

Quantum Mechanics II

The Schrödinger Equation in Central Potential

The generalization of the Schrödinger Equation to 3D involves three dimensional position and momentum operators $\hat{\vec{X}} = (\hat{x}, \hat{y}, \hat{z})$ & $\hat{\vec{P}} = (\hat{P}_x, \hat{P}_y, \hat{P}_z)$ with

$$[\hat{x}_i, \hat{p}_j] = i\hbar \hat{1} \delta_{ij}$$

$$[\hat{x}_i, \hat{x}_j] = [\hat{p}_i, \hat{p}_j] = \hat{0}$$

In the coordinate representation these two vector operators are given by:

$$\hat{\vec{X}} \longrightarrow \vec{x}$$

$$\hat{\vec{P}} \longrightarrow -i\hbar \vec{\nabla}$$

And so the Schrödinger equation becomes:

$$i\hbar \frac{\partial \Psi(\vec{x}, t)}{\partial t} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(\vec{x}, t) + V(\vec{x}) \Psi(\vec{x}, t)$$

For general potentials $V(\vec{x})$ this is a hard equation to solve exactly. In a later course, we shall develop techniques to solve this equation approximately. But for now we look at the three dimensional case that we can solve exactly.

The class of potentials for which V is just a function of $r = |\vec{x}| = \sqrt{x^2 + y^2 + z^2}$ are called central potentials. When we have such a system the Hamiltonian is symmetric under rotation. When that happens the SE decomposes into three uncoupled ODEs.

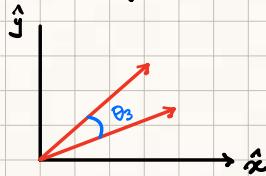
Under rotation about the origin in \mathbb{R}^3 a position vector $\vec{x} = (x, y, z)$ changes as:

$$x'_i = \sum_j R_{ij} x_j \quad \text{where } R \text{ is a } 3 \times 3 \text{ orthogonal matrix with determinant 1.}$$

$R^T R = I \Rightarrow |\vec{x}'| = |\vec{x}|$. $\det R = 1 \Rightarrow$ The transformation is continuously connected to the identity matrix $\mathbb{1}$.

For example a rotation by an angle θ about the z-axis in the counter-clockwise sense is

given by $R_z(\theta) = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$



Similarly $R_x(\theta) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & \cos\theta \end{pmatrix}$ and $R_y(\theta) = \begin{pmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{pmatrix}$

Any arbitrary rotation in 3D can be expressed as composition of 3 independent rotations (Euler's theorem).

Rotational Invariance in Operator Language:

In the position representation it is straightforward to see that any Hamiltonian for which the potential is central is left invariant by a rigid rotation. This is because, in addition to the potential, the Laplacian $\vec{\nabla}^2 = \sum_i \frac{\partial^2}{\partial x_i^2}$ is also invariant under rotation. But it's worth investigating how rotational invariance is manifested at the abstract operator level.

Suppose we have a quantum system which undergoes a rotation. This means that the coordinates \vec{x} describing the system undergo some rotation described by a 3×3 rotation matrix.

We expect that this will induce some transformation on the Hilbert space \mathcal{H} . Therefore there must exist an operator $\hat{U}(R)$ corresponding to the matrix R :

$$\begin{array}{ccc} R & \xrightarrow{\quad} & \hat{U}(R) \\ \downarrow & & \downarrow \\ \text{acts on } \mathbb{R}^3 & & \text{acts on } \mathcal{H} \end{array}$$

We assume that this transformation does not destroy any information about the system we must assume that $\hat{U}(R)$ is unitary. This ensures that

normalization of states do not change:

$$|\psi\rangle \xrightarrow{R} |\psi_R\rangle = U(R)|\psi\rangle$$

$$\begin{aligned}\langle \psi_R | \psi_R \rangle &= \langle \psi | U^\dagger U | \psi \rangle \\ &= \langle \psi | \psi \rangle\end{aligned}$$

Operators change in the following way: Consider the expectation value of a scalar operator:

$$\langle \hat{O} \rangle = \langle \psi | \hat{O} | \psi \rangle. \text{ Physically this should be invariant under a rotation.}$$

For example, $\langle \hat{O} \rangle = \langle H \rangle = E$, could be the average energy. Rotation invariance implies:

$$\langle \psi_R | \hat{O}_R | \psi_R \rangle = \langle \psi | \hat{O} | \psi \rangle$$

$$\text{So } \hat{O} \xrightarrow{R} \hat{O}_R = \hat{U}(R) \hat{O} \hat{U}^\dagger(R)$$

For a small rotation, parametrized by three parameters $\vec{\theta}$, we can write the rotation matrix as:

$$R_{ij} \approx \delta_{ij} - i \theta_k J_{ij}^k = \delta_{ij} - \theta_k \epsilon_{ijk}$$

where $J_{ij}^k = -i \epsilon_{ijk}$ are the generators of rotation for $k=1,2,3$.

This means that for small $\vec{\theta}$ we have

$$\hat{U}(0) \approx \hat{1} - i \vec{\theta} \cdot \frac{\hat{L}}{\hbar}$$

$\hat{L} = (\hat{L}_x, \hat{L}_y, \hat{L}_z)$ vector operator. $\hat{L} \rightarrow$ Generator of rotation on Hil.

Since $U \rightarrow$ Unitary $\Rightarrow \vec{\theta} \cdot \hat{L} \rightarrow$ Hermitian. $\vec{\theta} \sim$ arbitrary real angles.

$\Rightarrow \hat{L} \rightarrow$ Hermitian.

Rotational invariance means $[\hat{H}, \hat{U}(R)] = 0$

\Leftrightarrow

$$[\hat{H}, \frac{\hat{L}}{\hbar}] = 0$$

\hat{L} is defined
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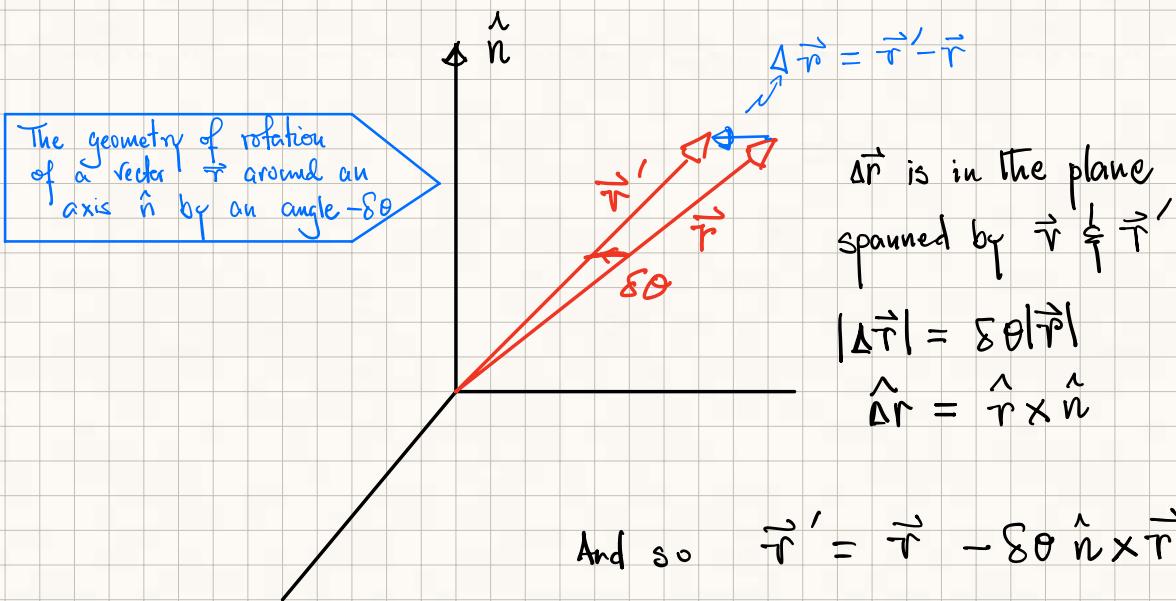
Since \hat{L} is a hermitian operator it is potentially an observable. And indeed it is. The generator of rotation in 3D satisfy

$$[J_i, J_j] = i\epsilon_{ijk} J_k$$

As a result \hat{L} also must satisfy the same algebra:

$$[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk} \hat{L}_k \quad [\text{See below for a proof.}]$$

