The Schrödinger Equation in 3D : HYDROGEN ATOM

(Bransden book.)

In various occasions earlier, for example in the square well potential, Harmonic oscillators, we had briefly introduced the Schrödinger equation in 3-dimensions. Mainly we focussed on the cases where the 3D Schrödinger equation separates into three independent Schrödinger equations for each dimensions by virtue of the separation of variable method applicable where the potential term $V(\vec{r})$ does not involve any cross term between different coordinates. Then the total solution was just a product of three solutions of individual dimensions. After a brief recapitulations of this case in cartesian coordinates, we will move to spherical harmonics case and discuss the result for free particle via separation of radial and angular variables, and finally we we talk about hydrogen atom case under a central potential $V(r)$. Heleum atom will be discussed in next course where the difficulties to deal with two or more particles will be introduced.

The Schrödinger equation (time independent) that we want to solve is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right]\Psi(\vec{r}) = E\,\Psi(\vec{r}) \quad ---(1)$$

(A) Cartesian Coordinates: As we have learned before also that its always a choice of what coordinate system we want to use and we choose a suitable coordinate system based on observation of the potential energy term $V(\vec{r})$ and its symmetry. For a potential $V(\vec{r})$ in which all three three cartesian coordinates do not mix, its needless to say that cartesian coordinates will simplify the problem. The K.E. term is always separable in any coordinates, since the Laplacian is $\nabla^2 = \nabla_x^2 + \nabla_y^2 + \nabla_y^2$ is separable. So, when $V(\vec{r}) = V(x) + V(y) + V(z)$, the Hamiltonian splits into:

$$H = \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right] + (x \to y) + (x \to z)$$
$$= H_x + H_y + H_z. \quad ---(2).$$

Similarly, the Schrödinger equation (eigenvalue equation being a 2nd order PDE) is also solvable through a separation of variable

$$\Psi(\vec{r}) = X(x)\,Y(y)\,Z(z). \quad ---(3).$$

This gives three independent Schrödinger equations

$$H_x X(x) = E_x X(x) \;;\; H_y Y(y) = E_y Y(y) \;;\; H_z (z) = E_z Z(y) \quad ---(4)$$

where the total energy eigenvalue of the product wavefunction is $E = E_x + E_y + E_z$ --- (5). (Note that $E_{x,y,z}$ are just different symbols, E_x does <u>not</u> imply its a function of x, its constant in space).

(Aa) Free particles: $V(x) = 0$.

For free particles, we know the solution of eq (4), which are the plane wave solutions in all directions:

$$X(x) = A e^{ik_x x} + B e^{-ik_x x}, \text{ where } k_x = \sqrt{\frac{2mE_x}{\hbar^2}} \text{ and so on.}$$

We take $E_x \geq 0$ which gives oscillatory or scattering solutions and $E_x < 0$ gives decaying or amplifying solutions, but we discard the amplifying solutions because they are not normalizable or unphysical. The plane wave solutions are also not normalizable, but we put it in a box or imposed periodic boundary condition to normalize them. We will revisit that here.

Then the total wavefunction is

$$\psi_{\vec{k}}(\vec{r}) = X(x)\, Y(y)\, Z(z)$$
$$= C\, e^{i\vec{k}\cdot\vec{r}} \quad ---- (5)$$

where $\vec{k} = (k_x, k_y, k_z)$ span over $\pm$ ranges, and C is the normalization constant. The total energy is

$$E_{\vec{k}} = E_x + E_y + E_z = \frac{\hbar^2}{2m} k_x^2 + k_y^2 + k_z^2 = \frac{\hbar^2 k^2}{2m} \quad -- (6).$$

Its clear from eq (6) that there is an infinite degeneracy associated with every energy eigenvalues. Because a given k can be obtained by various combinations of k_x, k_y & k_z, and those solutions are linearly independent. The energy spectrum is so far continuous, but the wave function is not yet normalizable. As we have seen earlier, in the process of choosing only normalizable solutions or putting the boundary conditions to normalize them, we obtain discrete set of solutions.

- Normalization of the wave function in eq (5).

$$\int \psi^*_{\vec{k}}(\vec{r})\, \psi_{\vec{k}'}(\vec{r})\, d^3r = \int \psi^*_{k_x}(x)\, \psi_{k_x'}(x)\, dx \int (\,)\, dy \int (\,)\, dz$$

$$= \delta(k_x - k_x')\, \delta(k_y - k_y')\, \delta(k_z - k_z')$$

$$= \delta^3(\vec{k} - \vec{k}') \quad \text{---} \; (7).$$

A notation for three dimensional delta function, given by

$$\delta^3(\vec{k} - \vec{k}') = \left[\frac{1}{(2\pi)} \int e^{i(k_x - k_x')x}\, dx\right] \left[x \to y\right] \left[x \to z\right].$$

$$= \frac{1}{(2\pi)^3} \int e^{i(\vec{k} - \vec{k}')\cdot\vec{r}}\, d^3r \quad \text{---} \; (8).$$

Therefore, the normalization 'c' in eq (5) is $c = \frac{1}{\sqrt{(2\pi)^3}}$

And we obtain the normalization in real space as

$$\int \psi^*_{\vec{k}}(\vec{r})\, \psi_{\vec{k}}(\vec{r}\,')\, d^3k = \frac{1}{(2\pi)^3}\int e^{i\vec{k}\cdot(\vec{r}-\vec{r}\,')}\, d^3k$$

$$= \delta^3(\vec{r}-\vec{r}\,') \quad \cdots (9).$$

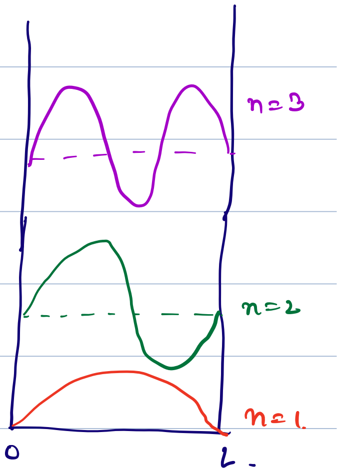
We can see that the R.H.S of eq (9) is not 1 as we expect for a normalizable solution. So, what we did earlier is that we imposed a boundary condition that pretend the free particle is confined in a box of length L_x, L_y, L_z such that only those wave vectors are allowed which the corresponding wavelength is such that we have nodes of the plane waves at the two boundaries. The other, although somewhat equivalent, boundary condition is the periodic boundary condition, which says, only those wavevectors are allowed for which the wave function is periodic in length L_x, L_y, L_z as $\psi(x+L_x, y+L_y, z+L_z) = \psi(x, y, z)$. Solving for this boundary condition, we get $k_x = \frac{2\pi}{L_x} n_x$, $k_y = \frac{2\pi}{L_y} n_y$, $k_z = \frac{2\pi}{L_z} n_z$, where n_i are integers. The energy is $E = \frac{\hbar^2 k^2}{2m} = \frac{h^2 k^2}{2mL^2}(n_x^2 + n_y^2 + n_z^2)$, for $L = L_x = L_y = L_z$. We impose the integration limit in eq (7) from $r = 0$ to L, which gives

$$\int_0^L dx \int_0^L dy \int_0^L dz\, |\psi_k(\vec{r})|^2 = 1. \Rightarrow \boxed{\psi_k(\vec{r}) = \frac{1}{\sqrt{L^3}}\, e^{i\vec{k}\cdot\vec{r}}}.$$

$$--- (10).$$

(A6) Particle in a 3D box

We had studied earlier particle in a 1D box, which can now be trivially generalized to 3D box.



As we saw in 1D case also, particle in a box is the same boundary condition as the box normalization we mentioned above. The potential is zero inside the box and infinity at the walls, which makes the wavefunction to vanish there.. This means $X(x) = 0$ at $x \leq 0$ & $x \geq L$, and the same for $Y(y)$ & $Z(z)$. This puts further constraint on the allowed values of k that we obtained above for the periodic boundary condition, that $k_x = \frac{\pi}{L} n_x$, $k_y = \frac{\pi}{L} n_y$ & $k_z = \frac{\pi}{L} n_z$, where $n = 1, 2, 3 \ldots$ Then we obtained the wavefunction as $X_{n_x}(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi}{L} n_x x\right)$ and similar for Y & Z. The full wavefunction is

$$\psi_{n_x n_y n_z}(\vec{r}) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{\pi}{L} n_x x\right) \sin\left(\frac{\pi}{L} n_y y\right) \sin\left(\frac{\pi}{L} n_z z\right) \quad \text{---} (11)$$

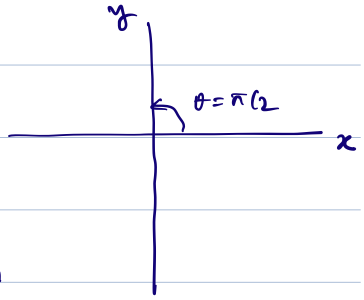
with energy eigenvalues

$$E_{n_x, n_y, n_z} = \frac{\hbar^2 \pi^2}{2mL^3}\left(n_x^2 + n_y^2 + n_z^2\right) \quad \text{---} (12).$$

$$= \frac{\hbar^2 \pi^2}{2mL^3} n^2 \quad \text{where } n = \sqrt{n_x^2 + n_y^2 + n_z^2} = \text{integer}$$

H.W: It's now easy to evaluate the degeneracy by counting for a given value of n how many combinations of (n_x, n_y, n_z) we can obtain.

This degeneracy is clearly a manifestation of the <u>discrete</u> rotational symmetry of the box when $L_x = L_y = L_z$. Lets say we make a rotation about the z-axis by angle $\theta = m\pi/2$, where m is an integer, the wavefunction $\Psi(\vec{r})$ remains invariant. Note that the Hamiltonian being a free particle is invariant under any continuous rotation, but the boundary condition is only invariant under discrete rotation, and hence the wavefunction is. So, for $\theta = \pi/2$ rotation about the z-axis $X(x) \to Y(y)$ and $Y(y) \to X(-x)$ and $Z(z) \to Z(z)$. But now we see a problem that $X(-x) = -X(x)$ according to the wavefunction form in eq (11). So, we actually don't get back to the same wavefunction, but obtain a phase difference of π. To realize the discrete rotational symmetry, we should shift the axis of rotation with respect to the center of the box, or equivalently the center of reference frame can be shifted to the center of box as we did in chapter 3. Since the result, symmetries etc should be independent of the choice of reference frame, the lesson we learn is that the choice of coordinate system can sometimes makes certain symmetry manifest or hidden. In the new coordinate, the wavefunction will also have parity, i.e., $x \to -x$, or $y \to -y$, $z \to -z$, the wavefunction is symmetric. Parity here is nothing but a discrete rotation by $\theta = \pi$, and so on.



(Ac) 3D Harmonic Oscillator:

We also talked briefly about a 3D simple Harmonic oscillator in the corresponding chapter. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2.$$

$$= \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}m\omega_x^2 x^2\right) + (y) + (z).$$

$$= H_x + H_y + H_z. \quad \text{---(13)}$$

where the frequency of oscillation along three directions are $\omega_\mu = \sqrt{\frac{k_\mu}{m}}$. We have already solved each of H_μ earlier in two different methods and now we just multiply their wavefunction and add their eigen values.

$$\psi_{n_x,n_y,n_z}(\vec{r}) = N_{n_x}N_{n_y}N_z\, e^{-\frac{1}{2}\alpha_x x^2 - \frac{1}{2}\alpha_y y^2 - \frac{1}{2}\alpha_z z^2}$$

$$\times H_{n_x}(\alpha_x x)\, H_{n_y}(\alpha_y y)\, H_{n_z}(\alpha_z z) \quad \text{--(14)}$$

where $\alpha_\mu = \left(\frac{m k_\mu}{\hbar^2}\right)^{1/4}$ and $N_\mu = \left(\frac{\alpha_\mu}{\sqrt{\pi}\, 2^{n_\mu} n_\mu!}\right)^{1/2}$.

= variance of the w.f along the μ^{th} direction for the g.s.

The energy $E_{n_x,n_y,n_z} = (n_x+\frac{1}{2})\hbar\omega_x + (n_y+\frac{1}{2})\hbar\omega_y + (n_z+\frac{1}{2})n_z$

$= (n_x + n_y + n_z + 3/2)\hbar\omega$ when $\omega_x = \omega_y = n_z = \omega$.

