$$\widehat{H} = \widehat{K}_{nucleus} + \widehat{K}_{electron} + \widehat{V} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2\psi}{\partial x_1^2} + \frac{\partial^2\psi}{\partial y_1^2} + \frac{\partial^2\psi}{\partial z_1^2}\right) - \frac{\hbar^2}{2m_2}\left(\frac{\partial^2\psi}{\partial x_2^2} + \frac{\partial^2\psi}{\partial y_2^2} + \frac{\partial^2\psi}{\partial z_2^2}\right) + \left[\widehat{V}(x_1, y_1, z_1, x_2, y_2, z_2) - E\right]\psi = 0$$

$$\psi \equiv \psi(x_1, y_1, z_1, x_2, y_2, z_2); \quad \widehat{V} = -\frac{e^2}{4\pi\varepsilon_0[(x_2 - x_1)^2 + (y_2 - y_1)^2 + (z_2 - z_1)^2]^{1/2}} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

Since the force exerted by the proton and electron on each other are directed along the straight line joining them, the potential energy function depends only on the relative coordinates.

For simplicity, let's consider $x = x_2 - x_1, \ y = y_2 - y_1, \ z = z_2 - z_1$

COM: $\quad X = \dfrac{m_1 x_1 + m_2 x_2}{m_1 + m_2}, \qquad Y = \dfrac{m_1 y_1 + m_2 y_2}{m_1 + m_2}, \qquad Z = \dfrac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$

$$\frac{\partial\psi(x,y,z;X,Y,Z)}{\partial x_1} = \frac{\partial\psi}{\partial X}\frac{\partial X}{\partial x_1} + \frac{\partial\psi}{\partial x}\frac{\partial x}{\partial x_1} = \left(\frac{m_1}{m_1+m_2}\frac{\partial}{\partial X} - \frac{\partial}{\partial x}\right)\psi$$
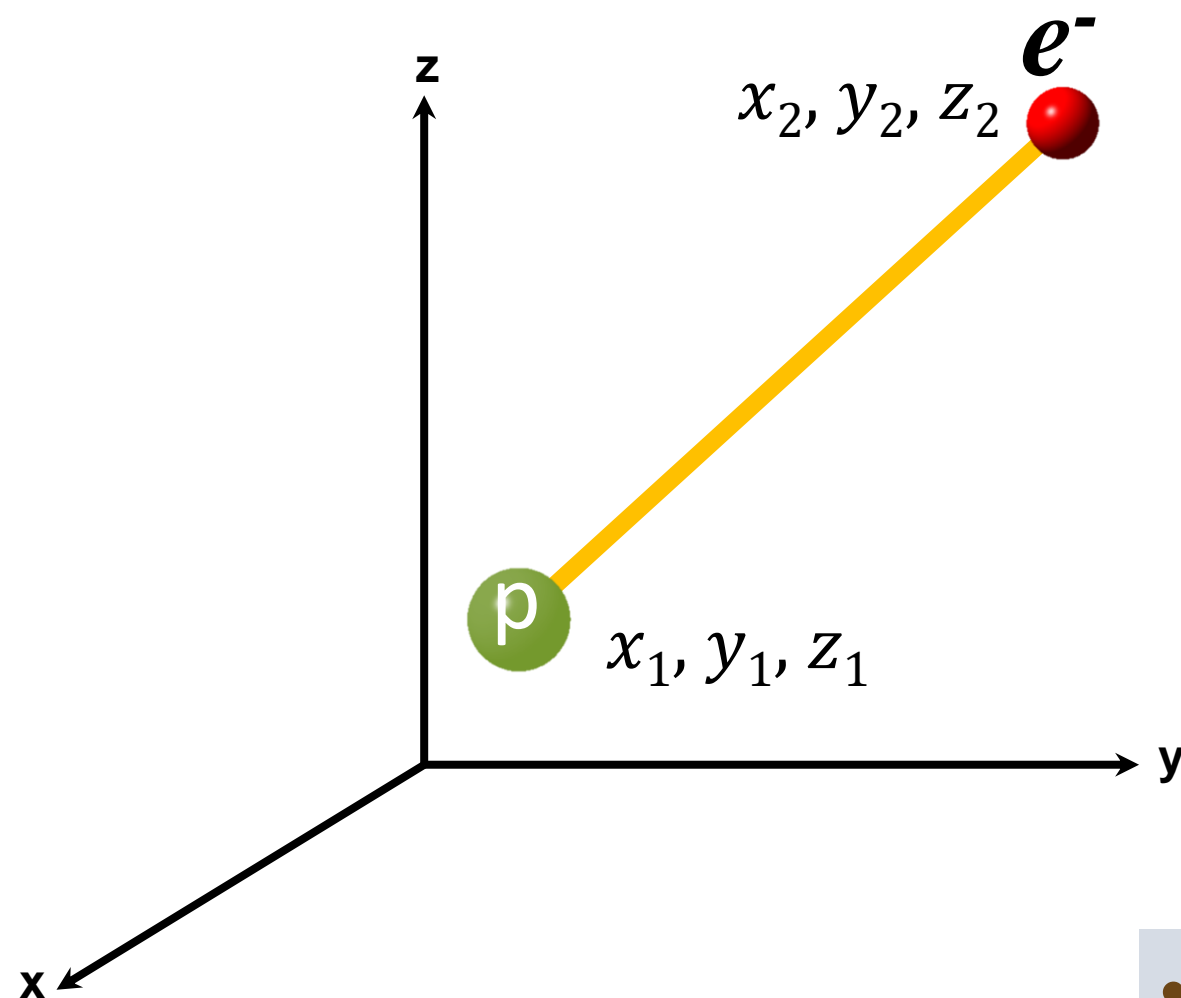
$$\frac{\partial^2\psi(x,y,z;X,Y,Z)}{\partial x_1^2} = \left(\frac{m_1^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} - \frac{2m_1}{m_1+m_2}\frac{\partial^2}{\partial X\partial x} + \frac{\partial^2}{\partial x^2}\right)\psi, \qquad \frac{\partial^2\psi(x,y,z;X,Y,Z)}{\partial x_2^2} = \left(\frac{m_2^2}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} + \frac{2m_2}{m_1+m_2}\frac{\partial^2}{\partial X\partial x} + \frac{\partial^2}{\partial x^2}\right)\psi$$

$\Rightarrow$

$$\frac{1}{m_1}\frac{\partial^2\psi}{\partial x_1^2} + \frac{1}{m_2}\frac{\partial^2\psi}{\partial x_2^2} = \left(\frac{m_1}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} - \frac{2}{m_1+m_2}\frac{\partial^2}{\partial X\partial x} + \frac{\partial^2}{m_1\partial x^2} + \frac{m_2}{(m_1+m_2)^2}\frac{\partial^2}{\partial X^2} + \frac{2}{m_1+m_2}\frac{\partial^2}{\partial X\partial x} + \frac{\partial^2}{m_2\partial x^2}\right)\psi = \left(\frac{1}{m_1+m_2}\frac{\partial^2}{\partial X^2} + \left(\frac{1}{m_1} + \frac{1}{m_2}\right)\frac{\partial^2}{\partial x^2}\right)\psi$$

Similarly for other terms.

z

x_2, y_2, z_2 **e⁻**

p

x_1, y_1, z_1

y

x

Total mass: $M_T = (m_1 + m_2)$ and reducd mass $\dfrac{1}{\mu} = \left(\dfrac{1}{m_1} + \dfrac{1}{m_2}\right)$

