ECE 162A
Mat 162A

Lecture #9: 3D Solutions. Expectation Values

Read Chapter 3,8 of French/Taylor

3 Dimensional Time Independent Schroedinger Equation

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

$$=E\psi(x,y,z)$$

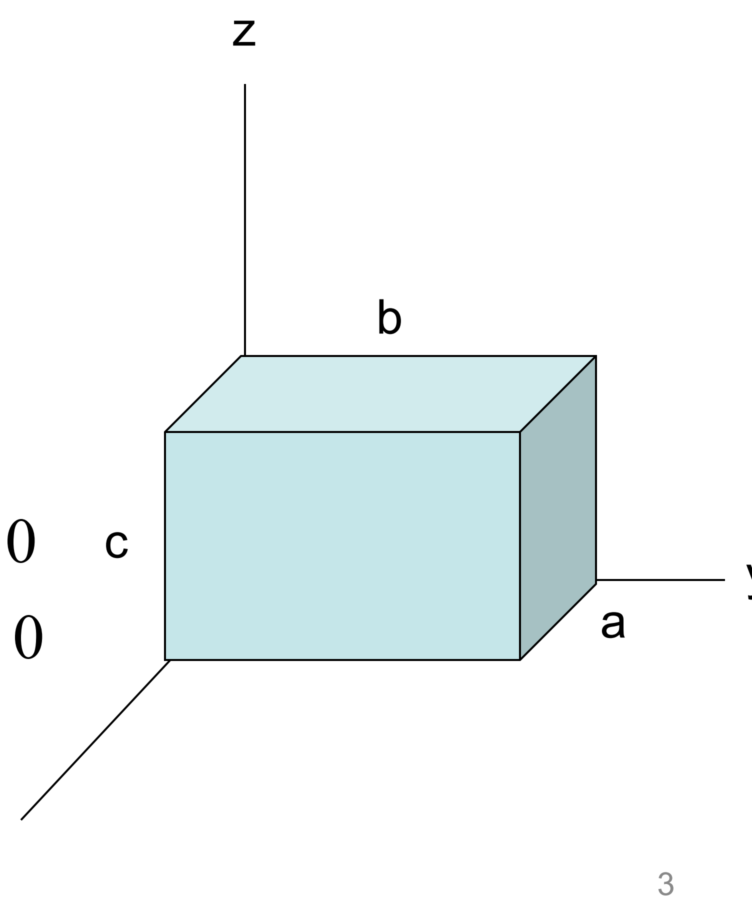
$$-\frac{\hbar^2}{2m}\nabla^2\psi+V\psi=E\psi$$

Free Particle in a 3D Box

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

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

$$Boundary\,Conditions:$$
$$\psi(0,y,z)=\psi(x,0,z)=\psi(x,y,0)=0$$
$$\psi(a,y,z)=\psi(x,b,z)=\psi(x,y,c)=0$$



Separation of Variables

- Voltage is separable
- Boundary conditions are separable

So try:

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

3D Particle in a Box

$$-\frac{\hbar^2 YZ}{2m}\frac{d^2X}{dx^2}-\frac{\hbar^2 XZ}{2m}\frac{d^2Y}{dy^2}-\frac{\hbar^2 XY}{2m}\frac{d^2Z}{dz^2}=EXYZ$$

$Divide \quad by \quad XYZ$

$$-\frac{\hbar^2}{2mX}\frac{d^2X}{dx^2}-\frac{\hbar^2}{2mY}\frac{d^2Y}{dy^2}-\frac{\hbar^2}{2mZ}\frac{d^2Z}{dz^2}=E$$

$FunctionofX \quad FunctionofY \quad FunctionofZ = Const.$

$$E_x + E_y + E_z = E$$

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_x X$$

$$X = e^{ikx}$$

$$\psi = e^{ikx}e^{iky}e^{ikz} = e^{ikx+iky+ikz}$$

Simplest to use Sines and Cosines to match boundary conditions

$$X(x) = \sin \frac{n_x \pi x}{a} \quad n_x = 1,2,3,...$$

$$Y(y) = \sin \frac{n_y \pi y}{b} \quad n_y = 1,2,3,...$$

$$Z(z) = \sin \frac{n_z \pi z}{c} \quad n_z = 1,2,3,...$$

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

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

Time Dependence of Solution

- Solve for stationary solutions $\psi_n(x)$ with energies E_n

$$\Psi(x,t) = \sum_n A_n \psi_n(x) e^{-i\omega_n t}$$

$$\omega_n = E_n / \hbar$$

- Find the values for A_n that satisfy the intial conditions.

