Hydrogen atom

Note Title 04-11-2009

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}$$

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

$$\psi(r, \theta, \varphi) = R(r)\, Y_{\ell m}(\theta, \varphi)$$

$$L^2 Y_{\ell m}(\theta, \varphi) = \ell(\ell+1)\hbar^2 Y_{\ell m}$$

$$L_z Y_{lm} = m\hbar Y_{lm}$$

Radial Schrödinger equation

$$\left\{ -\frac{\hbar^2}{2m}\left(\frac{d}{dr} r^2 \frac{d}{dr}\right) - E + V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right\} R = 0$$

$$V \to -\frac{Ze^2}{r}$$

no m dependence

Radial momentum p_r ✓

$$\frac{p_r^2}{2m} + \frac{p_\ell^2}{2M}$$

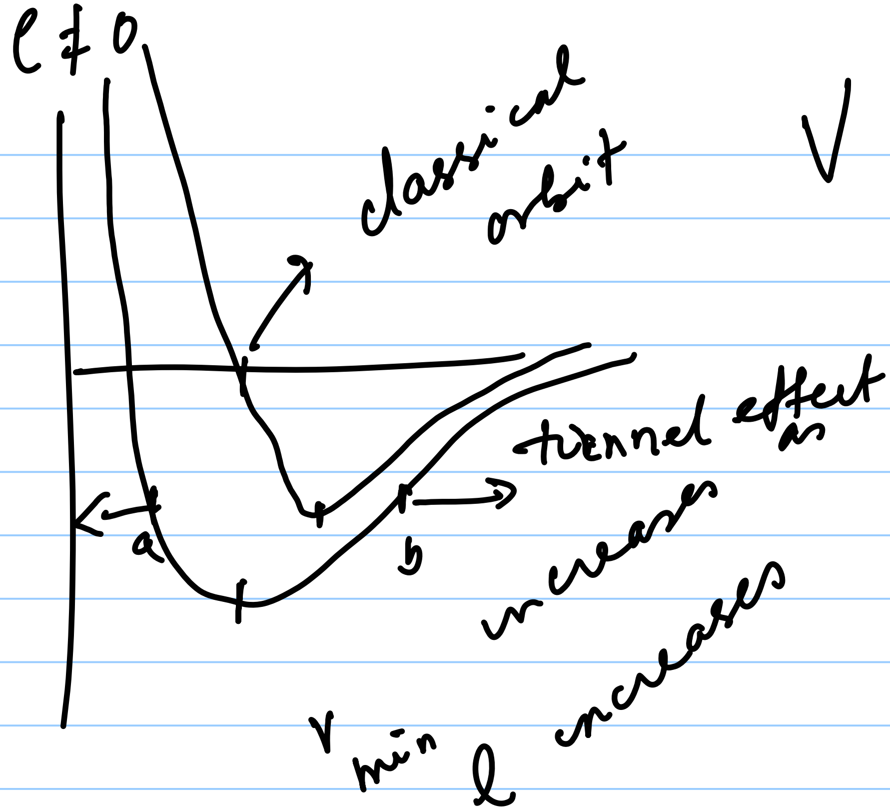
a $\qquad p_\ell$

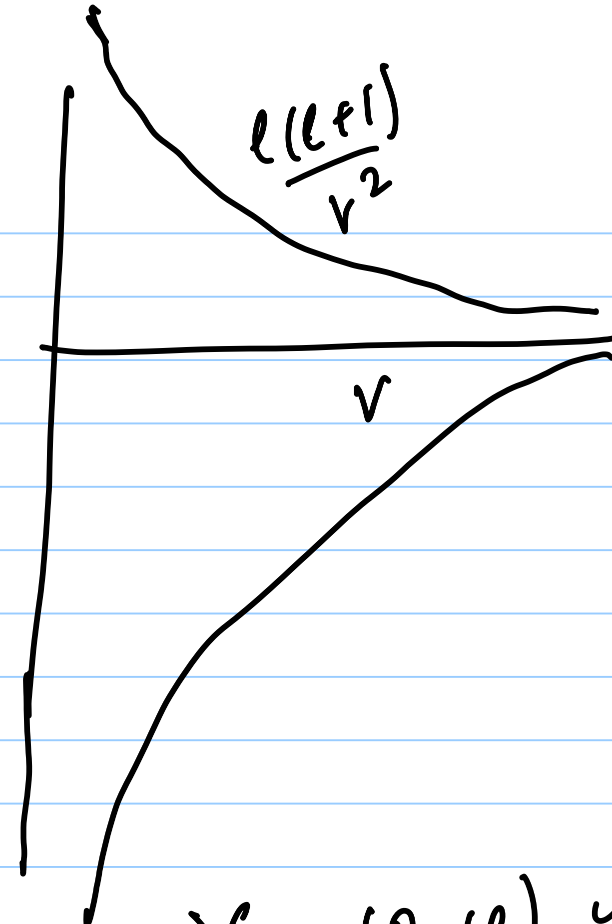
constant $= \left\{ \frac{p_r^2}{2m} + \frac{(p_\ell r)^2}{2m r^2} \right.$ angular momentum

