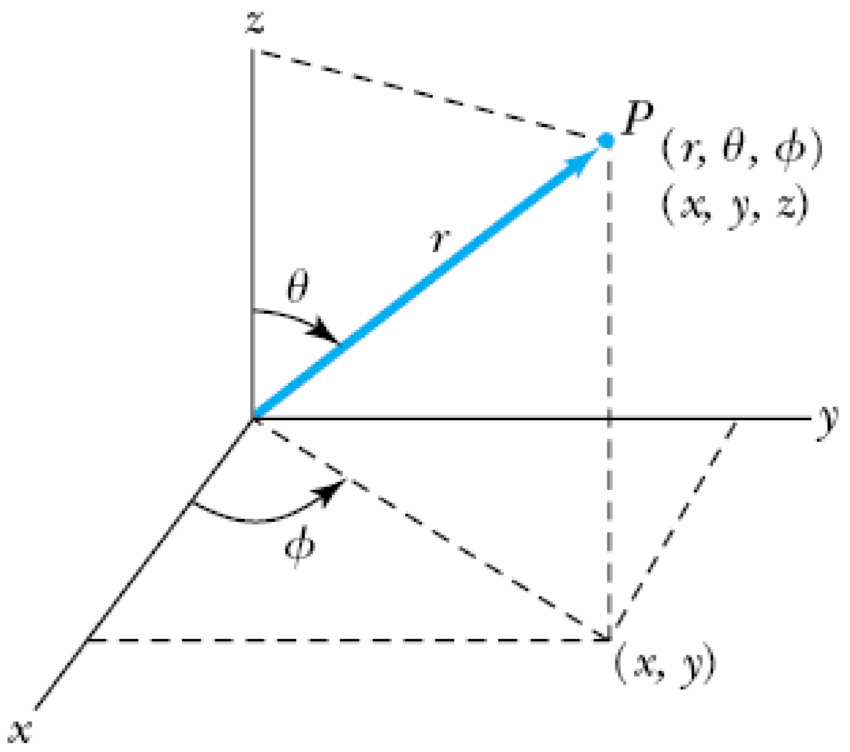
The Hydrogen Atom

Spherical Coordinates

•The potential (central force) *V*(*r*) depends on the distance *r* between the proton and electron.

Transform to spherical polar coordinates because of the radial symmetry.



$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \cos^{-1}\frac{z}{r} \quad \text{(Polar angle)}$$

$$\phi = \tan^{-1}\frac{y}{x} \quad \text{(Azimuthal angle)}$$

Solution of the Radial Equation

$$\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

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

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$\hat{H}R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi)$$

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

Dividing throughout by RY

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}-\frac{1}{Y}\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]Y+V(r)=E$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}-\frac{1}{Y}\frac{\hbar^2}{2\mu r^2}\Lambda^2 Y+V(r)=E$$

$$-\frac{\hbar^2}{2\mu r^2}\Lambda^2 Y=\frac{\hbar^2}{2\mu r^2}l(l+1)Y$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}+\frac{\hbar^2}{2\mu r^2}l(l+1)+V(r)=E$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r}+\left[\frac{\hbar^2}{2\mu r^2}l(l+1)-\frac{Ze^2}{4\pi\varepsilon_0 r}\right]=E$$

$$V_{eff} = \frac{\hbar^2}{2\mu r^2} l(l+1) - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + V_{eff} = E$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + V_{eff}R = ER$$

$$\frac{\partial^2 R}{\partial r^2} + \frac{2}{r}\frac{\partial R}{\partial r} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}\right)R = 0$$

Define

$$u = rR$$

$$\frac{1}{r}\frac{\partial^2 u}{\partial r^2} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}\right)R = 0$$

$$\frac{\partial^2 u}{\partial r^2} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}\right)rR = 0$$

$$\frac{\partial^2 u}{\partial r^2} + \frac{2\mu}{\hbar^2}\left(E - V_{eff}\right)u = 0$$

