Chapter 12

The Hydrogen Atom

Hydrogen atom : contains one electron, one proton

Hydrogen like atom : " " " , allowing for a nucleus, more complicated than a single proton

The Schrödinger becomes a one-particle equ. after the center of mass motion is separated out.

The Schrödinger equ. for two-particle system:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + V(r)\psi = E\psi \qquad (1)$$

where $\psi = \psi(\bar{r}_1, \bar{r}_2)$ but $V = V(r)$ (2)

$$\bar{r} = \bar{r}_1 - \bar{r}_2 \qquad (3)$$

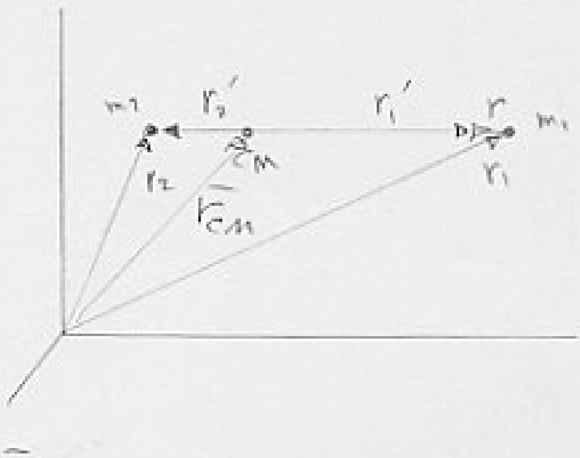
$$\nabla_1^2\psi = \frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2}$$

$$\nabla_2^2\psi = \dots \qquad (4)$$

Now $\bar{F}_1 = m_1 \dfrac{d^2\bar{r}_1}{dt^2}$

$\bar{F}_2 = m_2 \dfrac{d^2\bar{r}_2}{dt^2}$ (5)

$\bar{F}_1 = -\bar{F}_2$



By def.; $\bar{r}_{CM} = \dfrac{\bar{r}_1 m_1 + \bar{r}_2 m_2}{m_1+m_2}$ (6)

$M = m_1 + m_2$

$\bar{F}_1 + \bar{F}_2 = 0 \longrightarrow$ C.M. has a const velocity

Let $\bar{r}_{CM} = 0$ (7)

$$\begin{cases} \dfrac{d^2\bar{r}_{CM}}{dt^2} = \dfrac{1}{m_1+m_2}\underbrace{\left(m_1 \dfrac{d^2\bar{r}_1}{dt^2} + m_2 \dfrac{d^2\bar{r}_2}{dt^2}\right)}_{0} = 0 \\ \rightarrow \dfrac{d\bar{r}_{CM}}{dt} = \text{const.} \end{cases}$$

(3) (7)(6) $\longrightarrow \bar{r}_1' = \bar{r}\dfrac{m_2}{m_1+m_2}$, $\bar{r}_2' = -\bar{r}\dfrac{m_1}{m_1+m_2}$ (8)

Remark: Note that, if $\bar{r}_{CM} = 0 \longrightarrow \begin{cases} r_1' \to r_1 \\ r_2' \to r_2 \end{cases}$

Now $\bar{r}_1 = \bar{r}_{CM} + \bar{r}\dfrac{m_2}{m_1+m_2}$ $\bar{r}_2 = r_{CM} - \bar{r}\dfrac{m_1}{m_1+m_2}$ (9)

$$\bar{F}_1 = m_1 \frac{d^2\bar{r}_1}{dt^2} = 0 + \frac{d^2\bar{r}}{dt^2}\frac{m_1 m_2}{m_1+m_2}$$

$\rightarrow \bar{F}_1 = \mu \dfrac{d^2 r}{dt^2}$ $\mu = \dfrac{m_1 m_2}{m_1+m_2}$ (10)

Now $\dfrac{\partial \psi}{\partial x_1} = \dfrac{\partial \psi}{\partial x}\dfrac{\partial x}{\partial x_1} + \dfrac{\partial \psi}{\partial x_c}\dfrac{\partial x_c}{\partial x_1}$ (11)

