I. THE SOLUTION OF THE SCHRÖDINGER EQUATION IN THREE DIMENSIONS

A. Infinite square well in three dimensions

Consider the three-dimensional time-idependent Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})\,. \tag{1}$$

This is a three-dimensional partial differential equation and the approach to the solution of this equation depends very much on the character of the potential.

A simple example of this is to consider the three-dimensional version of a particle in a cubical box. The potenital is

$$\begin{aligned} V(\vec{r}) &= 0 \qquad\qquad \text{if} \quad 0 < x < L, \quad 0 < y < L, \quad 0 < z < L \\ V(\vec{r}) &= \infty \qquad\qquad \text{otherwise} \end{aligned} \tag{2}$$

The Schrödinger equation for this potential can be written in Cartesian coordinates as

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\psi(x,y,z) = E\psi(x,y,z), \qquad 0 \le x,y,z \le L \tag{3}$$

Similarly to one-dimensional case, the boundary conditions are

$$\psi(x,y,z) = 0 \quad \text{if} \quad \begin{cases} x < 0 \ \text{ or } \ x > L \\ \qquad \text{or} \\ y < 0 \ \text{ or } \ y > L \\ \qquad \text{or} \\ z < 0 \ \text{ or } \ z > L \end{cases}$$

which means that the wave function vanishes outside the box (and by continuity, on the sides of the box).

This equation can be solved using separation of variables by trying the ansatz

$$\psi(x,y,z) = X(x)Y(y)Z(z)\,. \tag{4}$$

Substituting this into the Schrödinger equation and dividing by the wave function gives

$$-\frac{\hbar^2}{2mX(x)}\frac{\partial^2 X(x)}{\partial x^2} - \frac{\hbar^2}{2mY(y)}\frac{\partial^2 Y(y)}{\partial y^2} - \frac{\hbar^2}{2mZ(z)}\frac{\partial^2 Z(z)}{\partial z^2} = E\,. \tag{5}$$

This clearly results in a separation of the three coordinates. If this equation is to be true for all possible values of x, y and z, it is necessary that each separated term be constant. This allows us, for example, to write

$$-\frac{\hbar^2}{2mX_{n_x}(x)}\frac{\partial^2 X_{n_1}(x)}{\partial x^2} \;=\; E_{n_1}\,, \tag{6}$$

or

$$-\frac{\hbar^2}{2m}\frac{\partial^2 X_{n_x}(x)}{\partial x^2} \;=\; E_{n_x}X_{n_x}(x)\,. \tag{7}$$

This is the equation for one-dimensional box with (normalized) solutions

$$X_{n_1}(x) \;=\; \sqrt{\frac{2}{L}}\sin k_1 x, \qquad k_1 \;=\; \frac{\pi n_1}{L} \tag{8}$$

vanishing at $x = 0, L$. The eigenvalue $E_{n_1} = \frac{\hbar^2 k_1^2}{2m} = \frac{p_x^2}{2m}$ where $p_x \equiv \hbar k_1$. Similarly, we get

$$\begin{aligned} Y_{n_2}(y) &= \sqrt{\frac{2}{L}}\sin k_2 y, \qquad k_2 = \frac{\pi n_2}{L}, \qquad E_{n_2} = \frac{\hbar^2 k_2^2}{2m} = \frac{p_y^2}{2m} \\ Z_{n_3}(z) &= \sqrt{\frac{2}{L}}\sin k_3 z, \qquad k_3 = \frac{\pi n_3}{L}, \qquad E_{n_3} = \frac{\hbar^2 k_3^2}{2m} = \frac{p_z^2}{2m} \end{aligned} \tag{9}$$

Thus, the solution of Schrödinger equation (5) is

$$\psi_{n_1,n_2,n_3}(x,y,z) \;=\; \Big(\frac{2}{L}\Big)^{\frac{3}{2}}\sin k_1 x \sin k_2 y \sin k_3 z \tag{10}$$

with energy

$$E_{n_1,n_2,n_3} \;=\; \frac{p_x^2 + p_y^2 + p_z^2}{2m} \;=\; \frac{\pi^2\hbar^2}{2m}(n_1^2 + n_2^2 + n_3^2) \tag{11}$$

The energy and wave function are characterized by three quantum numbers, each arising from a boundary condition on one of the coordinates.

In general, there are multiple combinations of n_1, n_2, n_3 leading to the same energy (14). An energy level that has more than one wave function associated with it is said to be degenerate. The ground state for this potential is non-degenerate

$$\psi_{111}(x,y,z) \;=\; \Big(\frac{2}{L}\Big)^{\frac{3}{2}}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}, \qquad E_0 \;=\; 3\frac{\hbar^2\pi^2}{2m} \tag{12}$$

but already the first excited state with energy $E_1 = 6\frac{\hbar^2\pi^2}{2m}$ has degeneracy 3:

$$\begin{aligned} \psi_{211} &= \Big(\frac{2}{L}\Big)^{\frac{3}{2}}\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{\pi z}{L}, \qquad E = 6\frac{\hbar^2\pi^2}{2m} \\ \psi_{121} &= \Big(\frac{2}{L}\Big)^{\frac{3}{2}}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}\sin\frac{\pi z}{L}, \qquad E = 6\frac{\hbar^2\pi^2}{2m} \\ \psi_{112} &= \Big(\frac{2}{L}\Big)^{\frac{3}{2}}\sin\frac{\pi x}{L}\sin\frac{\pi y}{L}\sin\frac{2\pi z}{L}, \qquad E = 6\frac{\hbar^2\pi^2}{2m} \end{aligned} \tag{13}$$

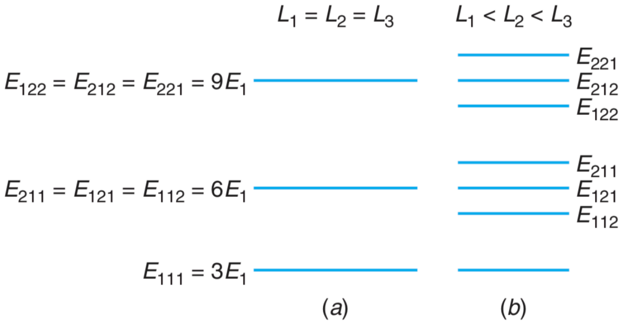


Figure 7-1 Energy-level diagram for (*a*) cubic infinite square well potential and (*b*) noncubic infinite square well. In the cubic well, the energy levels above the ground state are threefold degenerate; i.e., there are three wave functions having the same energy. The degeneracy is removed when the symmetry of the potential is removed, as in (*b*). The diagram is only schematic, and none of the levels in (*b*) necessarily has the same value of the energy as any level in (*a*).