$m_1 = m_N$ and v $m_2 = m_e$

$$-\frac{\hbar^2}{2M_T}\left(\frac{\partial^2\psi}{\partial X^2} + \frac{\partial^2\psi}{\partial Y^2} + \frac{\partial^2\psi}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \left[\hat{V}(x,y,z) - E\right]\psi = 0$$
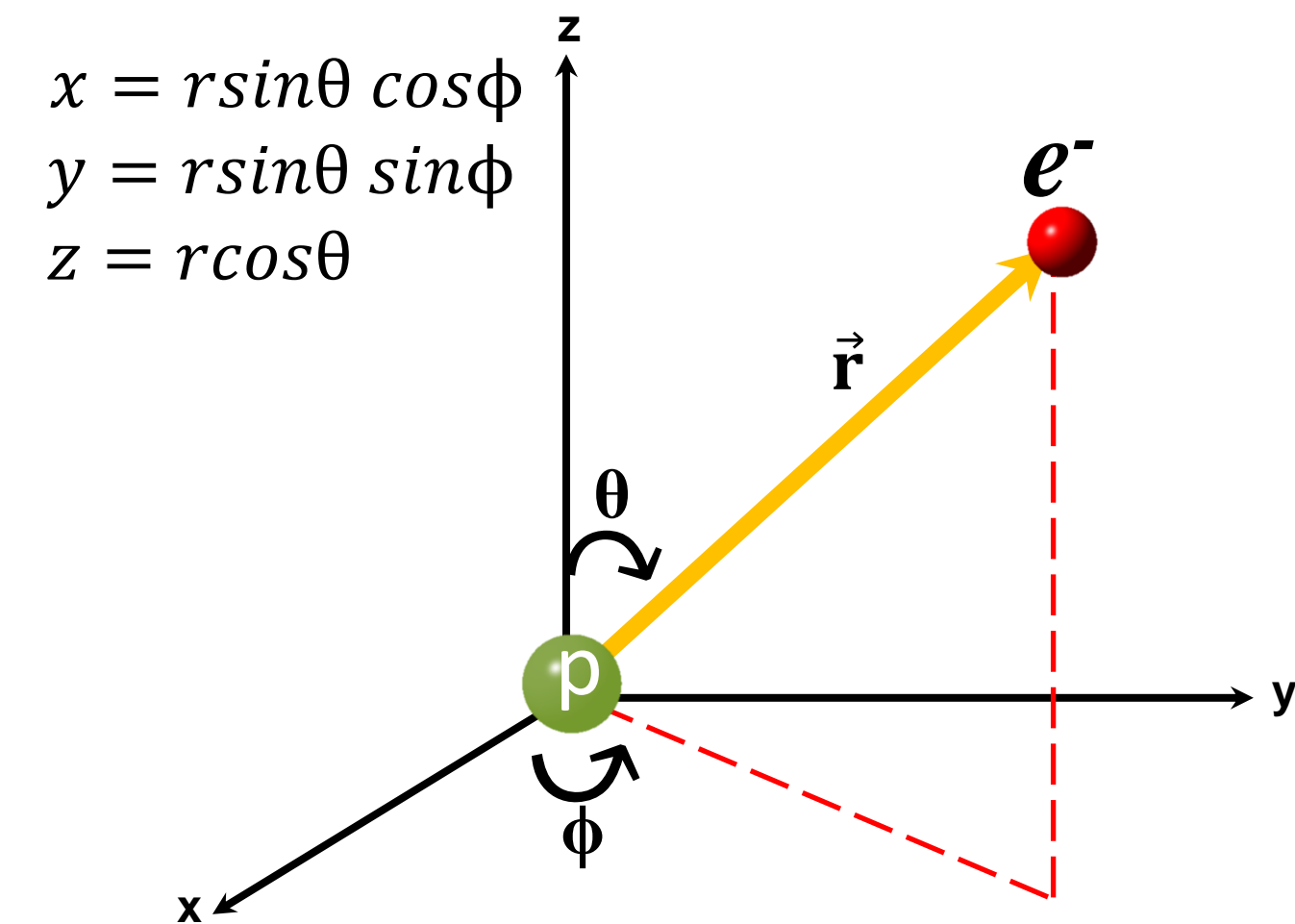
$$\hat{V}(r \equiv (x,y,z)) = -\frac{e^2}{4\pi\varepsilon_0(x^2+y^2+z^2)^{1/2}} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- **If we assume that the centre-of-mass of the whole system is fixed, then the kinetic energy of the total system will become zero**

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + \left[\hat{V}(x,y,z) - E\right]\psi = 0$$

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi + \left[\hat{V}(x,y,z) - E\right]\psi = 0$$

Schrödinger equation for a particle of reduced mass $\mu\left(= \dfrac{m_e m_N}{m_e + mN}\right)$ moving around a fixed centre at $x = y = z = 0$.

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

$$\hat{H} = \hat{K}_{nucleus} + \hat{K}_{electron} + \hat{V} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

- Since a hydrogenlike atom is spherically symmetric, it is more convenient to use spherical coordinates and write the Schrödinger equation as

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) + \left[\hat{V}(r) - E\right]\psi(r,\theta,\phi) = 0$$

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

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} - \frac{\hat{L}^2}{r^2\hbar^2} \qquad \hat{L}^2 = -\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

[Operator for the square of angular momentum]

$$\Rightarrow \quad -\frac{\hbar^2}{2\mu}\left[\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) - \frac{\hat{L}^2\psi}{r^2\hbar^2}\right] + \left[-\frac{e^2}{4\pi\varepsilon_0 r} - E\right]\psi = 0$$

- The angular dependence of the operator is contained in $\hat{L}^2$, whose eigenvalues and eigenfunctions are already known (through rigid rotor example).
- This clearly suggests us to solve the above Sch. Eq. by separation of variables by writing

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

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$$-\frac{\hbar^2}{2\mu}\left[\left(\frac{\partial^2[R(r)Y(\theta,\phi)]}{\partial r^2}+\frac{2}{r}\frac{\partial[R(r)Y(\theta,\phi)]}{\partial r}\right)-\frac{\hat{L}^2[R(r)Y(\theta,\phi)]}{r^2\hbar^2}\right]+\left[-\frac{e^2}{4\pi\varepsilon_0 r}-E\right]R(r)Y(\theta,\phi)=0$$

$$-\frac{\hbar^2}{2\mu}\left[\left(Y\frac{\partial^2 R}{\partial r^2}+Y\frac{2}{r}\frac{\partial R}{\partial r}\right)-R\frac{\hat{L}^2 Y}{r^2\hbar^2}\right]+\left[-\frac{e^2}{4\pi\varepsilon_0 r}-E\right]RY=0$$

Multiplying both sides by r^2/RY

$$-\frac{\hbar^2}{2\mu}\left(\frac{r^2}{R}\frac{\partial^2 R}{\partial r^2}+\frac{2r}{R}\frac{\partial R}{\partial r}\right)+\frac{1}{Y}\frac{\hat{L}^2 Y}{2\mu}+r^2\left[-\frac{e^2}{4\pi\varepsilon_0 r}-E\right]=0$$

Only angular part

$$\Rightarrow \frac{1}{Y}\frac{\hat{L}^2 Y}{2\mu}=\text{constant} \qquad \hat{L}^2 Y(\theta,\phi)=\ell(\ell+1)\hbar^2\,Y(\theta,\phi) \qquad \text{where } \ell=0,1,2\dots$$

$$\Rightarrow \hat{L}^2 Y_\ell^{m_\ell}(\theta,\phi)=\ell(\ell+1)\hbar^2\,Y_\ell^{m_\ell}(\theta,\phi)$$

$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2 R(r)}{\partial r^2}+\frac{2}{r}\frac{\partial R(r)}{\partial r}\right)+\left[\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}-\frac{e^2}{4\pi\varepsilon_0 r}-E\right]R(r)=0$$

Radial wave equation

Radial wave equation:

