

Topic 1D - The Hydrogen Atom

Schrödinger Eq. Solutions for “Hydrogen-Like” Atoms

For the H-atom, the energy of the electron in its n^{th} energy state, as given by the solution to the Schrödinger Equation, is:

$$E = -\frac{m_e e^4}{8\epsilon_0^2 n^2 h^2} = -\frac{h\mathcal{R}}{n^2} \quad \left(= -h\nu \times \frac{1}{n^2} \right)$$

where \mathcal{R} (the Rydberg constant) = $\frac{m_e e^4}{8h^3 \epsilon_0^2} = 3.29 \times 10^{15} \text{ Hz}$

For all one-electron atoms (e.g., H, He⁺, Li²⁺, etc.),

$$E = -\frac{Z^2 e^4 m_e}{8\epsilon_0^2 n^2 h^2} = -\frac{Z^2 h\mathcal{R}}{n^2}$$

where Z is the nuclear charge (+1, +2, +3, etc.).

There are n^2 independent solutions to the Schrödinger Equation for the H-atom. In polar coordinates, they have the form:

$$\psi_{nlm}(\mathbf{r}, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi) \Rightarrow \text{“Orbital”}$$

where $\psi_{nlm}(\mathbf{r}, \theta, \phi)$ is the overall wave function, containing the quantum numbers n , ℓ , and m ; $R_{nl}(r)$ is the “radial” portion of the wave function, which depends on only the quantum numbers n and ℓ , and $Y_{lm}(\theta, \phi)$ is the “angular” portion of the wave function, which depends on only the quantum numbers ℓ and m .

The three quantum numbers are:

n = Principal quantum number (= 1, 2, 3, ...)

ℓ = Angular Momentum quantum number (= 0, 1, 2, ..., $n-1$)

m = Magnetic quantum number (= $-\ell$, ..., 0, ..., $+\ell$)

For one-electron atoms, the electron energy depends only on n .

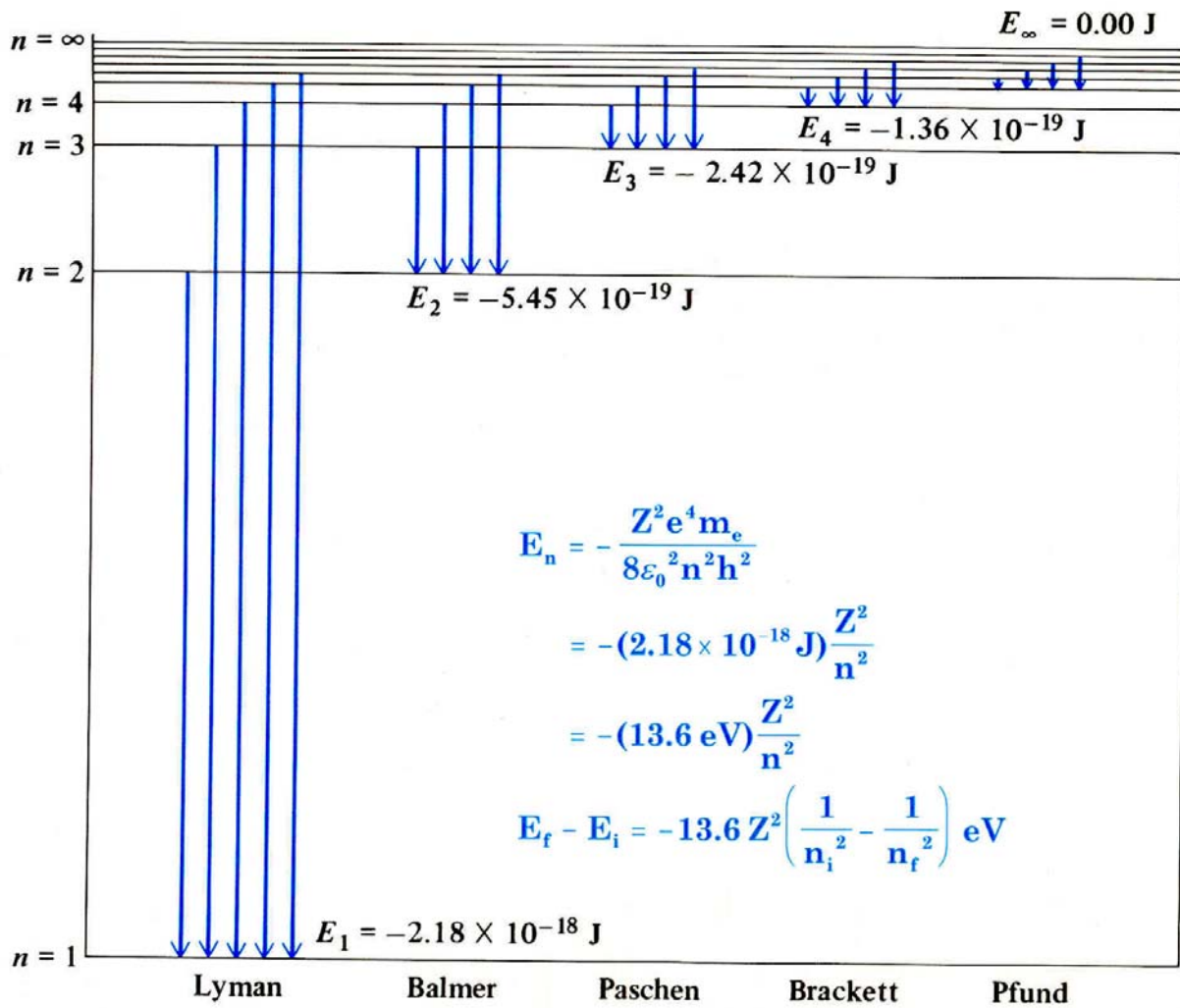
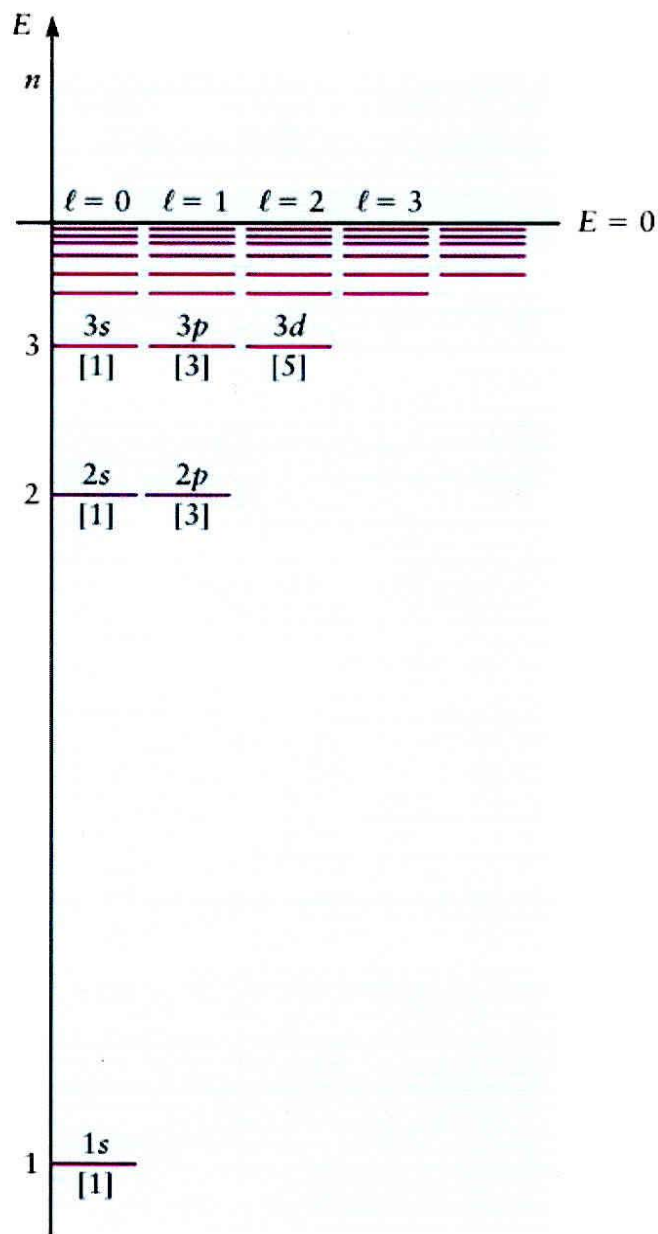