$\bar{r} = \bar{r}_1 - \bar{r}_2 \longrightarrow \bar{x} = \bar{x}_1 - \bar{x}_2 \longrightarrow \dfrac{\partial x}{\partial x_1} = 1$ (12)

Also (6) $\rightarrow \dfrac{\partial x_c}{\partial x_1} = \dfrac{m_1}{m_1+m_2}$ (13)

$$(11)(12)(13) \longrightarrow \frac{\partial \psi}{\partial x_1} = \frac{\partial \psi}{\partial x} + \frac{\partial \psi}{\partial x_c}\frac{m_1}{m_1+m_2} \quad (14)$$

$$\rightarrow \frac{\partial^2 \psi}{\partial x_1^2} = \frac{\partial}{\partial x_1}\left(\frac{\partial \psi}{\partial x_1}\right) = \frac{\partial}{\partial x}\left(\frac{\partial \psi}{\partial x_1}\right)\frac{\partial x}{\partial x_1} + \frac{\partial}{\partial x_c}\left(\frac{\partial \psi}{\partial x_1}\right)\frac{\partial x_c}{\partial x_1} \quad (15)$$

$$\frac{\partial^2 \psi}{\partial x_1^2} = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial x \partial x_c}\cdot\frac{2m_1}{m_1+m_2} + \frac{\partial^2 \psi}{\partial x_c^2}\left(\frac{m_1}{m_1+m_2}\right)^2 \quad (16)$$

Similarly;

$$\frac{\partial^2 \psi}{\partial x_2^2} = \frac{\partial^2 \psi}{\partial x^2} - \frac{\partial^2 \psi}{\partial x \partial x_c}\cdot\frac{2m_2}{m_1+m_2} + \frac{\partial^2 \psi}{\partial x_c^2}\left(\frac{m_2}{m_1+m_2}\right)^2 \quad (17)$$

$$\rightarrow$$

$$-\frac{\hbar^2}{\mu}\left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial \psi^2}{\partial z^2}\right) - \frac{\hbar^2}{2(m_1+m_2)}\left(\frac{\partial^2 \psi}{\partial x_c^2} + \frac{\partial^2 \psi}{\partial y_c^2} + \frac{\partial^2 \psi}{\partial z_c^2}\right)$$

$$+ V\psi = E\psi \quad (18)$$

Since V is a func. of relative coord. only, we can write;

$$\psi(r, r_c) = \psi_0(r)\,\psi_c(r_c) \quad (19)$$

$$(18)(19) \rightarrow \underbrace{\left[-\frac{\hbar^2}{2\mu}\frac{\nabla^2\psi_0}{\psi_0} + V\right]}_{} + \underbrace{\left[-\frac{\hbar^2}{2(m_1+m_2)}\cdot\frac{\nabla^2\psi_c}{\psi_c}\right]}_{} = E \quad (20)$$

indep.

$$\rightarrow \quad -\frac{\hbar^2}{2\mu}\nabla^2\psi_0 + V\psi_0 = E_0\psi$$

$$-\frac{\hbar^2}{2M}\nabla^2\psi_c = E_c\psi \quad (21)$$

where $E = E_0 + E_c$

Now $$V(r) = -\frac{Ze^2}{r} \qquad (22)$$

and the radial Schrödinger equ.;

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr}\right)R + \frac{2\mu}{\hbar^2}\left[E + \frac{Ze^2}{r} - \frac{l(l+1)\hbar^2}{2\mu r^2}\right]R = 0 \qquad (23)$$

For bound states $E < 0$

Let $$\rho \equiv \left(\frac{8\mu|E|}{\hbar^2}\right)^{1/2} r \qquad (24)$$

$$(23)(24) \longrightarrow \frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{l(l+1)}{\rho^2}R + \left(\frac{\lambda}{\rho} - \frac{1}{4}\right)R = 0 \qquad (25)$$

where $$\lambda = \frac{Ze^2}{\hbar}\left(\frac{\mu}{2|E|}\right)^{1/2} = Z\alpha\left(\frac{\mu c^2}{2|E|}\right)^{1/2} \qquad (26)$$

