

# Quantum Chemistry

CML101  
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## 9 Postulates of Quantum Mechanics

### 9.1 Postulate I: The Wavefunction

The state of the system is described as fully as possible by the wavefunction  $\psi(r_1, r_2, \dots, t)$  where  $r_1, r_2, \dots$  are the locations of the particles and  $t$  is time.

$\psi(r_1, r_2, \dots, t) \rightarrow$  time-dependent wavefunction

$\psi(r_1, r_2, \dots) \rightarrow$  time-independent wavefunction

#### 9.1.1 Born Interpretation

For a system described by the wavefunction  $\psi(r_1, r_2, \dots)$  the probability of finding particle 1 in the volume element  $d\tau_1$  at  $r_1$ , particle 2 in the volume element  $d\tau_2$  at  $r_2$ , etc. is proportional to  $|\psi|^2 d\tau_1 d\tau_2 \dots$

$|\psi|^2 \rightarrow$  probability density

$\psi \rightarrow$  probability amplitude. It has no physical significance

#### 9.1.2 Normalisation Condition

A wavefunction is said to be normalised if  $\int \psi^* \psi d\tau = 1$

Hence the normalisation constant  $N$  (which when multiplied to the wavefunction normalises it) is equal to  $\frac{1}{(\int \psi^* \psi d\tau)^{1/2}}$ . If this integral has a finite value, the wavefunction is **square-integrable**.

#### 9.1.3 Constraints on Wavefunction

- $\psi$  must not be infinite over a finite region
- $\psi$  must be single-valued
- $\psi$  must be continuous
- $\frac{d\psi}{dx}$  must be continuous

## 9.2 Postulate II: Quantum Mechanical Operators

For each observable property  $\Omega$  of a system there is a corresponding operator  $\hat{\Omega}$  built from the following position and momentum operators:

- $\hat{\mathbf{x}} = x \times$
- $\hat{\mathbf{p}} = -i\hbar\nabla$  or in special case of one dimension  $\hat{\mathbf{p}}_x = -i\hbar\frac{\partial}{\partial x}$

All the operators we encounter are linear i.e.  $\hat{\Omega}(\psi_1 + \psi_2) = \hat{\Omega}(\psi_1) + \hat{\Omega}(\psi_2)$

### Time-independent Schrodinger Equation

$$\hat{\mathbf{H}}\psi = E\psi$$

where,

$\hat{\mathbf{H}} = \frac{-\hbar^2}{2m}\nabla^2 + V$  is the hamiltonian operator corresponding to total energy of system.

$E$  is the total energy of system

This suggests the form of the **eigenvalue equation**

$$\hat{\Omega}\psi = \omega\psi$$

where,

$\hat{\Omega}$  is a operator corresponding to an observable

$\omega$  is called observable or **eigenvalue** of operator. It is always a real value.

$\psi$  is the wavefunction and also called as **eigenfunction** of the operator

## 9.3 Postulate III: Eigenvalues and Eigenfunctions

If the system is described by a wavefunction  $\psi$  that is an eigenfunction of  $\hat{\Omega}$  such that  $\hat{\Omega}\psi = \omega\psi$  then the outcome of a measurement of  $\Omega$  will be the eigenvalue  $\omega$ . Operator  $\hat{\Omega}$  has to be Hermitian and observable  $\omega$  has to be purely real.

$$\int \psi_1^* \hat{\Omega} \psi_2 dx = \left[ \int \psi_2^* \hat{\Omega} \psi_1 dx \right]^* \quad \forall \psi_1, \psi_2$$

The momentum and position operators are hermitian. Sum and product of two hermitian operators is also hermitian.