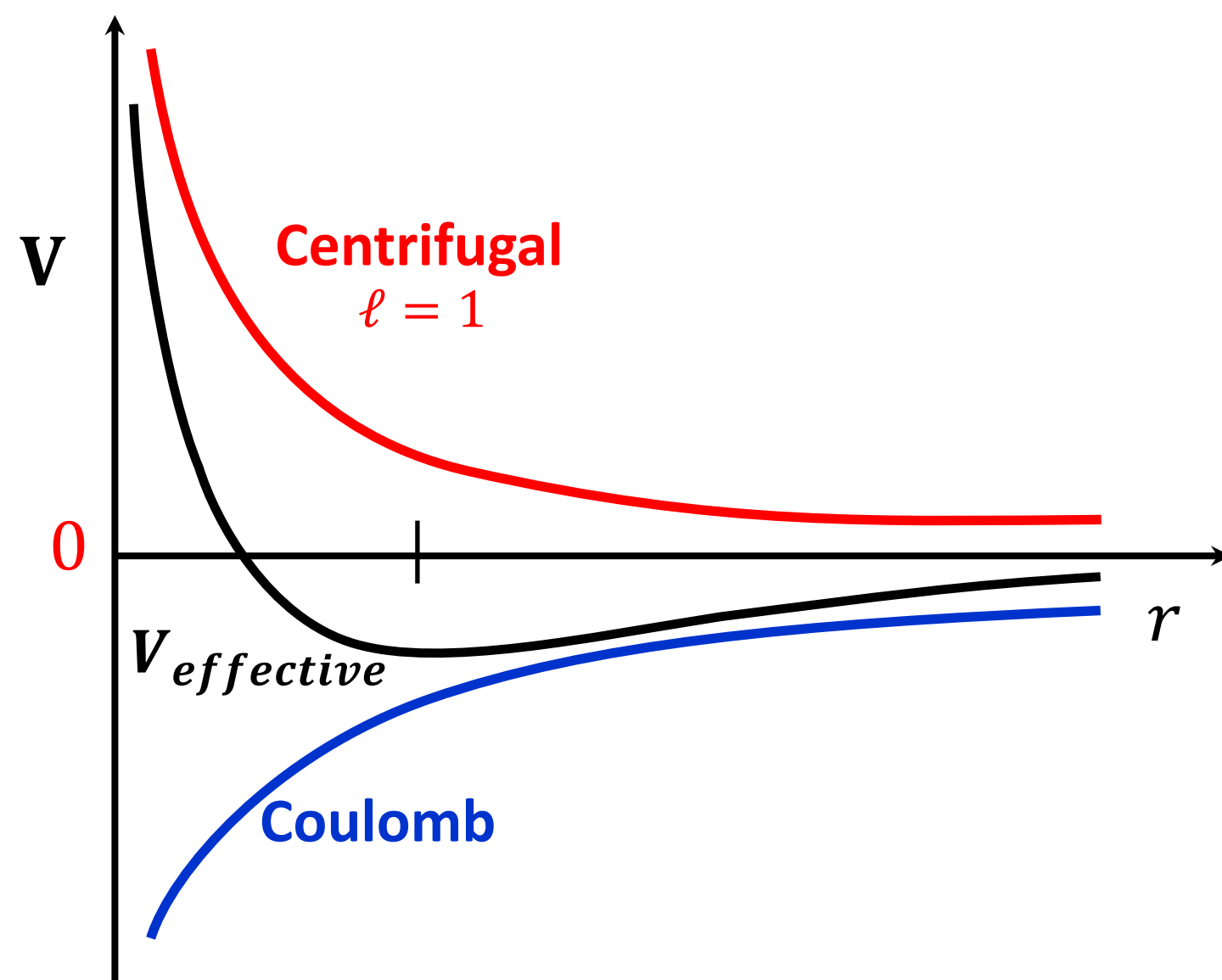$$-\frac{\hbar^2}{2\mu}\left(\frac{\partial^2 R(r)}{\partial r^2}+\frac{2}{r}\frac{\partial R(r)}{\partial r}\right)+\left[V_{effective}-E\right]R(r)=0$$

$$V_{effective}=\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}-\frac{e^2}{4\pi\varepsilon_0 r}$$

Repulsive   **Attractive**

Centrifugal potential energy function   **Coulomb potential energy function**
due to orbital motion of the electron

- For $\ell=0$ only attractive part exists
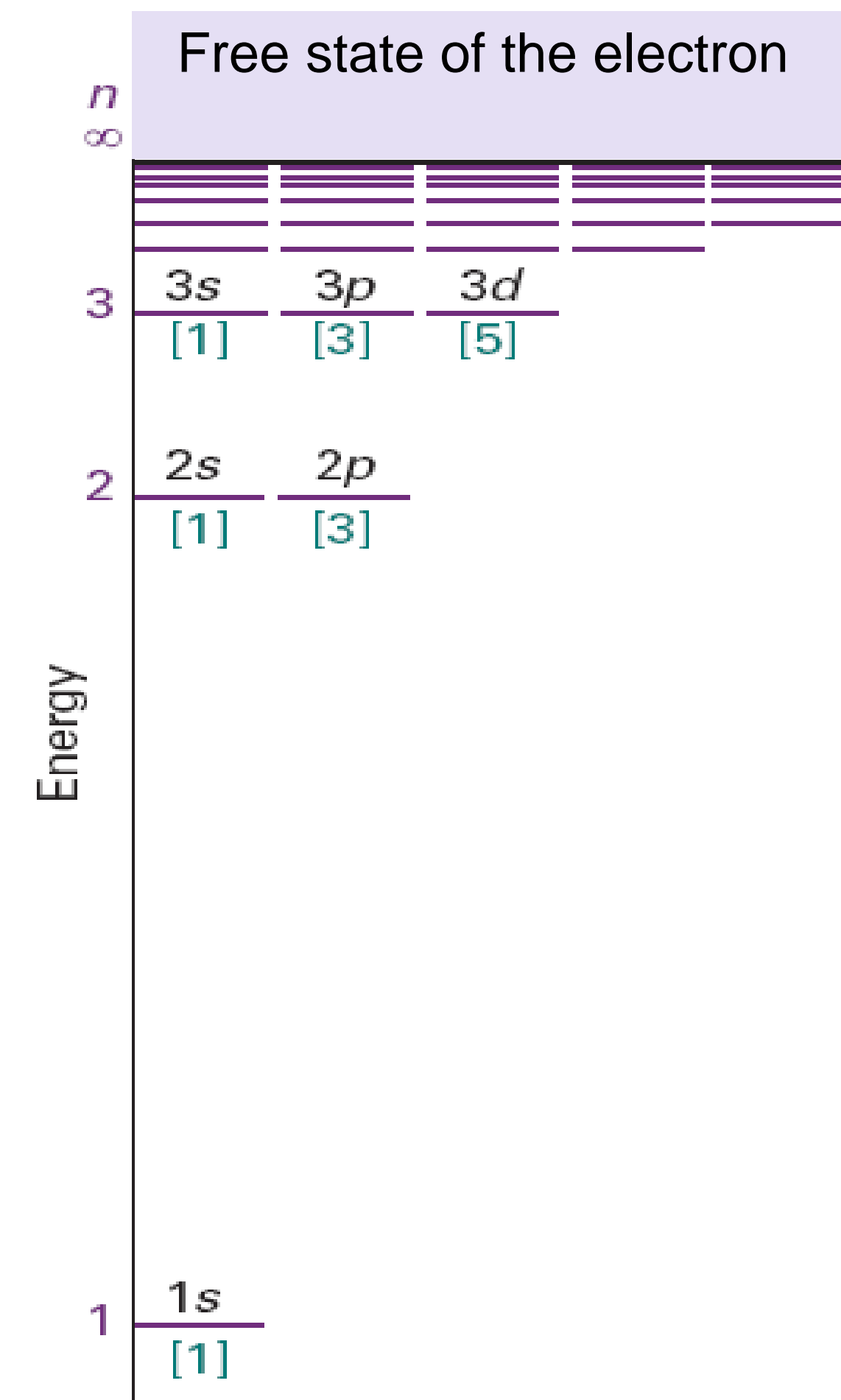- For $\ell\neq 0$ both repulsive and attractive parts exist

