Quantum Mechanics in 3D. The Hydrogen Atom

1. Introduction
   - 3D isotropic harmonic oscillator
   - degeneracy of energy levels in 3D problems

2. Angular momentum
   - quantization of angular momentum and spherical harmonics
   - example: diatomic molecule

3. Motion in a central potential field and the hydrogen atom

Introduction:
3D Isotropic Harmonic Oscillator

3D Isotropic Harmonic Oscillator

Particle acted upon a central force $\bar{F} = -k\bar{r}$, where $k = m\omega^2$

$$V(x,y,z) = \frac{1}{2} m\omega^2 r^2 = \frac{1}{2} m\omega^2 \left(x^2 + y^2 + z^2 \right) =$$

$$= \frac{1}{2} m\omega x^2 + \frac{1}{2} m\omega^2 y^2 + \frac{1}{2} m\omega^2 z^2$$

Since the terms with *x*, *y*, *z* are separated, the Hamiltonian can be written as

$$\hat{H}(x,y,z) = \hat{H}_1(x) + \hat{H}_1(y) + \hat{H}_1(z)$$

where $\hat{H}_1(x) = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2$ (analogously for *y* and *z*).

We will therefore look for solutions to the 3D stationary Schrödinger equation

$$\hat{H}(x,y,z) \, \psi(x,y,z) = E \, \psi(x,y,z)$$

in the form

$$\psi(x,y,z) = \psi^{(x)}(x) \, \psi^{(y)}(y) \, \psi^{(z)}(z)$$

Separation of Variables

Separation of variables in the Schrödinger equation

$$\hat{H}(x,y,z)\,\psi^{(x)}(x)\,\psi^{(y)}(y)\,\psi^{(z)}(z) = E\,\psi^{(x)}(x)\,\psi^{(y)}(y)\,\psi^{(z)}(z)$$

gives

$$\frac{\hat{H}_1(x)\,\psi^{(x)}(x)}{\psi^{(x)}(x)} + \frac{\hat{H}_1(y)\,\psi^{(y)}(y)}{\psi^{(y)}(y)} + \frac{\hat{H}_1(z)\,\psi^{(z)}(z)}{\psi^{(z)}(z)} = E$$

Since x, y, z are independent each of the three terms on the lhs needs to be equal to a constant. Hence the 3D Schrödinger equation splits into three Schrödinger equations for 1D harmonic oscillators

$$\begin{cases} \hat{H}_1(x)\,\psi^{(x)}(x) = E^{(x)}\psi^{(x)}(x) \\ \hat{H}_1(y)\,\psi^{(y)}(y) = E^{(y)}\psi^{(y)}(y) \\ \hat{H}_1(z)\,\psi^{(z)}(z) = E^{(z)}\psi^{(z)}(z) \end{cases}$$

where $E = E^{(x)} + E^{(y)} + E^{(z)}$ and

$$E^{(x)} = E^{(x)}_{n_x} = \hbar\omega\left(n_x + \tfrac{1}{2}\right)$$

$$\psi^{(x)}(x) = \psi^{(x)}_{n_x} = C_{n_x} H_{n_x}\left(\tfrac{x}{x_0}\right) e^{-\frac{1}{2}\left(\frac{x}{x_0}\right)^2}$$

$$n_x = 0, 1, 2, \ldots \qquad \text{(analogously for } y \text{ and } z\text{)}$$

Degeneracy of Energy Levels

Solution of the 3D problem

$$\Psi_{(n_x, n_y, n_z)}(x, y, z) = C_{(n_x, n_y, n_z)} H_{n_x}\left(\frac{x}{x_o}\right) H_{n_y}\left(\frac{y}{y_o}\right) H_{n_z}\left(\frac{z}{z_o}\right) e^{-\frac{1}{2}\left[\left(\frac{x}{x_o}\right)^2 + \left(\frac{y}{y_o}\right)^2 + \left(\frac{z}{z_o}\right)^2\right]}$$

$$N = 0, 1, 2, \ldots$$

$$E_{(n_x, n_y, n_z)} = \hbar\omega\left(n_x + n_y + n_z + \frac{3}{2}\right)$$
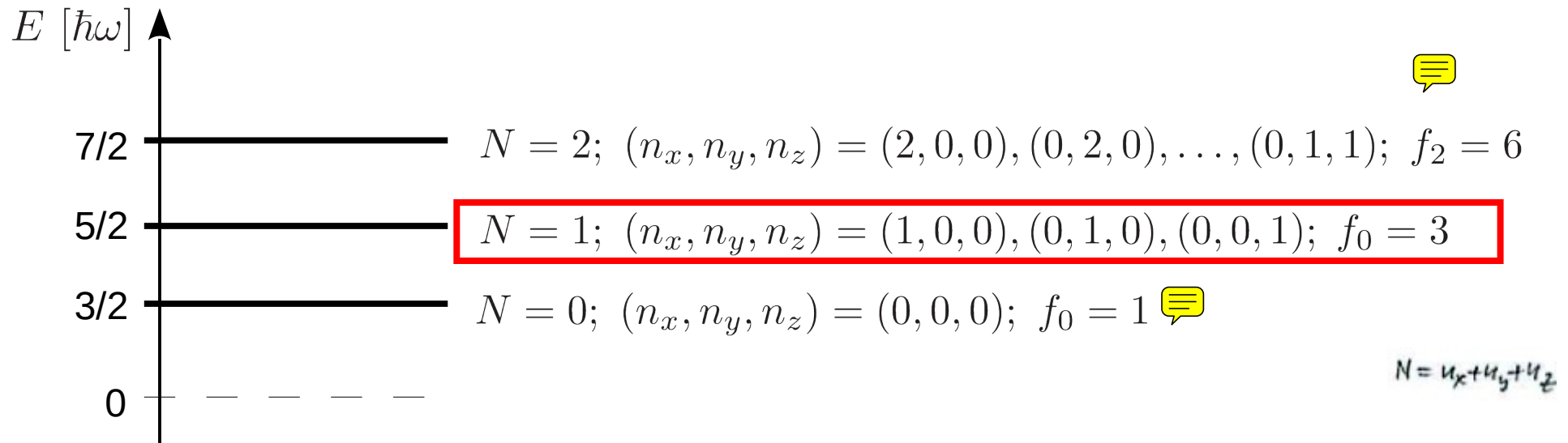
here $(x_o = y_o = z_o)$

where $n_x, n_y, n_z = 0, 1, 2, \ldots$

Discussion

- wave function is a <mark>product of three wave functions</mark> of 1D harmonic oscillators with the same natural angular frequency <mark>ω</mark>

- energy spectrum is discrete, with equally-spaced energy levels separated by $\hbar\omega$

- the ground-state energy is not zero (zero-point oscillations) and is three times the value for the 1D problem $\boxed{3} \times \hbar\omega/2$

- energy levels are **_degenerate_**: <mark>there is more than one wavefunction</mark> corresponding to one eignevalue for excited states

Degeneracy of Energy Levels

Energy levels are said to be **degenerate** if *different combinations of quantum numbers* (here n_x, n_y, and n_z), that is *different eigenfunctions*, represent states with *the same energy*.