The degeneracy is related to the symmetry of the problem, and anything that destroys or breaks the symmetry will also destroy or remove the degeneracy. If, for example, we considered a non-cubical box $V = 0$ for $0 < x < L_1$, $0 < y < L_2$, $0 < z < L_3$, the boundary condition at the walls would lead to the quantum conditions

$$k_1 L_1 \;=\; \pi n_1, \qquad k_2 L_2 \;=\; \pi n_2, \qquad k_3 L_3 \;=\; \pi n_3$$

and we will get

$$E_{n_1,n_2,n_3} \;=\; \frac{\hbar^2 \pi^2}{2m}(n_1^2 + n_2^2 + n_3^2) \tag{14}$$

Let us prove that wave functions corresponding to different energies are orthogonal

$$\int dV\;\psi^*_{m_1,m_2,m_3}(x,y,z)\psi_{n_1,n_2,n_3}(x,y,z) \;=\; 0 \qquad \text{if} \;\; E_{m_1,m_2,m_3} \neq E_{n_1,n_2,n_3} \tag{15}$$

Proof: consider

$$\int dV\;\psi^*_{m_1,m_2,m_3}(x,y,z)\hat{H}\psi_{n_1,n_2,n_3}(x,y,z) \;=$$
$$=\;\int dV\;\psi^*_{m_1,m_2,m_3}(x,y,z)\Big[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Big]\psi_{n_1,n_2,n_3}(x,y,z)$$

$$= E_{n_1,n_2,n_3} \int dV \ \psi^*_{m_1,m_2,m_3}(x,y,z)\psi_{n_1,n_2,n_3}(x,y,z) \tag{16}$$

because $\psi_{n_1,n_2,n_3}(x,y,z)$ is a solution of Schrödinger equation (3) with eigenvalue E_{n_1,n_2,n_3}. On the other hand, we can integrate r.h.s. of Eq. (16) two times by parts and get

$$\begin{aligned}
&\int dV \ \psi^*_{m_1,m_2,m_3}(x,y,z)\hat{H}\psi_{n_1,n_2,n_3}(x,y,z) \\
&= \int dV \ \psi^*_{m_1,m_2,m_3}(x,y,z)\Big[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Big]\psi_{n_1,n_2,n_3}(x,y,z) \\
&= \int dV \ \psi_{n_1,n_2,n_3}(x,y,z)\Big[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Big]\psi^*_{m_1,m_2,m_3}(x,y,z) \\
&= E_{m_1,m_2,m_3} \int dV \ \psi_{n_1,n_2,n_3}(x,y,z)\psi^*_{m_1,m_2,m_3}(x,y,z)
\end{aligned} \tag{17}$$

since $\psi^*_{m_1,m_2,m_3}(x,y,z)$ is a solution of Schrödinger equation (3) with eigenvalue E_{m_1,m_2,m_3} (recall that energies are real). Comparing two expressions (16) and (17) we see that

$$\int dV \ \psi^*_{m_1,m_2,m_3}(x,y,z)\psi_{n_1,n_2,n_3}(x,y,z) \ = \ 0 \tag{18}$$

unless $E_{m_1,m_2,m_3} = E_{n_1,n_2,n_3}$. This is a general property: wave functions corresponding to states with different energies are orthogonal.

Mathematical statement: eigenfunctions of a *Hermitian* operator corresponding to different eigenvalues are orthogonal. (Hermitian operator ≡ operator with only real eigenvalues).

II. THE SCHRÖDINGER EQUATION WITH A CENTRAL POTENTIAL

We now consider the solution of the three-dimensional time-independent Schrödinger equation for a central potential

$$V(\boldsymbol{r}) = V(|\boldsymbol{r}|) = V(r)\,. \tag{19}$$

For example, for Coulomb potential of electron $V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}$ where Ze is the charge of the nucleus.

Since the potential depends only on the distance from the origin, the Hamiltonian is spherically symmetric. It is therefore convenient to represent the Schrödinger equation in terms of the standard spherical coordinate system shown in Fig. 4.

$$\left.\begin{array}{lcl} x &=& r\sin\theta\cos\phi \\ y &=& r\sin\theta\sin\phi \\ z &=& r\cos\phi \end{array}\right\} \Leftrightarrow \left\{\begin{array}{lcl} r &=& \sqrt{x^2+y^2+z^2} \\ \theta &=& \arccos\frac{z}{r} \\ \phi &=& \arctan\frac{y}{x} \end{array}\right. \tag{20}$$

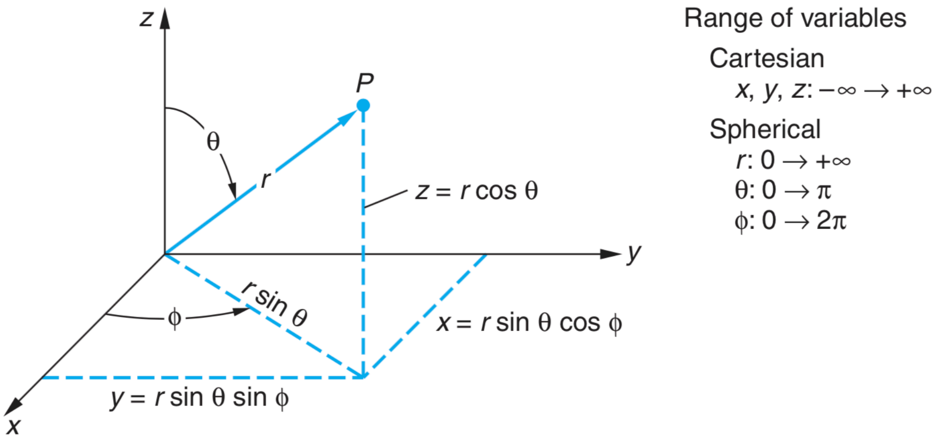


FIG. 1. The spherical coordinate system.

