Hydrogen Atom

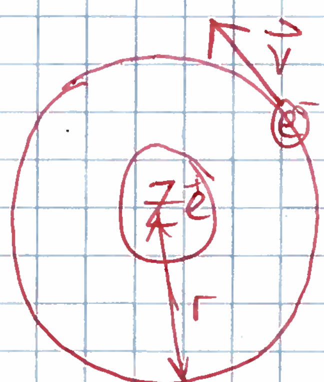
Rydberg Formula (empirical)

Atomic hydrogen emits light with a discrete set of wavelengths.

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$ where n_1 & n_2 are integers.

R = Rydberg constant $\sim 1.097 \times 10^7\ m^{-1}$

Bohr: A ~~planetary~~ planetary model of atom:



Classical Picture: $F = \frac{Zke^2}{r^2}$

Acceleration $= \frac{v^2}{r}$ (centripetal)

$F = ma \Rightarrow \boxed{\frac{Zke^2}{r^2} = \frac{mv^2}{r}} \Rightarrow \boxed{\frac{Zke^2}{r} = mv^2}$

Also $\frac{Zke^2}{2r} = \frac{1}{2}mv^2 = KE$

$$U = -\frac{ke^2 Z}{r}$$

$\therefore$ Total energy $= KE + U = -\frac{ke^2 Z}{2r}$

Angular Momentum: $L = mvr$

Bohr Assumed that L is quantized.

$$L \stackrel{?}{=} n\hbar \,, \quad n = \text{integer} \quad \text{(Bohr guess)}$$

Actually, $L = \sqrt{\hbar^2 \ell(\ell+1)} = \hbar\sqrt{\ell(\ell+1)}$, ℓ = integer,

So Bohr guessed incorrectly.

Nevertheless, with Bohr assumption,

$$L = mvr = n\hbar \Rightarrow \cancel{r_n = \frac{n\hbar}{mv}} \quad v = \frac{n\hbar}{mr}$$

$$\cancel{E = KE + U = -\frac{ke^2 Z}{2r} = -\frac{ke^2 Z}{2n\hbar}}$$

$$\therefore \frac{Zke^2}{r} = \frac{m n^2\hbar^2}{m^2 r^2}$$

$$\boxed{r = \frac{n^2\hbar^2}{mZke^2} = \frac{n^2}{Z}a_0}$$

where a_0 = Bohr radius $= \frac{\hbar^2}{mke^2}$

$\cancel{v = n\hbar}$

$$\text{Total Energy} = KE + U = -\frac{ke^2 Z}{2r} = -\frac{ke^2 Z}{2\left(\frac{n^2 a_0}{Z}\right)}$$

$$= -\frac{ke^2 Z^2}{2a_0}\frac{1}{n^2}$$

$\rightarrow$ 13.6 eV for $Z=1$

If electrons transition from n_2 to n_1, then they emit light with energy

$$\Delta E = -\underbrace{\frac{ke^2 Z^2}{2a}}_{(13.6\,eV)}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) = h\nu = \frac{hc}{\lambda}$$

$$\frac{1}{\lambda} = \frac{13.6\,eV}{\underbrace{hc}_{1240\,eV\cdot nm}}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

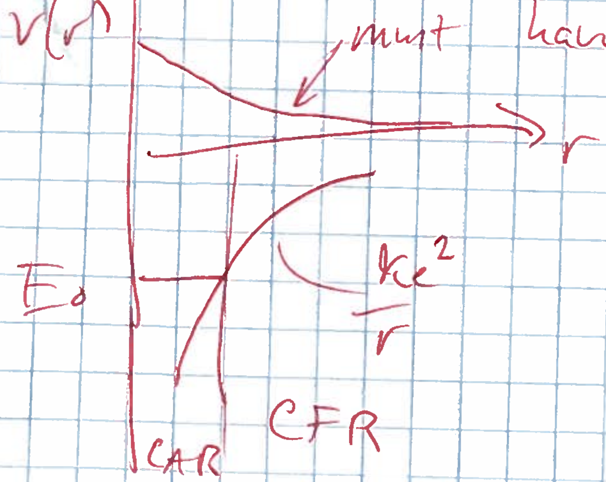
$$= \frac{13.6\,eV}{(1240\,eV\cdot nm)}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= \frac{13.6\,eV}{(1.24\times10^{-4}\,eV\,cm)}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

$$= 1.097\,cm^{-1}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Bohr's Semiclassical Approach gives the correct result for the energy levels of H atom, He^+ ~~ato~~ ion, ect, even though his angular momentum guess was wrong.

With the full QM, energy eigenstates are quantized for bound states ~~because~~ due to the normalization condition on $|\psi|^2$.



Since $V(r)$ is a central potential, we know that

$$\phi(r,\theta,\varphi) = R(r)\, Y_l^m(\theta,\varphi)$$

and $R(r)$ = radial wavefunction = $\frac{u(r)}{r}$

where $u(r)$ satisfies the radial equation

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

with $V(r) = -\frac{kZe^2}{r}$

Simplify notation: $\kappa \equiv \dfrac{\sqrt{-2mE}}{\hbar}$ (E is negative)

$\rho \equiv \kappa r$ (dimensionless distance)

$\rho_0 = \dfrac{2mZe^2k}{\hbar^2\kappa}$ [note that ρ_0 determines E:

E =

Then $\dfrac{d^2u}{d\rho^2} = \left[1 - \dfrac{\rho_0}{\rho} + \dfrac{\ell(\ell+1)}{\rho^2}\right]u$

Guess solution:

$$u(\rho) = \rho^{\ell+1}e^{-\rho}\underbrace{\left[\sum_{j=0}^{\infty} c_j\rho^j\right]}$$

Some power series polynomial. The question is: what are the c_j?

Answer: Substitute the guess into the radial eq.

Result:

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty}(j+1)c_{j+1}\rho^j$$
$$-2\sum_{j=0}^{\infty} jc_j\rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j\rho^j = \emptyset.$$

For this to equal zero, each power of ρ^j must have zero as its coefficient. This means

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + \left[\rho_0 - 2(l+1)\right]c_j = \phi$$

or $$c_{j+1} = \left[\frac{2(j+l+1) - \rho_0}{(j+1)(j+2l+2)}\right] c_j \Leftarrow$$ "Recursion Formula for c_j"

Given c_0, this formula gives c_1.
Then c_1 gives c_2
Then c_2 gives c_3.
etc.

But this is dangerous, because then the series might go to infinity as $\rho \to \infty$
(This means $r \to \infty$).

There ~~can~~ would be ~~a~~ unnormalizable solution

To make sure the radial wavefunction is normalizable, we must have some coefficient c_{jmax} which equals zero, so that

$c_{jmax+1} = \phi$
$c_{jmax+2} = \phi$

Then $u(r)$ will be normalizable