$= (n + \frac{3}{2})\hbar\omega$ --(15)

where $n_x, n_y, n_z \in 0, 1, 2, \cdots$. Clearly again, for a given value of n, there will be degeneracy determined by the # of combinations of (n_x, n_y, n_z).

Continuous Rotational Symmetry : Unlike the particle in a cubic box which had the discrete rotational symmetry, the 3D S.H.O with isotropic spring constants $K_x = K_y = K_z = k$ enjoys a continuous rotational symmetry. The potential energy

$$V(\vec{r}) = \frac{1}{2} k (x^2 + y^2 + z^2) = \frac{1}{2} k r^2, \quad \cdots (16)$$

is clearly independent of the angular variable. Therefore, the theory has full 3D continuous rotational symmetry. This means $[H, L_\mu] = 0$, where L_μ are the three angular momentum components. But since L_μ do not commute, we found in the previous section that there are two operators L^2, L_z which commute with each other and we have obtain their simultaneous eigenstate $|l\, m\rangle$ to denote the eigenstate of the Hamiltonian. Now, since the Hilbert space dimension of the energy eigenstates must be the same, therefore, the Hilbert space in the previous description of $|n_x n_y n_z\rangle$ must coincide with that of $|l m\rangle$. Therefore, the degeneracy of the $|n_x n_y n_z\rangle$ basis must also coincide with the degeneracy of the $|l m\rangle$ states. Since H commutes with all three L_μ components, therefore we anticipate that all m-multiplets of a given l values must be degenerate. This is indeed the case that all the degenerate energy eigenstates $|n_x n_y n_z\rangle$ can be grouped into different angular momentum states of distinct l-values with $(2l+1)$-fold degeneracy. Is it all true? Are we not missing something? Notice the mismatch in the number of degrees of freedom (i.e, the quantum numbers).

n	$E_n(\hbar\omega)$	$(n_x\ n_y\ n_z)$	Degeneracy	$\neq (2l+1)$	l	m
0	$\frac{3}{2}$	$(0\ 0\ 0)$	1	1	0	0
1	$\frac{5}{2}$	$(0\ 0\ 1)$	3	3	1	-1
		$(0\ 1\ 0)$				0
		$(1\ 0\ 0)$				1
2	$7/2$	$(0\ 0\ 2)$	6	6	$5/2$	$-5/2$
		$(0\ 2\ 0)$				$-3/2$
		$(2\ 0\ 0)$				$-1/2$
		$(0\ 1\ 1)$				$1/2$
		$(1\ 0\ 1)$				$3/2$
		$(1\ 1\ 0)$				$5/2$

We see that trouble starts arising from the 2nd excited states that if we want to map to all energy eigenstates to distinct orbital angular states, we see that we are not getting a simple integer values of l, but a integer and half-integer values. Therefore, it suggests that all components of the orbital angular momentum are not conserved. Also the mapping of different (n_x, n_n, n_z) values. This is because the number operators $\hat{n}_\mu$ do not commute with the angular momentum L_μ. and hence the above conjecture that angular momentum states are also the energy eigenstates is not correct. The problem lies in the fact that in the angular momentum basis we are only looking into two angular degrees of freedom, while in the number operator basis we looked into all three cartesian coordinates and via the restrictions that only normalizable solutions along all three directions are allowed. This makes the energy quantized and integer values of n_x, n_y, n_z arose. In the spherical coordinates, we have only looked into the two angular variables and studied their quantization. We have not yet studied whether the radial part of the wavefunction is all normalizable or not. In fact we will discover below that the restriction on the normalizibility along r gives a quantum number (also denoted by n) which has to be account for in addition to l, m to denote all the energy eigenstates as $\psi_{nlm}(r,\theta,\phi)$. Then we will get a complete matching between $\psi_{nlm}(r,\theta,\phi) \rightarrow \psi_{n_x n_y n_z}(x,y,z)$. Then the number of degrees of freedom, which is the number of quantum numbers matches on both sides. Its not an hard-and-fast rule that the number of quantum numbers have to match. Sometimes quantum numbers are also associated with different conserved operators, such as number operators in the case of Harmonic oscillator, or angular momentum L^2, L_z etc. But here the quantum numbers are associated with normalizability in 3D spatial domain. Since the number of orthogonal unit vectors remain same, so their quantum numbers too. The same quantum number n also arises for Hydrogen atom, in fact, for any central field potential $V(r)$ which is rotationally invariant.

B. Spherical Coordinates & Central Potential

In this section, we will study the same Schrödinger equation in spherical coordinates (r, θ, ϕ), but only restrict ourselves to the central potential $V(r)$. Because, for central field potential, its more justified to switch to the spherical coordinates to take advantage of the rotational symmetry of the Theory. The Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$$

$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \underbrace{\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \underbrace{\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}}_{\frac{1}{\hbar^2 r^2\sin^2\theta}L_z^2}}_{-\frac{\vec{L}^2}{\hbar^2 r^2}}\right] + V(r). \qquad \text{--- (17).}$$

- One thing we notice in eq(17) is that the three coordinates are *not* separable in this case. More appropriately, we will see below that, the two angular variables (θ, ϕ) are not separable from each other, while r-variable will be separable. (This is actually due to the fact that the generators of the rotations L_μ are not all independent, but related to each other by a commutation relation that we saw in the previous chapter). [Therefore, much like what we did earlier in the cartesian coordinate case of $\psi_{n_x n_y n_z}(x,y,z) = X_{n_x}(x)\, Y_{n_y}(y)\, Z_{n_z}(z)$ where the quantum numbers n_x, n_y, n_z obtained by only considering normalizable solutions in the corresponding x, y, z direction, a similar approach of $\Psi_{n_r n_\theta n_\varphi}(r,\theta,\varphi) = R_{n_r}(r)\,\Theta_{n_\theta}(\theta)\,\Phi_{n_\varphi}(\varphi)$ is not going to work here.]

- But we already gained some insight in the previous chapter that there however two operators $\vec{L}^2$, L_z which commute with each other and give two quantum numbers (l,m) for their simultaneous eigenstates $|lm\rangle$. We had also learned that the projection of this abstract eigenket in the (θ,φ) coordinates gives the wave function $Y_{lm}(\theta,\varphi) = \langle\theta,\varphi|lm\rangle$ which are the well known spherical harmonics. Can we use this wavefunction $Y_{lm}(\theta,\varphi)$ for our present Hamiltonian in case of $\Theta_{n_\theta}(\theta)\,\Phi_{n_\varphi}(\varphi)$ wavefunctions? Of course! Because the Hamiltonian H commutes with both $\vec{L}^2$ & L_z:

$$[H,\vec{L}^2] = [H,L_z] = 0 \quad \text{---} \quad (18).$$

So, the Hamiltonian and $\vec{L}^2$, L_z share the same eigenfunctions and we write

$$\Psi_{n_r lm} = G_{n_r lm}(r,\theta,\varphi)\,Y_{lm}(\theta,\varphi) \quad \text{--} \quad (19).$$

Notice that we have not simply written $R_{n_r}(r)\,Y_{lm}(\theta,\varphi)$ form, because we do not know yet whether after substituting $Y_{lm}(\theta,\varphi)$, the (θ,φ) & r variable will separate from each other, and even if it does, whether the r-part of the Hamiltonian, H_r, will or will not depend on the (l,m) quantum number. Therefore, eq (19) is so far the most general form of the wavefunction after taking into account the rotational invariance of the theory. The values of l & m are determined by the operators $\vec{L}^2$ & L_z and are already evaluated to be integer. The remaing quantum number n_r, which we will simply denote by n, is to be then evaluated by imposing the boundary condition on the radial part of the wavefunction, e.g. by demanding that only those solutions are allowed which gives normalizable (ei, decaying) solution in r.

Recaling that $\vec{L}^2 \psi_{nlm} = \vec{L}^2 G_{nlm} Y_{lm} = l(l+1)\hbar^2 \psi_{nlm}$, we apply the Hamiltonian H in eq(17) on the wavefunction in eq(19) we get the eigenvalue equation as

$$\left[-\frac{\hbar^2}{2m} \underbrace{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{l(l+1)\hbar^2}{2mr^2} - V(r)}_{H_r(r)}\right] G_{nlm}(r,\theta,\phi)\, Y_{lm}(\theta,\phi)$$

$$= E_{nlm}\, G_{nlm}(r,\theta,\phi)\, Y_{lm}(\theta,\phi). \quad \text{--- (20)}$$

It is now clear that in the form of the wavefunction written in eq(19), the r-variable separates out and hence Y_{lm} can be dropped out from both sides in eq(20) and we can also conclude that G does not depend on (θ,ϕ) and it depends on n (to be determined), l, but does not depend on 'm'. So, we define

$$G_{nlm}(r,\theta,\phi) \equiv R_{nl}(r) \quad \text{--- (21).}$$

and $$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_{lm}(\theta,\phi) \quad \text{--- (22).}$$

We have already evaluated $Y_{\ell m}(\theta,\phi)$ is the previous chapter to be the spherical harmonics, and ℓ, m are quantized because of the periodic boundary condition that $Y_{\ell m}(\theta,\phi+2\pi p) = Y_{\ell m}(\theta,\phi)$ and $Y_{\ell m}(\theta+\pi,\phi) = Y_{\ell m}(\theta,\phi)$. ℓ takes all positive integer values $0, 1, 2, \cdots$, which are the quantized total angular momentum associated with $\vec{L}^2$, while $m\hbar$ are the quantized angular momentum momentum for rotation about the z-axis (randomly chosen axis), and m takes values $-\ell, -\ell+1, \cdots \ell-1, \ell$, i.e., $(2\ell+1)$ values. $Y_{\ell m}$ are also orthonormalized, and form a Hilbert space by itself since L^2 & L_z are linear, Hermitian operators.

So, we only have to worry about the radial part of the wavefunction, its normalizability, and the quantum number 'n'. Clearly, $R_{n\ell}(r)$ depends on the form of the central field potential $V(r)$ and any associated boundary conditions.

- To make the differential equation look nicer we make a substitution:

$$R_{n\ell}(r) = \frac{u_{n\ell}(r)}{r} \quad \cdots (23).$$

This gives

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{n\ell}}{dr^2} + \underbrace{\left[\underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}}_{\text{called Centrifugal barrier}} + V(r)\right]}_{V_{eff}(r)} u_{n\ell} = E\, u_{n\ell} \quad \cdots (24).$$

We now have a 1D schrödinger equation that we solved earlier under an effective "potential" $V_{eff}(r) = \frac{l(l+1)\hbar^2}{2mr^2} + V(r)$.

