Tema 11: The electron in a central field

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Schrodinger equation for the H atom

$$V(r) \; = \; -\frac{Ze^2}{r} \qquad (\text{units } / \;\; 4\pi\epsilon_0 \; = \; 1)$$

- Nucleus charge $Ze \; + \; 1 \; e^-$ (hydrogenic atom)
  Ex.: H,D,T,He^+,Li^{++}...
- Two body problem $($nucleus $+ \; e^-) \; \rightarrow$ C.M. problem + relative problem
- Originally

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r_1}, \vec{r_2}; t) \; = \; \left[-\frac{\hbar^2}{2m_1} \nabla^2_{r_1} - \frac{\hbar^2}{2m_2} \nabla^2_{r_2} \; + \; V(\vec{r_1}, \vec{r_2}; t) \right] \; \Psi(\vec{r_1}, \vec{r_2}; t)$$

but

$$V(\vec{r_1}, \vec{r_2}; t) \; = \; V(|\vec{r_1} - \vec{r_2}|)$$

We define

$$\vec{R} \; = \; \frac{m_1 \vec{r_1} + m_2 \vec{r_2}}{m_1 + m_2} \quad ; \quad \vec{r} \; = \; \vec{r_1} - \vec{r_2}$$

(C.M.) (Relative)

$$\frac{1}{2m_1} \nabla^2_{r_1} + \frac{1}{2m_2} \nabla^2_{r_2} \; = \; \frac{1}{2\mu} \nabla^2_r + \frac{1}{2M} \nabla^2_R$$

where $M \; = \; m_1 + m_2$ (total) ; $\mu \; = \; \frac{m_1 \; m_2}{m_1 + m_2}$ (reduced)
In the new coordinates

$$i\hbar \, \frac{\partial}{\partial t} \, \Phi(\vec{r}, \vec{R}; t) \; = \; \left[-\frac{\hbar^2}{2M} \nabla^2_R - \frac{\hbar^2}{2\mu} \nabla^2_r \; + \; V(r) \right] \; \Phi(\vec{r}, \vec{R}; t)$$

We can separate variables $\Phi(\vec{r}, \vec{R}; t) \; = \; \phi(\vec{r}) \; \Psi(\vec{R}) \; T(t)$

For eigenstates of $\hat{H}$ $\left(\hat{H} \neq \hat{H}(t) \rightarrow T(t) = e^{-\frac{iEt}{\hbar}} \right)$

$$-\frac{\hbar^2}{2M}\nabla_R^2 \, \Psi(\vec{R}) = E_R \Psi(\vec{R})$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 + V(r)\right] \phi(\vec{r}) = E_r \phi(\vec{r})$$

where $E = E_r + E_R$

- Free motion of the center of mass
- The relative motion of the system $Ze + 1\ e^-$ is subjected to attractive potential $V(r)$
- We will study the relative problem (we're not interested in excitations coming from the C.M. motion)

We must solve (we ignore subscripts r in $\vec{\nabla}$ and E from now on)

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(r)\right] \phi(\vec{r}) = E\phi(\vec{r}) \quad ; \quad V(r) = -\frac{Ze^2}{r}$$

Central potencial $\quad \phi(\vec{r}) = R(r)\, Y_l^m(\theta, \varphi)$

Radial Eq.: $-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \left(V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right) R(r) = E\ R(r)$

Change $u(r) = rR(r)$

$$-\frac{\hbar^2}{2\mu}\frac{d^2u}{dr^2} + \left[V(r) + \frac{l(l+1)\hbar^2}{2\mu r^2}\right] u(r) = E\ u(r) \quad ; \quad u(0) = 0$$

or, equivalently

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

We define $x \;=\; \frac{2r}{r_0}$ (dimensionless) where $r_0 \;=\; \frac{\hbar}{\sqrt{2\ \mu\ |E|}}$

