CHAPTER 2: PARTICLE IN A CENTRAL POTENTIAL. THE HYDROGEN ATOM

(From Cohen-Tannoudji, Chapter VII)

A. STATIONARY STATES OF A PARTICLE IN A CENTRAL POTENTIAL

We will be dealing with the following three topics:

A) Stationary states of a particle in a central potential

$V(\vec{r})$ is invariant under any rotation about the origin, that is $[H, L_k] = 0$, and thus the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ are also eigenfunctions of H.

**B) Motion of the center of mass and relative motion for a system of two interacting particles**

(i) a two particle system in which interaction energy depends only on the particles' relative position can be replaced by a simpler problem of one fictitious particle;

(ii) in addition, when the interaction depends only on the distance between particles, then the fictitious particle's motion is governed by a central potential.

C) Exactly solvable problems

(i) $V(\vec{r})$ is a Coulomb potential: hydrogen, deuterium, tritium, He^+, Li^+;

(ii) $V(\vec{r})$ is a quadratic potential: isotropic three-dimensional harmonic oscillator.

1. Outline of the problem

a. REVIEW OF SOME CLASSICAL RESULTS
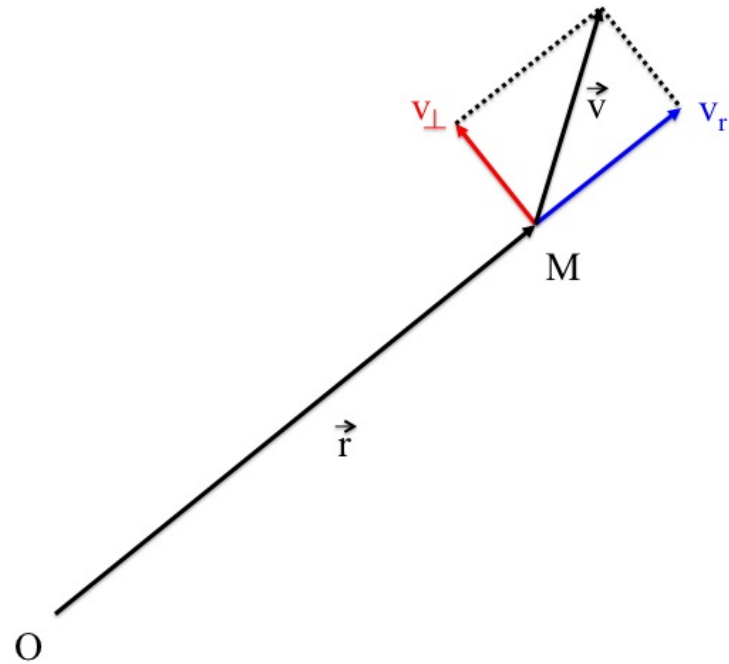
Force on the particle located at the point M

$$\vec{F} = -\vec{\nabla}V(r) = -\frac{\mathrm{d}V}{\mathrm{d}r}\frac{\vec{r}}{r} \tag{2.1}$$

is always directed to the origin O. In this case the angular momentum theorem implies that the angular momentum $\vec{\mathcal{L}} = \vec{r} \times \vec{p}$ is *a constant of motion*:

$$\frac{\mathrm{d}\vec{\mathcal{L}}}{\mathrm{d}t} = \vec{0} \tag{2.2}$$

and the particle trajectory is on the plane through the origin and perpendicular to $\vec{\mathcal{L}}$.

Let us consider now the position and velocity of the particle at time t. The velocity can be decomposed into the radial v_r and tangential velocity $\vec{v}_\perp$ defined through the relations

$$v_r = \frac{\mathrm{d}r}{\mathrm{d}t} \tag{2.3}$$

$$\left|\vec{r} \times \vec{v}\right| = r\left|\vec{v}_\perp\right| \tag{2.4}$$

so that the modulus of the angular momentum is given as

$$\left|\vec{\mathcal{L}}\right| = \left|\vec{r} \times \mu\vec{v}\right| = \mu r\left|\vec{v}_\perp\right| \tag{2.5}$$

The total energy of the particle

$$E \;=\; \frac{1}{2}\mu\vec{v}^2 + V(r) = \frac{1}{2}\mu\vec{v}_r^2 + \frac{1}{2}\mu\vec{v}_\perp^2 + V(r) \tag{2.6}$$

can be rewritten as

$$E \;=\; \frac{1}{2}\mu v_r^2 + \frac{\vec{\mathcal{L}}^2}{2\mu r^2} + V(r) \tag{2.7}$$

which follows from

$$\vec{\mathcal{L}}^2 \;=\; \left|\vec{\mathcal{L}}^2\right| = \mu^2 r^2 \left|\vec{v}_\perp\right|^2 = r^2 p_\perp^2 \tag{2.8}$$

The classical Hamiltonian of the system is then

$$\mathcal{H} \;=\; \frac{p_r^2}{2\mu} + \frac{\vec{\mathcal{L}}^2}{2\mu r^2} + V(r) \tag{2.9}$$

where the momentum

$$p_r \;=\; \mu\frac{\mathrm{d}r}{\mathrm{d}t} \tag{2.10}$$

is conjugate to the radial coordinate r, and $\vec{\mathcal{L}}^2$ can be expressed using the spherical coordinates r, θ and ϕ as

$$\vec{\mathcal{L}}^2 \;=\; p_\theta^2 + \frac{1}{\sin^2\theta}p_\phi^2 \tag{2.11}$$

$\vec{\mathcal{L}}^2$ is a constant of motion as $V(r)$ depends only on r and not on θ and ϕ that is the kinetic energy associated with tangential motion $T_\perp = \frac{1}{2}\mu v_\perp^2$ is a constant in the Hamiltonian. That is $\vec{\mathcal{L}}^2$ plays the role of a parameter

$$\frac{\mathrm{d}p_r}{\mathrm{d}t} = \mu\frac{\mathrm{d}^2 r}{\mathrm{d}t^2} = -\frac{\partial \mathcal{H}}{\partial r} = \frac{\vec{\mathcal{L}}^2}{\mu r^3} - \frac{\mathrm{d}V}{\mathrm{d}r} \qquad (2.12)$$

and this allows us to regard this problem as equivalent to a one-dimensional problem (with $0 \le r < \infty$) with a particle of mass μ in the effective potential

$$V_{\mathrm{eff}}(r) = V(r) + \frac{\vec{\mathcal{L}}^2}{2\mu r^2} \qquad (2.13)$$

b. THE QUANTUM MECHANICAL HAMILTONIAN

The eigenvalue problem in the coordinate representation is given as

$$\left[-\frac{\hbar^2}{2\mu}\Delta + V(r) \right] \varphi(\vec{r}) = E\varphi(\vec{r}) \qquad (2.14)$$

where the Laplacian Δ in spherical coordinates is

$$\Delta = \frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right) \qquad (2.15)$$

Recall that

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \frac{1}{\tan\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \right) \qquad (2.16)$$

and you can write down the quantum mechanical Hamiltonian in the form analogous to the one we found in the classical case

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2\mu r^2}\hat{L}^2 + V(r)$$

The eigenvalue equation then becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2\mu r^2}\hat{L}^2 + V(r)\right]\varphi(r,\theta,\phi) = E\varphi(r,\theta,\phi) \qquad (2.17)$$

2. Separation of Variables

a. ANGULAR DEPENDENCE OF THE EIGENFUNCTIONS

The three components of the angular momentum operator $\hat{\vec{L}}$ act only on the angular variables θ and ϕ and thus they commute with all operators that depend on r only. In addition they commute with $\hat{L}^2$, so the three components of the angular momentum are constants of motion:

$$\left[\hat{H}, \hat{\vec{L}}\right] = 0 \tag{2.18}$$

Obviously also $\left[\hat{H}, \hat{L}^2\right] = 0$, so we can choose the complete set of commuting observables to be represented by the operators

$$\hat{H}, \hat{L}^2, \text{ and } \hat{L}_z$$

We therefore require the eigenfunctions $\varphi(r, \theta, \phi)$ to be simultaneous eigenfunctions of this C.S.C.O. Their eigenvalue equations

$$
\begin{align}
\hat{H}\varphi(\vec{r}) &= E\varphi(\vec{r}) \tag{2.19} \\
\hat{L}^2\varphi(\vec{r}) &= l(l+1)\hbar^2\varphi(\vec{r}) \tag{2.20} \\
\hat{L}_z\varphi(\vec{r}) &= m\hbar\varphi(\vec{r}) \tag{2.21}
\end{align}
$$

now constitute a system of differential equations that must be solved simultaneously.

We know the general form of the eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ for a fixed value of the quantum numbers l and m which is given by the spherical harmonics $Y_l^m(\theta, \phi)$. Thus the general solution will be of the following form

$$
\varphi(\vec{r}) = R(r)Y_l^m(\theta, \phi) \tag{2.22}
$$

and the remaining problem is to determine the radial function $R(r)$ such that $\varphi(\vec{r})$ is an eigenfunction of $\hat{H}$.

b. THE RADIAL EQUATION

Inserting $\varphi(\vec{r}) = R(r)Y_l^m(\theta, \phi)$ into the eigenvalue equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + \frac{1}{2\mu r^2}\hat{L}^2 + V(r) \right]\varphi(r, \theta, \phi) = E\varphi(r, \theta, \phi) \qquad (2.23)$$

we can formulate the eigenvalue equation for the function of the radial coordinate $R(r)$ only

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right]R(r) = ER(r) \qquad (2.24)$$

We note at this point that the Laplacian is not necessarily defined at $r = 0$. In order for $\varphi(\vec{r}) = R(r)Y_l^m(\theta, \phi)$ to be the solution of the eigenvalue problem, we need to make sure that the behavior of the solutions $R(r)$ at $r = 0$ is sufficiently regular.

Now we face the eigenvalue problem, i.e. represented by a differential equation, which depends only on r and l as parameters, i.e. we are looking for eigenvalues and eigenvectors of $\hat{H}_l$ which is different for different values of l.