This motivates us to identify \hat{L}_i as angular momentum. We call \hat{L} orbital angular momentum to distinguish it from spin angular momentum to be introduced in the next chapter. We can draw the analogy with planetary motion where the angular momentum due to the motion of the planets around a central star is the orbital angular momentum while the diurnal motion of the planets around its axis gives rise to its spin angular momentum.



$$\text{And so } \vec{r}' = \vec{r} - \delta\theta \hat{n} \times \vec{r}$$

Vector Operators:

Under a rotation the position vector \vec{x} transforms as $x_i \rightarrow x'_i = \sum_j R_{ij} x_j$. In physics an object that transforms in this way is called a vector. Other examples of vector include momentum, acceleration etc. A vector is also supposed to transform under parity $P = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ as $\vec{x} \rightarrow -\vec{x}$.

It is clear that both \vec{P} & $\vec{\alpha}$ do that but angular momentum $\vec{J} = \vec{x} \times \vec{P}$ does not. This is why angular momentum is known as a pseudo-vector.

We derive the transformation property of a vector operator under rotation by noting that if \hat{O} is a vector operator and $|q'\rangle = \hat{U}(R)|q\rangle$ then for a small rotation $\delta\theta$

$$\begin{aligned} \langle q' | \hat{O} | q' \rangle - \langle q | \hat{O} | q \rangle &= \delta\theta \times \langle q | \hat{O} | q \rangle \quad [\text{See above fig.}] \\ \Rightarrow \hat{U}(R)^\dagger \hat{O} \hat{U}(R) - \hat{O} &= \delta\theta \times \hat{O} \\ \Rightarrow \cancel{\hat{O}} + \frac{i}{\hbar} \sum_i \delta\theta_i [\hat{L}_i, \hat{O}] - \cancel{\hat{O}} &= \delta\theta \times \hat{O} \\ \Rightarrow \frac{i}{\hbar} \sum_i \delta\theta_i [\hat{L}_i, \hat{O}_j] &= (\delta\theta \times \hat{O})_j \\ &= \sum_{i,k} \epsilon_{ijk} \delta\theta_i \hat{O}_k \\ \Rightarrow \frac{i}{\hbar} [\hat{L}_i, \hat{O}_j] &= \sum_k \epsilon_{ijk} \hat{O}_k \\ \Rightarrow [\hat{L}_i, \hat{O}_j] &= i\hbar \epsilon_{ijk} \hat{O}_k \end{aligned}$$

Operators that transform in this way under rotations are called (pseudo) vector operators.

When $\hat{O} = \hat{L}$ we get the angular momentum algebra:

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k$$

Symmetry under a Transformation:

When $\hat{H} \notin \hat{L}$ commute, we see that

$$\langle \psi(t) | \hat{L} | \psi(t) \rangle = \langle \psi(0) | e^{\frac{i}{\hbar} \hat{H} t} \hat{L} e^{-\frac{i}{\hbar} \hat{H} t} | \psi(0) \rangle = \langle \psi(0) | \hat{L} | \psi(0) \rangle.$$

This means that $\langle \hat{L} \rangle(t) \equiv \langle \psi(t) | \hat{L} | \psi(t) \rangle$ does not change with time:

$$\frac{d}{dt} \langle \hat{L} \rangle = 0$$

Such a quantity is called a constant of motion or a conserved quantity

Thus for a rotationally symmetric system the angular momentum is conserved. This is a particular example of a more general theorem known as **Noether's Theorem** which states that for any continuous symmetry of a system there exists a conserved quantity.

The Generator of Translation:

Suppose we translate a system in space: $x \rightarrow x+a$, where $a \in \mathbb{R}$ is a constant parameter. Then the

wave function transform as $\psi(x) \rightarrow \psi'(x) = \psi(x-a)$

$$\begin{aligned} \text{For small } a: \quad \psi'(x) &= \psi(x) - a \frac{d\psi}{dx} + O(a^2) \\ &\simeq \psi(x) - \frac{i}{\hbar} a \left(-i \frac{\hbar}{\imath} \frac{d}{dx} \right) \psi(x) \\ &= \left(\hat{I} - \frac{i}{\hbar} a \hat{P} \right) \psi(x) \end{aligned}$$

Thus for finite a we can write

$$\psi(x-a) = e^{\frac{-i}{\hbar} a \hat{P}} \psi(x)$$

Thus we see that \hat{P} generates spatial translations: $\hat{u}_x(a) = e^{\frac{i}{\hbar} a \hat{P}}$

Suppose $V(x) = \text{Constant}$ Then $[\hat{H}, \hat{u}_p] = 0 \Rightarrow$ Momentum $\langle \hat{P} \rangle$ is conserved.

Comment:

1. We see that the \hat{P} operator generates translation. In a similar way it is easy to show that \hat{L} generates rotations provided

$$\hat{L} = \hat{x} \times \hat{p}.$$

Orbital Angular Momentum:

We just learned that for a rotationally invariant system angular momentum $\hat{\vec{L}}$ is a conserved observable. We also know the relationship that the components of $\hat{\vec{L}}$ must satisfy:

$$[\hat{L}_i, \hat{L}_j] = i\hbar \epsilon_{ijk} \hat{L}_k$$

How do we construct such operators?

We should expect this new observable to be the angular momentum of the system. Classically we have $\vec{L} = \vec{x} \times \vec{p}$

And therefore we try

$$\hat{\vec{L}} = \hat{\vec{x}} \times \hat{\vec{p}}$$

$$\Rightarrow \hat{L}_i = \epsilon_{ijk} \hat{x}_j \hat{p}_k$$

$$\hat{L}_x = \hat{y} \hat{p}_z - \hat{z} \hat{p}_y$$

$$\hat{L}_y = \hat{z} \hat{p}_x - \hat{x} \hat{p}_z$$

$$\hat{L}_z = \hat{x} \hat{p}_y - \hat{y} \hat{p}_x$$

using $[\hat{x}_i, \hat{p}_j] = i\hbar \delta_{ij}$ one can derive $[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$ etc.

Since $\hat{L}_x, \hat{L}_y, \hat{L}_z$ are not compatible variable we can't measure them simultaneously with arbitrary precision. However $\hat{L}^2 = \hat{L}_x \hat{L}_x + \hat{L}_y \hat{L}_y + \hat{L}_z \hat{L}_z$ commutes with \hat{L}_i so we can simultaneously diagonalize \hat{L}^2 and one component of $\hat{\vec{L}}$.

Note: Two variables (observables) are compatible if they commute. Thus one can measure them simultaneously with arbitrary precision.