$$\omega(x) \;=\; u(r) \quad ; \quad \omega(0) \;=\; 0$$

$\omega(x)$ satisfies

$$\omega'' \;+\; \left[\frac{1}{4}\frac{E}{|E|} + \frac{A}{x} - \frac{l(l+1)}{x^2}\right]\omega \;=\; 0$$

$$A \;=\; \sqrt{\frac{\mu Z^2 e^4}{2\hbar^2|E|}} \;=\; \frac{Ze^2}{2|E|r_0}$$

We will study bound states $\rightarrow \quad E < 0$

$$\omega'' \;+\; \left[-\frac{1}{4} + \frac{A}{x} - \frac{l(l+1)}{x^2}\right]\omega \;=\; 0 \tag{1}$$

- a) For $x \;\rightarrow\; \infty$ (1) $\Rightarrow\ \omega'' \;-\; \frac{\omega}{4} \;=\; 0$

$$\omega(x) \;=\; C\ e^{\frac{x}{2}} \;+\; D\ e^{-\frac{x}{2}}$$

$$\lim_{x\,\rightarrow\,\infty} e^{\frac{x}{2}} \;=\; \infty \;\Rightarrow\; R \;\rightarrow\; \infty$$

- b) For $x \;\rightarrow\; 0$ (1) $\Rightarrow\ \omega'' \;-\; \frac{l(l+1)}{x^2}\ \omega \;=\; 0$

  x^{-l} y x^{l+1} are particular solutions

general solution $\omega(x) \;=\; a\ x^{l+1} \;+\; b\ x^{-l}$

- i) $\omega(x) = x^{-l}$; $R \approx \frac{\omega}{x} = x^{-(l+1)}$; $\omega(0) \neq 0 \; \forall l$ $R(r \to 0) \to \infty$ **solution not valid**
- ii) $\omega(x) = x^{l+1} \to 0$ cuando $x \to 0$; $R \approx \frac{\omega}{x} = x^{l}$ when $x \to 0$ **valid**
- c) $\forall x$ $\omega(x) = x^{l+1} \, e^{-\frac{x}{2}} \, f_l(x)$ brought to (1)

$$\left[x\frac{d^2}{dx^2} + (2l + 2 - x)\frac{d}{dx} - (l+1-A)\right] f_l(x) = 0 \tag{2}$$

Laplace Eq.. Its regular solution is the confluent hypergeometric series of the first kind $F(l+1-A;\; 2l+2;\; x)$

We make $f_l(x) = \sum_{p=0}^{\infty} b_p \, x^p$

$$\sum_{p=2}^{\infty} p(p-1)\; b_p x^{p-1} + \sum_{p=1}^{\infty}(2l+2)\; p\; b_p x^{p-1} - \sum_{p=1}^{\infty} p\; b_p\; x^p - \sum_{p=0}^{\infty}(l+1-A)\; b_p\; x^p = 0$$

It leads to

$$b_{p+1} = \frac{l+1-A+p}{(p+1)(2l+2+p)}\, b_p \qquad \text{recurrence relation}$$

$$\lim_{p \to \infty} \frac{b_{p+1}}{b_p} = \frac{1}{p} \quad \to$$

$f_l(x)$ is equivalent to $e^x = \sum_{p=0}^{\infty} \frac{1}{p!}\, x^p \;\to$

in $\omega(x)$ there is $e^{-\frac{x}{2}}\, e^x \;\to$ asymptotic dependence is not acceptable for $x \to \infty$ $\to$ the expansion must be cut $\Rightarrow$ polynomial

