9. SPHERICALLY SYMMETRIC POTENTIALS

Many systems have a potential energy function that is invariant under rotations about an origin - the potentials depend only upon the distance from the origin, $r = |\vec{r}|$, an are known as 'spherically symmetric'.

We showed earlier that the kinetic energy in three-dimensions can be expressed in terms of radial derivatives & the orbital angular momentum operator

$$\frac{\vec{p}^2}{2\mu} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial r}\right] + \frac{\vec{L}^2}{2\mu r^2}$$

The Hamiltonian with a spherically symmetric potential is

$$H = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r}\frac{\partial}{\partial r}\right] + \frac{\vec{L}^2}{2\mu r^2} + V(r)$$

It is easy to show then that L_z, L^2 commute with this Hamiltonian

$[H, L^2] = [H, L_z] = 0$ so the eigenstates of L^2, L_z are stationary and the eigenvalues are good quantum numbers

$$L^2 Y_\ell^m = \ell(\ell+1)\hbar^2 Y_\ell^m \quad ; \quad L_z Y_\ell^m = m\hbar Y_\ell^m$$

Suppose we guess at eigenfunctions of H of the following form: $\phi(\vec{r}) = R(r)\, Y_\ell^m(\theta,\phi)$

then $$H\phi = \left(-\frac{\hbar^2}{2\mu}\left[\frac{1}{r}\frac{d}{dr}\left(r\frac{d}{dr}\right) + \frac{1}{r}\frac{d}{dr} - \frac{\ell(\ell+1)}{r^2}\right]R(r) + V(r)R(r)\right)Y_\ell^m = E\, R(r)\, Y_\ell^m$$

the absence of any dependence upon m implies that all $2\ell+1$ values of m correspond to degenerate states.

The "radial wavefunction" $R(r)$ must satisfy

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

We shall solve this equation, subject to constraints on $R(r)$. We shall insist (with one exception) that the potential $V(r)$ goes to zero at $r\to\infty$ faster than $1/r$ & that $\lim_{r\to 0} r^2 V(r) = 0$ so that the potential is not more singular than $1/r^2$ at the origin.

Solving the differential equation can be aided by introducing the function

$u(r) = r \cdot R(r)$ which satisfies

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

This equation bears a strong resemblence to the one-dimensional Schrödinger eqn with a modified potential

$$V(r) \rightarrow V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2} .$$

If $R(r)$ is to be finite at the coordinate origin we require $\underline{u(0) = 0}$.

- At small r, for potentials less singular than $1/r^2$ we have

$$\frac{d^2u}{dr^2} - \frac{l(l+1)}{r^2}u(r) \simeq 0$$

for $u(r) \sim r^{\alpha}$ $\rightarrow \alpha(\alpha-1) - l(l+1) = 0 \quad \Rightarrow \alpha = l+1, -l$

$$u(r\to 0) \sim \begin{cases} r^{l+1} & \text{"regular soln", satisfies } u(0)=0 \\ 1/r^{l} & \text{"irregular soln", violates } u(0)=0 \end{cases}$$

- At large r, only the kinetic energy is relevant,

$$\frac{d^2u}{dr^2} + \frac{2\mu E}{\hbar^2}u \simeq 0$$

& since the wavefunction must be normalisible

$$1 = \int d^3\vec{r}\, |\varphi(\vec{r})|^2 = \int d\Omega\, Y_l^{m*} Y_l^{m} \int_0^\infty r^2 dr\, |R(r)|^2 = \int_0^\infty r^2 dr\, |R(r)|^2 = \int_0^\infty dr\, |u(r)|^2 ,$$

the function $u(r)$ must vanish at infinity, $\underline{u(r\to\infty) \to 0}$.