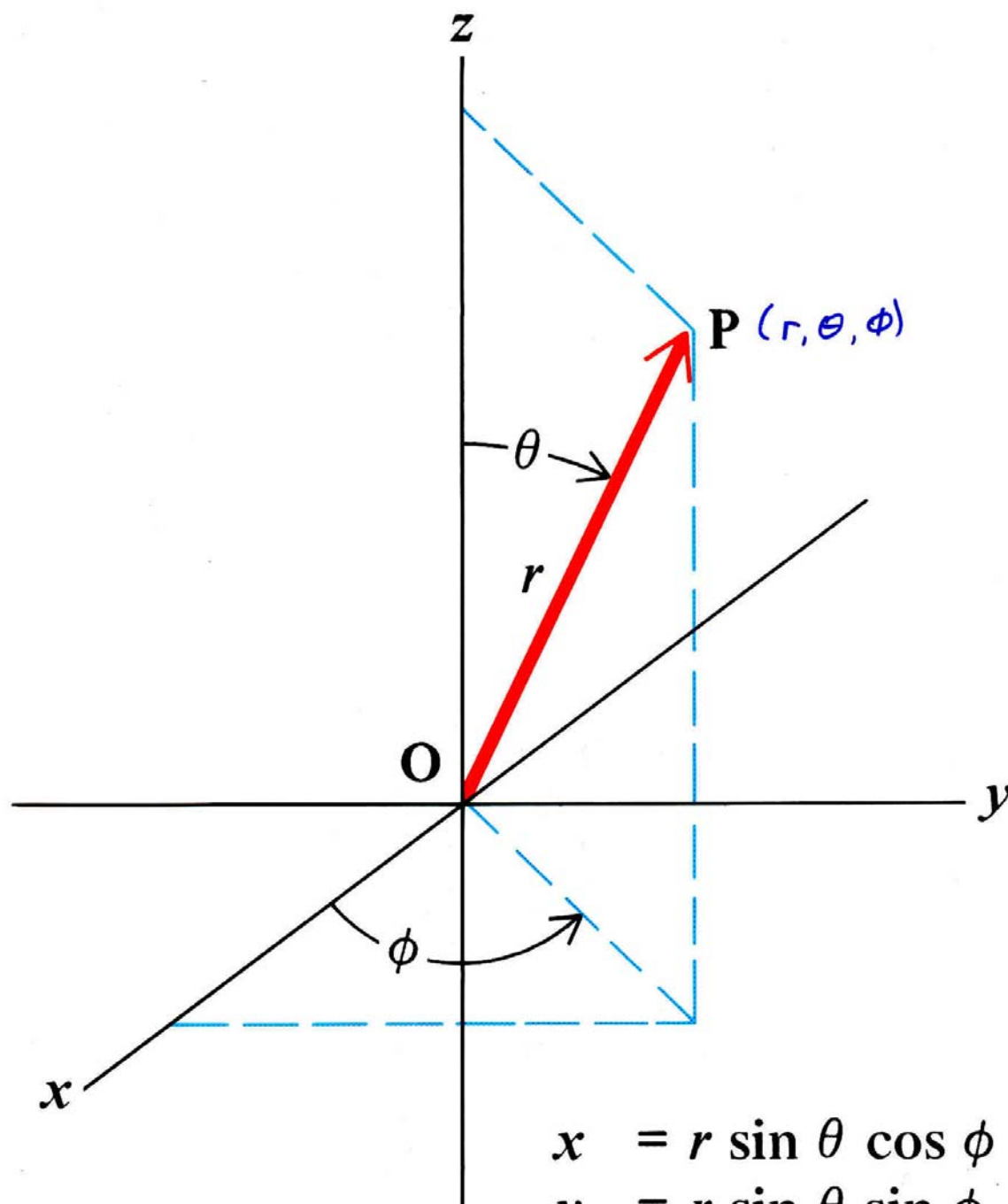
TABLE 5.1 Allowed Values of Quantum Numbers for One-Electron Atoms

n	1	2	3
ℓ	0	0, 1	0, 1, 2
m	0	0, -1, +1	0, -1, 0, +1, +2
Number of degenerate states for each ℓ	1	1, 3	1, 3, 5
Number of degenerate states for each n	1	4	9