It can be demonstrated that for $f(x,y,z) \;=\; F(r,\theta,\phi)$

$$\Big(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\Big)F(r,\theta,\phi) \;=\; \Big(\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big)F(r,\theta,\phi) \tag{21}$$

and therefore the statiponary Schrödinger equation in spherical coordinates can be written as

$$\left\{-\frac{\hbar^2}{2m}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]+V(r)\right\}\psi(r,\theta,\phi) \;=\; E\psi(r,\theta,\phi)\,. \tag{22}$$

This can be simplified by treating it as a mathematical problem. We will proceed to do this and then will explore the physical consequences afterward.

A. Solution of Schrödinger equation in spherical potential by separation of variables

The standard approach to solving partial differential equations is to use the method of separation of variables, which we have already used several times. We assume that the wave function is a product of functions each depending upon a single variable. Let

$$\psi(r,\theta,\phi) = R(r)P(\theta)Q(\phi)\,. \tag{23}$$

Substituting this into (22), dividing both sides by $R(r)P(\theta)Q(\phi)$ and multiplying both sides by $\frac{2m}{\hbar^2}\, r^2 \sin^2\theta$ gives

$$\frac{r\sin^2\theta}{R(r)}\frac{\partial^2}{\partial r^2}\, rR(r) + \frac{\sin\theta}{P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}P(\theta)\right) + \frac{2m}{\hbar^2}\, r^2\sin^2\theta\,(E - V(r)) + \frac{1}{Q(\phi)}\frac{\partial^2}{\partial\phi^2}\, Q(\phi) = 0\,. \tag{24}$$

Note that only the last term depends upon ϕ and that no other variable appears in this term. This equation can be true for all values of r, θ and ϕ only if the last term is equal to a constant. Let

$$\frac{1}{Q(\phi)}\frac{\partial^2}{\partial\phi^2}\, Q(\phi) = -m^2\,. \tag{25}$$

This is can be rewritten as

$$\frac{\partial^2}{\partial\phi^2}\, Q(\phi) + m^2 Q(\phi) = 0\,. \tag{26}$$

This is the familiar harmonic equation that has solutions of the form

$$Q(\phi) = e^{im\phi}\,. \tag{27}$$

Since the solution must satisfy $Q(\phi) = Q(\phi + 2\pi)$, the constant m must be an integer.

Using (25) in (24), and dividing both sides by $\sin^2\theta$ gives

$$\frac{r}{R(r)}\frac{\partial^2}{\partial r^2}\, rR(r) + \frac{2m}{\hbar^2} r^2\,(E - V(r)) + \frac{1}{\sin\theta P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\, P(\theta)\right) - \frac{m^2}{\sin^2\theta} = 0\,. \tag{28}$$

Here the first two terms depend only upon r while the third and fourth terms depend only upon θ. For this equation to be satisfied for all possible values of r and θ, the third and forth terms must add to a constant. Let

$$\frac{1}{\sin\theta P(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\, P(\theta)\right) - \frac{m^2}{\sin^2\theta} = -l(l+1)\,. \tag{29}$$

(we will show later that l is integer). This can be rewritten as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\, P(\theta)\right) - \frac{m^2}{\sin^2\theta}P(\theta) + l(l+1)P(\theta) = 0\,. \tag{30}$$

The solution to this equation is simplified by changing variables to $x = \cos\theta$. In terms of the new variable (30) becomes

$$\frac{\partial}{\partial x}\left(\left(1 - x^2\right)\frac{\partial}{\partial x}P(x)\right) + \left(l(l+1) - \frac{m^2}{1 - x^2}\right)P(x) = 0\,. \tag{31}$$

This is Legendre's equation and is known to have finite solutions on the interval $-1 \leq x \leq 1$ only if l is an integer with $l \geq 0$.

First consider the solutions for m=0. These solutions are the Legendre polynomials $P_l(x)$. Traditionally these polynomials are normalized such that

$$P_l(1) = 1 \tag{32}$$

and the first few solutions are

$$P_0(x) = 1 \tag{33}$$

$$P_1(x) = x \tag{34}$$

$$P_2(x) = \frac{1}{2}\left(3x^2 - 1\right) \tag{35}$$

$$P_3(x) = \frac{1}{2}\left(5x^3 - 3x\right) \tag{36}$$

Note that these are polynomials of order l and that they are even when l is even and odd when l is odd.

For $m \neq 0$, the solutions to (31) are the associated Legendre functions. For $m > 0$ the associated Legendre functions are given by

$$P_l^m(x) = \left(1 - x^2\right)^{\frac{m}{2}} \frac{d^m}{dx^m} P_l(x)\,. \tag{37}$$

$$P_l^{-m}(x) \equiv (-1)^m \frac{(l-m)!}{(l+m)!} P_l^m(x)\,. \tag{38}$$

The permissable values of m are then given by $-l \leq m \leq l$.