* bound states, $E<0$: $\frac{2\mu E}{\hbar^2} = -K^2$ & $u(r\to\infty) \sim e^{-Kr}$

* continuum states, $E>0$: $\frac{2\mu E}{\hbar^2} = k^2$ & $u(r\to\infty) \sim e^{\pm ikr}$

(only normalisible in the "box"-sense)

A FREE PARTICLE IN THREE-DIMENSIONS

Consider the case $V(r)=0$ – this system is clearly spherically symmetric & has solutions for $E>0$.

$$\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]R(r)+k^2R(r)=0 \qquad \left(k^2=\frac{2\mu E}{\hbar^2}\right)$$

Changing to the dimensionless variable $\rho=kr$; $\dfrac{d^2R}{d\rho^2}+\dfrac{2}{\rho}\dfrac{dR}{d\rho}-\left(\dfrac{l(l+1)}{\rho^2}-1\right)R=0$

- $l=0$, $R(\rho)=\dfrac{w(\rho)}{\rho}$; $\dfrac{d^2w}{d\rho^2}+w=0 \Rightarrow w=\begin{cases}\cos\rho\\ \sin\rho\end{cases}$

$$R(\rho)=\begin{cases}(\cos\rho)/\rho \xrightarrow[\rho\to0]{} \sim 1/\rho & \text{"irregular soln"}\\ (\sin\rho)/\rho \xrightarrow[\rho\to0]{} \sim 1 & \text{"regular soln"}\end{cases}$$

- for general l, the solutions are known as the "spherical Bessel functions"

"regular soln" $$j_l(\rho)=(-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\left(\frac{\sin\rho}{\rho}\right)=\begin{cases}(\sin\rho)/\rho & (l=0)\\ \frac{\sin\rho}{\rho^2}-\frac{\cos\rho}{\rho} & (l=1)\\ \vdots\end{cases}$$

"irregular soln" $$n_l(\rho)=-(-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\left(\frac{\cos\rho}{\rho}\right)=\begin{cases}-\cos\rho/\rho & (l=0)\\ -\frac{\cos\rho}{\rho^2}-\frac{\sin\rho}{\rho} & (l=1)\\ \vdots\end{cases}$$

"spherical Neumann functions"

→ important linear combinations, the "spherical Hankel functions"

$$h_l^{(1)}=j_l(\rho)+i\,n_l(\rho) \qquad (\text{"of the first type"})$$

$$h_l^{(2)}=j_l(\rho)-i\,n_l(\rho) \qquad (\text{"of the second type"})$$

$$h_l^{(1)}=\begin{cases}e^{i\rho}/i\rho & (l=0)\\ -\frac{e^{i\rho}}{\rho}\left(1+\frac{i}{\rho}\right) & (l=1)\\ \vdots\end{cases}$$

* for small ρ $(\rho\ll l)$ $j_l(\rho)\sim\rho^l/(2l+1)!!$ & $n_l(\rho)\sim-\dfrac{(2l-1)!!}{\rho^{l+1}}$

* for large ρ $(\rho\gg l)$ $j_l(\rho)\sim\dfrac{1}{\rho}\sin\left(\rho-l\dfrac{\pi}{2}\right)$ & $n_l(\rho)\sim-\dfrac{1}{\rho}\cos\left(\rho-l\pi/2\right)$

& $h_l^{(1)}(\rho)\sim\dfrac{-i}{\rho}e^{i(\rho-l\pi/2)}$

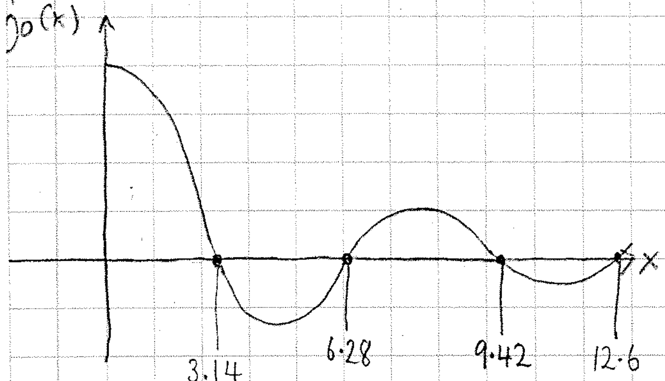
THE SPHERICAL INFINITE POTENTIAL WELL

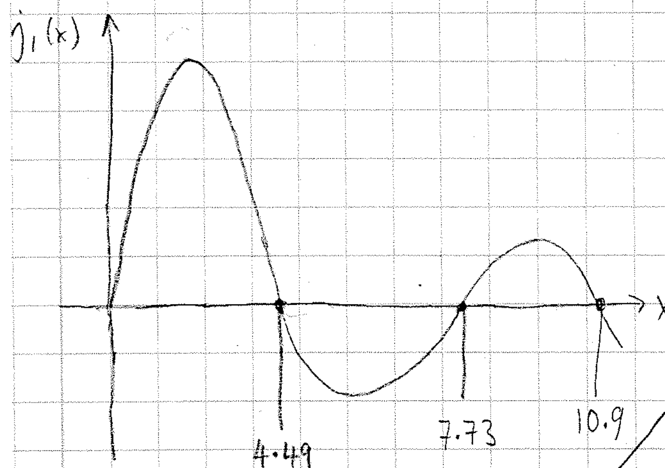
$$V(r) = \begin{cases} 0 & r<a \\ \infty & r>a \end{cases} \qquad \left(\frac{2\mu E}{\hbar^2} = k^2 \right)$$

