– Two particle systems –

We have two <u>different</u> particles of masses m_1 and m_2. The Hamiltonian $\hat{H}(\hat{\underline{r}}_1, \hat{\underline{r}}_2)$ is simply given by the sum of the two kinetic energies:

$$\hat{K} = \hat{K}_1 + \hat{K}_2 = \frac{\hat{\underline{p}}_1^2}{2m_1} + \frac{\hat{\underline{p}}_2^2}{2m_2}$$

and the potential energy

$$V(\hat{\underline{r}}_1, \hat{\underline{r}}_2)$$

Therefore,

$$\boxed{\hat{H}(\hat{\underline{r}}_1, \hat{\underline{r}}_2) = \frac{1}{2m_1}\hat{\underline{p}}_1^2 + \frac{1}{2m_2}\hat{\underline{p}}_2^2 + V(\hat{\underline{r}}_1, \hat{\underline{r}}_2)}$$

If the two particles do not interact $V(\hat{\underline{r}}_1, \hat{\underline{r}}_2) = 0$ and the time-independent Schrödinger equation (SE) becomes separable

$$\hat{H}(\hat{\underline{r}}_1, \hat{\underline{r}}_2)\Psi(\underline{r}_1, \underline{r}_2) = E\,\Psi(\underline{r}_1, \underline{r}_2)$$

$$\Psi(\underline{r}_1, \underline{r}_2) = \Psi_1(\underline{r}_1)\Psi_2(\underline{r}_2) \quad , \quad E = E_1 + E_2 \leftarrow \text{arbitrary split}$$

$$\left(\frac{\hat{\underline{p}}_1^2}{2m_1} + \frac{\hat{\underline{p}}_2^2}{2m_2}\right)\Psi_1(\underline{r}_1)\Psi_2(\underline{r}_2) = (E_1 + E_2)\Psi_1\Psi_2$$

$$\Leftrightarrow \quad \frac{\hat{\underline{p}}_1^2\Psi_1}{2m_1}\Psi_2 + \frac{\hat{\underline{p}}_2^2\Psi_2}{2m_2}\Psi_1 = (E_1 + E_2)\Psi_1\Psi_2$$

This equation takes the form of two independent equations:

$$\left(-\frac{\hbar^2}{2m_1}\nabla^2\psi_1 - E_1\psi_1\right)\psi_2 + \left(-\frac{\hbar^2}{2m_2}\nabla^2\psi_2 - E_2\psi_2\right)\psi_1 = 0$$

The probability to find particle 1 around $\underline{r}_1$ and particle 2 around $\underline{r}_2$ is:

$$dP(\underline{r}_1, \underline{r}_2) = |\psi_1(\underline{r}_1)|^2 |\psi_2(\underline{r}_2)|^2 d^3r_1 d^3r_2$$
$$= dP_1(\underline{r}_1)\, dP_2(\underline{r}_2)$$

In terms of Bra and Ket, we clearly have:

$$\psi_1(\underline{r}_1)\psi_2(\underline{r}_2) = \langle \underline{r}_1|\psi_1\rangle\langle \underline{r}_2|\psi_2\rangle$$

This is the structure → of a direct product

$$= \left(\langle \underline{r}_1| \otimes \langle \underline{r}_2|\right)\left(|\psi_1\rangle \otimes |\psi_2\rangle\right)$$

It is customary to use the short-hand

$$\langle \underline{r}_1| \otimes \langle \underline{r}_2| = \langle \underline{r}_1|\langle \underline{r}_2| = \langle \underline{r}_1, \underline{r}_2| \leftarrow \text{equivalents writings}$$

$$|\psi_1\rangle \otimes |\psi_2\rangle = |\psi_1\rangle|\psi_2\rangle = |\psi_1, \psi_2\rangle \leftarrow \text{equivalents writings}$$

This generalizes to n particles:

$$\langle \underline{r}_1|\langle \underline{r}_2| \cdots \langle \underline{r}_n|$$

