5. Hydrogen atom

5.1. Hydrogen atom – according to the Schrödinger theory

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

Solve the Schrödinger eq

$$\psi_{n\ell m}(r,\theta.\phi) = \frac{u_{n\ell}(r)}{r} Y_{\ell m}(\theta,\phi) = R_{n\ell}(r) Y_{\ell m}(\theta,\phi) \quad (1)$$

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

$$E_n = -\left[\frac{m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{2n^2} = \frac{-E_1}{2n^2} \qquad n = 1, 2, 3 \cdots (3)$$

In atomic units, the quantities $m = \hbar = e = 1$, then the square bracket $[\ ] = 1$,

$$E_n = -\frac{1}{2n^2} \quad [\text{in atomic units}]$$

$\underline{1}$ atomic unit in energy $= 2 \times 13.6\ eV$

Thus the binding energies of hydrogen atom is

$$E_n = -\frac{13.6}{n^2}\ eV \qquad n = 1, 2, \cdots \quad (4)$$

In the above model, the proton mass is assumed to be infinite.

Generalization: (1) If the mass of proton is considered, the mass m in Eq. (3) should be replaced by the ~~red~~ reduced mass

(2) If the charge of the nucleus is Z, the binding energy (4) is multiplied by Z^2.

(3) In a medium, the effective interaction is reduced by K, which is the <u>dielectric constant</u>, the binding energy is reduced by $(1/K^2)$

Carry out homework #4 problem 5 to see how these results appear in real examples

5.2. Beyond the Schrödinger theory

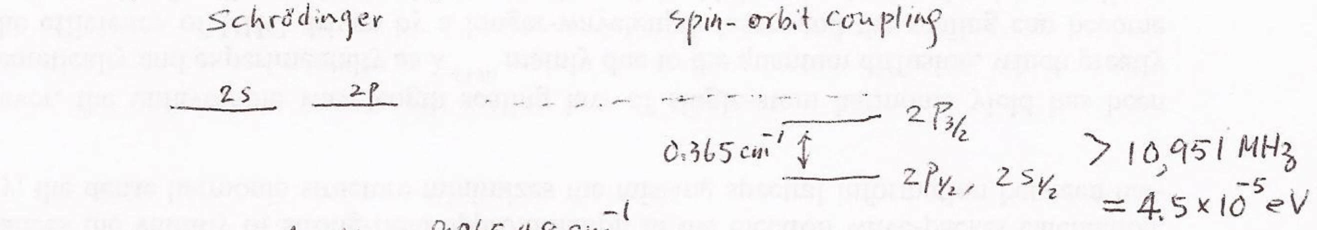
(1) electron has spin, thus the total wavefunction has the form $R_{n\ell}(r)\, Y_{\ell m_\ell}(\theta,\phi) \begin{Bmatrix} \chi^+ \\ \chi^- \end{Bmatrix}$ where χ is spin (½) function

Total electron angular momentum

$$\vec{J} = \vec{l} + \vec{S} \qquad S = \tfrac{1}{2}$$

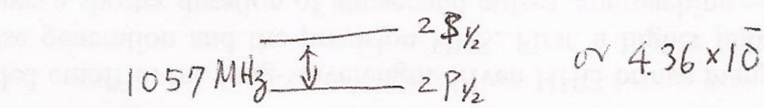
Need to learn how to add two angular momenta.

(2) spin-orbit coupling → leading to fine structure



$$1\text{ eV} = 8065.48\text{ cm}^{-1}$$
$$= 2.42 \times 10^{8}\text{ MHz}$$

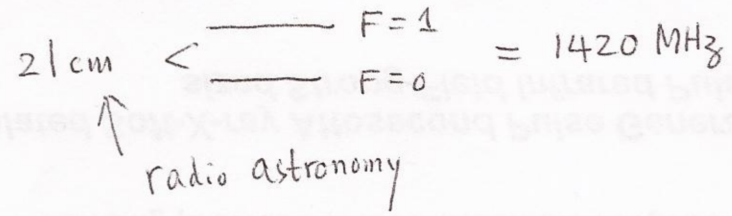
(3) Lamb shift



(4) hyperfine structure of the ground state of hydrogen

$$\vec{F} = \vec{J} + \vec{S}_p$$

↑ spin (= ½) of the proton



5.3. solving the radial eq. of a hydrogen atom

Only key steps are outlined (SI units)

