CHAPTER 1: PARTICLE STATES IN A CENTRAL POTENTIAL

1. Schrödinger Equation for a Central Potential

Any of one component of angular momentum $\mathbf{L} = \mathbf{x} \times \mathbf{p} \equiv -i\hbar \mathbf{x} \times \nabla$ commutes with the Hamiltonian **H**. $\mathbf{L}^2$ also commutes with **H**.

In polar coordinates,

$$
\begin{aligned}
L_1 &= i\hbar \left(\sin\phi \frac{\partial}{\partial\theta} + \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \\
L_2 &= i\hbar \left(-\cos\phi \frac{\partial}{\partial\theta} + \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\
L_3 &= -i\hbar \frac{\partial}{\partial\phi}
\end{aligned} \tag{1}
$$

What does this have to do with the Schrödinger equation?

$$
\mathbf{L}^2 = -\hbar^2 \left[r^2 \nabla^2 - \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \right] \tag{2}
$$

or in other words:

$$
\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \frac{\mathbf{L}^2}{\hbar^2 r^2} \tag{3}
$$

Then Schrödinger equation takes the form:

$$
E\psi(\mathbf{x}) = -\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\mathbf{x})}{\partial r} \right) + \frac{1}{2\mu r^2} \mathbf{L}^2 \psi(\mathbf{x}) + V(r)\psi(\mathbf{x}) \tag{4}
$$

As long as $V(r)$ is not extremely singular at $r = 0$, the wave function can be expressed as a power series in the Cartesian components.

$$
\psi(\mathbf{x}) \to r^l Y(\theta, \phi) \tag{5}
$$

then,

$$
\mathbf{L}^2 \psi(\mathbf{x}) = \hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi(\mathbf{x})}{\partial r} \right) + 2\mu r^2 \left[E - V(r) \right] \psi(\mathbf{x}) \tag{6}
$$

In the limit $r \to 0$, as long as the potential is less singular than $1/r^2$, the second term on the right side vanishes as $r \to 0$ more rapidly than ψ, so ψ satisfy the eigenvalue equation

$$
\mathbf{L}^2 \psi(\mathbf{x}) \to \hbar^2 l(l+1)\psi \tag{7}
$$

Hence, the eigenvalue of $\hat{H}$ can only be $\hbar^2 l(l+1)$.

Since $\mathbf{L}^2$ acts only on angles,such

$$
\psi(\mathbf{x}) = R(r) Y(\theta, \phi) \tag{8}
$$

where $R(r)$ is a function of r satisfying

$$R(r) \propto r^l \quad \text{for} \quad r \to 0 \tag{9}$$

and $Y(\theta,\phi)$ is a function of θ and ϕ satisfying

$$\mathbf{L}^2 Y = \hbar^2 l(l+1) Y \tag{10}$$

If we also require ψ to be an eigenfunction of L_3 with eigenvalue denoted $\hbar m$

then

$$L_3 Y = \hbar m Y \tag{11}$$

Equation 1.3 shows that $Y(\theta,\phi)$ must then have a ϕ-dependence

$$Y(\theta,\phi) = e^{im\phi} \times \text{function of} \quad \theta \tag{12}$$

The condition that $Y(\theta,\phi)$ must have the same value at $\phi = 0$ and $\phi = 2\pi$ requires then m be an integer.

2. Spherical Harmonics

The angular part of the wave function will therefore be labeled with l and m, as $Y_l^m(\theta,\phi)$.

Use Eq.3 and act on $r^l Y_l^m$, and according to Eq.10,

$$\nabla^2 \left(r^l Y_l^m\right) = 0 \tag{13}$$

Finally, recall that $r^l Y_l^m(\theta,\phi)$ is a homogeneous polynomial of order l in the Cartesian components of the coordinate vector $\mathbf{x}$. Equivalently, it can be written as a homogeneous polynomial of order l in

$$x_\pm \equiv x_1 \pm i x_2 = r \sin\theta e^{\pm i\phi} \quad \text{and} \quad x_3 = r\cos\theta \tag{14}$$

Thus Eq.11 tells us that Y_l^m must contain numbers $\nu_\pm$ of factors of $x_\pm$ such that

$$m = \nu_+ - \nu_- \tag{15}$$

Since the total number of factors of x_+, x_- and x_3 is l, the index m is a positive or negative integer, with a maximum value l and a minimum value $-l$.

Whether Y_l^m is uniquely determined by the values of l and m ?

For a given l , m takes $2l+1$ values. And we have

$$N_l = \sum_{\nu_+=0}^{l} \sum_{\nu_-=0}^{l-\nu_+} 1 = \frac{1}{2}(l+1)(l+2) \tag{16}$$

Recall Eq.13,

$$N_l - N_{l-2} = 2l + 1 \tag{17}$$

Thus, there is only one independent polynomial for each l and m.