### 9.3.1 Orthogonality of Eigenfunctions

**Eigenfunctions corresponding to different eigenvalues of the same Hermitian operator are orthogonal.** To say that two different functions  $\psi_i$  and  $\psi_j$  are orthogonal means that the integral (over all space) of their product is zero:

$$\int \psi_i^* \psi_j \, d\tau = 0$$

in a special case when both functions are normalised,

$$\int \psi_i^* \psi_j \, d\tau = \delta_{ij}$$

## 9.4 Postulate IV: Basis Set Postulate

**The set of functions  $\psi_k$  which are eigenfunctions of the eigenvalue equation form a complete set of linearly independent functions. They can be said to form a basis set in terms of which any wavefunction representing the system can be expressed:**

$$\psi = \sum_{k=1}^{\infty} c_k \psi_k$$

This implies that any wavefunction  $\psi$  representing a physical system can be expressed as a linear combination of the eigenfunctions of any physical observable of the system. This is the Fourier Series of  $\psi$  and its existence is ensured by Dirichlet's Theorem. You can find the constant  $c_m$  by Fourier's trick: Multiply both sides by some  $\psi_m^*$  and integrate.

$$\int_0^{\infty} \psi_m^* \psi \, dx = \sum_{k=1}^{\infty} c_k \int_0^{\infty} \psi_m^* \psi_k \, dx = \sum_{k=1}^{\infty} c_k \delta_{m,k} = c_m$$

$$\therefore c_m = \int_0^{\infty} \psi_m^* \psi \, dx$$

## 9.5 Postulate V: Predicting Experiments

**When the value of an observable  $\Omega$  is measured for a system that is described by a wavefunction which is a linear combination,  $\psi = \sum_k c_k \psi_k$ , each measurement of  $\Omega$  gives**

one of the eigenvalues  $\omega_k$  with a probability proportional to  $|c_k|^2$ . If  $\psi$  is normalised, then this probability is equal to  $|c_k|^2$ .

The mean of the measurements of  $\Omega$  is equal to expectation value of the operator  $\hat{\Omega}$

$$\langle \Omega \rangle = \frac{\int \psi^* \hat{\Omega} \psi d\tau}{\int \psi^* \psi d\tau}$$

for a normalised wavefunction, the denominator is unity. If  $\psi$  is an eigenfunction of  $\hat{\Omega}$  then each measurement and consequently expectation value will be equal to it's eigenvalue  $\omega$ .

In the case of  $\psi = \sum_k c_k \psi_k$ , the expectation value is ( $\psi$  is normalised)

$$\langle \Omega \rangle = \sum_k |c_k|^2 \omega_k$$

## 10 The Uncertainty Principle

### Heisenberg Uncertainty Principle

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}$$

where,

$$\Delta X = \left[ \langle X^2 \rangle - \langle X \rangle^2 \right]^{1/2}$$

Note that there is no such constraint on say,  $p_y$  and  $x$

### 10.1 General Form of Uncertainty principle

Two observables  $\Omega_1$  and  $\Omega_2$  are complementary if  $\hat{\Omega}_1 \hat{\Omega}_2 \psi \neq \hat{\Omega}_2 \hat{\Omega}_1 \psi$

The commutator of the two operators is defined as their difference:  $[\hat{\Omega}_1, \hat{\Omega}_2] = \hat{\Omega}_1 \hat{\Omega}_2 - \hat{\Omega}_2 \hat{\Omega}_1$ . If two operators commute then their commutator is 0.

### General Uncertainty Principle

$$(\Delta \Omega_1)^2 (\Delta \Omega_2)^2 \geq \left( \frac{1}{2i} \langle [\hat{\Omega}_1, \hat{\Omega}_2] \rangle \right)^2$$

from which it immediately follows that

$$\Delta\Omega_1\Delta\Omega_2 \geq \left| \frac{1}{2i} \langle [\hat{\Omega}_1, \hat{\Omega}_2] \rangle \right|$$

## 11 Motion in 1D

A particle with net motion is described by a complex wavefunction. A wavefunction that is purely real corresponds to zero net motion. Because purely real wavefunction can be described as a linear combination of wavefunctions which are conjugates of each other. This gives an expectation value of 0 to linear momentum

For a freely moving particle in one dimension, Schrodinger's equation is

$$-\frac{\hbar}{2m} \frac{d^2\psi(x)}{dx^2} = E\psi(x)$$

Solving this we get the general solutions as,

$$\begin{aligned} \psi_k &= Ae^{ikx} + Be^{-ikx} \\ E_k &= \frac{k^2\hbar^2}{2m} \end{aligned}$$

It follows that in this case, energy is **not** quantized.