The Position Representation of a Rotationally Invariant Hamiltonian:

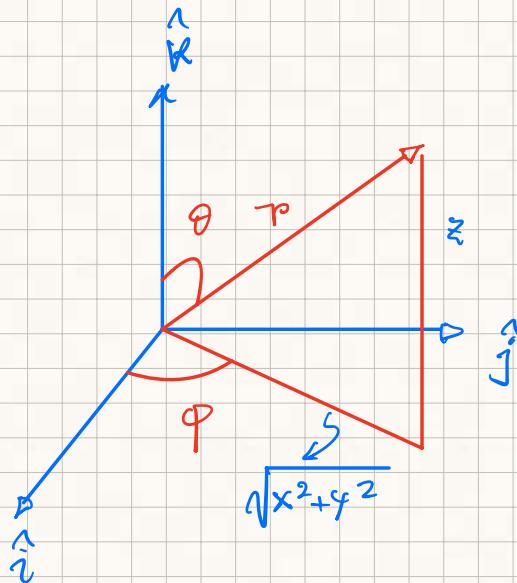
For a rotationally invariant system it makes sense to express the Hamiltonian in spherical polar coordinates.

Cartesian coordinates

$$\begin{cases} x = r \sin\theta \cos\phi \\ y = r \sin\theta \sin\phi \\ z = r \cos\theta \end{cases}$$

Spherical Polar coordinates

$$\begin{cases} r = \sqrt{x^2 + y^2 + z^2} \\ \tan\phi = \frac{y}{x} \\ \tan\theta = \sqrt{\frac{x^2 + y^2}{z^2}} \end{cases}$$



We first express \hat{L}_x , \hat{L}_y & \hat{L}_z in spherical polar coordinates.

$$\hat{L}_x = -i\hbar \left\{ -\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right\}$$

$$\hat{L}_y = -i\hbar \left\{ \cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right\}$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

(Show)

Note that these operators do not depend on r and thus only affect changes on the θ & ϕ

dependence of the wavefunction. Now we express the Laplacian in spherical polar coordinates:

$$\text{The Laplacian } \vec{\nabla}^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

in the spherical polar coordinates:

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

Since we know that $[\hat{H}, \hat{L}] = 0$ we expect \hat{H} to depend on the scalar combination

\hat{L}^2 . And indeed it turns out that

$$\hat{L}^2 = -\hbar^2 \left\{ \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) \right\} \quad (\text{show})$$

and so:

$$\frac{\hat{P}^2}{2m} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 = \frac{1}{2mT^2} \hat{L}^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial T^2} - \frac{\hbar^2}{mT} \frac{\partial}{\partial T}$$

Relationship Between the \hat{L}^2 & \hat{P}^2 operators

Recall that \hat{p}^2 in the position representation is given by:

$$\hat{p}^2 = (-i\hbar\vec{\nabla})^2 = -\hbar^2 \vec{\nabla}^2$$

Thus up to a constant the \hat{P}^2 operator is the Laplacian operator. There is a close link between $\vec{\nabla}^2$ & the \hat{L}^2 operator which is an important ingredient in the quantum mechanics of rotationally invariant systems.

Let us first derive the relationship between \hat{L}^2 & \hat{P}^2 first:

$$\hat{L}_i = \sum_{jk} \epsilon_{ijk} \hat{x}_j \hat{p}_k$$

$$\begin{aligned} \text{So, } \hat{L}^2 &= \sum_L \hat{L}_L \hat{L}_L = \sum_{ijk} (\epsilon_{ijk} \hat{x}_j \hat{p}_k) \sum_{mn} \epsilon_{lmn} \hat{x}_m \hat{p}_n \\ &= \sum_{ijklmn} \epsilon_{ijk} \hat{x}_j \hat{p}_k \epsilon_{lmn} \hat{x}_m \hat{p}_n \\ &= \sum_{jkmn} (\delta_{jm} \delta_{kn} - \delta_{jn} \delta_{km}) \hat{x}_j \hat{p}_k \hat{x}_m \hat{p}_n \\ &= \sum_{jkmn} (\delta_{jm} \delta_{kn} \hat{x}_j (\hat{x}_m \hat{p}_k - i\hbar \delta_{mk}) \hat{p}_n - \delta_{jn} \delta_{km} \hat{x}_j \hat{p}_k (\hat{p}_n \hat{x}_m + i\hbar \delta_{nm})) \\ &= \sum_{m,n} (\hat{x}_m (\hat{x}_m \hat{p}_n - i\hbar \delta_{mn}) \hat{p}_n - \hat{x}_n \hat{p}_m (\hat{p}_n \hat{x}_m + i\hbar \delta_{nm})) \\ &= \hat{x}^2 \hat{p}^2 - i\hbar \hat{x} \cdot \hat{p} - \sum_{m,n} \hat{x}_n \hat{p}_n \hat{p}_m \hat{x}_m - i\hbar \hat{x} \cdot \hat{p} \\ &= \hat{x}^2 \hat{p}^2 - 2i\hbar \hat{x} \cdot \hat{p} - \sum_m (\hat{x} \cdot \hat{p}) (\delta_{mm} i\hbar) + (\hat{x} \cdot \hat{p})^2 \\ &= \hat{x}^2 \hat{p}^2 - (\hat{x} \cdot \hat{p})^2 - 2i\hbar \hat{x} \cdot \hat{p} + 3i\hbar \hat{x} \cdot \hat{p} \\ &= \hat{x}^2 \hat{p}^2 - (\hat{x} \cdot \hat{p})^2 + i\hbar \hat{x} \cdot \hat{p} \end{aligned}$$

$$\text{Now } \hat{\vec{p}}^2 = -\hbar^2 \nabla^2 \Rightarrow \hat{\vec{x}}^2 \hat{\vec{p}}^2 = -\hbar^2 r^2 \nabla^2$$

$$\hat{\vec{x}} \cdot \hat{\vec{p}} = -i\hbar \vec{r} \cdot \vec{\nabla} = -i\hbar r \frac{\partial}{\partial r} \Rightarrow i\hbar \hat{\vec{x}} \cdot \hat{\vec{p}} = \hbar^2 r \frac{\partial}{\partial r}$$

$$(\hat{\vec{x}} \cdot \hat{\vec{p}})^2 = -\hbar^2 r \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) = -\hbar^2 r \frac{\partial}{\partial r} - \hbar^2 r^2 \frac{\partial^2}{\partial r^2}$$

$$\text{So } \hat{L}^2 = +2\hbar^2 r^2 \frac{\partial^2}{\partial r^2} + \hbar^2 r \frac{\partial}{\partial r} - \hbar^2 r^2 \nabla^2$$

$$\Rightarrow \frac{\hat{P}^2}{2m} = -\frac{\hbar^2 \nabla^2}{2m} = \frac{1}{2mr^2} \hat{L}^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{mr} \frac{\partial}{\partial r}$$

Thus we can write the Schrödinger equation for central potentials in a manifestly spherically symmetric form:

$$\hat{L}^2 = -\hbar^2 \left\{ \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \right\}$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial r^2} - \frac{\hbar^2}{m r} \frac{1}{r} \frac{\partial \Psi}{\partial r} + \frac{1}{2mr^2} \hat{L}^2 \Psi + V(r) \Psi = E \Psi$$

$$\frac{\partial^2 \Psi}{\partial r^2} + \frac{2}{r} \frac{\partial \Psi}{\partial r} - \frac{1}{\hbar^2 r^2} \hat{L}^2 \Psi + \frac{2m}{\hbar^2} [E - V(r)] \Psi = 0$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{1}{r^2} \left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Psi}{\partial \phi^2} \right\} + \frac{2m}{\hbar^2} [E - V(r)] \Psi = 0$$