If $\psi(\underline{r}_1, \ldots, \underline{r}_n)$ is <u>not</u> separable, we simply write:

$$\psi(\underline{r}_1, \ldots, \underline{r}_n) = \langle \underline{r}_1, \ldots, \underline{r}_n|\psi\rangle$$

Now, let $V(\hat{\underline{r}}_1, \hat{\underline{r}}_2) \neq 0$

We change variables:

$$\hat{\underline{P}} \equiv \hat{\underline{P}}_1 + \hat{\underline{P}}_2$$

$$\hat{\underline{r}} \equiv \hat{\underline{r}}_1 - \hat{\underline{r}}_2 \quad \leftarrow \text{relative coordinates}$$

$$\hat{\underline{R}} = \frac{m_1 \hat{\underline{r}}_1 + m_2 \hat{\underline{r}}_2}{m_1 + m_2} \quad \leftarrow \text{center of mass coordinates}$$

$M = m_1 + m_2$ = Total mass.

A straightforward calculation shows that

$$[\hat{P}_a, \hat{R}_b] = -i\hbar \delta_{ab} \quad (a, b = 1, 2, 3)$$

The variable canonically conjugate to $\hat{\underline{r}}$, is:

$$\begin{aligned} \hat{\mathbf{p}} &= \mu (\mathbf{v}_1 - \mathbf{v}_2) \\ &= \frac{m_1 m_2}{m_1 + m_2} \left(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2} \right) = \frac{m_2 \mathbf{p}_1 - m_1 \mathbf{p}_2}{M} \end{aligned}$$

because $$[\hat{p}_a, \hat{r}_b] = \left[\frac{m_2 \hat{P}_{1a} - m_1 \hat{P}_{2a}}{M}, \hat{r}_{1b} - \hat{r}_{2b} \right]$$

Remembering that operators of different particles commute, we have

$$[\hat{p}_a, \hat{r}_b] = \frac{m_2}{M} [\hat{P}_{1a}, \hat{r}_{1b}] + \frac{m_1}{M} [\hat{P}_{2a}, \hat{r}_{2b}] = \overbrace{\frac{m_2 + m_1}{M}}^{=1} (-i\hbar \delta_{ab})$$

$$= -i\hbar \delta_{ab}$$

Then we can rewrite

$$\begin{cases} \underline{\hat{P}}_1 = \underline{\hat{p}} + \frac{m_1}{M}\underline{\hat{P}} \\ \underline{\hat{P}}_2 = -\underline{\hat{p}} + \frac{m_2}{M}\underline{\hat{P}} \end{cases}$$

from which we calculate the kinetic energy in the form:

$$\frac{1}{2m_1}\underline{\hat{P}}_1^2 + \frac{1}{2m_2}\underline{\hat{P}}_2^2 = \frac{1}{2m_1}\left(\underline{\hat{p}} + \frac{m_1}{M}\underline{\hat{P}}\right)^2 + \frac{1}{2m_2}\left(-\underline{\hat{p}} + \frac{m_2}{M}\underline{\hat{P}}\right)^2$$

$$= \underline{\hat{p}}^2\left(\frac{1}{2m_1} + \frac{1}{2m_2}\right) + \underline{\hat{P}}^2 \underbrace{\frac{m_1+m_2}{2M^2}}_{= \frac{M}{2M^2} = \frac{1}{2M}}$$

$$\equiv \frac{\underline{\hat{P}}^2}{2M} + \frac{\underline{\hat{p}}^2}{2\mu}$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$ is the reduced mass.