The last equation is called the radial equation

$$E_n = -\left(\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\right)\frac{1}{n^2} \qquad n = 1, 2, \ldots$$

$$\rho = 2Zr/na_0$$

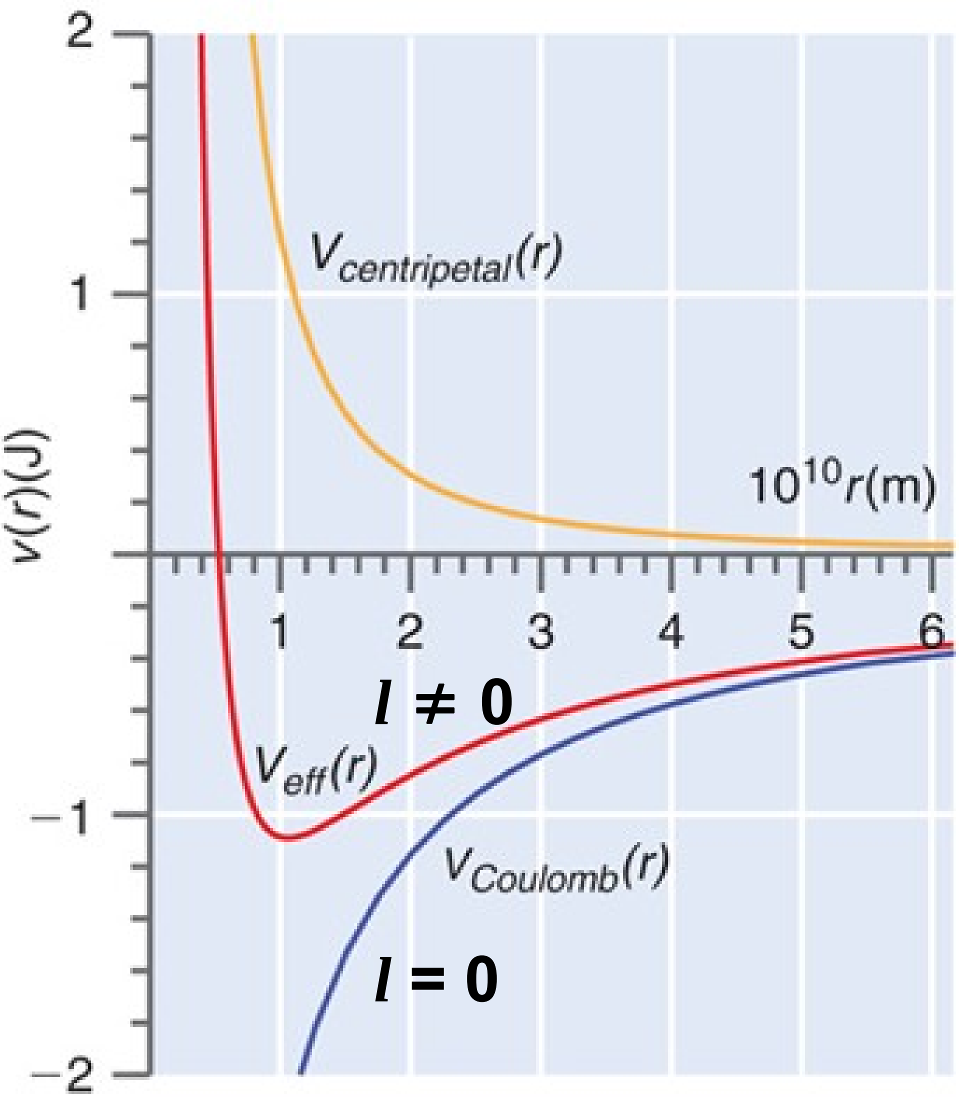
$$a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{m_e e^2}$$

Bohr's radius

In a precise calculation, the Bohr radius a_0, which depends on the mass of the electron, should be replaced by a, in which the reduced mass μ appears instead. Very little error is introduced by using a_0 in place of a in this and the other equations.