- The minimum of $V_{effective}$ is at around 1 Å
- $r\rightarrow\infty$, both the terms converge to zero
- $r\rightarrow 0$, repulsive term dominates

Solution of the Radial Wave Equation: Electronic Energy Levels

Radial wave equation can be solved for a well-behaved function near the nucleus and away from the nucleus. It turns out that with these boundary conditions, the expression for the energy eigenvalue is
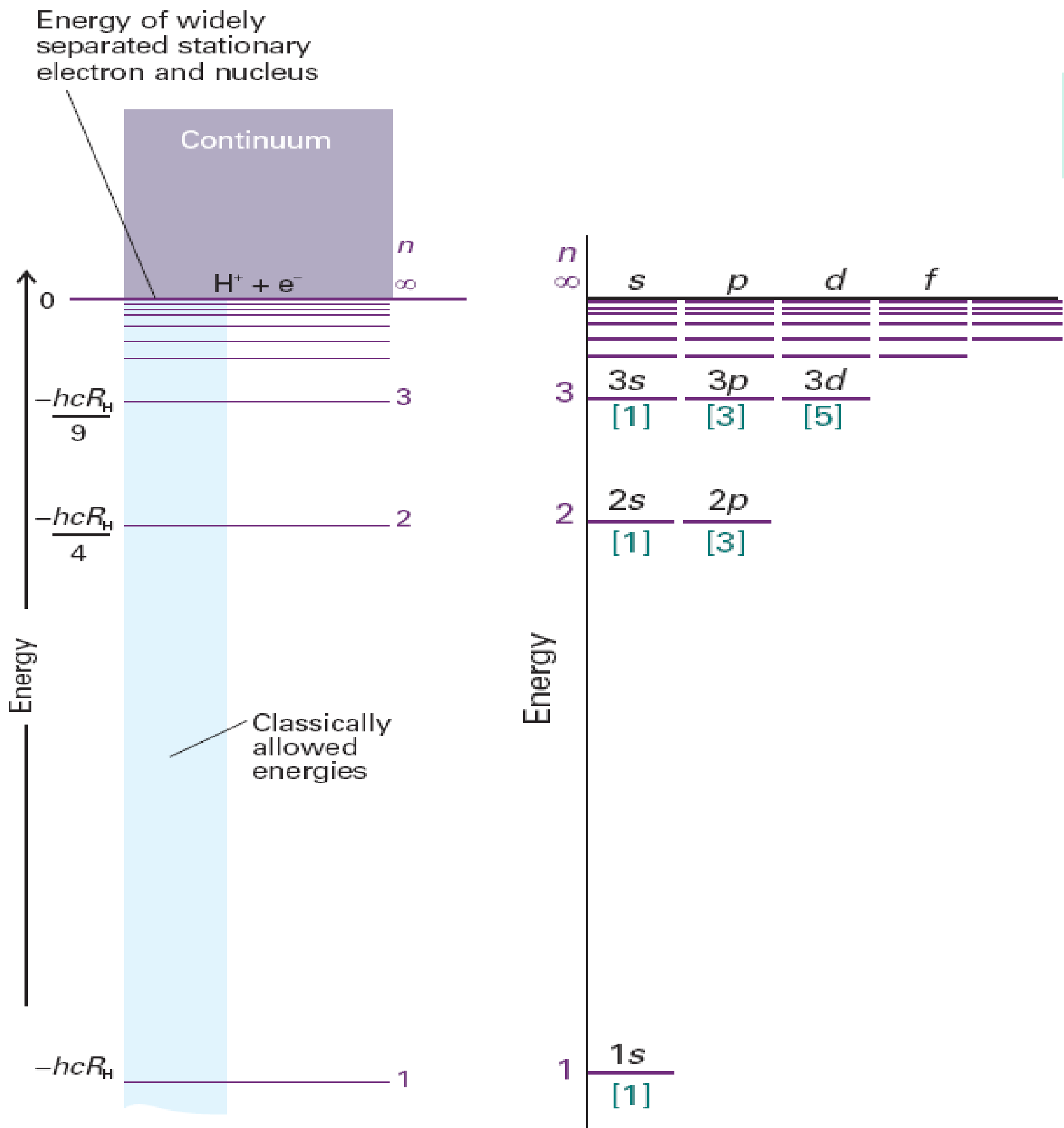
Free state of the electron

n
∞

$$E_n = -\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2 \hbar^2}\frac{1}{n^2}$$

where $n = 1, 2, 3 \ldots \infty$ are the principal quantum numbers and $Z = 1$ for H atom

3 | 3s | 3p | 3d
  | [1] | [3] | [5]

- Note that E_n does not depend on ℓ. However, while solving the eqn., it is found that $n > \ell$.

  More precisely, $0 \leq \ell \leq (n-1)$.

2 | 2s | 2p
  | [1] | [3]

- Since mass of the nucleus (m_N) is much higher than the mass of electron (m_e) $[m_N \gg m_e]$,

  $\mu \approx m_e$. Therefore, we can write

Energy

$$E_n = -\frac{m_e e^4}{2(4\pi\varepsilon_0)^2 \hbar^2}\frac{1}{n^2} = -\frac{e^2}{2(4\pi\varepsilon_0)a_0}\frac{1}{n^2}$$

where $a_0 = \frac{\hbar^2(4\pi\varepsilon_0)}{m_e e^2} = 0.529$ Å is **Bohr radius**

- Similarly, in terms of Rydberg constant (R_H) for hydrogen atom, the energy eigenvalue

$$E_n = -hcR_H\frac{1}{n^2}$$

where $R_H = \frac{\mu e^4}{2(4\pi\varepsilon_0)^2 \hbar^2} = 1.096775 \times 10^5\ cm^{-1}$

1 | 1s
  | [1]

Electronic Energy Levels of Hydrogen Atom

Solution of the Radial Wave Equation: Electronic Energy Levels

$$\Delta E_n = E_{n_2} - E_{n_1} = -\frac{e^2}{2(4\pi\varepsilon_0)a_0}\left[\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2}\right]$$

Solution of the Radial Wave Equation: Shapes of the Wavefunctions

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

Radial part   Angular part

- **Example: 1s orbital**

$$R_{n,\ell}(r) = N_{n,\ell}\; r^\ell e^{-\frac{r}{na_0}} L_{n,\ell}$$

$$\psi_{1s} = \frac{1}{(\pi a_0^3)^{1/2}} e^{-r/a_0}$$

Normalization component

Exponentially decaying function

Laguerre polynomial

Polynomial in *r*

- Asymptotic solution when $r \to 0$ is r^l

- Asymptotic solution when $r \to \infty$ is $e^{-\frac{r}{na_0}}$

- Polynomial L_{nl} of degree $(n - l - 1)$ for intermediate r

- **The quantum numbers n and ℓ can be determined from the form of the radial wavefunction**

- **Number of radial nodes $(n - \ell - 1)$ is determined by degree of $L_{n,\ell}$**

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Solution of the Radial Wave Equation: Shapes of the Wavefunctions

● Radial node

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

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

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

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}}\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