Solutions to Spherically Symmetric Systems :

One can say a lot about the forms of the solution without explicitly specifying the spherically symmetric potential $V(r)$. To do so one assumes that the solution is separable:

$$\Psi(\vec{r}) = R(r) Y(\theta, \phi)$$

$$\frac{1}{R(r)} \left[\frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \frac{2m}{\hbar^2} [E - V(r)] r^2 R(r) \right] = -\frac{1}{Y(\theta, \phi)} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y(\theta, \phi)}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y(\theta, \phi)}{\partial \phi^2} \right]$$

Since the left hand side only depends on r while the right hand side only depends of

$\theta \nmid \phi$ this equation can only be satisfied if both sides are equal to some constant λ :

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} + \frac{2m}{\hbar^2} [E - V(r)] r^2 R(r) - \frac{\lambda}{r^2} R(r) \right) = 0$$

and

$$\begin{aligned} -\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y}{\partial\theta} \right) - \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial\phi^2} &= \lambda Y \\ \Rightarrow \hat{L}^2 Y(\theta, \phi) &= \lambda Y(\theta, \phi) \end{aligned}$$

This last equation is independent of the energy E and the potential energy $V(r)$. Thus the angular dependence of $Y(\theta, \phi)$ for a spherically symmetric system is solely determined by spherical symmetry. The solutions to the equation $\hat{L}^2 Y = \lambda Y$ independent of E or the form of $V(r)$.

Recall that $[\hat{L}^2, \hat{L}_i] = 0$ and therefore we can choose $Y(\theta, \phi)$ to be simultaneous eigenfunctions of both \hat{L}^2 & one of the \hat{L}_i operators which we choose to be \hat{L}_z .

Further simplification is achieved by adopting the ansatz:

$$Y(\theta, \phi) = P(\theta) \Phi(\phi).$$

Then $\hat{L}^2 Y = \lambda Y$ becomes

$$\frac{1}{P(\theta)} \left[\sin\theta \frac{1}{\partial\theta} \left(\sin\theta \frac{dP(\theta)}{d\theta} \right) \right] + \lambda \sin^2\theta = m^2 \quad \left\{ \begin{array}{l} m^2 \rightarrow \text{some} \\ \text{constant?} \end{array} \right.$$

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

We require the wavefunction to be single valued and so the solution to this equation is

$$\Phi(\phi) = e^{\pm im\phi} \quad \text{where } m \text{ is an integer.}$$

Before we solve the equation for the θ variables let us determine the constant λ .

Note that we have seen that the angular part of the Schrödinger equation for a spherically symmetric potential is independent of the energy E as well as $V(r)$.

Thus if we solve for the angular part of Laplace's equation:

$$\nabla^2 \Psi = 0$$

Then we have solved it for all systems with spherically symmetric potentials.

We are assuming that our solution has the form:

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

Thus in Cartesian coordinates we can write it as a homogeneous polynomial of degree l :

$$\Psi_l = \sum_{p+q+r=l} a_{pqr} x^p y^q z^r$$

where a_{pqr} are coefficients which must be chosen so that $\nabla^2 \Psi = 0$ is satisfied.

Since l is fixed and $p+q+r=l$, we can choose only two of the positive integers $p, q \neq r$. So for a given p , q can take values: $0, 1, \dots, l-p$. But p can take any value from 0 to l . Thus p can take $(l+1)$ values. So the total number of combinations is:

$$\begin{array}{cccccc} (l+1) & + & l & + & l-1 & + \dots + 1 \\ p=0 & & p=1 & & p=2 & & p=l \end{array} = \frac{1}{2} (l+1)(l+2)$$

Thus there are $\frac{1}{2}(l+1)(l+2)$ linearly independent polynomial terms. But the Laplacian acting on Ψ_l gives a polynomial of degree $l-2$. Thus we get

$\frac{1}{2}(l-1)l$ constraints and so the number of linearly independent solutions

is :

$$\begin{aligned} \frac{1}{2}(l+1)(l+2) - \frac{1}{2}(l-1)l &= \frac{1}{2} (\cancel{l^2} + 3l + 2 - \cancel{l^2} + l) \\ &= \frac{1}{2} (4l + 2) \\ &= (2l + 1) \end{aligned}$$

Explicitly these polynomials are:

$$l=0 : 1$$

$$l=1 : x, y, z$$

$$l=2 : xy, yz, zx, x^2 - y^2, 2z^2 - x^2 - y^2$$

$$l=3 : x(x^2 - 3z^2), x(x^2 - 3y^2), y(y^2 - 3x^2), y(y^2 - 3z^2), z(z^2 - 3x^2), z(z^2 - 3y^2), xyz$$

etc.

In spherical polar coordinates we can write:

$$\Psi_l = r^l Y_l(\theta, \phi)$$

$Y_l(\theta, \phi)$ is called a spherical harmonic of order l .

Now if we write Laplace's equation in spherical polar coordinates

$$\nabla^2 \Psi_l = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi_l}{\partial r} \right) - \frac{1}{r^2} \Psi_l = 0$$

$$\Rightarrow (l(l+1) - \lambda) \frac{\Psi_l}{r^2} = 0$$

$$\Rightarrow \lambda = l(l+1).$$

$$\text{Thus we see that } \nabla^2 Y_l(\theta, \phi) = l(l+1) \frac{1}{r^2} Y_l(\theta, \phi).$$

The equation for θ :

$$\begin{aligned} & \frac{1}{H(\theta)} \left[\sin \theta \frac{d}{d\theta} \left(\sin \theta \frac{dH(\theta)}{d\theta} \right) + \lambda \sin^2 \theta \right] = m^2 \\ & \Rightarrow \frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{dH(\theta)}{d\theta} \right) + \left[\lambda - \frac{m^2}{\sin^2 \theta} \right] H(\theta) = 0 \end{aligned}$$

It is convenient to change the variables to $\mu = \cos \theta$, so that as $0 \leq \theta \leq \pi$,

$$1 \leq \mu \leq -1. \text{ Then } d\mu = -\sin \theta d\theta \text{ and } \frac{d}{d\theta} = \frac{d\mu}{d\theta} \frac{d}{d\mu} = -(1-\mu^2)^{-\frac{1}{2}} \frac{d}{d\mu}$$

Then the diff. equation becomes

$$+\frac{1}{1-\mu^2} \frac{d}{d\mu} \left[(1-\mu^2) \frac{dP(\mu)}{d\mu} \right] + \left[\lambda - \frac{m^2}{1-\mu^2} \right] P(\mu) = 0$$

Thus we get for $\mu = \cos \theta$:

$$\frac{d}{d\mu} \left[(1-\mu^2) \frac{dP(\mu)}{d\mu} \right] + \left\{ \lambda - \frac{m^2}{1-\mu^2} \right\} P(\mu) = 0$$

For $m=0$ this becomes the Legendre differential equation:

$$\boxed{\frac{d}{d\mu} \left[(1-\mu^2) \frac{dP(\mu)}{d\mu} \right] + \lambda P(\mu) = 0}$$

Note that as a second order differential equation, for every value of the parameter λ there are two linearly independent solutions.