In the state space $\mathcal{E}_{\vec{r}}$, we consider subspaces $\mathcal{E}(l, m)$ for fixed values of l and m, and study the eigenvalue equation of $\hat{H}$ in each of these subspaces:

- the equation is the same in the $(2l + 1)$ subspaces $\mathcal{E}(l, m)$ associated with l;

- $E_{k,l}$ are eigenvalues of $\hat{H}_l$ in a given $\mathcal{E}(l, m)$, and they can be discrete or continuous depending on k which represents various eigenvalues with the same value of l;

- $R_{k,l}(r)$ are eigenfunctions of $\hat{H}_l$ in $\mathcal{E}(l, m)$.

The eigenvalue equation (i.e. the differential equation)

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2}{dr^2}r + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] R_{k,l}(r) \;=\; E_{k,l}R_{k,l}(r) \qquad (2.25)$$

can be satisfied by taking

$$R_{k,l}(r) \;=\; \frac{1}{r}u_{k,l}(r) \qquad (2.26)$$
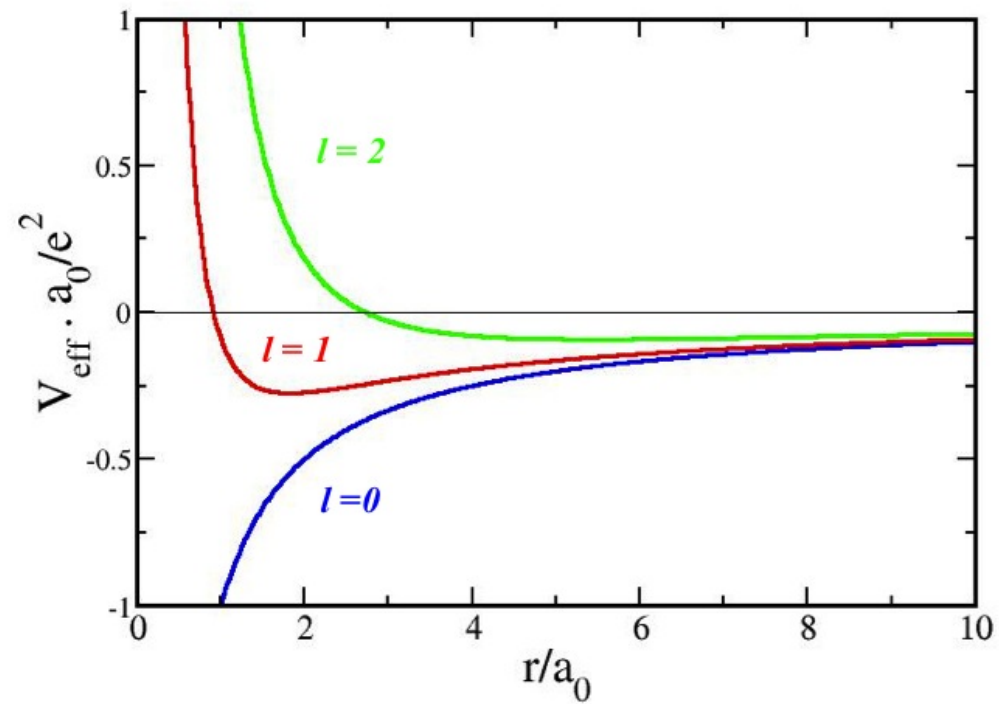
and by multiplying both sides of the equation by r

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] u_{k,l}(r) = E_{k,l}u_{k,l}(r)$$

Note that the last two terms in the square bracket constitute the effective potential

$$V_{\text{eff}}(r) \;=\; V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} \tag{2.27}$$

As $r \geq 0$ then $l(l+1)\hbar^2/2\mu r^2 \geq 0$ and thus the term $l(l+1)\hbar^2/2\mu r^2$ always repels the particle from the origin. We call this term *centrifugal potential*.

Examples of V_{eff} for $l = 0,\ 1,\ 2$:

c. BEHAVIOR OF THE SOLUTIONS OF THE RADIAL EQUATION AT THE ORIGIN

We have to examine the behavior of $R(r)$ at $r = 0$ to know whether they really are solutions of the eigenvalue problem. We assume

- $V(r)$ is for $r \to 0$ either finite or approaches infinity less rapidly than $\frac{1}{r}$;

- for $r \to 0$ the radial function $R_{k,l}(r) \sim C r^s$

Substituting $R_{k,l}(r)$ into the eigenvalue equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] R_{k,l}(r) \quad = \quad E_{k,l} R_{k,l}(r) \tag{2.28}$$

we get

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2}r(Cr^s) + \frac{l(l+1)\hbar^2}{2\mu r^2}(Cr^s) + V(r)(Cr^s) \quad = \quad E_{k,l}(Cr^s) \tag{2.29}$$

$$-\frac{\hbar^2}{2\mu}(s+1)\,s\,r^{s-2} + \frac{l(l+1)\hbar^2}{2\mu}r^{s-2} + V(r)r^s \quad = \quad E_{k,l}r^s \tag{2.30}$$

and setting the coefficients of the dominant term to zero we get

$$-s(s+1) + l(l+1) \quad = \quad 0 \tag{2.31}$$

The equation $-s(s+1) + l(l+1) = 0$ has two solutions

$$\begin{cases} \text{either} & s = l \\ \text{or} & s = -(l+1) \end{cases} \qquad (2.32)$$

that is, for a given $E_{k,l}$, there are therefore two linearly independent solutions of the eigenvalue equation above behaving at $r \to 0$ like

1. r^l, or

2. $\frac{1}{r^{l+1}}$.

However we have to reject the solution $\frac{1}{r^{l+1}}$ as this diverges for $r = 0$ and is thus physically unacceptable.

The acceptable solution of the eigenvalue problem converges to zero at $r = 0$ for all values of l (recall that $R_{k,l}(r) = \frac{1}{r}u_{k,l}(r)$):

$$u_{k,l}(r) \underset{r \to 0}{\sim} Cr^{l+1} \tag{2.33}$$

Consequently, to the eigenvalue equation we have to add a condition

$$\boxed{u_{k,l}(0) = 0.}$$

3. Stationary states of a particle in a central potential

a. QUANTUM NUMBERS

Summary:

- The eigenfunctions of $\hat{H}$ are required to be the simultaneous eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$ which determines their angular dependence

$$\varphi_{k,l,m}(\vec{r}) = R_{k,l}(r)Y_l^m(\theta, \phi) = \frac{1}{r}u_{k,l}(r)Y_l^m(\theta, \phi).$$

- The eigenvalue equation of $\hat{H}$ is replaced by a differential equation involving only the radial coordinate r and depending on a parameter l.

In addition:

In principle the functions $\varphi(r, \theta, \phi)$ must be square integrable

$$\int \left| \varphi_{k,l,m}(r, \theta, \phi) \right|^2 r^2 \mathrm{d}r \, \mathrm{d}\Omega \;\; = \;\; 1 \qquad (2.34)$$

and we can separately integrate their radial and angular component

$$\int \left| \varphi_{k,l,m}(r, \theta, \phi) \right|^2 r^2 \mathrm{d}r \, \mathrm{d}\Omega \;\; = \;\; \int_0^\infty r^2 \mathrm{d}r \left| R_{k,l}(r) \right|^2 \int \mathrm{d}\Omega \left| Y_l^m(\theta, \phi) \right|^2 \qquad (2.35)$$

The spherical harmonics $Y_l^m(\theta, \phi)$ are already normalized, so the normalization condition reduces to

$$\int_0^\infty r^2 \mathrm{d}r \left| R_{k,l}(r) \right|^2 \;\; = \;\; \int_0^\infty \mathrm{d}r \left| u_{k,l}(r) \right|^2 = 1 \qquad (2.36)$$

We note that if the spectrum has a continuous part, i.e. k is a continuous index, then

$$\int_0^\infty r^2 dr\, R_{k',l}^*(r) R_{k,l}(r) = \int_0^\infty dr\, u_{k',l}^*(r) u_{k,l}(r) = \delta\left(k' - k\right) \qquad (2.37)$$

where $\delta\left(k' - k\right)$ is δ-function. Since this is not a square integrable function, the normalization integral diverges for $k = k'$.

An eigenfunction

$$\varphi_{k,l,m}\left(\vec{r}\right) = R_{k,l}(r) Y_l^m\left(\theta, \phi\right)$$

depends on three parameters as it is a simultaneous eigenfunction of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$ with eigenvalues E_k, $l(l+1)\hbar^2$, and $m\hbar$.

We call these parameters - k, l and m - *quantum numbers*:

k - a radial quantum number,

l - an azimuthal quantum number,

m - a magnetic quantum number.

The radial part $R_{k,l}(r) = \frac{1}{r}u_{k,l}(r)$ of $\varphi_{k,l,m}(\vec{r})$ are independent of m and are given by the eigenvalue equation

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r)\right]u_{k,l}(r) = E_{k,l}u_{k,l}(r)$$

The angular part depends only on l and m, and it does NOT depend on the form of the potential $V(r)$.

b. DEGENERACY OF THE ENERGY LEVELS

$(2l + 1)$ orthogonal functions $\varphi_{k,l,m}(\vec{r})$ with k and l fixed and m varying from $-l$ to $+l$ are eigenfunctions of $\hat{H}$ with the same eigenvalue $E_{k,l}$.

That is $E_{k,l}$ is at least $(2l + 1)$-fold degenerate. This is called *essential degeneracy* as it exists for all $V(r)$ and is due to the fact that $\hat{H}$ depends on $\hat{L}^2$ but not on $\hat{L}_z$.

It is also possible that $E_{k,l} = E_{k',l'}$ for $l \neq l'$. This occurs for certain potentials and it is called *accidental degeneracy*.

Remarks:

For a fixed l, the radial equation has at most one solution which is physically accept-
able. This is ensured by the condition $u_{k,l}(0) = 0$.