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

$$R_{30} = 2\left(\frac{Z}{3a_0}\right)^{\frac{3}{2}}\left(1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2}\right) e^{-Zr/3a_0}$$
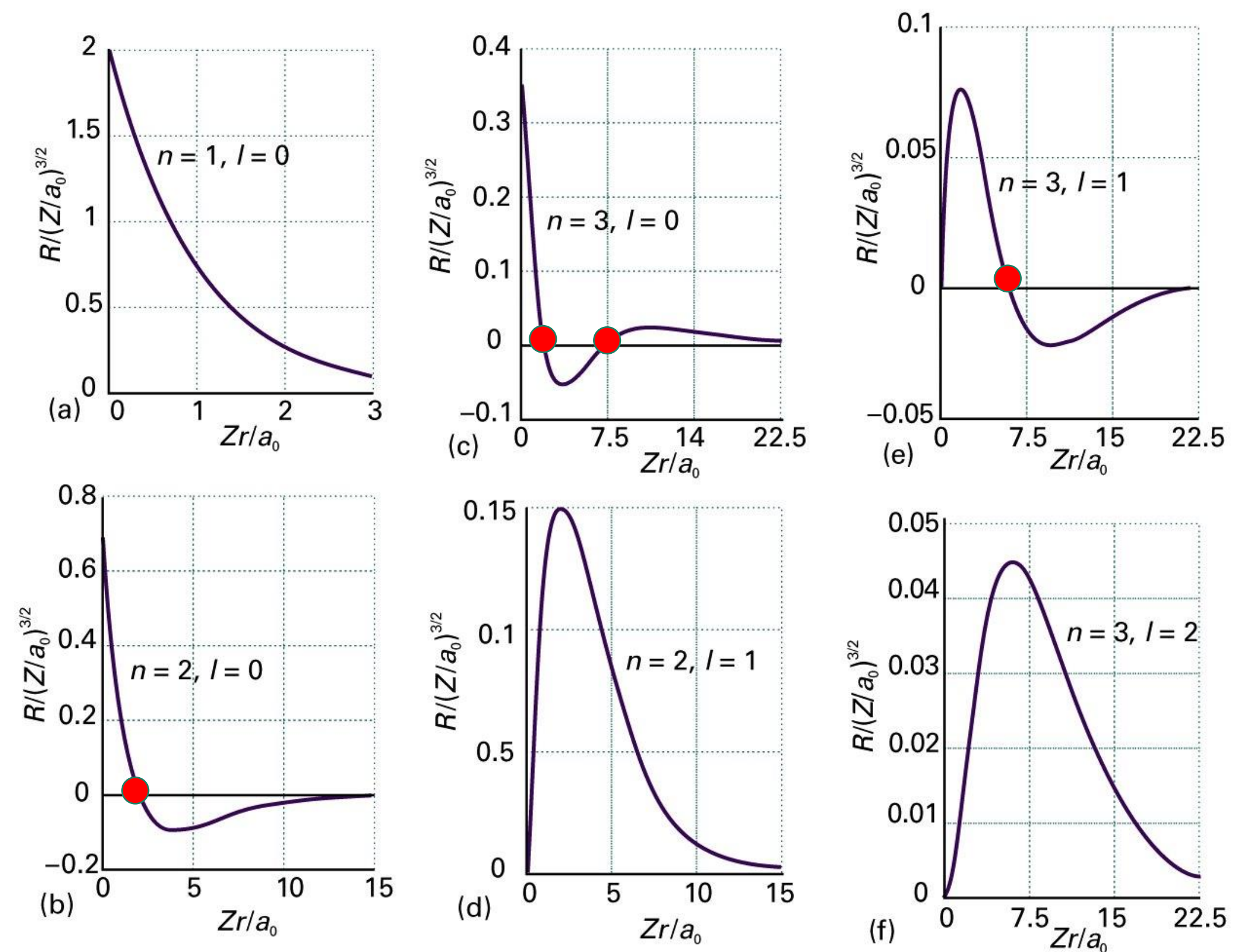
Figure 10-4
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi_{n,\ell,m_\ell}^* (r,\theta,\phi)\, \psi_{n,'\ell,'m_\ell'}\, (r,\theta,\phi)\, r^2 dr\, \sin\theta\, d\theta d\phi = \delta_{n,n'}\delta_{\ell,\ell,'}\, \delta_{m_\ell,m_\ell'}$$

$$= 1 \text{ when } n = n' \text{and } \ell = \ell' \text{ and } m_\ell = m_\ell'$$

$$= 0 \text{ when } n \neq n' \text{or } \ell \neq \ell' \text{ or } m_\ell \neq m_\ell'$$

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

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} R_{n,\ell}^* (r)\, Y_\ell^{m_\ell *}(\theta,\phi) R_{n,\ell}(r) Y_\ell^{m_\ell}(\theta,\phi)\, r^2 dr\, \sin\theta\, d\theta d\phi = 1$$

$$\therefore \quad \int_0^\pi \int_0^{2\pi} Y_\ell^{m_\ell *}(\theta,\phi)\, Y_\ell^{m_\ell}(\theta,\phi)\, \sin\theta\, d\theta d\phi = 1$$

$$\therefore \quad \int_0^\infty R_{n,\ell}^* (r)R_{n,\ell}(r)\, r^2 dr = 1$$

Probability that the electron described by $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ lies between r and $r+dr$

- How probability is distributed radially?
- The radial distribution function $P(r)$ gives the probability that the electron will be found anywhere in a shell of radius r.
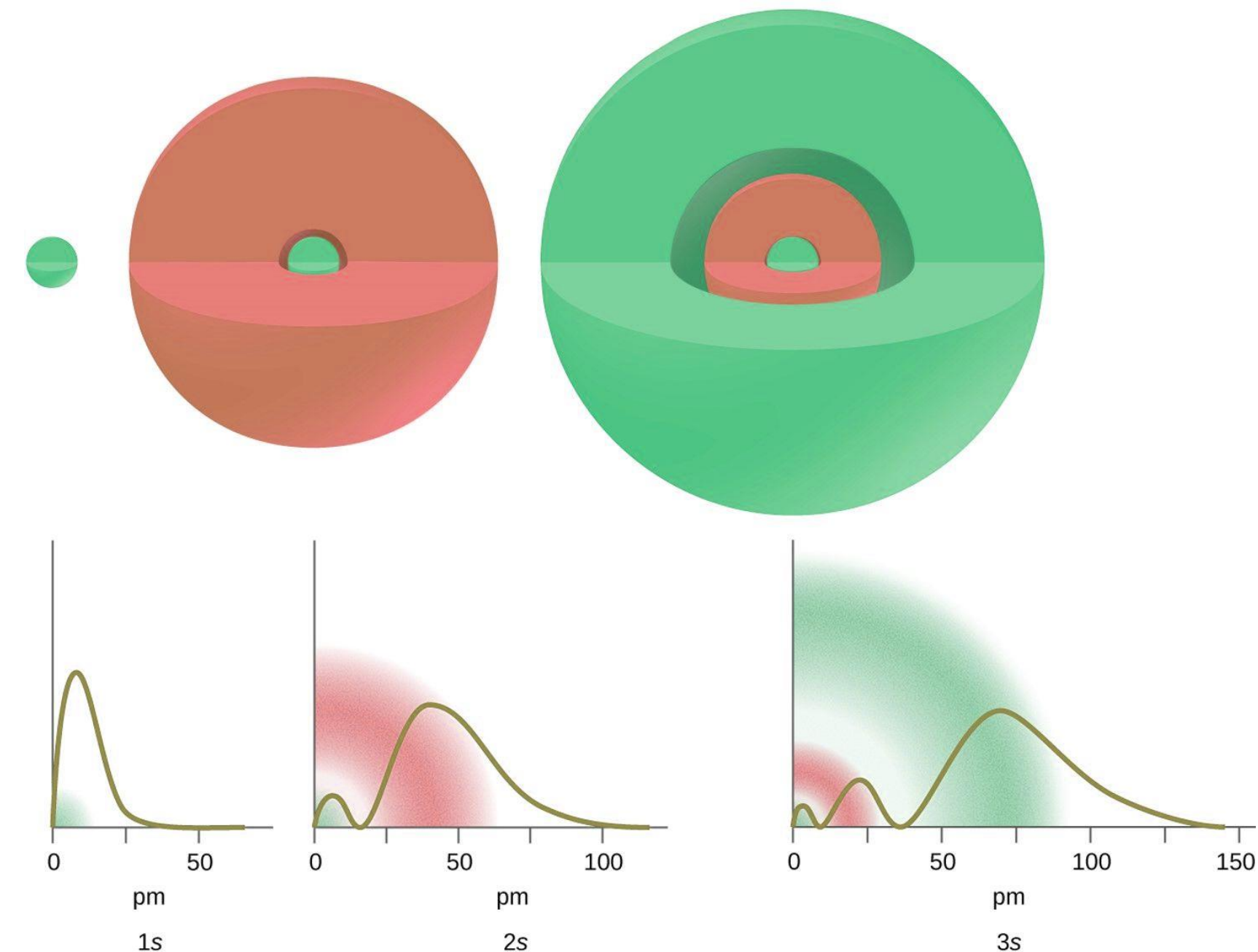
$$P(r)dr = \int_0^\pi \int_0^{2\pi} \psi_{n,\ell,m_\ell}^*(r,\theta,\phi)\,\psi_{n,'\ell,'m_\ell'}(r,\theta,\phi)\,r^2 dr\,\sin\theta\,d\theta d\phi$$