B. Spherical Harmonics

We now have solutions for angular functions $Q(\phi)$ and $P(\theta)$. It is convenient to combine these into a single normalized function of both angles. These functions are called the *spherical harmonics* and are defined as

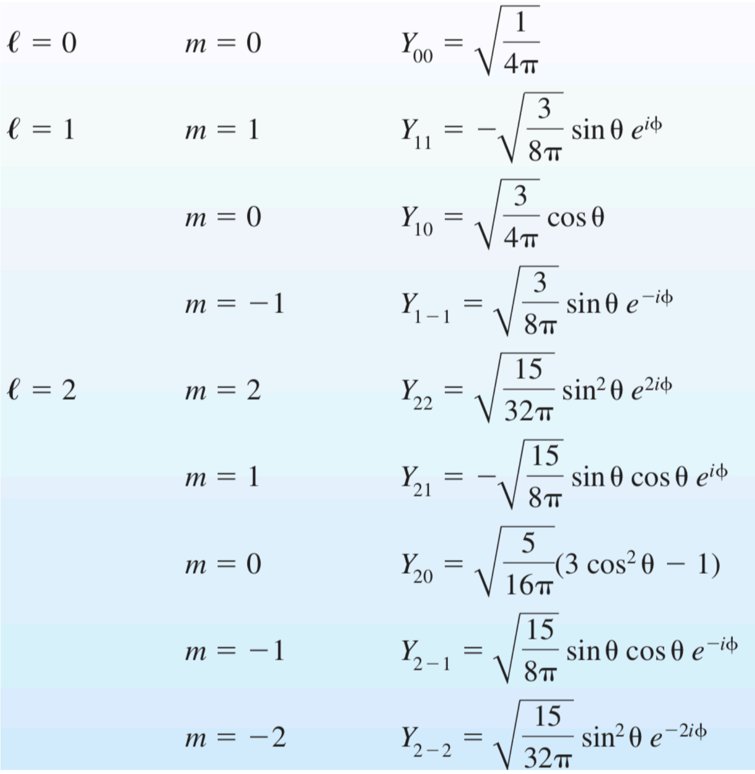
$$Y_{lm}(\theta,\phi) = (-1)^m \left[\frac{(2l+1)(l-m)!}{4\pi(l+m)!}\right]^{\frac{1}{2}} P_l^m(\cos\theta) e^{im\phi}\,. \tag{39}$$

In particular,

$$Y_{l0}(\theta,\phi) = \sqrt{\frac{2l+1}{4\pi}}\, P_l(cos\theta) \tag{40}$$

As we saw above, spherical harmonics are solutions of the equation

$$-\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]Y_{lm}(\theta,\phi) \;=\; l(l+1)Y_{lm}(\theta,\phi) \tag{41}$$



$\ell = 0$	$m = 0$	$Y_{00} = \sqrt{\frac{1}{4\pi}}$
$\ell = 1$	$m = 1$	$Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin\theta\, e^{i\phi}$
	$m = 0$	$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta$
	$m = -1$	$Y_{1-1} = \sqrt{\frac{3}{8\pi}} \sin\theta\, e^{-i\phi}$
$\ell = 2$	$m = 2$	$Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{2i\phi}$
	$m = 1$	$Y_{21} = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{i\phi}$
	$m = 0$	$Y_{20} = \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$
	$m = -1$	$Y_{2-1} = \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta\, e^{-i\phi}$
	$m = -2$	$Y_{2-2} = \sqrt{\frac{15}{32\pi}} \sin^2\theta\, e^{-2i\phi}$

FIG. 2. First few spherical harmonics.

The spherical harmonics are *orthonormal* (≡ orthogonal and normalized)

$$\int d\Omega\, Y^*_{l'm'}(\theta,\phi) Y_{lm}(\theta,\phi) \;\equiv \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi\, Y^*_{l'm'}(\theta,\phi) Y_{lm}(\theta,\phi) \;=\; \delta_{ll'}\delta_{mm'} \tag{42}$$

where δ_{mn} is the Kronecker symbol: $\delta_{mn} = 1$ if $m = n$ and $\delta_{mn} = 0$ otherwise.

We will see later that the differential operator in the l.h.s. of this equation has a meaning of operator of square of angular momentum (up to factor $\hbar^2$).

III. QUANTIZATION OF ANGULAR MOMENTUM

From our discussion of Rutherford scattering in classical mechanics:

For a particle in central potential, the classical motion lies in a fixed plane perpendicular to angular momentum $\vec{L}$, which contains the coordinate origin.

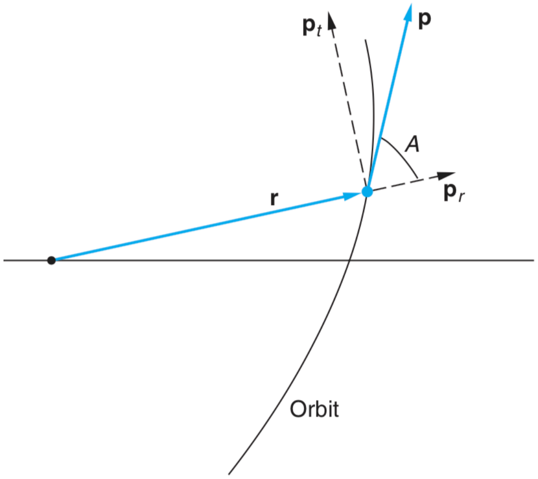


Figure 7-3 The orbit of a classical particle with $V = V(r)$ lies in a plane perpendicular to **L**. The components of the momentum **p** parallel and perpendicular to **r** are $\mathbf{p}_\mathbf{r}$ and $\mathbf{p}_\mathbf{t}$, respectively. The momentum **p** makes an angle A with the displacement **r**.

FIG. 3. Motion of a classical particle in the central potential.

Moreover, assuming the motion occurs in the x, y plane, we have derived that due to the conservation of angular momentum

$$L_z \;=\; mr^2\dot{\phi} \;=\; \text{const} \tag{43}$$

the problem of motion of a particle in a central potential $V(r)$ can be reduced to 1-dimensional problem with an "effective potential":

$$V_{\text{eff}}(r) \;\equiv\; V(r) + \frac{m}{2}\frac{L^2}{m^2r^2} \tag{44}$$

Thus, the energy of a particle in central potential is equal to the energy of a particle moving in one dimension (at $r > 0$) in the effective potential $V_{\text{eff}}(r)$

$$E \;=\; \frac{m}{2}\dot{r}^2 + V_{\text{eff}}(r) \tag{45}$$

For our purposes, it is convenient to rewrite this formula in terms of components of momentum

$$E \;=\; \frac{p_r^2}{2m} + V_{\text{eff}}(r) \;=\; \frac{p_r^2}{2m} + \frac{L^2}{2mr^2} + V(r) \tag{46}$$

where $p_r = m\dot{r}$ is the component of momentum along the radial direction.