Further note that $\mu \rightarrow -\mu$ is a symmetry of the equation. Since it is a linear equation this implies that $P(\mu)$ is either an odd function or an even function of μ .

Since $\mu \rightarrow -\mu$ means $\cos \theta \rightarrow -\cos \theta \Rightarrow \theta \rightarrow \pi - \theta$, $z \rightarrow -z$.

Thus we see that these functions are symmetric or antisymmetric with respect to reflection in the xy-plane.

Let us attempt a series solution:

$$P(\mu) = \sum_{n=0}^{\infty} a_n \mu^n$$

Plugging this into the LDE we obtain:

$$\frac{d}{d\mu} (1-\mu^2) \left(\sum_n n a_n \mu^{n-1} \right) + \lambda \sum_n a_n \mu^n = 0$$

$$\sum_n n(n-1) a_n \mu^{n-2} - \sum_n n(n+1) a_n \mu^n + \lambda \sum_n a_n \mu^n = 0$$

$$\sum_n (n+2)(n+1) a_{n+2} \mu^n - \sum_n n(n+1) a_n \mu^n + \lambda \sum_n a_n \mu^n = 0$$

$$(n+1)(n+2) a_{n+2} + [\lambda - n(n+1)] a_n = 0$$

Recurrence Relation

If $a_1 = 0$ and $a_0 \neq 0$ then we get an even function.

If $a_1 \neq 0$ and $a_0 = 0$ we get an odd function.

$$\text{As } n \rightarrow \infty \quad \frac{a_{n+2}}{a_n} \rightarrow \frac{n}{n+2}$$

Thus for large n the solution $\sim \sum_n \frac{\mu^n}{n}$ for either even or odd n .

Recall that $\log(1-x^2) = -2 \left\{ \frac{x^2}{2} + \frac{x^4}{4} + \frac{x^6}{6} + \dots \right\}$ for $|x| < 1$

and $\log\left(\frac{1+x}{1-x}\right) = 2 \left\{ x + \frac{x^3}{3} + \frac{x^5}{5} + \dots \right\}$ for $|x| < 1$

Thus we see that our series will diverge at $\mu = \pm 1$ if the series does not termi-

note. But if the series terminates at some value of $n = l$ then it must be that

$$\lambda = l(l+1). \quad l=0, 1, 2, 3, \dots$$

and then solution $P(\mu)$ is regular at $\mu = \pm 1$.

Thus we find a different way to justify $\lambda = l(l+1)$.

Since l labels the eigenvalue of the \vec{L}^2 operator, we interpret l as the orbital angular momentum. In chemistry $l=0, 1, 2, 3, \dots$ correspond to the $s, p, d, f \dots$ orbital labels.

The solutions to the Legendre differential equation are given by:

$$P_l(\mu) = \frac{1}{2^l \cdot l!} \frac{d^l}{d\mu^l} (\mu^2 - 1)^l$$

and they are known as the Legendre polynomials. Here are some of the first Legendre polynomials:

$$P_0(\mu) = 1$$

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

$$P_1(\mu) = \mu$$

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

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

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

We expect $P_l(\mu)$ to be orthogonal for different values of l :

$$\int_{-1}^{+1} P_l(\mu) P_{l'}(\mu) d\mu = \frac{2}{2l+1} \delta_{ll'}$$

The generating function for $P_l(\mu)$ is :

$$\begin{aligned} Z(x) &= \frac{1}{(1-2\mu x+x^2)^{1/2}} \\ &= \sum_{n=0}^{\infty} P_n(\mu) x^n \quad |x| < 1 \end{aligned}$$

$$\text{Then } \left. \frac{1}{l!} \frac{d^l}{dx^l} Z(x) \right|_{x=0} = P_l(\mu)$$

The Associated Legendre Polynomials:

So far we have only deduced the solutions for $m=0$. For $m \neq 0$ the equation to be solved is

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

Regular physical solutions only exist for $|m| \leq l$ and they are called the associated Legendre polynomials for $m > 0$.

$$P_e^m(\mu) = (1-\mu^2)^{m/2} \frac{d^m P_e(\mu)}{d\mu^m} = \frac{1}{2^l \cdot l!} (1-\mu^2)^{m/2} \frac{d^{l+m}}{d\mu^{l+m}} (\mu^2 - 1)^l$$

Since the differential equation for $P_e^m(\mu)$ is invariant under $m \rightarrow -m$, the $P_e^m(\mu)$ for negative m must be given by the same formula above but with $|m|$ replacing m .

Some of the associated Legendre polynomials:

$$P_e^0(\mu) = P_e(\mu)$$

$$P_e^1(\mu) = \sqrt{1-\mu^2}, \quad P_e^1(\mu) = 3\mu \sqrt{1-\mu^2}, \quad P_e^2(\mu) = 3(1-\mu^2).$$

Spherical Harmonics:

We can now write down the solutions to the angular part of the Schrödinger equation for central potentials:

$$\vec{L}^2 Y(\theta, \phi) = l(l+1) \vec{r}^2 Y(\theta, \phi)$$

with
$$Y_l^m(\theta, \phi) = N_{lm} e^{im\phi} P_e^m(\cos\theta)$$

$\xrightarrow{\theta \text{ dependence}}$
 $\xrightarrow{\phi \text{ dependence}}$

Since $Y(\theta, \phi)$ live on S^2 , we choose to normalize them with respect to the area

measure on the round S^2 :

$$\int_0^{2\pi} \int_0^\pi [Y_l^m(\theta, \phi)]^* Y_{l'}^{m'}(\theta, \phi) \sin\theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$

$$\text{Then } N_{cm} = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} (-i)^m e^{im\phi} P_l^m (\cos\theta)$$

$$\text{Then } \vec{L}^2 Y_l^m(\theta, \phi) = l(l+1) \hbar^2 Y_l^m(\theta, \phi)$$

$$L_z Y_l^m(\theta, \phi) = m \hbar Y_l^m(\theta, \phi)$$

$l \rightarrow$ total orbital angular momentum quantum number

$-l \leq m \leq l \rightarrow$ z-component of the orbital angular momentum quantum number.

$l=0, 1, 2, 3, \dots$ labels the whole irreducible Hilbert space.

For given l , $m=0, \pm 1, \pm 2, \dots, \pm l$ labels the basis states.

\vec{L}^2 is a degenerate operator and $l>0$ is a degenerate 'eigenvalue' with degeneracy $(2l+1)$ which are the possible number of values of m .

The First Few Spherical Harmonics

$$1. \quad Y_0^0 = (4\pi)^{-1/2}$$

\sim

0

$$2. \quad Y_1^{\pm 1} = \mp (3/8\pi)^{1/2} \sin\theta e^{\pm i\phi}$$

{

$$Y_1^0 = (3/4\pi)^{1/2} \cos\theta$$

π

Orbital angular momentum

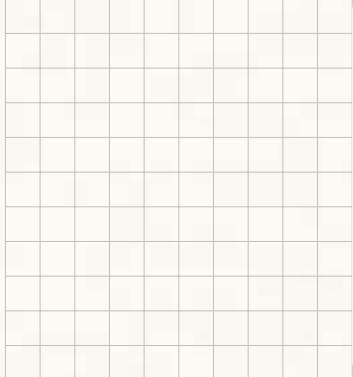
$$3. \quad Y_2^{\pm 2} = (15/32\pi)^{1/2} \sin^2\theta e^{\pm 2i\phi}$$

{

$$Y_2^{\pm 1} = \mp (15/8\pi)^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$$

2π

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$



Representation of the possible states of a system with $l=3$.