### 11.1 Particle in a 1D box

Particle is confined between  $x = 0$  and  $x = L$ . Hence potential energy is:

$$V = \begin{cases} 0 & \text{if } x \in (0, L) \\ \infty & \text{if } x \in (-\infty, 0] \cup [L, \infty) \end{cases}$$

For particle inside walls, wavefunction will be same as that for free motion. It would be more convenient to write  $\psi_k = Ae^{ikx} + Be^{-ikx}$  as  $\psi_k = C \sin kx + D \cos kx$  where  $C = (A - B)i$ ,  $D = (A + B)$ . For particle outside walls, wavefunction is 0.

$$\psi_k(x) = \begin{cases} C \sin kx + D \cos kx & \text{if } x \in (0, L) \\ 0 & \text{if } x \in (-\infty, 0] \cup [L, \infty) \end{cases}$$

At the moment, it seems that  $k$  can take any value.

### 11.1.1 Restricting values of $k$

For continuity of wavefunction, it must satisfy the following boundary conditions:

- $\psi_k(0) = 0$
- $\psi_k(L) = 0$

First condition implies that  $D = 0$  and second condition implies  $k = \frac{n\pi}{L}$ . normalising the wavefunction gives  $C = (\frac{2}{L})^{1/2}$ . This will quantize the system by allowing only discrete values.

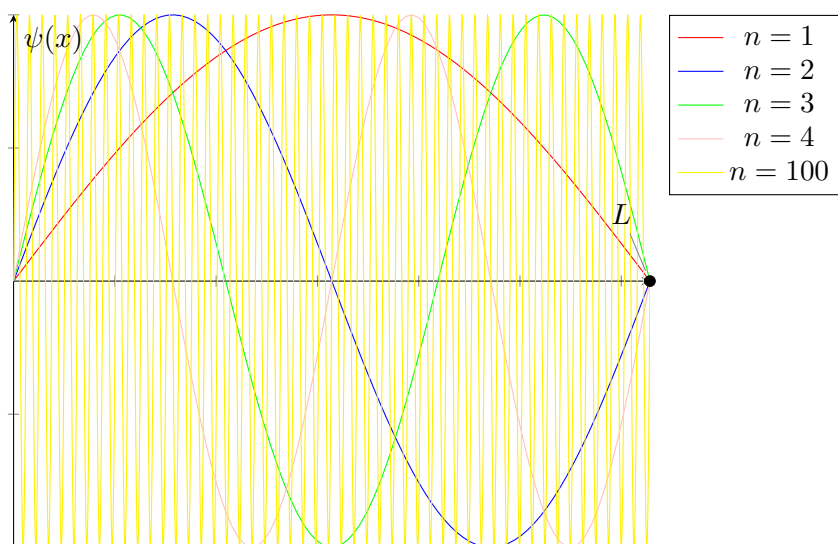
$$\psi_n(x) = \begin{cases} (\frac{2}{L})^{1/2} \sin \frac{n\pi x}{L} & \text{if } x \in (0, L) \\ 0 & \text{if } x \in (-\infty, 0] \cup [L, \infty) \end{cases}$$

and

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad \text{where } n = 1, 2, 3, \dots$$

### 11.1.2 Properties of Wavefunction

**Nodes are points where the wavefunction passes through zero (not merely reaching zero, as at the walls).** This particular wavefunction has  $n - 1$  nodes.



The probability density  $\psi^2(x)$  becomes more uniform as  $n$  increases, provided we ignore the fine detail of the increasingly rapid oscillations. The probability density at high quantum numbers reflects the classical result that a particle bouncing between the walls spends, on the average, equal times at all points. Thus classical mechanics emerges from quantum mechanics as high quantum numbers are reached.