The resulting energy-level diagram of the H-atom (or any other one-electron atom) shows the degeneracy ($2\ell + 1$) for each value of ℓ :



Polar Coordinates:



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

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

$$x^2 + y^2 + z^2 = r^2$$

For each value of the principal quantum number, n , there are n^2 independent solutions to the Schrödinger Equation for the H-atom. In polar coordinates, these solutions have the form:

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m}(\theta, \phi) \rightarrow \text{“Orbital”}$$

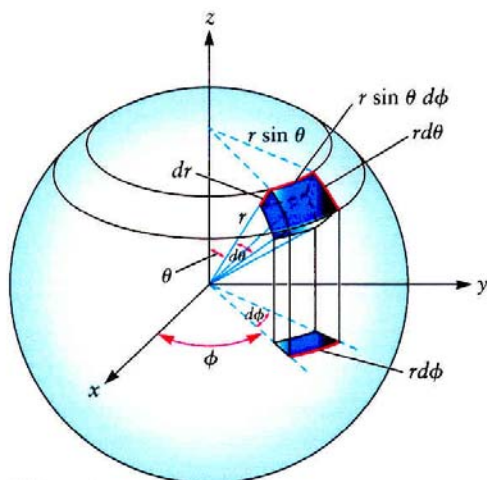
where $\psi_{n\ell m}(r, \theta, \phi)$ is the overall wave function, containing the quantum numbers n , ℓ , and m ; $R_{n\ell}(r)$ is the “radial” (*i.e.*, “size”) portion of the wave function, which depends only on the quantum numbers n and ℓ , and $Y_{\ell m}(\theta, \phi)$ is the “angular” (*i.e.*, “shape”) portion of the wave function, which depends only on the quantum numbers ℓ and m .

The probability of locating the electron at a particular point in the atom is given by the square of the wave function:

$$[\psi_{n\ell m}(r, \theta, \phi)]^2 dV = [R_{n\ell}(r)]^2 [Y_{\ell m}(\theta, \phi)]^2 dV$$

where dV is an infinitesimal three-dimensional volume located at the position (r, θ, ϕ) for an electron in the quantum state given by n, ℓ, m . The spherical volume element dV is given by:

$$dV = r^2 \sin \theta \, dr \, d\theta \, d\phi$$



The wave function $\psi_{n\ell m}(r, \theta, \phi)$ for an electron in the quantum state (n, ℓ, m) is called an “orbital.”

TABLE 3.2

Hydrogen atom orbitals*

n	l	m	Orbital label	Orbital function ($\rho = r/a_0$)
1	0	0	1s	$\frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-\rho}$
2	0	0	2s	$\frac{1}{4\sqrt{2\pi}} a_0^{-3/2} (2 - \rho) e^{-\rho/2}$
2	1	0	$2p_z$	$\frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \rho e^{-\rho/2} \cos\theta$
2	1	± 1	$2p_x$	$\frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \rho e^{-\rho/2} \sin\theta \cos\phi$
			$2p_y$	$\frac{1}{4\sqrt{2\pi}} a_0^{-3/2} \rho e^{-\rho/2} \sin\theta \sin\phi$
3	0	0	3s	$\frac{1}{81\sqrt{3\pi}} a_0^{-3/2} (27 - 18\rho + 2\rho^2) e^{-\rho/3}$
3	1	0	$3p_z$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} (6 - \rho) \rho e^{-\rho/3} \cos\theta$
3	1	± 1	$3p_x$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} (6 - \rho) \rho e^{-\rho/3} \sin\theta \cos\phi$
			$3p_y$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} (6 - \rho) \rho e^{-\rho/3} \sin\theta \sin\phi$
3	2	0	$3d_{z^2}$	$\frac{1}{81\sqrt{6\pi}} a_0^{-3/2} \rho^2 e^{-\rho/3} (3 \cos^2\theta - 1)$
3	2	± 1	$3d_{xz}$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} \rho^2 e^{-\rho/3} \sin\theta \cos\theta \cos\phi$
			$3d_{yz}$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} \rho^2 e^{-\rho/3} \sin\theta \cos\theta \sin\phi$
3	2	± 2	$3d_{xy}$	$\frac{\sqrt{2}}{81\sqrt{\pi}} a_0^{-3/2} \rho^2 e^{-\rho/3} \sin^2\theta \cos\phi \sin\phi$