These functions, denoted $Y_l^m(\theta, \phi)$, with $-l \leq m \leq +l$, are known as **spherical harmonics**.

$$Y_l^m(\theta, \phi) \propto P_l^{|m|}(\theta) e^{im\phi} \tag{18}$$

For $l \leq 2$,

$$\begin{aligned} Y_0^0 &= \sqrt{\frac{1}{4\pi}} \\ Y_1^1 &= -\sqrt{\frac{3}{8\pi}}(\hat{x}_1 + i\hat{x}_2) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi} \\ Y_1^0 &= -\sqrt{\frac{3}{4\pi}}\hat{x}_3 = -\sqrt{\frac{3}{4\pi}} \cos\theta \\ Y_1^{-1} &= -\sqrt{\frac{3}{8\pi}}(\hat{x}_1 - i\hat{x}_2) = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi} \end{aligned} \tag{19}$$

We also note the space-inversion(or "**parity**") property of the wave function.

Under the transformation $\hat{x} \to -\hat{x}$, the spherical harmonics change by just a sign factor $(-1)^l$:

$$Y_l^m(\pi - \theta, \pi + \phi) = (-1)^l Y_l^m(\theta, \phi) \tag{20}$$

<u>3. The Hydrogen Atom</u>

Since we have Eq.8, $\psi(\mathbf{x}) = R(r)Y(\theta, \phi)$, and associate it with Eq.10, $\mathbf{L}^2 Y = \hbar^2 l(l+1) Y$

we can get Schrödinger equation;

$$E\,R(r) = -\frac{\hbar^2}{2\mu r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}R(r)}{\mathrm{d}r}\right) + \frac{\hbar^2 l(l+1)}{2\mu r^2} R(r) + V(r)R(r) \tag{21}$$

The equation above can be made to look more like the Schrödinger equation in one dimension by defining a new radial wave function

$$u(r) \equiv rR(r) \tag{22}$$

Then Eq.20 takes the form

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2 u(r)}{\mathrm{d}r^2} + \left[V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right] r(r) = E\,u(r) \tag{23}$$

Consider $V(r) = -Ze^2/r$

$$-\frac{\mathrm{d}^2 u(r)}{\mathrm{d}r^2}+\left[-\frac{2m_e Ze^2}{r\hbar^2}+\frac{l(l+1)}{r^2}\right]u(r)=-\kappa^2 u(r) \tag{24}$$

where κ is defined by

$$E=-\frac{\hbar^2\kappa^2}{2m_e}, \quad \kappa>0 \tag{25}$$

We can write this in dimensionless form by introducing

$$\rho \equiv \kappa r \tag{26}$$

After dividing by κ^2, Eq.23 becomes

$$-\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2}+\left[-\frac{\xi}{\rho}+\frac{l(l+1)}{\rho^2}\right]u=-u \tag{27}$$

where

$$\xi \equiv \frac{2m_e Ze^2}{\kappa\hbar^2} \tag{28}$$

We must look for a solution that decreases as ρ^{l+1} for $\rho \to 0$, and like $\exp(-\rho)$ for $\rho \to \infty$, so let's replace u with a new function $F(\rho)$, defined by

$$u=\rho^{l+1}\exp(-\rho)F(\rho) \tag{29}$$

The radial wave equation (26) thus becomes

$$\frac{\mathrm{d}^2 F}{\mathrm{d}\rho^2}-2\left(1-\frac{l+1}{\rho}\right)\frac{\mathrm{d}F}{\mathrm{d}\rho}+\left(\frac{\xi-2l-2}{\rho}\right)F=0 \tag{30}$$

Let's try a power-series solution

$$F=\sum_{s=0}^{\infty}a_s\rho^s, \tag{31}$$

Then Eq.29 becomes,

$$\sum_{s=0}^{\infty}a_s\left[s(s-1)\rho^{s-2}-2s\rho^{s-1}+2s(l+1)\rho^{s-2}+(\xi-2l-2)\rho^{s-1}\right]=0 \tag{32}$$

After redefining s as $s+1$,

$$\sum_{s=0}^{\infty}\rho^{s-1}\left[s(s+1)a_{s+1}-2sa_s+2(s+1)(l+1)a_{s+1}+(\xi-2l-2)a_s\right]=0 \tag{33}$$

Thus

$$(s+2l+2)(s+1)a_{s+1}=(-\xi+2s+2l+2)a_s \tag{34}$$

Let us consider the asymptotic behavior of this power series for large ρ.

For $s \to \infty$:

$$a_{s+1}/a_s \to 2/s \tag{35}$$

we have

$$a_s \approx C\ 2^s/(s+B)! \tag{36}$$

Thus we expect that asymptotically

$$F(\rho) \approx C \sum_{s=0}^{\infty} \frac{(2\rho)^s}{(s+B)!} \to C(2\rho)^{-B} e^{2\rho} \tag{37}$$

Aside from constants and powers of ρ, $u \approx \exp(\rho)$, which is ***inconsistent*** with Eq.28.