### 11.1.3 Properties of Observables

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin \frac{n\pi x}{L} = \frac{1}{2i} \left(\frac{2}{L}\right)^{1/2} (e^{ikx} + e^{-ikx})$$

It follows that linear momentum will be  $k\hbar$  for half measurements and  $-k\hbar$  for other half. So expectation value is 0. Which we could even obtain directly by integration:

$$\langle p \rangle = \frac{-2i\hbar n\pi}{L^2} \int_0^L \sin \frac{n\pi x}{L} \cos \frac{n\pi x}{L} dx = 0$$

Because  $n$  cannot be zero, the lowest energy that the particle may possess is not zero (as would be allowed by classical mechanics) but this lowest, irremovable energy is called the **zero-point energy**. The physical origin of the zero-point energy can be explained in two ways:

- The Heisenberg uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region (which in this case is true)
- If the wavefunction is to be zero at the walls, but smooth, continuous, and not zero everywhere, then it must be curved, and curvature in a wavefunction implies the possession of kinetic energy.

## 12 Motion in 2D and 3D

### 12.1 Motion in 2D box

Let the region of box be  $\{(x, y) \mid 0 < x < L_1, 0 < y < L_2\}$ . Schrodinger's equation will be

$$\frac{-\hbar^2}{2m} \left( \frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} \right) = E\psi$$

#### 12.1.1 Separation of Variables

Assume that  $\psi$  can be written as a product of two function  $X(x)$  and  $Y(y)$ . I.e.  $\psi(x, y) = X(x)Y(y)$ .

Substituting this in Schrodinger's equation, dividing both sides by  $XY$  and rearranging,

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} = -\frac{2mE}{\hbar^2}$$

The first term on the left is independent of  $y$ , so if  $y$  is varied only the second term of the two on the left can change. But the sum of these two terms is a constant given by the right-hand side of the equation. Hence both the terms of left are constants. We can then break it like this:

$$\frac{1}{X} \frac{d^2 X}{dx^2} = -\frac{2mE_X}{\hbar^2} \quad \text{and} \quad \frac{1}{Y} \frac{d^2 Y}{dy^2} = -\frac{2mE_Y}{\hbar^2}$$

$$-\frac{\hbar^2}{2m} \frac{d^2 X}{dx^2} = E_X X \quad \text{and} \quad -\frac{\hbar^2}{2m} \frac{d^2 Y}{dy^2} = E_Y Y$$

where,

$$E = E_X + E_Y$$

This is exactly the equation for a particle in 1D box. So we can directly write the wavefunction easily:

### 2D box

$$\psi_{n_1, n_2}(x, y) = \begin{cases} \frac{2}{(L_1 L_2)^{1/2}} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} & \text{for } 0 < x < L_1, 0 < y < L_2 \\ 0 & \text{otherwise} \end{cases}$$

Similarly,  $E = E_x + E_y$

$$E_{n_1, n_2} = \frac{h^2}{8m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} \right)$$

### 12.1.2 Degeneracy

Now consider a situation where  $L_1 = L_2 = L$ . Then  $n_1 = 1, n_2 = 2$  and  $n_2 = 1, n_1 = 2$  will yield different wavefunctions but same energy. The technical term for different wavefunctions with same energy is **degeneracy**. In this case, we say the state is **double degenerate**.

Each occurrence of degeneracy is related to a symmetry of the system. In this case it's rotating the box by  $90^\circ$  changes  $\psi_{1,2}$  into  $\psi_{2,1}$ .

### 12.1.3 Multiplicity

**Multiplicity is defined as  $2S + 1$  where  $S$  is total spin angular momentum quantum number.** Multiplicity tells the number of permitted values of  $m_s$ , the spin quantum number. For



electron in atom, multiplicity = 2, because only  $m_s = 1/2$  and  $m_s = -1/2$  are allowed.