$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)R+\left(-E+V(r)\right)R=0$$

one dimensional $V_{eff} = -\frac{Ze^2}{r} + \frac{l(l+1)}{r^2}$

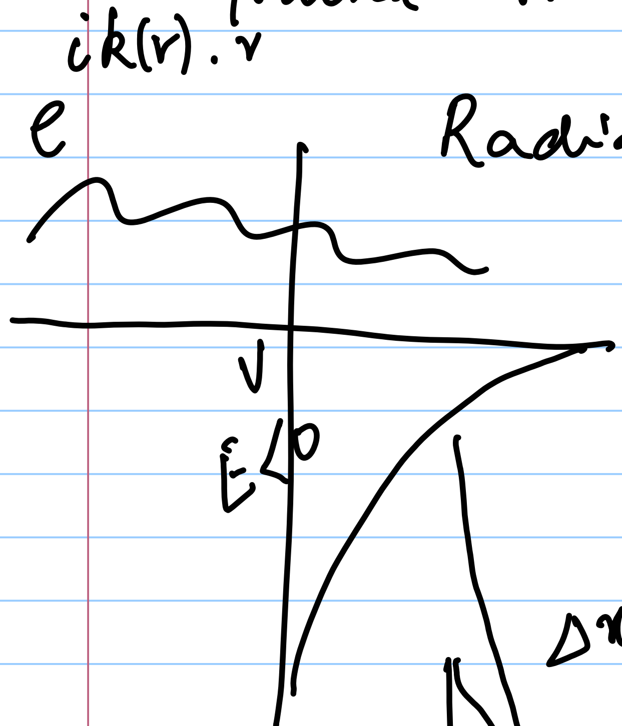
one dimensional SE
$$-\frac{\hbar^2}{2m}\left(\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}+V_{eff}\right)R = ER$$





$l = 0$, spherically symmetric. $Y_{lm}(\theta, \varphi)$ is indep of θ, & φ

Ground state spherically symmetric solution:

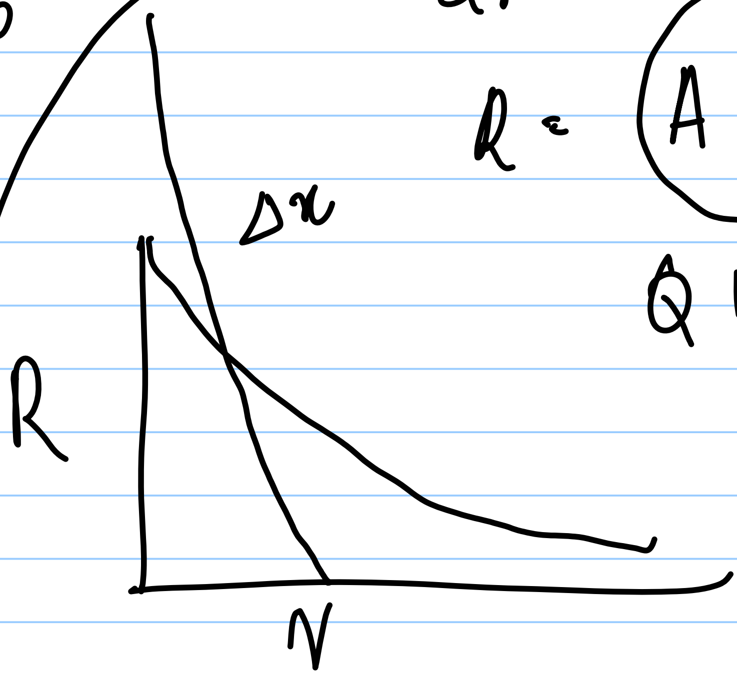


Radial S.E and look at it as $r \to \infty$

$$\frac{d^2R}{dr^2} = \alpha^2 R \qquad \alpha = \frac{-2mE}{\hbar^2}$$

$$R = A e^{\alpha r} + \boxed{B e^{-\alpha r}} \quad \text{for } r \to \infty$$

QM not acceptable



$$= Be^{-\alpha r}$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) - \frac{Ze^2}{r}R = ER$$

$$① \quad -\alpha^2 Be^{-\alpha r} + \frac{2}{r}\left(-\alpha Be^{-\alpha r}\right) + \frac{2m}{\hbar^2}\left(\frac{Ze^2}{r} + E\right)Be^{-\alpha r} = 0$$

$$\underbrace{\left(\alpha^2 + \frac{2mE}{\hbar^2}\right)} + \frac{1}{r}\underbrace{\left(\frac{2mZe^2}{\hbar^2} - 2\alpha\right)} = 0$$

independently zero

$$\alpha^2 = -\frac{2mE}{\hbar^2} \qquad \bigg/ \qquad \frac{2mZe^2}{\hbar^2} - 2\alpha = 0$$

$$E = \boxed{-Z^2 \frac{me^4}{\hbar^2}} \longrightarrow$$ Grand state energy of the H-atom