$$= \int_0^\pi \int_0^{2\pi} Y_\ell^{m_\ell*}(\theta,\phi)\,Y_\ell^{m_\ell}(\theta,\phi)\,\sin\theta\,d\theta d\phi \left|R_{n,\ell}(r)\right|^2 r^2 dr$$

$$\left|R_{n,\ell}(r)\right|^2 = R_{n,\ell}^*(r)R_{n,\ell}(r)$$

$$\because \quad \int_0^\pi \int_0^{2\pi} Y_\ell^{m_\ell*}(\theta,\phi)\,Y_\ell^{m_\ell}(\theta,\phi)\,\sin\theta\,d\theta d\phi = 1$$

$$P(r)dr = \left|R_{n,\ell}(r)\right|^2 r^2 dr$$

$$\int_0^\infty P(r)dr = \int_0^\infty R_{n,\ell}^*(r)R_{n,\ell}(r)\,r^2 dr = \int_0^\infty \left|R_{n,\ell}(r)\right|^2 r^2 dr = 1$$

Probability between r_1 and r_2 $= \int_{r_1}^{r_2} P(r)dr = \int_{r_1}^{r_2}\left|R_{n,\ell}(r)\right|^2 r^2 dr$
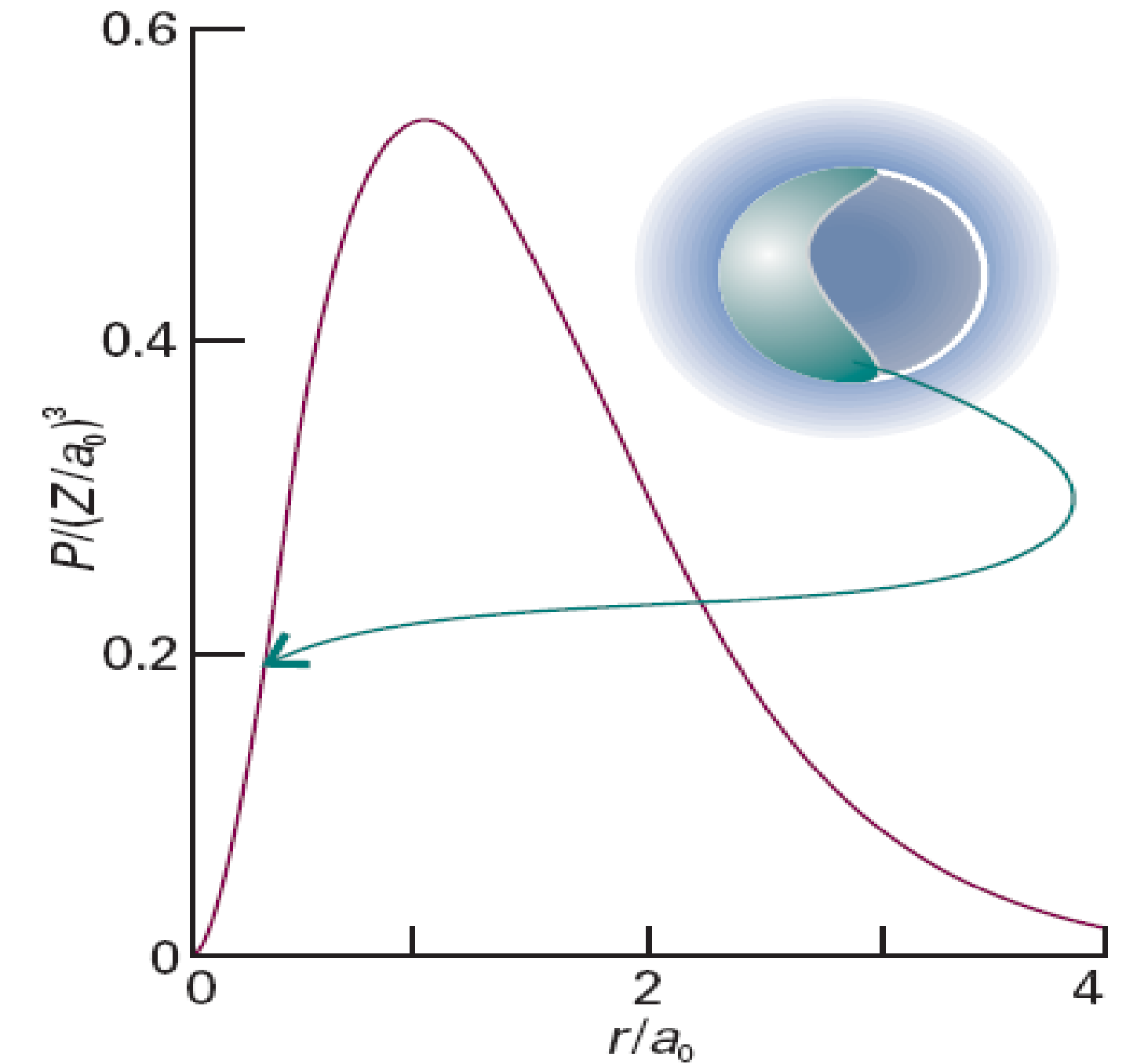

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Probability that the electron described by $\psi_{n,\ell,m_\ell}(r,\theta,\phi)$ lies between r and $r+dr$

$$P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

Let's interpret this expression:

1 Because $r^2 = 0$ at the nucleus, at the nucleus $P(0) = 0$.

2 As $r \to \infty$, $P(r) \to 0$ on account of the exponential term.

3 The increase in r^2 and the decrease in the exponential factor means that P passes through a maximum at an intermediate radius

For a **1s** electron in hydrogen, P is a maximum when r is equal to the Bohr radius a_0.

