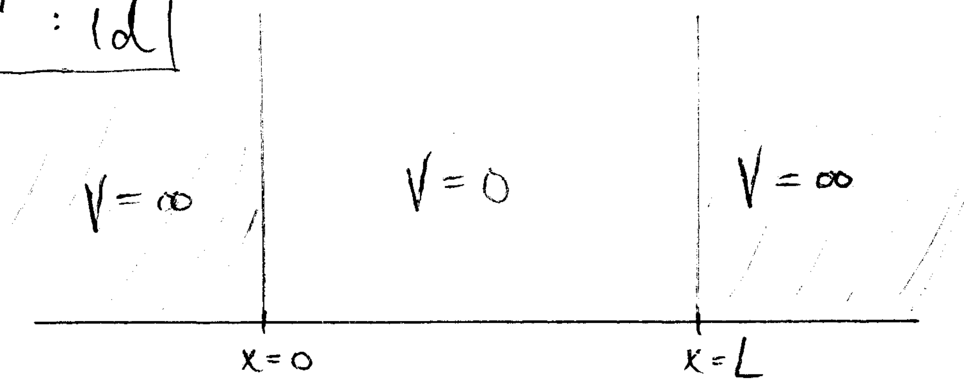
To summarize, the stationary ("allowed") states of a particle in the potential energy V are given by Schroedinger's time-independent equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n + V\psi_n = E_n\psi_n$$

where the constant En is the energy of the particle in that state (will prove later).

Section 2. Some Simple Problems

Particle in a "Box" : 1d



$\psi = 0$ for $x<0$ and for $x>L$ because the potential in these regions is ∞.

For $0 \le x \le L$, equation for the stationary states is

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = E\psi \Longrightarrow \frac{\partial^2\psi}{\partial x^2} = -\frac{2mE}{\hbar^2}\psi$$

subject to "boundary conditions"

$$\psi(0)=0 \quad \text{and} \quad \psi(L)=0$$

because $\psi(x)$ must be a continuous function.

The general solution to this differential equation is

$$\psi(x) = A\sin\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2}x\right] + B\cos\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2}x\right]$$

The complex exponential does not go to 0 so cannot use it.
(prob. density is $e^{i-x}\cdot e^{-i-x}=1$, so won't do because prob. $=0$ for some regions)

Also $B=0$ since $\psi(0)$ must $=0$.

Therefore $\psi = A \sin\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2} x\right]$

To satisfy the B.C. at $x = L$ we must have $\left(\frac{2mE}{\hbar^2}\right)^{1/2} L = n\pi$, $n \in \mathbb{Z}$

Solving for E, we get a discrete set of possible energies :

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Now substitute this E_n back into ψ to get the corresponding states

normalization constant

$$\psi_n = A_n \sin\left(\frac{n\pi x}{L}\right)$$

Constant A_n is determined by normalizing ψ_n

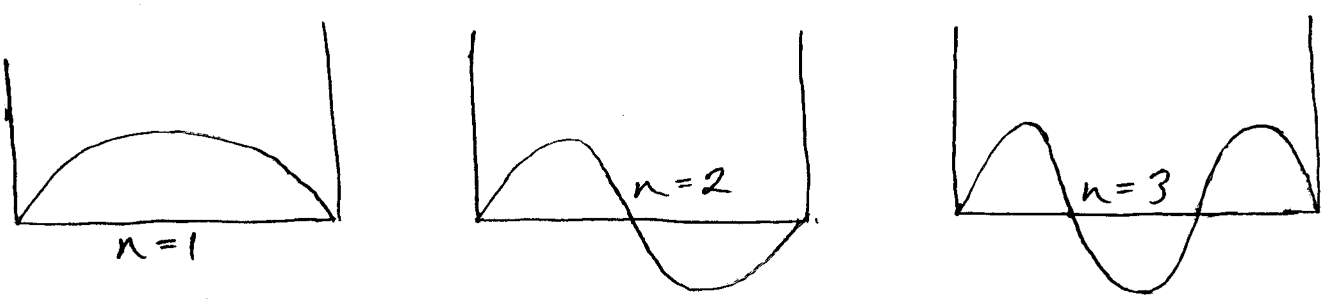
$$1 = \int_0^L |\psi_n|^2 \, dx = A_n^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = A_n^2 \cdot L/2$$

$$\Rightarrow A_n = (2/L)^{1/2}$$

The normalized stationary states are

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \quad , \ n \in \mathbb{Z}, \ n > 0 .$$

