Some Algebra:

$M = m_e + m_p$ $\qquad\qquad$ $\mu = \frac{m_e m_p}{m_e + m_p}$

$\vec{R} = \vec{X} + \vec{Y} + \vec{Z}$ $\qquad\qquad$ $\vec{r} = \vec{x} + \vec{y} + \vec{z}$

$X = \frac{m_e x_e + m_p x_p}{m_e + m_p}$ $\qquad\qquad$ $x = x_p - x_e$

$Y = \frac{m_e y_e + m_p y_p}{m_e + m_p}$ $\qquad\qquad$ $y = y_p - y_e$

$Z = \frac{m_e z_e + m_p z_p}{m_e + m_p}$ $\qquad\qquad$ $z = z_p - z_e$

(center of mass) $\qquad\qquad$ (relative coordinates)

Consider 1-D: $(m_e + m_p)\dot{X}^2 = (m_e+m_p)\left(\frac{1}{m_e+m_p}\right)^2 *$

$$(m_e^2\dot{x}_e^2 + m_p^2\dot{x}_p^2 + 2m_e m_p \dot{x}_e \dot{x}_p)$$

$$\frac{m_e m_p}{m_e + m_p}\dot{x}^2 = \frac{m_e m_p}{m_e + m_p}\left(\dot{x}_p^2 + \dot{x}_e^2 - 2\dot{x}_e\dot{x}_p\right)$$

now: $$M\dot{X}^2 + \mu\dot{x}^2 = \frac{1}{m_e+m_p}\left[m_e^2\dot{x}_e^2 + m_p^2\dot{x}_p^2 + m_e m_p(\dot{x}_p^2 + \dot{x}_e^2)\right]$$
$$= \frac{1}{m_e+m_p}\left[(m_e+m_p)m_e\dot{x}_e^2 + (m_e+m_p)m_p\dot{x}_p^2\right]$$
$$= m_e\dot{x}_e^2 + m_p\dot{x}_p^2 \qquad \underline{\text{equivalence}}$$

$$\mathcal{H}\Psi(R,r) = \left[\frac{-\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}\right]\Psi(R,r) = E_T\Psi(R,r)$$

$\Psi = \chi(R)\psi(r)$: $$\frac{-\hbar^2}{2M}\nabla_R^2\chi(R)\psi(r) = \left[\frac{\hbar^2}{2\mu}\nabla_r^2 + \frac{Ze^2}{r}\right]\chi(R)\psi(r) + E_T\chi(R)\psi$$

divide thru by $\Psi = \chi\cdot\psi$; each side constant because independent:

$$-\frac{1}{\chi(R)}\frac{\hbar^2}{2M}\nabla_R^2\chi(R) = E_{KE} = \frac{1}{\psi(r)}\left[\frac{\hbar^2}{2\mu}\nabla_r^2 + \frac{Ze^2}{r}\right]\psi(r) + E_T$$

1) $\nabla_R^2\chi(R) = -\frac{2ME_{KE}}{\hbar^2}\chi(R) \Longrightarrow \chi(R) = \exp\left(i\frac{\sqrt{2mE'}}{\hbar}R\right)$

2) $\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{Ze^2}{r}\right]\psi(r) = (E_T - E_{KE})\psi(r) = E\psi(r)$

(recall: $\nabla_r^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$)

Handout

④

Sol'n to Separation of Variables for H-atom

$$\nabla^2 = \left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

put ∇^2 in $\mathcal{H}$ and then multiply by $r^2\sin^2\theta$ to get ϕ equation separated: $\Psi = R(r)\Theta(\theta)\Phi(\phi)$

again, divide thru by Ψ; when set up get: $(\mathcal{H}-E)\Psi=0$

$$0 = \left[\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{\partial^2}{\partial\phi^2} - \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{r}+E\right)r^2\sin^2\theta\right]R\Theta\Phi$$

divide through by Ψ & multiply by $r^2\sin^2\theta$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R(r) + \frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta(\theta) - \frac{2\mu}{\hbar^2}\left(\frac{Ze^2}{r}+E\right)r^2\sin^2\theta = -\frac{1}{\Phi}\frac{\partial^2}{\partial\phi^2}\Phi$$

let each side be equal to a constant: m^2

all ϕ dependence is separated on the right (below ①)

Do the same thing to left hand side, divide thru by $\sin^2\theta$ to separate R + Θ

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R - \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{r}+E\right) = -\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta + m^2/\sin^2\theta$$

Each side again constant – fct. of diff. variables

let this one equal: λ

① $\frac{\partial^2}{\partial\phi^2}\Phi = -m^2\Phi \longrightarrow \Phi = e^{im\phi}$ $m = 0, \pm1, \pm2 \ldots$

② $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta - \frac{m^2}{\sin^2\theta}\Theta + \lambda\Theta = 0 \longrightarrow$ Legendre Poly.

