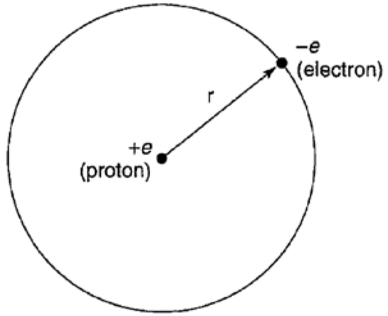
4.2: The Hydrogen Atom

Consider an electron orbiting a proton fixed at the origin of coordinates. The potential is (ε_0 = vacuum permittivity):

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



The radial equation for "$u(r)$" [remember $R(r) = u(r)/r$] becomes:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu}$$

The exact solution of the Hydrogen atom potential is important because it much influences on the understanding of all atoms (periodic table).

We will focus on bound states i.e. $E<0$ (there are also scattering states).

Thus, the combination used many times becomes:

$$\boxed{\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}}$$

$1/\kappa^2 = -\hbar^2/2mE$

If you divide all by E, and move the effective potential to the right, you get:

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{l(l+1)}{(\kappa r)^2}\right]u$$ Check!

This suggests $\boxed{\rho \equiv \kappa r}$ may be useful, and also

(dimensionless)

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

The exact radial equation then becomes "simpler":

$$\boxed{\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u}$$

As done time ago for the "second" solution of the 1D harmonic oscillator (using the Hermite polynomials), we will study special cases expecting to simplify the problem:

Consider ρ large: $$\frac{d^2u}{d\rho^2} = u \longrightarrow u(\rho) \sim Ae^{-\rho}$$

Unphysical diverging solutions discarded.

Consider ρ small: $$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \longrightarrow u(\rho) \sim C\rho^{l+1}$$

Knowing the two asymptotic limits of ρ large and small, it makes sense to try a new definition:

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho)$$

$\rho = \kappa r$ so we know all solutions will decay exponentially

$$\boxed{\rho \frac{d^2 v}{d\rho^2} + 2(l + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(l+1)]v = 0}$$

Exactly as done for the Hermite polynomials of 1D oscillator (second method) we try a series expansion:

$$\boxed{v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j}$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j$$

$$\frac{d^2v}{d\rho^2} = \sum_{j=0}^{\infty} j(j+1) c_{j+1} \rho^{j-1}$$

* **Verify** change in notation from *j* to *j+1* by expanding the first few terms!

Introducing these eqs. into the diff equation we arrive to a recursive relation for the coefficients Eq.4.63:

$$\boxed{c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j}$$

At very large *j*, then: $c_{j+1} \cong \frac{2}{j+1} c_j$

At large j, it can be shown (see book) that the coefficients generate a growing exponential e^{ρ}. The SAME happened in Ch. 2, 1D harmonic oscillator (revisit those lectures).

Then, we must truncate the series (as done with the Hermite polynomials). Long story short, there is an upper limit in j beyond which:

$$\boxed{c_{(j_{max}+1)} = 0}$$

c_0 only, then j_{max}=0
c_0 and c_1 only, then j_{max}=1
c_0, c_1, c_2, …

Thus, the series expansion with j running in principle to ∞, becomes in practice a polynomial.

You may recall that "magically" from that condition, the quantized levels of the 1D oscillator were deduced. Here is the SAME story.

Here, the recursive relation from 2 pages back is repeated:

$$\boxed{c_{j+1} = \left\{ \frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)} \right\} c_j}$$

Then: $$\underbrace{2(j_{\max} + l + 1)} - \rho_0 = 0$$

Call this "*n*" (1,2,3,...). I.e. $\rho_0 = 2n$.
Minimum angular momentum l is 0. Min j_{max} is 0. You can achieve the same "*n*" with various j_{max} and l.

Remember

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$$

and $$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$$

Amazingly, by this procedure we arrive to the very famous **Bohr's formula**:

$$\boxed{E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}}$$

n=1,2,3,...

$$E_n = -\underbrace{\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]}_{\boxed{E_1 = -13.6 \text{ eV}}}\frac{1}{n^2}$$

(eV = 1.6 10^{-19} Joules)

Moreover, since $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$ then it can be shown:

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}$$ where $\underbrace{\boxed{a = 0.529 \times 10^{-10} \text{ m}}}$

Bohr's radius.

The angstrom scale, and thus the typical atomic size, emerges.

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho)$$

$$\rho \equiv \kappa r = (1/an)\, r$$

Angstrom is the "natural" size of atoms. Remarkable agreement with reality!

OPTIONAL HW for 6 points: In order to transform the spherical harmonics to the canonical ones often used in chemistry and in condensed matter, we have to linearly combine them, as shown below.

$\ell = 1$ [edit]

$$Y_{1,-1} = p_y = i\sqrt{\frac{1}{2}}\left(Y_1^{-1} + Y_1^{1}\right) = \sqrt{\frac{3}{4\pi}} \cdot \frac{y}{r}$$

$$Y_{1,0} = p_z = Y_1^{0} = \sqrt{\frac{3}{4\pi}} \cdot \frac{z}{r}$$

$$Y_{1,1} = p_x = \sqrt{\frac{1}{2}}\left(Y_1^{-1} - Y_1^{1}\right) = \sqrt{\frac{3}{4\pi}} \cdot \frac{x}{r}$$

$\ell = 2$ [edit]

$$Y_{2,-2} = d_{xy} = i\sqrt{\frac{1}{2}}\left(Y_2^{-2} - Y_2^{2}\right) = \frac{1}{2}\sqrt{\frac{15}{\pi}} \cdot \frac{xy}{r^2}$$

$$Y_{2,-1} = d_{yz} = i\sqrt{\frac{1}{2}}\left(Y_2^{-1} + Y_2^{1}\right) = \frac{1}{2}\sqrt{\frac{15}{\pi}} \cdot \frac{y \cdot z}{r^2}$$

$$Y_{2,0} = d_{z^2} = Y_2^{0} = \frac{1}{4}\sqrt{\frac{5}{\pi}} \cdot \frac{3z^2 - r^2}{r^2}$$

$$Y_{2,1} = d_{xz} = \sqrt{\frac{1}{2}}\left(Y_2^{-1} - Y_2^{1}\right) = \frac{1}{2}\sqrt{\frac{15}{\pi}} \cdot \frac{x \cdot z}{r^2}$$

$$Y_{2,2} = d_{x^2-y^2} = \sqrt{\frac{1}{2}}\left(Y_2^{-2} + Y_2^{2}\right) = \frac{1}{4}\sqrt{\frac{15}{\pi}} \cdot \frac{x^2 - y^2}{r^2}$$

Note that in spherical coordinates, for instance $z=r\cos(\theta)$. Thus, z/r in p_z is r independent and p_z then becomes just $\cos(\theta)$ and because is ϕ independent, then we get the familiar shape.

All the rest are r-indep. as well, because x and y in spherical also are proportional to r, and the r's cancel out everywhere.