the solution regular at $r=0$ is $R(r) = N \cdot j_\ell(kr)$.

The wavefunction at $r=a$ must be zero $\Rightarrow j_\ell(ka) = 0$

$\left[\begin{array}{l} \text{compare to} \\ \sin\frac{ka}{2} = 0 \text{ , } \cos\frac{ka}{2} = 0 \\ \text{in one dimension} \\ \rightarrow k = n\pi/a \end{array}\right]$





Zeroes of the spherical Bessel function

$j_0(x)$: 3.14, 6.28, 9.42, 12.6 ...

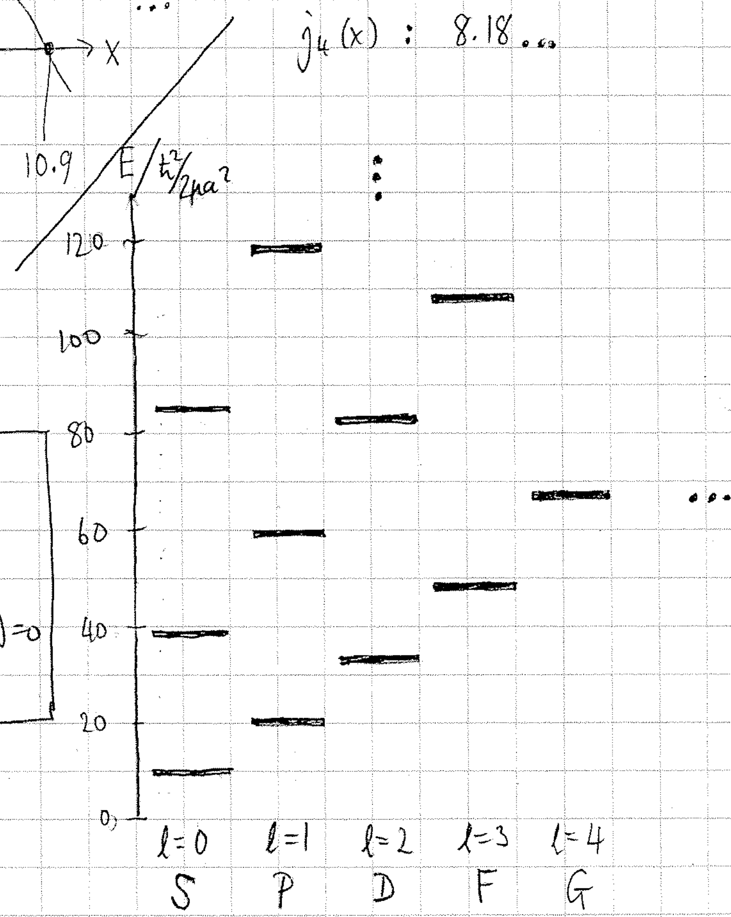
$j_1(x)$: 4.49, 7.73, 10.9 ...

$j_2(x)$: 5.76, 9.10 ...

$j_3(x)$: 6.99, 10.42 ...

$j_4(x)$: 8.18 ...

$$\boxed{\begin{array}{l} \phi_{n\ell m}(r) = N\, j_\ell(k_{n\ell} \cdot r)\, Y_\ell^m(\theta,\phi) \\ \qquad k_{n\ell} \text{ satisfies } j_\ell(k_{n\ell}\, a) = 0 \end{array}}$$



$\boxed{\text{THE SPHERICAL SQUARE WELL POTENTIAL}}$

$$V(r) = \begin{cases} -V_0 & r<a \\ 0 & r>a \end{cases}$$

· We'll consider bound state solutions $-V_0 < E < 0$.