The only way to avoid this is to require that the power series terminates.

$$\xi = 2n \geq l+1 \quad \text{see right hand of Eq. 33} \tag{38}$$

Although the wave functions depend on l and m, the energy only depend on n. with $\xi = 2n$, Eq.27 gives

$$\kappa_n = \frac{2m_e Z e^2}{\xi \hbar^2} = \frac{1}{na} \tag{39}$$

where a is *Bohr radius*

$$a = \frac{\hbar^2}{m_e Z e^2} = 5.2918 \times 10^{-10} Z^{-1} \mathrm{m} \tag{40}$$

Finally,

$$E_n = -\frac{\hbar^2 \kappa_n^2}{2m_e} = -\frac{\hbar^2}{2m_e a^2 n^2} = -\frac{m_e Z^2 e^4}{2\hbar^2 n^2} = -\frac{13.6057 Z^2 \mathrm{eV}}{n^2} \tag{41}$$

For each n we have l values running from 0 to $n-1$, and for each l we have $2l+1$ values of m. The total number of states with energy E_n is

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \tag{42}$$

The rate at which a state represented by a wave function ψ decays by single-photon emission into a state represented by a wave function ψ' is proportion to $|\int \psi'^* \mathbf{x} \psi|^2$. If we change the variable of integration from $\mathbf{x}$ to $-\mathbf{x}$, the wave functions ψ and ψ' change by factors $(-1)^l$ and $(-1)^{l'}$, and so the whole integrand changes by a factor

$$(-1)^{l+l'+1} \tag{43}$$

So the signs $(-1)^l$ and $(-1)^{l'}$ must be opposite. Thus $2p$ orbital can transit to $1s$, but $2s$ can't transit to $1s$ by only emitting one photon.

4. The two body problem

The two-body problem is equivalent to a one body problem, with the electron mass replaced with a reduced mass:

$$\mu = \frac{m_e m_N}{m_e + m_N} \tag{44}$$

The Hamiltonian for one-electron atom is

$$H = \frac{\mathbf{P}_e^2}{2m_e} + \frac{\mathbf{P}_N^2}{2m_N} + V(\mathbf{x}_e - \mathbf{x}_N) \tag{45}$$

We introduce a relative coordinate $\mathbf{x}$ and a center-of-mass coordinate $\mathbf{X}$ by

$$\mathbf{x} \equiv \mathbf{x}_e - \mathbf{x}_N, \quad \mathbf{X} \equiv \frac{m_e \mathbf{x}_e + m_N \mathbf{x}_N}{m_e + m_N} \tag{46}$$

and a relative momentum $\mathbf{p}$ and a total momentum $\mathbf{P}$ by

$$\mathbf{p} \equiv \mu \left(\frac{\mathbf{p}_e}{m_e} - \frac{\mathbf{p}_N}{m_N} \right), \quad \mathbf{P} \equiv \mathbf{p}_e + \mathbf{p}_N \tag{47}$$

Then Hamiltonian may be written

$$H = \frac{\mathbf{p}^2}{2\mu} + \frac{\mathbf{P}^2}{2(m_e + m_N)} + V(\mathbf{x}) \tag{48}$$

where

$$\mathbf{p} = -i\hbar \nabla_{\mathbf{x}}, \quad \mathbf{P} = -i\hbar \nabla_{\mathbf{X}} \tag{49}$$

So the momenta and the coordinates satisfy the commutation relations

$$[x_i, p_j] = [X_i, P_j] = i\hbar \delta_{ij}, \quad [x_i, P_j] = [X_i, p_j] = 0 \tag{50}$$

Such a wave function will have the form

$$\psi(\mathbf{x}, \mathbf{X}) = e^{i\mathbf{P}\cdot\mathbf{X}/\hbar} \psi(\mathbf{x}) \tag{51}$$

and $\psi(\mathbf{x})$ is a wave function for an internal energy $\mathcal{E}$, satisfying the one-particle Schrödinger equation

$$-\frac{\hbar^2 \nabla_x^2 \psi(\mathbf{x})}{2\mu} + V(\mathbf{x})\psi(\mathbf{x}) = \mathcal{E}\psi(\mathbf{x}) \tag{52}$$

The total energy is just the internal energy $\mathcal{E}$ of the atom, plus the kinetic energy of its overall motion:

$$E = \mathcal{E} + \frac{\mathbf{P}^2}{2(m_e + m_N)} \tag{53}$$

For hydrogen and deuteron,

$$\mu_{pe} = 0.99945 m_e, \quad \mu_{de} = 0.99973 m_e. \tag{54}$$

This tiny difference is enough to produce a detectable split in the frequencies of light emitted from a mixture of ordinary hydrogen and deuterium.