$Be^{-\alpha r}$ is a solution of the radial Schrödinger equation

$$\alpha = Z \frac{me^2}{\hbar^2} = \frac{1}{a_0} = \frac{Z}{a_0}$$

a_0: Bohr radius

$$\psi_{1s} = Be^{-\alpha r}$$

Normalization

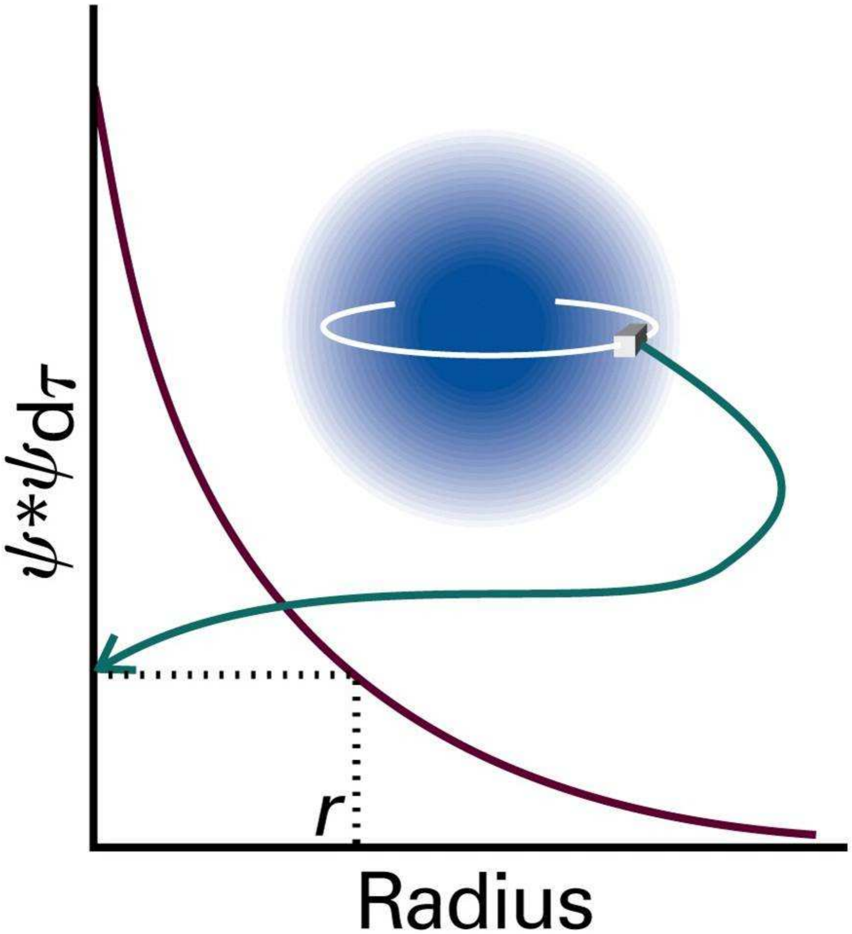
$$\int \psi_{1s}^* \psi_{1s}\, r^2\, dr \underbrace{\int Y_{lm}^* Y_{lm} \sin\theta\, d\theta\, d\phi}_{1}$$

Prob. — Born interpretation

Radial distribution function $\left\{ r^2 R_{nl}(r)^2 = r^2 e^{-2\alpha r} \right.$