For $\rho \rightarrow$ large

$$(25) \longrightarrow \frac{d^2R}{d\rho^2} - \frac{1}{4}R \simeq 0 \qquad (27)$$

$$\longrightarrow R \sim e^{-\rho/2} \qquad (28)$$

$$R(\rho) = e^{-\rho/2}\, G(\rho) \qquad (29)$$

$$(29) \text{ in } (25) \longrightarrow \frac{d^2G}{d\rho^2} - \left(1 - \frac{2}{\rho}\right)\frac{dG}{d\rho} + \left[\frac{\lambda - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right]G = 0 \qquad (30)$$

In chap. 11 we established that for the pots. satisfying

$$\lim_{r\to 0} r^2 V(r) = 0$$

$$u(r) \sim r^{l+1} \longrightarrow R(r) \sim r^{l} \sim \rho^{l} \quad (31)$$

$$\longrightarrow G(\rho) = \rho^{l} \sum_{n=0}^{\infty} a_n \rho^{n} \quad (32)$$

Let $H(\rho) = \sum_{n=0}^{\infty} a_n \rho^n \quad (33)$

$$G(\rho) = \rho^{l} H(\rho) \quad (34)$$

$$(34) \text{ in } (30) \longrightarrow \frac{d^2H}{d\rho^2} + \left(\frac{2l+2}{\rho} - 1\right)\frac{dH}{d\rho} + \frac{\lambda - 1 - l}{\rho} H = 0 \quad (35)$$

$$(33)(35) \rightarrow \sum_{n=0}^{\infty} \left[n(n-1) a_n \rho^{n-2} + n a_n \rho^{n-1}\left(\frac{2l+2}{\rho} - 1\right) + (\lambda - 1 - l) a_n \rho^{n-1} \right] = 0 \quad (36)$$

The coffs. of each power must independently vanish.

$$\rightarrow \sum_{n=0}^{\infty} \left\{ (n+1)\left[n a_{n+1} + (2l+2) a_{n+1} \right] + (\lambda - 1 - l - n) a_n \right\} \rho^{n-1} = 0 \quad (37)$$

$$\rightarrow \frac{a_{n+1}}{a_n} = \frac{n + l + 1 - \lambda}{(n+1)(n+2l+2)} \quad (38)$$

For $n \longrightarrow$ large : $\dfrac{a_{n+1}}{a_n} \simeq \dfrac{1}{n} \quad (39)$

Now since $e^{x} = \sum_{n=0}^{\infty} \frac{x^n}{n!}$

The coeff. of x^{n+1} : $\frac{1}{(n+1)!}$

" " " x^n : $\frac{1}{n!}$ $\longrightarrow \frac{\frac{1}{(n+1)!}}{\frac{1}{n!}} = \frac{1}{n+1}$

$\frac{1}{n+1} \approx \frac{1}{n}$ for large n

$\longrightarrow$ the series $H(\rho) \sim e^{\rho}$ (not well behaved at infinity)

$\xrightarrow{\text{Conclusion}}$ The series $H(\rho) = \sum_{=0}^{\infty} a_n \rho^n$ must terminate for a given ℓ for some $n = n_r$ (i.e. it should be a polynomial);

i.e.
$$\lambda = n_r + \ell + 1 \qquad (40)$$

Let us introduce the principal quantum number n defined by;
$$n = n_r + \ell + 1 \qquad (41)$$

Then since $n_r \geqslant 0$

$$\rightarrow \begin{cases} \text{i)} \ n \geqslant \ell + 1 \\ \text{ii)} \ n \text{ is an integer} \\ \text{iii)} \ \lambda = n \text{ implies that } E = -\frac{1}{2}\mu c^2 \frac{(Z\alpha)^2}{n^2} \end{cases}$$
(42)

Now let $m_1 \equiv m$ the mass of electron
$m_2 = M$ " " " nucleus $\rightarrow \mu = \frac{mM}{m+M}$

$$\omega_{ij} = \frac{E_i - E_j}{\hbar} = \frac{mc^2/2\hbar}{1 + m/M} (Z\alpha)^2 \left(\frac{1}{n_i^2} - \frac{1}{n_j^2} \right) \qquad (43)$$

These transition frequencies differ slightly for different hydrogenlike atom.