Now, rewriting

$$\psi(\underline{r}_1, \underline{r}_2) = \phi(\underline{r}, \underline{R}) \ ; \quad V(\underline{r}_1, \underline{r}_2) = U(\underline{r}, \underline{R})$$

the SE becomes

$$\left[\frac{\underline{\hat{p}}^2}{2\mu} + \frac{\underline{\hat{P}}^2}{2M} + U(\underline{r}, \underline{R})\right]\phi(\underline{r}, \underline{R}) = E\,\phi(\underline{r}, \underline{R})$$

Often, the potential energy depends only on the <u>relative distance</u> between the particles, that is:

$$U(\underline{r}, \underline{R}) = U(\underline{r})$$

and the Hamiltonian takes the form

$$\hat{H} = \hat{H}_R + \hat{H}_r$$

where

$$\hat{H}_R = \frac{\hat{P}^2}{2M} \quad \leftarrow \text{purely kinetic}$$

$$\hat{H}_r = \frac{\hat{p}^2}{2\mu} + U(\hat{r})$$

Therefore, we look for a factorable solution

$$\begin{cases} \phi(\underline{r}, \underline{R}) = u(\underline{r})\, \varphi(\underline{R}) \\ E = E_R + E_r \end{cases}$$

with

and the SE separates:

$$\boxed{\begin{aligned} -\frac{\hbar^2}{2M} \nabla_R^2 \varphi(\underline{R}) &= E_R \varphi(\underline{R}) && (1.5a) \\ -\frac{\hbar^2}{2\mu} \nabla_r^2 u(\underline{r}) + U(\underline{r})\, u(\underline{r}) &= E_r\, u(\underline{r}) && (1.5b) \end{aligned}}$$

The solution of (1.52) is simply an eigenstate of linear momentum $\hat{\underline{P}}$:

$$\left(\hat{\underline{P}}^2 \varphi\right)(\underline{R}) = 2M E_R \, \varphi(\underline{R})$$
$$\equiv \underline{P}^2 \varphi(\underline{R})$$

where $\underline{P}^2 = P_x^2 + P_y^2 + P_z^2 \equiv 2M E_R \Rightarrow \boxed{E_R = \frac{P^2}{2M}}$

number, NOT operator

and $$\varphi(\underline{R}) = \exp\left[\frac{i}{\hbar} \underline{P} \cdot \underline{R}\right]$$

The corresponding time-dependent wave function is, as usual,

$$\varphi(\underline{R}) \exp\left(-\frac{i}{\hbar} E_R t\right) = \underbrace{\exp\left[\frac{i}{\hbar}\left(\underline{P} \cdot \underline{R} - \frac{P^2}{2M} t\right)\right]}$$

This is a plane wave, representing the free-propagation of the center of mass of the two-particle system.

This relation is true for any form of the energy potential $U(\underline{r})$. Now we specialize to the so-called "central potential" case, where

$$U(\underline{r}) = V(|\underline{r}|) = V(r) \quad \text{where } r = |\underline{r}|$$

In this case it is useful to solve 1.5b) in spherical coordinates:

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

$$\equiv \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{L}^2}{\hbar^2 r^2}$$

The SE is therefore:

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)u(\underline{r}) + \frac{\hat{L}^2}{2\mu r^2}u(\underline{r}) + V(r)u(\underline{r}) = E_r u(\underline{r})$$

We know that the spherical harmonics $Y_{\ell m}(\theta, \phi)$ are eigenstates of $\hat{L}^2$ with eigenvalue $\ell(\ell+1)\hbar^2$. So we rewrite:

This symbol now denotes a function. It has nothing to do with the center of mass radius R!

$$u(\underline{r}) = \widetilde{R}(r)\, Y_{\ell m}(\theta, \phi)$$

where $R(r)$ obeys the ordinary differential equation:

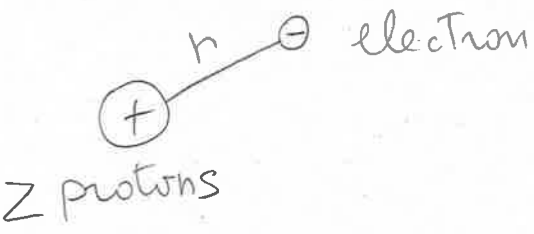
$$-\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right)R(r) + V(r)R(r) = E_r R(r)$$

So, the eigenvalues E_r will depend certainly from the index ℓ (because of the term $-\frac{\ell(\ell+1)}{r^2}$).