The Radial Equation: General Considerations

The radial part of the Schrödinger equation can be written as:

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

Note that radial equation depends on l so the solutions are labelled by both E & l .

We can gain a lot of insight into the solution by rewriting this equation in terms of $u_{EL}^{(r)}$ defined by:

$$R_{EL}(r) = \frac{u_{EL}(r)}{r}$$

Then the equation above looks like:

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{EL}(r)}{dr^2} + \left[\frac{l(l+1)}{2mr^2} + V(r) \right] u_{EL}(r) = E u_{EL}(r) \quad (*)$$

Now recall that $\int d^3x |\psi(\vec{x})|^2 = 1 \Leftrightarrow \int d^2\theta |Y_l^m|^2 = 1 \Rightarrow$

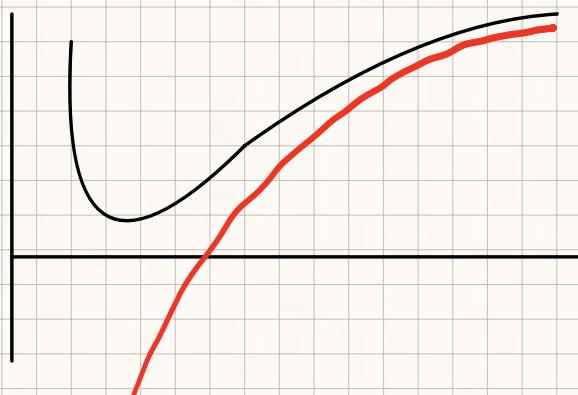
$$\int_0^\infty dr r^2 R_{EL}^*(r) R_{EL}(r) = 1 \Rightarrow \int_0^\infty dr |u_{EL}(r)|^2 = 1$$

unit sphere

Thus we can treat (*) as a one-dimensional problem in an effective potential:

$$V_{\text{eff}}(r) \equiv \frac{l(l+1)}{2mr^2} + V(r)$$

Note that unless $V(r)$ is negative and highly singular as $r \rightarrow 0$, the potential energy term dominates. Graphically



This means that any particle with non-zero angular momentum sees an 'angular momentum barrier' towards $r \rightarrow 0$ and so only particles in $l=0$ states are likely to be found there.

To obtain more insight we assume that our potential satisfies $\lim_{r \rightarrow 0} r^2 V(r) = 0$.

Then, as we approach $r \rightarrow 0$ the radial equation takes the form:

$$\frac{d^2 u_{El}(r)}{dr^2} = \frac{l(l+1)}{r^2} u_{El}(r)$$

So in the $r \rightarrow 0$ limit the solution potentially becomes $u = A r^{l+1} + B r^{-l}$. But since r^{-l} is singular in the $r \rightarrow 0$ limit we may experience some physical problem at the origin. If we examine the divergence of the probability current there we get from $\vec{j} \cdot \hat{r} = \frac{\hbar}{m} \text{Im}(\psi^* \frac{\partial}{\partial r} \psi) = \frac{\hbar}{m} R_{El}(r) \frac{d}{dr} R_{El}(r)$

For $u(r) \sim r^{l+1}$ we get the current leakage from a small sphere around $r=0$ given by $4\pi r^2 j_r \sim l r^{l+1}$ which $\rightarrow 0$ as $r \rightarrow 0$. But on the other hand for $u(r) \sim r^{-l}$ we get $4\pi r^2 j_r \sim (l+1) r^{-2l-1} \rightarrow \infty$ as $r \rightarrow 0$. Thus we set $B=0$ and settle on the solution $u_{El}(r) \sim r^{l+1}$ as $r \rightarrow 0$ or $R_{El}(r) \rightarrow r^l$ as $r \rightarrow 0$.

The fact that $R_{El}(r) \rightarrow 0$ for $r \rightarrow 0$ if $l \neq 0$ is reflective of the angular momentum barrier.

Next we examine the properties of the solution when $V(r) \rightarrow 0$ as $r \rightarrow \infty$ (the Coulomb potential is an example). Then asymptotically the equation becomes

$$\frac{d^2 u_E}{dr^2} = k^2 u_E \quad \text{with} \quad k = \frac{-2mE}{\hbar^2}$$

Since $E < 0$ for bounded states we have $k^2 > 0$ and the physical solution is $u_E(r) \sim e^{-kr}$

Putting these two behaviours together in a single solution:

$$u_{E_l}(r) = \rho^{l+1} e^{-\rho} w(\rho) \quad \text{where } \rho \equiv kT$$

we get for $w(\rho)$:

$$\frac{d^2 w}{d\rho^2} + 2\left(\frac{l+1}{\rho} - 1\right) \frac{dw}{d\rho} + \left[\frac{V}{E} - \frac{2(l+1)}{\rho}\right] w = 0$$

This analysis will come in handy when we examine the hydrogen atom which we turn to next.

The Hydrogen Atom:

The hydrogen atom is one of fundamental building blocks of our universe. It is also one of the few real world quantum mechanical problems one can solve exactly. The hydrogen atom was also one of the spectacular successes of the 'old' (pre-Schrödinger/Heisenberg equations) quantum theory. That treatment was due to Niels Bohr but it involved the ad hoc assumptions of:

1. Quantization angular momentum of the electron orbits.
2. Non-radiating electron orbits around the nucleus.

Bohr's atomic model was a huge success in explaining the spectrum of the hydrogen atom. However some discrepancy remained some of which were fixed by introducing elliptical orbits. However, one needs the full power of quantum mechanics for a full analysis of the problem. There are even very subtle effects such as the Lamb shift that needs to go beyond quantum mechanics and one needs to apply quantum field theory.

The Schrödinger Equation:

The hydrogen atom is a two-body problem. It involves a proton and an electron both of which are fermions with spin $\frac{1}{2}\hbar$. In our first analysis we shall ignore their spins. In this approximation the Hamiltonian is

$$H = \frac{\vec{p}_1^2}{2m_1} + \frac{\vec{p}_2^2}{2m_2} - \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \quad \left[\text{we are using CGS system of units.} \right]$$

And so the Schrödinger equation is:

$$H\Psi = -\frac{\hbar^2}{2m_1} \vec{\nabla}_1^2 \Psi - \frac{\hbar^2}{2m_2} \vec{\nabla}_2^2 \Psi - \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \Psi = E_t \Psi$$

Here the subscripts 1 & 2 refer to the proton and electron, respectively. Recall that this is similar to the Kepler problem of the motion of a planet around another star. We expect the motion to separate into a centre of mass degree of freedom \neq a motion around the centre of mass.

This is effected by introducing new variables:

$$\vec{R} = (x, y, z) = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \quad \begin{matrix} \sim \text{position vector of the} \\ \text{COM} \end{matrix}$$

and $\vec{r} = (x, y, z) = \vec{r}_1 - \vec{r}_2 \quad \sim \text{Relative position of the particles}$

We can solve these by

$$\vec{r}_1 = \vec{R} + \frac{m_1}{m_1 + m_2} \vec{r} \quad \text{and} \quad \vec{r}_2 = \vec{R} - \frac{m_2}{m_1 + m_2} \vec{r}$$

in which $m = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass.

[In the limit $m_1 \rightarrow \infty$, $m = m_2$.]