4π

Bohr radius



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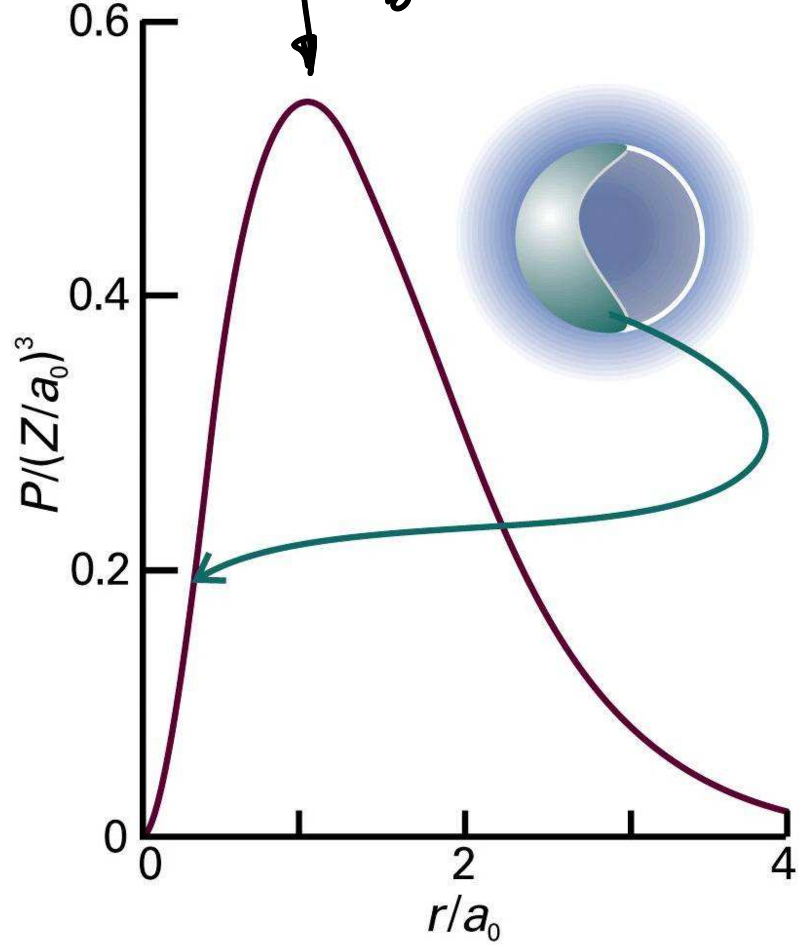

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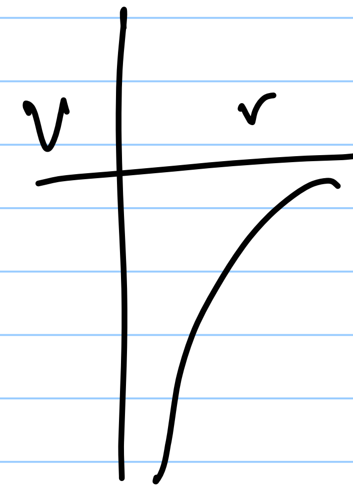
Spherically symmetric excited state