For the sake of clarity, from now on we rename:

$$E_r \rightarrow E$$

— The HYDROGEN-like atoms —



$Z=1 \Rightarrow$ Hydrogen

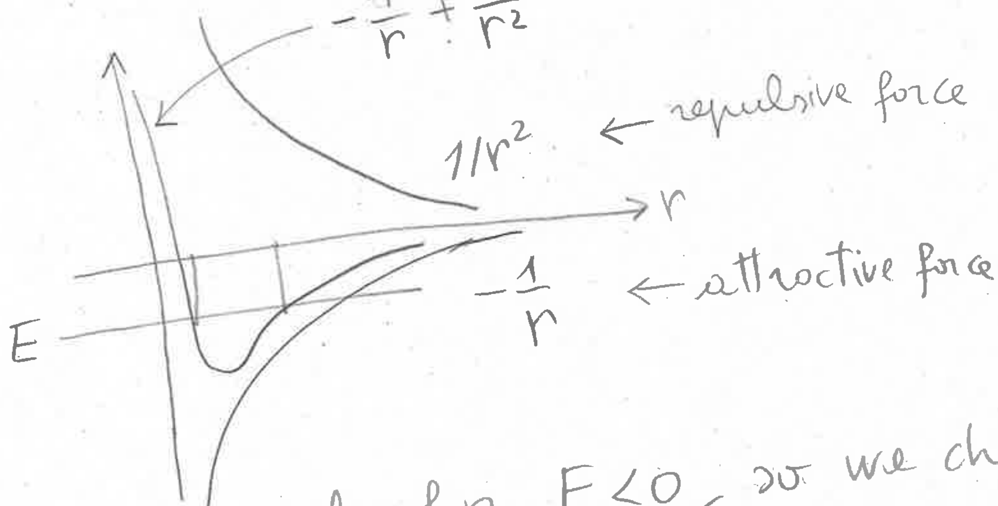
$$U(r) = -\frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$$

e = electronic charge

and the RADIAL SE is:

$$\left[\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + \frac{2\mu}{\hbar^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2}\right)\right]R(r) = 0$$

What is the form of the potential?



we expect bound states only for $E<0$, so we choose

$$E = -|E| < 0$$

and we introduce the dimensionless variable

$$\rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}\, r$$

and SE becomes:

$$\boxed{\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)R = 0} \quad 1.8)$$

where $\lambda \equiv \frac{Ze^2}{4\pi\epsilon_0\hbar}\sqrt{\frac{\mu}{2|E|}} = Z\alpha\sqrt{\frac{\mu c^2}{2|E|}}$

where $\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \simeq \frac{1}{137}$ ≡ fine-structure constant

- Solving the equation -

We begin by studying the large ρ behavior:

$$\frac{1}{\rho}, \frac{1}{\rho^2} \to 0 \Rightarrow$$

$$\Rightarrow 1.8) \longrightarrow \frac{d^2R}{d\rho^2} - \frac{1}{4}R = 0$$

The solution (well behaving at infinity) is

$$R(\rho) \propto e^{-\rho/2}$$

So, it is convenient to define the function $G(\rho)$ via:

$$\boxed{R(\rho) \equiv e^{-\rho/2}\, G(\rho)} \quad 2.8)$$

Substituting 2.8 into 1.8 we find, after some manipulation:

$$\frac{d^2 G}{d\rho^2} - \left(1 - \frac{2}{\rho}\right)\frac{dG}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right] G = 0 \qquad 1.9)$$

– Homework: Do explicitly the missing calculations above.

