Consider the Electron

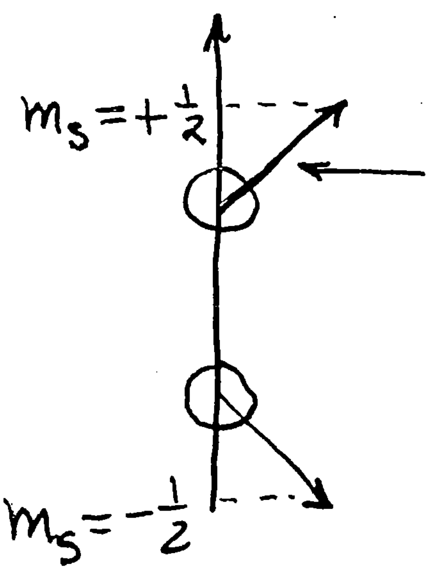
It also has "Spin" angular momentum

$$S = 1/2$$

$$\underline{\text{Magnitude of}} \ \underline{\text{spin angular momentum}} = \left[s(s+1)\right]^{1/2} \hbar$$

$$\text{Component along } z\text{-axis} = m_s \hbar$$

$$g_s = \text{degeneracy} = 2s+1 = 2\left(\tfrac{1}{2}\right)+1 = 2$$



$$= \sqrt{\tfrac{1}{2}\left(\tfrac{3}{2}\right)}\,\hbar = \sqrt{s(s+1)}\,\hbar$$

$$= \sqrt{\tfrac{3}{4}}\,\hbar$$

Atomic Structure & Spectra

Spectrum of atomic hydrogen:

$$\frac{1}{\lambda} = R_H \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

$n_2 = n_1+1, n_1+2, n_1+3, \ldots$

R_H = Rydberg Constant

$= 109677 \text{ cm}^{-1}$

Balmer Series — visible region of spectrum

$n_1 = 2$

Lyman Series — ultraviolet

$n_1 = 1$

Paschen Series — I.R.

Bohr Model of H atom

Assumptions:

- electrons in orbits don't radiate
- do so only if they change by discrete frequencies
- built on Planck-Einstein relationship: energy difference related to $h\nu$

1) $E_2 - E_1 = h\nu$

2) Angular momentum of electron can only have values $l_n = n\hbar$

3) Coulombic force 

$$F = -\frac{(Ze)e}{r^2}$$

Z = nuclear charge

4) Use $F = ma$

Bohr Model (Cont.)

Centripetal acceleration / centrifugal force

$= \frac{mv^2}{r}$

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}$$

$$mv^2 r = Ze^2$$

$$l_a = mvr = n\hbar$$

$$v = \frac{n\hbar}{mr}$$

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

$$\frac{n^2\hbar^2}{mr} = Ze^2$$

$$r = \frac{n^2\hbar^2}{mZe^2}$$

$\therefore$ restricted to orbits where $n = 1, 2, \ldots$

Bohr Model (cont.)

Smallest Allowed orbit

$$r_0 \equiv a_0 = \frac{(1)^2 \hbar^2}{me^2}$$

$Z = +1$ for H atom

Bohr Radius $= a_0 = 0.529$ Å

Energy

$$T = \frac{1}{2} m v^2 \qquad v^2 = \frac{n^2 \hbar^2}{m^2 r^2}$$

$$r = \frac{n^2 \hbar^2}{m Z e^2}$$

$$T = \frac{1}{2} \frac{Ze^2}{r} \qquad m r v^2 = Ze^2$$

$$F = -\frac{\partial V}{\partial r} \qquad V = -\int_\infty^r F\,dr = +\int_\infty^r \frac{Ze^2}{r^2}\,dr$$

$$= -\frac{Ze^2}{r}$$

$$E = T + V = \frac{1}{2}\frac{Ze^2}{r} - \frac{Ze^2}{r} = -\frac{1}{2}\frac{Ze^2}{r}$$