$b_{n'} \neq 0$; $b_{n'+1} = 0$; n' integer, order of the polynomial

$$l+1-A+n' \;=\; 0 \qquad ; \qquad n' \;=\; 0,1,2\cdots$$

l is an integer $\Rightarrow$ $A = integer \equiv n$ **principal quantum number**

$$A \;\equiv\; n \;=\; l+1+n' \qquad ; \qquad n \;=\; 1,2,3,\cdots$$

$$n \;\geq\; l+1 \quad \rightarrow \quad l \;\leq\; n-1 \quad ; \quad l \;=\; 0,1,2\cdots,\; n-1$$

$$A \;=\; \sqrt{\frac{\mu Z^2 e^4}{2\hbar^2 |E|}}$$

Bound states $\rightarrow$ $E_n \;=\; -\frac{\mu Z^2 e^4}{2n^2\hbar^2}$

E_n are independent of l

For $\mu \;=\; m_e$ and $Z \;=\; 1$

$$\rightarrow\; E_1 \;=\; -13.6\; eV \;;\; E_2 \;=\; \frac{E_1}{4}\;\cdots$$

$$f_l \quad\rightarrow\quad f_{nl} \quad\rightarrow\quad R_{nl}$$

n=1	l=0 (=1s)		$R_{10}Y_0^0$	E_1	deg.1
n=2	l=0 (=2s)		$R_{20}Y_0^0$	E_2	deg.4
	l=1 (=2p)		$R_{21}Y_1^1, R_{21}Y_1^0, R_{21}Y_1^{-1}$		
n=3	l=0 (=3s)		$R_{30}Y_0^0$	E_3	deg.9
	l=1 (=3p)		$R_{31}Y_1^1, R_{31}Y_1^0, R_{31}Y_1^{-1}$		
	l=2 (=3d)		$R_{32}Y_2^m;\; m=0,\pm1,\pm2$		

For a given n $\rightarrow$ degeneracy $=$ n^2

$$\sum_{l=0}^{n-1}(2l+1) \;=\; n^2$$

Energies do not depend on m or l

$$\omega_{nl}(x) \;=\; x^{l+1}e^{-\frac{x}{2}} \times \text{polynomial of degree } \; n-l-1$$

polynomials are the **associated Laguerre polynomials**: $L_j^k(x)$ satisfying the associated Laguerre differential equation

$$x\frac{d^2L_j^k}{dx^2} \;+\; (k+1-x)\frac{dL_j^k}{dx} \;+\; (j-k)L_j^k \;=\; 0 \tag{3}$$

They can be obtained from the Laguerre polynomials $L_j(x)$ (of order j, solution of the Laguerre differential equation):

$$L_j(x) \;=\; e^x \; \frac{d^j(x^j \; e^{-x})}{dx^j}$$

$$L_j^k(x) \;=\; \frac{d^kL_j(x)}{dx^k}$$

If we compare (2) with (3)

$$k \;=\; 2l+1 \qquad ; \qquad j \;=\; n \;+\; l$$

$$f_{nl}(x) \;=\; L_{n+l}^{2l+1}(x)$$

$$\omega_{nl}(x) \;\sim\; x^{l+1}e^{-\frac{x}{2}} \; L_{n+l}^{2l+1}(x)$$

We define $a_0 \;=\; \frac{\hbar^2}{\mu e^2}$ $(=\; 0.528$ Å if $\mu \;=\; m_e$, radius of the first Bohr orbit for H

Then $r_0 \;=\; \frac{na_0}{Z}$; $x \;=\; \frac{2Zr}{na_0}$

$$u_{nl}(r) \;=\; \left(\frac{2Zr}{na_0}\right)^{l+1} e^{-\frac{Zr}{na_0}} \; L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right)$$

$$R_{nl}(r) \;=\; -A_{nl}\;\frac{2Z}{na_0}\;\left(\frac{2Zr}{na_0}\right)^{l} e^{-\frac{Zr}{na_0}} \; L_{n+l}^{2l+1}\left(\frac{2Zr}{na_0}\right) \qquad \text{(normal.)}$$

$$A_{nl} = \sqrt{\frac{2Z}{na_0}} \sqrt{\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}}$$

$$L_{n+l}^{2l+1}(x) = \sum_{p=0}^{n-l-1} (-)^{p+1} \frac{\left[(n+l)!\right]^2 \, x^p}{(n-l-1-p)!(2l+1+p)!\, p!} \tag{4}$$

