11/4/98

Lecture 27 H Atom cont.

H atom

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\psi_{n\ell m}(r,\theta,\phi) = E_n \, \psi_{n\ell m}(r,\theta,\phi)$$

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

Full wave function

$$\psi_{n\ell m} = \frac{U_{n\ell}(r)}{r} Y_\ell^m(\theta,\phi)$$

$$\int_0^\infty |U_{n\ell}(r)|^2 dr = 1$$

$$\kappa = \sqrt{\frac{-2mE_n}{\hbar^2}} \qquad \rho = \kappa r$$

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

$$U_{n\ell}(r) = U(r) = \rho^{\ell+1} e^{-\rho} V(\rho)$$

$$V(\rho) = \sum_{j=0}^{\infty} a_j \rho^j$$

Plug into Sch. eq. and find

$$a_{j+1} = \left[\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right] a_j$$

Consider large j limit

$$a_{j+1} \sim \frac{2}{j} a_j$$

$$a_j \sim \frac{2^j}{j!} A$$

If series does not terminate

$$v(\rho) \sim A \sum \frac{2^j \rho^j}{j!} \sim A e^{2\rho}$$

so $U(\rho) \sim \rho^{l+1} e^{\rho}$ not normalizable

$\Rightarrow$ Series must terminate for some j_{max}

$$a_{j_{max}+1} = 0$$

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

or $\boxed{\rho_0 = 2n}$

Define principle quantum # $n = j_{max} + l + 1$

$$\rho_0 = 2n = me^2/(2\pi\epsilon_0 \hbar^2 \kappa)$$

and $-\hbar^2\kappa^2/2m = E$

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

$n = 1, 2, 3 \ldots$ Bohr Formula

$E_n = E_1/n^2$ $\quad E_1 = -\frac{mc^2}{2}\left(\frac{e^2}{4\pi\epsilon_0 \hbar c}\right)^2$

multiply and divide by c^2

$$mc^2 = 0.511 \text{ MeV} = 0.511 \times 10^6 \text{ eV}$$

$V = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \Rightarrow \frac{e^2}{4\pi\epsilon_0}$ has units energy-length

2

$\hbar c$ = units energy - length also

So

$$\alpha \equiv \frac{e^2}{4\pi\epsilon_0}\frac{1}{\hbar c} \approx 1/137.036$$

is dimensionless fine structure constant sets strength of E+M interaction.

$$E_1 = -\frac{mc^2}{2}\alpha^2 = -13.6 \text{ eV}$$

Need to add 13.6 eV to H atom to ionize the electron.

$$\kappa = \frac{1}{an}$$

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} = \frac{\hbar c}{\alpha mc^2} = 5.29 \times 10^4 \text{ Fm}$$

$$= \boxed{0.529 \times 10^{-10} \text{ m}}$$

$\hbar c = 197.33$ MeV - Fm

$mc^2 = 0.511$ MeV

$$\rho = \frac{r}{an} \qquad \psi \sim e^{-\rho}$$

Thus a determines size of atoms and is called Bohr radius

Ground state $n = 1 = j_{max} + l + 1$

$\Rightarrow l = j_{max} = 0 \qquad V(\rho) = a_0$ a const

$$U_{nl} = a_0\rho^{l+1}e^{-\rho} = a_0\kappa r e^{-r/a}$$

$$U_{10} = \frac{a_0}{a} r e^{-r/a}$$

$$\psi_{100}(r,\theta,\phi) = \frac{u_{10}(r)}{r} Y_0^0(\theta,\phi)$$

$$Y_0^0 = \sqrt{\frac{1}{4\pi}}$$

Normalized ground state $\boxed{\psi_{100} = \frac{1}{\pi^{1/2} a^{3/2}} e^{-r/a}}$

2^{nd} energy level. $E_2 = \frac{E_1}{2^2} = \frac{-13.6}{4} = -3.4 eV$

Two choices $j_{max} + l + 1 = 2$

(a) $l = 1$, $j_{max} = 0$ P wave or P state

(b) $l = 0$, $j_{max} = 1$ 2^{nd} S state

Note $l = 0$ S waves

1 P waves

2 D waves

3 F waves

Old spectroscopic notation

Look at $l = 0$ $j_{max} = 1$

$$a_1 = \left[\frac{2(0+0+1) - \rho_0}{1(2)}\right] a_0 \qquad \begin{matrix} j=0 \\ l=0 \end{matrix}$$

$$\rho_0 = 2n = 4$$

$a_1 = -a_0$ and $a_2 = 0$

$$u_{20}(r) = \rho e^{-\rho} a_0 [1 - \rho]$$

In general wave func. is exp. times poly. 4

associated Laguerre polynomial

$$L^{p}_{q-p}(x) = (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

and

$$L_q(x) = e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$$

$$\boxed{\psi_{n\ell m} = \left[\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2} e^{-\frac{r}{na}} (2\rho)^\ell L^{2\ell+1}_{n-\ell-1}(2\rho)\, Y^m_\ell(\theta, \phi)}$$

$$\rho = \frac{r}{na}$$

$$R_{n\ell}(r) = \frac{u_{n\ell}(r)}{r}$$

$$\int_0^\infty r^2 dr \, |R_{n\ell}|^2 = 1$$

$$R_{10} = 2a^{-3/2} e^{-r/a}$$ ground state

$$R_{20} = \frac{1}{2^{1/2} a^{3/2}} e^{-r/2a} \left[1 - \frac{r}{2a}\right]$$ 2s state

$$R_{21} = \frac{1}{(24)^{1/2} a^{3/2}} \frac{r}{a} e^{-r/2a}$$ 2p state

Spectrum of Hydrogen

Consider a transition from $E_i = \frac{E_1}{i^2}$

to $E_f = \frac{E_1}{f^2}$

The atom can emit a photon of energy

$$E_\gamma = E_i - E_f = -13.6\,\text{eV}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

and the energy of the photon is related to its frequency

$$\boxed{E_\gamma = h\nu \quad \text{Planck Formula}} \qquad \lambda = c/\nu$$

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

R = Rydberg constant $= \frac{m}{4\pi c \hbar^3}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2$

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

Transitions to $n_f = 1$ are in ultraviolet and are called Lyman Series

Transitions to $n = 2$ are called Balmer Series