Solution of the Radial Wave Equation: Shapes of the Wavefunctions

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

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

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

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

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

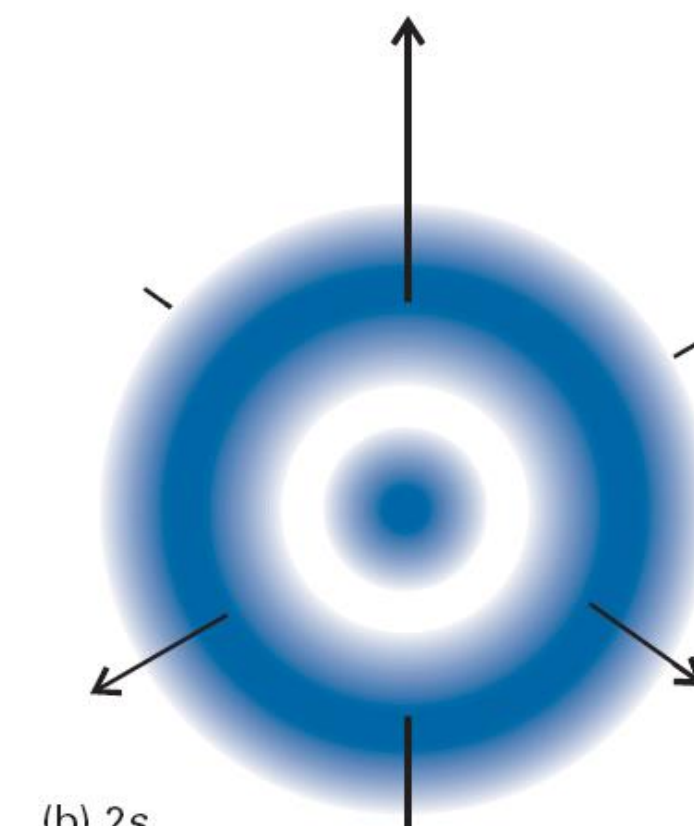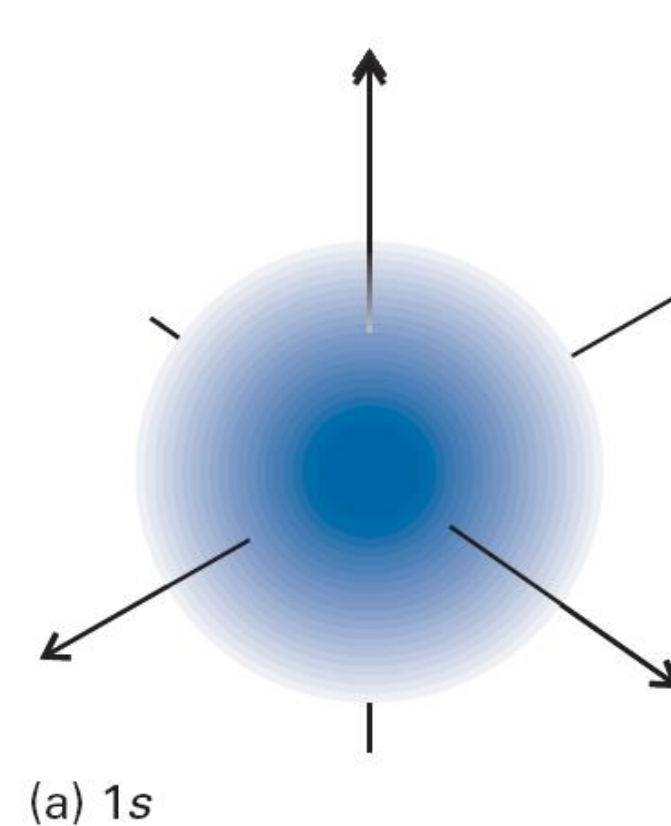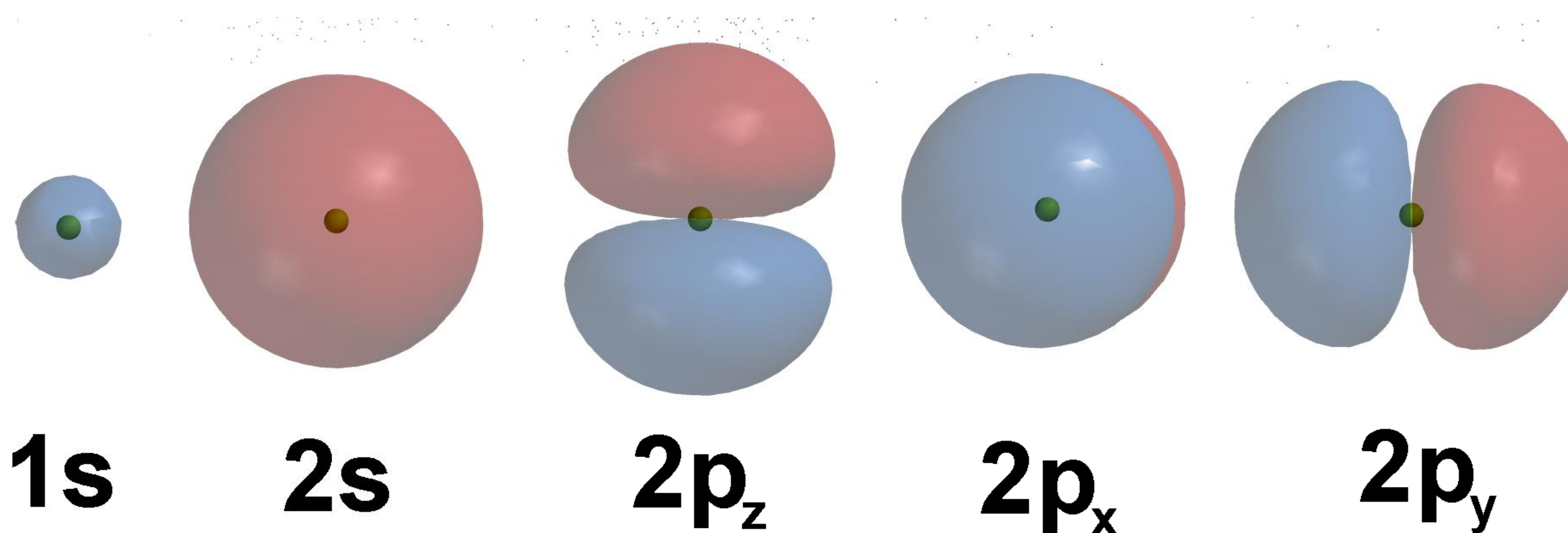$$Y_2^1 = -\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{i\phi}$$

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

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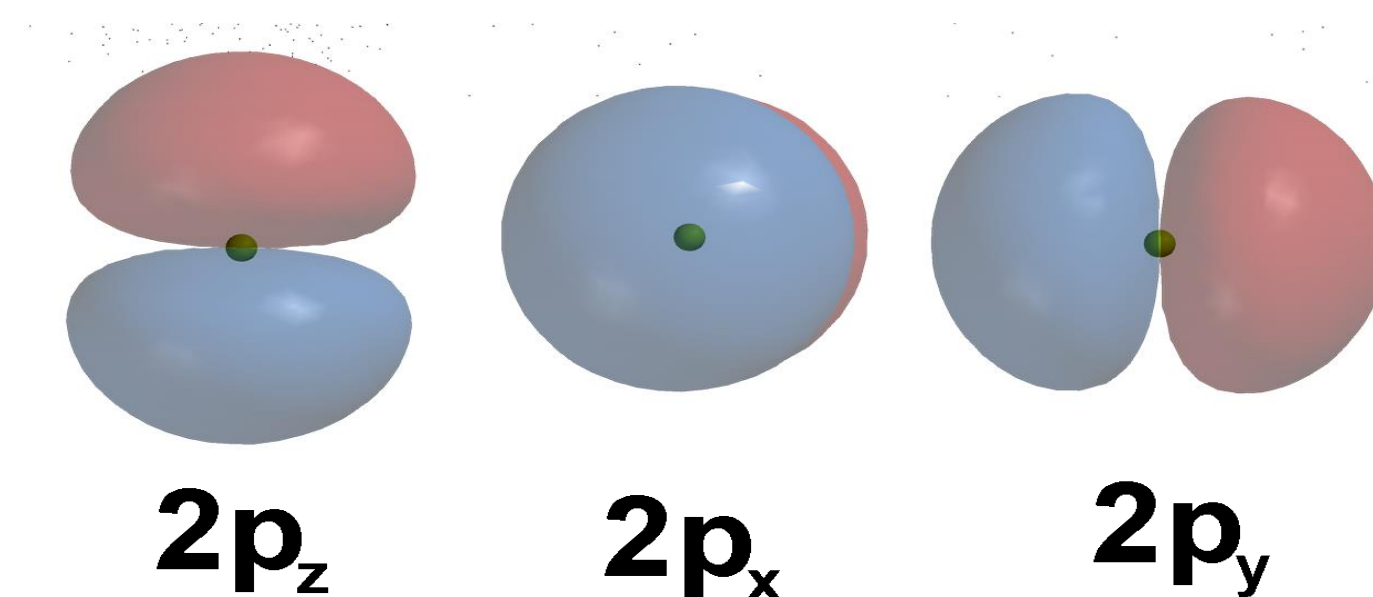
$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{-2i\phi}$$

