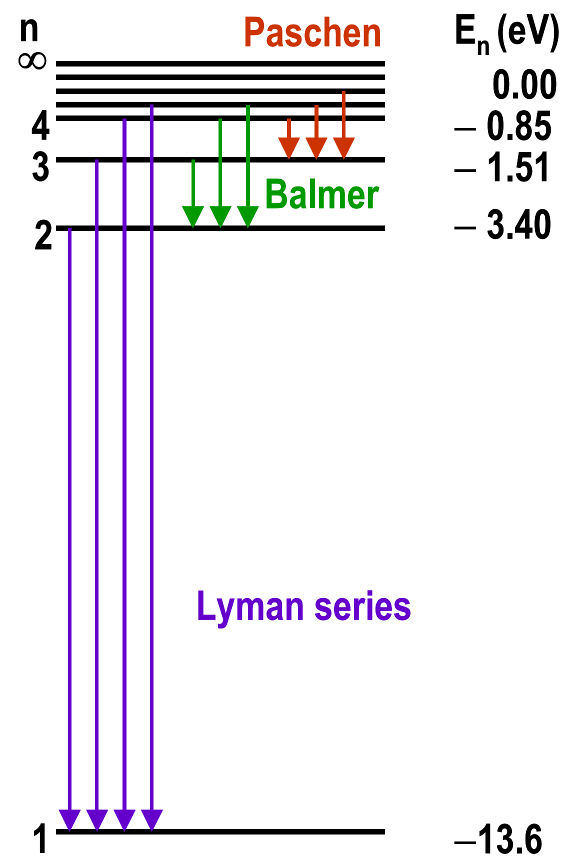
3.1-d: Hydrogen Spectra

- Later, we will learn about selection rules for transition. For the principal quantum number, *n*, Δn can be any positive (absorption) or negative (for emission) integer, resulting in the very rich form of the H atom spectrum. The Rydberg formula

$$\omega = R_H \cdot \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \qquad \text{where } R_H = \frac{2\pi^2 \mu_e e^4}{(4\pi\varepsilon_o)^2 h^3 c} = 109{,}737\ \text{cm}^{-1} \qquad \text{and } n_1 < n_2$$

- Emission lines fall in characteristic spectral regions
  - The Lyman series ($n1 = 1$) in the ultraviolet
  - The Balmer series ($n1 = 2$) in the visible
  - The Paschen series ($n1 = 3$) in the near IR

<u>*The Balmer series*</u>



- Absorption frequencies coincide with those for emission
- Transitions having $n_1 \neq 1$ are observed only after preparation of the excited state by some means, such as electrical discharge.
- The ionization limit in absorption corresponds to a final quantum number $n_2 = \infty$. From the ground state, $I_o = R_H$, or 13.6 eV

3.1-e: The H-Atom Orbitals

$$\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\varphi)$$

Imaginary functions

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot e^{-r/a_o}$$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(2-\frac{r}{a_o}\right)\cdot e^{-r/2a_o}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r}{a_o}\cdot e^{-r/2a_o}\cdot cos\theta$$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r}{a_o}\cdot e^{-r/2a_o}\cdot sin\theta\cdot e^{\pm i\varphi}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(27-18\frac{r}{a_o}+2\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}$$

$$\psi_{310} = \frac{1}{81}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(6\frac{r}{a_o}-\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}\cdot cos\theta$$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(6\frac{r}{a_o}-\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}\cdot sin\theta\cdot e^{\pm 2i\varphi}$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r^2}{a_o^{\,2}}\cdot e^{-r/3a_o}\cdot\left(3cos^2\theta-1\right)$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r^2}{a_o^{\,2}}\cdot e^{-r/3a_o}\cdot sin\theta\cdot cos\theta\cdot e^{\pm i\varphi}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r^2}{a_o^{\,2}}\cdot e^{-r/3a_o}\cdot sin^2\theta\cdot e^{\pm 2i\varphi}$$

$$\boxed{\psi_{n\ell m_\ell}(r,\theta,\varphi) = R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\varphi)}$$