Let us look then at the Schrödinger equation (22)

$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r - \frac{\hbar^2}{2m}\left[\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r)\right\}\psi(r,\theta,\phi) \;=\; E\psi(r,\theta,\phi)\,. \tag{47}$$

It is possible to show that quantum mechanical operator corresponding to p_r^2 is

$$\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$$

and comparing Eqs. (46) and (47) we see that the second term in the l.h.s. of Eq. (47) should be identified with operator of square angular momentum

$$\hat{L}^2\psi(r,\theta,\phi) \;=\; -\hbar^2\Big[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\Big(\sin\theta\frac{\partial}{\partial\theta}\Big) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\Big]\psi(r,\theta,\phi) \tag{48}$$

As we saw from the solution of Eq. (41), eigenfunctions of this operators are spherical harmonics and eigenvalues are $l(l+1)$:

$$\hat{L}^2 Y_{lm}(\theta,\phi) \;=\; \hbar^2 l(l+1) Y_{lm}(\theta,\phi) \tag{49}$$

Thus, we have the very important result that, for all potentials where $V = V(r)$ the angular momentum is quantized and its allowed magnitudes (eigenvalues) are given by

$$L = |\vec{L}| = \hbar\sqrt{l(l+1)} \tag{50}$$

where l is referred to as the angular momentum quantum number or the orbital quantum number.

In addition, from the form of the operator of z-component of angular momentum (see Table 6-1)

$$\hat{L}_z \;=\; -i\hbar\frac{\partial}{\partial\phi} \tag{51}$$

we see that the z component of the angular momentum is also quantized

$$\hat{L}_z e^{\pm im\phi} \;=\; m\hbar e^{\pm im\phi} \tag{52}$$

and its allowed values are given by

$$L_z \;=\; m\hbar, \qquad m \;=\; 0, \pm 1, \pm 2, ... \pm l \tag{53}$$

The physical significance of Equation (50) is that the angular momentum L, whose magnitude is quantized with values $\hbar\sqrt{l(l+1)}$, can only point in those directions in space such that the projection of L on the z axis is one or another of the values given by $m\hbar$. Thus, L is also space quantized. The quantum number m is referred to as the magnetic quantum number.

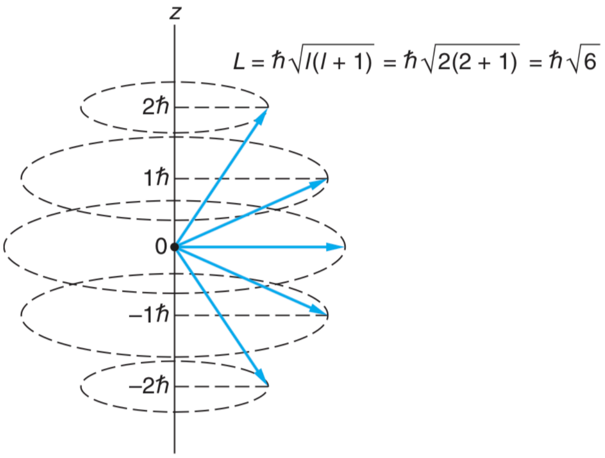


Figure 7-4 Vector model illustrating the possible orientations of **L** in space and the possible values of L_z for the case where $\ell = 2$.

FIG. 4. Quantization of vector of spin.

IV. THE COULOMB POTENTIAL

A. The Radial Equation

Substituting (29) into (28) gives

$$\frac{r}{R(r)}\frac{\partial^2}{\partial r^2} rR(r) + \frac{2m}{\hbar^2} r^2 \left(E - V(r)\right) - l(l+1) = 0\,, \tag{54}$$

which can be rewritten as

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2}r - \frac{l(l+1)}{r^2}\right) R(r) + V(r)R(r) = ER(r)\,. \tag{55}$$

This is the eigenvalue equation for the radial coordinate and since it explicitly depends upon the integer l, the eigenfunctions will in general be represented by $R_{nl}(r)$ where n is the energy quantum number.

The complete solutions of the Schrödinger equation can then written as

$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{56}$$

where the particular form of $R_{nl}(r)$ will depend upon the choice of potential $V(r)$. Note that the wave function not only depends on the energy quantum n but also on l and m.

The wave functions for bound states must be normalizable. That is

$$\int d^3r \psi^*_{nlm}(\boldsymbol{r})\psi_{nlm}(\boldsymbol{r}) = 1 \,. \tag{57}$$

This implies that

$$1 = \int_0^\infty dr\, r^2 R^2_{nl}(r) \int_0^{2\pi} d\phi \int_0^\pi d\theta \;\; \sin\theta \; Y^*_{lm}(\theta,\phi) Y_{lm}(\theta,\phi) = \int_0^\infty dr\, r^2 R^2_{nl}(r) \,. \tag{58}$$

Also, the wave functions are orthogonal, so we have the *orthonormal set* $\psi_{nlm}(r,\theta,\phi)$

$$\begin{aligned} &\int d^3x \psi^*_{n'l'm'}(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) \\ &= \int_0^\infty dr\, r^2 R^*_{n'l'}(r) R_{nl}(r) \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin\theta \; Y^*_{lm}(\theta,\phi) Y_{lm}(\theta,\phi) \;=\; \delta_{nn'}\delta_{ll'}\delta_{mm'} \end{aligned} \tag{59}$$

B. Radial equation for Coulomb potential

A simple version of hydrogen-like atoms can be obtained by solving the Schrödinger equation with a Coulomb potential

$$V(r) = -\frac{Zke^2}{r} \,. \tag{60}$$

Strictly speaking, the parameter m in the Schrödinger equation for the electron in the atom should be a "reduced mass" $m = \frac{m_{\text{electron}} M_{\text{nucleus}}}{m_{\text{electron}} + M_{\text{nucleus}}}$ but since $M_{\text{nucleus}} \gg m_{\text{electron}}$ our m can be identified with electron's mass.