Motion of a Particle in a Box

$$\psi(x) = A_1 \sin(\frac{\pi x}{L}) + A_2 \sin(\frac{2\pi x}{L}) + \cdots$$

$$E_n = E_0 n^2$$

$$Special\ case A_1 = A_2 = 1; others\ \ 0$$

$$\Psi(x,t) = \sin(\frac{\pi x}{L})e^{i\omega t} + \sin(\frac{2\pi x}{L})e^{4i\omega t}$$

Wave function evolution

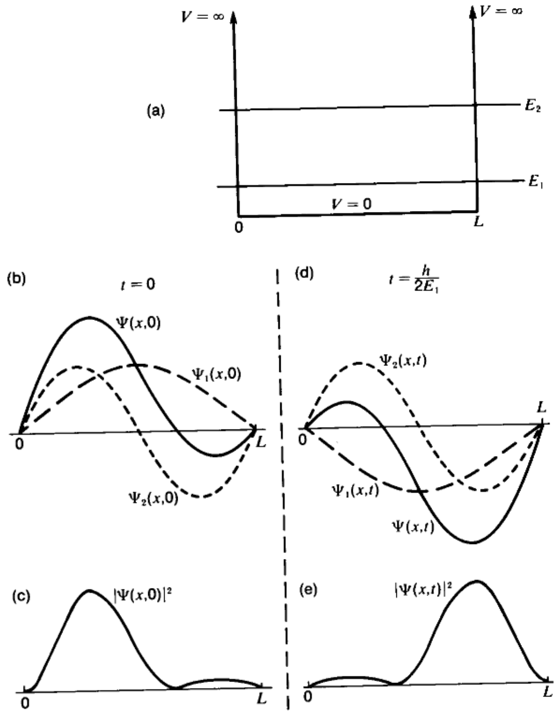


Fig. 8-1 Superposition of the lowest stationary states of an infinite square well. (a) Potential energy function for the well, with the two lowest energy eigenvalues shown. (b) Eigenfunctions for the two lowest energy states (broken lines) and the superposition of these functions (solid line), at $t = 0$. (c) Probability density function at $t = 0$ for the superposition shown in (b). (d) and (e) Plots corresponding to (b) and (c) for the later time $t = h/(2E_1)$.

ing $E = 0$ at the bottom of the well)

$$E_n = \frac{n^2h^2}{8mL^2}$$

Therefore,

$$\omega_2 = \frac{E_2}{\hbar} = 4\frac{E_1}{\hbar} = 4\omega_1$$

Thus one half-cycle for ω_1 occupies the same time as two complete cycles for ω_2. This means that between $t = 0$ and $t = h/2E_1$ the relative signs of the two components reverse, as

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Time Evolution

$$\psi(x) = \sin(\frac{\pi x}{L}) + \sin(\frac{2\pi x}{L}) = f_1 + f_2$$

$$\Psi(x,t) = f_1 e^{i\omega t} + \ f_2 e^{4i\omega t}$$

$$\left|\Psi(x,t)\right|^2 = f_1^2 + f_2^2 + 2 f_1 f_2 \cos((E_2 - E_1)t/\hbar)$$