Also these permitted values of spin quantum number are  $\{-S, -S + 1, -S + 2, \dots, S\}$

## 12.2 Motion in 3D box

Using similar separation of variables we get the following:

### 3D box

$$\psi_{n_1, n_2, n_3}(x, y, z) = \begin{cases} \frac{2\sqrt{2}}{(L_1 L_2 L_3)^{1/2}} \sin \frac{n_1 \pi x}{L_1} \sin \frac{n_2 \pi y}{L_2} \sin \frac{n_3 \pi z}{L_3} & \text{for } 0 < x < L_1, 0 < y < L_2, 0 < z < L_3 \\ 0 & \text{otherwise} \end{cases}$$

Similarly,  $E = E_x + E_y + E_z$

$$E_{n_1, n_2, n_3} = \frac{h^2}{8m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right)$$

## 13 Particle on a Ring

Let the particle move in a circle of radius  $r$  in the  $x, y$  plane and having a linear momentum  $p$  at some instant. The angular momentum along  $z$  axis is

$$J_z = \pm pr$$

Let moment of inertia of system be  $I$ . Then kinetic energy is

$$E = \frac{J_z^2}{2I}$$

This equation is valid for any body having moment of inertia  $I$  rotating in a plane, not just a particle.

### 13.1 Quantised Rotation

Since  $p = h/\lambda$  by de Broglie relation, we get

$$J_z = \pm \frac{hr}{\lambda}$$

$$E = \frac{h^2 r^2}{2I \lambda^2}$$

Because wavefunction must be single valued, it must repeat after a complete rotation. Hence, an integer number of wavelengths must fit the circumference of the ring.

$$n\lambda = 2\pi r \quad , \quad n = 0, 1, 2, \dots$$

$n = 0$  corresponds to  $\lambda = \infty$ , a wave that has constant height. Applying this constraint to  $J_z$  and  $E$  gives:

$$J_z = \pm \frac{nh}{2\pi} = m_l \hbar \quad , \quad m = 0, \pm 1, \pm 2, \dots$$

$$E = \frac{m_l^2 \hbar^2}{2I} \quad , \quad m = 0, \pm 1, \pm 2, \dots$$

A few observations:

- States with a given nonzero value of  $|m_l|$  are doubly degenerate because of  $\pm$ .
- Only the state described by  $m_l = 0$  is non-degenerate, consistent with the interpretation that, when  $m_l$  is zero, the particle has an infinite wavelength and is stationary
- Each state can be occupied by 2 electrons even for  $m_l = 0$
- There is no zero-point energy in this system: the lowest possible energy is  $E_0 = 0$

## 13.2 Wavefunction

Solving the PDE  $-\frac{\hbar^2}{2I} \frac{d^2\psi}{d\phi^2} = E\psi$ , gives us the state of system

### Particle on a ring

$$\psi_{m_l}(\phi) = \frac{e^{im_l\phi}}{(2\pi)^{1/2}}$$

$$J_z = m_l \hbar$$

$$E_{m_l} = \frac{m_l^2 \hbar^2}{2I}$$

where,  $m_l = 0, \pm 1, \pm 2, \dots$

## 14 Dirac Notation

$$|\psi\rangle = \sum_{i=0}^n a_i |\hat{\psi}_i\rangle$$

This is called a **ket**. It is a column vector with coefficients  $a_i$  (which may be complex) along the unit basis vectors  $|\hat{\psi}_i\rangle$ . We can write  $|\psi\rangle$  as a column vector:

$$|\psi\rangle = \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_n \end{bmatrix} \quad (1)$$

A **bra** is a row vector which consists of complex conjugates of  $a_i$ . It is shown as  $\langle\psi|$

$$\langle\psi| = [a_1^* \quad a_2^* \quad \dots \quad a_n^*] \quad (2)$$

Scalar product of  $\langle\psi_i|$  and  $|\psi_j\rangle$  is just written as  $\langle\psi_i|\psi_j\rangle = \sum_{i=0}^n a_i^* b_i$ . The order of scalar product matters if the coefficients are complex numbers because  $\langle\psi_i|\psi_j\rangle = \langle\psi_j|\psi_i\rangle^*$

It follows that if the wavefunctions are normalised,  $\langle\psi_i|\psi_j\rangle = \delta_{ij}$

**Because  $\langle\psi|$  and  $|\psi\rangle$  exist in different mathematical spaces, we cannot add or subtract them.**

### 14.1 Observables and Operators

The eigenvalue equation can be written as:

$$\hat{\Omega} |\psi\rangle = \omega |\psi\rangle$$

where  $\psi$  is an **eigenvector** of  $\hat{\Omega}$ .