$E\ [\hbar\omega]$

7/2 $N = 2;\ (n_x, n_y, n_z) = (2,0,0),(0,2,0),\ldots,(0,1,1);\ f_2 = 6$

5/2 $N = 1;\ (n_x, n_y, n_z) = (1,0,0),(0,1,0),(0,0,1);\ f_0 = 3$

3/2 $N = 0;\ (n_x, n_y, n_z) = (0,0,0);\ f_0 = 1$

0

$N = n_x + n_y + n_z$

Degeneracy of the *N*-th state is f_N-fold, where $\quad f_N = \dfrac{(N+1)(N+2)}{2}$

Note. Degeneracy is lifted if the oscillator is non-isotropic, i.e.

$$V(x,y,z) = \tfrac{1}{2} m\omega_x^2 x^2 + \tfrac{1}{2} m\omega_y^2 y^2 + \tfrac{1}{2} m\omega_z^2 z^2 \qquad \omega_x \neq \omega_y \neq \omega_z$$

Angular Momentum

Orbital Angular Momentum

$$\text{classical mechanics} \qquad\qquad \text{quantum mechanics}$$

$$\bar{L} = \bar{r} \times \bar{p} \qquad \xrightarrow{\text{replace with operators}} \qquad \hat{L} = \hat{\bar{r}} \times \hat{\bar{p}}$$

where $\hat{\bar{r}} = \bar{r}$ 3D position operator

$$\hat{\bar{p}} = -i\hbar \nabla = -i\hbar \left(\tfrac{\partial}{\partial x}, \tfrac{\partial}{\partial y}, \tfrac{\partial}{\partial z} \right)$$ 3D momentum operator

In the Cartesian coordinate system, the explicit form of the components of the (orbital) angular momentum operator

$$\hat{L}_x = \hat{y}\,\hat{p}_z - \hat{z}\,\hat{p}_y = -i\hbar \left(y \tfrac{\partial}{\partial z} - z \tfrac{\partial}{\partial y} \right)$$

$$\hat{L}_y = \hat{z}\,\hat{p}_x - \hat{x}\,\hat{p}_z = -i\hbar \left(z \tfrac{\partial}{\partial x} - x \tfrac{\partial}{\partial z} \right)$$

$$\hat{L}_z = \hat{x}\,\hat{p}_y - \hat{y}\,\hat{p}_x = -i\hbar \left(x \tfrac{\partial}{\partial y} - y \tfrac{\partial}{\partial x} \right)$$

Fact. Components of the orbital angular momentum do not commute with each other [see recitation class for a calculation of these commutators].

Consequently, two Cartesian components of the angular momentum cannot be measured simultaneously with arbitrarily small uncertainty.

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$

$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

Orbital Angular Momentum

In quantum mechanics the magnitude (squared) of the orbital angular momentum is represented by the operator

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Fact. L^2 commutes with L_α (where $\alpha = x$, y, or z).

$$[\hat{L}^2, \hat{L}_z] = [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_z] = [\hat{L}_x^2, \hat{L}_z] + [\hat{L}_y^2, \hat{L}_z] + \underbrace{[\hat{L}_z^2, \hat{L}_z]}_{0} =$$

$$= \hat{L}_x \underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar\hat{L}_y} + \underbrace{[\hat{L}_x, \hat{L}_z]}_{-i\hbar\hat{L}_y} \hat{L}_x + \hat{L}_y \underbrace{[\hat{L}_y, \hat{L}_z]}_{i\hbar L_x} + \underbrace{[\hat{L}_y, \hat{L}_z]}_{i\hbar L_x} \hat{L}_y =$$

$$= -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x + i\hbar\hat{L}_y L_x + i\hbar L_x\hat{L}_y \equiv 0$$
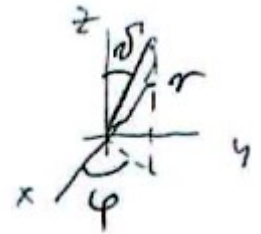
Consequences
- ➜ L^2 and L_z are compatible physical quantities (same for L^2 and L_x or L^2 and L_y)
- ➜ operators L^2 and L_z have common eigenfunctions

Angular Momentum in Spherical Coordinates

All problems we are going to discuss, will have spherical symmetry, hence the spherical coordinates are convenient.

The *z*-axis is chosen to represent the direction in case of any symmetry breaking (e.g, if we had a uniform magnetic field in the problem, it would be pointing in the z-axis direction). Then the operators representing L^2 and L_z are

(*z*- component)
$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \varphi}$$

(magnitude squared)
$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta}\left(\sin\vartheta \frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial\varphi^2} \right]$$

$$\underbrace{\hspace{6cm}}_{\Delta_{\vartheta,\varphi} \;-\; \text{Laplacian on a sphere}}$$

$$= -\hbar^2 \left[\frac{\partial^2}{\partial\vartheta^2} + \cot\vartheta \frac{\partial}{\partial\vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial\varphi^2} \right]$$

What are their eigenvalues (possible outcomes of measurements of L^2 and L_z) and the corresponding eigenfunctions?

(a) Eigenvalues and Eigenfunctions of L_z

Eigenvalue problem $\quad \hat{L}_z \phi = \hbar m \phi$, that is $\quad -i\hbar \frac{\partial}{\partial \varphi} \phi(\varphi) = \hbar m \phi(\varphi)$

Solution $\quad \boxed{\phi(\varphi) = C e^{im\varphi}}$

The function ϕ should be periodic with period 2π, i.e. $\quad \phi(\varphi + 2\pi) = \phi(\varphi)$
(rotation by 2π does not change anything). Hence

$$e^{i 2\pi m} = 1 \qquad \text{that is} \qquad \boxed{m = 0, \pm 1, \pm 2, \ldots}$$

Normalization on the interval $[0, 2\pi]$

$$\langle \phi_m, \phi_{m'} \rangle = |C|^2 \int_0^{2\pi} e^{i(m-m')\varphi} d\varphi = |C|^2 2\pi \delta_{mm'} \implies |C|^2 = \frac{1}{2\pi}$$

Summary

eigenvalues $\hbar m$, $m = 0, \pm 1, \pm 2, \ldots$; *eigenfunctions* $\phi_m(\varphi) = \frac{1}{\sqrt{2\pi}} e^{im\varphi}$