Urey and collaborations (1932) discovered the deuterium using the slight difference between the hydrogen spectrum and deuterium spectrum.

(42) $\longrightarrow$ The energy states for a given l are $(2l+1)$-fold degenerate (the radial equ. does not depend on $\underline{m}$).

The radial equ. does depend on l, but there is no l-dependence for E $\longrightarrow$ there is additional degeneracy. This is called accidental degeneracy.

In Cl. M. for $V \sim \frac{1}{r}$: The orbits consist of ellipses that maintain their orientation in space.

If $V \rightarrow \frac{1}{r^{1+\epsilon}}$: We have precessing orbits

The source of these modifications?

For example the perturbations due to other planets, in the Kepler prob.

In Q.M., too, there are perturbations, so that l-degeneracy is <u>not really</u> what is observed

In first approx., <u>however</u>, for a given n, we have

$$l = 0, 1, 2, \dots (n-1)$$

$$\sum_{l=0}^{n-1} (2l+1) = n^2 \qquad \text{Total degeneracy}$$

Real degeneracy $= 2n^2$ due to possible spin orientation (44)

Now, let us return to the diff. equ. If we set $\lambda = n$ in (38);

$$a_{k+1} = \frac{k+l+1-n}{(k+1)(k+2l+2)} a_k \qquad (45)$$

$$\rightarrow a_{k+1} = (-1)^{k+1} \frac{n-(k+l+1)}{(k+1)(k+2l+2)} \cdot \frac{n-(k+l)}{k(k+2l+1)} \cdots \frac{n-(l+1)}{l(2l+2)} a_0 \qquad (46)$$

With the help of this we can obtain the power series expansion for $H(\rho)$.

Equivalently, we observe that the equ for $H(\rho)$ is that for the associated Laguerre polynomials:

$$H(\rho) = L_{n-\ell-1}^{(2\ell+1)}(\rho) \qquad (47)$$

$$R(\rho) = e^{-\rho/2} G(\rho) = e^{-\rho/2} \rho^{\ell} H(\rho) = e^{-\rho/2} \rho^{\ell} \sum_{n=0}^{\infty} a_n \rho^n \qquad (48)$$

or, $$R(\rho) = e^{-\rho/2} \rho^{\ell} L_{n-\ell-1}^{(2\ell+1)}(\rho) \qquad (48)'$$

let $$a_0 = \frac{\hbar}{\mu c \alpha} \qquad (49)$$

$R_{n\ell}(r)$:

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

$$R_{20}(r) = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \qquad (50)$$

$$R_{30}(r) = 2\left(\frac{Z}{3a_0}\right)^{3/2}\left[1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2}\right] e^{-Zr/3a_0}$$

$$R_{31}(r) = \frac{4\sqrt{2}}{3}\left(\frac{Z}{3a_0}\right)^{3/2} \frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$$

$$R_{32}(r) = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

The following quantitative features emerge from the sampling of eigensolutions:

a) The behavior of r^l for <u>small r</u>, which forces the wave func. to stay <u>small</u> for a range of radii that increases with l, is a consequence of the centrifugal repulsive barrier that keeps the electrons from coming close to the nucleus.

b) The recursion relation (38) shows that $H(\rho)$ is a polynomial of deg. $n_r = n-l-1$

$\longrightarrow$ $H(\rho)$ has n_r radial nodes (zeros)

$\longrightarrow$ There will be $n-l$ bumps in the probability density distribution $P(r) = r^2 [R_{nl}(r)]^2$ (51)

For $l = n-1$ $\longrightarrow$ only one bump

(48') or (50) $\longrightarrow$ $R_{n,n-1}(r) \sim r^{n-1} e^{-Zr/a_0 n}$ (52)

$\rightarrow P(r) \sim r^{2n} e^{-2Zr/a_0 n}$ (53)

The peak of $P(r)$ is determined by

$$\frac{dP(r)}{dr} = \left(2n\,r^{2n-1} - \frac{2Z}{a_0 n} r^{2n}\right) e^{-2Zr/a_0 n} = 0$$

$$\rightarrow r = \frac{n^2 a_0}{Z} \qquad (54)$$

which is the Bohr atom value for circular orbits.

smaller values of l give probability distributions with more bumps.