We will focus on the bound state solutions of the Schrödinger equation which will occur for negative energies. That is where $E = -|E|$. In this case we can write the radial equation as

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r}\frac{d^2}{dr^2} r - \frac{l(l+1)}{r^2}\right) R(r) - \frac{Zke^2}{r} R(r) = -|E| R(r) \,. \tag{61}$$

Multiplying both sides by $-\frac{2m}{\hbar^2}$, moving all terms to the left-hand side and expanding the second derivative term gives

$$\left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2mZe^2}{\hbar^2 r} - \frac{2m|E|}{\hbar^2}\right) R(r) = 0 \,. \tag{62}$$

It is convenient to define a dimensionless radial variable

$$\rho = \sqrt{\frac{8m|E|}{\hbar^2}}\, r \,. \tag{63}$$

The radial wave equation in terms of ρ is then

$$\left(\frac{d^2}{d\rho^2} + \frac{2}{\rho}\frac{d}{d\rho} - \frac{l(l+1)}{\rho^2} + \frac{\lambda}{\rho} - \frac{1}{4}\right) R(\rho) = 0\,, \tag{64}$$

where

$$\lambda = \frac{2mZke^2}{\beta\hbar^2} = \frac{Zke^2}{\hbar}\sqrt{\frac{m}{2|E|}} = Z\alpha\sqrt{\frac{mc^2}{2|E|}}\,, \tag{65}$$

and

$$\alpha = \frac{e^2k}{\hbar c} \simeq \frac{1}{137} \tag{66}$$

is the fine structure constant ($k \equiv \frac{1}{4\pi\epsilon_0}$).

It can be demonstrated that in order for the function $R(\rho)$ to be normalizable (see Eq. (58) the constant λ must be integer greater than l

$$\lambda = n = n' + l + 1 \tag{67}$$

where $n' \geq 0$ is called *radial quantum number* and n *total quantum number*.

Using our previous definition (65) of λ we get

$$n = Z\alpha\sqrt{\frac{mc^2}{2|E|}}\,. \tag{68}$$

and therefore

$$E_n = -|E_n| = -\frac{Z^2\alpha^2mc^2}{2n^2}\,, \tag{69}$$

which is in agreement with the energy spectrum of the Bohr atom.

For future use, we will also need the explicit form of the dimensionles variable ρ

$$\rho = \frac{\sqrt{8m|E|}}{\hbar} = \frac{2Z}{a_0 n} \tag{70}$$

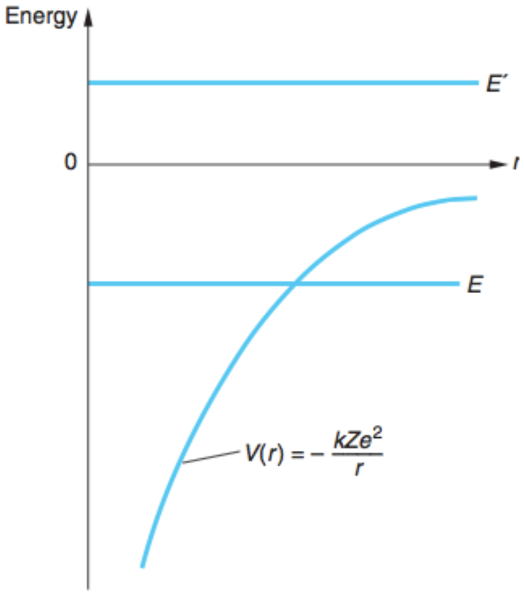


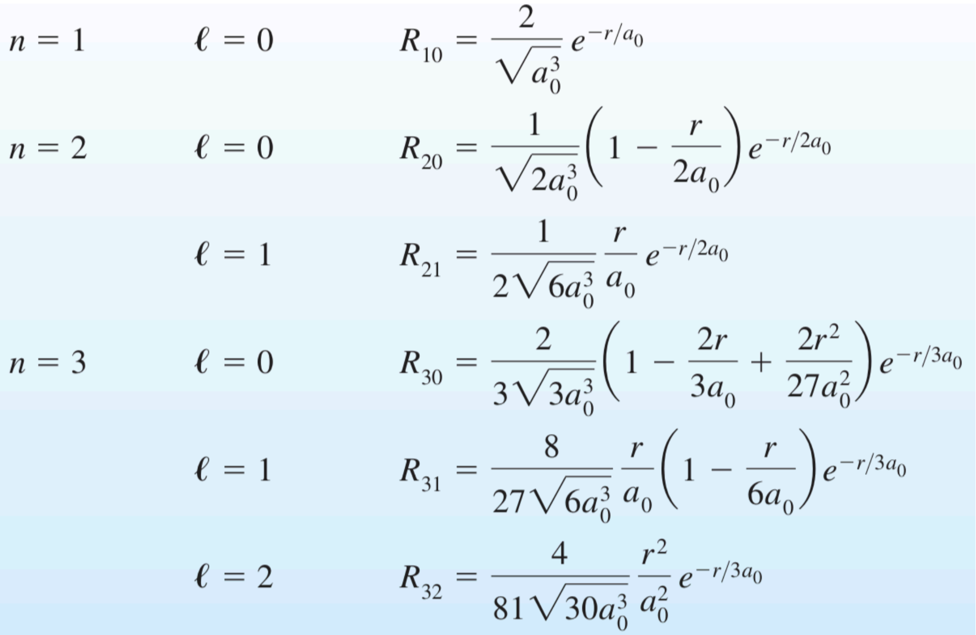
Figure 7-5 Potential energy of an electron in a hydrogen atom. If the total energy is greater than zero, as E', the electron is not bound and the energy is not quantized. If the total energy is less than zero, as E, the electron is bound. Then, as in one-dimensional problems, only certain discrete values of the total energy lead to well-behaved wave functions.