(b) Eigenvalues and Eigenfunctions of L^2

Eigenvalue problem $\hat{L}^2 Y = \hbar^2 \ell(\ell+1) Y$ in spherical coordinates

$$-\hbar^2 \left[\frac{\partial^2}{\partial \vartheta^2} + \cot\vartheta \frac{\partial}{\partial \vartheta} + \frac{1}{\sin^2\vartheta} \frac{\partial^2}{\partial \varphi^2} \right] Y(\vartheta, \varphi) = \hbar^2 \ell(\ell+1) \, Y(\vartheta, \varphi)$$

Recall that operators L^2 and L_z have common eigenfunctions, hence look for

$$Y(\vartheta, \varphi) = Y_{\ell m}(\vartheta, \varphi) = \Theta_{\ell m}(\vartheta) \, \Phi_m(\varphi)$$

Result (for details [optional*] see e.g. Liboff)

$$Y_{\ell m}(\vartheta, \varphi) = \sqrt{\frac{(\ell - |m|)!}{(\ell + |m|)!} \frac{2\ell+1}{4\pi}} \, (-1)^{\frac{m+|m|}{2}} P_\ell^{|m|}(\cos\vartheta) \, e^{im\varphi}$$

where $\ell = 0, 1, 2, \dots$; $m = -\ell, -\ell+1, \dots, 0, \dots, \ell-1, \ell$

and $P_\ell^{|m|}(u) = (1-u^2)^{\frac{|m|}{2}} \frac{d^{|m|}}{du^{|m|}} P_\ell(u)$ Legendre's polynomial (see ODE class) are the

associated Legendre polynomials

(b) Eigenvalues and Eigenfunctions of L^2

Eigenfunctions of L^2 $\quad Y_{\ell m}(\vartheta, \varphi)$ $\quad$ are called the **spherical harmonics**.

Note that $l=0, 1, 2,...$ and $m=-l, -l+1,..., 0,..., l-1, l$, i.e. for each value of l there is $(2l+1)$ spherical harmonics distinguished by m.

Properties of spherical harmonics

→ a few first

$$Y_{0,0}(\vartheta, \varphi) = \frac{1}{\sqrt{4\pi}} \quad ; \qquad Y_{1,0}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos\vartheta$$

$$Y_{1,\pm 1}(\vartheta, \varphi) = \mp \sqrt{\frac{3}{4\pi}} \sin\vartheta \, e^{\pm i\varphi}$$

$$Y_{2,0}(\vartheta, \varphi) = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2\vartheta - \frac{1}{2} \right)$$

$$Y_{2,\pm 1}(\vartheta, \varphi) = \mp \sqrt{\frac{15}{8\pi}} \sin\vartheta \cos\vartheta \, e^{\pm i\varphi}$$

$$Y_{2,\pm 2}(\vartheta, \varphi) = \sqrt{\frac{15}{32\pi}} \sin^2\vartheta \, e^{\pm i2\varphi}$$

→ orthogonality

$$\langle Y_{\ell m}, Y_{\ell' m'} \rangle = \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin\vartheta \underbrace{}_{\text{Jacobian}} Y_{\ell m}^*(\vartheta, \varphi) Y_{\ell m}(\vartheta, \varphi) = \delta_{\ell \ell'} \, \delta_{m m'}$$

Spherical Harmonics

$$Y_{0,0}(\vartheta, \varphi) = \frac{1}{\sqrt{4\pi}} \quad , \qquad Y_{1,0}(\vartheta, \varphi) = \sqrt{\frac{3}{4\pi}} \cos \vartheta$$

$$Y_{1,\pm1}(\vartheta, \varphi) = \mp \sqrt{\frac{3}{4\pi}} \sin \vartheta \, e^{\pm i\varphi}$$

$$Y_{2,0}(\vartheta, \varphi) = \sqrt{\frac{5}{4\pi}} \left(\frac{3}{2} \cos^2 \vartheta - \frac{1}{2} \right)$$

$$Y_{2,\pm1}(\vartheta, \varphi) = \mp \sqrt{\frac{15}{8\pi}} \sin \vartheta \cos \vartheta \, e^{\pm i\varphi}$$

$$Y_{2,\pm2}(\vartheta, \varphi) = \sqrt{\frac{15}{32\pi}} \sin^2 \vartheta \, e^{\pm i2\varphi}$$

$|Y_0^0(\theta, \phi)|^2$

$|Y_1^0(\theta, \phi)|^2$ $|Y_1^1(\theta, \phi)|^2$
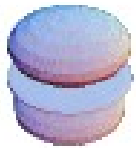
$|Y_2^0(\theta, \phi)|^2$ $|Y_2^1(\theta, \phi)|^2$ $|Y_2^2(\theta, \phi)|^2$

$|Y_3^0(\theta, \phi)|^2$ $|Y_3^1(\theta, \phi)|^2$ $|Y_3^2(\theta, \phi)|^2$ $|Y_3^3(\theta, \phi)|^2$

http://www.st-andrews.ac.uk/physics/quvis/simulations_phys/ph45_Spherical_Harmonics.html

Source: wolfram.com

Summary

Summary: Spherical harmonics are common eigenfunctions
of operators L^2 and L_z

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

$$\hat{L}_z Y_{\ell m}(\vartheta, \varphi) = \underline{\hbar m} Y_{\ell m}(\vartheta, \varphi)$$

where $l=0, 1, 2,...$ and $m=-l, -l+1,..., 0,..., l-1, l$.

Comment. The condition $|m| \leq l$ follows from the interpretation of
the eigenvalues as possible outcomes of measurements.

$\hbar^2 m^2$ — possible outcome of measurement of L_z^2

$\hbar^2 \ell(\ell+1)$ — possible outcome of measurement of $L^2 = L_x^2 + L_y^2 + L_z^2$

Hence $\quad m^2 \leq \ell(\ell+1) < \left(\ell + \frac{1}{2}\right)^2 \quad$ and $\quad |m| < \ell + \frac{1}{2}$. But m, ℓ – integers,

hence eventually $|m| \leq \ell$.