The behavior of the solutions as $r \to \infty$ follows from the behavior of the potential
$V(r \to \infty) \to 0$. The negative values of $E_{k,l}$ form a discrete set.

B. MOTION OF THE CENTER OF MASS AND RELATIVE MOTION FOR A SYSTEM OF TWO INTERACTING PARTICLES

1. Motion of the center of mass and relative motion in classical mechanics

Let us consider two spinless particles with masses m_1 and m_2 and positions $\vec{r}_1$ and $\vec{r}_2$ respectively, and assume that the force between the particles is derived from the potential $V(r) = V(\vec{r}_1 - \vec{r}_2)$.

in classical mechanics the system is described by the Lagrangian

$$\pounds\left(\vec{r}_1, \dot{\vec{r}}_1; \vec{r}_2, \dot{\vec{r}}_2\right) = T - V = \frac{1}{2}m_1\dot{\vec{r}}_1^2 + \frac{1}{2}m_2\dot{\vec{r}}_2^2 - V\left(\vec{r}_1 - \vec{r}_2\right). \qquad (2.38)$$

The momental of the particles are

$$\vec{p}_1 = m_1\dot{\vec{r}}_1 \qquad (2.39)$$

$$\vec{p}_2 = m_2\dot{\vec{r}}_2 \qquad (2.40)$$

The study of the motion of the two particles is simplified by introducing
(i) center of mass coordinates

$$\vec{r}_G = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2} \tag{2.41}$$

(ii) relative coordinates

$$\vec{r} = \vec{r}_1 - \vec{r}_2 \tag{2.42}$$

where

$$\vec{r}_1 = \vec{r}_G + \frac{m_2}{m_1 + m_2} \vec{r} \tag{2.43}$$

$$\vec{r}_2 = \vec{r}_G - \frac{m_1}{m_1 + m_2} \vec{r} \tag{2.44}$$

The Lagrangian can now be rewritten as follows

$$
\begin{aligned}
£\left(\vec{r}_G, \dot{\vec{r}}_G; \vec{r}, \dot{\vec{r}}\right) &= \frac{1}{2}m_1\left[\dot{\vec{r}}_G + \frac{m_2}{m_1 + m_2}\dot{\vec{r}}\right]^2 + \frac{1}{2}m_2\left[\dot{\vec{r}}_G - \frac{m_1}{m_1 + m_2}\dot{\vec{r}}\right]^2 - V(\vec{r}) \\
&= \frac{1}{2}M\dot{\vec{r}}_G^2 + \frac{1}{2}\mu\dot{\vec{r}}^2 - V(\vec{r}) \qquad (2.45)
\end{aligned}
$$

where M is the total mass of the system and μ is the reduced mass (i.e. the geometric mean of m_1 and m_2):

$$
M = m_1 + m_2 \qquad (2.46)
$$

$$
\mu = \frac{m_1 m_2}{m_1 + m_2} \qquad (2.47)
$$

$$
\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad (2.48)
$$

Conjugate momenta are the total momentum and the relative momentum defined as

$$\vec{p}_G = M\dot{\vec{r}}_G = m_1\dot{\vec{r}}_1 + m_2\dot{\vec{r}}_2 = \vec{p}_1 + \vec{p}_2 \tag{2.49}$$

$$\vec{p} = \mu\dot{\vec{r}} = \frac{m_2\vec{p}_1 - m_1\vec{p}_2}{m_1 + m_2} \tag{2.50}$$

$$\frac{\vec{p}}{\mu} = \frac{\vec{p}_1}{m_1} - \frac{\vec{p}_2}{m_2} \tag{2.51}$$

The classical Hamiltonian and the equations of motion are

$$\mathcal{H}\left(\vec{r}_G, \vec{p}_G; \vec{r}, \vec{p}\right) \;=\; \frac{\vec{p}_G^{\,2}}{2M} + \frac{\vec{p}^{\,2}}{2\mu} + V\left(\vec{r}\right) \tag{2.52}$$

$$\dot{\vec{p}}_G \;=\; \vec{0} \tag{2.53}$$

$$\dot{\vec{p}} \;=\; -\vec{\nabla} V\left(\vec{r}\right) \tag{2.54}$$

where $\frac{\vec{p}_G^{\,2}}{2M}$ is the kinetic energy of a *fictitious* particle with mass M and position in the center of mass which is, as indicated by $\dot{\vec{p}}_G = \vec{0}$, in uniform rectilinear motion.

In the center of mass frame (which is in uniform rectilinear motion $\dot{\vec{p}}_G = \vec{0}$) the total momentum $\vec{p}_G = 0$ so the Hamiltonian reduces to

$$\mathcal{H}_r = \frac{\vec{p}^2}{2\mu} + V(\vec{r}) \tag{2.55}$$

which characterizes the energy associated with the relative motion of the two particles.

Here a new fictitious particle, *relative particle*, is introduced with the mass μ (the reduced mass of the original particles) and the relative coordinate $\vec{r}$ and momentum $\vec{p}$. This relative particle behaves as being a subject of a potential $V(r)$ equal to the potential energy of interaction between two real particles.

The study of the relative motion of two interacting particles reduces to study of a motion of a single fictitious particle characterized by μ, $\vec{r}$ and $\vec{p}$.

2. Separation of variables in quantum mechanics
a. OBSERVABLES ASSOCIATED WITH THE CENTER OF MASS AND THE RELATIVE PARTICLE

The observables $\hat{\vec{R}}_1$, $\hat{\vec{R}}_2$, $\hat{\vec{P}}_1$, and $\hat{\vec{P}}_2$ satisfy the canonical commutation relations, e.g. the x components (similarly relations hold for the other components)

$$\left[\hat{X}_1, \hat{P}_{1x}\right] = i\hbar \tag{2.56}$$

$$\left[\hat{X}_2, \hat{P}_{2x}\right] = i\hbar \tag{2.57}$$

We can define new coordinates and momenta

$$\hat{\vec{R}}_G = \frac{m_1\hat{\vec{R}}_1 + m_2\hat{\vec{R}}_2}{m_1 + m_2} \tag{2.58}$$

$$\hat{\vec{R}} = \hat{\vec{R}}_1 - \hat{\vec{R}}_2 \tag{2.59}$$

$$\hat{\vec{P}}_G = \hat{\vec{P}}_1 + \hat{\vec{P}}_2 \tag{2.60}$$

$$\hat{\vec{P}} = \frac{m_2\hat{\vec{P}}_1 - m_1\hat{\vec{P}}_2}{m_1 + m_2} \tag{2.61}$$

which satisfy the following commutation relations, e.g. the x components (and similarly for the other components)

$$\left[\hat{X}_G, \hat{P}_{Gx}\right] = i\hbar \tag{2.62}$$

$$\left[\hat{X}, \hat{P}_x\right] = i\hbar \tag{2.63}$$

b. EIGENVALUES AND EIGENFUNCTIONS OF THE HAMILTONIAN

The Hamiltonian

$$\hat{H} \;=\; \frac{\hat{\vec{P}}_1^{\,2}}{2m_1} + \frac{\hat{\vec{P}}_2^{\,2}}{2m_2} + V\!\left(\hat{\vec{R}}_1 - \hat{\vec{R}}_2\right) \tag{2.64}$$

can be rewritten in terms of the new coordinates as

$$\hat{H} \;=\; \frac{\hat{\vec{P}}_G^{\,2}}{2M} + \frac{\hat{\vec{P}}^{\,2}}{2\mu} + V\!\left(\hat{\vec{R}}\right) \tag{2.65}$$

This can be expressed as the sum

$$\hat{H} \;=\; \hat{H}_G + \hat{H}_r \tag{2.66}$$

where

$$\hat{H}_G \;=\; \frac{\hat{\vec{P}}_G^{\,2}}{2M} \tag{2.67}$$

$$\hat{H}_r \;=\; \frac{\hat{\vec{P}}^{\,2}}{2\mu} + V\!\left(\hat{\vec{R}}\right) \tag{2.68}$$

$\hat{H}_G$ and $\hat{H}_r$ commute

$$\left[\hat{H}_G, \hat{H}_r\right] = 0 \tag{2.69}$$

and thus satisfy the eigenvalue equations with the common eigenvector

$$\hat{H}_G|\varphi\rangle = E_G|\varphi\rangle \tag{2.70}$$

$$\hat{H}_r|\varphi\rangle = E_r|\varphi\rangle \tag{2.71}$$

which imply that

$$\hat{H}|\varphi\rangle = E|\varphi\rangle \tag{2.72}$$

where

$$E = E_G + E_r \tag{2.73}$$

Consider $\{|\vec{r}_G, \vec{r}\rangle\}$ representation with the basis vectors common to the observables $\hat{\vec{R}}_G$ and $\hat{\vec{R}}$, $\phi(\vec{r}_G, \vec{r})$:

$$\hat{\vec{R}}_G \phi(\vec{r}_G, \vec{r}) = \vec{r}_G \phi(\vec{r}_G, \vec{r}) \tag{2.74}$$

$$\hat{\vec{R}} \phi(\vec{r}_G, \vec{r}) = \vec{r} \phi(\vec{r}_G, \vec{r}) \tag{2.75}$$

The conjugate momenta are

$$\hat{\vec{P}}_G = \frac{\hbar}{i} \vec{\nabla}_G \tag{2.76}$$

$$\hat{\vec{P}} = \frac{\hbar}{i} \vec{\nabla} \tag{2.77}$$

The state space factorizes into the tensor product $\mathcal{E} = \mathcal{E}_{\vec{r}_G} \otimes \mathcal{E}_{\vec{r}}$ and the Hamiltonians $\hat{H}_G$ and $\hat{H}_r$ appear as extensions to $\mathcal{E}$ acting on $\mathcal{E}_{\vec{r}_G}$ and $\mathcal{E}_{\vec{r}}$ respectively.