Only the regular solution is acceptable for $r<a$:

$$\underline{R(r<a) = A\, j_l(kr)} \qquad \left(k = \sqrt{\frac{2m}{\hbar^2}(E+V_0)}\right)$$

For $r>a$, both the regular & irregular solutions are acceptable, but only in a combination that decreases exponentially (to make the wavefunction normalisable)

for $E<0$, $\tilde{k} = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{-2m|E|}{\hbar^2}} = i\kappa$

the Hankel functions are $h_l^{(1)}(i\kappa r) \sim e^{-\kappa r}$ ✓ ; $h_l^{(2)}(i\kappa r) \sim e^{\kappa r}$ ✗

$$\underline{R(r>a) = B\, h_l^{(1)}(i\kappa r)} \qquad \left(\kappa = \sqrt{\frac{2m|E|}{\hbar^2}}\right)$$

The wavefunction & its first derivative must match at $r=a$:

$$\left.\begin{aligned} A\, j_l(ka) &= B\, h_l^{(1)}(i\kappa a) \\ A k\, j_l'(ka) &= i\kappa B\, h_l^{(1)\prime}(i\kappa a) \end{aligned}\right\} \quad \boxed{k\,\frac{j_l'(ka)}{j_l(ka)} = i\kappa\,\frac{h_l^{(1)\prime}(i\kappa a)}{h_l^{(1)}(i\kappa a)}}$$

$\rightarrow$ trancendental equation for E.

e.g. $\boxed{l=0}$: $j_0'(ka) = \frac{\cos ka}{ka} - \frac{\sin ka}{(ka)^2}$, $\quad h_0^{(1)\prime}(i\kappa a) = \frac{e^{-\kappa a}}{i\kappa a}\left(1+\frac{i}{i\kappa a}\right) = \frac{e^{-\kappa a}}{i\kappa a}\left(1+\frac{1}{\kappa a}\right)$

$j_0(ka) = \frac{\sin ka}{ka}$, $\quad h_0^{(1)}(i\kappa a) = e^{-\kappa a}/-\kappa a$

$$\Rightarrow \quad k\cdot\left(\cot ka - \frac{1}{ka}\right) = \left(1+1/\kappa a\right)\frac{i\kappa}{i\kappa a}\cdot(-\kappa a) = -\kappa\left(1+1/\kappa a\right)$$

$$k\cot ka - \cancel{1/a} = -\kappa - \cancel{1/a} \quad \Rightarrow \quad \underline{k\cot ka = -\kappa}$$

compare this to the one-dimensional case (odd solution) – same with $a_{1D} \to 2a$

Only has a solution if $a^2 V_0 > \hbar^2\pi^2/8m$.

* continuum ($E>0$) solutions

- for $r<a$, can only have the regular solution $R_\ell(r<a) = A\, j_\ell(Kr)$. $\left(K^2 = \frac{2m}{\hbar^2}(E+V_0)\right)$
- for $r>a$, both the regular & irregular solutions are acceptable

$$R_\ell(r>a) = B\, j_\ell(kr) + C\, n_\ell(kr) \quad \left(k^2 = \frac{2mE}{\hbar^2}\right)$$

matching the wavefunction & its derivative will fix the ratio C/B. We won't do it explicitly, but it can be done.

In the limit $r>>a$ (& $kr>>\ell$) $\quad R_\ell(r\to\infty) \to \frac{B}{2ikr}\left(e^{i(kr-\ell\pi/2)} - e^{-i(kr-\ell\pi/2)}\right)$

$$- \frac{C}{2kr}\left(e^{i(kr-\ell\pi/2)} + e^{-i(kr-\ell\pi/2)}\right)$$

$$R_\ell(r\to\infty) \to \frac{-C+iB}{2kr}\left(e^{-i(kr-\ell\pi/2)} + \frac{C+iB}{C-iB}\, e^{i(kr-\ell\pi/2)}\right)$$

"spherical wave from $r=\infty$ to $r=0$" INCOMING

"spherical wave from $r=0$ to $r=\infty$" OUTGOING

$$* \; \phi \propto \frac{e^{\pm ikr}}{r} Y_\ell^M(\theta,\phi)$$

radial flux:

$$j_r = \hat{r}\cdot\frac{\hbar}{2i\mu}\left[\phi^*\vec{\nabla}\phi - \phi\vec{\nabla}\phi^*\right]$$

$$= \frac{\hbar}{2i\mu}\left[\phi^*\frac{\partial}{\partial r}\phi - \phi\frac{\partial}{\partial r}\phi^*\right] = \pm\frac{\hbar k}{\mu}\,|Y_\ell^M(\theta,\phi)|^2$$

$$\Rightarrow \underline{\int d\Omega\, j_r = \pm\frac{\hbar k}{\mu}}$$

in the case of no potential, we match a j_ℓ to an equivalent j_ℓ & $C=0$ so that $\frac{C+iB}{C-iB} = -1$. In general $\left|\frac{C+iB}{C-iB}\right| = 1$ so we can write