Even for ^{1}H, $a = 1.0005\ a_0$

The effective potential, V_{eff}

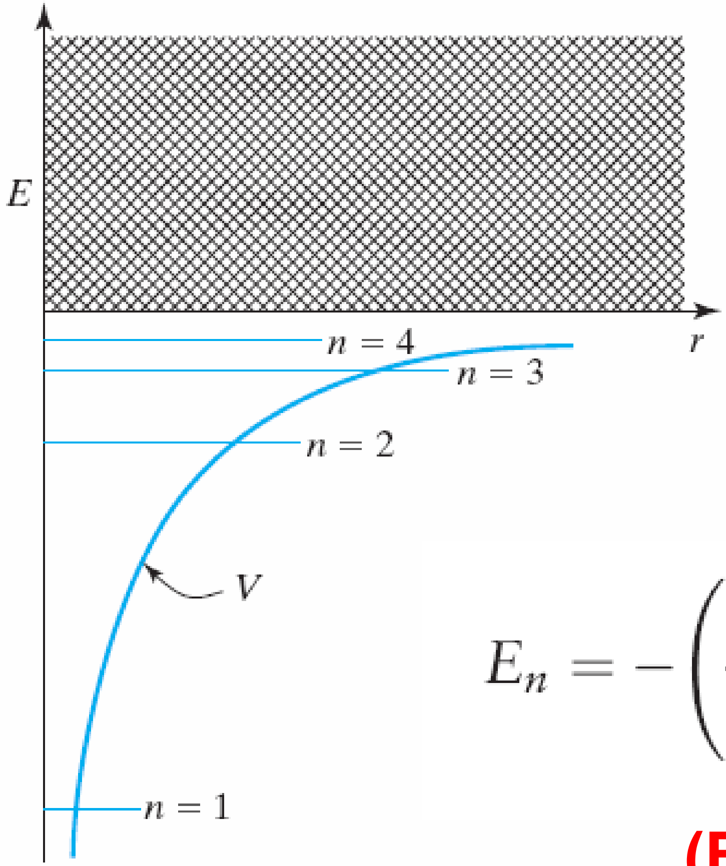


$$V_{\text{eff}} = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}$$

Centripetal potential

Coulomb Potential

Bound States



Shows the potential-energy curve and some of the allowed energy levels for the hydrogen atom (*Z* = 1).

The crosshatching indicates that all positive energies are allowed

$$E_n = -\left(\frac{Z^2 \mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\right)\frac{1}{n^2} \qquad n = 1, 2, \ldots$$

(Bound states)

$$\rho_n \equiv \frac{2Zr}{a_0 n}$$

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

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

$$R_{21}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{2\sqrt{6}}\, \rho_n$$

$$R_{30}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{9\sqrt{3}}\, (6 - 6\rho_n + \rho_n^2)$$

$$R_{31}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{9\sqrt{6}}\, (4 - \rho_n)\, \rho_n$$

$$R_{32}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{9\sqrt{30}}\, \rho_n^2$$

$$R_{40}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{96}\, (24 - 36\rho_n + 12\rho_n^2 - \rho_n^3)$$

$$R_{41}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{32\sqrt{15}}\, (20 - 10\rho_n + \rho_n^2)\, \rho_n$$

$$R_{42}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{96\sqrt{5}}\, (6 - \rho_n)\, \rho_n^2$$

$$R_{43}(r) = \left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho_n/2}\, \frac{1}{96\sqrt{35}}\, \rho_n^3$$