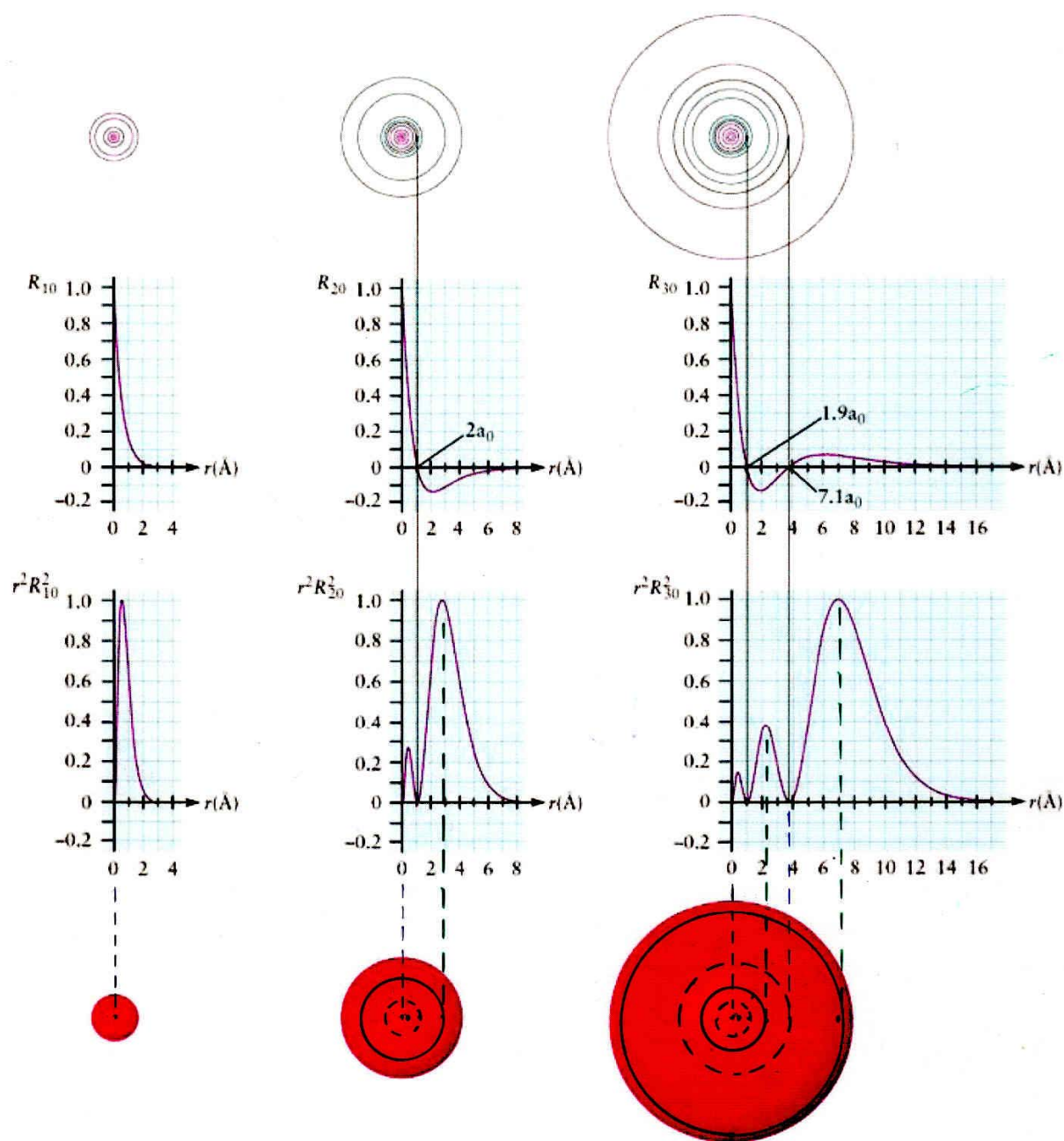


FIGURE 5.4 Four representations of hydrogen s orbitals. (a) A contour plot of the wave function amplitude for a hydrogen atom in its 1s, 2s, and 3s states. The contours identify points at which ψ takes on ± 0.05 , ± 0.1 , ± 0.3 , ± 0.5 , ± 0.7 , and ± 0.9 of its maximum value. Contours with positive phase are shown in red; those with negative phase are shown in blue. Nodal contours, where the amplitude of the wave function is zero, are shown in black. They are connected to the nodes in the lower plots by the vertical green lines. (b) The radial wave functions plotted against distance from the nucleus, r . (c) The radial probability density, equal to the square of the radial wave function multiplied by r^2 . (d) The “size” of the orbitals, as represented by spheres whose radius is the distance at which the probability falls to 0.05 of its maximum value.

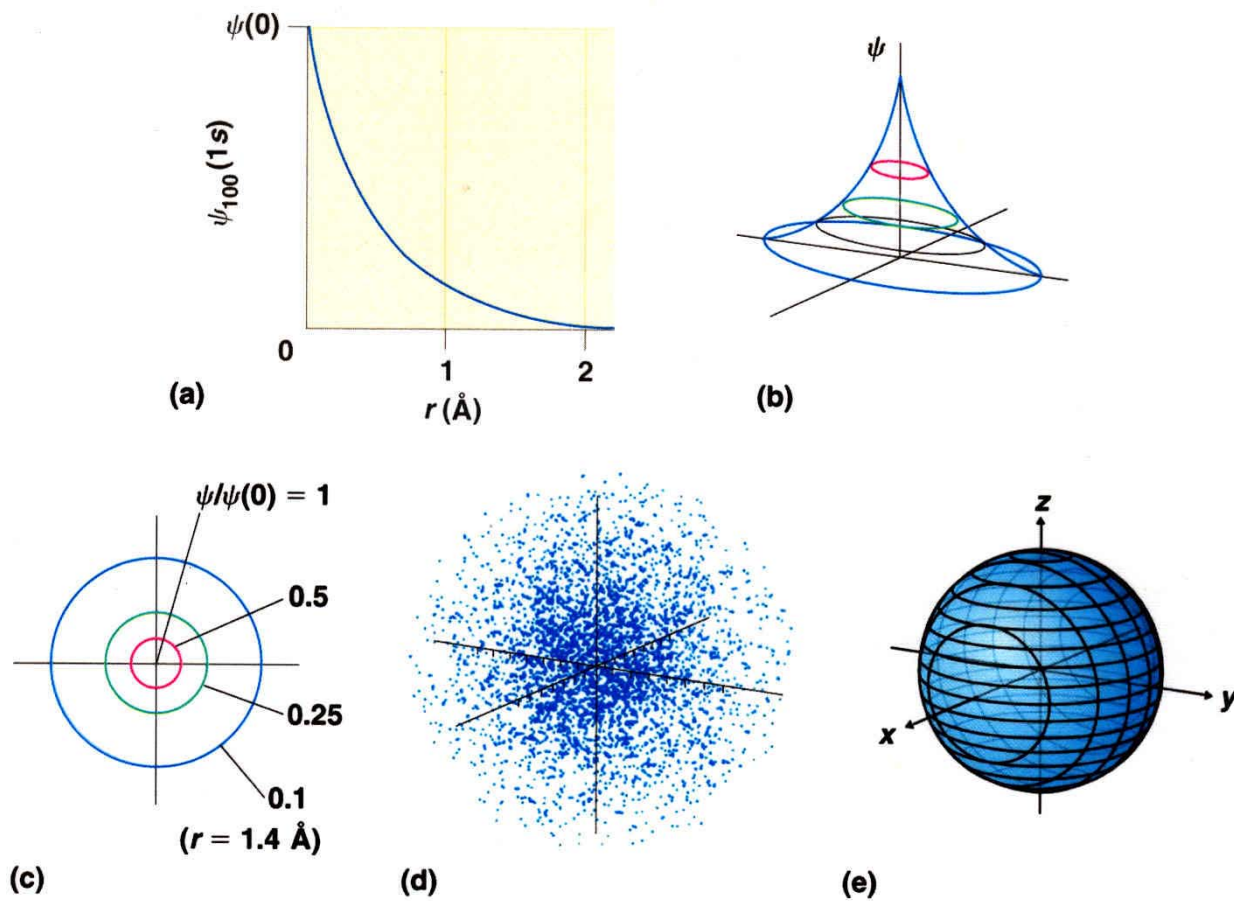
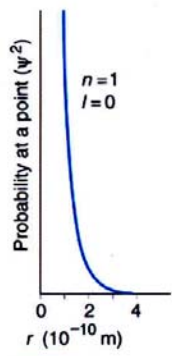
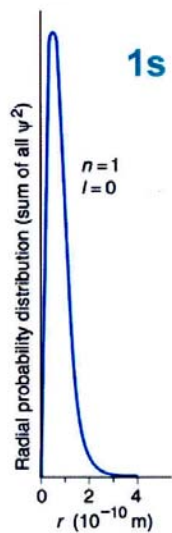