Bohr Model (cont.)

$$E = -\frac{1}{2}\frac{Ze^2}{r}$$

$$r = \frac{n^2\hbar^2}{mZe^2}$$

$$\therefore \quad E = -\frac{mZ^2e^4}{2n^2\hbar^2}$$

$$h\nu = E_2 - E_1 = \frac{me^4}{2\hbar^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\nu = \frac{c}{\lambda}$$

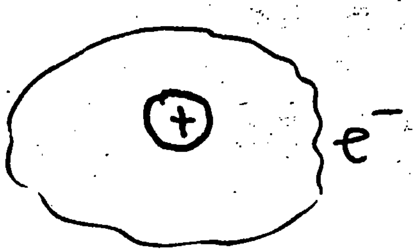
$$\frac{1}{\lambda} = \frac{2\pi^2 me^4}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$109737 \ \mathrm{cm}^{-1}$

Compared to $R_H = 109677 \ \mathrm{cm}^{-1}$

Schrödinger Eq. H-atom

Formal Solution



∴ 6 – Coordinates

– motion of atom ⇒ translation (c.m.)

+ motion of electron about the proton

partial differential Eq. in 3 variables

∴ Can factor into:

– angular function – rotational motion

– radial function

Sch. Eq. — H Atom (cont.)

$$H\Psi = E\Psi$$

$$H = -\left(\hbar^2/2m_e\right)\nabla_e^2 - \left(\frac{\hbar^2}{2m_N}\right)\nabla_N^2 + V(r)$$

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

Vacuum permittivity
8.854×10^{-12}
$J^{-1} C^2 m^{-1}$

Transform:

$$H = -\left(\frac{\hbar^2}{2m}\right)\nabla_{c.m.}^2 - \left(\frac{\hbar^2}{2\underline{\underline{\mu}}}\right)\underbrace{\nabla^2}_{} + V(r)$$

$m = m_N + m_e$

K.E. and mass of atom as a whole

Coordinates of electron relative to nucleus

H Atom (Cont.)

$$-\left(\frac{\hbar^2}{2\mu}\right)\nabla^2\Psi + V(r)\,\Psi = E\Psi$$

for internal structure of the atom

Take full Eq. – do a separation of variables
– obtain motion of μ about c.m.