Now, let us consider the opposite limit $\rho \to 0$. In this case $1 - \frac{2}{\rho} \approx -\frac{2}{\rho}$

and $\frac{1}{\rho}\left[\lambda - 1 - \frac{l(l+1)}{\rho}\right] \approx -\frac{l(l+1)}{\rho^2}$

and 1.9) reduces to:

$$\frac{d^2 G}{d\rho^2} + \frac{2}{\rho}\frac{dG}{d\rho} - \frac{l(l+1)}{\rho^2} G \approx 0 \qquad 2.9)$$

If we take: $G \propto \rho^l$, then $\frac{dG}{d\rho} = l\rho^{l-1}$

$$\frac{d^2 G}{d\rho^2} = l(l-1)\rho^{l-2}$$

and

$$2.9) \rightarrow l(l-1)\rho^{l-2} + \frac{2}{\rho} l \rho^{l-1} - \frac{l(l+1)}{\rho^2}\rho^l = 0 \quad \checkmark$$

So, now we introduce the new function $H(\rho)$ via:

$$\boxed{G(\rho) \equiv \rho^l H(\rho)} \qquad 3.9)$$

Substituting 3.9) into 1.9) we get:

$$\boxed{\frac{d^2H}{d\rho^2} + \left(\frac{2\ell+2}{\rho} - 1\right)\frac{dH}{d\rho} + \frac{\lambda-\ell-1}{\rho}H = 0} \qquad 1.10)$$

To find H, let us try a power expansion:

$$H(\rho) = \sum_{k=0}^{\infty} a_k \rho^k \qquad 2.10)$$

Replacing this in 1.10) we obtain

$$\sum_{k=0}^{\infty} a_k\left[k(k-1)\rho^{k-2} + k\left(\frac{2\ell+2}{\rho} - 1\right)\rho^{k-1} + (\lambda-\ell-1)\rho^{k-1}\right] = 0$$

$$\Leftrightarrow \underbrace{\sum_{k=0}^{\infty} a_k \rho^{k-2}\underbrace{\left[k(k-1) + 2k(\ell+1)\right]}_{\text{this term is zero for } k=0 \text{ so we can start the sum from 1:}}} + \sum_{k=0}^{\infty} a_k \rho^{k-1}(-k+\lambda-\ell-1) = 0$$

$$= \sum_{k=1}^{\infty} a_k k \rho^{k-2}\left[k-1+2(\ell+1)\right] \quad \Leftarrow \text{define } q = k-1 \Rightarrow k = q+1$$

$$= \sum_{q=0}^{\infty} a_{q+1}(q+1)\rho^{k-1}\left[q+2(\ell+1)\right]$$

Eventually we get: (going back to index k)

$$\sum_{k=0}^{\infty} \rho^{k-1}\left[(k+1)(k+2\ell+2)a_{k+1} + (\lambda-\ell-1-k)a_k\right] = 0$$

The coefficients of each power of ρ must necessarily vanish separately. This leads to a recursion relation:

$$\frac{a_{k+1}}{a_k} = \frac{k+\ell+1-\lambda}{(k+2\ell+2)(k+1)} \sim \frac{k}{k^2} = \frac{1}{k} \quad \text{for large } k$$

If the series

$$H(\rho) = \sum_{k=0}^{\infty} a_k \rho^k$$

does not terminate for some $k = n_r$, then

$$a_{k+2} = \frac{a_{k+1}}{k+1} = \frac{a_k}{(k+1)k} = \frac{a_{k-1}}{(k+1)k(k-1)} \dots \Rightarrow a_{k+1} \sim \frac{1}{k!}$$

for large k

This means that:

$$H(\rho) \simeq \sum_{k=0}^{n_r} a_k \rho^k + \sum_{k=N+1}^{\infty} \frac{\rho^k}{k!}$$

$$\simeq (\text{polynomial in } \rho) + e^{\rho}$$

this is unphysical for $\rho \to \infty$, therefore we require the series to stop at $k = n_r$.