$$\Psi_{2s} = R_{2s} = (b - r)\, e^{-ar}$$

$\uparrow$

one node



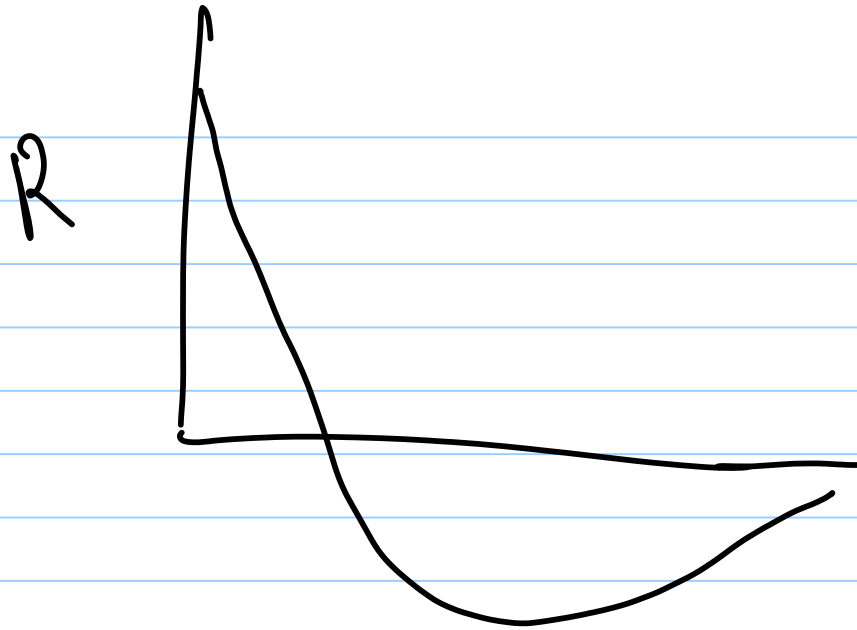
$r^2 \Psi_{2s}^2$

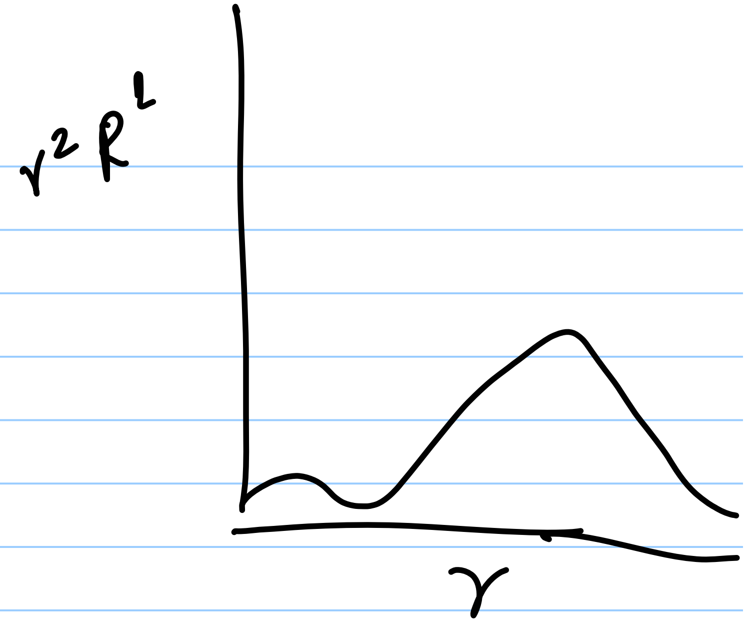
$r^2 R^2$

$$a = Z/2a_0$$

$$b = \frac{2a_0}{Z}$$

$$E_2 = -\frac{1}{4}\frac{Z^2 e^2}{2a_0}$$


R


$r^2 R^2$
r

State with no spherical symmetry (first excited state)

$x R(r), \quad y R(r), \quad z R(r)$

ϕ

$r \sin\theta \quad \cos\varphi$

e^{-Zr/na_0}

Table 10.1 Hydrogenic radial wavefunctions

Orbital	n	l	$R_{n,l}$
1s	1	0	$2\left(\frac{Z}{a}\right)^{3/2} e^{-\rho/2}$
2s	2	0	$\frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)e^{-\rho/2}$
2p	2	1	$\frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}$
3s	3	0	$\frac{1}{243^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(6-6\rho+\rho^2)e^{-\rho/2}$
3p	3	1	$\frac{1}{486^{1/2}}\left(\frac{Z}{a}\right)^{3/2}(4-\rho)\rho e^{-\rho/2}$
3d	3	2	$\frac{1}{2430^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho^2 e^{-\rho/2}$

$\rho = (2Z/na)r$ with $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$. For an infinitely heavy nucleus (or one that may be assumed to be so), $\mu = m_e$ and $a = a_0$, the Bohr radius. The full wavefunction is obtained by multiplying R by the appropriate Y given in Table 9.3.

$r^2 = l$

$l=2$, 1

$e^{-\rho/2} = e^{-\frac{2Zr}{2a_0}} = e^{-\frac{Zr}{a_0}}$

$e^{-Zr/2a_0} \times \left(2 - 2\frac{Zr}{2a_0}\right)$

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As $r \to 0$, $\quad \psi \sim r^{\ell}$

As $r \to \infty$, $\quad \psi \sim 0 \quad (e^{-Zr/na_0})$

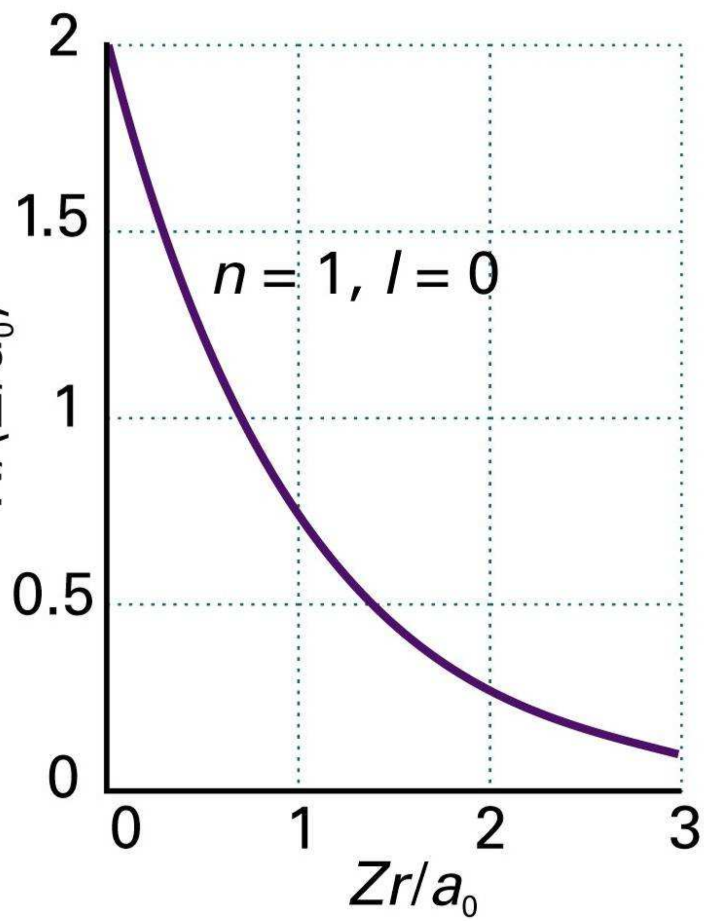
$$R_{n\ell} = N\, e^{-Zr/na_0}\, r^{\ell} \underbrace{(\text{polynomial in } r)}_{\#\text{ of nodes}}$$