Multiplying both sides by  $\langle\psi|$  gives

$$\langle\psi|\hat{\Omega}|\psi\rangle = \langle\psi|\omega|\psi\rangle = \omega \langle\psi|\psi\rangle$$

because  $\omega$  is just a scalar real value. And if  $\langle\psi|$  is normalised, we can easily write the expectation value of  $\omega$  in state  $\psi$ .

### Expectation Value

$$\langle \omega \rangle_\psi = \langle \psi | \hat{\Omega} | \psi \rangle = \int \psi^* \hat{\Omega} \psi \, d\tau$$

This is the derivation for expectation value in Postulate V.

Properties of operators (some already discussed before):

- Operators are linear  $\hat{\Omega}(|\psi_1\rangle + |\psi_2\rangle) = \hat{\Omega}|\psi_1\rangle + \hat{\Omega}|\psi_2\rangle$
- Operators with real eigenvalues are Hermitian  $\langle \psi_1 | \hat{\Omega} | \psi_2 \rangle = \langle \psi_2 | \hat{\Omega} | \psi_1 \rangle$
- Hermitian operator with a set of eigenvectors which have different eigenvalues are orthogonal  $\langle \psi_i | \psi_j \rangle = 0$
- There exists a set of eigenvectors of both operators  $\hat{\Omega}_1$  and  $\hat{\Omega}_2 \iff$  these operators commute,  $[\hat{\Omega}_1, \hat{\Omega}_2] = 0$

### Proof

$$\hat{\Omega}_1 |\psi\rangle = \omega_1 |\psi\rangle$$

$$\hat{\Omega}_2 |\psi\rangle = \omega_2 |\psi\rangle$$

Multiplying first equation by  $\hat{\Omega}_2$  and second equation by  $\hat{\Omega}_1$  gives,

$$\hat{\Omega}_2 \hat{\Omega}_1 |\psi\rangle = \omega_1 \hat{\Omega}_2 |\psi\rangle = \omega_1 \omega_2 |\psi\rangle$$

$$\hat{\Omega}_1 \hat{\Omega}_2 |\psi\rangle = \omega_2 \hat{\Omega}_1 |\psi\rangle = \omega_2 \omega_1 |\psi\rangle$$

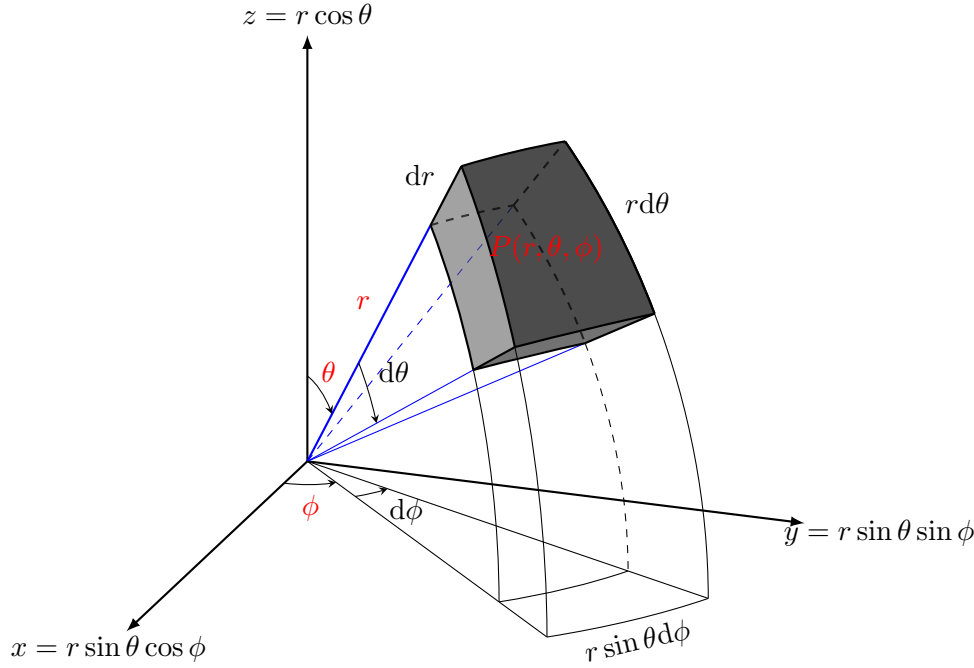
Subtracting them gives the required result.