5. The Harmonic Oscillator

Let's consider a particle of mass M in a potential

$$V(r) = \frac{1}{2} M \omega^2 r^2 \tag{55}$$

There are four reason it is worth considering

1. Historical Reason: This is the problem studied by Heisenberg introducing *Matrix Mechanics*
2. This theory provides a nice illustration of how we can find energy levels and radiative transition amplitudes by algebraic methods, ***without having to solve second-order differential equations***.
3. The harmonic potential is used in models of atomic nuclei.
4. The methods described here is useful for dealing with **the energy levels of electrons in magnetic fields** and for calculating **the properties of photons**.

The Schrödinger equation is here

$$E\,\psi = -\frac{\hbar^2}{2M} \nabla^2 \psi + \frac{1}{2} M \omega^2 r^2 \psi \tag{56}$$

we can write this equation in another form

$$\sum_{i=1}^{3} \left(-\frac{\hbar^2}{2M} \frac{\partial^2 \psi}{\partial x_i^2} + \frac{M \omega^2 x_i^2 \psi}{2} \right) = E\,\psi \tag{57}$$

This has separable solutions, of the form

$$\psi(\mathbf{x}) = \psi_{n_1}(x_1) \psi_{n_2}(x_2) \psi_{n_3}(x_3) \tag{58}$$

where $\psi_n(x)$ is a solution of the one-dimensional Schrödinger equation

$$-\frac{\hbar^2}{2M} \frac{\partial^2 \psi_n(x)}{\partial x^2} + \frac{M \omega^2 x^2 \psi_n(x)}{2} = E_n \psi_n(x) \tag{59}$$

The energy is the sum.

$$E = E_1 + E_2 + E_3 \tag{60}$$

To solve this problem, we introduce so-called lowering and raising operators

$$a_i \equiv \frac{1}{\sqrt{2M\hbar\omega}}\left(-i\hbar\frac{\partial}{\partial x_i} - iM\omega x_i\right) \tag{61}$$

$$a_i^\dagger \equiv \frac{1}{\sqrt{2M\hbar\omega}}\left(-i\hbar\frac{\partial}{\partial x_i} + iM\omega x_i\right) \tag{62}$$

These operators obey the commutation relations

$$\left[a_i, a_j^\dagger\right] = \delta_{ij} \tag{63}$$

and

$$[a_i, a_j] = \left[a_i^\dagger, a_j^\dagger\right] = 0 \tag{64}$$

Also, the one-dimensional Hamiltonian here is

$$H_i \equiv -\frac{\hbar^2}{2M}\nabla_i^2 + \frac{M\omega^2 x_i^2}{2} = \hbar\omega\left[a_i^\dagger a_i + \frac{1}{2}\right] \tag{65}$$

Now

$$[H_i, a_i] = -\hbar\omega a_i, \quad [H_i, a_i^\dagger] = +\hbar\omega a_i^\dagger \tag{66}$$

Hence if ψ represents a state with energy E, then $a_i\psi$ represents a state with energy $E-\hbar\omega$, and $a_i^\dagger\psi$ represents a state with energy $E+\hbar\omega$.

There must be a wave function $\psi_0(x_i)$ for which $a_i\psi_0 = 0$; it is

$$\psi_0(x_i) \propto \exp(-M\omega x_i^2/2\hbar) \tag{67}$$

And

$$\psi_{n_i}(x_i) \propto a_i^{\dagger n_i}\psi_0(x_i) \propto H_{n_i}(x_i)\exp(-M\omega x_i^2/2\hbar) \tag{68}$$

where $H_n(x)$ is a polynomial of order n in x. These polynomials satisfy the parity condition

$$H_n(-x) = (-1)^n H_n(x) \tag{69}$$

The general wave function representing a state of definite energy is therefore

$$\psi_{n_1n_2n_3}(\mathbf{x}) \propto a_1^{\dagger n_1} a_2^{\dagger n_2} a_3^{\dagger n_3} \propto H_{n_1}(x_1)H_{n_2}(x_2)H_{n_3}(x_3)\exp(-M\omega r^2/2\hbar) \tag{70}$$

and the state has energy

$$E_{n_1n_2n_3} = \hbar\omega\left[\sum_i\left(a_i^\dagger a_i + \frac{1}{2}\right)\right] = \hbar\omega\left[N + \frac{3}{2}\right] \tag{71}$$

where $N = n_1 + n_2 + n_3$.

The degeneracy $\mathcal{N}_n$

$$\mathcal{N}_n = \sum_{n_1=0}^{N} \sum_{n_2=0}^{N-n_1} 1 = \sum_{n_1=0}^{N} (N - n_1 + 1) = \frac{(N+1)(N+2)}{2} \tag{72}$$