Summary

The fact that $l=0, 1, 2,...$ and $m=-l, -l+1,..., 0,..., l-1, l$ implies, that the projection of the angular momentum onto the z-axis is quantized, i.e. the orbital angular momentum can only point in these directions in space such that its projection on the axis is $-l, -l+1,..., 0,..., l-1, l$ (in the units of ℏ).
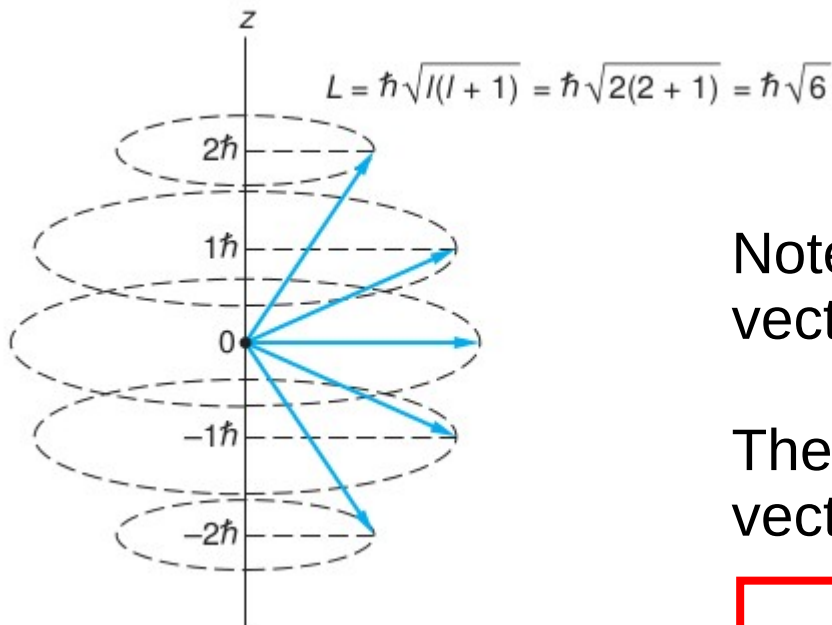
$$L = \hbar\sqrt{l(l+1)} = \hbar\sqrt{2(2+1)} = \hbar\sqrt{6}$$

FIGURE 7-4 Vector model illustrating the possible orientations of **L** in space and the possible values of L_z for the case where $\ell = 2$.

Note that the orbital angular momentum vector never points in the z (nor -z) direction!

The angle between the angular momentum vector and the z axis

$$\cos\theta = \frac{L_z}{L} = \frac{m\hbar}{\hbar\sqrt{l(l+1)}} = \frac{m}{\sqrt{l(l+1)}}$$

Example: The Rigid Rotor

Diatomic molecule rotating about its center of mass

➔ assume constant distance between atoms – rigid rotor

➔ two degrees of freedom: angles defining the direction of the axis

➔ energy = kinetic energy of rotational motion about the center of mass

$r_1 + r_2 = \text{const}$
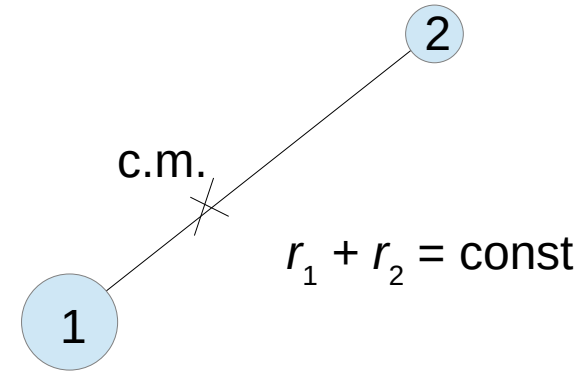
$$K = \frac{1}{2}I\omega^2 \overset{L=I\omega}{=} \frac{L^2}{2I}$$

moment of inertia about the center of mass

$$I = \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2$$

Hamiltonian $\quad \hat{H} = \dfrac{\hat{L}^2}{2I}$

Schrödinger equation $\quad \dfrac{\hat{L}^2}{2I}\psi = E\psi \qquad \Longleftrightarrow \qquad \hat{L}^2\psi = 2IE\psi$

eigenproblem for L^2

Example: The Rigid Rotor

$$\hat{L}^2 \psi = 2IE\psi$$

the Schrödinger equation is equivalent to the eigenproblem for L^2!

Solution

➔ eigenfunctions: spherical harmonics

➔ eigenvalues $\quad 2IE = \hbar^2 l(l+1), \qquad l = 0, 1, 2, \dots$

Hence, the energy levels of a rotating diatomic molecule

$$E_l = \frac{\hbar^2 l(l+1)}{2I}, \qquad l = 0, 1, 2, \dots$$
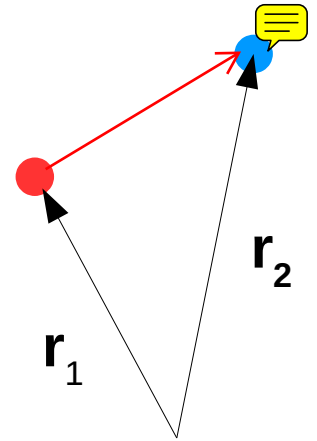
rotational levels

The Hydrogen Atom

Introduction

proton + electron = QM two-body problem
with a central force (Coulomb force)

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

By introducing

$$\bar{r} = \bar{r}_1 - \bar{r}_2 \quad - \text{relative position}$$

$$\bar{r}_{cm} = \frac{m_1\bar{r}_1 + m_2\bar{r}_2}{m_1 + m_2} \quad - \text{position of the center of mass}$$

the two-body problem can be reduced to two independent problems

(1) motion of the center of mass (free particle)

(2) relative motion – motion of an object with mass
in the central potential field V(r)
of the Coulomb force

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

"reduced mass"

Note that in the H atom mass of the proton
is much greater than that of electron, therefore $\mu \approx m_{electron}$.   * see Liboff, sec. 10.5 and 10.6 for details

Schrödinger Equation

We are interested in the relative motion. The stationary Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu} \nabla^2 + V(r) \right] \psi(\vec{r}) = E\psi(\vec{r})$$

Coulomb potential (central)

In spherical coordinates

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

$$\text{recall:} \quad = -\frac{\hat{L}^2}{\hbar^2}$$

Hence

$$\frac{\hat{p}_r^2}{2m} \longleftarrow \text{radial momentum}$$

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{L}^2}{2\mu r^2} + V(r) \right] \psi(r,\vartheta,\varphi) = E\psi(r,\vartheta,\varphi)$$

$$\hat{H}$$

Observation: Both operators representing L^2 and L_z commute with the Hamiltonian, hence they have common eigenfunctions. Therefore look for solutions in the form

