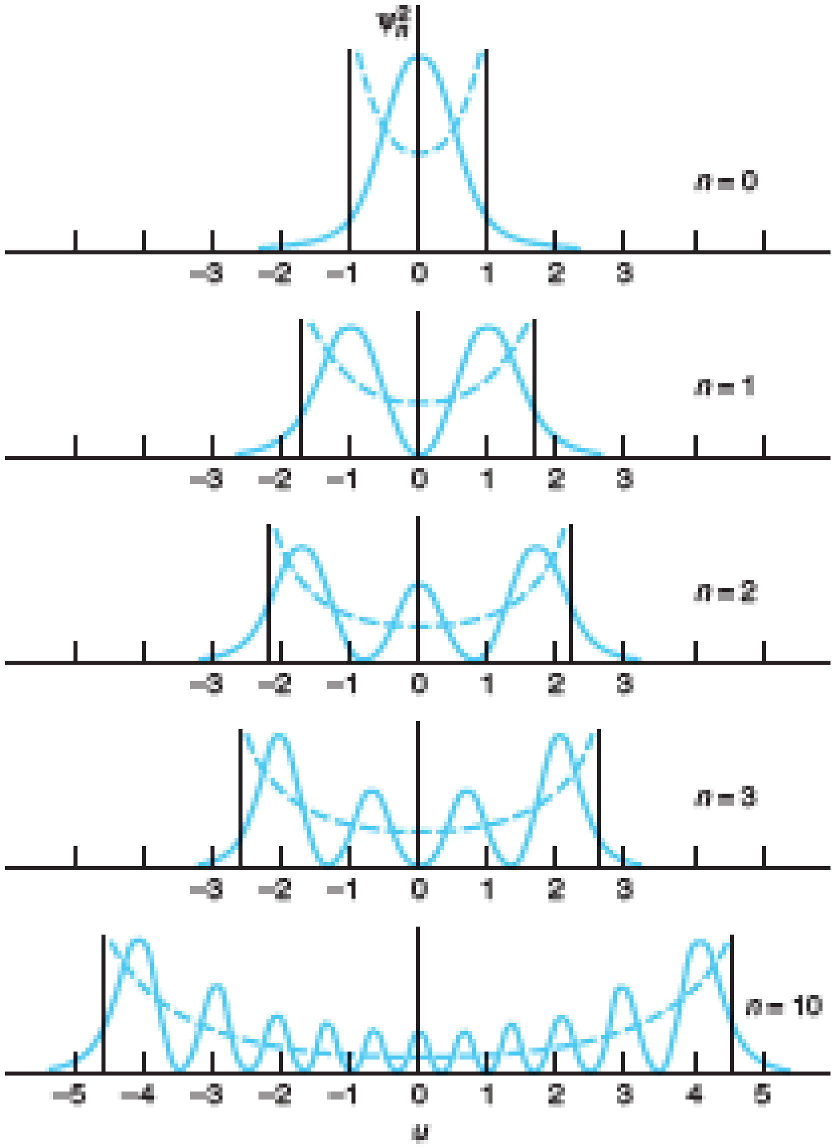
SIMPLE HARMONIC OSCILLATYOR



$$\psi_0(x) = A_0 e^{-m\omega x^2/2\hbar}$$

$$\psi_1(x) = A_1 \sqrt{\frac{m\omega}{\hbar}} e^{-m\omega x^2/2\hbar}$$

$$\psi_2(x) = A_2\left(1 - \frac{2m\omega x^2}{\hbar}\right) e^{-m\omega x^2/2\hbar}$$

- For the harmonic oscillator ground state n = 0, the Hermite polynomial Hn(x) $H_0 = 1$. Find (a) the normalization constant C_0
- (b) $\langle x^2 \rangle$
- (c) $\langle V(x) \rangle$ for this state. (Hint: Use the Probability Integral in Appendix B1 to compute the needed integrals.).