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{l(l+1)\hbar^2}{2mr^2}\right]u = Eu \quad (5)$$

Define $\kappa = \frac{1}{\hbar}\sqrt{-2mE}$

$$\rho \equiv \kappa r \qquad \rho_0 = \frac{me^2}{2\pi\epsilon_0 \hbar^2 \kappa}$$

$$(5) \rightarrow \quad \frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]u \quad (6)$$

Asymptotic form of (6) $\rho \to \infty$

$$\frac{d^2u}{d\rho^2} = u$$

$$u(\rho) = Ae^{-\rho} + Be^{\rho} \leftarrow \text{not acceptable}$$

$$u(\rho) \xrightarrow[\rho \to \infty]{} Ae^{-\rho}$$

Near the origin, (6) becomes

$$\frac{du}{d\rho^2} = \frac{l(l+1)}{\rho^2}u$$

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \leftarrow \text{to avoid divergence } D = 0$$

Seek solution

$$u(\rho) = \rho^{l+1} e^{-\rho} v(\rho) \quad (7)$$

In terms of $v(\rho)$

$$\rho \frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + \left[\rho_0 - 2(l+1)\right]v = 0 \quad (8)$$

The solution of eq. (8) is called Laguerre polynomial

$$v(\rho) = L^{2l+1}_{n-l-1}(2\rho)$$

Putting all together, the hydrogenic wavefunction

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{\quad}\left(\frac{2r}{na}\right)^{l} e^{-2r/na} L^{2l+1}_{n-l-1}(2r/na)\, Y_{lm}(\theta,\phi)$$

See eq. [4.89]

$$\boxed{a = \frac{4\pi\epsilon_0 \hbar^2}{me^2} = 0.53\,\text{Å}}$$

↑ Bohr radius

The eigenvalues

$$E_n = -\frac{E_1}{2n^2} \qquad n = 1, 2, 3, \cdots$$

$$E_1 = 27.21\,\text{eV}$$

How to designate an eigenstate?

$$\psi_{nlm}(r,\theta,\phi) = |nlm\rangle$$

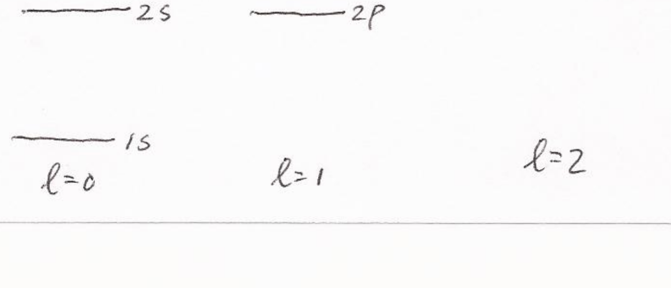
$n = 1, 2, \cdots$

For a given n, $l = 0, 1, 2, \cdots (n-1)$

For a given l, $m = -l, \cdots, +l$

$$\begin{cases} l=0 & s \\ l=1 & p \\ l=2 & d \\ l=3 & f \end{cases}$$

Typical energy levels



5.4 Getting comfortable with atomic hydrogen

(1) Take a look at the wavefunction $R_{n\ell}(r)$ and density $r^2 R_{n\ell}^2(r)$ on next page