## 15 Hydrogenic Atom

Schrodinger Equation in cartesian will be (we assume that nucleus is at rest and only electrostatic interactions are present):

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi - \frac{Ze^2}{4\pi\epsilon_0 \sqrt{x^2 + y^2 + z^2}} = E\psi$$

We cannot solve this PDE, hence we switch to spherical coordinates



Putting spherical coordinates in original equation gives us an apparently complicated looking equation

$$-\frac{\hbar^2}{2m_e} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right] - \frac{Ze^2}{4\pi\epsilon_0 r} \psi = E\psi$$

But surprisingly, we can separate variables and assume a wavefunction of the form  $\psi(r, \theta, \phi) = \underbrace{R(r)}_{\text{Radial}} \cdot \underbrace{\Theta(\theta) \cdot \Phi(\phi)}_{\text{Angular}}$  to solve it.

## 15.1 Radial Wavefunction

The radial part depends on  $n$  and  $l$ .

### Radial Part of Wavefunction

$$R_{n,l}(r) = N_{n,l} L_{n,l} r^l e^{-\frac{Zr}{na_0}}$$

- $N_{n,l}$  is a normalisation constant dependant on  $n$  and  $l$ .
- $L_{n,l}$  is called an **associated Laguerre polynomial** of degree  $n - l - 1$  which corresponds to  $n - l - 1$  radial nodes. **Node is a point where wavefunction passes through 0, not just achieves 0.** Hence,  $r = 0$  and  $r = \infty$  are not nodes.

- Asymptotic solution when  $r \rightarrow 0$  is  $r^l$ .
- Asymptotic solution when  $r \rightarrow \infty$  is  $e^{-\frac{r}{na_0}}$
- $a_0$  is Bohr radius = 52.9pm
- Expected value of radius of electron is:

$$\langle r_{n,l} \rangle = \frac{a_0}{2} [3n^2 - l(l+1)]$$

- Probability of finding an electron in a spherical shell at radius  $r = r^2 |R(r)|^2 dr$
- Energy depends only on  $n$ ,  $E_n = \text{PE}_n + \text{KE}_n = -\frac{Z^2 m_e e^4}{\hbar^2 n^2} + \frac{Z^2 m_e e^4}{2\hbar^2 n^2} = -\frac{Z^2 m_e e^4}{2\hbar^2 n^2} = \frac{-13.6 Z^2}{n^2} \text{eV}$

## 15.2 Angular Wavefunction

The angular part depends on  $l$  and  $m$ .

### Angular Part of Wavefunction

$$\Theta(\theta) \cdot \Phi(\phi) = c f(\theta) e^{im\phi}$$

- $c$  is a constant
- $l$  is equal to maximum sum of power of trigonometric functions in  $f(\theta)$  in one term. **This corresponds to  $l$  angular nodes.**  $\sin(\theta) \cos^2(\theta) \implies l = 3$ ,  $(\cos(\theta) \sin^3 \theta - 1) \implies l = 4$
- $m$  is given in the exponent part.

## 15.3 Quantum Numbers and Graphs

Read from notebook

## 16 Common Integrals

- $\int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$
- $\int_0^\infty e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}}$
- $\int_0^\infty x e^{-ax^2} dx = \frac{1}{2a}$
- $\int_0^\infty x^n e^{-ax^2} dx = \frac{d}{da} \left( \int_0^\infty -x^{n-2} e^{-ax^2} dx \right)$

## 17 Common Operators

- **Energy:**  $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}$
- **Linear Momentum:**  $\hat{\mathbf{p}}_x = -i\hbar\frac{\partial}{\partial x}$
- **Electric dipole moment:**  $\hat{\mu}_x = -ex \times$
- **Angular Momentum:**  $\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}, \quad L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right), \quad L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right),$   
 $L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$