Chapter 4: QM in three dimensions

In principle, the generalization 1D to 3D is simple:

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

where we follow the same rules of 1D, but now in 3D:

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

Written in a compact form we obtain:

gradient operator

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

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 in 3D is:

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

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

where in Cartesian coordinates $d^3\mathbf{r} = dx\,dy\,dz$

The time independent Sch. Eq. is:

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

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, due to completeness and orthonormality:

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

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

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

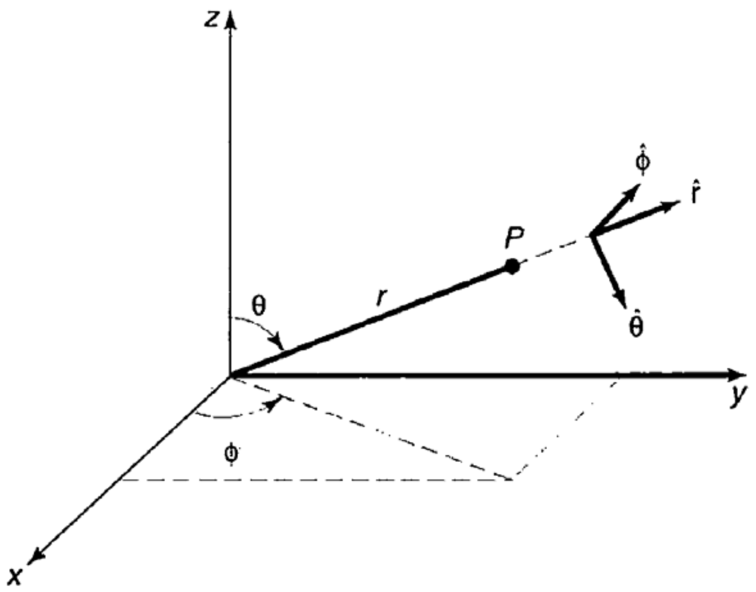
Once again, expectation values behave like classical variables:

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

Once again, there are uncertainty inequalities:

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

4.1.1: However, 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:

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

function of r only

function of r and θ only

function of r, θ, and ϕ

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

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

How do we even start addressing this difficult diff. eq.? As usual, try first separation of variables between radial and angular coordinates:

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

Simplification:
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(θ,φ) and multiply all by $(-2mr^2/\hbar^2)$:

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:

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

Because 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:

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

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

The angular component is more “fun” (physicists talking) and we will study that first. It leads to all the weird shapes of orbitals. Plus, it is independent of *V(r)* i.e. generic for many problems.

Moving $Y(\theta, \phi)\sin^2(\theta)$ to the other side, we focus on the **4.1.2** Angular Equation which is the SAME for any potential V(r):

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

Let us once again try separation of variables, followed by the canonical division by $\Theta\Phi$:

$$Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$$

$$\underbrace{\left\{\frac{1}{\Theta}\left[\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right)\right] + l(l+1)\sin^2\theta\right\}}_{\text{function of } \theta \text{ only}} + \underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}}_{\text{function of } \phi \text{ only}} = 0$$

function of θ only

Total derivative notation used, instead of partial, because unknown function depends only on θ

function of ϕ only

As in several occasions before, then this means:

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right]+l(l+1)\sin^2\theta=m^2$$

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

Thus, up to now via the trick of the separation of variables we have managed to write the single huge Sch. Eq. in spherical coordinates, into three separated equations.

In doing so, we introduced three unknown constants *E* (energy of the stationary states that likely will have an index *n* for bound states), plus *l(l+1)* and *m*.

Thus, solutions will have THREE labels: *n,l,m*.
We say "three quantum numbers".

Fortunately, the equation for ϕ is easy!