$$\psi = R_{n\ell}(r)\, Y_{\ell m}(\theta, \varphi)$$

$$E = -\frac{1}{n^2}\frac{Z^2 e^2}{2 a_0}$$

independent of ℓ & m

special case for H-atom



no radial nodes

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e^{-r/a_0}

$\psi_{ns} \neq 0$ at $r=0$

2 radial nodes
0 angular nodes

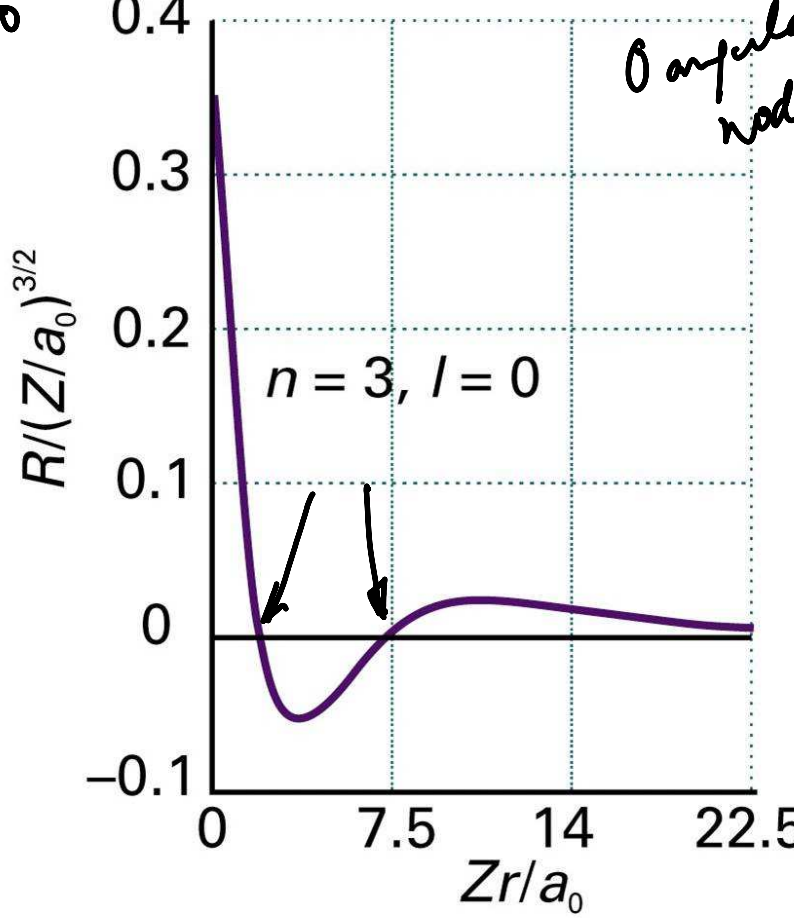

Figure 10-4c
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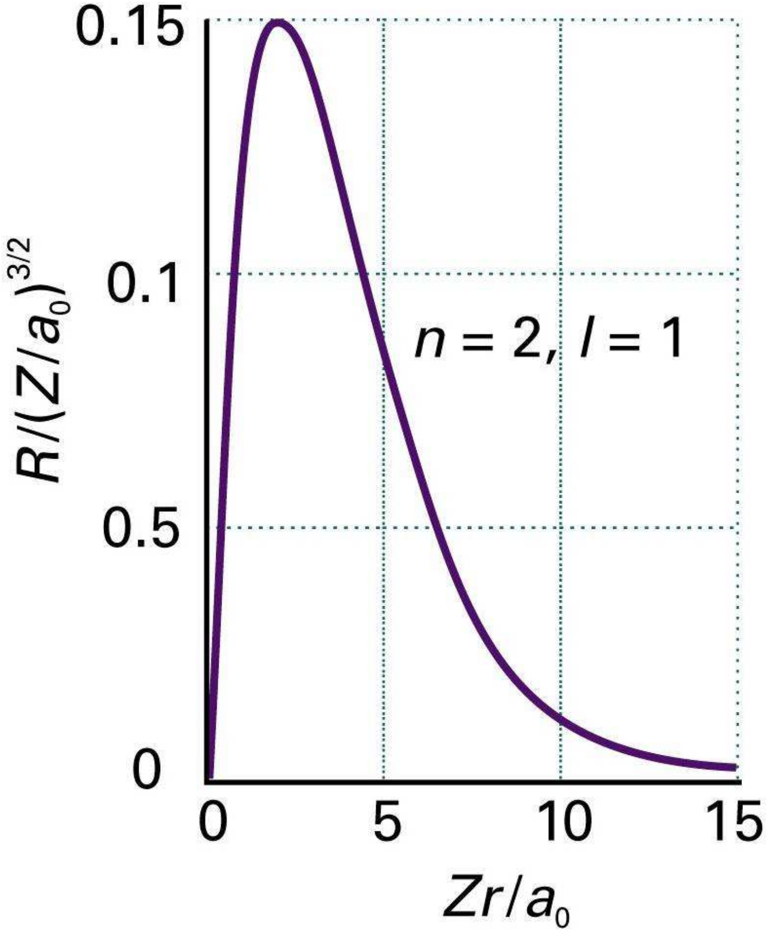
2p

