### 6.1.1 Infinite square well potential

$V = 0$ for $0 < x < L_x$ and $0 < y < L_y$ and $0 < z < L_z$ and $\infty$ elsewhere. Inside the well then we have

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

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

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

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

$$X(x) = \sqrt{\frac{2}{L_x}} \sin n_x \pi x / L_x \quad E_x = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2}$$

$$Y(x) = \sqrt{\frac{2}{L_y}} \sin n_y \pi x / L_y \quad E_y = \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2}$$

$$Z(x) = \sqrt{\frac{2}{L_z}} \sin n_z \pi x / L_z \quad E_z = \frac{n_z^2 \pi^2 \hbar^2}{2mL_z^2}$$

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

$$E = E_x + E_y + E_z = \frac{n_x^2 \pi^2 \hbar^2}{2mL_x^2} + \frac{n_y^2 \pi^2 \hbar^2}{2mL_y^2} + \frac{n_z^2 \pi^2 \hbar^2}{2mL_z^2}$$

$$= \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

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

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

The ground state has $n_x = n_y = n_z = 1$ so $n^2 = 3$ and there is only one wavefunction with this energy $E = 3\hbar^2\pi^2/(2mL^2)$ (degeneracy one or non-degenerate)
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 $E = 6\hbar^2\pi^2/(2mL^2)$ so the level is three fold degenerate.
we get degeneracies because of the *symmetry* of the potential. Each dimension has its own quantization condition. If the dimensions are the same then rotating the wave around gives the same energy as before.

## 6.2 Schroedinger in 3D spherical polars

so we now want to transform the Schroedinger equation into spherical polar coordinates. Becasue we often have potentials

$$V(x,y,z) = V(r) = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$$

we can't do separation of variables because the potential can't be split into separate x,y,z terms. Instead the most natural coordinates to use are spherical polar coordinates, where the variables are $(r, \theta\phi)$, the potential is simply $V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$ i.e. this is a function only of $r$ and not of $\theta$ or $\phi$ so this is separable in these coordinates.
so we need to take our 3D cartesian Schroedinger equation and transform to spherical polar coordinates where

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

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

$$z = r\cos\theta$$

and $r^2 = x^2 + y^2 + z^2$.
and when we do the volume integrals, we go from

$$\int_{x=-\infty}^{+\infty}\int_{y=-\infty}^{+\infty}\int_{z=-\infty}^{+\infty} dxdydz = \int_{r=0}^{+\infty}\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} r^2\sin\theta drd\theta d\phi$$

that means probability of finding the electron is now within VOLUME $dV$ of its position. so before we had probability of finding it within $dx$ of $x$ is $\psi^*(x)\psi(x)dx$, but now we have probability of finding it within $dV$ of its current position is $\psi^*\psi dV$. so for cartesian is $\psi^*(x,y,z)\psi(x,y,z)dxdydz$ and for spherical polars its $\psi^*(r,\theta,\phi)\psi(r,\theta,\phi)r^2\sin\theta drd\theta d\phi$. A probability density in some coordintate is then integrated over all the rest of the coordinates e.g. radial probability density is $\int_\theta\int_\phi \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)r^2\sin\theta d\theta d\phi$
we want to transform from

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

changing coodinates (the slow way is via the chain rule)

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

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

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

So, lets try separating variables in this! let $\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) = R(r)Y(\theta,\phi)$ in the time independent Schroedinger equation.

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

$$\frac{1}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial\psi}{\partial r}\Big) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial\psi}{\partial\theta}\Big) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} - \frac{2m}{\hbar^2}(V(\underline{r}) - E)\psi = 0$$

$$\frac{Y}{r^2}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R}{\partial r}\Big)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial Y}{\partial\theta}\Big)+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}-\frac{2m}{\hbar^2}(V(\underline{r})-E)RY=0$$

$$\frac{1}{R}\frac{\partial}{\partial r}\Big(r^2\frac{\partial R}{\partial r}\Big)-\frac{2mr^2}{\hbar^2}(V(\underline{r})-E)=-\Big(\frac{1}{Y\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial Y}{\partial\theta}\Big)+\frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\Big)$$

the rhs is a function only of $r$, the lhs is a function only of $\theta, \phi$. the only way these two can be equal to each other is if NEITHER has any $r, \theta, \phi$ dependance i.e. its a constant.