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \;\Rightarrow\; \Phi(\phi) = e^{im\phi}$$

Because "physics" has to be the same after a 2π rotation then we impose:

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

which leads to quantization of m (discrete values):

$$m = 0, \pm 1, \pm 2, \ldots.$$

The second angular equation is NOT easy:

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + [l(l+1)\sin^2\theta - m^2]\Theta = 0$$

The solution is simply given to you:

$$\Theta(\theta) = A P_l^m(\cos\theta)$$

Called the **associated Legendre function** (not polynomials)

For m=0, they are just called the **Legendre polynomials** (yes, now polynomials).

These m=0 polynomials will be given to you. At most you will be asked to prove that indeed they are solutions. Using the very common notation $cos(\theta) = x$:

$$P_0 = 1$$

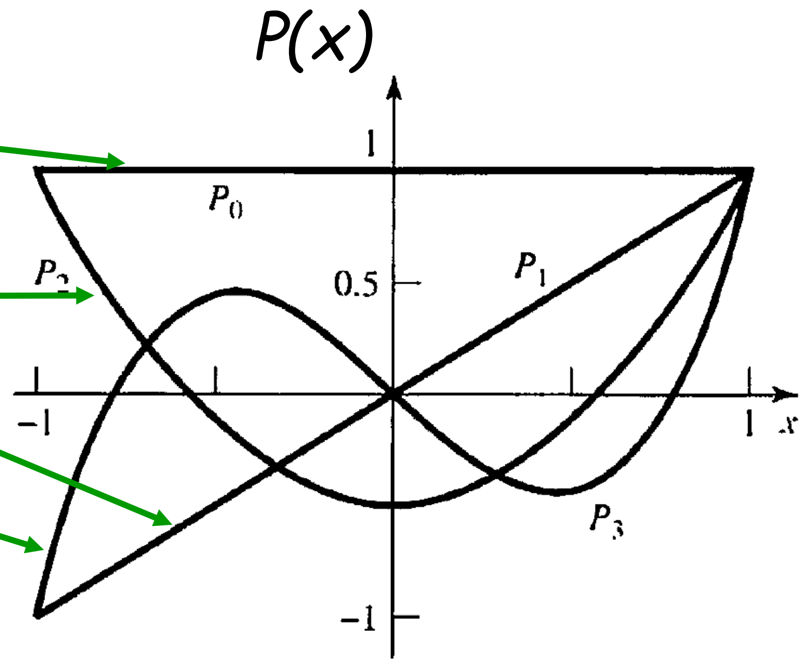
$$P_1 = x$$

$$P_2 = \frac{1}{2}(3x^2 - 1)$$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$



These polynomials can be divided in even and odd.

But we need the entire associated Legendre functions (i.e. arbitrary m). Just accept the following formula:

$$P_l^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x)$$

l=2, m=0

$$P_2^0(x) = \frac{1}{2}(3x^2-1),$$

l=2, m=1 or -1

$$P_2^1(x) = (1-x^2)^{1/2}\frac{d}{dx}\left[\frac{1}{2}(3x^2-1)\right] = 3x\sqrt{1-x^2},$$

$$P_2^2(x) = (1-x^2)\left(\frac{d}{dx}\right)^2\left[\frac{1}{2}(3x^2-1)\right] = 3(1-x^2),$$

l=2, m=2 or -2

Not a polynomial. But note $(1-x^2)$ is simply $\sin^2(\theta)$!

Note that in the formula of previous page "*l*" is the order of the polynomial, thus if $|m|>l$, we obtain a zero after the derivatives are made.

$$P_l^m(x) \equiv (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_l(x)$$

As a consequence we have the following constraints:

$$l = 0,\ 1,\ 2,\ldots;\quad m = -l,\ -l+1,\ \ldots,\ -1,\ 0,\ 1,\ \ldots,\ l-1,\ l$$

For each integer "*l*", there are $(2l+1)$ values of m.

All associated Legendre functions you may need will be given to you in exams (in HW you may have to look for them in tables or you may google them):

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

If you graph these functions, the "orbitals" that you have seen many times before since high school start appearing!