Real functions

$$\psi_{2p_x}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r}{a_o}\cdot e^{-r/2a_o}\cdot sin\,\theta\cdot cos\,\varphi$$

$$\psi_{2p_y}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r}{a_o}\cdot e^{-r/2a_o}\cdot sin\,\theta\cdot sin\,\varphi$$

$$\psi_{2p_z}(r,\theta,\varphi) = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\frac{r}{a_o}\cdot e^{-r/2a_o}\cdot cos\,\theta$$

$$\psi_{3p_x}(r,\theta,\varphi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(6\frac{r}{a_o}-\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}\cdot sin\,\theta\cdot cos\,\varphi$$

$$\psi_{3p_y}(r,\theta,\varphi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(6\frac{r}{a_o}-\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}\cdot sin\,\theta\cdot sin\,\varphi$$

$$\psi_{3p_z}(r,\theta,\varphi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\cdot\left(6\frac{r}{a_o}-\frac{r^2}{a_o^{\,2}}\right)\cdot e^{-r/3a_o}\cdot cos\,\theta$$

$$\psi_{n\ell m_\ell}(\mathrm{r},\theta,\varphi) = \mathrm{R}_{n\ell}(\mathrm{r}) \cdot \mathrm{Y}_{\ell m_\ell}(\theta,\varphi)$$

Real functions

$$\psi_{3d_{z^2}}(r,\theta,\varphi) = \frac{1}{81\sqrt{6\pi}}\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^{\ 2}} \cdot e^{-r/3a_o} \cdot \left(3\cos^2\theta - 1\right)$$

$$\psi_{3d_{xz}}(r,\theta,\varphi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^{\ 2}} \cdot e^{-r/3a_o} \cdot \sin\theta \cdot \cos\theta \cdot \cos\varphi$$

$$\psi_{3d_{yz}}(r,\theta,\varphi) = \frac{1}{81\sqrt{\pi}}\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^{\ 2}} \cdot e^{-r/3a_o} \cdot \sin\theta \cdot \cos\theta \cdot \sin\varphi$$

$$\psi_{3d_{x^2-y^2}}(r,\theta,\varphi) = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^{\ 2}} \cdot e^{-r/3a_o} \cdot \sin^2\theta \cdot \cos 2\varphi$$

$$\psi_{3d_{xy}}(r,\theta,\varphi) = \frac{1}{81\sqrt{2\pi}}\left(\frac{1}{a_o}\right)^{3/2}\frac{r^2}{a_o^{\ 2}} \cdot e^{-r/3a_o} \cdot \sin^2\theta \cdot \sin 2\varphi$$

•The wave functions

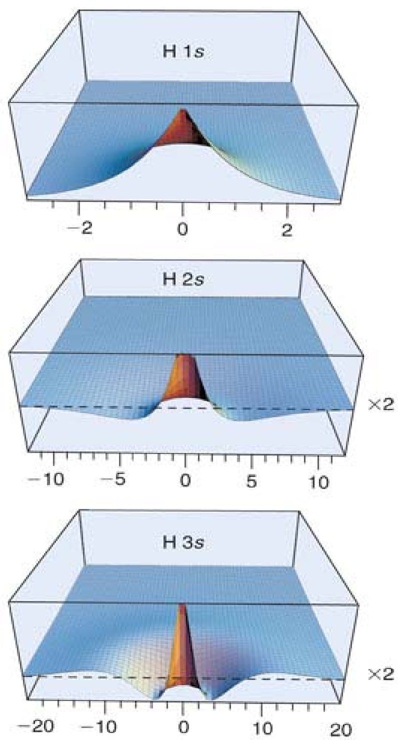
$$\psi_{n\ell m_\ell m_s}(r,\theta,\varphi,\delta) = R_{n\ell}(r)\cdot Y_{\ell m_\ell}(\theta,\varphi)\cdot\begin{Bmatrix}\alpha\\ \beta\end{Bmatrix}$$

where $R_{n,\ell}(r)$ = the radial wave function

and $Y_{\ell,m_\ell}(\theta,\varphi)$ = the angular wave function

$$Y_{\ell,m_\ell}(\theta,\varphi) \propto \Theta_{\ell,m_\ell}(\cos\theta)\cdot e^{im_\ell\varphi}$$