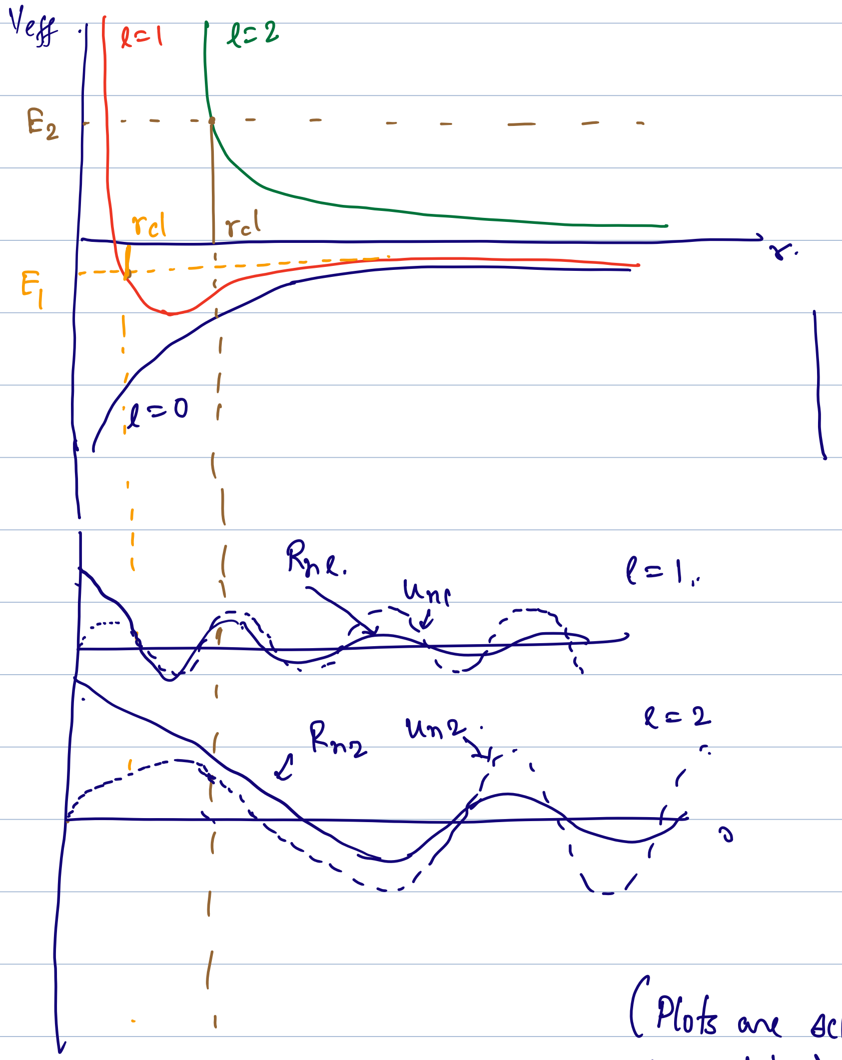
(Let me emphasize that although we denote it as "effective potential", but it should not be confused with the actual potential energy the particle experiences which is always $V(r)$. V_{eff} is defined just for mathematical analysis.). We also note that r takes only positive values.

- We want to look for normalizable solution such that $R_{nl}(r)$ does not diverge at both $r \to 0$ & $r \to \infty$. From eq (22), it's clear that $u_{nl}(r)$ then must go to zero as $r \to 0$, and it should go to zero faster than $r \to 0$ such that $R_{nl}(r)$ does not diverge as $r \to 0$. The same for $r \to \infty$ limit.

- Much like the 1D case, lets briefly discuss the behavior of solutions across "the classical turning point." Lets consider a Coulomb like interaction $V(r) = \pm \frac{a}{r}$ for attractive and repulsive cases. First of all, note that the "classical turning point" we are going to refer to for V_{eff} is again not the actual classical turning point w.r.to $V(r)$, but only for analogy and to predict the behavior of $u_{nl}(r)$ inside and outside this point.

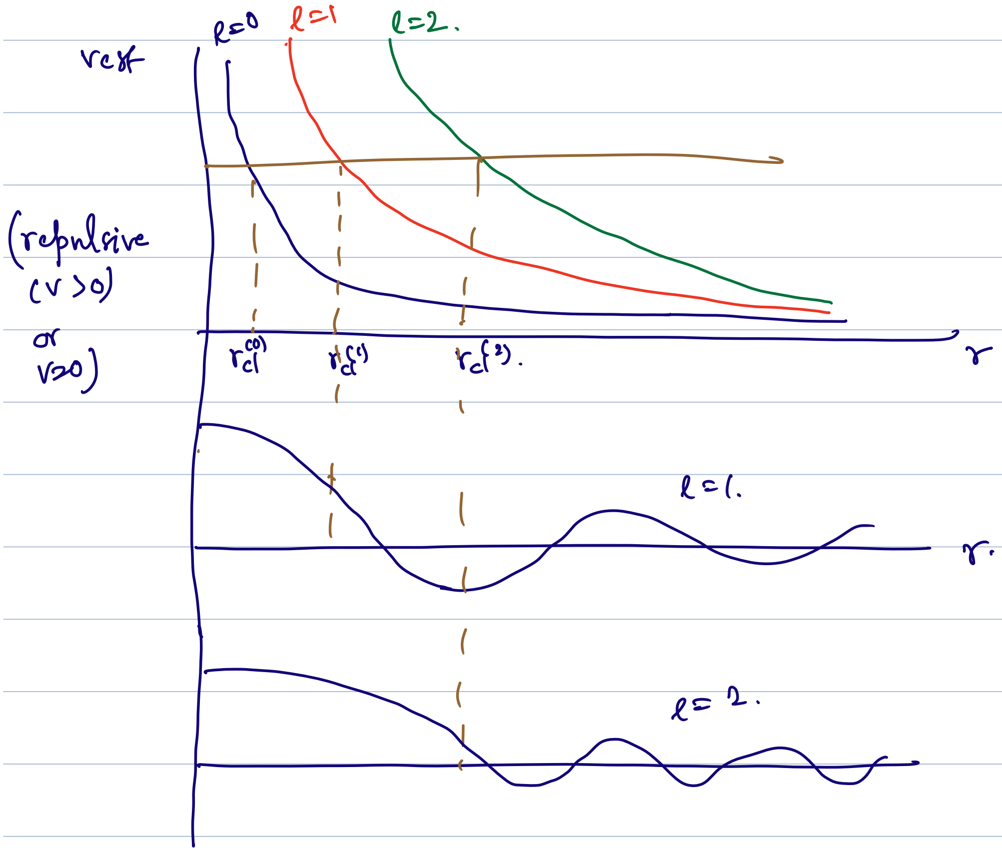
- Since eq (24) is a 2nd order PDE, we will have two linearly independent solutions. We will again consider the solutions which is not divergent both at $r \to 0$ & $r \to \infty$.

(Attractive $V(r)<0.$)



(Plots are schematic, some behavior near $r\to 0$ is not probably correct)

For attractive potential, there is a competition between $V(r)$ & centrifugal barrier $\ell(\ell+1)/r^2$, and that's important to obtain bound states for electrons to be confined with in an atom. As we see for some illustrative case above, for $\ell=1$, we have a bound state with negative total energy $E_1<0$ which however has to be greater than the minima of V_{eff}. Then when $E_1 = V_{eff}(r_{cl})$, we have the so called "classical turning point" like behavior. Inside this region, the K.E is negative, and hence we have decaying solution and outside the classical turning point we have scattering or oscillatory behavior of $u_{n\ell}(r)$. But thanks to the form $R_{n\ell}(r) = u_{n\ell}/r$, the actual radial wave function decays as $r \to \infty$. Therefore, we do not need to worry about its normalizibility, it will be normalizable.



For a repulsive potential or no potential form, there is no competition with the centrifugal barrier, because both have the same sign. Therefore, for any positive energy, we will have a bound state inside the so called "classical turning point", but a damped scattering/oscillatory behavior outside it. The solutions are normalizable.

(✱) We will consider four cases (a) Free particle where $V(r)=0$,
(b) Potential barrier / well like potential profile,
(c) Coulomb interaction $V(r) = -Ze^2/r$ and (d) spherical / isotropic Harmonic oscillator.

(Ba) Free Particle: $V(r) = 0$.

As we said, even for a free electron, there is a centrifugal barrier $\frac{\ell(\ell+1)\hbar^2}{2mr}$ under which the $u_{n\ell}(r)$ "wavefunction" has to be considered. We write eq (20) for $R_{n\ell}(r)$ as

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2} + k^2\right] R_{n\ell}(r) = 0. \quad \text{---} \quad (25)$$

where we have defined $E = \frac{\hbar^2 k^2}{2m}$.

- We rescale r to $\boxed{\rho = kr}$, which gives a spherical Bessel's differentential eq.

$$\left[\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} + \left(1 - \frac{\ell(\ell+1)}{\rho^2}\right)\right] R_{n\ell}(\rho) = 0. \quad \text{---} \quad (26).$$

The popular solutions of this differential eqn, that we solve in the mathematical physics course through series solution, has two linearly independent solutions :

Spherical Bessel functions: $j_\ell(\rho) = \sqrt{\frac{\pi}{2\rho}}\; J_{\ell+1/2}(\rho)$ ... (27a)

Spherical Neumann function: $n_\ell(r) = (-1)^{\ell+1}\sqrt{\frac{\pi}{2\rho}}\; J_{-\ell-1/2}(\rho)$ --(27b).

where $J_\ell(\rho)$ is the ordinary Bessel function of order ℓ. Eq (27) can also be expressed via differential eq as

$$j_\ell(\rho) = (-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\sin\rho}{\rho} \qquad n_\ell(\rho) = -(-\rho)^\ell \left(\frac{1}{\rho}\frac{d}{d\rho}\right)^\ell \frac{\cos\rho}{\rho}.$$

$$j_0(kr) = \frac{\sin kr}{kr}$$

$$j_1(kr) = \frac{\sin kr}{(kr)^2} - \frac{\cos kr}{kr}$$

$$j_2(kr) = \frac{3\sin kr}{(kr)^3} - \frac{3\cos kr}{(kr)^2} - \frac{\sin kr}{kr}$$

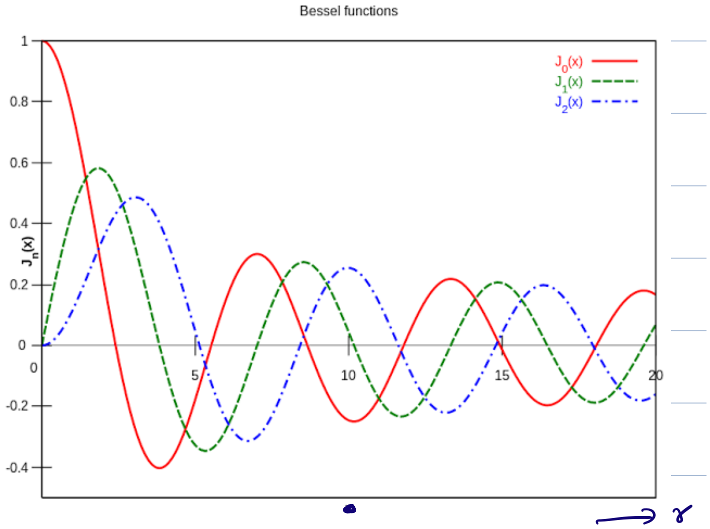
$n_l(\rho)$:

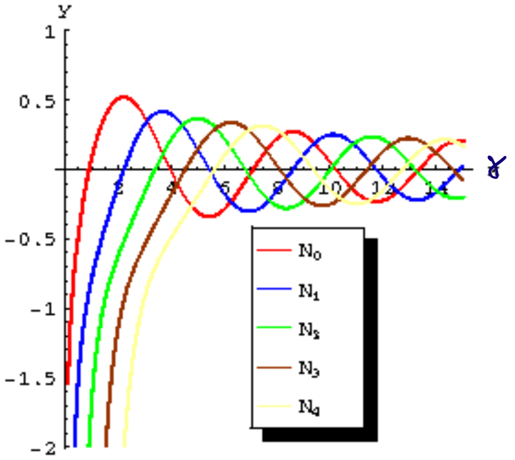
$$n_0(\rho) = -\frac{\cos\rho}{\rho}$$

$$n_1(\rho) = -\frac{\cos\rho}{\rho^2} - \frac{\sin\rho}{\rho}$$

$$n_2(\rho) = -\frac{3\cos\rho}{\rho^3} - \frac{3\sin\rho}{\rho^2} + \frac{\cos\rho}{\rho}$$

$\rho = kr.$





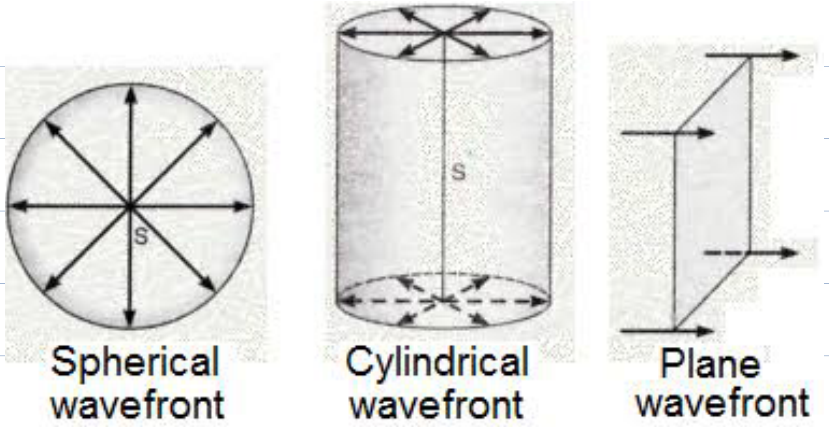
We notice that the Neumann functions have poles of order $(l+1)$ at $r=0$, and are therefore irregular functions, and not normalizable. The spherical Bessels functions $j_l(kr)$ are finite at $r=0$ and are regular and normalizable functions. Therefore, we only consider this solution and write

$$R_{nl}(r) = A\, j_l(kr) \quad --- (28).$$

we notice that $R_{nl}(r)$ for free particle has no n-dependence or one may say $n \equiv k \doteq$ quantum number as in the free electron case in the Cartesian coordinate. k can take any value between 0 to ∞ as in the case of cartesian coordinates for free electrons. The eigenenergy is $E_k = \hbar^2 k^2/2m$, which does not depend on l, m and hence is infinitely degenerate. The full wavefunction is then

$$\psi_{klm}(r,\theta,\phi) = A\, j_l(kr)\, Y_{lm}(\theta,\phi) \quad --- (29)$$

where A is the normalization constant. This is called spherical wave solution. Note that we are only talking about the magnitude of the momentum $k = \sqrt{k_x^2 + k_y^2 + k_z^2}$ in eq (29). For the spherical plane wave solution, all values of k is allowed and hence its not quantized as in the case of Cartesian coordinates. There is no lengthscale in the problem and hence position uncertainty Δr is infinity, while momentum $p_r \sim \hbar k$ is completely known, as we expect for the plane wave solution. Other two coordinates for spherical waves, i.e, θ, ϕ are also arbitrary as the corresponding conjugate variables $\bar{L}^2$ & L_z are completely known (eigenvalues l, m).