One can show they correspond to elliptical orbits in the large quantum number limit.

c) Given the wave fncs, we can calculate

$$\langle r^k \rangle = \int_0^\infty dr\, r^{2+k} \left[R_{nl}(r)\right]^2 \qquad (55)$$

Some useful expectation values:

$$\langle r \rangle = \frac{a_0}{2Z}\left[3n^2 - l(l+1)\right]$$

$$\langle r^2 \rangle = \frac{a_0^2 n^2}{2Z^2}\left[5n^2 + 1 - 3l(l+1)\right]$$

$$\langle \tfrac{1}{r} \rangle = \frac{Z}{a_0 n^2} \qquad (56)$$

$$\langle \tfrac{1}{r^2} \rangle = \frac{Z^2}{a_0^2 n^3 (l+\frac{1}{2})}$$

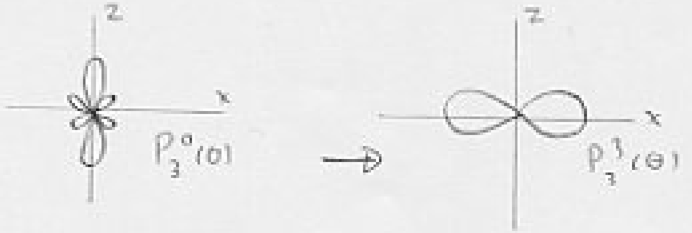
d) $$P(r,\theta,\varphi) \sim r^2 [R_{n\ell}(r)]^2 |Y_\ell^m(\theta,\varphi)|^2 \qquad (57)$$

Since $Y_\ell^m(\theta,\varphi) = (-1)^m \left[\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}\right]^{\frac{1}{2}} P_\ell^m(\cos\theta)\, e^{im\varphi}$

$$\rightarrow P(r,\theta,\varphi) \sim r^2 [R_{n\ell}(r)]^2\, P_\ell^m(\cos\theta)^2 \qquad (58)$$

As m increases $\longrightarrow$ $P_\ell^m(\cos\theta)$ shifts from z-axis toward the equatorial plane

i.e. For example



When $|m| = \ell$ $\longrightarrow |P_\ell^\ell(\cos\theta)|^2 \sim \sin^{2\ell}\theta$ (59) Peaked about $\theta = \frac{\pi}{2}$

It can be shown;

As ℓ increases $\longrightarrow$ the width of the peak decreases like $\ell^{-\frac{1}{2}}$

Conclusion $\longrightarrow$ $\ell \rightarrow$ large $\Longrightarrow$ width $\rightarrow 0$

$\longrightarrow$ classical picture of the planar orbits (i.e. definiteness)

The finite width of the peak (quantum mechanical aspect) can be understood from the following considerations:

i) When $|m| = l$ $\longrightarrow$ $L_z^2 = l^2$ $\quad (L_z|m=l\rangle = l|m=l\rangle)$

Since $L^2 = L_x^2 + L_y^2 + L_z^2$ and $L^2 = l(l+1)$ in units of $\hbar$

$$\longrightarrow L_x^2 + L_y^2 = l \qquad (60)$$

$\longrightarrow$ The angular momentum vector can never be perfectly oriented along an axis.

ii) Identically,

The degeneracy in m $\xrightarrow[\text{us}]{\text{allows}}$ to orient the orbit relative to some other axis

$\longrightarrow$ So that there is really no distinguished z-axis.

Thus a state that is an eigenstate of L_x with eigenvalue l will be oriented in the x-dir

$$L_x|m=l\rangle_x = l|m=l\rangle_x \qquad (61)$$

where $|m=\ell\rangle_x = \sum_m C_m |m\rangle_z$ (62)

But because of the degeneracy, the energy will be the same as for the z-oriented orbits.