The φ-dependence is important in giving rise to selection rules on changes in the quantum number m_ℓ



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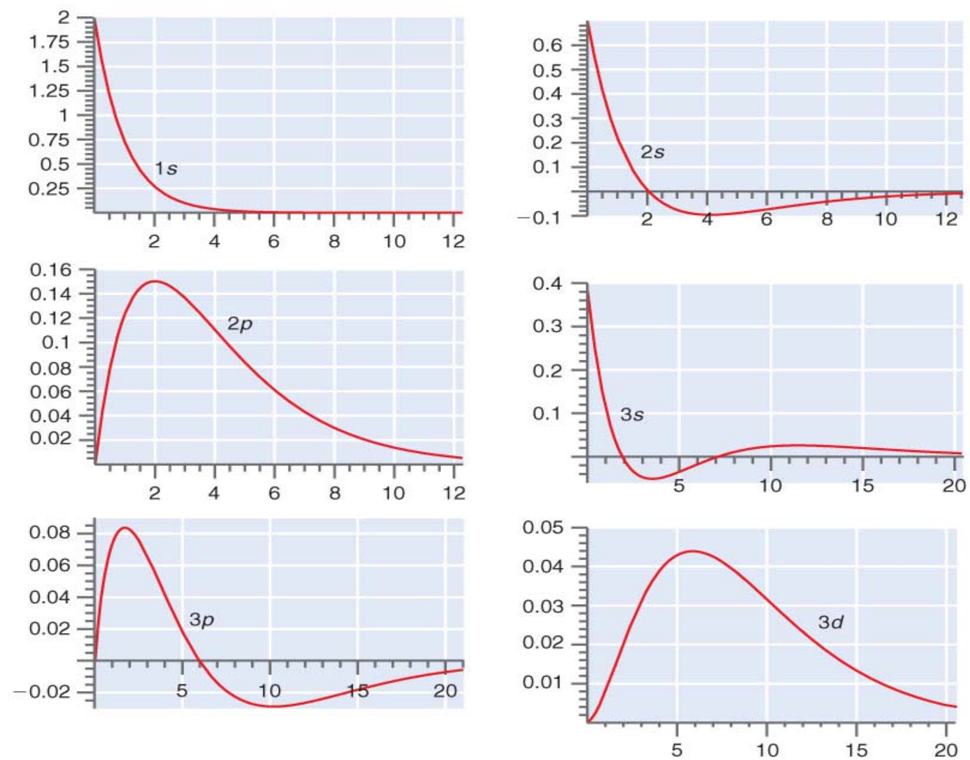