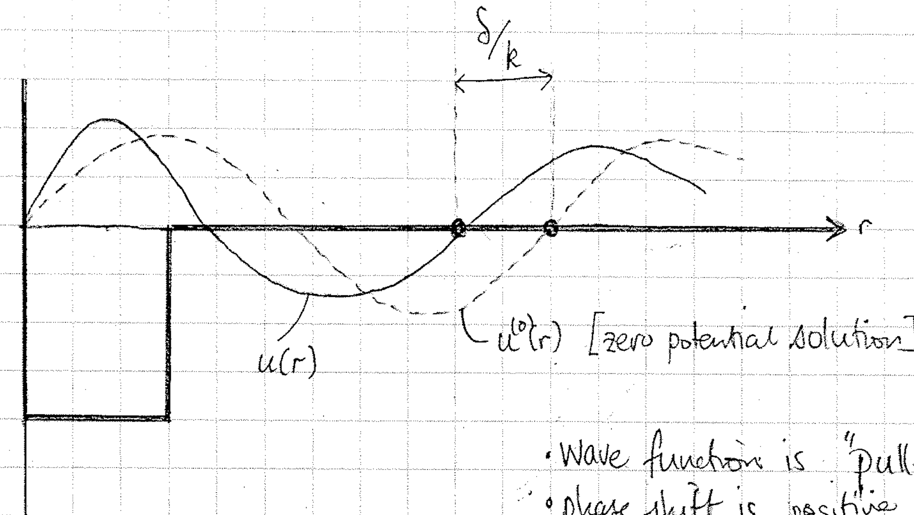
$$\frac{C+iB}{C-iB} = -e^{2i\delta_\ell(k)}$$

$$\& \; R_\ell(r\to\infty) \to \frac{N}{r}\sin\left(kr - \ell\frac{\pi}{2} + \delta_\ell(k)\right) \quad \text{(A)}$$

in the no potential case $\quad R_\ell^{(0)}(r\to\infty) \to \frac{N^{(0)}}{r}\sin(kr - \ell\pi/2)$

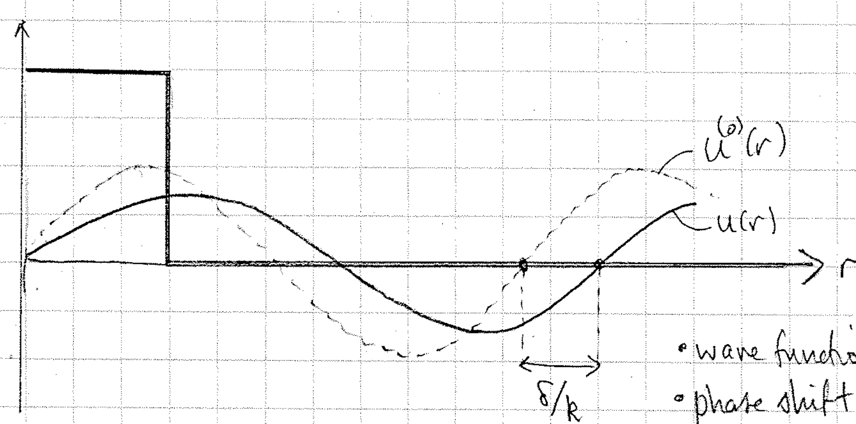
In fact equation (A) describes the asymptotic wave for any real potential, with the "phase shift" $\delta_\ell(k)$ describing scattering by the potential.

e.g. for an <u>attractive</u> square well



- wave function is "pulled in" to the potential
- phase shift is positive

e.g. for a <u>repulsive</u> square well



- wave function is "pushed out" of the potential
- phase shift is negative.

We will return to the phase shift as a parameterisation of scattering from potentials next semester.