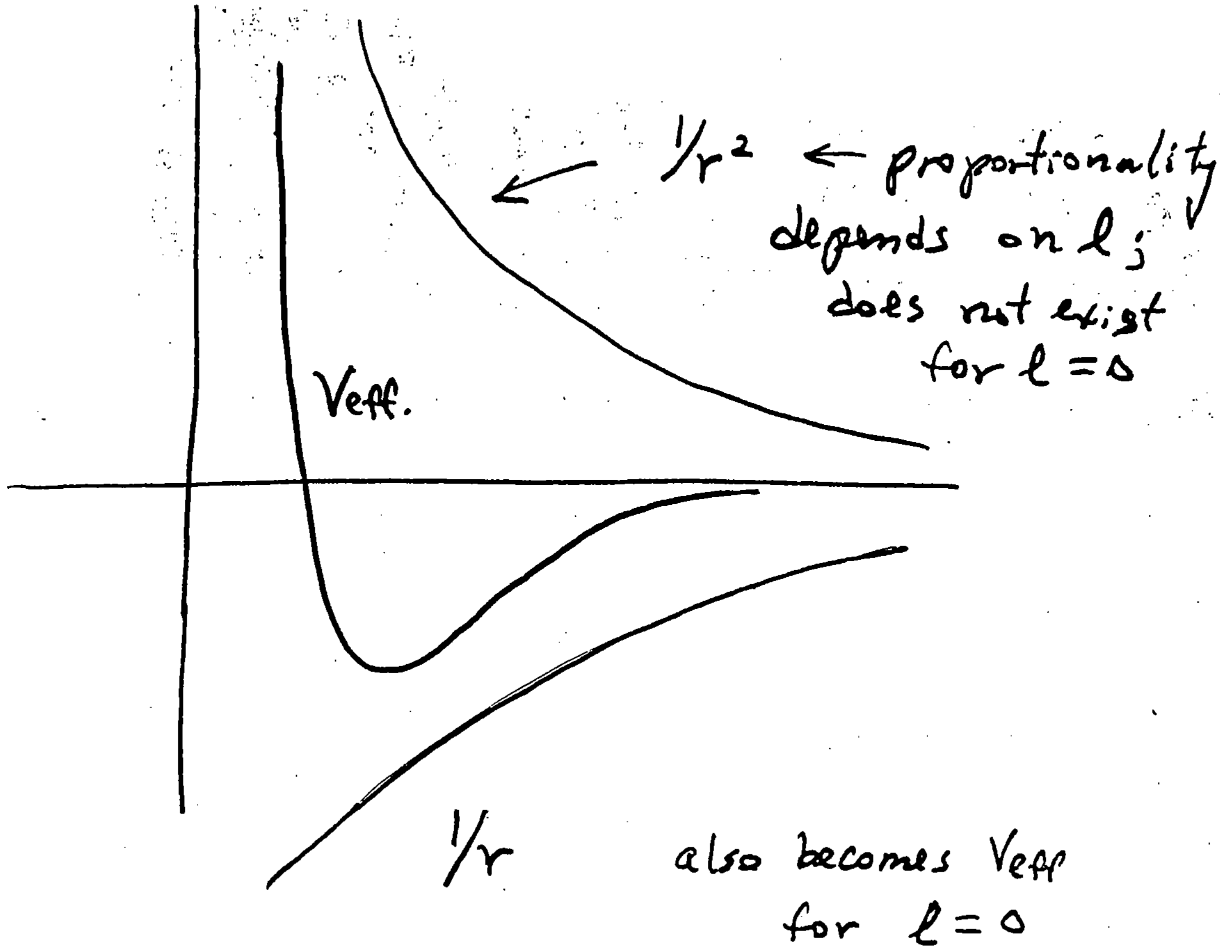
$$\Psi(r,\theta,\varphi) = R(r)\,Y(\theta,\varphi)$$

Radial Part of Solution – looks like Sch. Eq. with

$$V = -\left(\frac{Ze^2}{4\pi\epsilon_0 r}\right) + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}$$

Coulomb potential energy

Centrifugal force arising from angular moment of the electron around



$\therefore$ $\ell = 0$
& $\ell \neq 0$ wavefunctions very different near the nucleus

Gave Associated Laguerre Eq.

$n = 1, 2, \ldots$
$\ell < n-1$

H Atom

$$E = -\left(Z^2 e^4 / 32\pi^2 \epsilon_0^2 \hbar^2\right) \frac{1}{n^2}$$

Associated Laguerre Polynomials

$$R_{n,\ell}(\rho) = \rho^{\ell} L_{n,\ell}(\rho)\, e^{-\rho/2}$$

where $\rho = \left(\dfrac{\mu Z e^2}{2\pi \epsilon_0 \hbar^2}\right) \dfrac{r}{n}$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

$$\mu = \frac{m_e \cdot m_N}{m_e + m_N} \cong m_e$$

$$\Psi_{n,\ell,m_\ell} = R_{n,\ell}(r)\, Y_{\ell,m_\ell}(\theta,\varphi) \qquad \frac{m_e}{\mu} = 1.00054$$

1s: $R_{1,0} = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho/2}$

2s: $R_{2,0} = \left(1/2\sqrt{2}\right)\left(\frac{Z}{a_0}\right)^{3/2} (2-\rho)\, e^{-\rho/2}$

2p: $R_{2,1} = \left(1/2\sqrt{6}\right)\left(\frac{Z}{a_0}\right)^{3/2} \rho\, e^{-\rho/2}$