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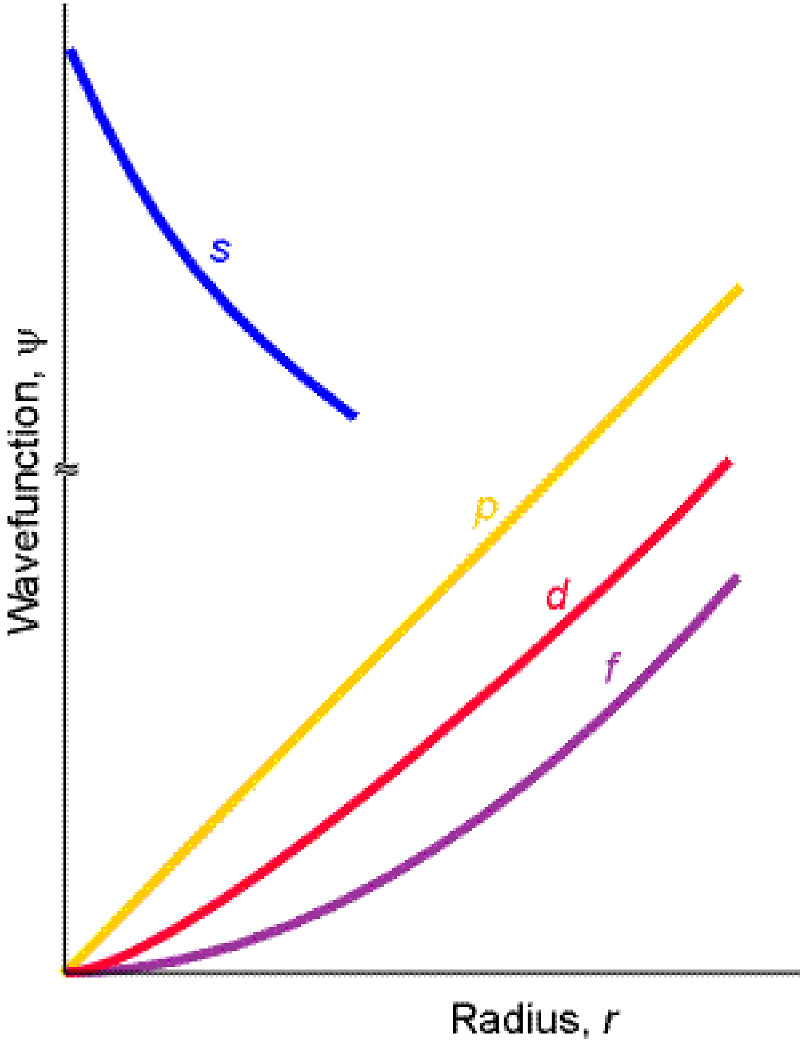
Behaviour of the orbitals near the nucleus



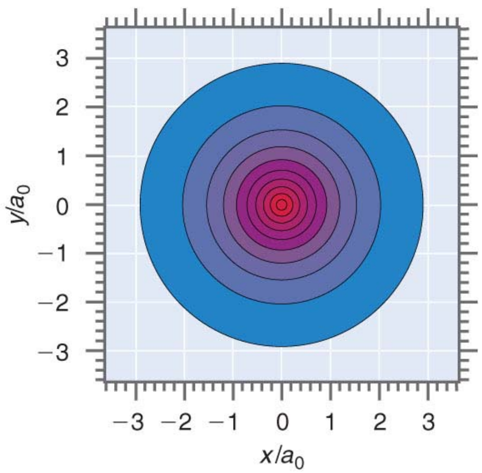
Close to the nucleus,

p orbitals are proportional to r
d orbitals are proportional to r^2
f orbitals are proportional to r^3

Electrons are progressively excluded from the neighborhood of the nucleus as l increases.

Note that the s orbital as a finite, non-zero value at the nucleus.

3.1-f: Contour Plots of the



(b)

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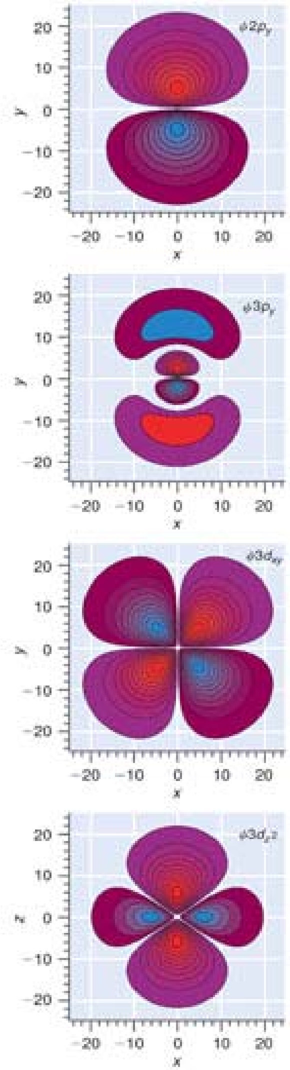