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

Schrödinger Equation
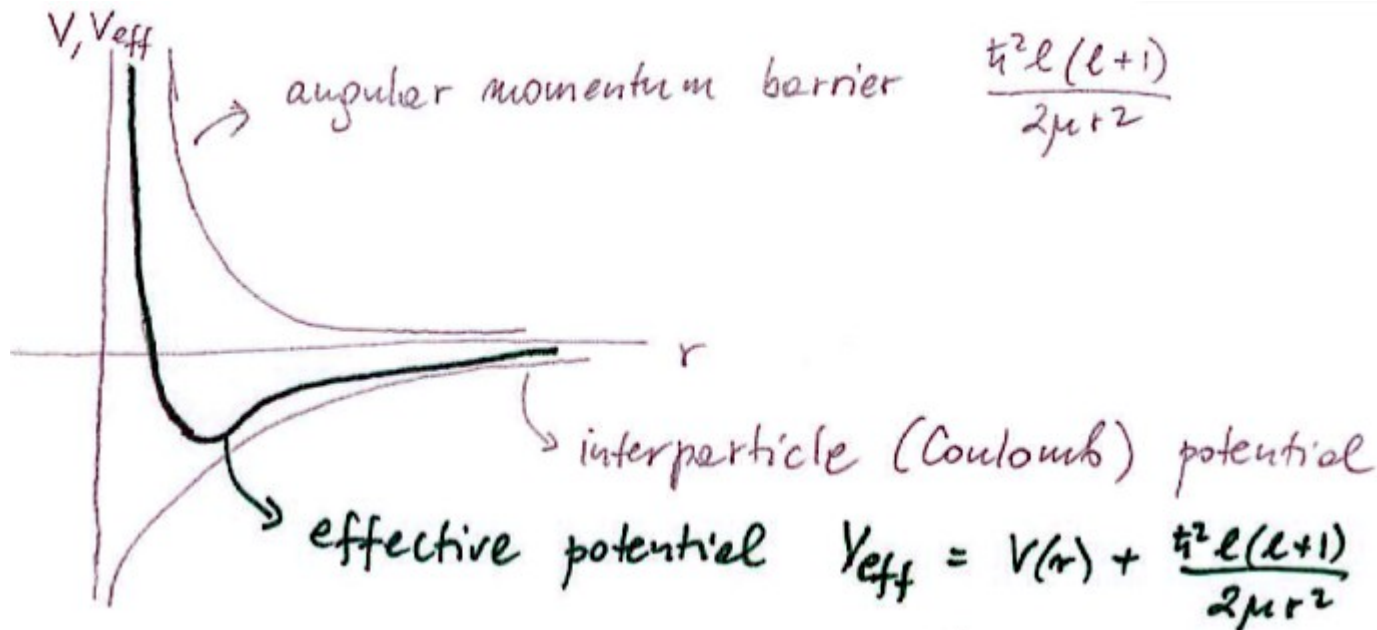
$$\psi = R(r)\, Y_{\ell m}(\vartheta, \varphi)$$

"radial" part   spherical harmonics

Hence the equation for the radial part

recall: $\hat{L}_z Y_{\ell m} = \hbar^2 \ell(\ell+1)\, Y_{\ell m}$

$$\left[-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \underbrace{\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)}_{V_{eff}(r)} \right] R(r) = E\, R(r)$$

V, V_{eff}

angular momentum barrier $\dfrac{\hbar^2\ell(\ell+1)}{2\mu r^2}$

r

interparticle (Coulomb) potential

effective potential $V_{eff} = V(r) + \dfrac{\hbar^2\ell(\ell+1)}{2\mu r^2}$

$l = 0, 1, 2, \ldots$

Schrödinger Equation. Solution

Solutions to the equation for the radial part giving a square-integrable wave function exist if

$$E = -\frac{E_1}{n^2}, \qquad n = 1, 2, 3, \ldots$$

$$l = 0, 1, 2, \ldots, n-1$$

$$m = -l, l-1+1, \ldots, 0, \ldots, l-1, l$$
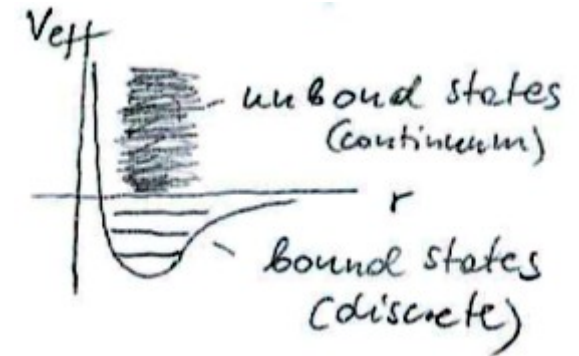
$$E_1 = \frac{\mu e^4}{32\pi^2\hbar^2\varepsilon_0} = 13.6 \text{ eV}$$

The corresponding radial function

$$R_{nl}(r) = A_{nl} e^{-\frac{r}{a_0 n}} r^l \mathcal{L}_{nl}\left(\frac{r}{a_0}\right)$$

where L_{nl} denote the associated Laguerre polynomials

Discussion of the Results: Energy Levels

$$E_n = -\frac{E_1}{n^2}, \qquad \psi(r, \vartheta, \phi) = Y_{lm}(\vartheta, \phi) R_{nl}(r)$$

$$n = 1, 2, 3, \ldots \qquad l = 0, 1, 2, \ldots, n-1$$

$$m = -l, l - 1 + 1, \ldots, 0, \ldots, l - 1, l$$

Features

➜ discrete spectrum of energy levels

➜ three quantum numbers: *n* (principal), *l* (orbital), *m* (magnetic)

➜ the energy depends **only** on the principal quantum number. Except for the ground state, there is more than one wave function corresponding to an energy level – energy levels are n^2-fold degenerate

$$f_n = \sum_{l=0}^{n-1} (2l + 1) = n^2$$

Discussion of the Results: Energy Levels

Features (contd)

➔ * for central forces that do not depend on the distance as $1/r^2$, the energy levels will depend on the orbital quantum number *l*

➔ the discussion can be generalized to find energy levels of H-like atoms (ions with *Z* protons in the nucleus and a single electron), then

$$E = -\frac{Z^2 E_1}{n^2}, \qquad n = 1, 2, 3, \ldots \quad l = 0, 1, 2, \ldots, n-1$$

$$m = -l, l - 1 + 1, \ldots, 0, \ldots, l - 1, l$$

➔ * if we place a hydrogen atom in an external magnetic field, the degeneracy due to *m* will be lifted, i.e. the energy levels will depend on *m* (an originally $(2l + 1)$-fold degenerate energy level will split into $(2l+1)$ energy levels); this is known as the *Zeeman effect*

(magnetic field breaks the symmetry, by distinguishing a direction in space)

Discussion of the Results: Energy Levels

allowed transitions between the energy levels must obey the *selection rules*

$$\Delta m = 0 \qquad \text{or} \qquad \pm 1$$

$$\Delta l = \pm 1$$

[* this result follows from the so-called time-dependent perturbation theory; probability of other transitions is zero]

Sharp
Principal
Diffuse
Fundamental
G, **H**,...