Figure 3.3

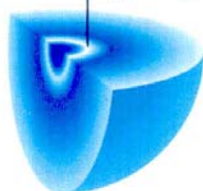
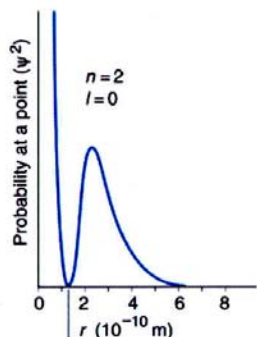
Graphic representations of the $1s$ orbital of the hydrogen atom. (a) 1-D ψ versus r . (b) 2-D "mountain" obtained by rotating the graph in (a) about the vertical axis. This represents the orbital amplitude in the x - y plane. (c) 2-D "contour map" of the orbital amplitude in the x - y plane obtained from the rings of constant altitude shown in (b). The contour values are fractions of the peak value at $r = 0$. This is what you would see looking down on (b) from above. (d) 3-D cloud whose density is proportional to orbital amplitude. (e) 3-D boundary surface diagram enclosing most of the cloud of (d).



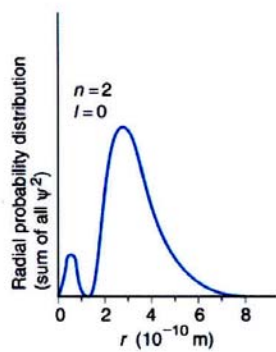
1s



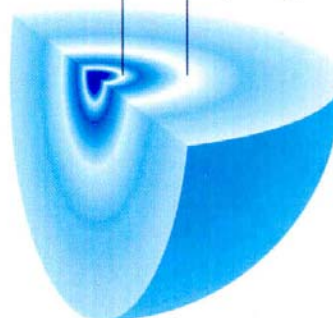
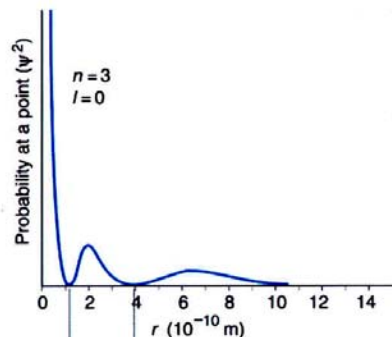
A 1s orbital