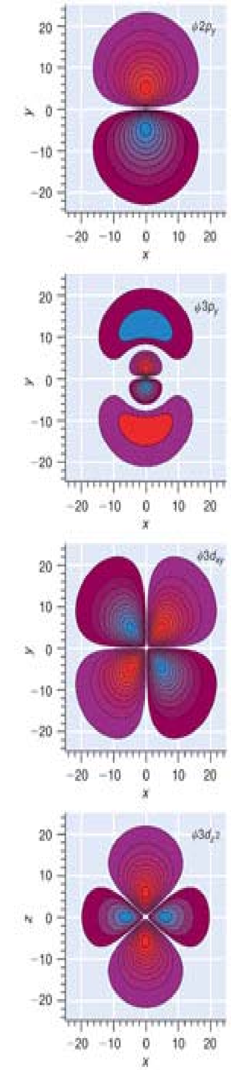

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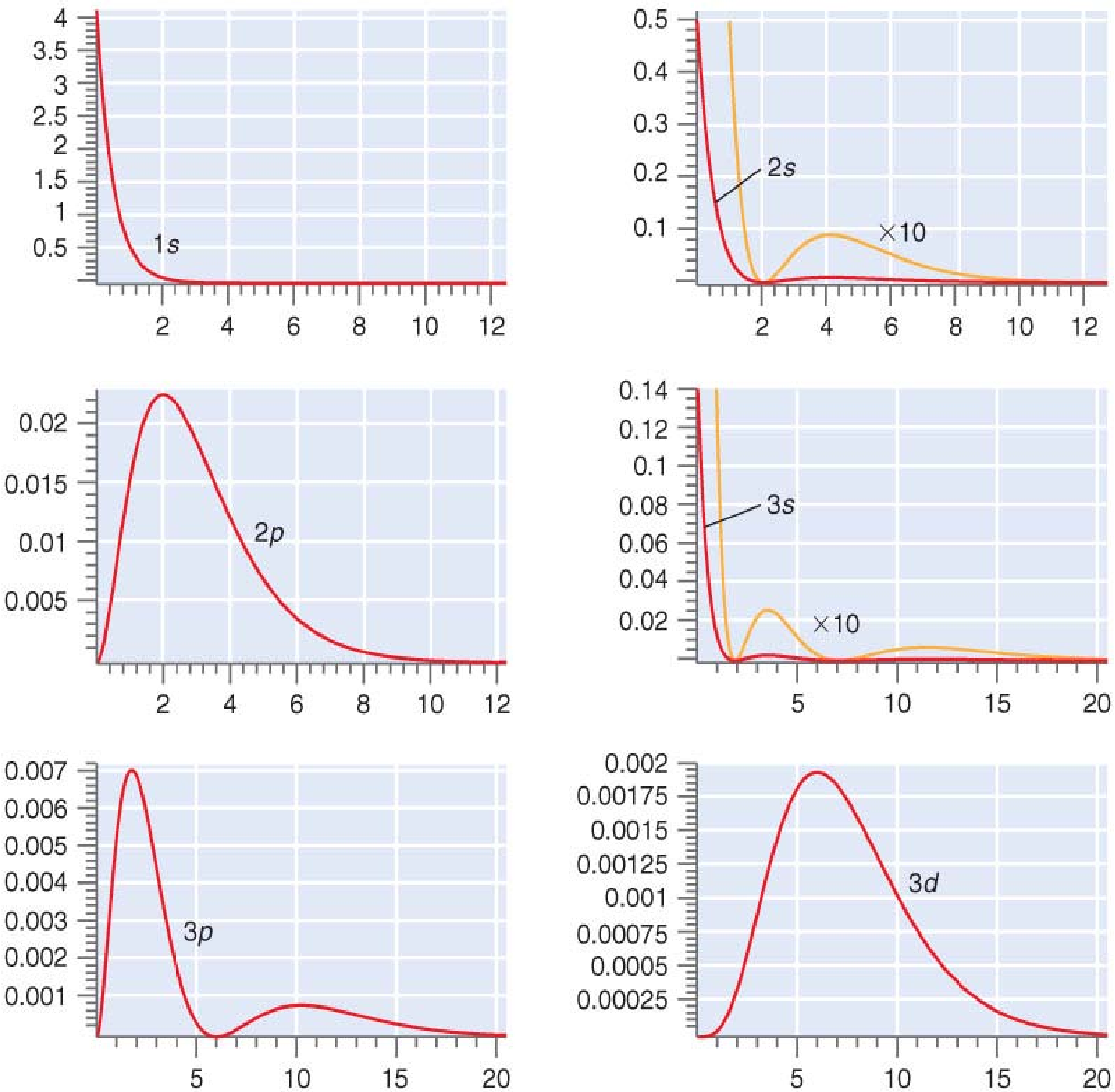
3.1-g: Probability Density Functions