(Point source)

(Line Source)

(Source at infinity)

Expansion of Plane waves in Spherical Harmonics:

We had solved for the $\psi(\vec{r})$ in the Cartesian coordinates and obtained plane wave solution as $e^{i\vec{k}\cdot\vec{r}}$. The same wavefunction in the spherical coordinates give eq (29). Therefore, one can express $e^{i\vec{k}\cdot\vec{r}}$ in terms of spherical waves as

$$\langle\vec{p}|\vec{r}\rangle = e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} C_{lm}\, j_l(kr)\, Y_{lm}(\theta,\phi) \quad \text{---}(30a)$$

$$= \sum_{l=0}^{\infty} a_l\, j_l(kr)\, P_l(\cos\theta) \quad \text{---}(30b)$$

where C_{lm} & a_l are the expansion coefficients. Eq (30b) is obtained by summing over m- since j_l does not depend on m. $P_l(\cos\theta)$ is the Legendre polynomial introduced in the previous chapter. a_l can be deduced from normalization and one gets $a_l = (2l+1)i^l$. So, we have

$$\boxed{e^{i\vec{k}\cdot\vec{r}} = \sum_{l=0}^{\infty}(2l+1)\, i^l\, j_l(kr)\, P_l(\cos\theta)} \quad \text{---}(31).$$

(Bb) 3D Square well or Rather spherical well:

$$V(r) = -V_0 \quad \text{for } r < a$$
$$= 0 \quad \text{for } r > 0.$$

For $E_1 > |V_0|$, we have positive K.E. everywhere and we will have scattering/oscillatory solutions everywhere. So, lets not consider it. There is no lengthscale in this case.

For $-V_0 \le E_2 < 0$, We now have a length scale (like a classical turning pt) in the problem, i.e. 'a'.

For $r<a$, we have positive K-E., and we expect oscillatory/scattering solution.

For $r \geq a$, we have negative K.E. and hence imaginary wave vector $(k=i\kappa)$ which we denote as inverse decay length $\kappa \sim 1/a$. We have to match the two wavefunctions and their 1st derivatives. This puts restrictions on the values of the wave vector and hence on the allowed energy levels, and thereby we achieve quantization. The resulting wavefunction is called "wave packet". The uncertainty in position is expected to be $\sim a$ and the spread in k, $\Delta k \sim 1/a \sim k$.

- For $r<a$, we have the radial part of the Schrödinger eq

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+\frac{\ell(\ell+1)\hbar^2}{2m}\right]R_{n\ell}(r)=\frac{\hbar^2k^2}{2m}R_{n\ell}(r) \quad \text{--- (32a)}$$

where we define the decay constant $k=\sqrt{\frac{2m(E+V_0)}{\hbar^2}}$ --- (32b)

The solution is $R_{n\ell}(r)=A\,j_\ell(kr)$ --- (32c).

n quantum number $\equiv k$

- For $r>a$, we have decaying solution

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+\frac{\ell(\ell+1)\hbar^2}{2m}\right]R_{n\ell}(r)=-\frac{\hbar^2\kappa^2}{2m}R_{n\ell}(r) \quad \text{--- (33a)}$$

where $\kappa=\sqrt{-\frac{2mE}{\hbar^2}}$ --- (33b)

$=$ imaginary for $E>0$

The solution is $R_{n\ell}(r)=B\left[j_\ell(i\kappa r)+i\,\eta_\ell(i\kappa r)\right]$

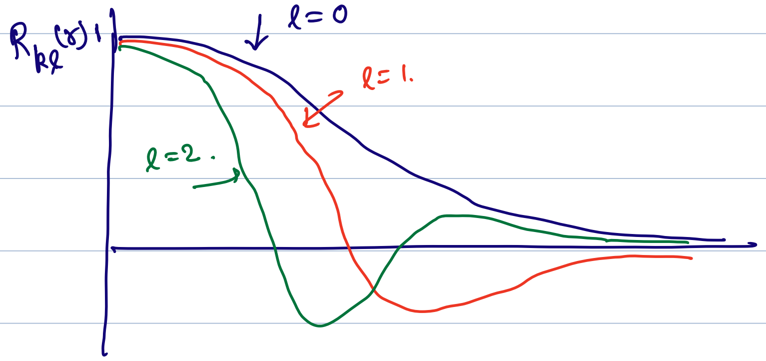
$=B\,h_\ell(i\kappa r)$ --- (33c)

where $h_\ell(i\kappa r)=j_\ell(i\kappa r)+i\,\eta_\ell(i\kappa r)$ is called the Hankel's function of first kind. Notice that here the Neumann function also contributes because this function was ruled out earlier since it has singularity at $r \to 0$. But now $r \to 0$ region is prohibited and hence η_ℓ is also an allowed solutions. Henkel function with imaginary argument has decaying solutions

$$h_0(i\kappa r) = -\frac{1}{\kappa r} e^{-\kappa r}$$
$$h_1(i\kappa r) = i\left(\frac{1}{\kappa r} + \frac{1}{\kappa^2 r^2}\right) e^{-\kappa r} \qquad -(34)$$
$$h_2(i\kappa r) = \left(\frac{1}{\kappa r} + \frac{3}{\kappa^2 r^2} + \frac{3}{\kappa^3 r^3}\right) e^{-\kappa r}$$

with a spread of the wavefunction roughly defined by the decay length κr.

- The energy eigenvalues will be quantized in which the restriction on the allowed values of k comes from the matching condition of the wavefunction & its first derivative at $r = a$. The wavefunction matching condition gives $\boxed{k \cot ka = -\kappa}$. We are not going to solve or discuss this solutions any further and only sketch some of the wave function:



(Bc) Hydrogen Atom

Finally we are going to study the motion of an electron under an attractive Coulomb interaction due to the nucleus of charge Ze, with $Z=1$ for the Hydrogen atom. The potential is

$$V(r) = -\frac{Ze^2}{(4\pi\epsilon_0)\, r} \qquad --- (35)$$

Here we consider the nucleus is at rest and hence we neglect its K-E term, only consider the K.E. of the electron. [A slightly more general formalism would be to consider the K-E of both the nucleus and electron as $-\frac{\hbar^2}{2M}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2$. Then since the only potential energy term is as in eq (35), which only depends on the relative distance between them r, therefore, we can go to the center of mass & relative coordinates as $\vec{R} = (\vec{r}_1 + \vec{r}_2)/2$ & $\vec{r} = (\vec{r}_1 - \vec{r}_2)/2$. Then the Hamiltonian becomes $-\frac{\hbar^2}{2M_{cm}}\nabla_R^2 - \frac{\hbar^2}{2M}\nabla_r^2 + V(r)$. We see that the center of mass coordinate, $\vec{R}$, becomes completely separable from the reduced coordinate $\vec{r}$, and the total wavefunction is $\psi(\vec{r}_1, \vec{r}_2) = \psi_{cm}(\vec{R})\, \psi_\mu(\vec{r})$. It's easy to see that $\psi_{cm}(\vec{R})$ has the spherical wave solution. We are here interested in finding $\psi_\mu(\vec{r})$. The Schrödinger equation for $\psi_\mu(\vec{r})$ is same as that of electron only except the electron mass m is replaced with the reduced mass $\mu = \frac{mM}{m+M} \approx m$ as $m \ll M$. So, we will just solve for the reduced mass μ with the rest same.]

- Hamiltonian of Hydroden atom $\left(\overset{\vec{r}_1}{\text{Nucleus}} + \overset{\vec{r}_2}{1 \text{ electron}}\right)$

$$\left[-\frac{\hbar^2}{2M}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\right]\psi(r_1, r_2) = E(r_1, r_2)$$

$$\underline{\vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2)}, \qquad \vec{r} = \frac{1}{2}(\vec{r}_1 - \vec{r}_2).$$

$$M_{cm} = \frac{M+m}{2} \qquad \frac{1}{\mu} = \frac{1}{M} + \frac{1}{m}.$$

$$\left[\underbrace{-\frac{\hbar^2}{2M_{cm}}\nabla_R^2}_{\text{CM cordinate.}} \underbrace{-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}}_{\text{relative cordinate}}\right]\psi(R, r) = E\psi(R, r)$$

$$\psi(R, r) = \underset{\substack{\uparrow \\ \text{not interested,} \\ \text{because we have} \\ \text{alread solved it above,}}}{\psi_{\text{Free}}(R)}\,\psi_{nlm}(r).$$

$$\boxed{\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi_{nlm}(\vec{r}) = E\,\psi_{nlm}(\vec{r})}$$

$$\psi_{nlm}(r) = R_{nl}(r)\,Y_{lm}(\theta, \phi)$$

$$R_{nl}(r) = \frac{u_{nl}(r)}{r}.$$

Lets go back to eq(24), and substitute for V(r),

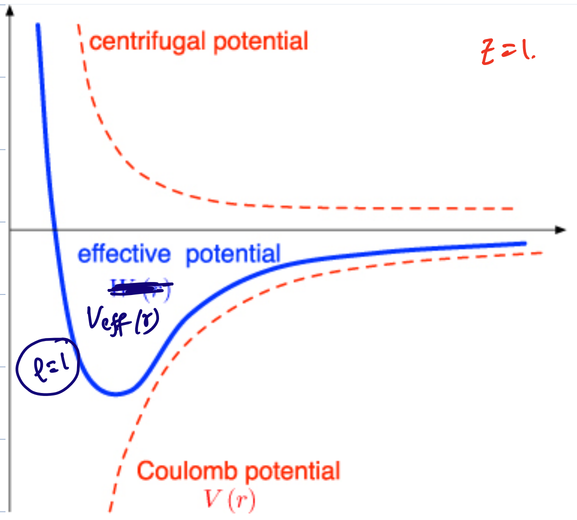
$$-\frac{\hbar^2}{2\mu}\frac{d^2u_{nl}}{dr^2}+\underbrace{\left[\frac{l(l+1)\hbar^2}{2mr^2}-\frac{Ze^2}{4\pi\epsilon_0 r}\right]}_{V_{eff}(r)}u_{nl}=E\,u_{nl}, \quad --- (36a)$$

which can be rewritten as

$$\frac{d^2}{dr^2}u_{nl}(r)-\frac{2\mu}{\hbar^2}V_{eff}(r)\,u_{nl}(r)-\frac{2\mu}{\hbar^2}E\,u_{nl}(r)=0 \quad --(36b)$$

Dim in $\frac{1}{L^2}$ $=\frac{1}{a^2}K^2$, $K=$ dimensionless.