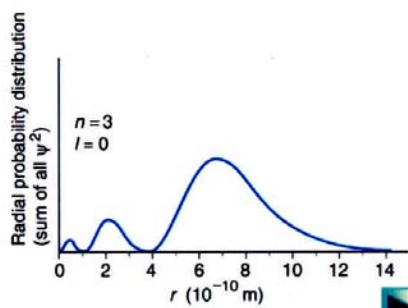
2s



B 2s orbital



3s



C 3s orbital



Figure 3.4: $n = 2$ Orbitals for Hydrogen

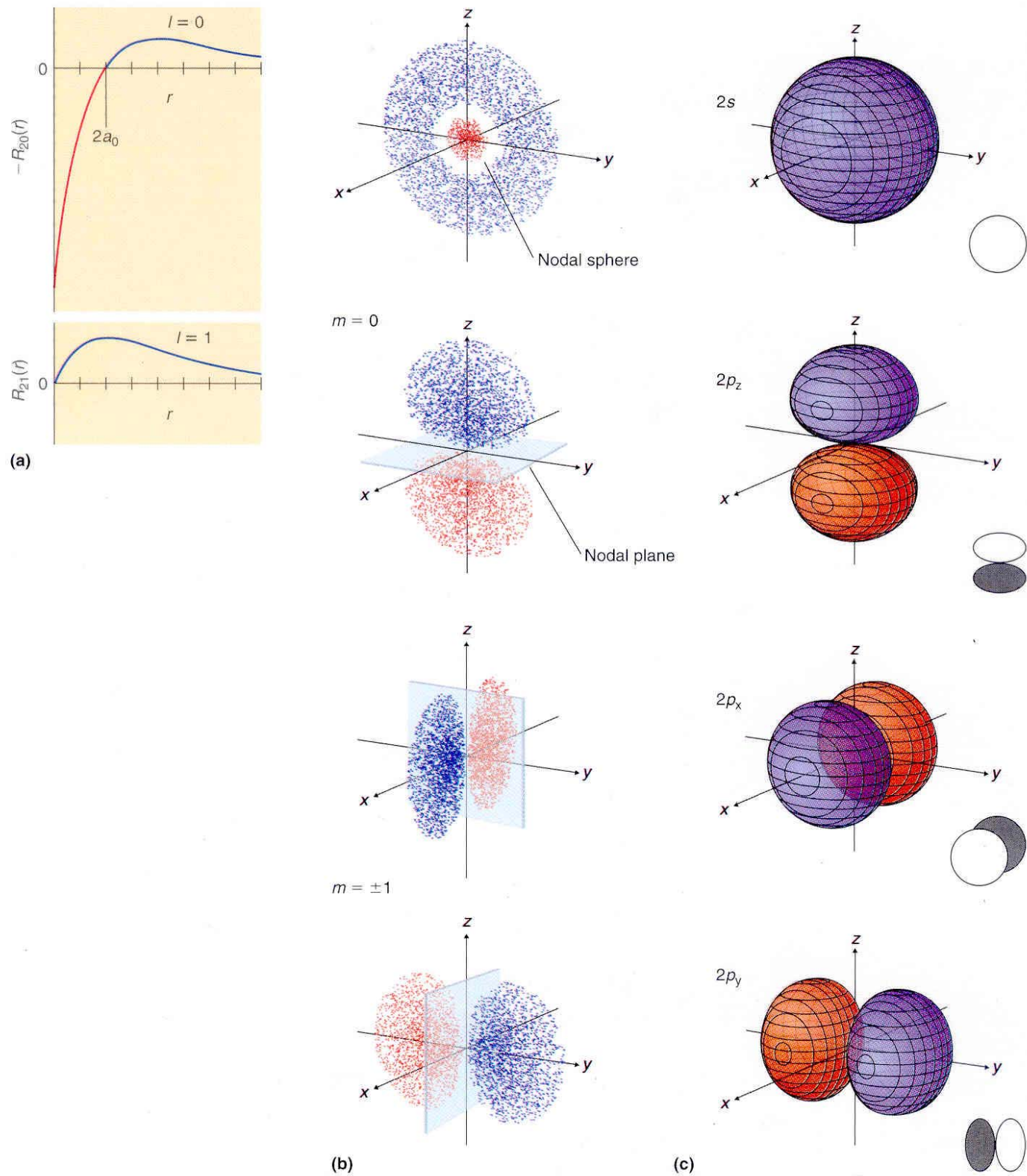