Easy to show that

$$\begin{aligned}\vec{\nabla}_1 &= \frac{m}{m_2} \vec{\nabla}_R + \vec{\nabla} \\ \vec{\nabla}_2 &= \frac{m}{m_1} \vec{\nabla}_R - \vec{\nabla}\end{aligned}\quad \left\{ \begin{array}{l} \vec{\nabla}_R = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \\ \vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \end{array} \right.$$

Schrödinger equation becomes:

$$\underbrace{-\frac{\hbar^2}{2(m_1+m_2)} \vec{\nabla}_R^2 \Psi}_{\text{in}} - \frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi - \frac{e^2}{r} \Psi = E_t \Psi$$

Separation of variables: $\Psi = \Phi(\vec{R}) \psi(\vec{r})$

$$\Rightarrow -\frac{\hbar^2}{2M} \vec{\nabla}_R^2 \Phi(\vec{R}) = E_c \Phi(\vec{R}) \quad \text{--- ①}$$

$$\Rightarrow -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi(\vec{r}) - \frac{e^2}{r} \psi(\vec{r}) = E \psi(\vec{r}) \quad \text{--- ②}$$

$$E_t = E_c + E$$

Solution to ①:

$$\Phi(\vec{R}) = \frac{1}{(\sqrt{2\pi\hbar})^3} e^{+i/\hbar \vec{P} \cdot \vec{R}}$$

$$\text{with } |\vec{P}| = \sqrt{2M E_c}$$

so we see the interesting equation is:

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

Let us use units which are natural for the hydrogen atom:

Energy measured in terms of ionization energy:

$$E \longrightarrow \frac{me^4}{2\hbar^2} E$$

And distance measured in terms of Bohr radius:

$$\vec{r} \longrightarrow \frac{\hbar^2}{me^2} \vec{r}$$

$$\frac{-\frac{\hbar^2}{2m} \frac{me^4}{\hbar^2} \vec{\nabla}^2 \psi - \frac{me^2}{\hbar^2} \frac{e^2}{r} \psi}{-\frac{me^4}{2\hbar^2} \vec{\nabla}^2 \psi - \frac{me^4}{\hbar^2} \frac{1}{r} \psi} = \frac{me^4}{2\hbar^2} E$$

$$-\frac{me^4}{2\hbar^2} \vec{\nabla}^2 \psi - \frac{me^4}{\hbar^2} \frac{1}{r} \psi = \frac{me^4}{2\hbar^2} E$$

$$\boxed{\vec{\nabla}^2 \psi + \left(\frac{2}{r} + E \right) \psi = 0}$$

Effectively we are using units in which $\hbar = 1$, $e^2 = 2$ and $m = \frac{1}{2}$.

Finding the solution to the radial equation:

The radial equation becomes, in terms of $u(r) = r R(r) \Rightarrow$

$$\frac{d^2 u}{dr^2} + \left[E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] u = 0$$

Compare with the radial equation from last lecture:

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{E_l}(r)}{dr^2} + \left[\frac{l(l+1)}{2mr^2} + V(r) \right] u_{E_l}(r) = E u_{E_l}(r) \quad (*)$$

Note that the potential $V = -\frac{2}{r}$ satisfies $\lim_{r \rightarrow \infty} r^2 V(r) = 0$ as well as

$$\lim_{r \rightarrow \infty} V(r) = 0.$$

Recall that we found that solution would have the form:

$$u = r^{l+1} w(r) e^{-kr}$$

with $K = \sqrt{-E}$ for bound states.

We saw that the ansatz for $w(r)$ should be

$$w(r) = \sum_{n=0}^{\infty} a_n r^n e^{-Kr}$$

But if we write $u = v(r) e^{-Kr}$ we get:

$$v(r) = \sum_{n=l+1}^{\infty} a_n r^n$$

The equation in terms of $v(r)$ is

$$\frac{d^2v}{dr^2} - 2K \frac{dv}{dr} + \left(\frac{2}{r} - \frac{l(l+1)}{r^2} \right) v = 0$$

Recursion relation (show): $a_{n+1} = 2 \frac{nK - l}{n(n+1) - l(l+1)} a_n$

$$\lim_{n \rightarrow \infty} \frac{a_{n+1}}{a_n} = \frac{2K}{n}$$

$$\Rightarrow \lim_{r \rightarrow \infty} v(r) \sim e^{2Kr}$$

Thus solution u blows up unless $nK - l = 0$ for some n :

$$\Rightarrow K = \frac{l}{n}$$

$$\Rightarrow E_n = -\frac{l}{n^2}$$

Restoring \hbar , e & m :

$$E_n = -\frac{me^4}{2n^2\hbar^2} \quad n = l+1, l+2, \dots$$

$n \rightarrow$ Principal quantum number

$l \rightarrow$ Orbital angular momentum number.

$$m \rightarrow \text{reduced mass: } \frac{m_e m_p}{m_e + m_p}$$

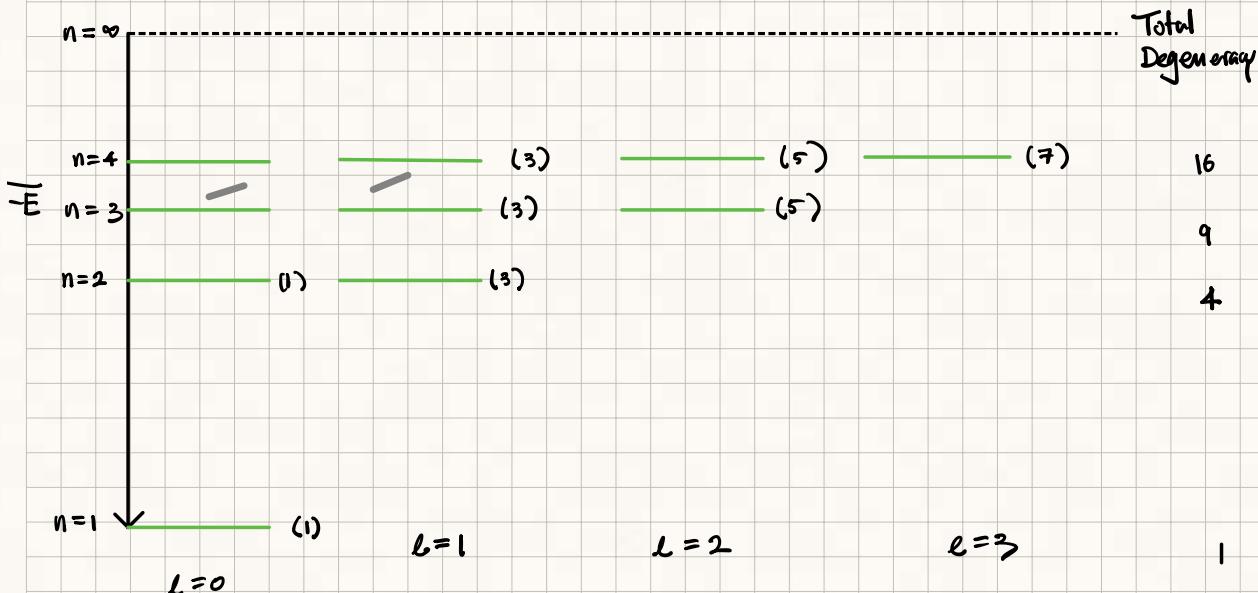
In MKS units the energy levels are given by:

$$E_n = -\frac{R}{n^2} \quad \text{with} \quad R = \frac{1}{2} m \left(\frac{e^2}{4\pi\epsilon_0\hbar} \right)^2 = 13.6056923 \text{ eV}$$

$R \rightarrow$ Rydberg constant - the ionization energy of a hydrogen atom.