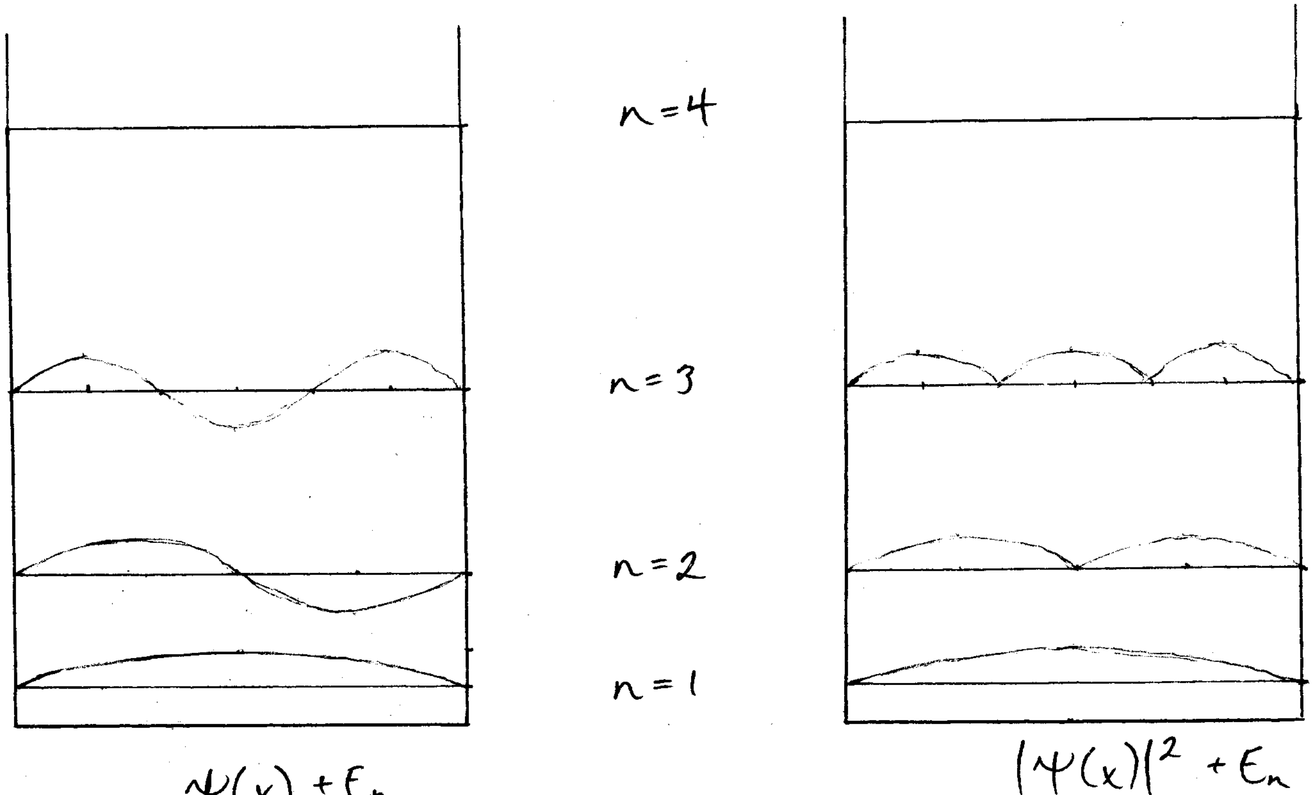
(Why don't we need $n \leq 0$?)



Note that there are $(n-1)$ nodes in the wavefunctions

ie ~~more~~ higher energy $\Rightarrow$ more nodes.

$E_n \propto n^2$. It is customary (see Fig 9.13, but this is not the "box" potential) to offset the wavefunction vertically by E_n:



Particle in a "Box": 3d

Denote edge lengths as a, b, c.