This means:

$$0 = a_{n_r+1} = a_{n_r} \frac{(n_r+\ell+1)-\lambda}{[n_r+2(\ell+1)](n_r+1)} = 0$$

This equation fixes the eigenvalue λ to

$$\boxed{\lambda = n_r + l + 1}$$ ← Integer number

The quantity n:

$$n \equiv n_r + l + 1$$

is called the PRINCIPAL quantum number

Since $l \geq 0$ and $n_r \geq 0$ ⇒ 1. $n \geq l+1$

2. n is an integer

3. $\lambda = n$ implies:

$$\lambda = Z\alpha\sqrt{\frac{\mu c^2}{2|E|}} = n \Rightarrow |E| = \frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2}$$

or

$$\boxed{E = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2}}$$

– The spectrum of Hydrogen atom –

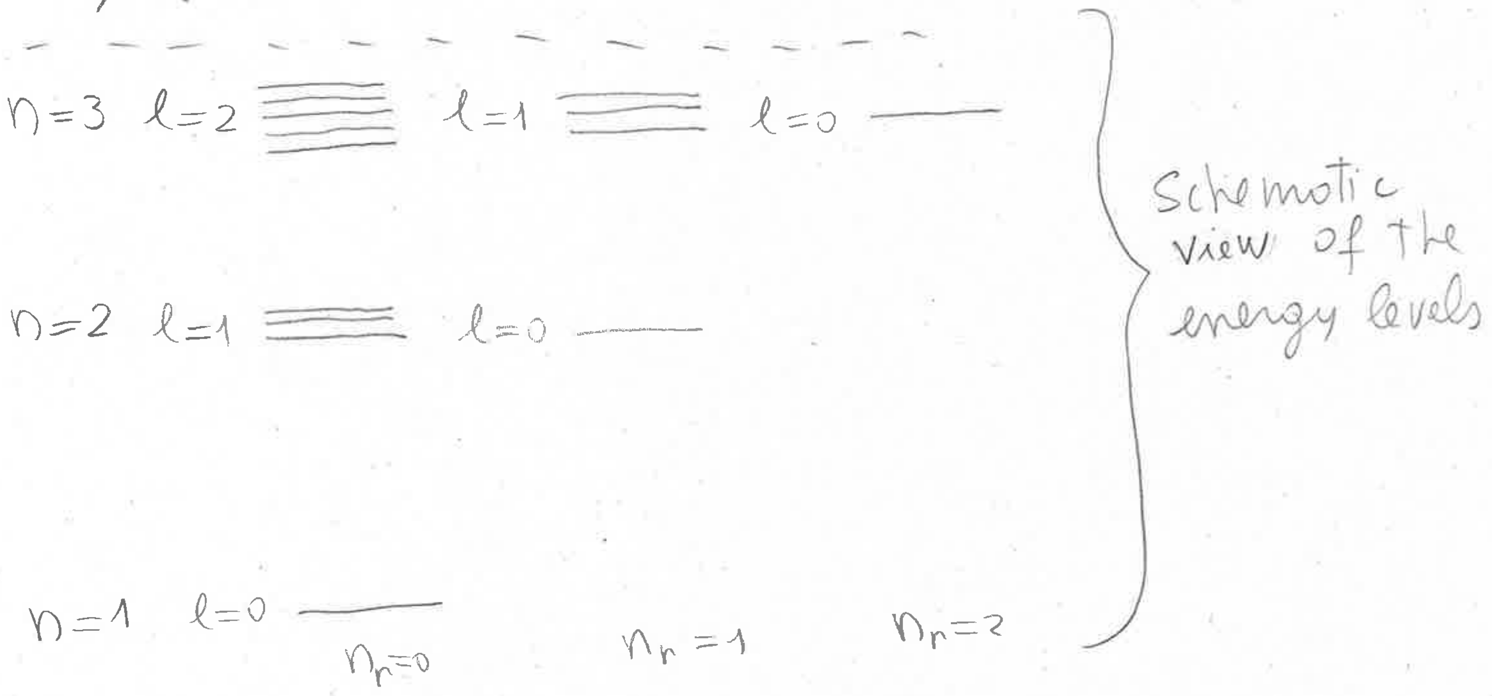
1. $n = n_r + l + 1 = 1 \Rightarrow \begin{cases} n_r = 0 \\ l = 0 \end{cases}$ There is a unique ground state.