$$R_{nl}(r) = \mathbf{N_{n,l}}\ \rho^{l} L_{n+l}^{2l+1}(\rho) e^{-\rho/2}$$

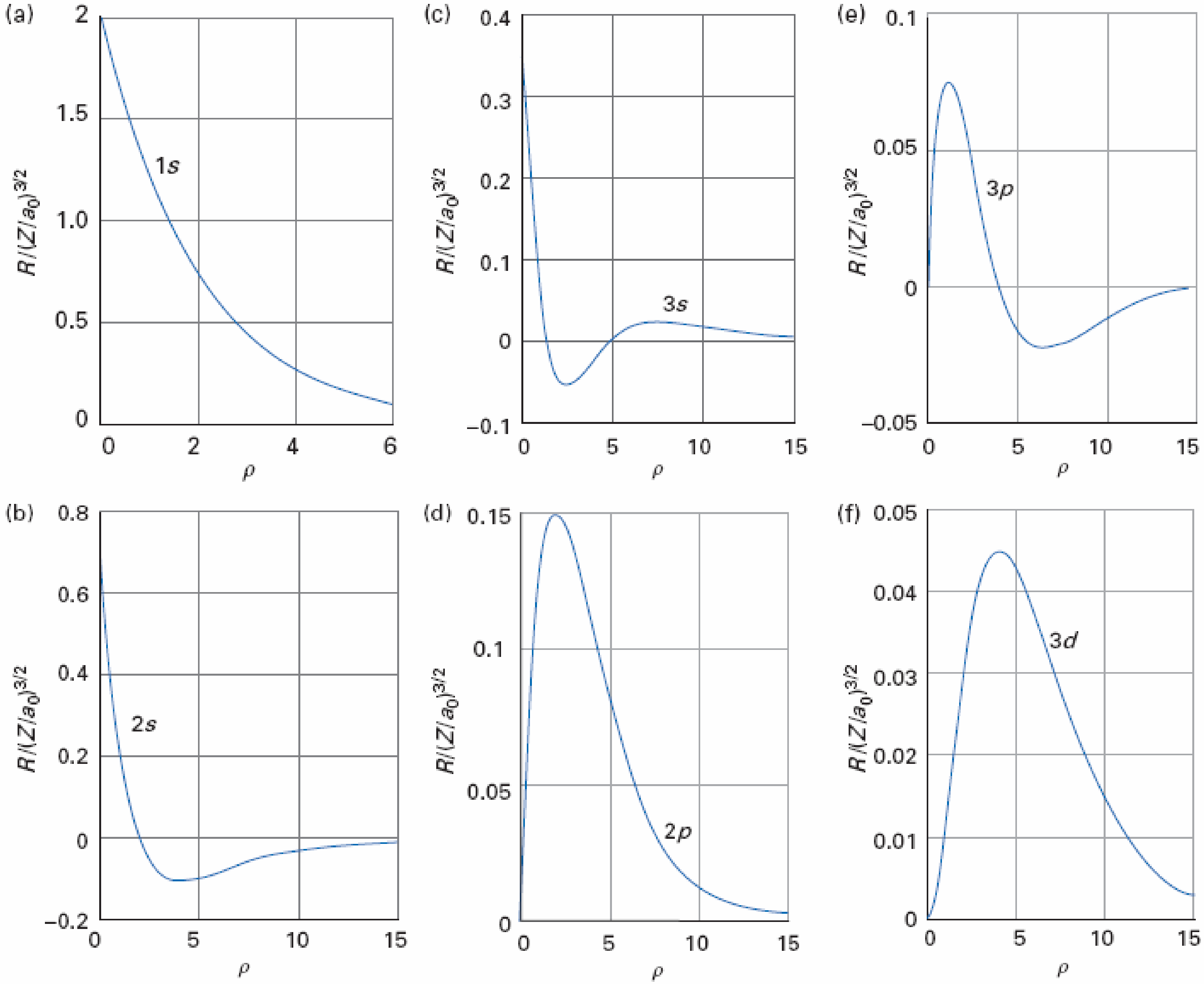


Illustration 3.1 Locating nodes

The zeros of the function with $n = 3$ and $l = 0$ occur where

$$6 - 6\rho + \rho^2 = 0 \quad \text{with } \rho = \left(\frac{2Z}{3a_0}\right)r$$

The zeros of this polynomial occur at $\rho = 3 \pm \sqrt{3}$, which corresponds to $r = (3 \pm \sqrt{3})(3a_0/2Z)$.

Quantum Numbers

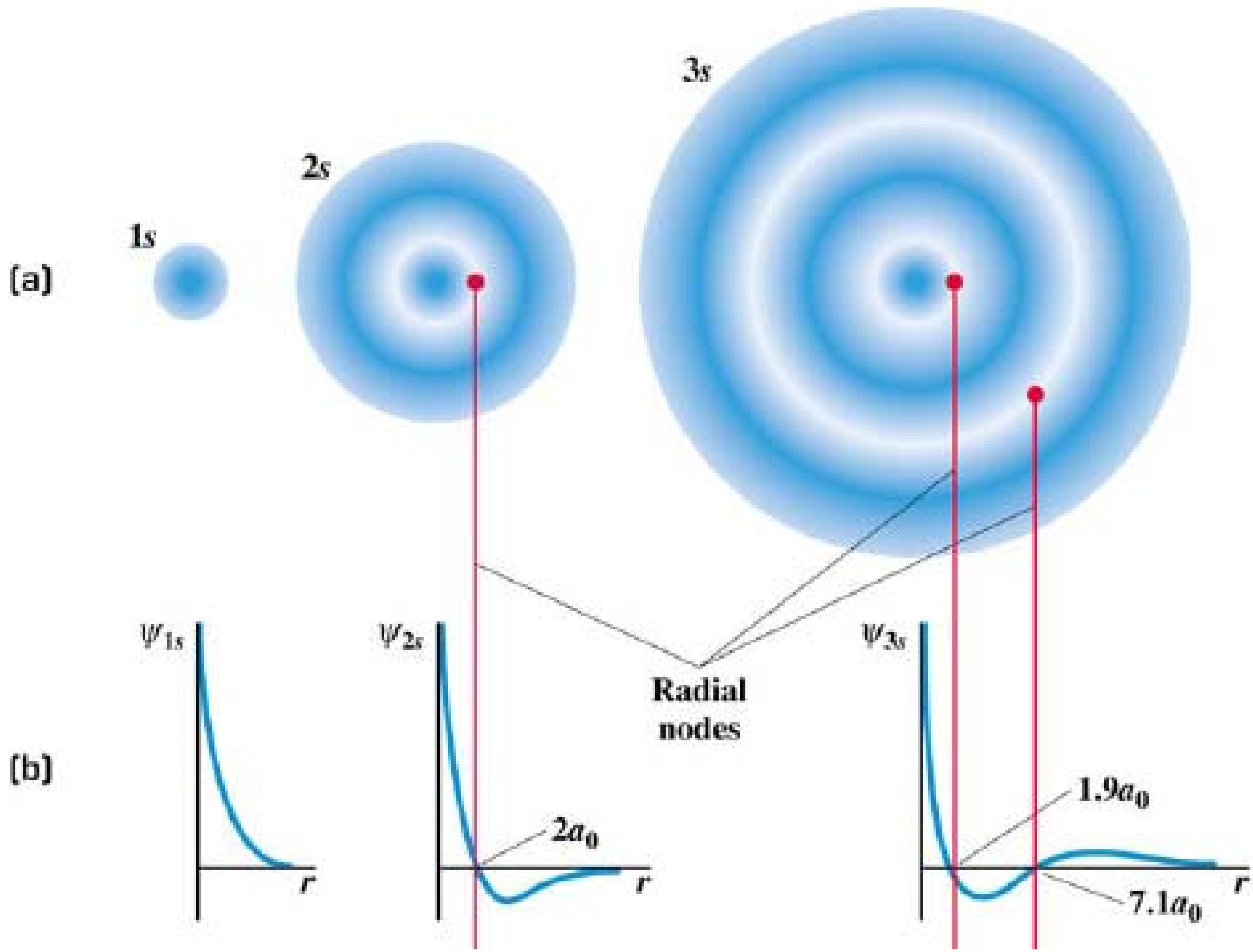
- The three quantum numbers:
  - n: Principal quantum number
  - ℓ: Orbital angular momentum quantum number
  - m_ℓ: Magnetic (azimuthal) quantum number