Inside the box $-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi$ since $V=0$

with B.C. $\psi(0,y,z)=0$; $\psi(a,y,z)=0$

$\psi(x,0,z)=0$; $\psi(x,b,z)=0$; $\psi(x,y,0)=0$; $\psi(x,y,c)=0$

This is a PDE. Try the only method we know: separation of variables

Try $\psi(x,y,z) = f(x)\,g(y)\,h(z)$.

Then, $\nabla^2 \psi = f''(x)g(y)h(z) + f(x)g''(y)h(z) + f(x)g(y)h''(z)$

$$= -\frac{2mE}{\hbar^2} f(x)g(y)h(z)$$

Divide through by $f(x)g(y)h(z)$ to get

$$\frac{f''(x)}{f(x)} + \frac{g''(y)}{g(y)} + \frac{h''(z)}{h(z)} = -\frac{2mE}{\hbar^2} = \text{constant}$$

Thus each individual term = constant

ie This can work only if each term on LHS is a constant.

Call them $-k_x, -k_y, -k_z$ respectively

We have $k_x + k_y + k_z = \frac{2mE}{\hbar^2}$ and ⊛

$$f''(x) = -k_x f(x)$$
$$g''(y) = -k_y g(y)$$
$$h''(z) = -k_z h(z)$$

Consider the x-equation: has solution $f(x) = A \cdot \sin(\sqrt{k_x}\, x)$

(cosine solution not allowed by $x = 0$ B.C.)

To satisfy B.C. at $x = a$, we must have $\sqrt{k_x}\, a = n_x \pi$, $n_x \in \mathbb{Z}$

$$\text{So } k_x = \frac{n_x^2 \pi^2}{a^2}$$

Similarly, $k_y = \frac{n_y^2 \pi^2}{b^2}$ and $k_z = \frac{n_z^2 \pi^2}{c^2}$

Plug into ⊛ to get $\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)\pi^2 = \frac{2mE}{\hbar^2}$

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

where, for reasons similar to 1d case, $n_x, n_y, n_z = 1, 2, 3, \ldots$

The normalized states are

$$\psi(x,y,z) = \left(\frac{8}{abc}\right)^{1/2} \sin\left(\frac{n_x \pi}{a} x\right) \sin\left(\frac{n_y \pi}{b} y\right) \sin\left(\frac{n_z \pi}{c} z\right)$$

If the box is a perfect cube then $a = b = c = L$ and E becomes

$$E = (n_x^2 + n_y^2 + n_z^2)\frac{\pi^2 \hbar^2}{2mL^2}$$

Now, we have degenerate energy levels — namely different states with the same energy.

n_x	n_y	n_z	$n_x^2+n_y^2+n_z^2 \propto E$	
1	1	1	3	
2	1	1	6	triple degeneracy
1	2	1	6	
1	1	2	6	
1	2	2	9	
2	1	2	9	
2	2	1	9	
3	1	1	11	
1	3	1	11	
1	1	3	11	
2	2	2	12	
⋮	⋮	⋮	⋮	

This is the simplest example of a general rule in quantum mechanics: Symmetry often implies degeneracy

Particle in a "Box" : Quantum Dots

Quantum dots, or fluorescent semiconductor nanocrystals, are revolutionizing biological imaging. The color of light emitted by a semiconductor material is determined by the width of the energy gap separating the conduction and valence energy bands.

In bulk semiconductors, this gap width is fixed by the identity (ie composition) of the material. For example, the band gap energy of bulk CdSe is 1.77 eV at 300 K.

Recall that a photon obeys $E = h\nu = hc/\lambda$ for the relationship between the energy gap and the frequency or wavelength.

If you want a different wavelength of light to be emitted, you need to find a different material.

However, the situation changes in the case of nanoscale semiconductor particles with sizes smaller than ~10 nm.

This size range corresponds to the regime of quantum confinement, for which the spatial extent of the electronic wavefunction is comparable with the dot size.

As a result of these geometrical constraints, electrons respond to changes in particle size by adjusting their energy. This phenomenon is called the quantum-size effect.