For $l \neq 0$

$R(r=0) = 0$

3d



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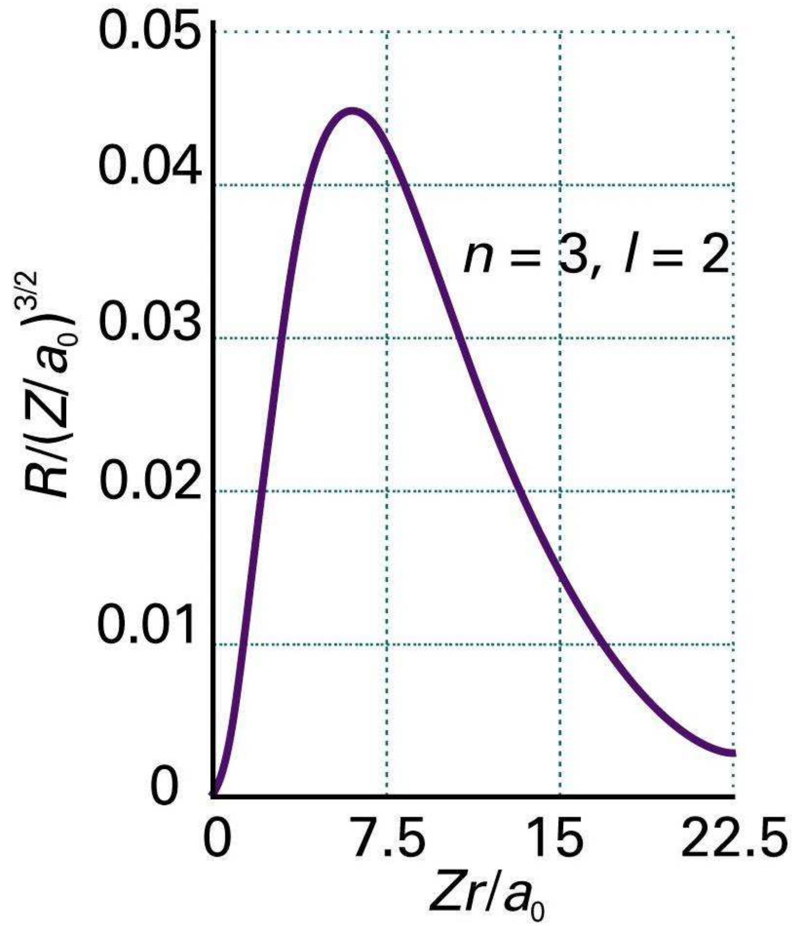