C. Degeneracy

Since the energy depends on on n and this in turn depends on n' and l, there will be states that are degenerate in energy. With $n' \geq 0$ and $l \geq 0$, then $n \geq 1$. This means that $0 \leq l \leq n-1$. Now for each value of l, $-l \leq m \leq l$, so there are $2l+1$ degenerate states for each l. The total degeneracy will then be given by

$$\sum_{l=0}^{n-1}(2l+1) = 2\frac{n(n-1)}{2} + n = n^2 \,. \tag{71}$$

While the degeneracy in m occurs of any central force, the degeneracy in l is characteristic of the Coulomb force.



$n = 1$	$\ell = 0$	$R_{10} = \frac{2}{\sqrt{a_0^3}}\, e^{-r/a_0}$
$n = 2$	$\ell = 0$	$R_{20} = \frac{1}{\sqrt{2a_0^3}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$
	$\ell = 1$	$R_{21} = \frac{1}{2\sqrt{6a_0^3}}\, \frac{r}{a_0}\, e^{-r/2a_0}$
$n = 3$	$\ell = 0$	$R_{30} = \frac{2}{3\sqrt{3a_0^3}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$
	$\ell = 1$	$R_{31} = \frac{8}{27\sqrt{6a_0^3}}\, \frac{r}{a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}$
	$\ell = 2$	$R_{32} = \frac{4}{81\sqrt{30a_0^3}}\, \frac{r^2}{a_0^2}\, e^{-r/3a_0}$

FIG. 5. First few radial functions for the Coulomb potential.

D. Radial Wave Functions

The general form of radial wave function for Coulomb potential is

$$R_{nl}(r) = -\left\{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{\frac{1}{2}} \rho^l e^{-\frac{\rho}{2}} L_{n+l}^{2l+1}(\rho)\,, \tag{72}$$

where

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = \frac{\hbar}{\alpha mc} \tag{73}$$

is the Bohr radius and $L_p^q(\rho)$ is so-called associated Laguerre polynomials.

E. Summary of Quantum numbers

The allowed values of and restrictions on the quantum numbers n, l and n associated with the variables r, θ, and ϕ are summarized as follows:

$$\begin{aligned} n &= 0, 1, 2, 3... \\ l &= 0, 1, 2, ...n - 1 \\ m &= -l, -l + 1, ... - 2, -1, 0, 1, 2...l \end{aligned} \tag{74}$$

The fact that the energy of the hydrogen atom depends only on the principal quantum number n and not on l is a peculiarity of the inverse-square force. It is related to the result in classical mechanics that the energy of a mass moving in an elliptical orbit in an inverse-square force field depends only on the major axis of the orbit and not on the eccentricity. The largest value of angular momentum $l = n-1$ corresponds most nearly to a circular orbit, whereas a small value of l corresponds to a highly eccentric orbit. The quantum number m is related to the z component of angular momentum. Since there is no preferred direction for the z axis for any central force, the energy cannot depend on m.

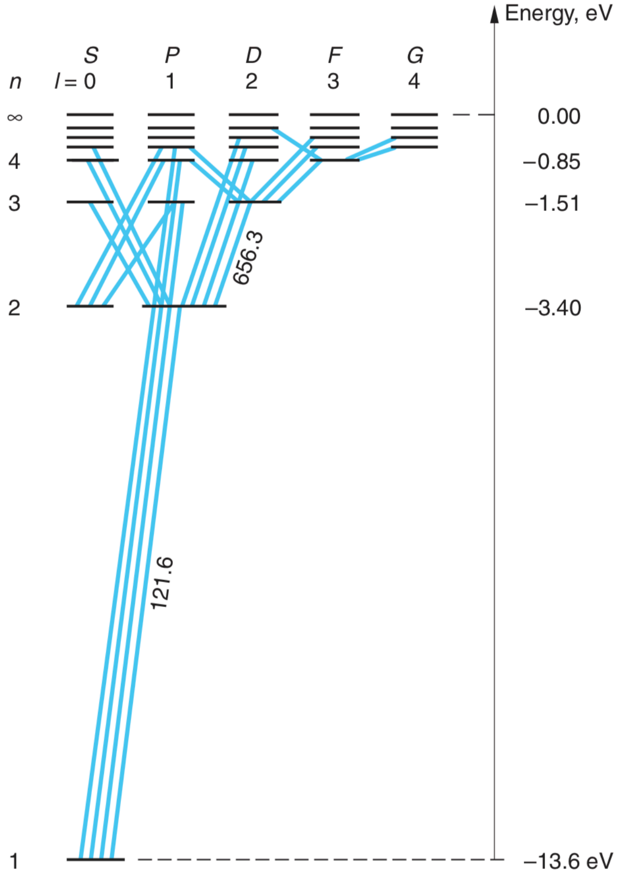


Figure 7-6 Energy-level diagram for the hydrogen atom, showing transitions obeying the selection rule $\Delta\ell = \pm 1$. States with the same n value but different ℓ value have the same energy, $-E_1/n^2$, where $E_1 = 13.6$ eV, as in the Bohr theory. The wavelengths of the Lyman $\alpha(n = 2 \rightarrow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

Figure 7-6 shows an energy-level diagram for hydrogen. These states are referred to by giving the value of n along with a code letter: S stands for $l = 0$, P for $l = 1$, D for $l = 2$, and F for$l = 3$. (These code letters are remnants of the spectroscopist's descriptions of various series of spectral lines as Sharp, Principal, Diffuse, and Fundamental.) The allowed electric dipole transitions between energy levels obey the selection rules

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

That the quantum number l of the atom must change by ± 1 when the atom emits or absorbs a photon results from conservation of angular momentum and the fact that the photon itself has an intrinsic angular momentum of $1\hbar$.