Eq (36b) takes the form of an 1D Schrödinger equation, except r goes from 0 to ∞. Lets take a look at the Veff potential:



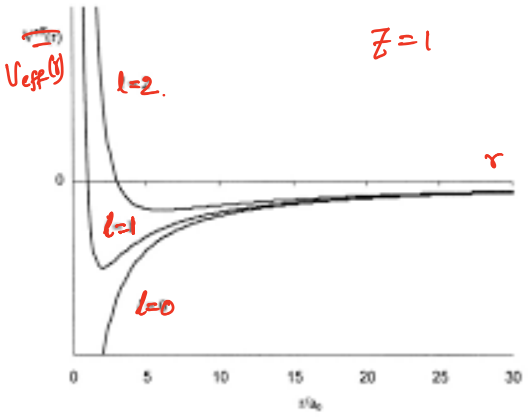
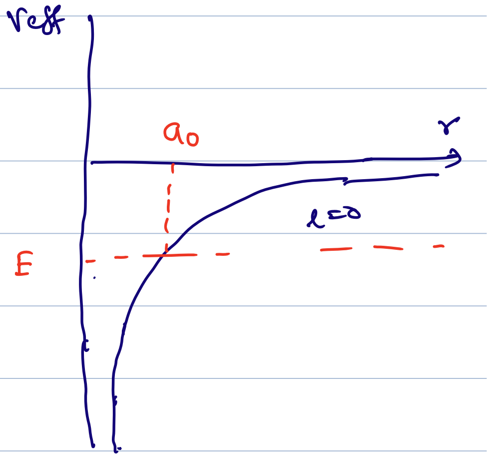


Figure 8-3. The effective potential (Equation 8-15) for a hydrogen atom is shown for an $l = 0$, $l = 1$, and $l = 2$ orbital. For $l = 0$, there is no repulsive potential and the attractive potential continues to increase (more negative) at small radial distances, r. For $l \neq 0$, the repulsive potential dominates at small radial distances.

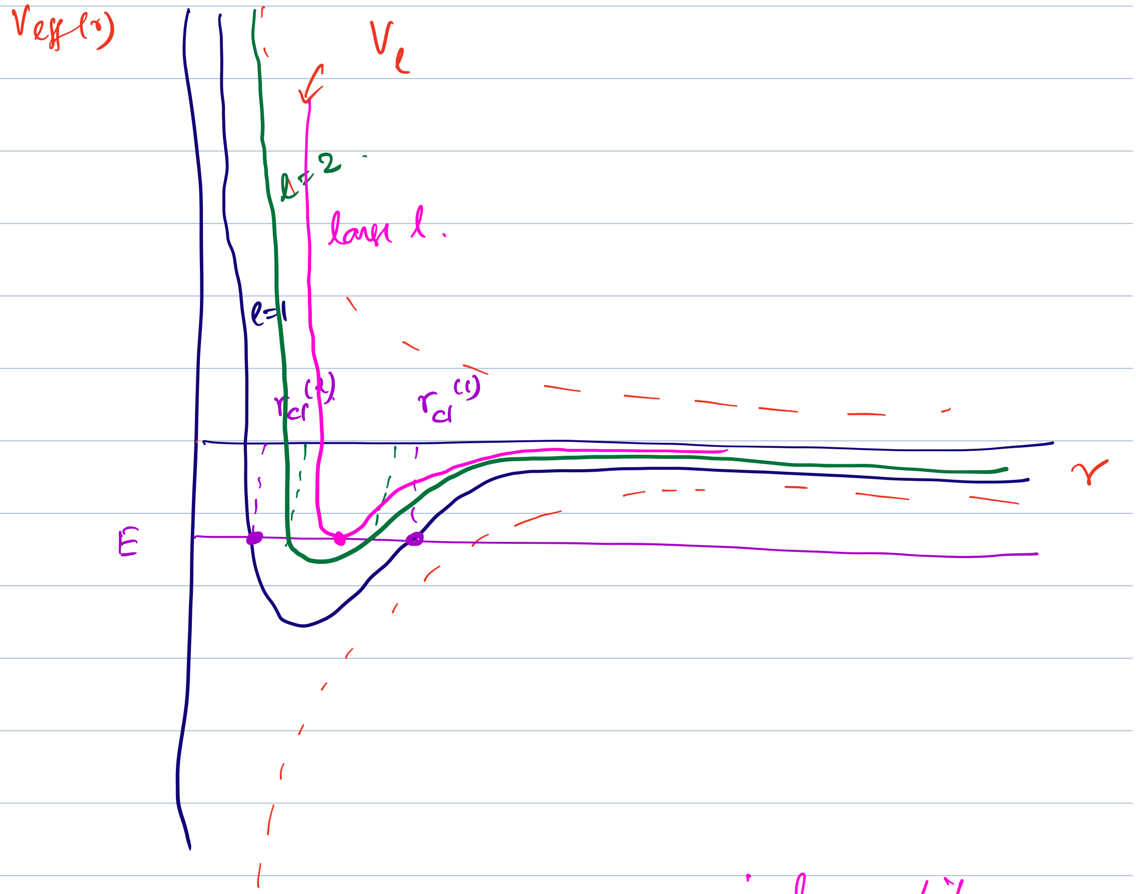
Since $V_{eff} \to 0$ as $r \to \infty$, therefore, the solution $u_{nl}(r)$ will be oscillatory or scattering wave at $r \to \infty$ for $E > 0$.

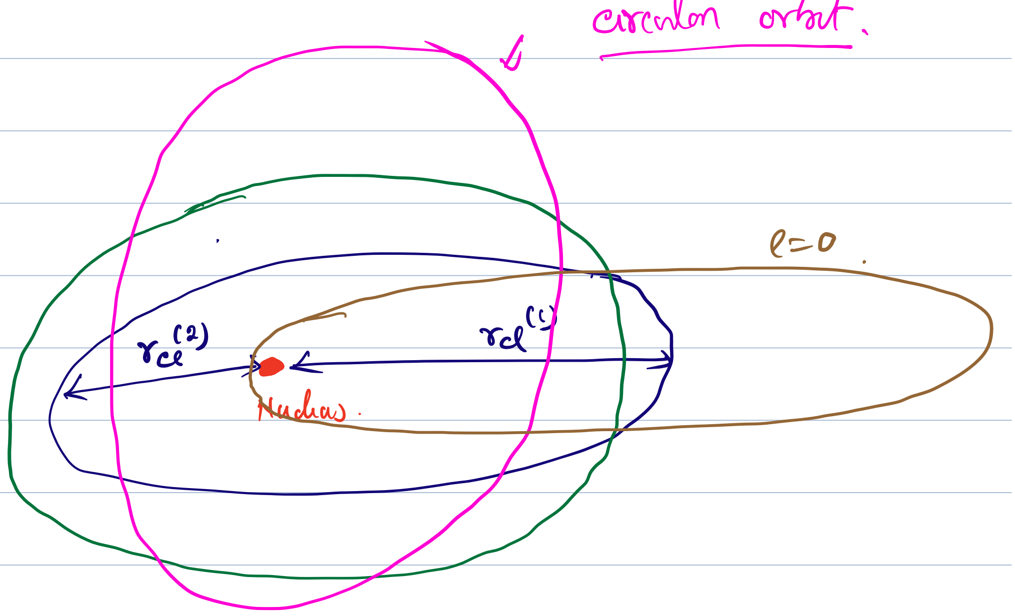
Here our focus is for <u>$E<0$</u> solutions. For $E<0$, we have a length scale, in the "classical turning point" for V_{eff}.

For $l=0$, the centrifugal barrier is zero, and the potential goes to $-\infty$ as $r \to 0$. Therefore for any value of $E<0$, we have a "classical turning point". The "classical turning point" for the hydrogen atom, having only one electron, is the Bohr radius "a_0". Therefore, 'a_0' is the length where the total energy matches with the potential energy, such that the electron has <u>no radial momentum</u>. From dimensional analysis we can estimate the total energy for a particle in a radius 'a' (as we did for the S.H.O case) is $E \sim \frac{\hbar^2}{\mu a_0^2} = V(a_0) = \frac{Ze^2}{4\pi\epsilon_0 a_0}$. This gives $\boxed{a_0 = \frac{4\pi\epsilon_0 \hbar^2}{Z\mu e^2}}^{*}$ which is exactly the Bohr radius we obtained earlier using angular momentum conservation. So, we expect oscillatory solution for the radial part u_{nl} for $r<a_0$ and decaying solution for $r>a_0$. This problem is hence characteristically similar to the potential well case we discussed in sec (B6) above, but instead of solving for different regions and matching the wavefunction at $r=a_0$, we can actually solve the Schrödinger equation (96) exactly through series solution.



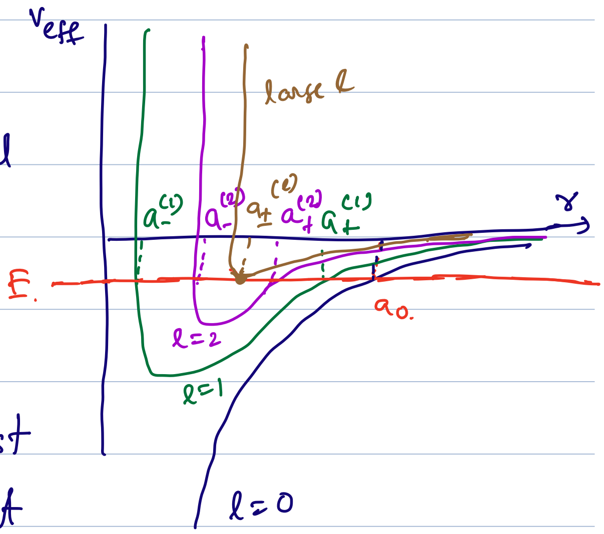
(For reduced mass μ, a_0 is called modified Bohr radius).


Veff(r)
Vℓ
ℓ=2
large ℓ.
ℓ=1
rcl(2)
rcl(1)
E
r

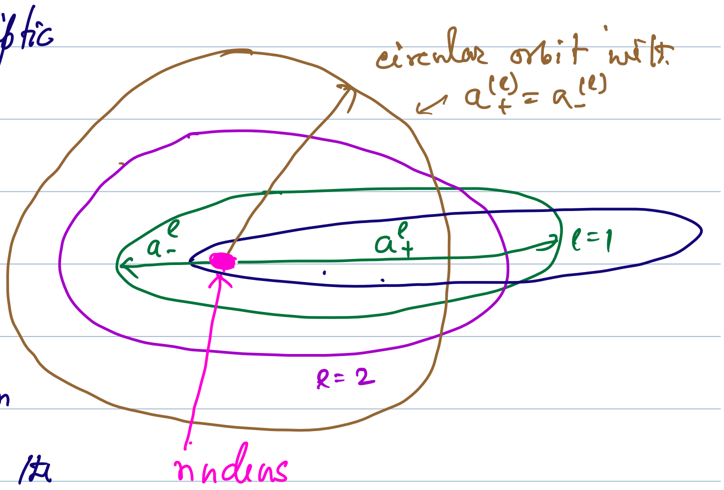

circular orbit.
ℓ=0.
rcl(2)
rcl(1)
Nucleus.

- For $l > 0$, we have two "classical turning points" $a_\pm$. This is because the effective potential has a minimum.

This is because for a fixed energy $E<0$, the effective potential profile cuts the E line at two points, denoted by $a_\pm^{(l)}$. These two points are actually related to the highest and lowest distance from the nucleus sitting at the focal point of the elliptic orbit.



As l increases, the minimum value of the potential decreases, and hence the difference between $a_\pm^{(l)}$ decreases. This means the orbit tends to become more circular. The orbit with highest possible l value, whose minimum coincides with energy at $r = a_+^{(l)} = a_-^{(l)}$, becomes fully circular orbit. No higher value of l is possible for this case, since then the electron will no longer have bound state radial wavefunction.



The average $\frac{a_+^{(l)}+a_-^{(l)}}{2} = n^2 a_0$, where n is some integer that we will find out later. The average is at the potential minimum, indep. of l.