③ $\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)R - \frac{2\mu r^2}{\hbar^2}\left(\frac{Ze^2}{r}+E\right)R - \lambda R = 0 \longrightarrow$ Laguerre Poly.

Handout

The Θ solutions — Associated Legendre Polynomials — $\Theta_{\ell m}(\theta)$ $\left(P_\ell^{|m|}(\cos\theta)\right)^{‡}$

ℓ	m	$\Theta_{\ell m}$
0	0	$\frac{1}{2}\sqrt{2}$
1	0	$(3/2)^{1/2}\cos\theta$
1	± 1	$(3/4)^{1/2}\sin\theta$
2	0	$(5/8)^{1/2}(3\cos^2\theta - 1)$
2	± 1	$(15/4)^{1/2}\sin\theta\cos\theta$
2	± 2	$(15/16)^{1/2}\sin^2\theta$

The Radial Solutions – exponential and a power times Associated Lequerre Polynomials – $R_{n\ell}(r)^{*}$

n	ℓ	$R_{n\ell}$ (note: $\sigma = \frac{Zr}{a_0}$, $a_0 = \frac{\hbar^2}{me^2}$)
1	0	$2(Z/a_0)^{3/2} e^{-\sigma}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}(2-\sigma)e^{-\sigma/2}$
2	1	$3^{-1/2}\left(\frac{Z}{2a_0}\right)^{3/2}\sigma e^{-\sigma/2}$
3	0	$\frac{2}{27}\left(Z/3a_0\right)^{3/2}(27-18\sigma+2\sigma^2)e^{-\sigma/3}$
3	1	$\frac{1}{81\sqrt{3}}\left(2Z/a_0\right)^{3/2}(6-\sigma)\sigma e^{-\sigma/3}$
3	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}\sigma^2 e^{-\sigma/3}$

*
$$R_{n\ell}(r) = \left[\frac{2Z^3}{n}\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2Zr}{na_0}\right)^{\ell} L_{n+\ell}^{2\ell+1}\left(\frac{2Zr}{na_0}\right) e^{-\frac{Zr}{na_0}}$$

$$L_r^s(\rho) = \frac{d^s}{d\rho^s}\left[L_r(\rho)\right] \;;\; L_r(\rho) = e^{\rho}\frac{d^r}{d\rho^r}\left[\rho^r e^{-\rho}\right]$$

‡
$$P_\ell^{|m|}(\cos\theta) = \frac{1}{2^\ell \ell!}(1-\cos^2\theta)^{|m|/2}\frac{d^{\ell+|m|}}{d(\cos\theta)^{\ell+|m|}}(\cos^2\theta - 1)^\ell$$

note: $n = 1, 2, 3 \cdots\cdots$; $\ell = 0, 1, \cdots n$; $\ell \geq |m|$

Handout

Real Wavefunctions (as opposed to complex)

$$\psi'_{real} = \frac{1}{\sqrt{2}}\left(\psi_{n\ell m} + \psi_{n\ell,-m}\right)$$

$$\psi''_{real} = \frac{i}{\sqrt{2}}\left(\psi_{n\ell m} - \psi_{n\ell,-m}\right)$$

Table 6.2 Real Hydrogenlike Wave Functions

$$\psi_{1s} = \frac{1}{\pi^{1/2}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$\psi_{2s} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$\psi_{2p_z} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\cos\theta$$

$$\psi_{2p_x} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\cos\varphi$$

$$\psi_{2p_y} = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{5/2} re^{-Zr/2a}\sin\theta\sin\varphi$$

$$\psi_{3s} = \frac{1}{81(3\pi)^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\left(27 - 18\frac{Zr}{a} + 2\frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}$$

$$\psi_{3p_z} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\cos\theta$$

$$\psi_{3p_x} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\cos\varphi$$

$$\psi_{3p_y} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{5/2}\left(6 - \frac{Zr}{a}\right)re^{-Zr/3a}\sin\theta\sin\varphi$$

$$\psi_{3d_{z^2}} = \frac{1}{81(6\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}(3\cos^2\theta - 1)$$

$$\psi_{3d_{xz}} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\cos\varphi$$

$$\psi_{3d_{yz}} = \frac{2^{1/2}}{81\pi^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin\theta\cos\theta\sin\varphi$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\cos 2\varphi$$

$$\psi_{3d_{xy}} = \frac{1}{81(2\pi)^{1/2}}\left(\frac{Z}{a}\right)^{7/2} r^2e^{-Zr/3a}\sin^2\theta\sin 2\varphi$$

from: Ira Levine, "Quantum Chemistry", Vol I
edition 2 — (1975)