(states with same *n*, but different *l* shown separately)

FIGURE 7-6 Energy-level diagram for the hydrogen atom, showing transitions obeying the selection rule $\Delta\ell = \pm 1$. States with the same *n* value but different ℓ value have the same energy, $-E_1/n^2$, where $E_1 = 13.6$ eV, as in the Bohr theory. The wavelengths of the Lyman α ($n = 2 \rightarrow n = 1$) and Balmer α ($n = 3 \rightarrow n = 2$) lines are shown in nm. Note that the latter has three possible transitions due to the ℓ degeneracy.
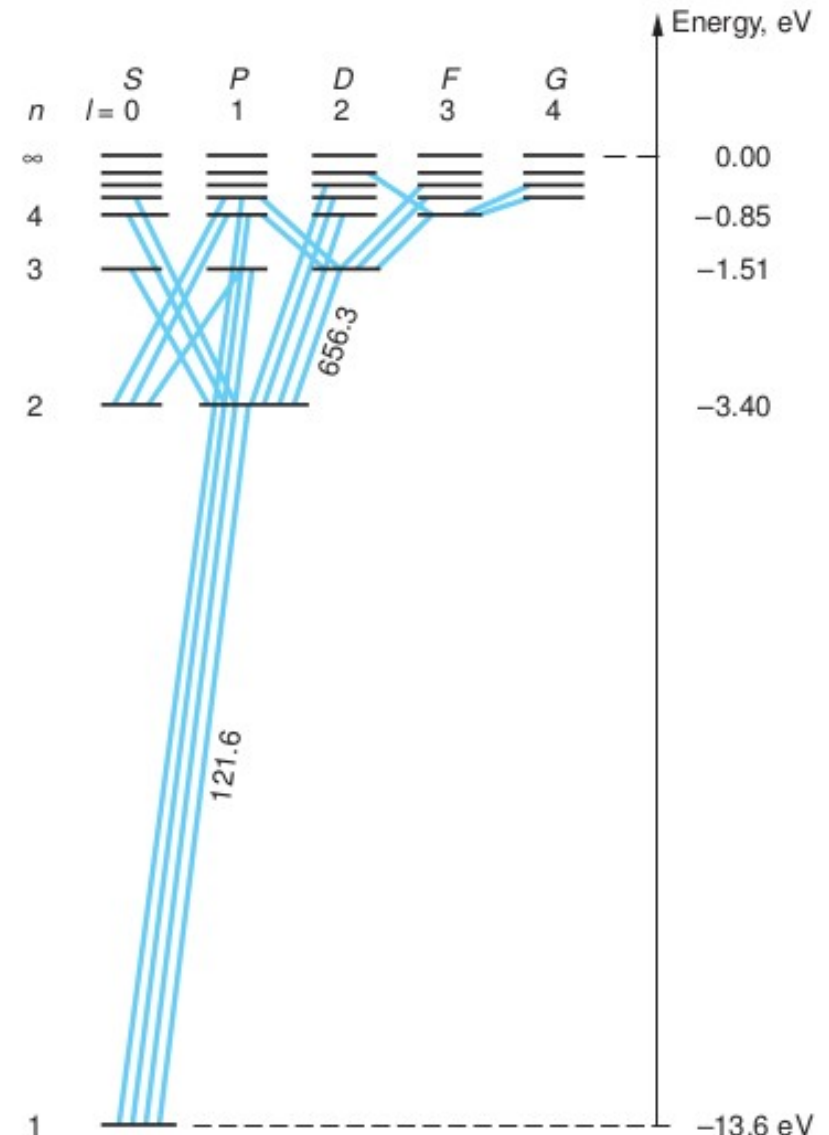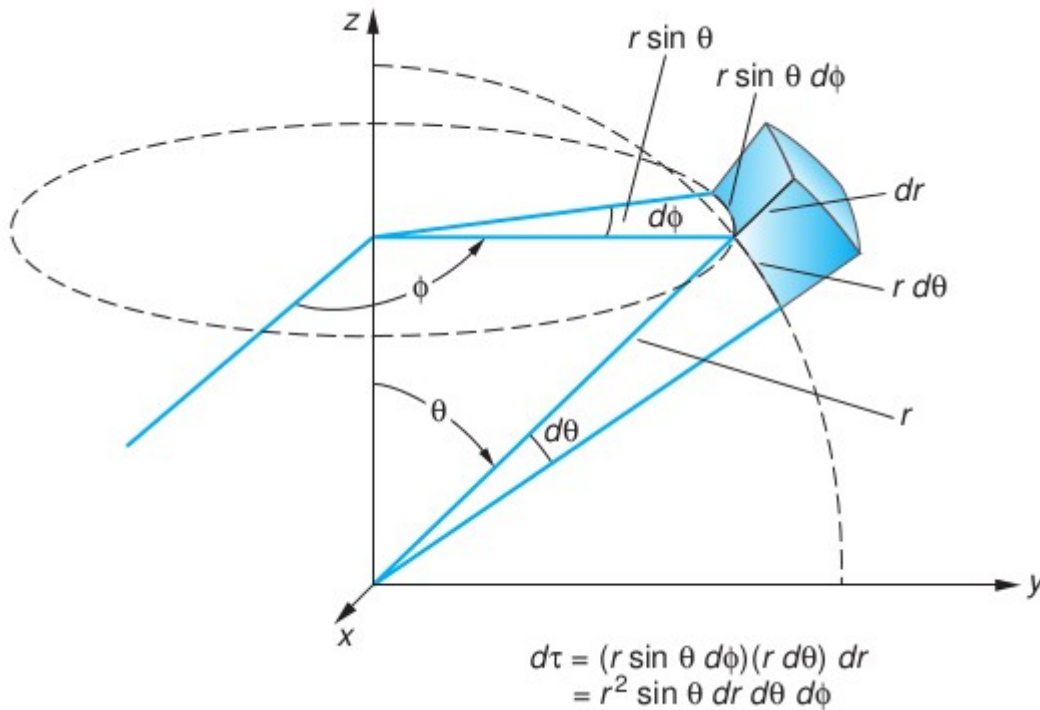
Discussion of the Results: Wave Functions

$$\psi(r, \vartheta, \phi) = Y_{lm}(\vartheta, \phi) R_{nl}(r)$$

Probability that the electron is in the infinitesimal element of volume $d\tau$ around the position (r, ϑ, ϕ) $\qquad |\psi|^2 \, d\tau$