Figure 3.5: $n = 3$ Orbitals for Hydrogen

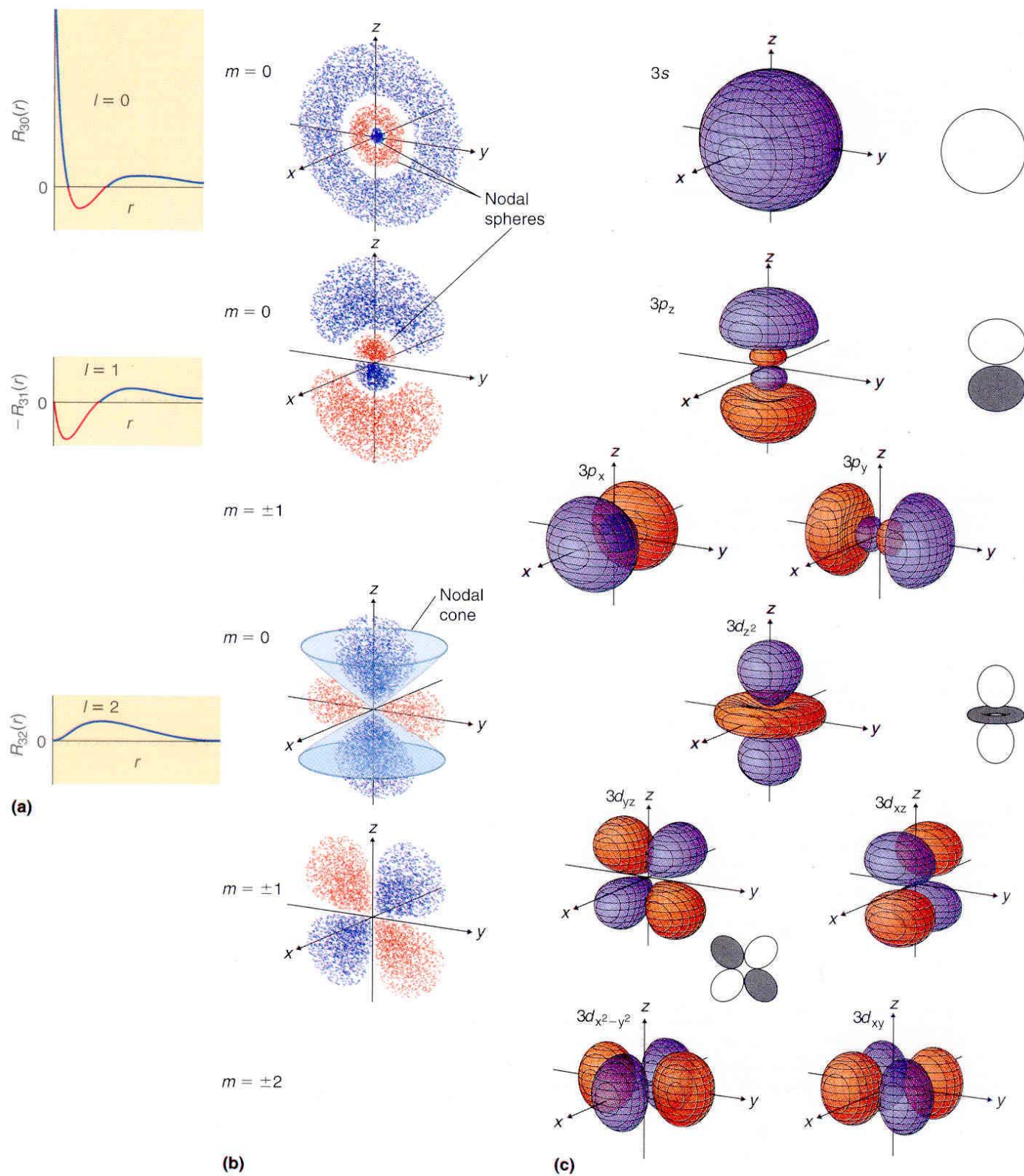
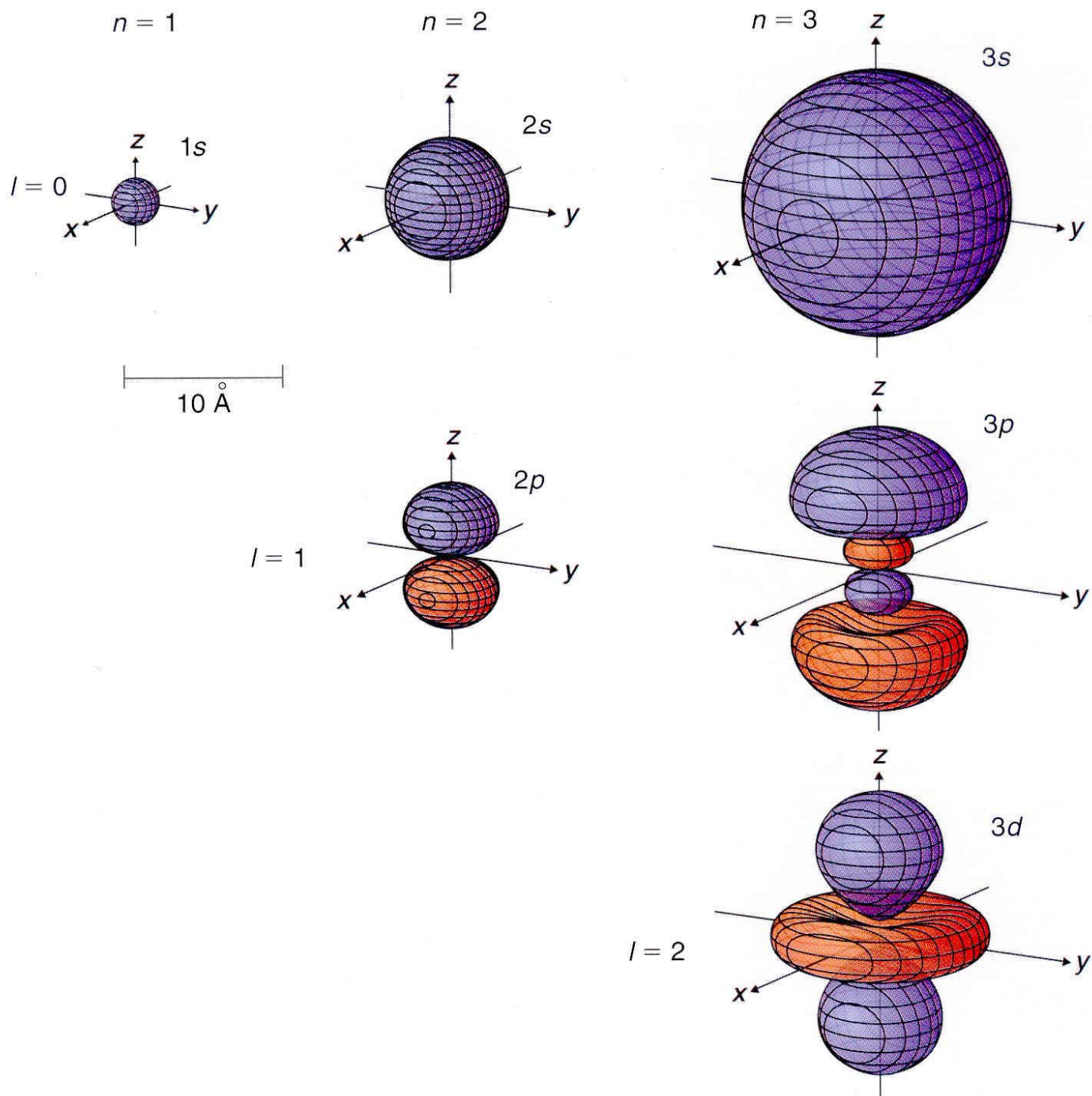
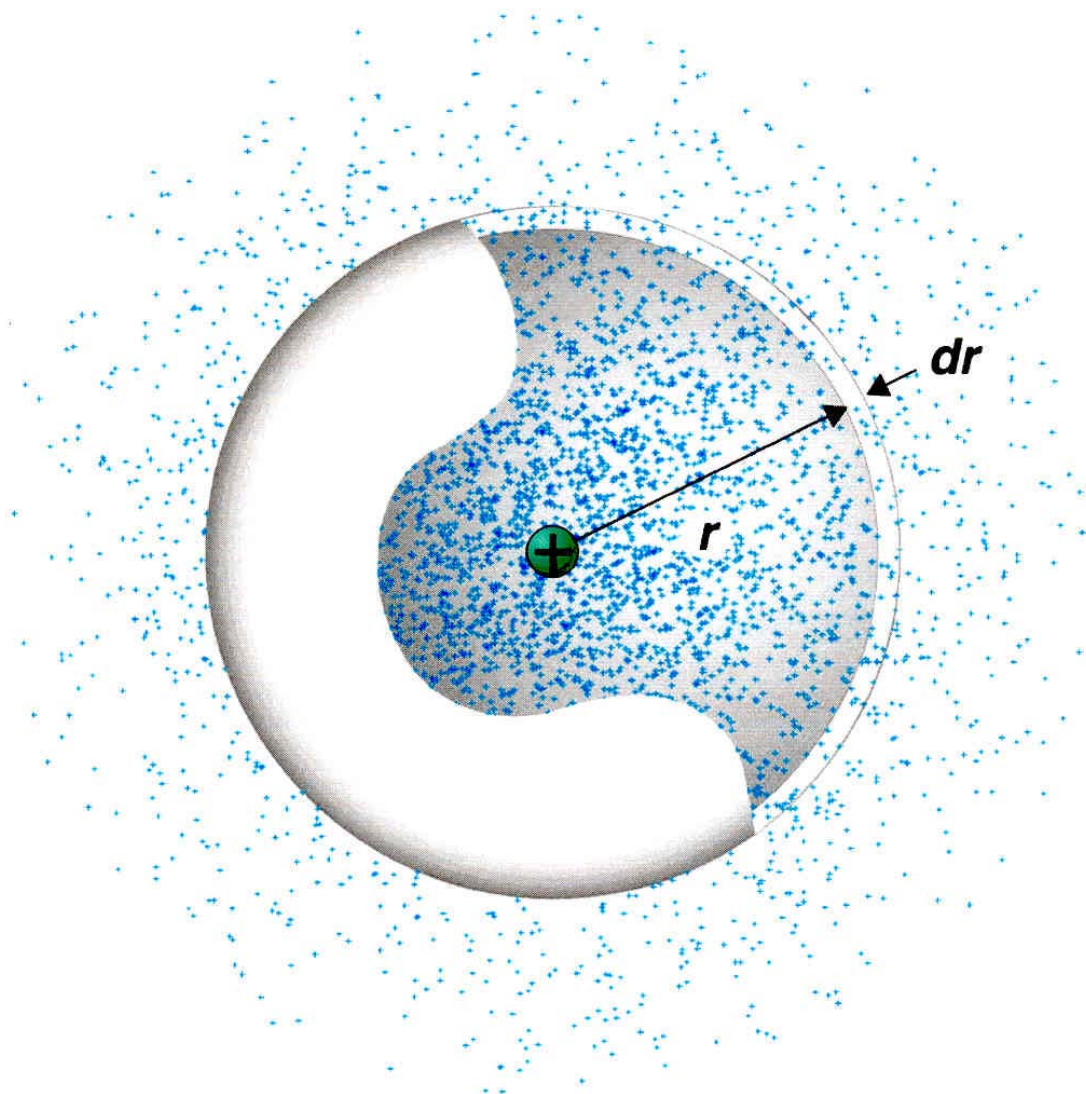