⊛ We will approach to solving the differential eqn (36b) in a similar way as we did for the 1D S.H.O case. We first make two substitutions to get of the length and energy dimensions. The first term has dimension of L^{-2}, the 2nd term $\frac{2ME}{\hbar^2}$ also then has the dimension of L^{-2}. So, we define a dimensionless "energy" quantity (K)

$$K^2 = -\frac{2\mu E}{\hbar^2} a_0^2 \Rightarrow E = -\frac{\hbar^2 K^2}{2\mu a_0^2} = -\frac{2Z^2e^2}{a_0} K^2$$

$$= -13.6\, Z^2 (2K)^2 \quad \text{---(37a)}$$

(in eV)

We also define a dimensionless "length" variable

$$\boxed{\rho = 2Z\frac{r}{a_0}} \qquad \text{— (37b)}$$

where the factor 2Z is added for our future convenience.

Then the differential eq (36b) becomes

$$\boxed{\left[\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} + \frac{1}{\rho}\right] u_{nl}(\rho) = K^2 u_{nl}(\rho)} \quad \text{---(38)}$$

Before we plunged into obtaining series solutions, one should always look at the behavior at the limiting values. Because, its not always possible to obtain a simple series solution everywhere, there might be more components in the solution which are needed to have the solutions converge at the potentially dangerous limits such as $r \to 0$ & $r \to \infty$ in our problem.

$$\frac{d^2}{dr^2} u_{n\ell}(r) - \frac{2\mu}{\hbar^2} V_{eff}(r)\, u_{n\ell}(r) - \boxed{\frac{2\mu}{\hbar^2} E}\, u_{n\ell}(r) = 0 \quad \text{--} (366)$$

Dim in $\frac{1}{L^2}$

$= \frac{1}{a^2} K^2$, K = dimensionless.

$$\left[\overset{a^2}{\downarrow}\frac{d^2}{dr^2} - \frac{2\mu}{\hbar^2}\overset{a^2}{\downarrow} V_{eff}(r) - \overset{a^2}{\downarrow} k^2\right] u_{n\ell}(r) = 0 .$$

- So, in the asymptotic limit of $r \to \infty$, i.e., $s \to \infty$, we see that the second and third terms on the R.H.S of eq (38) are negligible, and we are left with $\frac{d^2}{ds^2} u \underset{s\to\infty}{=} k^2 u$.

$$\Rightarrow \quad \boxed{u_{n\ell}(s) \xrightarrow[s\to\infty]{} e^{\pm ks}} \quad --- (39a)$$

Since '+' solution blows up at $s \to \infty$, we will only consider e^{-ks} solution. Substituting for k & s in eq (39a), we will get a decaying solution with decay length in terms of the Bohr radius a_0 as we anticipate.

- As $r \to 0$, ie, $s \to 0$, we do not want the radial wave function $R = u/r$ to diverge. Therefore, u must vanish faster than r, in an algebric powerlaw. Taking an ansatz of $u \sim s^p$ and substituting in eq (38), one can find that the power $p = \ell + 1$. Therefore, $u_{n\ell}(s) \xrightarrow[s\to 0]{} (ks)^{\ell+1}$ --- (39b).

- So, eqs (39a) & (39b) suggests us to make one more substitution of variable $\boxed{\xi = ks}$ = dimensionless variable. --- (39c).

This gives a differential eq as

$$\left[\frac{d^2}{d\xi^2} - \frac{\ell(\ell+1)}{\xi^2} + \frac{1}{k\xi}\right] u_{n\ell}(\xi) = u_{n\ell}(\xi) \quad -- (39d)$$

- Now we are ready to write down an ansatz solution for u_{nl}s

$$u_{nl}(\rho) = \rho^{l+1} e^{-\rho} L_{nl}(\rho) \quad ---- \quad (39e)$$

where $L(\rho)$ is some function of ρ and depends on 'n' the energy quantization number which we yet have to find out and l. We now hope that $L(\rho)$ will yield a series solution whose convergence condition obtained by the termination of the series at a finite term and that finite term will give a quantization condition on 'n'. This simply means, we hope $L(\rho)$ will turn out to be some polynomial in terms of (n, l) and that each (n, l) values would give orthogonal polynomial and end up being the eigenstates of the Hydrogen atom Hamiltonian. (This hope stems from our experience with the S.H.O. case. Spoiler alert, $L(\rho)$ will turn out to be Laguerre polynomials). Let us ignore the index 'nl' in L for simplicity in notation and store that information in our memory.

- Substituting the ansatz in eq (39c) in (39d), we rather get a long PDE as

$$\boxed{\rho \frac{d^2L}{d\rho^2} + 2(l+1-\rho)\frac{dL}{d\rho} + \left[\frac{1}{\kappa} - 2(l+1)\right] L = 0} \quad \text{---}(40a)$$

So, now we look for series solution of the form

$$L(\rho) = \sum_{i=0}^{\infty} c_i \rho^i \quad \text{---} \quad (40b)$$

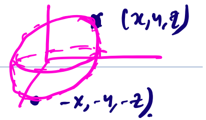
- We get $\sum_{i=0}^{\infty}\left[i(i-1)c_i\rho^{i-1} + 2(l+1-\rho)\, i\, c_i \rho^{i-1} + \left[\frac{1}{\kappa} - 2(l+1)\right] c_i \rho^i\right] = 0$ -(40c)

$$\sum_i \Big[\underbrace{\qquad\qquad}_{=0}\Big] \rho^i = 0.$$

Following the standard procedure of equating the coefficient of ρ^i to zero, we get the recursion relation:

$$\frac{c_{i+1}}{c_i} = \frac{2(i+l+1) - \frac{1}{\kappa}}{(i+1)(i+2l+2)} \quad \text{---}(40d)$$

(We notice a difference with the S.H.O case where the recursion relation was 2-steps between c_i & c_{i+2}, giving two unknown c_0, c_1 and decoupling the even and odd power polynomials. This was the result of the parity symmetry of the S.H.S between $x \to -x$. For the radial solution of the central potential the parity is lost and the variable r is only defined from 0 to ∞. The parity is actually there in the full Hamiltonian which require a



transformation for $(r, \theta, \phi) \to (r, \theta - \pi, \phi + \pi)$. This is the reason the solution $L(\rho)$ is not expected to have any definite parity and an one step recursion relation in eq(40d) makes sense).

- We ask the same question again, will the series $L(\rho)$ converge as $i \to \infty$? (More appropriately, will the term $\rho^{l+1} e^{-\rho} L(\rho)$ converge as $\rho \to \infty$?). Lets check the convergence criterion of L.

$$\frac{c_{i+1}}{c_i} \approx \frac{2i}{i\,(i+1)} = \frac{2}{i}.$$

This recursion relation for $i \to \infty$ is solvable and we get

$$c_i = \frac{2^i}{i!} c_0 \quad \text{as } i \to \infty$$

Then we get: $L(\rho) = \sum_{i=0}^{\infty} c_i \rho^i \underset{i \to \infty}{\cong} c_0 \sum_{i=0}^{\infty} \frac{2^i}{i!} \rho^i = c_0 e^{2\rho}$

So, the series $L(\rho)$ will blow up as $\rho \to \infty$ if we sum over all i. In other words, the series must truncate at finite values of i for a given value of k & l (very similar to the 1D S.H.O. case). What we are going to see is that for a given value of k & l, the polynomial must terminate at the N^{th} term such that $c_{N+1} = 0$, but $c_N \neq 0$. Then c_{N+2} and higher coefficients are also zero from the recursion relation and we will obtain a polynomial of degree N. For c_{N+1} to be zero while $c_N \neq 0$, the numerator of the recursion relation must vanish for $i = N$; i.e.

$$\boxed{(N+\ell+1) = \frac{1}{2K}} \qquad \text{--- (40e)}$$

(the dimensionless number)

That's it! Recall that Energy E depends on K (and some fundamental constants), and since since K is now quantized, <u>energy</u> is also quantized. ☺

<u>What are the possible values of K ?</u>

We know that the possible values of $\ell = 0, 1, 2, 3, \ldots$ due to quantization of angular momenta $\vec{L}^2$. And N is also positive integers $N = 0, 1, 2, 3, \ldots$. And as we can already anticipate from eq (40e), there will be multiple combinations of (ℓ, N) given the same value of K, i.e. there will be degeneracy in the energy eigenvalues.

We define $$\boxed{\frac{1}{2K} = N+\ell+1 = n} \qquad \text{--- (41)}$$

where 'n' called the <u>principle quantum number</u> that we have been looking for from the begining in $R_{n\ell}$, $u_{n\ell}$ functions. Since $N = 0, 1, 2, \ldots$; $\ell = 0, 1, 2, ; \geq 0$, $\underline{n \geq 1}$ and <u>integer</u>.

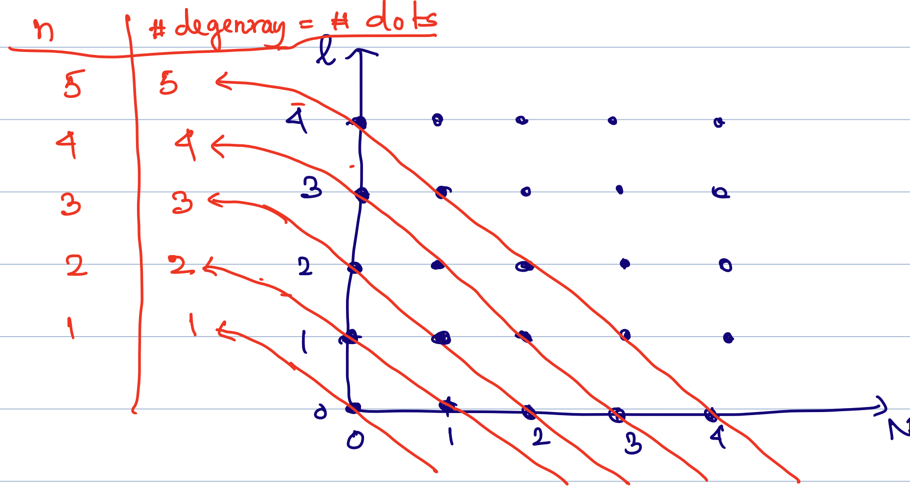
Energy: Now from eq (37a), we get

$$E = -\frac{\hbar^2 k^2}{2\mu a_0^2} = -\frac{2Z^2e^2}{a_0}k^2 \quad = -13.7\,Z^2(2k)^2 \quad \text{in ev)}$$

$$\Rightarrow \boxed{E_n = -\frac{Z^2e^2}{2a_0}\frac{1}{n^2}} \quad \text{where } n = 1, 2, 3, \ldots \qquad (42)$$

(This is exactly the result Bohr obtained by assuming angular momentum L_z being quantized as to $m\hbar$ values and that 'm' ended up in the energy quantization. But in the calculation of Schrödinger equation we got the same expression, however the quantum number 'n' is different, than 'm'. In fact, the angular momentum value 'm' does not appear in eq(42) and hence are degenerate).

- The possible values of n in terms of N, l can be organized as follows (one possible way, but there are also other ways)



Remember all points in (N, l) chart are allowed

- Therefore, for a given n, there are n possible combinations of (N, ℓ) and $N + \ell = n-1$. This puts the restriction on the maximum values of N & ℓ for a given value of n as

$$\left.\begin{aligned} 0 \leq \ell \leq n-1 \\ 0 \leq N \leq n-1 \end{aligned}\right\} \quad -(43)$$

So,

ℓ	0	1	2	---	$n-1$	← # of possible ℓ values
N	$n-1$	$n-2$	$n-3$	---	0	← # of possible N values.

- The energy levels only depend on 'n' and hence all possible ℓ values of 0 to $n-1$ are degenerate. Moreover, for each ℓ-values, there are $(2\ell+1)$ possible m-values also. This gives a total degeneracy of a n^{th} energy level as

$$\boxed{\text{Degeneracy}: \quad \sum_{\ell=0}^{n-1} (2\ell+1) = 2 \underbrace{\sum_{\ell=0}^{n-1} \ell}_{\frac{n(n-1)}{2}} + \underbrace{\sum_{\ell=0}^{n-1} 1}_{n} = 2\,\frac{n(n-1)}{2} + n = n^2 \quad -(44)}$$

- There is a well defined code letter corresponding to different orbitals with fixed 'l' values. They are defined as

l = 0 1 2 3 4 5 ...