Probability that the electron is a distance (r, $r+dr$) from the proton

$$P(r) \, dr \propto r^2 |R(r)|^2$$

Wave Function – The Ground State

$$\psi_{1,0,0}(r, \vartheta, \phi) = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-Zr/a_0}$$
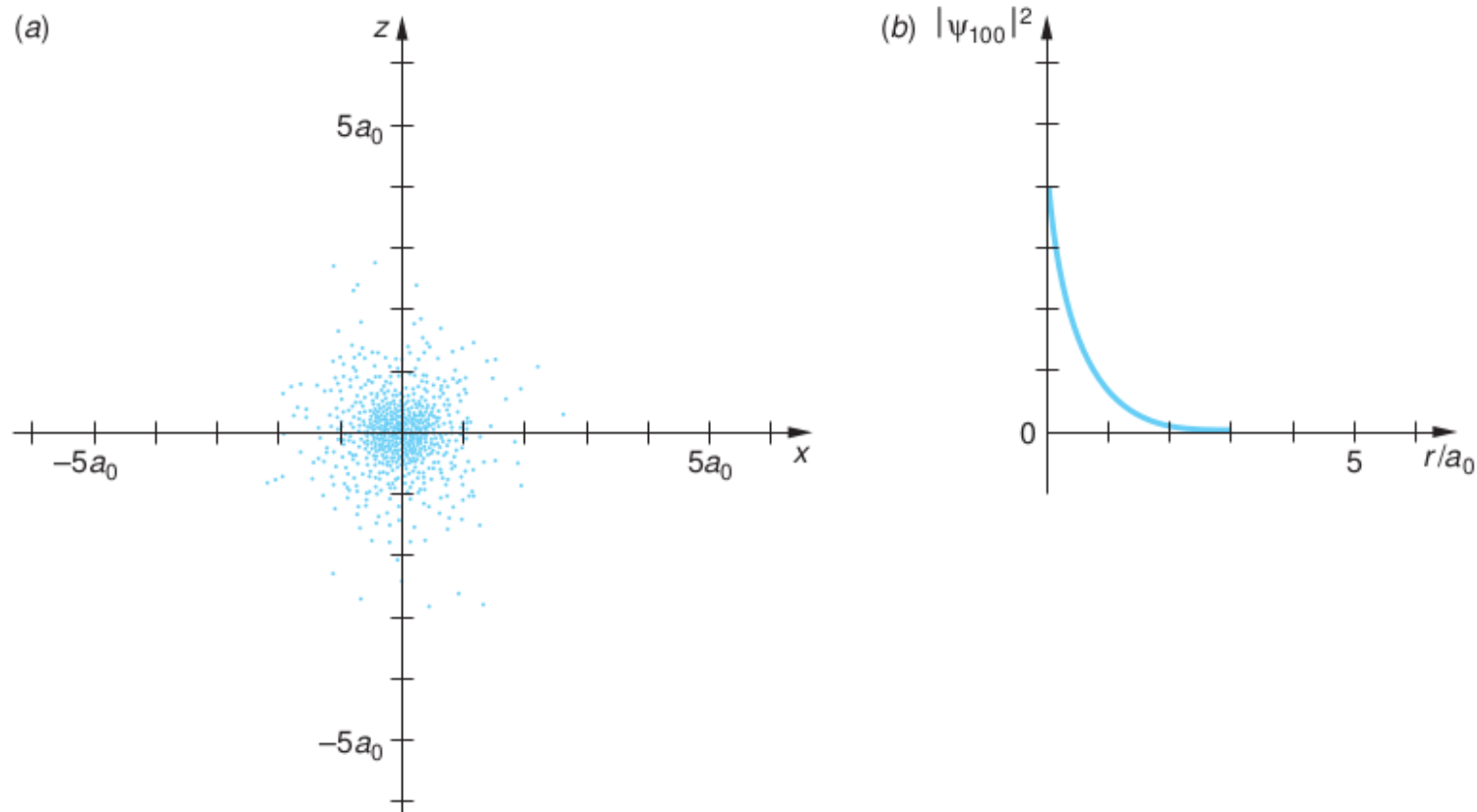

FIGURE 7-8 Probability density $\psi^*\psi$ for the ground state in hydrogen. The quantity $e\psi^*\psi$ can be thought of as the electron charge density in the atom. (*a*) The density is spherically symmetric, is greatest at the origin, and decreases exponentially with r. This computer-generated plot was made by making hundreds of "searches" for the hydrogen electron in the *x-z* plane (i.e., for $\phi = 0$), recording each finding with a dot. (*b*) The more conventional graph of the probability density $|\psi_{100}|^2$ vs. r/a_0. Compare the two graphs carefully. [*This computer-generated plot courtesy of Paul Doherty, The Exploratorium.*]
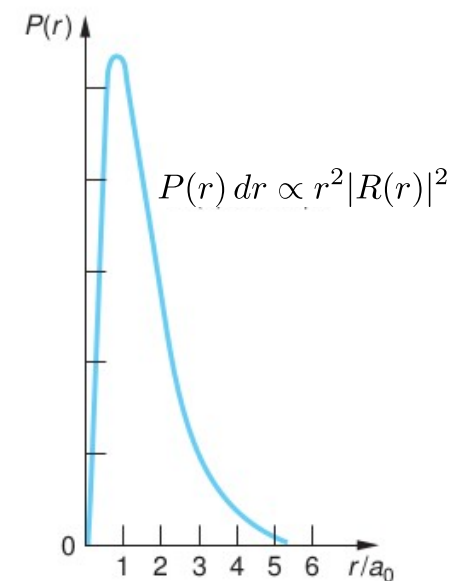
FIGURE 7-9 Radial probability density $P(r)$ versus r/a_0 for the ground state of the hydrogen atom. $P(r)$ is proportional to $r^2|\psi_{100}|^2$. The most probable distance r is the Bohr radius a_0.
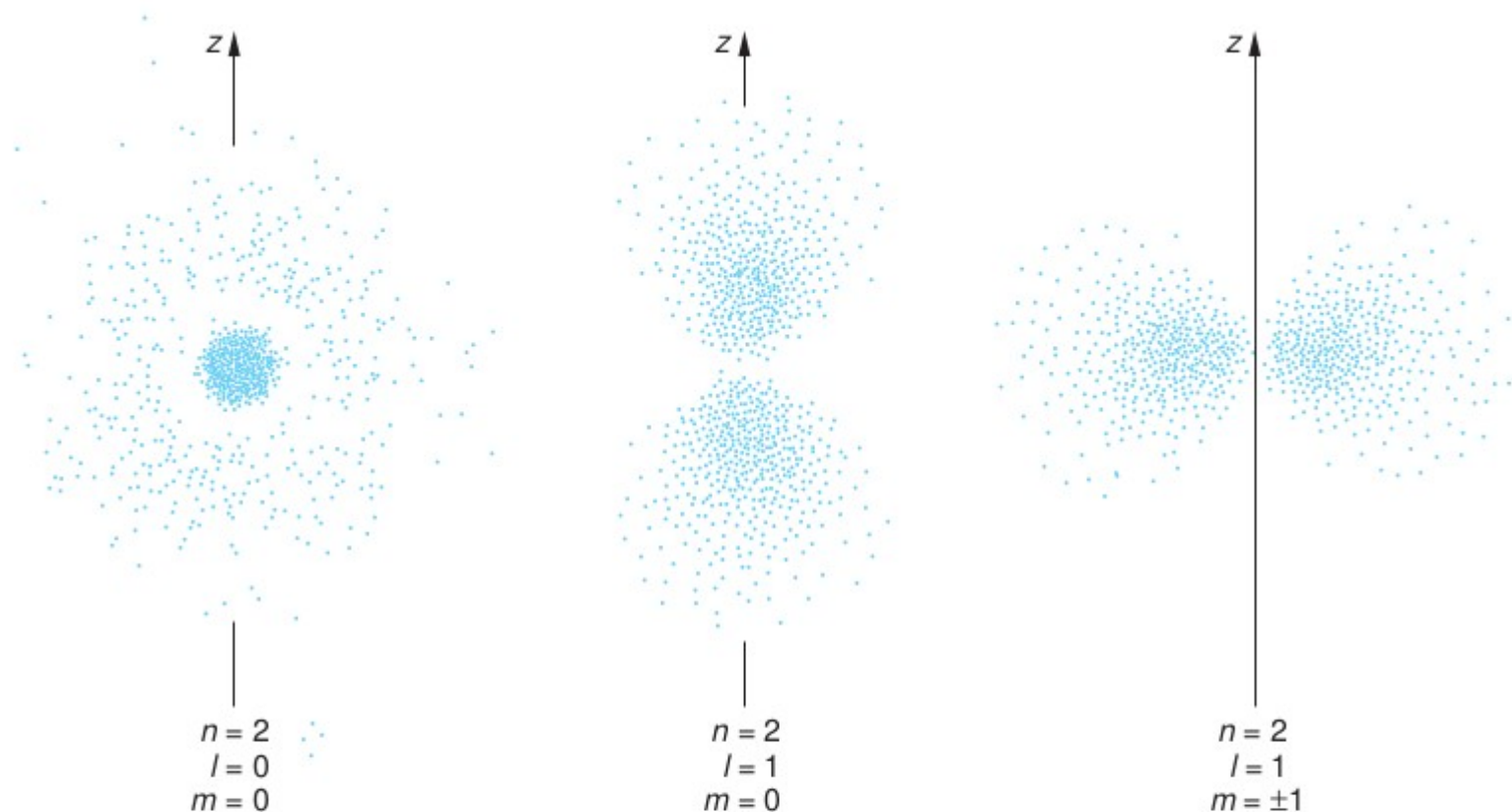
Wave Function – Excited States