- The restrictions for the quantum numbers:

  $n = 1, 2, 3, 4, \ldots$

  $\ell = 0, 1, 2, 3, \ldots, n - 1$

  $m_\ell = -\ell, -\ell + 1, \ldots, 0, 1, \ldots, \ell - 1, \ell$



(a)
1s
2s
3s
Radial nodes
(b)
ψ_{1s}
ψ_{2s}
ψ_{3s}
r
$2a_0$
$1.9a_0$
$7.1a_0$

Spherical Harmonics

Y_l^m's are the eigenfunctions to $\hat{H}\psi = E\psi$ for the rigid rotor problem.

$$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}} \cos\theta$$

$$Y_1^1 = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{i\phi}$$

$$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{\frac{1}{2}} \sin\theta e^{-i\phi}$$

$$Y_2^0 = \left(\frac{5}{16\pi}\right)^{\frac{1}{2}} \left(3\cos^2\theta - 1\right)$$

$$Y_2^{\pm 1} = \left(\frac{15}{8\pi}\right)^{\frac{1}{2}} \sin\theta\cos\theta e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{\frac{1}{2}} \sin^2\theta e^{\pm 2 i\phi}$$

$$\rho_n \equiv \frac{2Zr}{a_0 n}$$

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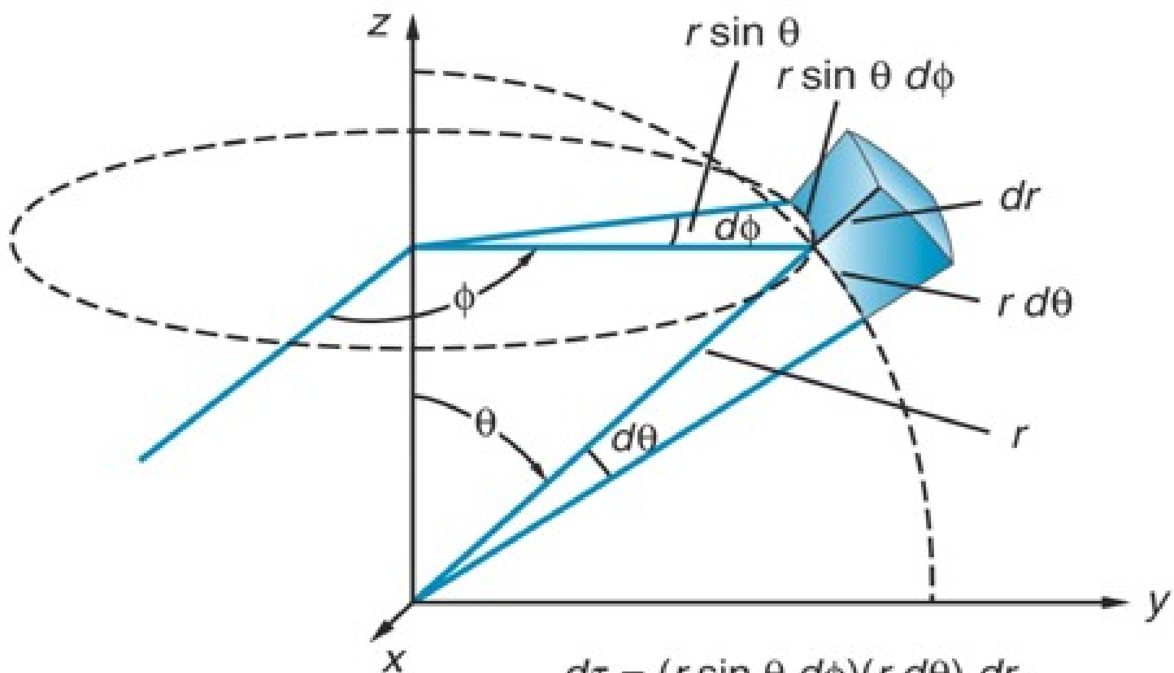
Think about how to write the total wavefunction