This implies

$$|\varphi\rangle \;=\; |\chi_G\rangle \otimes |\omega_r\rangle \tag{2.78}$$

where

$$\begin{cases} \hat{H}_G|\chi_G\rangle = E_G|\chi_G\rangle \\ |\chi_G\rangle \in \mathcal{E}_{\vec{r}_G} \end{cases} \tag{2.79}$$

and

$$\begin{cases} \hat{H}_r|\omega_r\rangle = E_r|\omega_r\rangle \\ |\omega_r\rangle \in \mathcal{E}_{\vec{r}} \end{cases} \tag{2.80}$$

(i) The eigenvalue equation

$$-\frac{\hbar^2}{2M}\Delta_G\,\chi_G\,(\vec{r}_G) \;=\; E_G\,\chi_G\,(\vec{r}_G) \tag{2.81}$$

describes the motion of a free fictitious particle and has the solution

$$\chi_G\,(\vec{r}_G) \;=\; \frac{1}{(2\pi\hbar)^{3/2}}e^{\frac{i}{\hbar}\vec{p}_G\cdot\vec{r}_G} \tag{2.82}$$

whose energy is

$$E_G \;=\; \frac{\vec{p}_G^{\,2}}{2M} \geq 0 \tag{2.83}$$

(ii) The eigenvalue equation

$$\left[-\frac{\hbar^2}{2\mu}\Delta + V(\vec{r})\right]\omega_r(\vec{r}) = E_r\omega_r(\vec{r}) \tag{2.84}$$

describes the behavior of the two interacting particles in the center of mass frame (which is equivalent to a single fictitious relative particle in central potential).

The interaction depends only on the distance between the particles $\left|\vec{r}_1 - \vec{r}_2\right|$ and not on the direction of $\vec{r}_1 - \vec{r}_2$.

The relative particle is subject to a central potential $V(\vec{r})$.

The total angular momentum of the system of two real particles is given as

$$\hat{\vec{J}} = \hat{\vec{L}}_1 + \hat{\vec{L}}_2 \tag{2.85}$$

$$\hat{\vec{L}}_1 = \hat{\vec{R}}_1 \times \hat{\vec{P}}_1 \tag{2.86}$$

$$\hat{\vec{L}}_2 = \hat{\vec{R}}_2 \times \hat{\vec{P}}_2 \tag{2.87}$$

and it can be written as

$$\hat{\vec{J}} = \hat{\vec{L}}_G + \hat{\vec{L}} \tag{2.88}$$

where

$$\hat{\vec{L}}_G = \hat{\vec{R}}_G \times \hat{\vec{P}}_G \tag{2.89}$$

$$\hat{\vec{L}} = \hat{\vec{R}} \times \hat{\vec{P}} \tag{2.90}$$

such that $\left[\hat{\vec{L}}_G, \hat{\vec{L}} \right] = 0$ and their components satisfy the standard angular momentum commutation relations.

C. THE HYDROGEN ATOM

1. Introduction

The hydrogen atom is the system of two particles: proton, with mass m_p and charge q, and electron, with mass m_e and charge $-q$

$$m_p = 1.7 \times 10^{-27} \text{ kg} \tag{2.91}$$
$$m_e = 0.9 \times 10^{-30} \text{ kg} \tag{2.92}$$
$$q = 1.6 \times 10^{-19} \text{ Coulomb} \tag{2.93}$$

interacting via the Coulomb potential

$$V(r) = -\frac{q^2}{4\pi\epsilon_0}\frac{1}{r} = -\frac{e^2}{r} \tag{2.94}$$

which depends on the distance r between proton and electron

The Hydrogen atom in the center of mass coordinate system:

Classically the Hamiltonian for the relative motion of the particles is

$$\mathcal{H}(\vec{r}, \vec{p}) = \frac{\vec{p}^2}{2\mu} - \frac{e^2}{r} \qquad (2.95)$$

with the reduced mass

$$\mu = \frac{m_e m_p}{m_e + m_p} \simeq m_e \left(1 - \frac{m_e}{m_p}\right) \qquad (2.96)$$

where $m_e/m_p \approx 1/1800$, so the center of mass is in almost in the same place as the proton and thus the relative particle can be identified with the electron.

2. The Bohr model

Niels Bohr postulated fixed classical orbits for motion of electron around proton

$$E \; = \; \frac{1}{2}\mu v^2 - \frac{e^2}{r} \tag{2.97}$$

The force, given as $\mu \times$ acceleration of circular motion, equals to the Coulomb force

$$\frac{\mu v^2}{r} \; = \; \frac{e^2}{r^2} \tag{2.98}$$

The quantization condition introduced empirically by Bohr is

$$\mu v r = n\hbar; \quad \text{where } n \text{ is a positive integer} \qquad (2.99)$$

implies (homework: derive these relations)

$$E_n = -\frac{1}{n^2}E_I \qquad (2.100)$$

$$(2.101)$$

$$r_n = n^2 a_0 \qquad (2.102)$$

$$(2.103)$$

$$v_n = \frac{1}{n}v_0 \qquad (2.104)$$

The values of the introduced constants are

$$E_I = \frac{\mu e^4}{2\hbar^2} \tag{2.105}$$

$$a_0 = \frac{\hbar^2}{\mu e^2} \tag{2.106}$$

$$v_0 = \frac{e^2}{\hbar} \tag{2.107}$$

$$E_I \simeq 13.6 \text{ eV} \tag{2.108}$$

$$a_0 \simeq 0.52 \text{ Å} \tag{2.109}$$

The Bohr model yielded the correct values for the energy levels of the hydrogen atom. Moreover, it provides correct value of the ionization energy E_I and the Bohr radium a_0 and thus correctly characterizes atomic dimensions.

However, its classical character prevents it to be the ultimate theory of the hydrogen atom which would be free of internal inconsistencies.

Quantum theory of the hydrogen atom is free of these inconsistencies.

3. Quantum mechanical theory of the hydrogen atom

Relative motion of the proton and electron is studied in the center of mass in which the eigenvalue equation has the following form

$$\left[-\frac{\hbar^2}{2\mu}\Delta - \frac{e^2}{r} \right] \varphi(\vec{r}) \;=\; E\varphi(\vec{r}) \tag{2.110}$$

The eigenfunctions

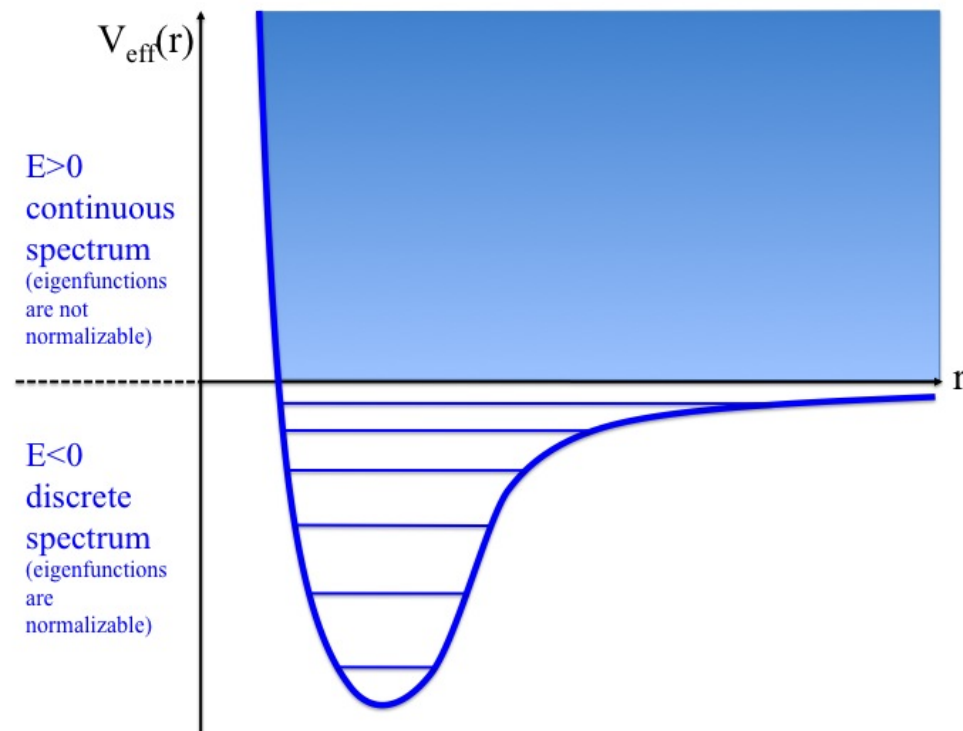$$\varphi_{k,l,m}(\vec{r}) \;=\; \frac{1}{r}u_{k,l}(r)Y_l^m(\theta,\phi) \tag{2.111}$$

where $u_{k,l}(r)$ satisfies

$$\left[-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{r} \right] u_{k,l}(r) = E u_{k,l}(r) \qquad (2.112)$$

and the condition

$$u_{k,l}(0) = 0 \qquad (2.113)$$

The spectrum include dicrete and continuous parts, for example:

a. CHANGE OF VARIABLES

It is convenient to work with dimensionless quantities which we define as

$$\rho = r/a_0 \tag{2.114}$$

$$\lambda_{k,l} = \sqrt{-E_{k,l}/E_I} \tag{2.115}$$

The radial eigenvalue equation becomes

$$\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{2}{\rho} - \lambda_{k,l}^2\right] u_{k,l}(\rho) = 0 \tag{2.116}$$

b. SOLVING THE RADIAL EQUATION

We will seek the solution by expanding $u_{k,l}(\rho)$ in power series but first we will have a look at its asymptotic behavior.

α. Asymptotic behavior

For $\rho \to \infty$ the terms in the eigenvalue equation above proportional to $1/\rho$ and $1/\rho^2$ are much smaller than $\lambda_{k,l}^2$, so we can neglect them obtaining

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - \lambda_{k,l}^2\right] u_{k,l}(\rho) = 0 \qquad (2.117)$$

At this limit the solution therefore is $e^{\pm\rho\lambda_{k,l}}$.