(a) 1s

(b) 2s

Representations of the 1s and 2s hydrogenic atomic orbitals in terms of their electron densities (as represented by the density of shading)

1s   2s   2p$_z$ 2p$_x$ 2p$_y$

$2p_z$ $2p_x$ $2p_y$

(f) p Orbitals

The three $2p$ orbitals are distinguished by the three different values that m_l can take when $l = 1$. Because the quantum number m_l tells us the orbital angular momentum around an axis, these different values of m_l denote orbitals in which the electron has different orbital angular momenta around an arbitrary z-axis but the same magnitude of that momentum (because l is the same for all three). The orbital with $m_l = 0$, for instance, has zero angular momentum around the z-axis. Its angular variation is proportional to $\cos \theta$, so the probability density, which is proportional to $\cos^2 \theta$, has its maximum value on either side of the nucleus along the z-axis (at $\theta = 0$ and 180°). The wavefunction of a $2p$-orbital with $m_l = 0$ is

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

$$\psi_{P_0} = R_{2,1}(r)Y_{1,0}(\theta,\phi) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta e^{-Zr/2a_0}$$

$$= r\cos\theta f(r)$$

where $f(r)$ is a function only of r. Because in spherical polar coordinates $z = r\cos\theta$, this wavefunction may also be written

$$\psi_{P_z} = zf(r) \qquad (10.23)$$

All p orbitals with $m_l = 0$ have wavefunctions of this form regardless of the value of n. This way of writing the orbital is the origin of the name 'p_z orbital': its boundary surface is shown in Fig. 10.15. The wavefunction is zero everywhere in the xy-plane, where $z = 0$, so the xy-plane is a **nodal plane** of the orbital: the wavefunction changes sign on going from one side of the plane to the other.

The wavefunctions of $2p$ orbitals with $m_l = \pm 1$ have the following form:

$$\psi_{P_{\pm 1}} = R_{2,1}(r)Y_{1,\pm 1}(\theta,\phi) = \mp\frac{1}{8\pi^{1/2}}\left(\frac{Z}{a_0}\right)^{5/2} re^{-Zr/2a_0}\sin\theta e^{\pm i\phi}$$

$$= \mp\frac{1}{2^{1/2}}r\sin\theta e^{\pm i\phi}f(r)$$

We saw in Chapter 8 that a moving particle can be described by a complex wavefunction. In the present case, the functions correspond to non-zero angular momentum about the z-axis: $e^{+i\phi}$ corresponds to clockwise rotation when viewed from below, and $e^{-i\phi}$ corresponds to counter-clockwise rotation (from the same viewpoint). They have zero amplitude where $\theta = 0$ and $180°$ (along the z-axis) and maximum amplitude at $90°$, which is in the xy-plane. To draw the functions it is usual to represent them as standing waves. To do so, we take the real linear combinations

$$\psi_{P_x} = -\frac{1}{2^{1/2}}(p_{+1} - p_{-1}) = r\sin\theta\cos\phi f(r) = xf(r)$$

$$(10.24)$$

$$\psi_{P_y} = \frac{i}{2^{1/2}}(p_{+1} + p_{-1}) = r\sin\theta\sin\phi f(r) = yf(r)$$

These linear combinations are indeed standing waves with no net orbital angular momentum around the z-axis, as they are superpositions of states with equal and opposite values of m_l. The p_x orbital has the same shape as a p_z orbital, but it is directed along the x-axis (see Fig. 10.15); the p_y orbital is similarly directed along the y-axis.

Average value of r (Mean radius):

$$\langle r \rangle = \int_{\text{all space}} \Psi^* \, r \, \Psi \, d\tau$$

Example: (i) For a $1s\ e^-$ in H-atom

$$\langle r \rangle_{1s} = i \int \Psi_{1s}^* \, r \, \Psi_{1s} \, d\tau = \int_0^\infty r^3 |R_{1,0}(r)|^2 dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$

$$= \frac{3}{2} a_0$$

$$= \frac{3}{2} * 0.529 \, \text{Å}$$

$$= 0.7935 \, \text{Å}$$

(ii) For $2s\ e^-$ in H-atom

$$\Psi_{2s}(r,\theta,\phi) = \frac{1}{\sqrt{32\pi}} \frac{1}{a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$\langle r \rangle_{2s} = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \int_0^\infty dr \, r^2 \, \Psi_{2s}^* \, r \, \Psi_{2s} \, dr$$

$$= \int_0^\infty r^3 |R_{2,0}(r)|^2 dr$$

$$= 6 a_0$$

$$= 3.174 \, \text{Å}$$

On average a $2s\ e^-$ is at much greater distance than a $1s\ e^-$.

General formula for ns electron in H-atom

$$\boxed{\langle r \rangle_{ns} = \frac{3}{2} a_0 n^2}$$

Radial Extent of Orbitals:

$$\langle r \rangle_{n,l} = \frac{n^2 a_0}{Z} \left[1 + \frac{1}{2}\left(1 - \frac{l(l+1)}{n^2}\right)\right] = \frac{a_0}{2Z}\left[3n^2 - l(l+1)\right]$$
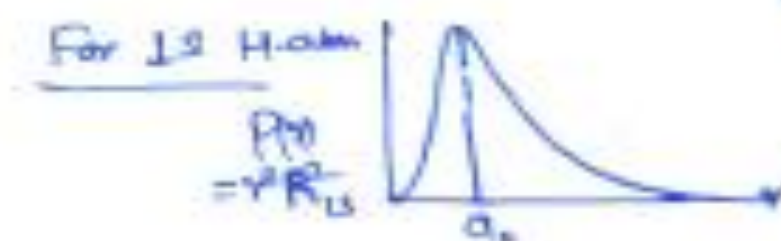
For a given n & Z

Ex: $4s\ e^-$ would $\langle r \rangle_{4s}$ greater than $4p\ e^-$ due l in the above eqn.

$$\boxed{\langle r \rangle_{4s} > \langle r \rangle_{4p}}$$

H.W: Calculate $\langle r \rangle_{2s}$, $\langle r \rangle_{2p}$ & $\langle r \rangle_{3s}$ and $\langle r \rangle_{3p}$ and arrange in increasing order

Most probable distance (r_{mp}): Value of r for which $P(r)$ is maximum

$$\text{i.e} \quad \frac{d\,P(r_{mp})}{dr} = 0$$

For 1s H-atom

$$P(r) = r^2 R_{1s}^2 = \frac{4 r^2}{a_0^3} e^{-2r/a_0}$$

$$\frac{d\,P(r_{mp})}{dr} = \frac{4}{a_0^3}\left[r_{mp}^2 e^{-2r_{mp}/a_0}\left(\frac{-2}{a_0}\right) + 2 r_{mp} e^{-2r_{mp}/a_0}\right] = 0$$

$$\Rightarrow \frac{r_{mp}}{a_0} e^{-2r_{mp}/a_0} = e^{-2r_{mp}/a_0}$$

$$\Rightarrow \boxed{r_{mp} = a_0}$$

General for Hydrogenic atom (1s e^-)

$$\boxed{r_{mp} = \frac{a_0}{Z}}$$

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