Figure 10-4f
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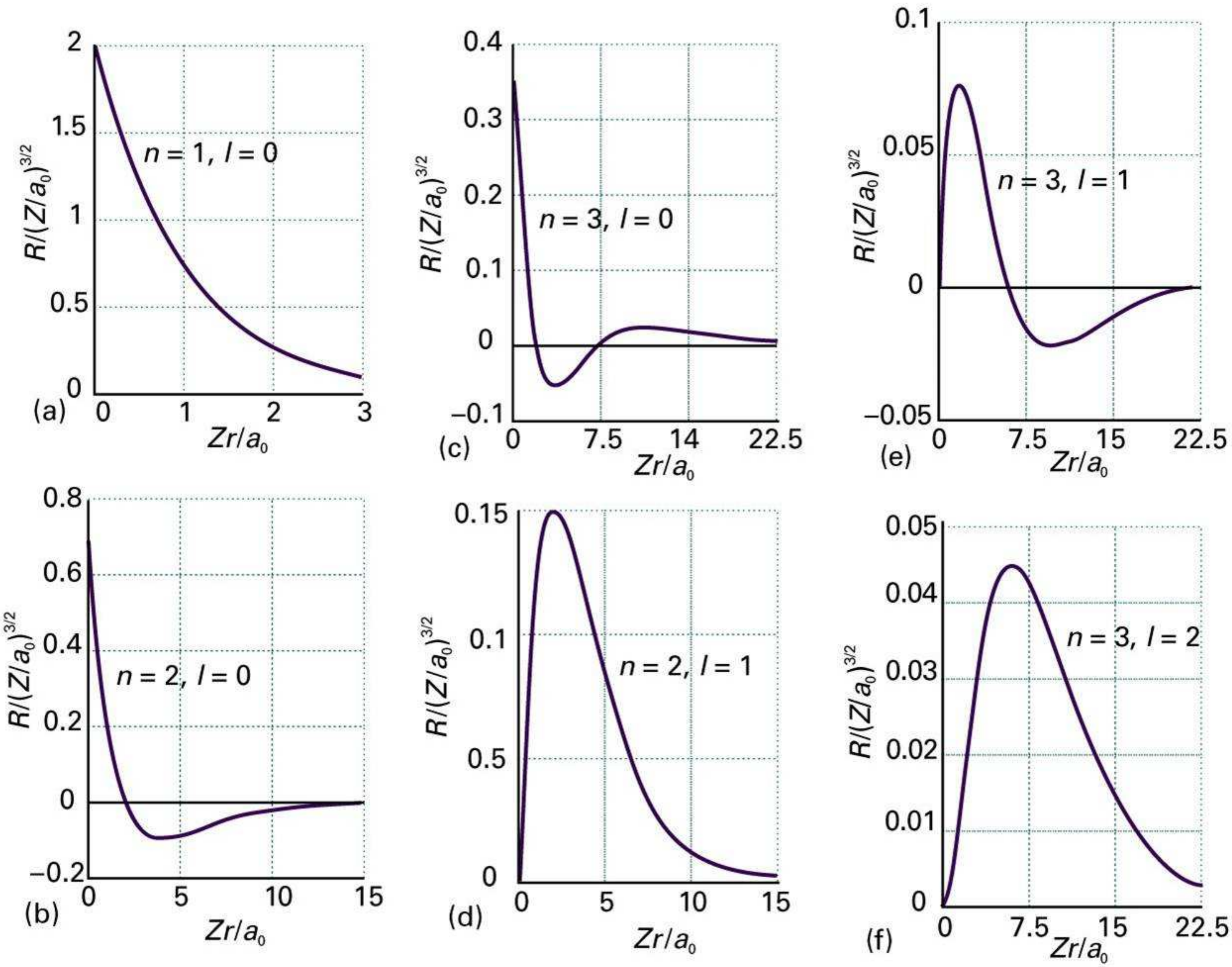

Figure 10-4
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1) Identify n, ℓ, m given the H-atom wave functions

$$\psi = (\text{linear fn}) \times e^{-\alpha x^2} \quad n = 1 \qquad \Delta n = \pm 1$$

$$\psi' = (\text{cubic}) \times e^{-\alpha x^2} \quad n = 3$$

2) E dep on Z, n

3) Prob of finding an electron at same pt, max prob of finding the electron

4) Expectation values of T, V, etc
x, y, z,

$$\psi_{1s} = e^{-r/a_0}$$

$$\int_0^\infty r^n e^{-\beta r}\, dr = \left(\frac{\partial}{\partial \beta}\right)^n \int_0^\infty e^{-\beta r}\, dr$$

$$= \frac{\partial^n}{\partial \beta^n} \int_0^\infty e^{-\beta r}\, dr$$

$$\langle x \rangle = 0$$

$$\langle r \sin\theta \cos\varphi \rangle$$

$$= \frac{\int e^{-r/a_0}\, r \sin\theta \cos\varphi\, e^{-r/a_0}\, r^2 \sin\theta\, dr\, d\theta\, d\varphi}{\int e^{-r/a_0} e^{-r/a_0} r^2 dr \sin\theta\, d\theta\, d\varphi}$$

$$\int_0^\infty e^{-r/2a_0} r^3\, dr$$

Multi electron atoms

He atom

e_1 •

• e_2

$+2e$ •

$FC0$

$$\hat{H} = \boxed{-\frac{\hbar^2}{2m_N}\nabla_N^2} - \frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + e^2/r_{12}$$

KE of the nucleus

KE of the 2 electrons

attrn of e_1 to nucleus

e_2 to nucleus

$e^2/r_{12} \rightarrow$ interelectronic repulsion

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e_2}^2 - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \cancel{\frac{e^2}{r_{12}}}$$

$$\hat{H}\psi = E\psi$$

$$\psi(x_1, y_1, z_1, x_2, y_2, z_2) \Rightarrow \psi_1(x_1, y_1, z_1)\,\psi_2(x_2, y_2, z_2$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = -\frac{\hbar^2}{2m_e}\nabla_{e_1}^2 - \frac{2e^2}{r_1} - \frac{\hbar^2}{2m_e}\nabla_{e}^2 - \frac{2e^2}{r_2}$$

$$\psi = \psi_{1s}^{(1)}(Z=2) \times \psi_{1s}^{(2)}(Z=2)$$

$$= N e^{-\frac{2r_1}{a_0}} e^{-\frac{2r_2}{a_0}}$$

$$E = 8 \times H_{1s} \approx 108.8\,eV$$

(exptl). 75 eV