THE COULOMB POTENTIAL

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

* bound state solutions, $E<0$, $E=-|E|$

change variables ; $\lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}}$ & $\rho = \sqrt{\frac{8\mu|E|}{\hbar^2}}\, r$

$$\Rightarrow \frac{d^2u}{d\rho^2} - \frac{1}{4}u - \frac{l(l+1)}{\rho^2}u + \frac{\lambda}{\rho}u = 0$$

in the $\rho \to \infty$ limit $\rightarrow \frac{d^2u}{d\rho^2} - \frac{1}{4}u = 0 \quad \Rightarrow u(\rho\to\infty) \sim e^{-\rho/2}$

propose the form $u(\rho) = f(\rho)e^{-\rho/2}$ where $f(\rho)$ must satisfy

$$f'' - f' + \left(\frac{\lambda}{\rho} - \frac{l(l+1)}{\rho^2}\right)f = 0$$

We proved earlier that near the origin we require $u_l(r\to 0) \sim r^{l+1}$

$\Rightarrow f(\rho) \sim \rho^{l+1}$

propose $f(\rho) = \rho^{l+1} g(\rho)$

$$\Rightarrow \boxed{g'' + \left(\frac{2(l+1)}{\rho} - 1\right)g' + \frac{\lambda-(l+1)}{\rho}g = 0}$$

this can be solved by power series expansion: $g(\rho) = \sum_{k=0} a_k \rho^k$

$$\Rightarrow \sum_k \Big(\underbrace{k(k-1)a_k\rho^{k-2} + 2(l+1)ka_k\rho^{k-2}}_{\text{shift } k\to k+1} - ka_k\rho^{k-1} + (\lambda-(l+1))a_k\rho^{k-1}\Big) = 0$$

$$\sum_k \Big(\left[k(k+1) + 2(l+1)(k+1)\right]a_{k+1} + \left[-k + (\lambda-(l+1))\right]a_k\Big)\rho^{k-1} = 0$$

$$\Rightarrow \underline{a_{k+1} = \frac{k-\lambda+l+1}{(k+1)(k+2l+2)}a_k}$$

as in the one-dimension harmonic oscillator case, to get a normalisable solution we require the polynomial to truncate. This means that for a given l there is a value of k for which $k-\lambda+l+1=0$, call this value $k=n$.

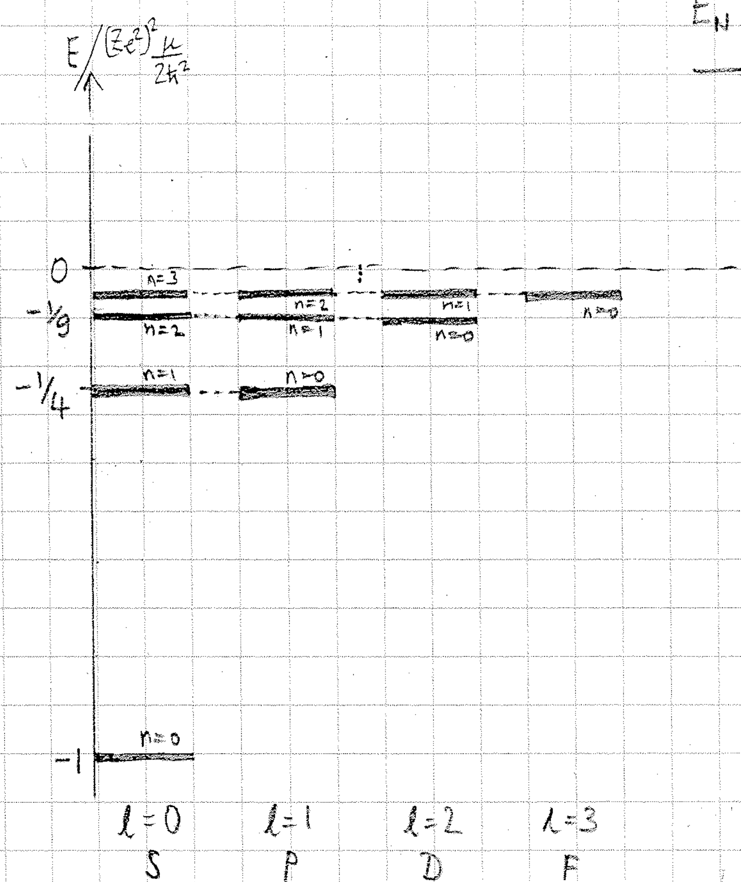
$\Rightarrow \underline{\lambda = n+l+1}$ & $a_{k+1} = \frac{k-n}{(k+1)(k+2l+2)}a_k$ $\quad$ <u>where $n\geq 0$</u>.