Comments:

1. The energy levels of the full quantum treatment of the hydrogen atom are exactly those of the Bohr atom ($m \rightarrow$ electron mass in the simplified $m_p = \infty$ version)
2. For a given n , $l < n$. This leads to the following degeneracy pattern in the energy levels:



3. The total number of degeneracy for a given value of n is

$$1 + 3 + 5 + \dots + (2n-1) = n^2$$

4. For a given n the degeneracy due to different values of l are called accidental as they are not due to any symmetry operator commuting with H . Any perturbation of the system which is t -dependent and is not of form $\frac{1}{t^n}$ will cause small shifts to the energy levels with different values of l .

Eg: $H = H_0 + H'$ $\xrightarrow{\text{Perturbation}} \sim \frac{\lambda}{t^n}$, $n \neq 1$. $\lambda \sim \text{small}$.

$\underbrace{\quad}_{\text{Hydrogen atom}}$

5. Historically the spectrum of the hydrogen atom consisted of different 'series':

$$\gamma = \frac{R}{h} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

$n' = 1$ Lyman series

$n' = 2$ Balmer series

$n' = 3$ Paschen Series

$n' = 4$ Brackett series

The Radial Wavefunctions :

Although we have used the convergence of the radial wavefunction to derive quantization of energy of the bound states ($E < 0$) we have not worked out the radial wavefunctions explicitly. The general analysis involves the theory of the Laguerre polynomials and it will be covered in assignment 3.

But the first few radial wavefunctions can be easily worked out by using the recursion relationship.

Thus $\Psi_{n,l,m}(r) = \underbrace{\frac{1}{r} u_{n,l}(r)}_{R_{n,l}(r)} Y_l^m(\theta, \phi)$ gives us (Show:)

$$u_{1,0} = 2r e^{-r}$$

$$u_{2,0} = \frac{1}{\sqrt{8}} e^{-r/2} r(2-r)$$

$$u_{2,1} = \frac{1}{\sqrt{24}} e^{-r/2} r^2$$

$$u_{3,0} = \frac{2}{81\sqrt{3}} e^{-r/3} r(27 - 18r + 2r^2), \quad u_{3,1} = \frac{4}{81\sqrt{6}} e^{-r/3} r^2 (6-r)$$

$$u_{3,2} = \frac{4}{81\sqrt{30}} e^{-r/3} r^3$$

In the picture below is shown the probability of finding the electron as a function of r .

If we combine with the radial wavefunctions the angular part:

The First Few Spherical Harmonics Orbital angular momentum

$$1. \quad Y_0^0 = (4\pi)^{-1/2} \quad \sim \quad 0$$

$$2. \quad Y_1^{\pm 1} = \mp (3/8\pi)^{1/2} \sin \theta e^{\pm i\phi} \quad \left. \begin{array}{c} \\ \end{array} \right\} \pi$$

$$Y_1^0 = (3/4\pi)^{1/2} \cos \theta$$

$$3. \quad Y_2^{\pm 2} = (15/32\pi)^{1/2} \sin^2 \theta e^{\pm 2i\phi} \quad \left. \begin{array}{c} \\ \\ \end{array} \right\} 2\pi$$

$$Y_2^{\pm 1} = \mp (15/8\pi)^{1/2} \sin \theta \cos \theta e^{\pm i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2 \theta - 1)$$

And then plot the probability distributions in three dimensions we then get:

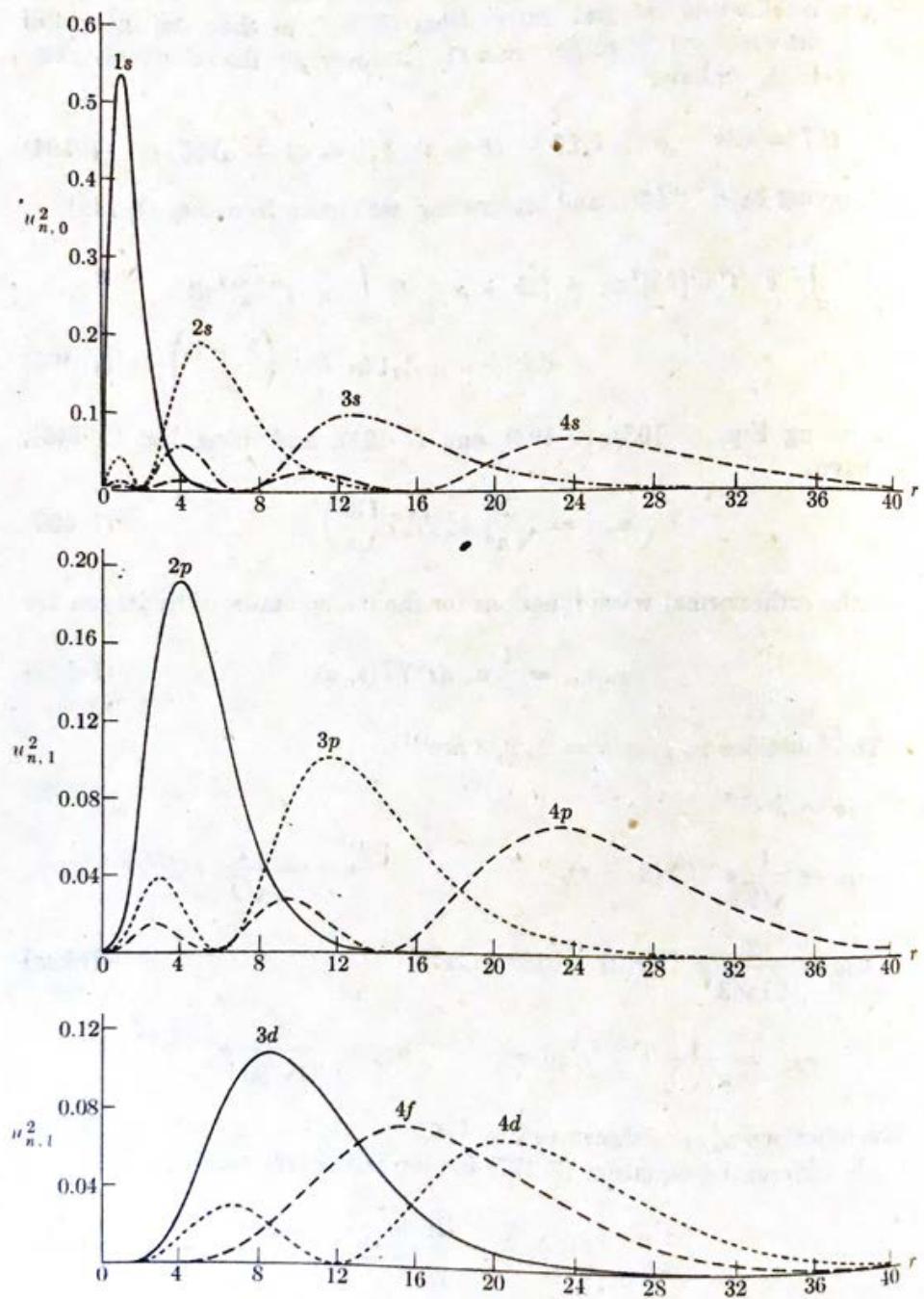


FIG. 7-6. The radial probability distribution function $u_{n,l}^2$ for several values of the quantum numbers n, l . (From E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1953, by permission.)