$$\psi^2_{n\ell m_\ell}(r,\theta,\varphi)$$



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- Shell model (the Bohr Atom) vs. Quantum mechanical model Knowledge of the location of the electron in the H-atom vs. knowledge of the probability of finding it in a small volume element at a specific location

- The probability $\propto \psi^* \psi d\tau$

- To what extent does the exact quantum mechanical solution resemble the shell model?

$\Rightarrow$ The radial distribution function

3.1-h: The Radial Distribution Function

- The probability of finding the electron in a particular region, r, θ and φ, in space

$$\psi^2_{n\ell m_\ell}(r,\theta,\varphi)\cdot r^2 \sin\theta\cdot dr\cdot d\theta\cdot d\varphi$$

- What we are really interested in is

"What is the probability of finding the electron at a particular value of r, regardless of the values of θ and φ?"

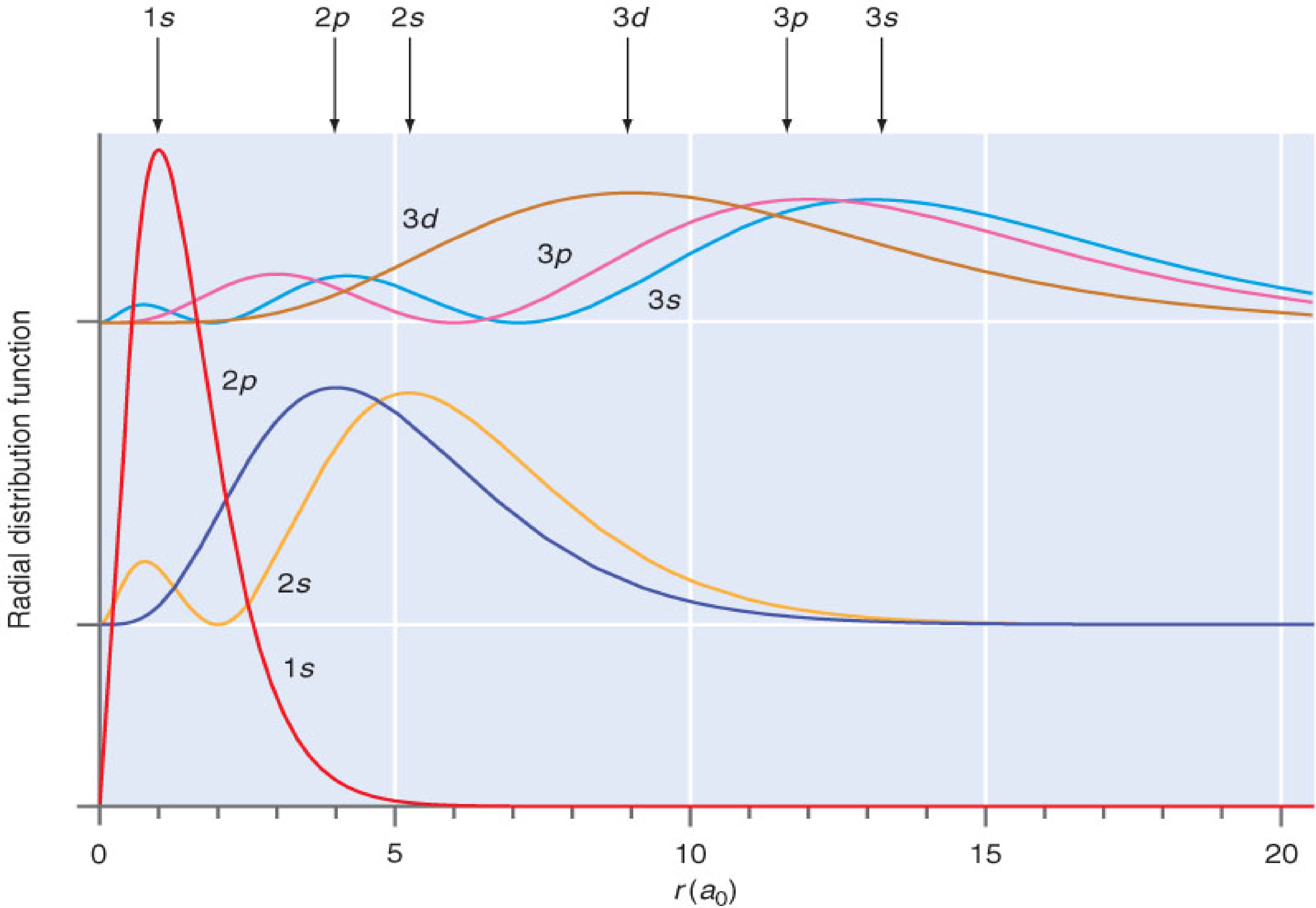
This can be obtained by integrating the probability density over all values of θ and φ