Done in class!

Total H atom wavefunctions are normalized and orthogonal:

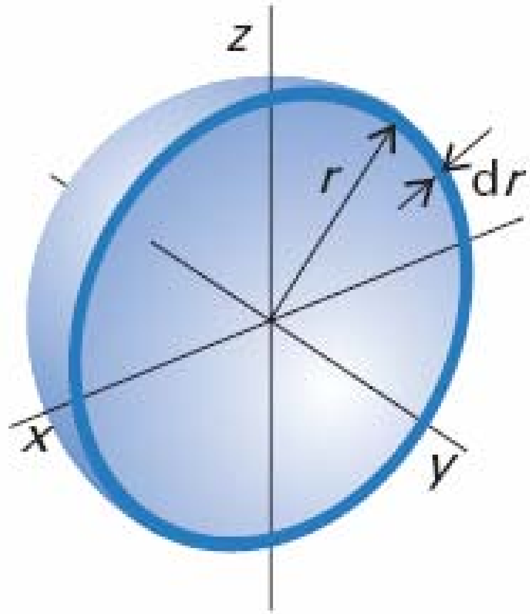
$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \; sin\theta \int_0^{\infty} drr^2 \psi^*_{nlm}(r,\theta,\phi)\psi^*_{n'l'm'}(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$



$$d\tau = (r \sin\theta \, d\phi)(r \, d\theta) \, dr$$
$$= r^2 \sin\theta \, dr \, d\theta \, d\phi$$

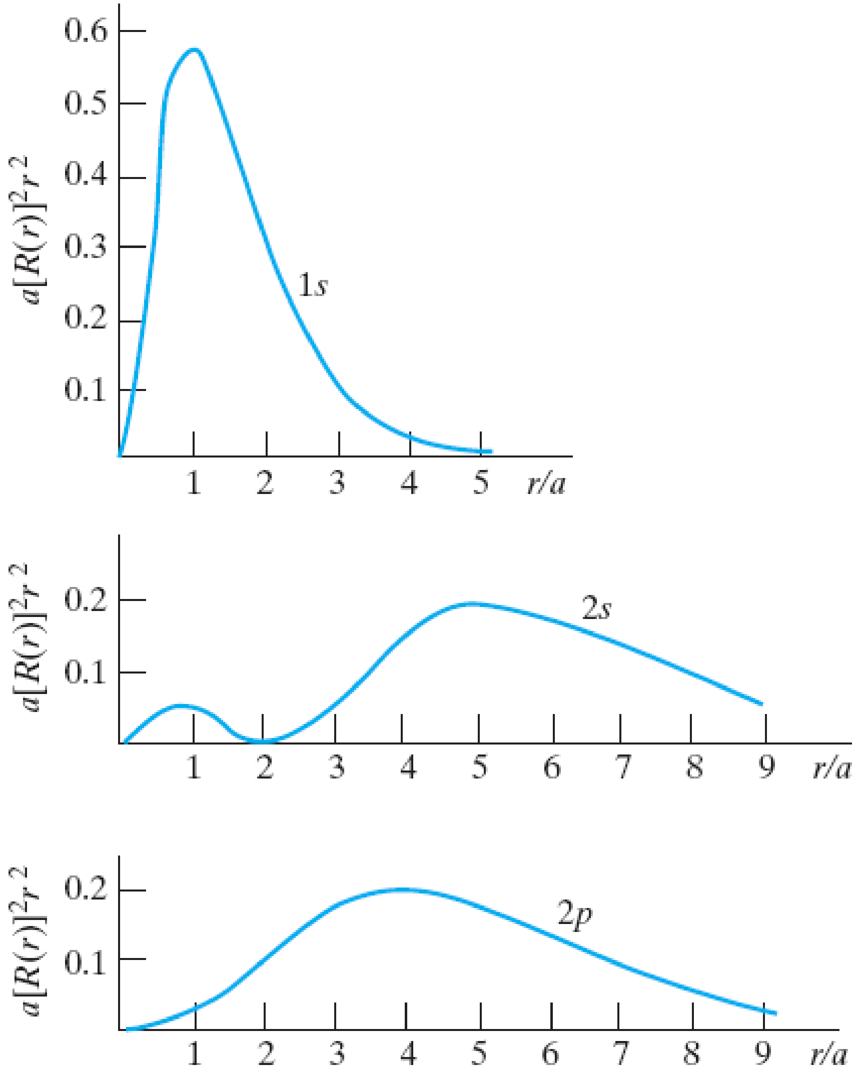
Volume element in spherical polar coordinates