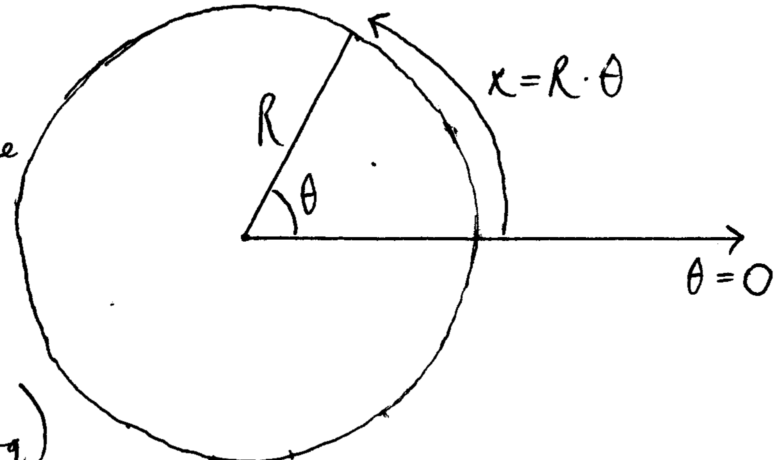
The quantum-size effect can be approximately described by the "particle in a box" model. How good is this approx.?

Good → see Weber, Phys. Rev. B 66 041305 (2002)

For a spherical quantum dot with radius R, this model predicts a size-dependent contribution to the energy gap proportional to $1/R^2$.

Hence the gap increases as the quantum dot size decreases.

Particle on a Ring



radius = R. V = 0 on ring

Use θ as the independent variable

Schroedinger's equation for stationary states is

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \psi(x)}{\partial x^2} = E\psi \quad (V=0 \text{ on ring})$$

where x is the distance along the circumference of the ring

$$x = R\theta \Rightarrow -\frac{\hbar^2}{2mR^2}\frac{\partial^2 \psi(\theta)}{\partial \theta^2} = E\psi \quad \text{or} \quad \frac{\partial^2 \psi}{\partial \theta^2} = -\frac{2mR^2E}{\hbar^2}\psi$$

subject to the B.C.

$$\psi(\theta=0) = \psi(\theta=2\pi)$$
$$\psi'(\theta=0) = \psi'(\theta=2\pi)$$
$$\psi''(\theta=0) = \psi''(\theta=2\pi)$$
$$\vdots$$

because θ = 0 and θ = 2π are the same point.

Both real and complex solutions are possible (sin, cos, e^i).

Use real representation ⇒ sin/cos

① $$\psi^{\sin} = A\sin\left[\left(\frac{2mR^2E}{\hbar^2}\right)^{1/2}\theta\right]$$

B.C. require that $2\pi\left(\frac{2mR^2E}{\hbar^2}\right)^{1/2} = 2n\pi$, $n \in \mathbb{Z}$

to satisfy both the ψ and ψ' B.C. because $\cos(2\pi n) = 1$.

Thus $\psi_n^{\sin} = A_n \sin n\theta \quad , n \in \mathbb{Z}, > 0$

and $E_n = \dfrac{n^2\hbar^2}{2mR^2}$

(Ignoring the normalization constant A_n)

(2) $\psi^{\cos} = B \cos\left[\left(\dfrac{2mR^2E}{\hbar^2}\right)^{1/2}\theta\right]$

with B.C. $2\pi\left(\dfrac{2mR^2E}{\hbar^2}\right)^{1/2} = 2n\pi \quad , n \in \mathbb{Z}$

giving $\psi_n^{\cos} = B_n \cos n\theta \quad , n \in \mathbb{Z}, \geq 0$ ($n=0$ gives a meaningful solution)

(Ignoring the normalization constant B_n)

Negative n values are redundant always because $|\psi|^2$ is what we see. But $n=0$ gives 1 for the cos solution, 0 for the sin solution, so look for when to include it.

Summary: ground state is just $\psi_0^{\cos} = 1$ with $E_0 = 0$

Excited states have energies $E_n = \dfrac{n^2\hbar^2}{2mR^2} \quad (n \in \mathbb{Z}, > 0)$

and are doubly degenerate with pair of states,

$\psi_n^{\sin} = \sin n\theta$, $\psi_n^{\cos} = \cos n\theta$ for each energy level (ignoring the normalization constants).

This is a useful model for cyclic π-electron systems.