(2) It can be shown

$$\langle r \rangle_{n\ell m} = a_0 \frac{n^2}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{\ell(\ell+1)}{n^2} \right] \right\}$$

roughly $\langle r \rangle \sim n^2$

Thus the orbital radius goes like n^2

(3) Some rough estimate

$$H = T + V = \frac{p^2}{2m} + V$$

$$\langle H \rangle_{n\ell m} = -\frac{1}{2n^2} = \frac{1}{2m} \langle p^2 \rangle_{n\ell m} + \left\langle -\frac{1}{4\pi\epsilon_0} \frac{1}{r} \right\rangle_{n\ell m}$$

$$\sim \frac{1}{n^2}$$

Thus $\langle v \rangle_{n\ell m} \sim \frac{1}{n}$

Classical estimate:

$$T = \frac{2\pi r}{v} \sim \frac{n^2}{1/n} = n^3$$

For 1s orbital

$$T = \frac{2\pi a_0}{\alpha c} \simeq 150 \times 10^{-18}\ \text{sec}$$

$$= 150\ \text{as}$$

↑ attoseconds

For $n = 100$

$$T = 150\ (\text{as}) \times 10^6 = 150\ \text{ps}$$

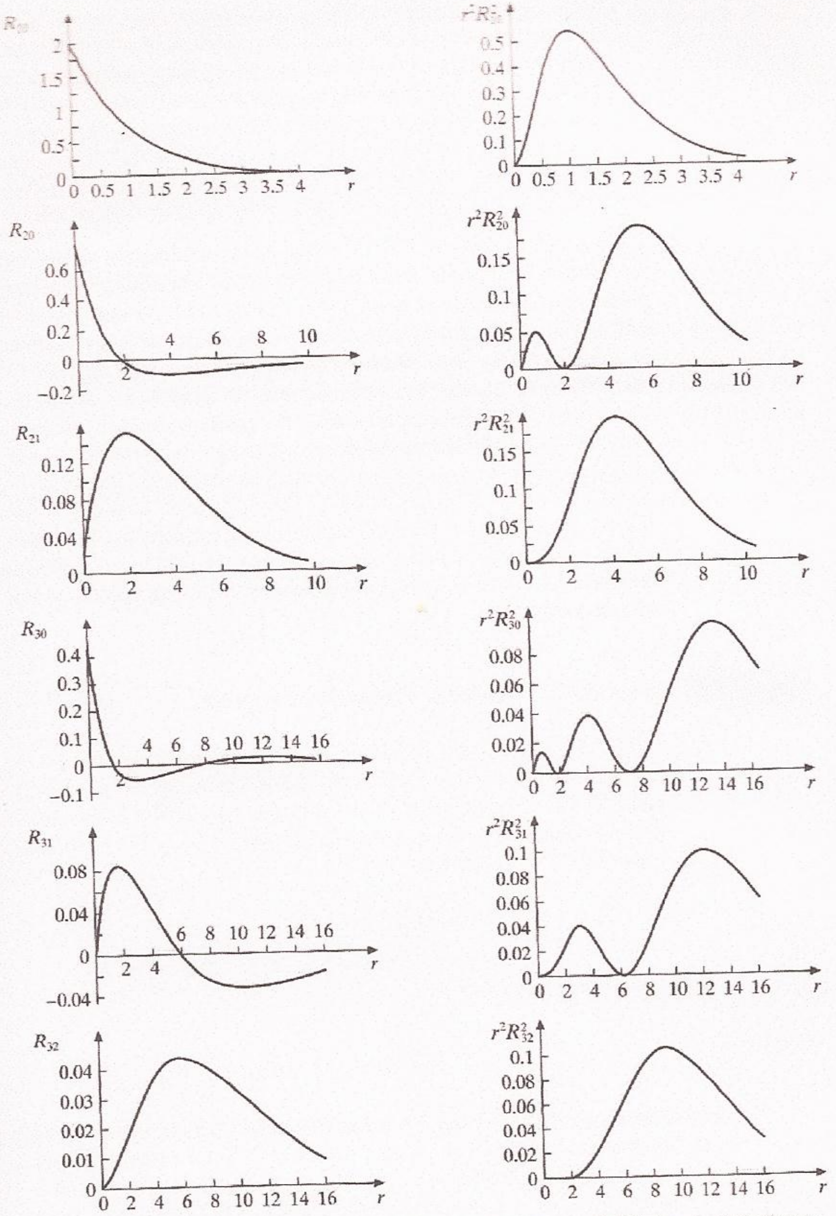


Figure 3.3 Radial functions $R_{nl}(r)$ and radial distribution functions $r^2R_{nl}^2(r)$ for atomic hydrogen.