Expectation Values

$$\langle x \rangle = \int x |\psi(x)|^2 dx = \int \psi^*(x) x \psi(x) dx$$

$$\langle x^2 \rangle = \int \psi^*(x) x^2 \psi(x) dx$$

$$\langle p \rangle = \int \psi^*(x) (-i\hbar \frac{d}{dx}) \psi(x) dx$$

$$\langle V \rangle = \int \psi^*(x) V(x) \psi(x) dx$$

Expectation Values

$$\langle x \rangle = \int x|\psi(x)|^2 dx = \int \psi^*(x) x \psi(x) dx$$

$$\langle x^2 \rangle = \int \psi^*(x) x^2 \psi(x) dx$$

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$$\langle V \rangle = \int \psi^*(x) V(x) \psi(x) dx$$

Calculate these for the lowest order solution for an infinite square well

Expectation Values

$$\langle x \rangle = \int x |\psi(x)|^2 dx$$

$1D$ *Infinite Square Well*

$$\psi_n = \sqrt{\frac{2}{L}} \sin(\frac{n\pi x}{L})$$

$$\langle x \rangle = \int x |\psi(x)|^2 dx = \frac{2}{L} \int_0^L x \sin^2(\frac{n\pi x}{L}) dx$$

$$\langle x \rangle = \frac{1}{L} \int_0^L x(1 - \cos(\frac{2n\pi x}{L}) dx$$

$$\langle x \rangle = \frac{1}{L} (\frac{x^2}{2} - \frac{x^2}{2} \cos(\frac{2n\pi x}{L}) + \frac{xL}{2n\pi} \sin(\frac{2n\pi x}{L}))\Big|_0^L$$

$$\langle x \rangle = \frac{1}{L} (\frac{L^2}{2}) = \frac{L}{2}$$

Hyrdrogen like solutions
3 Dimensional Time Independent Schroedinger Equation

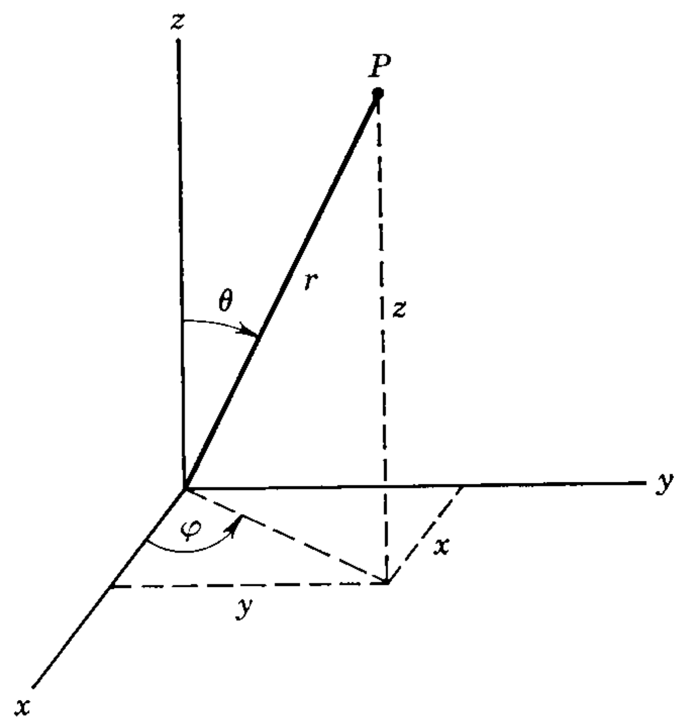
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)$$
$$=E\psi(x,y,z)$$

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

$$If\ V(x,y,x)=V(r)$$

$$Switch\ coordinate\ systems$$

Spherical Coordinates



$$r = \sqrt{x^2 + y^2 + z^2}$$

$$x = r\sin\theta\cos\phi$$

$$y = r\sin\theta\sin\phi$$

$$z = r\cos\theta$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r}) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial}{\partial\theta}) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi}$$

Transform

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}(\sin\theta \frac{\partial}{\partial \theta}) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2}{\partial^2 \phi}$$

Solution to SE in Spherical Coordinates

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

$$If\ V(r,\theta,\phi) = V(r) = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$$

Then try separation of variables

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

Substitute and divide by $R\Theta\Phi$

$$-\frac{\hbar^2}{2mR}\left(\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) + \frac{1}{\Theta r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi r^2\sin^2\theta}\frac{d^2\Phi}{d^2\phi} + V(r) = E$$

Separate ϕ dependence

$$\mathrm{Re}\,arrange:$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d^2\phi} = -\frac{2mr^2\sin^2\theta}{\hbar^2}(E - V(r)) - \frac{\sin^2\theta}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$$LHS\ is\ a\ function of\ \phi\ only.$$

Solution of Φ

$$\frac{1}{\Phi}\frac{d^2\Phi}{d^2\phi} = -m_l^2$$

$$\Phi = Ae^{im_l\phi}$$

Single valued means

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

Which means m_l *is an* integer.