Figure 3.6: Boundary Surfaces of Hydrogen Orbitals



Concept of the radial distribution function. The RDF is obtained by summing the electron density $|\psi|^2$ in the spherical shell.

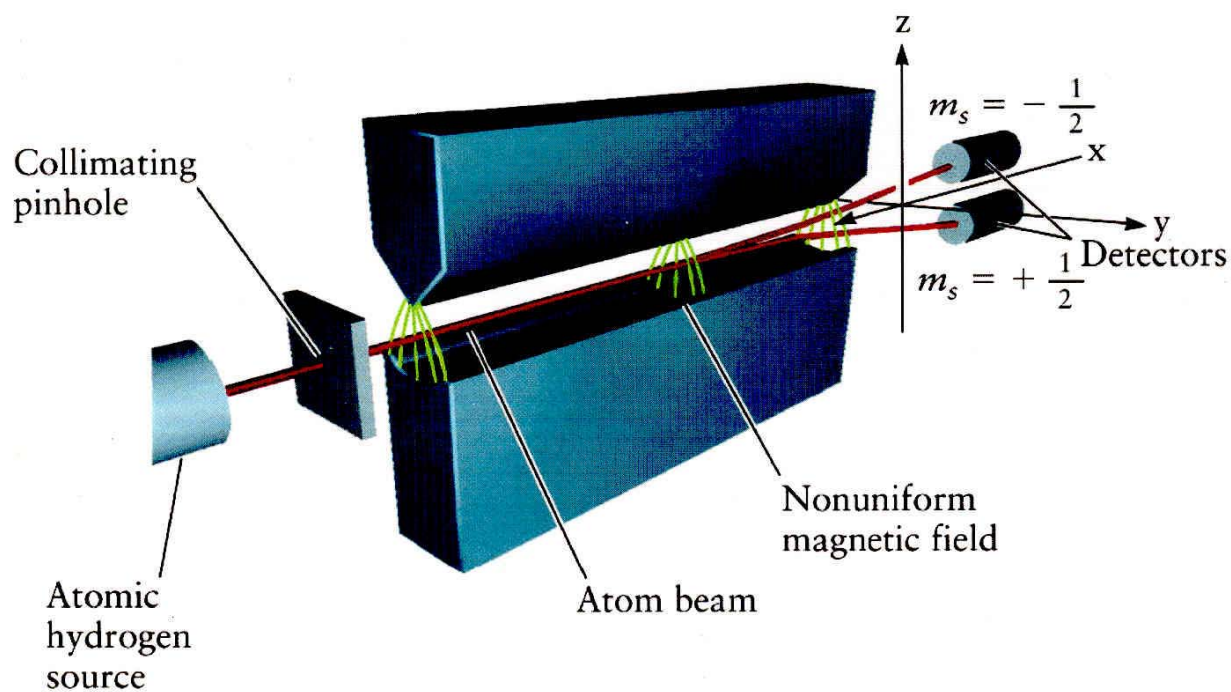


FIGURE 5.11 A beam of hydrogen atoms is split into two beams when it traverses a magnetic field, the value of which is not constant in the plane perpendicular to the path of the beam. The nonconstant field is created by the specially shaped cross section of the north and south poles of the magnet in the z - y plane. The green curved lines trace the pattern over which the field is varied. Regions where the green lines are closer together are regions of greater magnetic field. Atoms with spin quantum number $m_s = +\frac{1}{2}$ follow one trajectory, and those with $m_s = -\frac{1}{2}$ follow another.

Atomic Quantum Numbers

n	Principal Q.N.	(1, 2, 3, ...)
l	Angular Momentum Q.N.	(0, 1, 2, ..., n-1)
m_l	Magnetic Q.N.	(-l, ..., 0, ..., +l)
s	Spin "Q.N." (an intrinsic property)	($\frac{1}{2} \hbar$)
m_s	Spin Orientation Q.N.	($+\frac{1}{2}$, $-\frac{1}{2}$)

l and **m_l** describe an electron's orbital angular momentum.

s and **m_s** describe an electron's spin angular momentum.

n, **l**, and **m_l** result from the wave mechanical treatment of electrons in bound states.

s and **m_s** reflect an intrinsic property of the electron.