R_{nl} has n zeros:

- of order l in $r = 0$
- of order 1 in $r = \infty$
- of order $n-l-1$ between $0 < r < \infty$

$R_{nl}(r \to 0) \sim r^l$ *and* $R_{nl}(r) > 0$ close to the origin ($b_0 < 0$ see Eq. (4))

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

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

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

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

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

$$R_{32}(r) = \left(\frac{1}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{r}{a_0}\right)^2 e^{-r/3a_0}$$

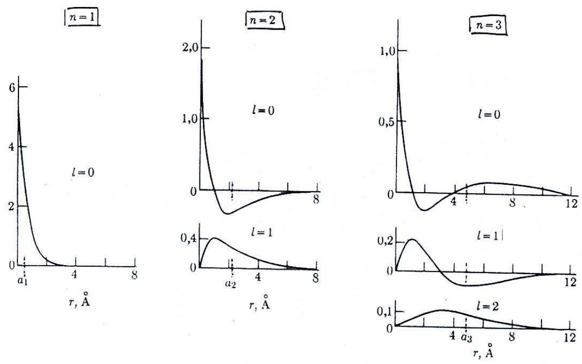


Fig. 3-12. Funciones radiales del hidrógeno para $n = 1$, 2 y 3. En cada caso, la ordenada de la curva es $[R_{nl}(r)\ \mathrm{m}^{-3/2}] \times 10^{-8}$.

a_i Radio clásico de la órbita $i = n^2 a_0$

n Nodos $\begin{cases} \text{orden } l \text{ en } r=0 \\ n-l-1 \quad 0<r<\infty \\ 1 \quad r=\infty \end{cases}$

Números cuánticos n	l	m_l	Eigenfunciones
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$
2	0	0	$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	0	$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta$
2	1	± 1	$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \operatorname{sen}\theta e^{\pm i\varphi}$
3	0	0	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$
3	1	0	$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta$
3	1	± 1	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6 - \frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0} \operatorname{sen}\theta e^{\pm i\varphi}$
3	2	0	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\theta - 1)$
3	2	± 1	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \operatorname{sen}\theta \cos\theta e^{\pm i\varphi}$
3	2	± 2	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \operatorname{sen}^2\theta e^{\pm 2i\varphi}$

Three-dimensional electron probability density

For eigenfunctions of $H,\ L^2\ and\ L_z$: the probability density

$$\Psi^*_{nlm_l}\ \Psi_{nlm_l}\ =\ R^*_{nl}\ \Theta^*_{lm_l}\ \Phi^*_{m_l}\ R_{nl}\ \Theta_{lm_l}\ \Phi_{m_l}$$

- The probability of finding the e^- in $d\tau$

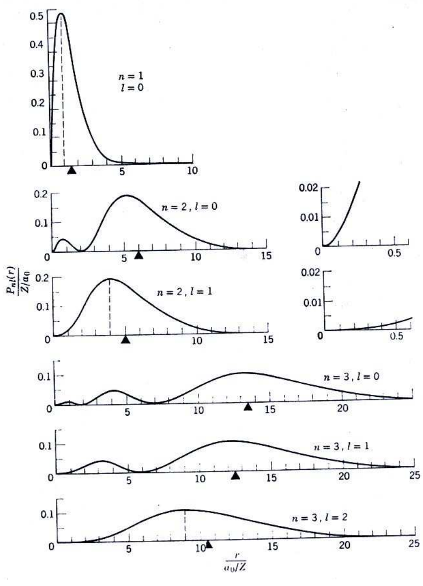
$$|\Psi_{nlm_l}|^2\ d\tau$$

pin spherical coordinates $d\tau\ =\ r^2\ \sin\theta\ dr\ d\theta\ d\phi$

- The radial probability of presence (probability of finding the e^- at distance between r and $r+dr$ from the nucleus, with any angle d θ and ϕ)

$$R^*_{nl}\ R_{nl}\ r^2\ dr\ \ =\ P_{nl}(r)\ dr$$

$P_{nl}(r)\ =\ |R_{nl}|^2\ r^2$ is the **radial probability density**



$$< r >_{nl} = \int_0^\infty R_{nl}^* \ r \ R_{nl} \ r^2 \ dr \ = \ \frac{n^2 a_0}{Z} \left\{ 1 + \frac{1}{2} \left[1 - \frac{l(l+1)}{n^2} \right] \right\}$$