Radial Probability Distribution Function

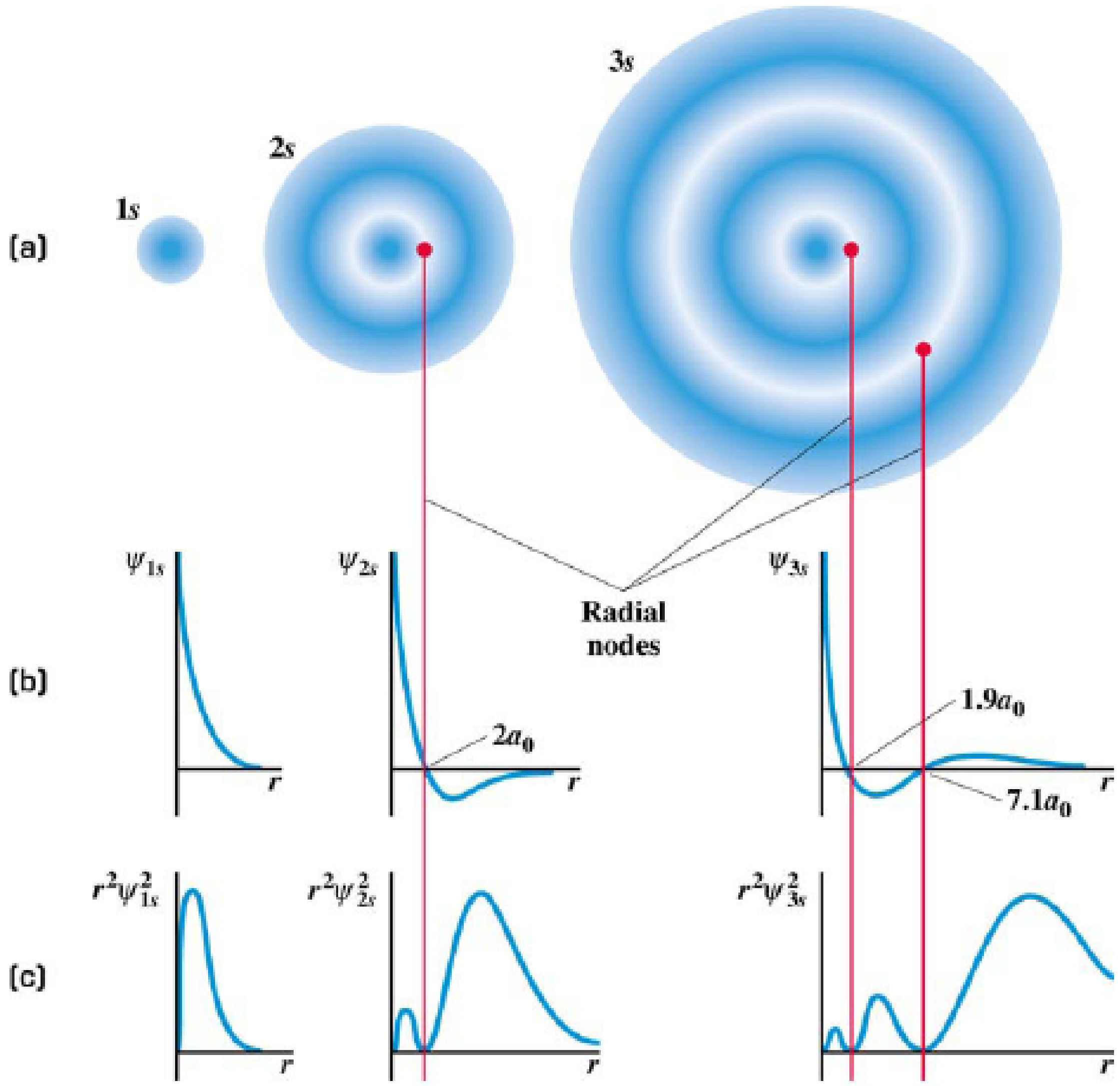


- The radial distribution function gives the probability that an electron will be found anywhere between two concentric spheres with radii that differ by ***dr***

FIGURE 6.9 Plots of the radial distribution function $[R_{nl}(r)]^2 r^2$ for the hydrogen atom.