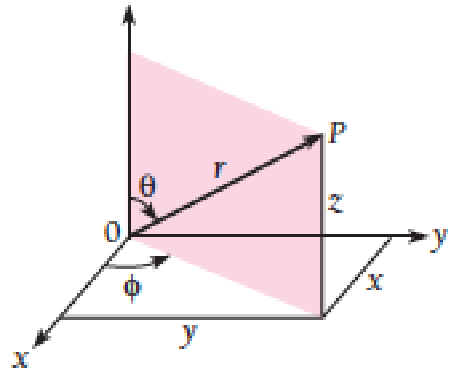
The general formula for $\langle x \rangle$ is

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,|\psi|^2\,dx$$

Quantum Theory of the Hydrogen Atom

- SCHRÖDINGER’S EQUATION FOR THE HYDROGEN ATOM

A hydrogen atom consists of a proton, a particle of electric charge e , and an electron, a particle of charge e which is 1836 times lighter than the proton. For the sake of convenience we shall consider the proton to be stationary, with the electron moving about in its vicinity but prevented from escaping by the proton’s electric field.



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

Schrödinger's equation for the electron in three dimensions

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}(E - U)\psi = 0$$

$$|p_x| = \hbar k_1 = n_1 \frac{\pi\hbar}{L} \qquad n_1 = 1, 2, \ . \ . \ .$$

$$|p_y| = \hbar k_2 = n_2 \frac{\pi\hbar}{L} \qquad n_2 = 1, 2, \ . \ . \ .$$

$$|p_z| = \hbar k_3 = n_3 \frac{\pi\hbar}{L} \qquad n_3 = 1, 2, \ . \ . \ .$$

Allowed values of momentum components for a particle in a box

Discrete energies allowed for a particle in a box

$$E = \frac{1}{2m}(|p_x|^2 + |p_y|^2 + |p_z|^2) = \frac{\pi^2\hbar^2}{2mL^2}\{n_1^2 + n_2^2 + n_3^2\}$$

The stationary states for particle in 3D box

$$\Psi(x, y, z, t) = A \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)e^{-i\omega t} \qquad \text{for } 0 < x, y, z < L$$
$$= 0 \qquad \text{otherwise}$$

Find the value of the multiplier A that normalizes the wave-function of Equation 8.10 having the lowest energy.

Solution The state of lowest energy is described by $n_1 = n_2 = n_3 = 1$, or $k_1 = k_2 = k_3 = \pi/L$. Since Ψ is nonzero only for $0 < x, y, z < L$, the probability density integrated over the volume of this cube must be unity:

$$1 = \int_0^L dx \int_0^L dy \int_0^L dz \, |\Psi(x, y, z, t)|^2$$

$$= A^2 \left\{ \int_0^L \sin^2(\pi x/L)\, dx \right\} \left\{ \int_0^L \sin^2(\pi y/L)\, dy \right\}$$

$$\times \left\{ \int_0^L \sin^2(\pi z/L)\, dz \right\}$$

Using $2 \sin^2 \theta = 1 - \cos 2\theta$ gives

$$\int_0^L \sin^2(\pi x/L)\, dx = \frac{L}{2} - \frac{L}{4\pi} \sin(2\pi x/L)\Big|_0^L = \frac{L}{2}$$

$$1 = A^2 \left(\frac{L}{2} \right)^3$$

$$A = \left(\frac{2}{L} \right)^{3/2}$$

Exercise 1 With what probability will the particle described by the wavefunction of Example 8.1 be found in the volume $0 < x, y, z < L/4$?

Answer 0.040,

Exercise 2 Modeling a defect trap in a crystal as a three-dimensional box with edge length 5.00 Å, find the values of momentum and energy for an electron bound to the defect site, assuming the electron is in the ground state.

Answer $|p_x| = |p_y| = |p_z| = 1.24\ \text{keV}/c$; $E = 4.51\ \text{eV}$

Degenerate Energy States

- The ground state which $n_1 = n_2 = n_3 = 1$, has energy

$$E_{111} = \frac{3\pi^2\hbar^2}{2mL^2}$$

- Whenever different states have the same energy, this energy level is said to be degenerate.