2. $n = n_r + l + 1 = 2 \Rightarrow \left.\begin{array}{l} \begin{cases} n_r = 1 \\ l = 0 \Rightarrow m = 0 \end{cases} \quad 1 \text{ state} \\ \begin{cases} n_r = 0 \\ l = 1 \Rightarrow m = 1, 0, -1 \end{cases} \quad 3 \text{ states} \end{array}\right\}$ 4-fold degenerate

3. $n = n_r + l + 1 = 3 \Rightarrow n_r + l = 2$

$$n_r + l = 2 \Leftrightarrow \begin{cases} \begin{cases} n_r = 2 \\ l = 0 \end{cases} & \text{1 state} \\ \begin{cases} n_r = 1 \\ l = 1 \Rightarrow m = \begin{cases} -1 \\ 0 \\ 1 \end{cases} \end{cases} & \text{3 states} \\ \begin{cases} n_r = 0 \\ l = 2 \Rightarrow m = \begin{cases} -2 \\ -1 \\ 0 \\ 1 \\ 2 \end{cases} \end{cases} & \text{5 states} \end{cases}$$

So, the level with $n = 3$ is 9-fold degenerate



In summary, for a given n, the degeneracy is:

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

The eigen functions

It turns out that the functions $H(\rho)$ are well-known in mathematics. They are called the associated Laguerre polynomials:

$$\boxed{H(\rho) = L_{n-\ell-1}^{(2\ell+1)}(\rho)}$$

whose series expansion is:

$$L_p^{\alpha}(\rho) = \sum_{m=0}^{n} \binom{n+\alpha}{p-m} \frac{(-\rho)^m}{m!}$$

and $y = L_p^{\alpha}(x)$ is a solution of:

$$x y'' + (\alpha + 1 - x) y' + p y = 0 \qquad (1.14)$$

If we multiply (1.10) by ρ, we obtain

$$\rho H'' + [(2\ell+1)+1-\rho] H' + (\lambda-\ell-1) H = 0$$

which coincides with (1.14) if:

$$\begin{cases} \alpha = 2\ell+1 \\ p = \lambda-\ell-1 \end{cases}$$

If we introduce the length

$$a_0 \equiv \frac{\hbar}{\mu c \alpha}$$

called the BOHR RADIUS of the ground state, we can write:

$R_{n\ell}(r)$:

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

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

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

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

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

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

Homework: calculate probability density $|\psi|^2$ and probability current $\vec{j}$ for the ground state $n_r=0$, $\ell=0$, and for the state $n_r=0$, $\ell=1$, $m=1$

Useful quantities to calculate via the moments of radial probability distribution:

$$\langle r^k \rangle = \int_0^\infty dr\, r^{k+2} \left[R_{n\ell}(r)\right]^2$$

In particular:

$$\langle r \rangle = \frac{a_0}{2Z}\left[3n^2 - \ell(\ell+1)\right]$$

$$\langle r^2 \rangle = \frac{a_0^2 n^2}{2Z^2}\left[5n^2 + 1 - 3\ell(\ell+1)\right]$$

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0 n^2}$$

$$\left\langle \frac{1}{r^2} \right\rangle = \frac{Z^2}{a_0^2 n^3 \left(\ell + \frac{1}{2}\right)}$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{a_0^3 n^3 \ell\left(\ell + \frac{1}{2}\right)(\ell+1)}$$