What next?

$$-m_l^2 = -\frac{2mr^2\sin^2\theta}{\hbar^2}(E - V(r)) - \frac{\sin^2\theta}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$$What \quad now?$$

Separation of r and θ

$$-m_l^2 = -\frac{2mr^2\sin^2\theta}{\hbar^2}(E-V(r)) - \frac{\sin^2\theta}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) - \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$$\mathrm{Re}\,arrange:$$

$$-\frac{2mr^2}{\hbar^2}(E-V(r)) + \frac{1}{R}\left(\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) \equiv l(l+1)$$

LHS is a function of r only and RHS is a function of θ only.

Solution of Θ

$$\frac{m_l^2\Theta}{\sin^2\theta} - \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) = l(l+1)\Theta$$

The solution is in Appendix N.
Use a power series expansion in cos θ.
The series terminates for

$$l = |m_l|, |m_l + 1|, \ldots$$

$$\Theta = \sin^{m_l}\theta\ F_{lm_l}(\cos\theta)$$

Solution of R

$$-\frac{2mr^2}{\hbar^2}(E-V(r))R+(\frac{d}{dr}(r^2\frac{dR}{dr}))=l(l+1)R$$

The solution is in Appendix N.
Use a power series expansion in r.
The series terminates for

$$E_n=-\frac{E_0}{n^2}$$

where

$$E_0=\frac{mZ^2e^4}{(4\pi\varepsilon_0)^2 2\hbar^2}=13.6eV$$

$$n=l+1,l+2,...$$

(Z=1)

$$R_{nl}(r)=e^{-Zr/na_0}(\frac{Zr}{a_0})^l G_{nl}(Zr/a_0)$$

G(x) is a polynomial in x

$$a_0=\frac{4\pi\varepsilon_0\hbar^2}{me^2}=.525A$$

Quantum numbers

•N,l,m_l are called quantum numbers

•The energy eigenvalue depends only on n, so
N is called the principle quantum number.

•The angular momentum depends on l, so
l is called the azimuthal quantum number.

•The energy in a magnetic field depends on m_l, so
m_l is called the magnetic quantum number.

$$E_n = -\frac{E_0}{n^2}$$

Examination of the solution

- The solution of the spherical potential has solutions for particular quantum numbers m_l,l,n,E where

$$|m_l| = 0,1,2,...$$

$$l = |m_l|, |m_l| + 1,...$$

$$n = l + 1, l + 2,...$$

Examination of the solution

- The solution of the spherical potential has solutions for particular quantum numbers m,l,n,E where

$$|m_l| = 0,1,2,\ldots$$
$$l = |m_l|, |m_l| + 1,\ldots$$
$$n = l + 1, l + 2,\ldots$$

- This is equivalent to

$$n = 1,2,3,\ldots$$
$$l = 0,1,2,\ldots n - 1$$
$$m_l = -l, -l + 1,\ldots 0 \ldots l - 1, l$$

Degeneracy of the solution

$$n = 1,2,3,\ldots$$

$$l = 0,1,2,\ldots n-1$$

$$m_l = -l,-l+1,\ldots 0 \ldots l-1,l$$

- For each value of n,
  - There are n possible values of l
- For each value of l
  - There are 2l+1 values of m_l
- For each value of n,
  - There are n^2 degenerate eigenfunctions.

- The 3D Schroedinger equation has 3 spacial variables (x,y,z) and one time variable, so there are 4 quantum numbers (n, l, m_l, E)

- If there had been 6 variables, then there would be 6 quantum numbers.