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2mL^2}$$

Schrödinger's equation in spherical polar coordinates

Hydrogen atom:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2m}{\hbar^2}(E-U)\psi=0$$

r = length of radius vector from origin

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

θ = angle between radius vector and $+z$ axis

= zenith angle

$= \cos^{-1}\frac{z}{\sqrt{x^2+y^2+z^2}}$

$= \cos^{-1}\frac{z}{r}$

ϕ = angle between the projection of the radius vector in the xy plane and the $+x$ axis, measured in the direction shown

= azimuth angle

$= \tan^{-1}\frac{y}{x}$

multiplying the entire equation by $r^2 \sin^2$

$$\sin^2\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial^2\psi}{\partial\phi^2}+\frac{2mr^2\sin^2\theta}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r}+E\right)\psi=0$$

the partial differential equation for the wave function of the electron in a hydrogen atom.

Electric potential energy

$$U=-\frac{e^2}{4\pi\epsilon_0 r}$$

Separation of variables for the stationary state wavefunction

$$\psi(\mathbf{r}) = \psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\sin^2\theta\left\{\frac{r^2}{R}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{1}{\Theta}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\frac{d\Theta}{d\theta}\right] + \frac{2mr^2}{\hbar^2}[E - U(r)]\right\}$$

divid by $R\Theta\Phi$

$$\frac{d^2\Phi}{d\phi^2} = -m_\ell^2\Phi(\phi)$$

m_l is the magnetic quantum number.

$$\frac{r^2}{R}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{2mr^2}{\hbar^2}[E - U(r)] = -\frac{1}{\Theta}\left[\frac{d^2\Theta}{d\theta^2} + \cot\theta\frac{d\Theta}{d\theta}\right] + \frac{m_\ell^2}{\sin^2\theta}$$

$$\frac{d^2\Theta}{d\theta^2} + \cot\theta \frac{d\Theta}{d\theta} - m_\ell^2 \csc^2\theta\, \Theta(\theta) = -\ell(\ell+1)\Theta(\theta)$$

l is called the orbital quantum number

Angular momentum and its z component are quantized

$$|\mathbf{L}| = \sqrt{\ell(\ell+1)}\hbar \qquad \ell = 0, 1, 2, \ldots$$

$\ell =$	0	1	2	3	4	5 . . .
Letter =	s	p	d	f	g	h . . .

$$L_z = m_\ell \hbar \qquad m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

Radial wave equation

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right] + \frac{\ell(\ell+1)\hbar^2}{2mr^2}R(r) + U(r)R(r) = ER(r)$$

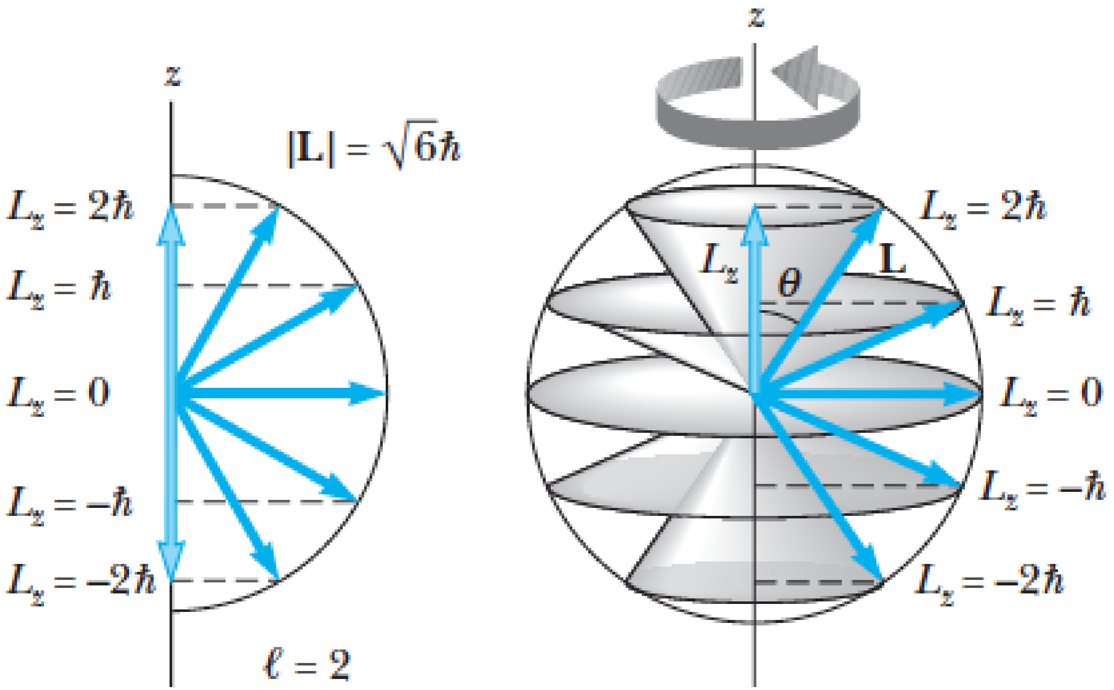
$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