$$P(r)\cdot dr = \int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\psi^2_{n\ell m_\ell}(r,\theta,\varphi)\cdot r^2 \sin\theta\cdot dr\cdot d\theta\cdot d\varphi$$

$$P(r)\cdot dr = r^2\cdot\left[R_{n\ell}(r)\right]^2\cdot dr$$

- The new function, P(r), is called the **radial distribution function**

The probability function of choice to determine the most likely radius to find the electron for a given orbital



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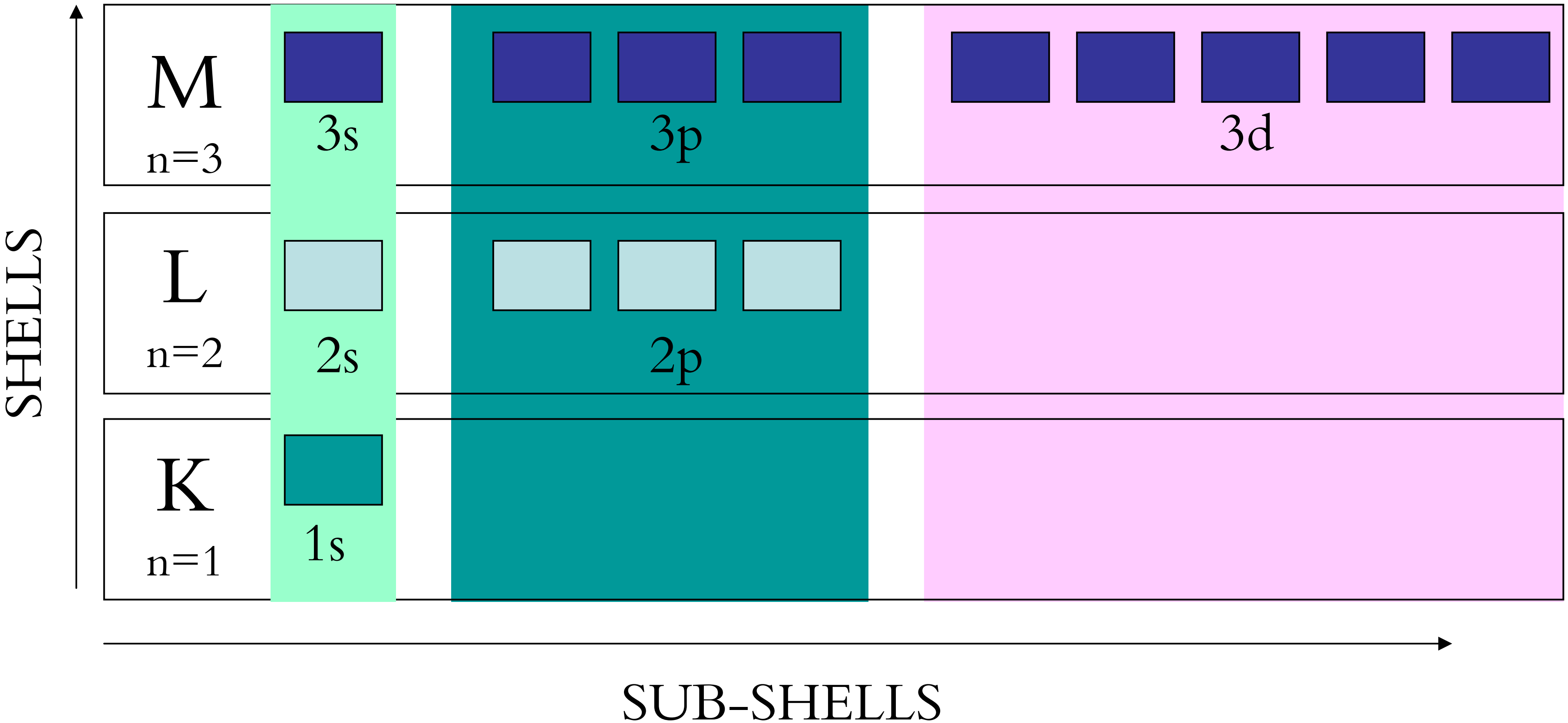
Old Convention: Shells vs. Sub-shells