If we consider the full eigenvalue equation, including the terms proportional to $1/\rho$ and $1/\rho^2$, we expect the solution to be given by $e^{\pm\rho\lambda_{k,l}}$ multiplied by a power of ρ.

We note the solution $e^{+\rho\lambda_{k,l}}$ must be rejected as it is not bounded at $\rho \to \infty$, and we are left with $e^{-\rho\lambda_{k,l}}$ as the only physically acceptable asymptotic solution.

The solution we are looking for is thus given as

$$u_{k,l}(\rho) \;=\; e^{-\rho\lambda_{k,l}}y_{k,l}(\rho) \tag{2.118}$$

where $y_{k,l}(\rho)$ must satisfy the equation

$$\left\{\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - 2\lambda_{k,l}\frac{\mathrm{d}}{\mathrm{d}\rho} + \left[\frac{2}{\rho} - \frac{l(l+1)}{\rho^2}\right]\right\} y_{k,l}(\rho) \;=\; 0 \tag{2.119}$$

and the condition

$$y_{k,l}(0) \;=\; 0. \tag{2.120}$$

β. Solutions in the form of power series

We expect the solution in the following form

$$y_{k,l}(\rho) \;=\; \rho^s \sum_{q=0}^{\infty} c_q \rho^q \tag{2.121}$$

where by definition

$$c_0 \;\neq\; 0 \tag{2.122}$$

The condition $y_{k,l}(0) = 0$ implies that $s > 0$. We first calculate the derivatives

$$\frac{\mathrm{d}}{\mathrm{d}\rho} y_{k,l}(\rho) \;=\; \sum_{q=0}^{\infty} (q+s) c_q \, \rho^{q+s-1} \tag{2.123}$$

$$\frac{\mathrm{d}^2}{\mathrm{d}\rho^2} y_{k,l}(\rho) \;=\; \sum_{q=0}^{\infty} (q+s)(q+s-1) c_q \, \rho^{q+s-2} \tag{2.124}$$

and we substitute these into the eigenvalue equation

$$\left\{ \frac{\mathrm{d}^2}{\mathrm{d}\rho^2} - 2\lambda_{k,l}\frac{\mathrm{d}}{\mathrm{d}\rho} + \left[\frac{2}{\rho} - \frac{l(l+1)}{\rho^2} \right] \right\} y_{k,l}(\rho) \;\; = \;\; 0 \qquad (2.125)$$

to get

$$\sum_{q=0}^{\infty}(q+s)(q+s-1)c_q\,\rho^{q+s-2} - 2\lambda_{k,l}\sum_{q=0}^{\infty}(q+s)c_q\,\rho^{q+s-1}$$

$$+ \left[\frac{2}{\rho} - \frac{l(l+1)}{\rho^2} \right]\sum_{q=0}^{\infty}c_q\,\rho^{q+s} = 0 \qquad (2.126)$$

In order for this equation to be zero, all its coefficients (at each power of ρ) must be zero.

The lowest order term is ρ^{s-2}. By taking its coefficient as zero we get (homework)

$$[-l(l + 1) + s(s - 1)]\, c_0 \;=\; 0 \tag{2.127}$$

which is satisfied, since $c_0 \neq 0$, by the following relations

$$\begin{cases} s = l + 1 \\ s = -l \end{cases} \tag{2.128}$$

and we choose as physically acceptable the condition

$$s = l + 1$$

(the other solution would be diverging for $\rho \to 0$).

By setting the coefficients of the general term in ρ^{q+s-2} we obtain the recurrence (homework)

$$q(q + 2l + 1)c_q = 2\Big[(q + l)\lambda_{k,l} - 1\Big]c_{q-1} \qquad (2.129)$$

If we fix c_0, we can calculate using this recursion all the other coefficients of the series c_1, c_2, ... c_q.

Since $c_q/c_{q-1} \to 0$ as $q \to \infty$, the series is convergent for all q.

Thus we have determined, for any value of $\lambda_{k,l}$, the solution of the eigenvalue equation for $y_{k,l}(\rho)$ with the condition $y_{k,l}(0) = 0$.

c. ENERGY QUANTIZATION. RADIAL FUNCTIONS

We require the preceding solution to have correct, i.e. physically acceptable, asymptotic behavior for $q \to \infty$. In this limit, the equation

$$q(q + 2l + 1)c_q \;\; = \;\; 2\Big[(q + l)\lambda_{k,l} - 1\Big]c_{q-1} \qquad (2.130)$$

reduces to

$$q^2 c_q \;\; \sim \;\; 2q\lambda_{k,l}c_{q-1} \qquad (2.131)$$

which implies that

$$\frac{c_q}{c_{q-1}} \underset{q \to \infty}{\sim} \frac{2\lambda_{k,l}}{q} \qquad (2.132)$$

Now consider

$$e^{2\rho\lambda_{k,l}} = \sum_{q=0}^{\infty} d_q \rho^q \qquad (2.133)$$

where

$$d_q = \frac{\left(2\lambda_{k,l}\right)^q}{q!} \qquad (2.134)$$

This implies that

$$\frac{d_q}{d_{q-1}} = \frac{2\lambda_{k,l}}{q} \qquad (2.135)$$

That is the series for $y_{k,l}(\rho)$ being considered behaves like $e^{2\rho\lambda_{k,l}}$ and thus

$$u_{k,l}(\rho) \quad = \quad e^{-\rho\lambda_{k,l}}y_{k,l}(\rho) = e^{+\rho\lambda_{k,l}} \tag{2.136}$$

which is not physically acceptable.

Consequently, we must reject all cases in which the expansion

$$y_{k,l}(\rho) \quad = \quad \rho^s \sum_{q=0}^{\infty} c_q \rho^q \tag{2.137}$$

is an infinite series.

That is the only possible values of $\lambda_{k,l}$ are those for which the expansion above reduces to a polynomial.

$u_{k,l}$ is than physically acceptable since its asymptotic behavior is dominated by $e^{-\rho\lambda_{k,l}}$.

Therefore we need an integer k such that *r.h.s.* of the equation

$$q(q + 2l + 1)c_q \;=\; 2\Big[(q + l)\lambda_{k,l} - 1\Big]c_{q-1} \tag{2.138}$$

goes to zero as $q = k$. Then $c_q = 0$ for $q \geq k$.

For fixed l, we label the corresponding values of $\lambda_{k,l}$ by this integer ($k \geq 1$ as c_0 never goes to zero).

By the equation above we have

$$\lambda_{k,l} \;=\; \frac{1}{k + l} \tag{2.139}$$

For a given l, the only negative energies possible are

$$E_{k,l} = \frac{-E_I}{(k+l)^2}; \qquad k = 1, 2, 3, \ldots \tag{2.140}$$

$y_{k,l}(\rho)$ is therefore a polynomial whose term of the lowest order is ρ^{l+1} and whose term of the highest order is ρ^{k+l}.

The various coefficients can be calculated in terms of c_0 by the recursion

$$c_q = -\frac{2(k-q)}{q(q+2l+1)(k+l)} c_{q-1} \tag{2.141}$$

or alternatively by the formula

$$c_q = (-1)^q \left(\frac{2}{k+l}\right)^q \frac{(k-1)!}{(k-q-1)!} \frac{(2l+1)!}{q!(q+2l+1)!} c_0 \tag{2.142}$$

$u_{k,l}(\rho)$ is then given as $e^{-\rho\lambda_{k,l}}y_{k,l}(\rho)$ and c_0 is determined by the normalization condition

$$\int_0^\infty dr \left|u_{k,l}(r)\right|^2 = 1 \tag{2.143}$$

Finally we obtain the true functions $R_{k,l}(r)$ by $\dfrac{u_{k,l}(r)}{r}$.

Examples:

$$R_{k=1,l=0}(r) = 2\left(a_0\right)^{-3/2}e^{-r/a_0} \tag{2.144}$$

$$R_{k=2,l=0}(r) = 2\left(2a_0\right)^{-3/2}\left(1 - \frac{r}{2a_0}\right)e^{-r/2a_0} \tag{2.145}$$

$$R_{k=1,l=1}(r) = \left(2a_0\right)^{-3/2}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-r/2a_0} \tag{2.146}$$

4. Discussion of the results

a. ORDER OF MAGNITUDE OF ATOMIC PARAMETERS

The ionization energy E_I and the Bohr radius a_0 play important roles in giving an order of magnitude of the energies and spatial extensions of the wavefunctions

$$E_I = \frac{1}{2}\alpha^2\mu c^2 \tag{2.147}$$

$$a_0 = \frac{1}{\alpha}\lambda_C \tag{2.148}$$

where

$$\alpha = \frac{e^2}{\hbar c} = \frac{q^2}{2\pi\epsilon_0\hbar c} \simeq \frac{1}{137} \tag{2.149}$$

$$\lambda_C = \frac{\hbar}{\mu c} \simeq \frac{\hbar}{m_e c} \simeq 3.8 \times 10^{-3}\ \text{Å} \tag{2.150}$$

The Bohr radius a_0 is about $100\times$ the Compton wavelength λ_C of electron.

The ionization potential $E_I \approx 10^{-5} - 10^{-4} \, \mu c^2$ where the rest-mass energy

$$\mu c^2 \approx m_e c^2 \quad \simeq \quad 0.51 \times 10^6 \text{ eV} \tag{2.151}$$

which implies

$$E_I \quad \ll \quad m_e c^2 \tag{2.152}$$

This condition justifies our choice of non-relativistic Schrödinger equation to describe the hydrogen atom.

b. ENERGY LEVELS

α. Possible values of the quantum numbers; degeneracies

For a fixed l, there exist an inifinite number of possible energy values with $k = 1, 2, 3...$ and each of these is at least $(2l+1)$-fold degenerate. This is the *essential* degeneracy. recall that this follows from the fact that the radial wavefunction depends on l but not on m.