SPACE QUANTIZATION

The fact that the direction of **L** is quantized with respect to an arbitrary axis (the z -axis) is referred to as space quantization.

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{\sqrt{\ell(\ell + 1)}}$$

The orientations of L are restricted (quantized)


z
$|\mathbf{L}| = \sqrt{6}\hbar$
$L_z = 2\hbar$
$L_z = \hbar$
$L_z = 0$
$L_z = -\hbar$
$L_z = -2\hbar$
$\ell = 2$
z
L_z
θ
$\mathbf{L}$
$L_z = 2\hbar$
$L_z = \hbar$
$L_z = 0$
$L_z = -\hbar$
$L_z = -2\hbar$

Consider an atomic electron in the $\ell = 3$ state. Calculate the magnitude $|\mathbf{L}|$ of the total angular momentum and the allowed values of L_z and θ.

$$|\mathbf{L}| = \sqrt{3(3+1)}\,\hbar = 2\sqrt{3}\,\hbar$$

The allowed values of L_z are $m_\ell \hbar$, with $m_\ell = 0, \pm 1, \pm 2,$ and ± 3. This gives

$$L_z = -3\hbar, -2\hbar, -\hbar, 0, \hbar, 2\hbar, 3\hbar$$

$$\cos\theta = \frac{L_z}{|\mathbf{L}|} = \frac{m_\ell}{2\sqrt{3}} \qquad \cos\theta = \pm 0.866, \quad \pm 0.577, \quad \pm 0.289, \quad \text{and} \quad 0$$

Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}}e^{-r/a_0}$
2	0	$\left(2-\frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta-1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta-3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta-1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Show that the hydrogen wave function ψ_{211} is normalized.

Strategy We refer to Equation (6.8) in Chapter 6 where we normalized the wave function in one dimension. Now we want to normalize the wave function in three dimensions in spherical polar coordinates. The normalization condition is

$$\int \psi^*_{n\ell m_\ell}\psi_{n\ell m_\ell}\, d\tau = 1 = \int \psi^*_{211}\psi_{211} r^2 \sin\theta\, dr\, d\theta\, d\phi \tag{7.18}$$

where $d\tau = r^2 \sin\theta\, dr\, d\theta\, d\phi$ is the volume element. We look up the wave function ψ_{211} using Tables 7.1 and 7.2.

$$\psi_{211} = R_{21}Y_{11} = \left[\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}\right]\left[\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta e^{i\phi}\right]$$

Solution We insert the wave function ψ_{211} into Equation (7.18), insert the integration limits for r, θ, and ϕ, and do the integration. First we find $\psi^*_{211}\psi_{211}$:

$$\psi^*_{211}\psi_{211} = \frac{1}{64\pi a_0^5} r^2 e^{-r/a_0}\sin^2\theta$$

where we have combined factors. The normalization condition from Equation (7.18) becomes

$$\int \psi^*_{211}\psi_{211} r^2 \sin\theta\, dr\, d\theta\, d\phi$$

$$= \frac{1}{64\pi a_0^5}\int_0^\infty r^4 e^{-r/a_0}\, dr \int_0^\pi \sin^3 d\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{64\pi a_0^5}[24a_0^5]\left[\frac{4}{3}\right][2\pi]$$

$$= 1$$

We have not shown all the steps in the integration, but we have shown the results of each integration in each of the square brackets. The integrals needed are in Appendix 3. The wave function is indeed normalized.