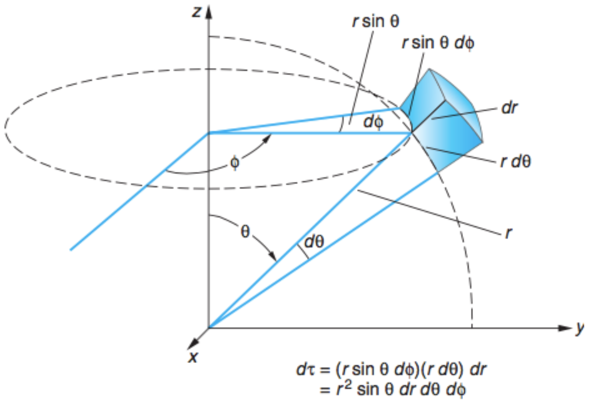


Figure 7-7 Volume element $d\tau$ in spherical coordinates.

V. WAVE FUNCTIONS OF THE HYDROGEN ATOM

1. *Ground state*

In general

$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r)Y_{lm}(\theta, \phi) \tag{75}$$

so for $n = 1$, $l = m = 0$ we get (the Laguerre polynomial is just 1 in this case)

$$\psi_{100}(\boldsymbol{r}) = C_{100}e^{-\frac{Z}{a_0}r} \tag{76}$$

where C is the normalization constant. From

$$1 = \int d^3x\, |\psi_{100}(\boldsymbol{r})|^2 = |C_{100}|^2 \int d^3x\; e^{-\frac{2Z}{a_0}r} = \frac{a_0^3}{Z^3\pi} \Rightarrow C_{100} = \frac{1}{\pi}(Z/a_0)^{\frac{3}{2}} \tag{77}$$

Probability to find electron in a spherical shell between r and $r + dr$

$$P(r)dr = |\psi|^2 4\pi r^2 dr = 4\pi r^2 C_{100}^2 e^{-2\frac{Zr}{a_0}}$$

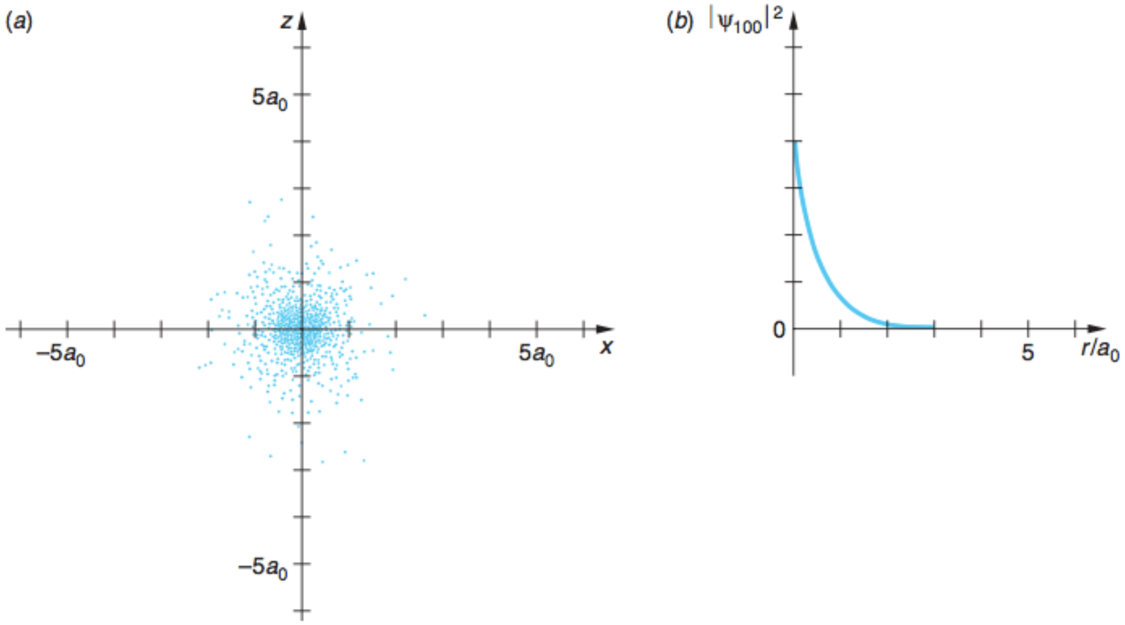


Figure 7-8 Probability density $\psi^*\psi$ for the ground state in hydrogen. The quantity $e\psi^*\psi$ can be thought of as the electron charge density in the atom. (*a*) The density is spherically symmetric, is greatest at the origin, and decreases exponentially with r. This computer-generated plot 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.*]

A. Excited states

In the first excited state, $n = 2$ and l an be either 0 or 1. For $l = m = 0$ again we have a spherically symmetric wave function, given by

$$\psi_{200}(\boldsymbol{r}) = C_{200}\Big(2 - \frac{Zr}{a_0}\Big)e^{-\frac{Z}{2a_0}r} \tag{78}$$

For $l = 1$, m can be 1, 0, or -1. The corresponding wave functions are

$$\begin{aligned}\psi_{210}(\boldsymbol{r}) &= C_{210}\frac{Zr}{a_0}e^{-\frac{Z}{2a_0}r}\cos\theta \\ \psi_{21\pm1}(\boldsymbol{r}) &= C_{210}\frac{Zr}{a_0}e^{-\frac{Z}{2a_0}r}\sin\theta e^{\pm i\phi}\end{aligned} \tag{79}$$

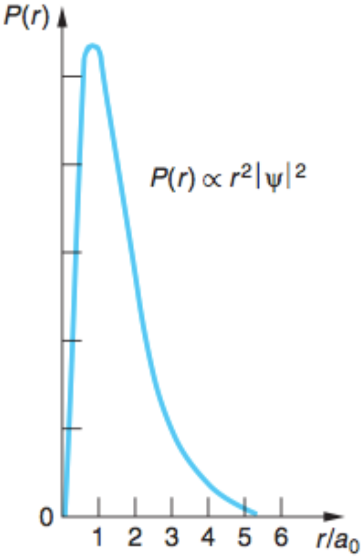


Figure 7-9 Radial probability density $P(r)$ versus r/a_0 for the ground state of the hydrogen atom. $P(r)$ is proportional to $r^2|\psi_{100}|^2$. The most probable distance r is the Bohr radius a_0.

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 2^2a_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.