Code letter = s p d f g h ...

We don't fill orbitals with higher than $l = 4$ angular momentum. The orbitals are then defined by n values followed by the code letter as n(code letter). For example, if we say 3p orbital, it means $n = 3$, $l = 2$; or 5d orbital means $n = 5$, $l = 2$.

$\boxed{N + l + 1 = n}$

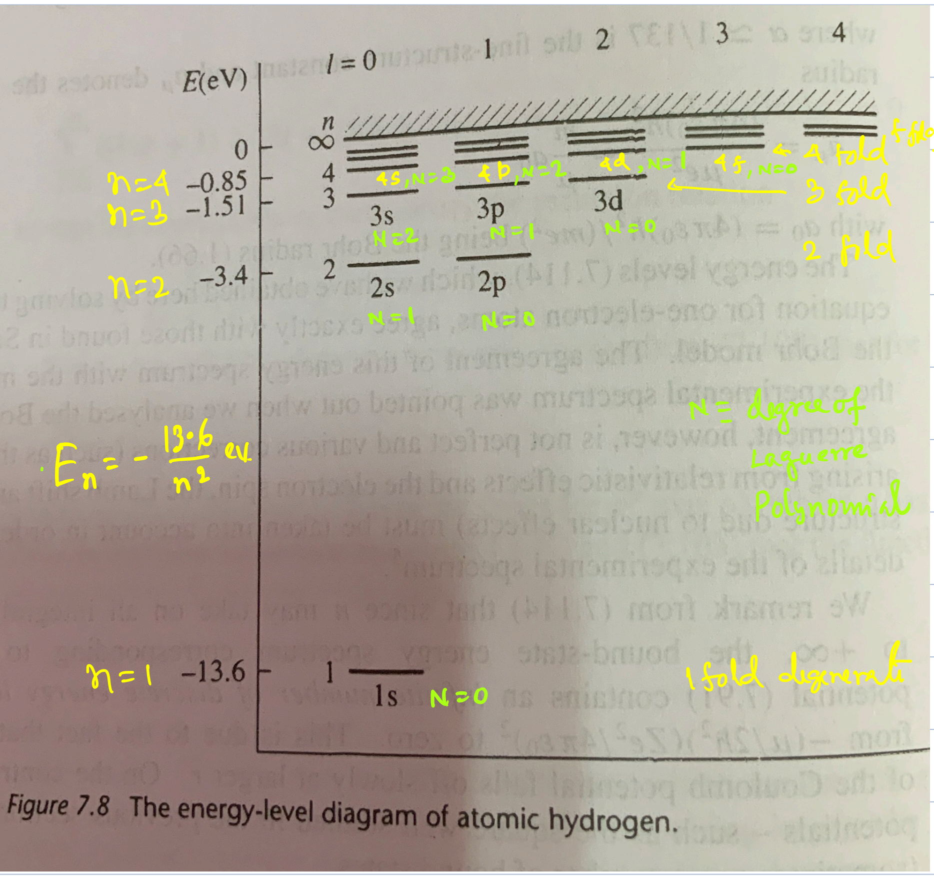


Figure 7.8 The energy-level diagram of atomic hydrogen.

Energy levels gets denser and denser as n- increases and hence in the limit of $n \to \infty$ we reach the classical limit as we also saw in chapter 1.

- The atom with the last occupied n-value being very large is called the Rydberg Atom. For the last electron, the other electrons inside screens the nucleus charge to an effective charge of $(Z-1)$. So, we have an effective H-atom problem.

Wavefunctions :

Now we can reverse all the change of variables and write the wavefunction in terms of three quantum numbers n, l, m as $\psi_{nlm}(r)$.

$$\rho = \kappa s = \kappa \frac{2Z}{a_0} r = \frac{Z}{n a_0} r. \qquad \text{---} (45a)$$

$$R_{nl}(r) = \frac{u_{nl}(r)}{r} = \frac{e^{-\rho} \rho^{l+1} L_{nl}(\rho)}{r}$$

$$= e^{-(Z/na_0) r} (Z/na_0)^{l+1} r^{l} L_{\underset{N}{\boxed{nl}}}\left(\frac{Z}{na_0} r\right) \text{---} (45b)$$

where L_{nl} is the Laguerre Polynomial of degree $N = n-l-1$. Laguerre polynomial is defined as.

$$
\begin{aligned}
L_0(x) &= 1 \\
L_1(x) &= -x+1 \\
L_2(x) &= x^2-4x+2 \\
L_3(x) &= -x^3+9x^2-18x+6 \\
L_4(x) &= x^4-16x^3+72x^2-96x+24 \\
L_5(x) &= -x^5+25x^4-200x^3+600x^2-600x+120 \\
L_6(x) &= x^6-36x^5+450x^4-2400x^3+5400x^2-4320x+720 \\
L_7(x) &= -x^7+49x^6-882x^5+7350x^4-29{,}400x^3+52{,}920x^2-35{,}280x+5040
\end{aligned}
$$

- This gives the radial wave functions, whose first few terms are

$R_{n\ell}$

N=0 $$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

N=1 $$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

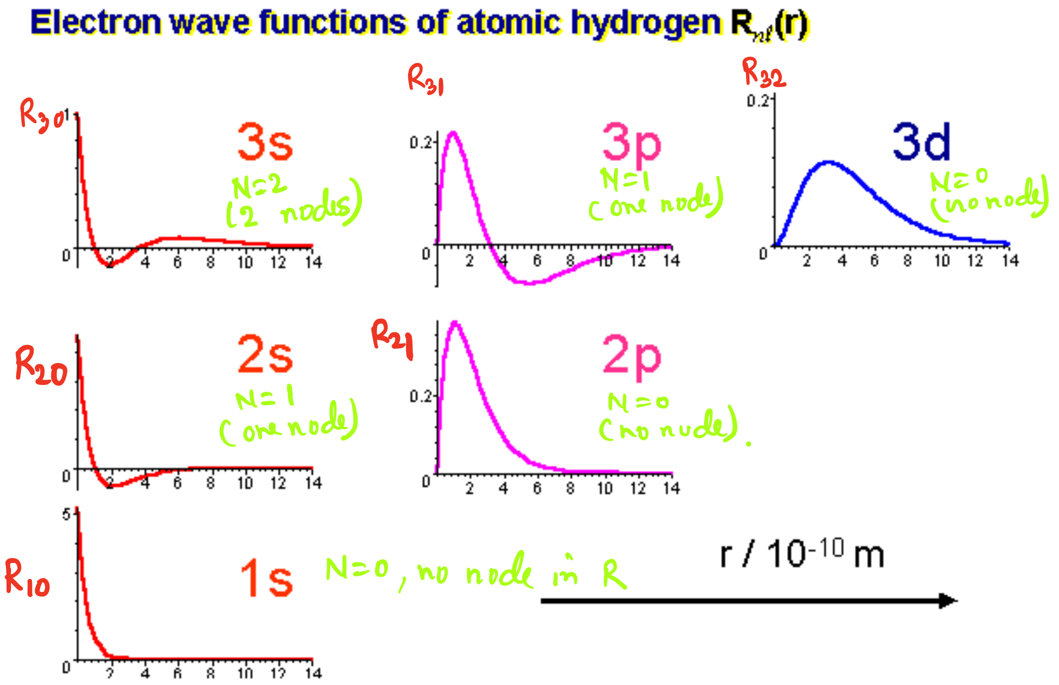
N=0 $$R_{20} = 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

N=0 $$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^{2} e^{-Zr/3a_0}$$

N=1 $$R_{31} = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)\left(1-\frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

N=0 $$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1-\frac{2Zr}{3a_0}+\frac{2\,(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$

We see that the spread of the radial w.f. depends on $\frac{na_0}{Z}$. So, the radial w.f. spreads more with increasing n, but decreases with higher atomic number.



Electron wave functions of atomic hydrogen $R_{n\ell}(r)$

$$\frac{1}{a_\mu^3}\int r\,|R_{1s}|^2 r^2\,dr = a_\mu^{\cancel{3}}$$

- The full wave function is then written as

$$\Psi_{n\ell m}(r,\theta,\varphi) = N\, R_{n\ell}(r)\, Y_{\ell m}(\theta,\varphi) \;, \quad \cdots (45c).$$

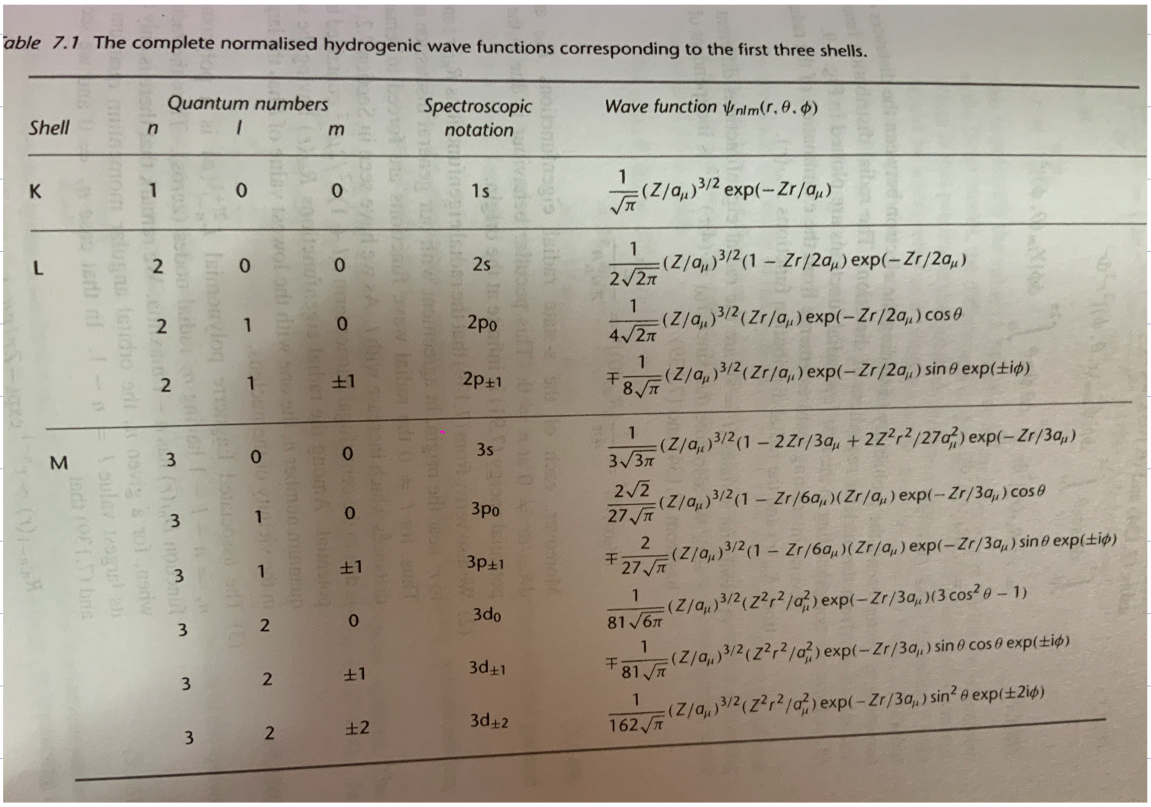
where N is a normalization constant.
The radial part is normalized in the r-direction as $\int_0^\infty |R_{n\ell}(r)|^2 r^2 dr = 1$. The spherical harmonics are normalized in the angular variables as $\int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi\, |Y_{\ell m}(\theta,\varphi)|^2 = 1$. This two normalization gives a value of the normalization that has a long-expression which we don't write here.

- The plots of $Y_{\ell m}$ are already given in the previous chapter.
- The wavefunction $\Psi_{n\ell m}$ contains now three quantum numbers: n = principle quantum number which is related to ensuring normalizability in the radial direction and makes the energy normalized in this quantum number.

ℓ = Orbital angular momentum quantum numbers, arising from the conservation of the total angular momentum $\vec{L}^2$.

m = z-component of the angular momentum conservation, and also related to the peridic boundary condition of the azimuthal angle ϕ.