H atom S orbitals



H-atom spectrum

$$E_n = -\left(\frac{\mu e^4}{32\pi^2 \varepsilon_0^2 \hbar^2}\right)\frac{Z^2}{n^2}$$

(for any hydrogen-like atom)

$$E_n = -hcR_H \frac{Z^2}{n^2}$$

(expressing R_H in cm^{-1})

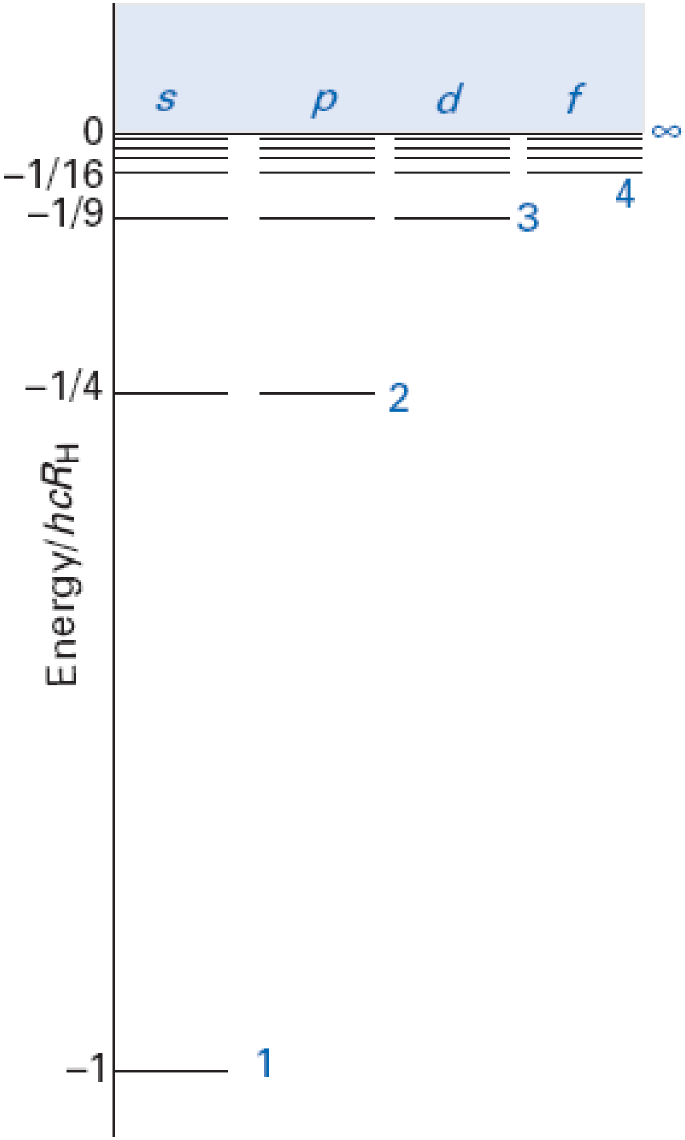
$$R_H = \frac{\mu e^4}{8\varepsilon_0^2 h^3 c}$$

(R_H is the Rydberg constant)

If one considers the reduced mass of electron and proton, R_H = 109677cm^{-1}

If one considers the mass of electron only ($\mu=m_e$), R_H = 109737cm^{-1}

For H-atom, Z = 1



For transition from n_2 to n_1

The wavenumber of the emitted radiation is

$$\tilde{\nu} = \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) R_H$$

$n_1 = 1, n_2 = 2, 3, \ldots$	Lyman series, ultraviolet
$n_1 = 2, n_2 = 3, 4, \ldots$	Balmer series, visible
$n_1 = 3, n_2 = 4, 5, \ldots$	Paschen series, infrared
$n_1 = 4, n_2 = 5, 6, \ldots$	Brackett series, far infrared
$n_1 = 5, n_2 = 6, 7, \ldots$	Pfund series, far infrared
$n_1 = 6, n_2 = 7, 8, \ldots$	Humphreys series, far infrared

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$ **(For H-atom, Z=1)**

$$E_n = -13.6\frac{Z^2}{n^2} \text{ eV}$$ **(For Hydrogen-like atom, Z≠1)**