There exist *accidental* degeneracies when $E_{k,l} = E_{k',l'}$ $(l \neq l')$ if $k + l = k' + l'$.

$E_{k,l}$ depends on $(k + l)$ rather than k and l separately (only for hydrogen). We set

$$n = k + l \tag{2.153}$$

which we call *principal* quantum number.

The energy levels are then

$$E_n = -\frac{1}{n^2}E_I \tag{2.154}$$

Since $k \geq 1$, there is only a finite number of the values of l associated with the same n, that is, if n is fixed $l = 0, 1, ..., n - 1$.

The shell n contains n subshells, each with $(2l + 1)$ orthogonal states.

The total degeneracy of the level n is given as

$$g_n = \sum_{l=0}^{n-1}(2l + 1) = 2\frac{(n - 1)n}{2} + n = n^2 \qquad (2.155)$$

β. Spectroscopic notation

The energy shells are labelled by $n = 1, 2..$or by the letters $K, L, ...$ The subshells are labelled by the corresponding number n followed by l in the spectroscopic notation:
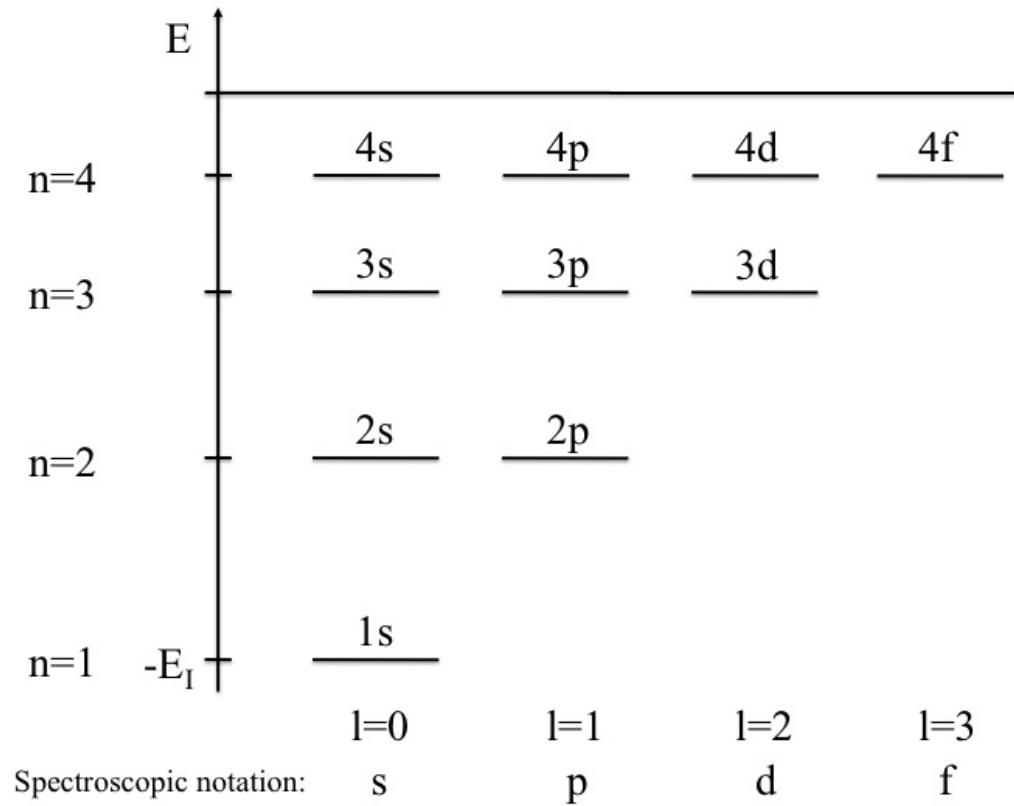
$$
\begin{aligned}
l &= 0 &\leftrightarrow&\quad s \\
l &= 1 &\leftrightarrow&\quad p \\
l &= 2 &\leftrightarrow&\quad d \\
l &= 3 &\leftrightarrow&\quad f \\
l &= 4 &\leftrightarrow&\quad g \\
&\ \vdots & &\quad \vdots
\end{aligned}
\tag{2.156}
$$

$$\text{alphabetical order} \tag{2.157}$$

Example:

The ground state is K shell with $1s$ subshell, the first excited state is L shell with the subshells $2s$ and $2p$, etc.
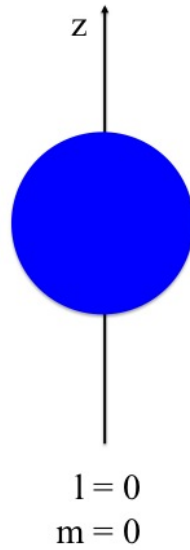
The hydrogen atom energy levels

c. WAVE FUNCTIONS

Wavefunctions are labeled by the quantum numbers n, l, and m which uniquely characterize the eigenfunctions $\phi_{n,l,m}(\vec{r})$ of the C.S.C.O. $\hat{H}$, $\hat{L}^2$, and $\hat{L}_z$.

α. *Angular dependence*

the angular dependence is given by the spherical harmonics $Y_l^m(\theta, \phi)$

β. Radial dependence

Since $n = k + l$, we can label the radial wavefunctions by n and l (rather than k and l)

$$R_{k=1,l=0} \equiv R_{n=1,l=0}; \tag{2.158}$$

$$R_{k=2,l=0} \equiv R_{n=2,l=0}; \tag{2.159}$$

$$R_{k=1,l=1} \equiv R_{n=2,l=1} \tag{2.160}$$

the behavior of $R_{n,l}(r)$ around $r = 0$ is r^l, so only states belonging to s subshell ($l = 0$) give a nonzero probability of presence at the origin.

The greater l is, the larger is the region around proton with negligible probability of finding an electron. This has interesting physical consequences (hyperfine structure,...).
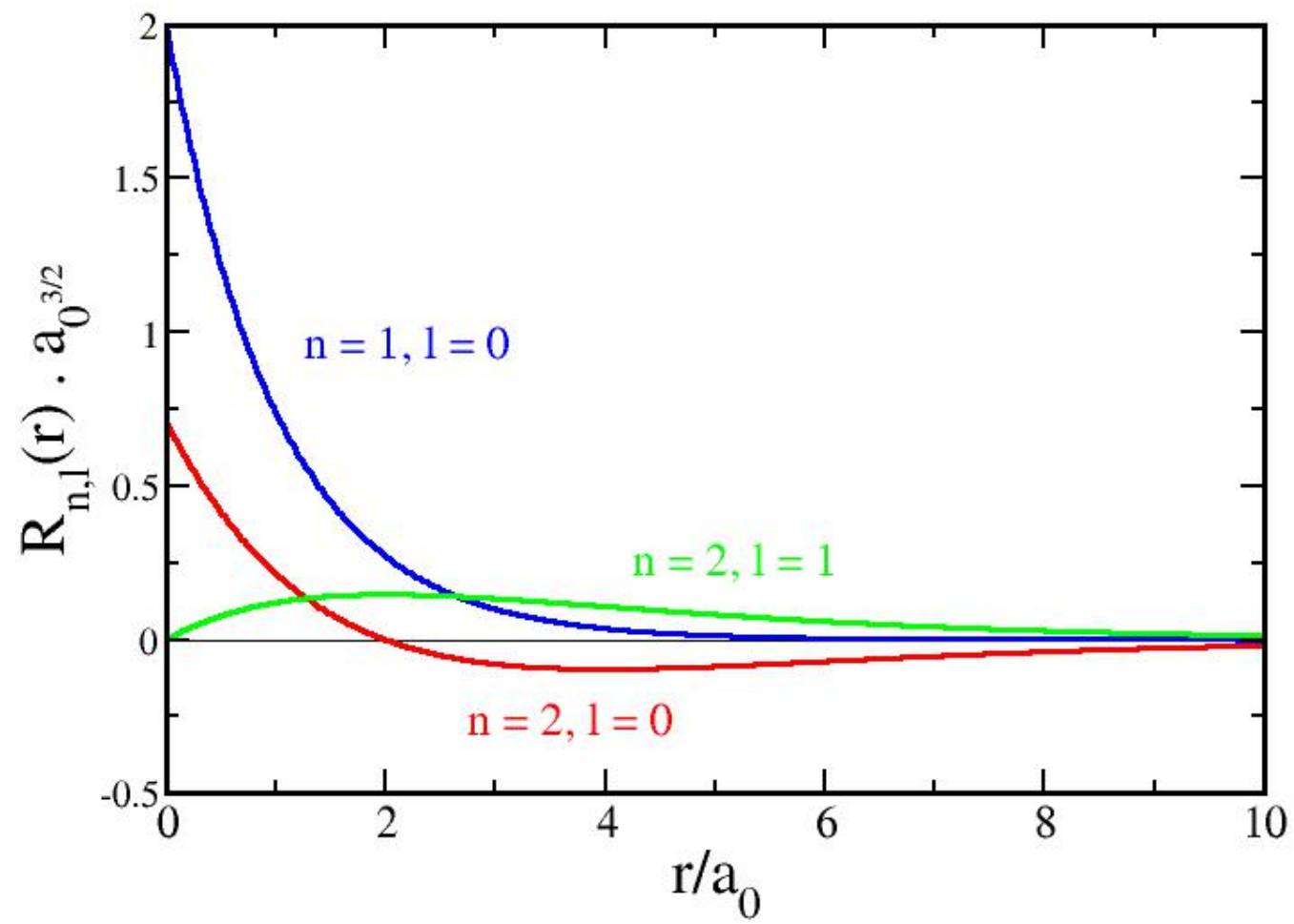
γ. Formula for successive Bohr radii $r_n = n^2 a_0$

Let us consider various states with $l = n - 1$, and calculate variation of probability density with r for each of the preceding levels in an infinitesimal solid angle $d\Omega$ about a fixed direction of polar angles θ and ϕ

$$
\begin{aligned}
d^3 \mathcal{P}(r, \theta, \phi) &= \left| \varphi_{n,l,m}(r, \theta, \phi) \right|^2 r^2 dr d\Omega & (2.161) \\
&= \left| R_{n,l}(r) \right|^2 r^2 dr \times \left| Y_l^m(\theta, \phi) \right|^2 d\Omega & (2.162)
\end{aligned}
$$

where the term $\left| R_{n,l}(r) \right|^2 r^2 dr$ is the probability density between r and $r + dr$.