SHELL	n =	1	2	3	4
		↕	↕	↕	↕
		K	L	M	N

4.1 Angular Momentum

a) General Properties: apply to all angular momenta.

Any property **M** is assigned as an angular momentum if it obeys the following relationships:

$$i)\ \hat{M}^2 = \hat{M}_x^2 + \hat{M}_y^2 + \hat{M}_z^2$$

$$ii)\ \left[\hat{M}_x, \hat{M}_y\right] = i\hbar\hat{M}_z; \left[\hat{M}_y, \hat{M}_z\right] = i\hbar\hat{M}_x; \left[\hat{M}_z, \hat{M}_x\right] = i\hbar\hat{M}_y$$

$$iii)\ \left[\hat{M}^2, \hat{M}_x\right] = \left[\hat{M}^2, \hat{M}_y\right] = \left[\hat{M}^2, \hat{M}_z\right] = 0$$

M has $\hat{M}_+ = \hat{M}_x + i\hat{M}_y$ Raising operator

$\hat{M}_- = \hat{M}_x - i\hat{M}_y$ Lowering operator

Two quantum numbers are needed because **M** has two properties:

$$\hat{M}^2\psi_{j,m_j} = j(j+1)\hbar^2\psi_{j,m_j} \qquad j = 0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$$

$$\hat{M}_z\psi_{j,m_j} = m_j\hbar\psi_{j,m_j} \qquad m_j = -j, -j+1, \ldots j-1, j$$

Note:

1.) j can have non-integer values in general

2.) m_j has symmetric values about 0

Also:

$$\langle \psi_{j,m_j+1} | \hat{M}_+ | \psi_{j,m_j} \rangle = \hbar\sqrt{j(j+1) - m_j(m_j+1)} = \hbar\sqrt{(j-m_j)(j+m_j+1)}$$

$$\langle \psi_{j,m_j-1} | \hat{M}_- | \psi_{j,m_j} \rangle = \hbar\sqrt{j(j+1) - m_j(m_j-1)} = \hbar\sqrt{(j+m_j)(j-m_j+1)}$$

Note: from the definitions of $\mathbf{M}_+$ and $\mathbf{M}_-$ one can readily show:

$$\hat{M}_x = \frac{(\hat{M}_+ + \hat{M}_-)}{2} \text{ and } \hat{M}_y = \frac{(\hat{M}_+ - \hat{M}_-)}{2i}$$

One specific example seen in C374a is Orbital Angular Momentum of the electron.

Here: $\hat{M} = \hat{L}$ and it operators on H-atom wave functions ψ_{n,ℓ,m_ℓ}

The quantum numbers here are integer:

$$\ell = 0,1,2,\ldots \quad m_\ell = -\ell,\ldots,+\ell$$