Can show that $\nabla^2_{r(xyz)} \rightarrow \nabla^2_{r(r,\theta,\phi)}$ gives:

$$\mathcal{H}\psi = \frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\psi$$

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

<u>separable</u> eqn because $\mathcal{H} \cong \mathcal{H}(r) + \mathcal{H}(\theta) + \mathcal{H}(\phi)$
(i.e. works if do one at a time – see sheet)

See Handout — use product wave function $\underline{\psi = R(r)\,\Theta(\theta)\,\Phi(\phi)}$

① $\underline{\frac{\partial^2}{\partial\phi^2}\Phi = -m^2\Phi}$ — sol'n easy same <u>form</u> as for free particle

$\Phi = e^{im\phi}$ $\quad m = 0, \pm1, \pm2 \cdots$

— integer so that single valued i.e.
$e^{im\phi} = e^{im(\phi+2\pi)} = e^{im\phi}\cdot \underbrace{e^{im2\pi}}_{1 \text{ if } m \text{ integ}}$

② $\underline{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\Theta - \frac{m^2}{\sin^2\theta}\Theta + \lambda\Theta = 0}$

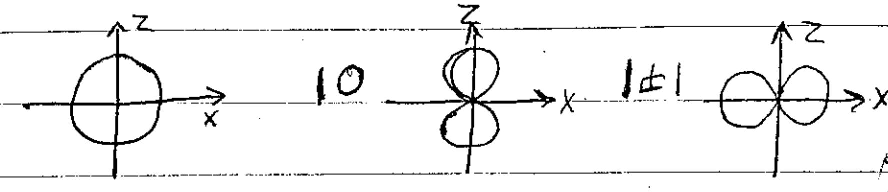
solution to this eqn if $\underline{\lambda = l(l+1)}$

$\underline{l = 0, 1, 2, 3}$ ---- (pos)

and $\underline{|m| \le l}$

sol'n called Legendre polynomials Θ_{lm}
(math books: $\Theta_{lm} = P_l^{|m|}$ – see sheet)

Shapes: 00



constant w/ θ $\qquad$ $\cos\theta$ $\qquad$ $\sin\theta$

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

note: $\lambda = l(l+1)$

- can be solved by combination of an exponential and a polynomial (L_{n+l}^{2l+1}) called associate LeGuerre polynomial
- restrictions: $n = 1, 2, 3, 4 \ldots$

$n \geq l+1$ or $0 \leq l \leq n-1$

and $n^2 = -\frac{Z^2 e^4 \mu}{2\hbar^2 E}$

$\therefore$ Energy must be quantized + get Bohr soln:

$$E_n = -\frac{Z^2 e^2 \mu}{2\hbar^2 n^2}$$

(note: $\mu \sim m_e$ since $m_e \ll m_p$)

Shapes of R + R^2 + r^2R^2 (sph. harm + ang mom eig fct)

in general: Radial function shape

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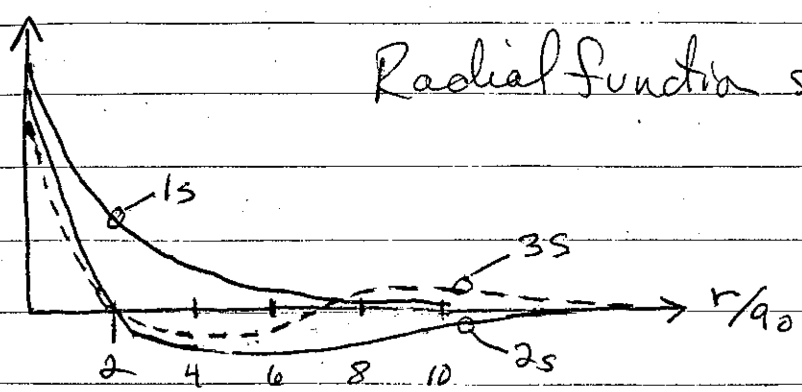

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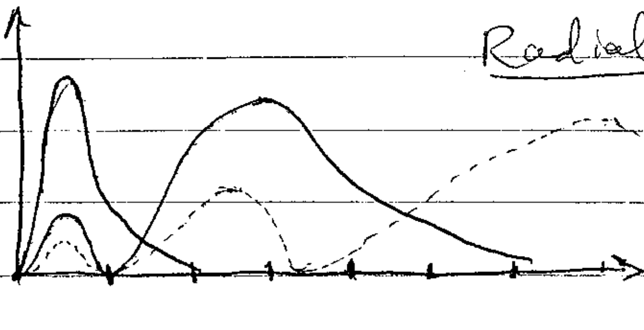
radial distribution r^2R^2

Radial distribution ~ probability of electron in a shell of dr at r



max 1s = a_0
2s = $5.2a_0$