FIGURE 7-11 Probability densities $\psi^*\psi$ for the $n = 2$ states in hydrogen. The probability is spherically symmetric for $\ell = 0$. It is proportional to $\cos^2\theta$ for $\ell = 1, m = 0$, and to $\sin^2\theta$ for $\ell = 1, m = \pm1$. The probability densities have rotational symmetry about the z axis. Thus, the three-dimensional charge density for the $\ell = 1, m = 0$ state is shaped roughly like a dumbbell, while that for the $\ell = 1, m = \pm1$ states resembles a doughnut, or toroid. The shapes of these distributions are typical for all atoms in S states ($\ell = 0$) and P states ($\ell = 1$) and play an important role in molecular bonding. [*This computer-generated plot courtesy of Paul Doherty, The Exploratorium.*]

Note. Wave functions of all states with l = 0 are spherically symmetric.

Wave Function – Excited States
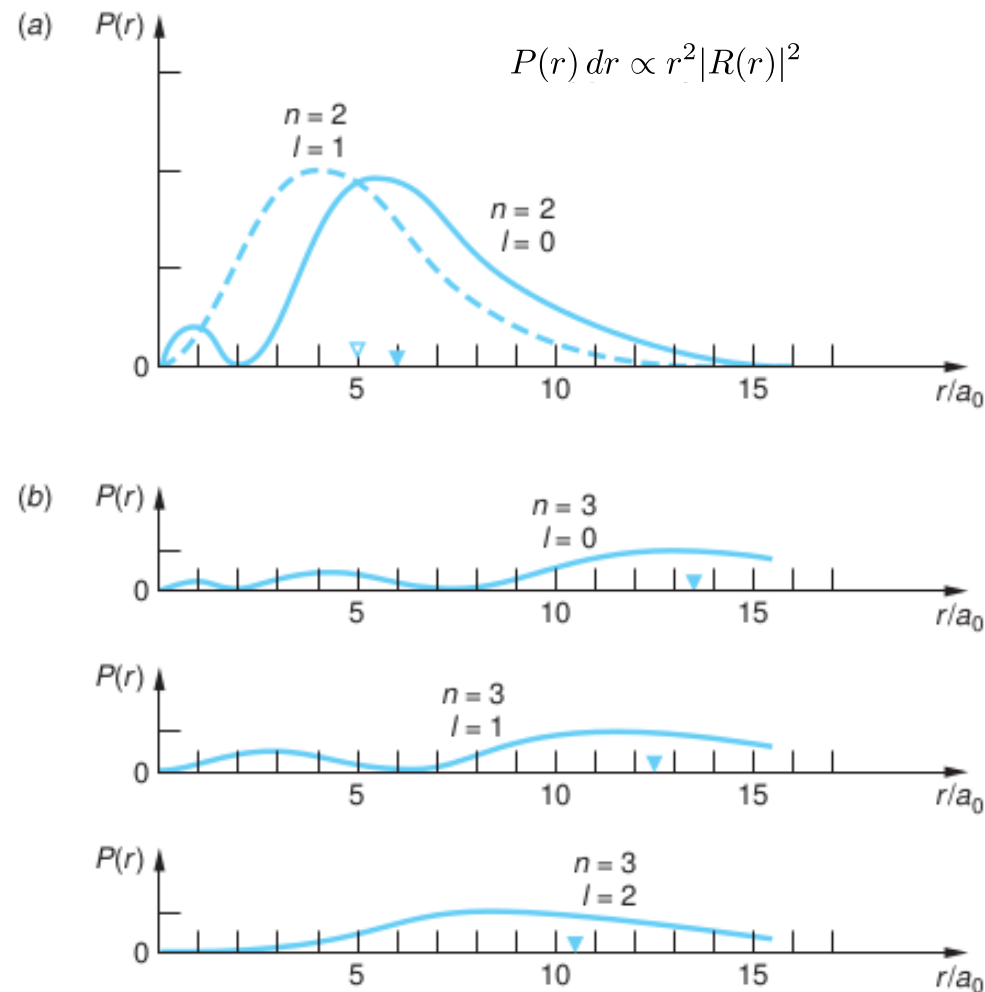

$$P(r)\,dr \propto r^2 |R(r)|^2$$

FIGURE 7-10 (a) Radial probability density $P(r)$ vs. r/a_0 for the $n=2$ states in hydrogen. $P(r)$ for $\ell = 1$ has a maximum at the Bohr value $2^2 a_0$. For $\ell = 0$, there is a maximum near this value and a smaller submaximum near the origin. The markers on the r/a_0 axis denote the values of $\langle r/a_0 \rangle$. (b) $P(r)$ vs. r/a_0 for the $n=3$ states in hydrogen.

Source: Tipler