Plot $\frac{P_{nl}(r)}{Z/a_0}$ vs. $\frac{r}{a_0/Z}$

- for l_{max} compatible with given n

$$r_{most\ probable} \ = \ \frac{n^2 \ a_0}{Z} \quad \text{(= Bohr radius, circular orbits)}$$

- $< r >_{nl}$ greater than the most probable value (black triangles)
- the scale $\rightarrow$ universal plot (valid for different values of μ and Z)

- for given n the behavior for $r \ \rightarrow \ 0$ depends on l

$$R(r) \ \sim \ r^l \quad ; \quad P(r) \ \sim \ r^{2(l+1)}$$

- $r <<$ probability of presence in the nucleus (we assume radius R_n) $\neq \ 0$ for $l \ = \ 0$ (for $l > 0$ negligible in comparison)

$$\int_0^{R_N} \frac{r^{2l+2}}{a_0^{2l+3}} dr \ \rightarrow \ \frac{1}{2l+3} \left(\frac{R_N}{a_0} \right)^{2l+3} \quad ; \quad \frac{R_N}{a_0} \ \sim \ 10^{-5}$$

- appreciable radial probability density within restricted range of r, longer interval for larger n

The probability density is independent of ϕ

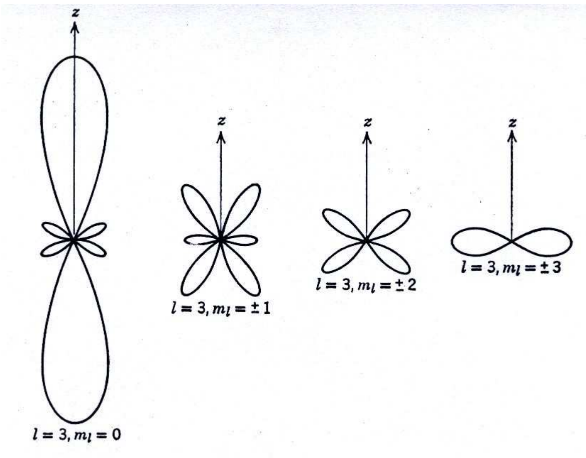
$$\Phi^*_{m_l}(\phi)\ \Phi_{m_l}(\phi) \ = \ 1$$

the angular dependence of the probability density comes from θ

$$\Theta^*(\theta)\ \Theta(\theta) \ \text{ drawn in polar diagram}$$

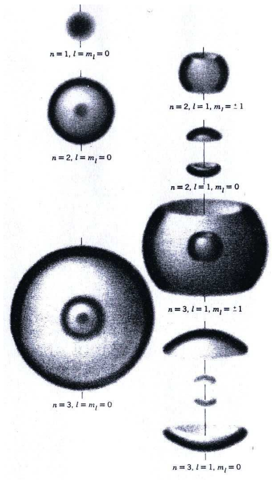
- $l \ = \ 0$ $|\Theta|^2$ is independent of θ $\rightarrow$ spherical symmetry
- $l \ \neq \ 0$
  - $m_l \ = \ \pm l$ location in the xy plane $(\theta \ = \ \frac{\pi}{2})$
  - $m_l \ = \ 0$ e^- quite located on axis z $(\theta \ = \ 0,\ \pi)$

24 / 28



Polar diagram of $\Theta^*(\theta)\ \Theta(\theta)$ (angular dependence of $|\Psi_{nlm_l}|^2$)

25 / 28



Probability density for an atom with one e^- (the line is the z axis)

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