6.2 Free particle in 3D

$$i\hbar\frac{\partial\Psi(\underline{r},t)}{\partial t} = E\Psi(\underline{r},t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\underline{r},t)$$

so our potential is not a function of time so we separate the time dependence out to get the time independent wavefunction which satisfies

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

if $V(\underline{r})$ is separable in cartesian coordinates we can write

$$\psi(\underline{r}) = \psi(x,y,z) = X(x)Y(y)Z(z)$$

$$\frac{-\hbar^2}{2m}\Big(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\Big)X(x)Y(y)Z(z) = EX(x)Y(y)Z(z)$$

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

each term is only a function of x or y or z, so these all must be constants in order to equal a constant at the end. so this results in the three equations

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

$$\frac{-\hbar^2}{2m}\frac{\partial^2 Y(x)}{\partial y^2} = E_y Y(y)$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2 Z(z)}{\partial z^2} = E_z Z(z)$$

each one of these is just the same as the 1D case. so we can write down the solution as

$$X(x) = A_x e^{ik_x x} \quad E_x = \frac{k_x^2\hbar^2}{2m}$$

similarly

$$Y(y) = A_y e^{ik_y y} \quad E_y = \frac{k_y^2\hbar^2}{2m}$$

$$Z(z) = A_z e^{ik_z z} \quad E_x = \frac{k_y^2 \hbar^2}{2m}$$

hence our full wavefunction is

$$\psi(x, y, z) = Ce^{ik_x x} e^{ik_y y} e^{ik_z z} = Ce^{i(k_x x + k_y y + k_z z)} = Ce^{i\underline{k}.\underline{r}}$$

where $\underline{k} = k_x \mathbf{i} + k_y \mathbf{j} + k_z \mathbf{k}$ and this will have energy

$$E = E_x + E_y + E_z = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{p^2}{2m}$$

where p is the magnitude of the linear momentum $\underline{p} = \hbar \underline{k}$

k_x, k_y, k_z can be +ve or -ve, depending on whether the wave is moving to the right or to the left. but E depends on k^2 so its always +ve. every non-negative value of E is allowed, so the spectrum is continuous. and for each value of E there are an infinite number of ways to make that energy by a different choice of k_x, k_y, k_z subject only to the condition that $k_x^2 + k_y^2 + k_z^2 = 2mE/\hbar^2$ i.e. there are infinitely many different orientations of the plane wave which give the same magnitude. It is infinitely degenerate, where degenerate means that there is more than one eigenvector which gives the same eigenvalue.

6.3 Infinite potential well in 3D

The time independent Schroedinger equation inside the region of the box is as above for a few particle i.e. the three equations

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

$$\frac{-\hbar^2}{2m} \frac{\partial^2 Y(x)}{\partial y^2} = E_y Y(y)$$

$$\frac{-\hbar^2}{2m} \frac{\partial^2 Z(z)}{\partial z^2} = E_z Z(z)$$

each one of these is just the same as the 1D case. so we can write down the solution as

$$X(x) = \sqrt{\frac{2}{L_x}} \sin n_x \pi x/L_x \quad E_x = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x}$$
$$Y(x) = \sqrt{\frac{2}{L_x}} \sin n_y \pi x/L_y \quad E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mL_y}$$
$$Z(x) = \sqrt{\frac{2}{L_x}} \sin n_z \pi x/L_z \quad E_z = \frac{n_z^2 \pi^2 \hbar^2}{2mL_z}$$

where the box extends from $0 - L_x$ on the x axis, $0 - L_y$ on the y axis and $0 - L_z$ on the z axis, so have volume $V = L_x L_y L_z$. hence the full wavefunction is

$$\psi(x, y, z) = X(x)Y(y)Z(z) = \sqrt{\frac{8}{L_x L_y L_z}} \sin(n_x \pi x/L_x) \sin(n_y \pi y/L_y) \sin(n_z \pi z/L_z)$$

where allowed energy levels are

$$E = E_x + E_y + E_z = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x} + \frac{n_y^2 \pi^2 \hbar^2}{2mL_y} + \frac{n_z^2 \pi^2 \hbar^2}{2mL_z}$$
$$= \frac{\pi^2 \hbar^2}{2m} (\frac{n_x^2}{L_x} + \frac{n_y^2}{L_y} + \frac{n_z^2}{L_z})$$

but we could of course have made our lives a lot easier by simply choosing a cube! so then

$$\psi_{\underline{n}}(x, y, z) = \sqrt{\frac{8}{V}} \sin(n_x \pi x/L) \sin(n_y \pi y/L) \sin(n_z \pi z/L)$$

with energy

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

The ground state has $n_x = n_y = n_z = 1$ so $n^2 = 3$ and there is only one wavefunction with this energy $E = 3\hbar^2 \pi^2/(2mL)$

The next energy level has one of the dimensions in the $n = 2$ state. but this could be either of n_x, n_y, n_z. so there are 3 possible different wavefunctions with this energy, where $(n_x, n_y, n_z) = (2, 1, 1)$, or (1,2,1) or (1,1,2). These all have $n^2 = 6$ so $E = 6\hbar^2 \pi^2/(2mL)$ so the level is three fold degenerate.

7 Schroedinger in 3D spherical polars

all very well to do this is cartesian coordinates, but we are really wanting to do potentials which are functions of radial distance since we are interested in atoms! so we really want to write the Schroedinger equation in 3D in spherical polar coordinates as our potential $V(r) \propto 1/r = (x^2 + y^2 + z^2)^{-1/2}$ which is NOT separable in cartesian coordinates but is in spherical polars.

so we need to take our 3D cartesian Schroedinger equation and transform to spherical polar coordinates. we know

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

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

so then we can do a 3D hamiltonian in spherical polar coordinates

$$H = \frac{-\hbar^2}{2m}\Big[\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial^2}{\partial\theta^2}\Big) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big] + V(\underline{r})$$

but from a few lectures ago we saw that

$$L^2 = -\hbar^2\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial^2}{\partial\theta^2}\Big) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]$$

so our 3D Schroedinger equation is

$$\Big[\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial}{\partial r}\Big) + \frac{L^2}{2mr^2} + V(\underline{r})\Big]\psi = E\psi$$