Chapter 4: QM in three dimensions

In principle, the generalization is simple:

$$\boxed{i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \;=[\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V(x,y,z)\;]\,\Psi}$$

where we follow the recipe of 1D now in 3D:

$$\boxed{p_x \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad p_y \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial y}, \quad p_z \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial z},}$$

Written in a compact form we get:

$$\mathbf{p} \to \frac{\hbar}{i}\nabla \xrightarrow{\text{gradient operator}} i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

where the Laplacian is:

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

The normalization remains:

$$\int |\Psi|^2\, d^3\mathbf{r} = 1$$

$\mathbf{r}=(x,y,z)$

where in Cartesian coordinates

$$d^3\mathbf{r} = dx\, dy\, dz$$

The time independent Sch. Eq. is:

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

Solutions are the stationary states, or eigenstates of the Hamiltonian, with the regular time dependence:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r})e^{-iE_n t/\hbar}$$

Any 3D wave function can be expanded similarly as in 1D:

$$\boxed{\Psi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r})e^{-iE_n t/\hbar}}$$

Once again, coordinates and momenta do not commute (i,j Cartesian coordinates x,y,z):

$$\boxed{[r_i\,,\,p_j\,] = -[p_i\,,\,r_j\,] = i\,\hbar\,\delta_{ij}\quad,\quad [r_i\,,\,r_j\,] = [p_i\,,\,p_j\,] = 0}$$

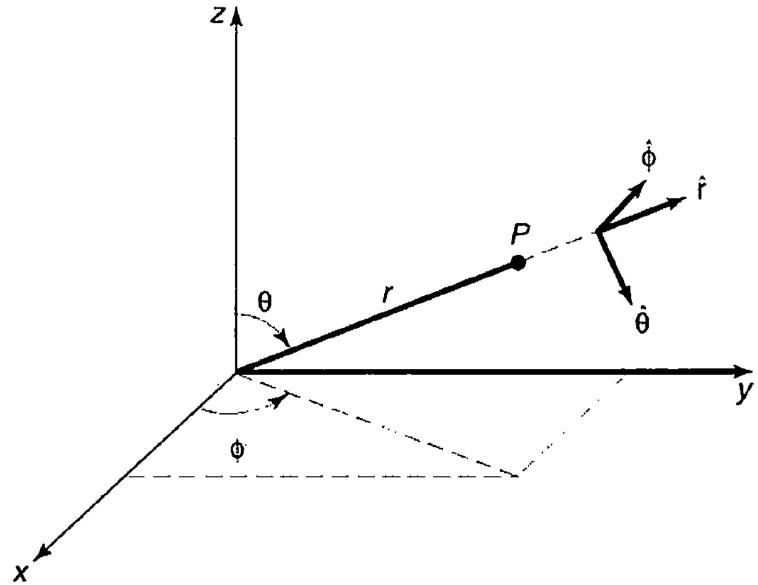
Once again, expectation values behave like classical variables:

$$\boxed{\frac{d}{dt}\langle\mathbf{r}\rangle = \frac{1}{m}\langle\mathbf{p}\rangle, \quad \text{and} \quad \frac{d}{dt}\langle\mathbf{p}\rangle = \langle -\nabla V\rangle}$$

Once again, there are uncertainty inequalities:

$$\boxed{\sigma_x\sigma_{p_x} \geq \hbar/2, \quad \sigma_y\,\sigma_{p_y} \geq \hbar/2, \quad \sigma_z\sigma_{p_z} \geq \hbar/2}$$

Spherical coordinates is what we need for the Hydrogen atom because of rotational invariance:



The Laplacian in spherical coordinates is "complicated". Without a proof just accept that:

$$\boxed{\nabla^2 = \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}_{\text{function of r only}} + \underbrace{\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)}_{\text{function of r and }\theta\text{ only}} + \underbrace{\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)}_{\text{function of r, }\theta\text{, and }\phi}}$$

After the "horrible" Laplacian is used, the Sch. Eq. becomes:

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

How do we even start addressing this mess? Try first separation of variables between radial and angular coordinates:

$$\boxed{\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)}$$

In many cases of interest V=V(r) only, like the H atom.

Use the proposed solution in the Hamiltonian …
and hope for the best:

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$
$$+VRY=ERY$$

Divide by $R(r)Y(\theta,\phi)$ and multiply all by $(-2mr^2/\hbar)$:

Only function of r:

$$\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]\right\}$$

Only function of angles θ and ϕ:

$$+\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=0.$$

Since the sum of a term that depends on r and a term that depends on angles gives zero, both must be constant and of opposite sign:

$$\boxed{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]=l(l+1);}$$

$$\boxed{\frac{1}{Y}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right\}=-l(l+1)}$$

The angular component is more “fun” (physicist talking) and we will study that first. It leads to all the weird shapes of orbitals.