The condition $l = n - 1$ implies $k = n - l = 1$, so $R_{n,l}(r)$ contains only one term in $(r/a_0)^{n-1}$ and the probability density

$$f_n(r) = \frac{r^2}{a_0^2} \left[\left(\frac{r}{a_0} \right)^{n-1} e^{-r/na_0} \right]^2 \tag{2.163}$$

$$= \left(\frac{r}{a_0} \right)^{2n} e^{-2r/na_0} \tag{2.164}$$

this function has a maximum for

$$r = r_n = n^2 a_0 \tag{2.165}$$

which is the Bohr radii of the Bohr orbit corresponding to the energy E_n.

The wavefunctions of the lowest energy levels:

$1s$ level	$\varphi_{n=1,l=0,m=0} = \dfrac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$
$2s$ level	$\varphi_{n=2,l=0,m=0} = \dfrac{1}{\sqrt{8\pi a_0^3}} \left(1 - \dfrac{r}{2a_0}\right) e^{-r/2a_0}$
$2p$ level	$\varphi_{n=2,l=1,m=1} = -\dfrac{1}{8\sqrt{\pi a_0^3}} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta e^{i\phi}$ $\varphi_{n=2,l=1,m=0} = \dfrac{1}{4\sqrt{2\pi a_0^3}} \dfrac{r}{a_0} e^{-r/2a_0} \cos\theta$ $\varphi_{n=2,l=1,m=-1} = \dfrac{1}{8\sqrt{\pi a_0^3}} \dfrac{r}{a_0} e^{-r/2a_0} \sin\theta e^{-i\phi}$

THE ISOTROPIC THREE-DIMENSIONAL HARMONIC OSCILLATOR

(Complement B_{VII})

Our objectives are:

1. Solving the radial equation

2. Finding energy levels and stationary wave functions

Consider a spinless particle of mass μ subjected to the potential

$$V(x, y, z) \;=\; \frac{1}{2}\mu\left[\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right] \tag{2.166}$$

where

$$\omega_x = \omega_y = \omega_z \;=\; \omega \tag{2.167}$$

The Hamiltonian is given as

$$\hat{H} \;=\; \frac{\hat{\vec{P}}^2}{2\mu} + V\left(\hat{\vec{R}}\right) \tag{2.168}$$

The standard solution relies on separating x, y and z coordinates in the coordinate representation and solving the system in a way analogous to solving the harmonic oscillator in one dimension. The energy eigenvalues found are

$$E_n \;=\; \left(n + \frac{3}{2}\right)\hbar\omega \tag{2.169}$$

their degree of degeneracy is

$$g_n \;=\; \frac{1}{2}(n+1)(n+2) \tag{2.170}$$

and the eigenfunctions associated with the eigenvalue E_n, $n = n_x = n_y = n_z$, are

$$\varphi_{n_x,n_y,n_z}(x,y,z) \;=\; \left(\frac{\beta^2}{\pi}\right)^{3/4}\frac{1}{\sqrt{2^{n_x+n_y+n_z}n_x!n_y!n_z!}}e^{-\frac{\beta^2}{2}\left(x^2+y^2+z^2\right)} \tag{2.171}$$

$$\times\; H_{n_x}(\beta x)H_{n_y}(\beta y)H_{n_z}(\beta z) \tag{2.172}$$

where

$$\beta = \sqrt{\frac{\mu\omega}{\hbar}}, \tag{2.173}$$

$$n = n_x + n_y + n_z \tag{2.174}$$

Since the oscillator is isotropic we can use the spherical coordinates; the potential becomes a central potential

$$V(\vec{r}) \to V(r) = \frac{1}{2}\mu\omega^2 r^2 \tag{2.175}$$

C.S.C.O. is given by $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$.

1. Solving the radial equation

$$\left[-\frac{\hbar^2}{2\mu} \frac{1}{r} \frac{\mathrm{d}^2}{\mathrm{d}r^2} r + \frac{1}{2}\mu\omega^2 r^2 + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R_{k,l}(r) \;=\; E_{k,l} R_{k,l}(r) \qquad (2.176)$$

$$R_{k,l}(r) \;=\; \frac{1}{r} u_{k,l}(r) \qquad (2.177)$$

$$\varepsilon_{k,l} \;=\; \frac{2\mu E_{k,l}}{\hbar^2} \qquad (2.178)$$

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \beta^4 r^2 - \frac{l(l+1)}{r^2} + \varepsilon_{k,l} \right] u_{k,l}(r) \;=\; 0 \qquad (2.179)$$

We also have to add the condition

$$u_{k,l}(0) \;=\; 0 \tag{2.180}$$

to get the physically acceptable behavior of the wavefunction at the origin $r = 0$.

Considering the asymptotic behavior for $r \to \infty$ simplifies the eigenvalue equation:

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \beta^4 r^2\right] u_{k,l}(r) \;\overset{\simeq}{\underset{r\to\infty}{}}\; 0 \tag{2.181}$$

whose two solutions are $e^{\beta^2 r^2/2}$ and $e^{-\beta^2 r^2/2}$, however only the latter is physically acceptable as it does not diverges for large r.

We therefore seek the eigenfunctions in the form

$$u_{k,l}(r) \;=\; e^{-\beta^2 r^2/2} y_{k,l}(r) \tag{2.182}$$

$y_{k,l}(r)$ must satisfy

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2}y_{k,l} - 2\beta^2 r \frac{\mathrm{d}}{\mathrm{d}r}y_{k,l} + \left[\varepsilon_{k,l} - \beta^2 - \frac{l(l+1)}{r^2}\right]y_{k,l}(r) = 0 \qquad (2.183)$$

$$y_{k,l}(0) = 0 \qquad (2.184)$$

We expand $y_{k,l}(r)$ into a power series

$$y_{k,l}(r) \;\; = \;\; r^s \sum_{q=0}^{\infty} a_q r^q \qquad (2.185)$$

where a_0 is by definition nonzero

$$a_0 \;\; \neq \;\; 0 \qquad (2.186)$$

We substitute $y_{k,l}(r)$ into the eigenvalue equation. The term of the lowest order is r^{s-2}. Its coefficient is zero if

$$[s(s-1) - l(l+1)]\, a_0 \;=\; 0 \tag{2.187}$$

which implies the physically acceptable (to satisfy $y_{k,l}(0) = 0$) solution

$$s \;=\; l+1 \tag{2.188}$$

The next term in the expansion is r^{s-1} and its coefficient equals to

$$[s(s+1) - l(l+1)]\, a_1 \tag{2.189}$$

Since s is fixed already, the coefficient can go to zero only if

$$a_1 \;=\; 0 \tag{2.190}$$

The general term in r^{q+s} is zero if

$$\left[(q+s+2)(q+s+1) - l(l+1)\right] a_{q+2} \tag{2.191}$$
$$+ \left[\varepsilon_{k,l} - \beta^2 - 2\beta^2(q+s)\right] a_q = 0 \tag{2.192}$$

or

$$(q+2)(q+2l+3)\, a_{q+2} = \left[(2q+2l+3)\beta^2 - \varepsilon_{k,l}\right] a_q \tag{2.193}$$

This recursion implies that all coefficients a_q of rank $q = odd$ are zero.

Coefficients of even rank are proportional to a_0.

If no coefficients on *r.h.s.* go to zero, then $y_{k,l}(r)$ has the form of an implicit power series for which

$$\frac{a_{q+2}}{a_q} \underset{q\to\infty}{\sim} \frac{2\beta^2}{q} \tag{2.194}$$

The behavior of the coefficients is the same as for the exponential function

$$e^{\beta^2 r^2} = \sum_{p=0}^{\infty} c_{2p} r^{2p} \tag{2.195}$$

with

$$c_{2p} = \frac{\beta^{2p}}{p!} \tag{2.196}$$

Then

$$\frac{c_{2p+2}}{c_{2p}} \underset{p \to \infty}{\sim} \frac{2\beta^2}{p} \tag{2.197}$$

and in this case the $y_{k,l}(r)$ would be dominated by $e^{\beta^2 r^2}$ which is not physically acceptable.

Physically acceptable cases are those in which there exists an even integer k, positive or zero, such that

$$\varepsilon_{k,l} = (2k + 2l + 3)\beta^2 \tag{2.198}$$

so the coefficients of the recursion of even rank greater than k are zero. Consequently the series for $y_{k,l}(r) = r^s \sum_{q=0}^{\infty} a_q r^q$ must be finite and thus reduces to a polynomial, and the radial function $u_{k,l}(r)$ decreases exponentially as r goes to infinity.

2. Energy levels and stationary wave functions

The energy eigenvalues are

$$E_{k,l} = \hbar\omega\left(k + l + \frac{3}{2}\right) \qquad (2.199)$$

where k is an even positive integer or zero. Since $E_{k,l}$ actually depends on

$$n = k + l \qquad (2.200)$$

we can rewrite it as

$$E_{k,l} = \hbar\omega\left(n + \frac{3}{2}\right) \qquad (2.201)$$

where k is an even positive integer or zero and l is any non-negative integer.