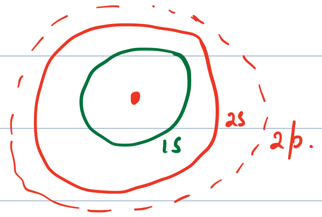
- Both (l, m) do not appear on the energy and hence each energy levels in a hydrogen atom are degenerate. In other atoms, having two or more electrons there are additional Coulomb interaction between the two electrons $e^2/|\vec{r}_1-\vec{r}_2|$. In solid where the atoms are peridically alligned, the degeneracy in l and m are lifted. You will learn them in QM-II and other Atomic physics or Condensed matter courses.



able 7.1 The complete normalised hydrogenic wave functions corresponding to the first three shells.

Shell	Quantum numbers			Spectroscopic notation	Wave function $\psi_{nlm}(r,\theta,\phi)$
	n	l	m		
K	1	0	0	1s	$\frac{1}{\sqrt{\pi}}(Z/a_\mu)^{3/2}\exp(-Zr/a_\mu)$
L	2	0	0	2s	$\frac{1}{2\sqrt{2\pi}}(Z/a_\mu)^{3/2}(1-Zr/2a_\mu)\exp(-Zr/2a_\mu)$
	2	1	0	$2p_0$	$\frac{1}{4\sqrt{2\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\cos\theta$
	2	1	±1	$2p_{\pm1}$	$\mp\frac{1}{8\sqrt{\pi}}(Z/a_\mu)^{3/2}(Zr/a_\mu)\exp(-Zr/2a_\mu)\sin\theta\exp(\pm i\phi)$
M	3	0	0	3s	$\frac{1}{3\sqrt{3\pi}}(Z/a_\mu)^{3/2}(1-2Zr/3a_\mu+2Z^2r^2/27a_\mu^2)\exp(-Zr/3a_\mu)$
	3	1	0	$3p_0$	$\frac{2\sqrt{2}}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\cos\theta$
	3	1	±1	$3p_{\pm1}$	$\mp\frac{2}{27\sqrt{\pi}}(Z/a_\mu)^{3/2}(1-Zr/6a_\mu)(Zr/a_\mu)\exp(-Zr/3a_\mu)\sin\theta\exp(\pm i\phi)$
	3	2	0	$3d_0$	$\frac{1}{81\sqrt{6\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)(3\cos^2\theta-1)$
	3	2	±1	$3d_{\pm1}$	$\mp\frac{1}{81\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin\theta\cos\theta\exp(\pm i\phi)$
	3	2	±2	$3d_{\pm2}$	$\frac{1}{162\sqrt{\pi}}(Z/a_\mu)^{3/2}(Z^2r^2/a_\mu^2)\exp(-Zr/3a_\mu)\sin^2\theta\exp(\pm 2i\phi)$

H.W. : (i) Since the potential $V(r)$ is a powerlaw of r, the virial theorem is applicable here. (Prove it).



(Bd) Spherical Harmonic Oscillator:

We have already solved the 3D Harmonic oscillator in the cartesian coordinates and by the virtue of separation of variable, we had exact solutions. We wanted to see the result for isotropic case where all three spring constants are the same and the potential is written as

$$V(r) = \frac{1}{2} k r^2 = \frac{1}{2} m \omega^2 r^2 \qquad - - - (46).$$

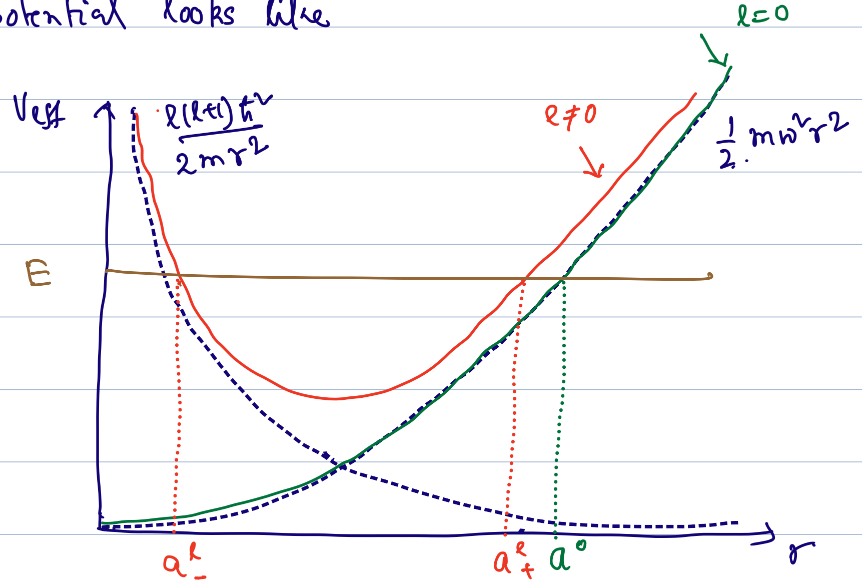
where $\omega = \sqrt{k/m}$.

Clearly the system now has the rotational symmetry and we can write the wave function as $\psi_{n_r l m}(r,\theta,\phi) = R_{n_r l}(r)\, Y_{lm}(\theta,\phi)$. Based on our experience with the previous Hydrogen atom case, we expect the same that the quantization of energy will depend on the quantization of the radial part, i.e, the energy will only depend on the quantum number 'n_r' that we only need to find out now. But we already know E_n by solving the Hamiltonian in the Cartesian coordinates. Since energy eigenvalues, being observable, is independent of the Hilbert space, so, it remains as $E_n = (n + 3/2)\hbar\omega$. Therefore, the eigenvalue of the number operator, i.e, n should be a function of n_r, l.

Let us look at the Schrödinger equation for $R_{n\ell} = \frac{u_{n\ell}}{r}$ that we derived in eq

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{n\ell}}{dr^2} + \Big[\underbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2} + \frac{1}{2}m\omega^2 r^2}_{V_{eff}(r)}\Big]u_{nr} = E\,u_{n\ell} \quad \text{---} \quad (47)$$

- We notice that both potentials are positive and the plot of the effective potential looks like



We notice that for finite values of ℓ, the effective potential has a minima at some finite r and there are two "classical turning points" $a^\ell_\pm$. Therefore, for finite ℓ, we will have elliptic orbits except when $E = \min(V_{eff})$. The elliptical orbits occur when $n_x \neq n_y \neq n_z$ for a given energy $E = (n+\frac{3}{2})\hbar\omega$. Clearly a circular orbit corresponds to $n_x = n_y = n_y = n_0$, which gives $E = (3n_0 + 3/2)\hbar\omega = 3(n_0 + 1/2)\hbar\omega = \min(V_{eff})$.

The general solution of eq (48) for general l can be obtained in the similar fashion, and we get the Confluent Hypergeometric polynomials as solution. The full solution is

$$R_{n_r l}(r) = N\ e^{-\alpha^2 r^2/2}\ r^l\ {}_1F_1\left(-n_r,\ l+\tfrac{3}{2},\ \alpha^2 r^2\right) \quad ---(48)$$

where ${}_1F_1$ is the Confluent Hypergeometric function of first kind. $\alpha = \sqrt{\frac{m\omega}{\hbar}}$ and N is the normalization constant.

- Proceeding similarly by making the n_r^{th} term to vanish in the recursion relation, we get the relation

$$\boxed{n = 2n_r + l}\ , \quad \text{where} \quad n_r = 0, 1, 2, \ldots$$

$$--(49) \qquad l = 0, 1, 2, \ldots$$

- The energy levels are $E_n = \left(n+\frac{3}{2}\right)\hbar\omega$, $n = 0, 1, 2, \ldots$ which has the same number of degeneracy as in in the Cartesian coordinates.

- Then the full wavefunction is

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\ Y_{lm}(\theta,\phi) \quad --(50)$$

where $n = \frac{n_r - l}{2}$, takes all positive integer values.

- **Degeneracy:** n :

n	n_r	l	$2l+1$	# of degeneracy.
0	0	0	1	1
1	0	1	3	3
2	1	0	1	
	0	2	5	6
3	1	1	3	
	0	3	7	10
4	2	0	1	
	1	2	5	15
	0	4	9	

- We notice that for a given energy level, ie, for a given n, there are restriction on the allowed values of n_r & l from eq(49).

→ For even n, l takes only even values as $2p$, where p takes $0, 1, 2, \ldots, n/2$.

→ For odd n, l takes only odd values as $2q+1$, where q takes values $0, 1, 2, \ldots, \frac{n-1}{2}$.

Then for each values of l, we have $(2l+1)$ distinct 'm' values which are degenerate. Therefore, the number of degeneracy is

→ For even n :

$$\sum_{p=0}^{n/2}\left(2\times \overset{\downarrow l}{2p}+1\right) = 4\sum_{p=0}^{n/2} p + \sum_{p=0}^{n/2} 1$$

$$= 4\cdot\frac{(n/2+1)\,n/2}{2} + \left(\frac{n}{2}+1\right)$$

$$= \frac{(n+2)\,n}{2} + \frac{n+2}{2}.$$

$$= \frac{(n+2)(n+1)}{2}.$$

→ For odd n,

$$\sum_{q=0}^{(n-1)/2}\left[2\times(\overset{\downarrow l}{2q+1})+1\right] = 4\sum_{q=0}^{(n-1)/2} q + 3\sum_{q=0}^{(n-1)/2} 1$$

$$= 4\,\frac{\left(\frac{n-1}{2}+1\right)\left(\frac{n-1}{2}\right)}{2} + 3\left(\frac{n-1}{2}+1\right)$$

$$= \frac{(n+1)(n-1)}{2} + 3\,\frac{n+1}{2}$$

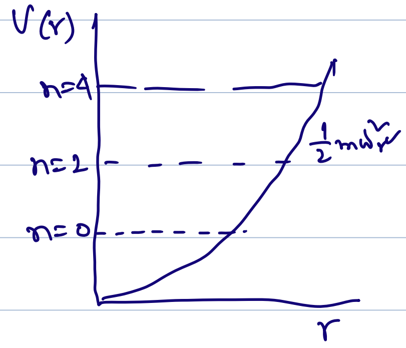
$$= \frac{(n+2)(n+1)}{2}$$

- Therefore, for both odd and even 'n', we have $\frac{(n+2)(n+1)}{2}$ number of degenerate states.

One can check that this degeneracy value matches exactly the value obtained from the combinations of (n_x, n_y, n_z) in the Cartesian case.

- We will not discuss the properties of the Confluent Hyper-geometric function for general l values. However the solution for $l=0$ matches the solution of the 1D S.H.O for odd parity functions. Because, for $l=0$, Eq(47) become

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{n_r,0}}{dr^2} + \frac{1}{2} m\omega^2 r^2 u_{n_r,0} = E\, u_{n_r,0} \quad --(48).$$



Except here r is defined only in the positive direction. This is equivalent to having an infinite potential barrier at $r=0$ and a 1D S.H.O for $r>0$. Therefore, all solutions of eq(48) must vanish as $r\to 0$. Therefore, the even parity solutions of the 1D S.H.O are not allowed here and only odd parity solutions exist. The eigenvalues remain the same as 1D S.H.O for odd integer $n = 2n_r+1$, with $n_r = 0, 1, 2, \cdots$. This gives the energy eigenvalues as

$$\begin{aligned} E_n &= \left(n+\tfrac{1}{2}\right)\hbar\omega \\ &= \left(2n_r+1+\tfrac{1}{2}\right)\hbar\omega. \\ &= \left(2n_r+\tfrac{3}{2}\right)\hbar\omega. \end{aligned}$$

This is exactly the solution we also obtained above $n = 2n_r + l$ for $l = 0$. The solutions are then written in terms of the Hermite polynomials with odd degrees, same as what we obtained for 1D S.H.O by replacing n with r. It is indeed the case that the Confluent Hypergeometric polynomial becomes Hermite polynomial for $l = 0$. In fact, Confluent Hypergeometric polynomial is a master polynomial from which many other known polynomials can be obtained at various limits that we will learn in some other course.

(3d) (i) Infinite spherical well (H.W).

$$V(r) = 0 \quad \text{for } r > a$$
$$= -\infty \quad \text{for } r < 0.$$

(ii) Spherical potential barrier:

$$V(r) = V_0 \quad r < a$$
$$= 0 \quad r > a.$$