Since both n & l can take positive integer values we have $\lambda = N = n+l+1$ where N is an integer

$$\Rightarrow N = \lambda = \frac{Ze^2}{\hbar}\sqrt{\frac{\mu}{2|E|}} \quad \Rightarrow |E| = \frac{(Ze^2)^2\mu}{2\hbar^2}\cdot\frac{1}{N^2}$$

So the bound state spectrum of the Coulombic potential

$$\underline{E_N = -\frac{(Ze^2)^2\mu}{2\hbar^2}\cdot\frac{1}{N^2}}.$$



Considerable degeneracy in the spectrum.

(this degeneracy reflects a symmetry of the $1/r$ potential, but not an obvious one!)

* eigenfunctions :

- $l=0$ $\rightarrow n=0$: $g(\rho) \propto 1$

  $\rightarrow n=1$: $a_1 = \frac{0-1}{1\cdot 2}a_0 = -\frac{1}{2}a_0 \Rightarrow g(\rho) \propto 1 - \rho/2$

  $\rightarrow n=2$: $a_2 = \frac{1-2}{2\cdot 3} = -\frac{1}{6}a_1$; $a_1 = \frac{0-2}{1\cdot 2} = -1 \Rightarrow g(\rho) \propto \left(1 - \rho + \rho^2/6\right)$

  ⋮

- $l=1$ $\rightarrow n=0$: $g(\rho) \propto 1$

  $\rightarrow n=1$: $a_1 = \frac{0-1}{1\cdot(4)}a_0 = -\frac{1}{4}a_0 \Rightarrow g(\rho) \propto 1 - \rho/4$

  ⋮

These polynomials are known as the "associated Laguerre polynomials" $g(\rho) = L^{(2l+1)}(\rho)$

In terms of the Bohr radius, $a_{Bohr} = \hbar^2/\mu e^2$, we have $\rho = \frac{2Z}{a_{Bohr}} \cdot \frac{1}{N} r$,

such that the wavefunctions are:

$$(N=1) \quad \phi_{00}(\vec{r}) = 2\left(\frac{Z}{a_{Bohr}}\right)^{3/2} e^{-Zr/a_{Bohr}} Y_0^0(\theta,\phi) \qquad \text{1-fold deg.}$$

$$(N=2) \quad \phi_{10}(\vec{r}) = 2\left(\frac{Z}{2a_{Bohr}}\right)^{3/2}\left(1-\frac{Z}{2a_{Bohr}} r\right) e^{-Zr/2a_{Bohr}} Y_0^0(\theta,\phi) \qquad \text{1-fold deg.}$$

$$(N=2) \quad \phi_{01}(\vec{r}) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_{Bohr}}\right)^{3/2} \frac{Zr}{a_{Bohr}} e^{-Zr/2a_{Bohr}} Y_1^m(\theta,\phi) \qquad \text{3-fold deg. } (m=-1,0,+1)$$

$$(N=3) \quad \phi_{20}(\vec{r}) = 2\left(\frac{Z}{3a_{Bohr}}\right)^{3/2}\left(1-\frac{2Zr}{3a_{Bohr}}+\frac{2}{27}\left(\frac{Zr}{a_{Bohr}}\right)^2\right) e^{-Zr/3a_{Bohr}} Y_0^0(\theta,\phi) \qquad \text{1-fold deg}$$

$$(N=3) \quad \phi_{11}(\vec{r}) = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_{Bohr}}\right)^{3/2} \frac{Zr}{a_{Bohr}}\left(1-\frac{Zr}{6a_{Bohr}}\right) e^{-Zr/3a_{Bohr}} Y_1^m(\theta,\phi) \qquad \text{3-fold deg. } (m=-1,0,+1)$$

$$(N=3) \quad \phi_{02}(\vec{r}) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_{Bohr}}\right)^{3/2}\left(\frac{Zr}{a_{Bohr}}\right)^2 e^{-Zr/3a_{Bohr}} Y_2^m(\theta,\phi) \qquad \text{5-fold deg. } (m=-2,-1,0,+1,+2)$$

$$\vdots$$