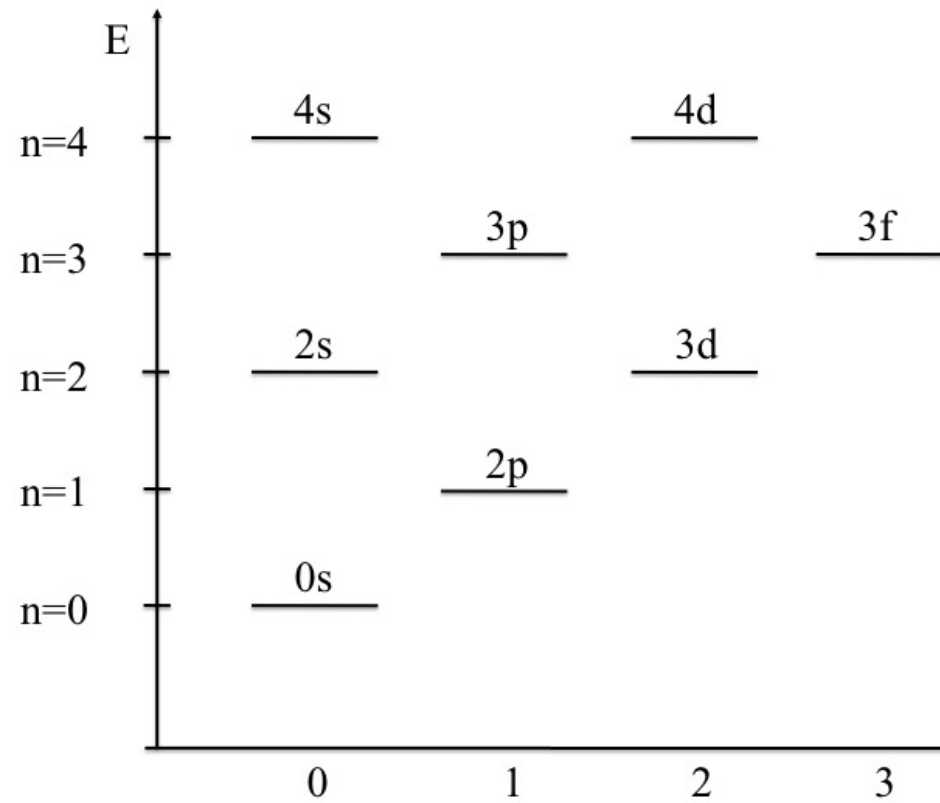Thus n can take only integral values, positive or zero:

$$(k, l) = (0, n), (2, n - 2), \ldots, (n - 2, 2), (n, 0) \qquad \text{if } n \text{ is even} \qquad (2.202)$$

$$(k, l) = (0, n), (2, n - 2), \ldots, (n - 3, 3), (n - 1, 1) \qquad \text{if } n \text{ is odd} \qquad (2.203)$$

This implies the values of l:

$$\begin{aligned}
n = 0 : \quad & l = 0 \\
n = 1 : \quad & l = 1 \\
n = 2 : \quad & l = 0, 2 \\
n = 3 : \quad & l = 1, 3 \\
n = 4 : \quad & l = 0, 2, 4
\end{aligned} \qquad (2.204)$$

$$E_n = (n + \tfrac{3}{2})\hbar\omega = \tfrac{3}{2}\hbar\omega, \tfrac{5}{2}\hbar\omega, \tfrac{7}{2}\hbar\omega, \tfrac{9}{2}\hbar\omega, \tfrac{11}{2}\hbar\omega, \ldots$$

For each pair (k, l) there exist one and only one radial wavefunction $u_{k,l}(r)$.

There is $(2l + 1)$ eigenfunctions of $\hat{H}$, $\hat{L}^2$ and $\hat{L}_z$:

$$\varphi_{k,l,m}(\vec{r}) \;=\; \frac{1}{r}u_{k,l}(r)Y_l^m(\theta, \phi) \tag{2.205}$$

and consequently the degree of degeneracy

$$g_n = \sum_{l=0,2,\ldots,n} (2l + 1) \qquad \text{if } n \text{ is even} \tag{2.206}$$

$$g_n = \sum_{l=1,3,\ldots,n} (2l + 1) \qquad \text{if } n \text{ is odd} \tag{2.207}$$

This specifically yields

$$\text{for even } n: \quad g_n = \sum_{p=0}^{n/2} (4p + 1) = \frac{1}{2}(n + 1)(n + 2) \qquad (2.208)$$

$$\text{for odd } n: \quad g_n = \sum_{p=0}^{(n-1)/2} (4p + 3) = \frac{1}{2}(n + 1)(n + 2) \qquad (2.209)$$

For each of the pair (k, l), we have one and only one $u_{k,l}(r)$ (to within a factor a_0), and thus $(2l + 1)$ common eigenfunctions of $\hat{H}$ and $\hat{L}^2$ with eigenvalues E_n and $l(l + 1)\hbar^2$.

Example: wavefunctions for the three lowest energy levels

(i) $E_0 = \frac{3}{2}\hbar\omega$

$$k = l = 0 \qquad (2.210)$$

$y_{0,0}(r)$ reduces to $a_0 r$ where a_0 is determined by normalization

$$\varphi_{0,0,0}(\vec{r}) = \left(\frac{\beta^2}{\pi}\right)^{3/4} e^{-\beta^2 r^2/2} \qquad (2.211)$$

The ground state is non-degenerate.

(ii) the first excited state $E_1 = \frac{5}{2}\hbar\omega$

This state is three-fold degenerate

$$\begin{cases} k = 0 \\ l = 1 \end{cases} \tag{2.212}$$

with $y_{0,1}(r) = a_0 r^2$.

The three eigenfunctions are

$$\varphi_{0,1,m}(\vec{r}) = \sqrt{\frac{8}{3}} \frac{\beta^{3/2}}{\pi^{1/4}} \beta r e^{-\beta^2 r^2/2} Y_1^m(\theta, \phi) \qquad m = 1, 0, -1 \tag{2.213}$$

The spherical harmonics $Y_l^m(\theta, \phi)$ are such that

$$rY_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}}z \tag{2.214}$$

$$\frac{r}{\sqrt{2}}\left[Y_1^{-1} - Y_1^1\right] = \sqrt{\frac{3}{4\pi}}x \tag{2.215}$$

$$\frac{r}{\sqrt{2}}\left[Y_1^{-1} + Y_1^1\right] = -i\sqrt{\frac{3}{4\pi}}y \tag{2.216}$$

and the Hermite polynomial of order 1 is

$$H_1(u) = 2u \tag{2.217}$$

so that the functions $\varphi_{0,1,m}$ are related to the functions φ_{n_x,n_y,n_z} of the basis given by the Hermite polynomials (Eq. (2.172)) by the equations

$$\varphi_{n_x=0,n_y=0,n_z=1} = \varphi_{k=0,l=1,m=0} \tag{2.218}$$

$$\varphi_{n_x=1,n_y=0,n_z=0} = \frac{1}{\sqrt{2}}\left[\varphi_{k=0,l=1,m=-1} - \varphi_{k=0,l=1,m=1}\right] \tag{2.219}$$

$$\varphi_{n_x=0,n_y=1,n_z=0} = \frac{i}{\sqrt{2}}\left[\varphi_{k=0,l=1,m=-1} + \varphi_{k=0,l=1,m=1}\right] \tag{2.220}$$

(iii) the second excited state $E_2 = \frac{7}{2}\hbar\omega$

This state is six-fold degenerate, and k and l can take the values

$$k = 0, \quad l = 2 \tag{2.221}$$
$$k = 2, \quad l = 0 \tag{2.222}$$

The function $y_{0,2}(r)$ is $a_0 r^3$, and the function $y_{2,0}(r)$

$$y_{2,0}(r) \;=\; a_0 r \left[1 - \frac{2}{3}\beta^2 r^2 \right] \tag{2.223}$$

the six basis functions in the eigenspace associated with E_2 are of the form

$$\varphi_{0,2,m}(\vec{r}) = \sqrt{\frac{16}{15}}\frac{\beta^{3/2}}{\pi^{1/4}}\beta^2 r^2 e^{-\beta^2 r^2/2} Y_2^m(\theta,\phi) \tag{2.224}$$

$$\varphi_{2,0,0}(\vec{r}) = \sqrt{\frac{3}{2}}\frac{\beta^{3/2}}{\pi^{1/4}}\left(1 - \frac{2}{3}\beta^2 r^2\right)\beta^2 r^2 e^{-\beta^2 r^2/2} \tag{2.225}$$

Through the explicite expressions for the spherical harmonics and the Hermite polynomials we can prove the relations:

$$\varphi_{k=2,l=0,m=0} = -\frac{1}{\sqrt{3}}\left[\varphi_{n_x=2,n_y=0,n_z=0} + \varphi_{n_x=0,n_y=2,n_z=0} + \varphi_{n_x=0,n_y=0,n_z=2}\right]$$

$$\frac{1}{\sqrt{2}}\left[\varphi_{k=0,l=2,m=2} + \varphi_{k=0,l=2,m=-2}\right] = -\frac{1}{\sqrt{2}}\left[\varphi_{n_x=2,n_y=0,n_z=0} - \varphi_{n_x=0,n_y=2,n_z=0}\right]$$

$$\frac{1}{\sqrt{2}}\left[\varphi_{k=0,l=2,m=2} - \varphi_{k=0,l=2,m=-2}\right] = i\varphi_{n_x=1,n_y=1,n_z=0}$$

$$\frac{1}{\sqrt{2}}\left[\varphi_{k=0,l=2,m=1} - \varphi_{k=0,l=2,m=-1}\right] = -\varphi_{n_x=1,n_y=0,n_z=1}$$

$$\frac{1}{\sqrt{2}}\left[\varphi_{k=0,l=2,m=1} + \varphi_{k=0,l=2,m=-1}\right] = -i\varphi_{n_x=0,n_y=1,n_z=1}$$

$$\varphi_{k=0,l=2,m=0} = \frac{2}{\sqrt{3}}\left[\varphi_{n_x=0,n_y=0,n_z=2} - \frac{1}{2}\varphi_{n_x=2,n_y=0,n_z=0} - \frac{1}{2}\varphi_{n_x=0,n_y=2,n_z=0}\right]$$