

results is known, and a large part of the methods and techniques of the subject is associated with attempts to reduce complex systems to combinations of simpler independent ones. This procedure is illustrated in the problem of the hydrogen atom, where it can be carried out exactly.

**7-7 The hydrogen atom.** The Hamiltonian function for the hydrogen atom is

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (7-163)$$

in which the subscripts 1 and 2 denote the electron and the proton, respectively. The wave function  $\Psi(\mathbf{r}_1, \mathbf{r}_2)$  depends upon six variables and is a solution of the Schrödinger equation

$$H\Psi = -\frac{\hbar^2}{2m_1}\nabla_1^2\Psi - \frac{\hbar^2}{2m_2}\nabla_2^2\Psi - \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}\Psi = E_i\Psi, \quad (7-164)$$

where  $E_i$  is the total energy.

The separation of the problem is accomplished by changing the variables to  $\mathbf{R}$  and  $\mathbf{r}$ , where

$$\mathbf{R} = [X, Y, Z] = \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2}{m_1 + m_2} \quad (7-165)$$

is the position vector of the center of mass, and

$$\mathbf{r} = [x, y, z] = \mathbf{r}_1 - \mathbf{r}_2 \quad (7-166)$$

is the separation between electron and proton. Solving for  $\mathbf{r}_1$  and  $\mathbf{r}_2$  in terms of  $\mathbf{R}$  and  $\mathbf{r}$ , we have

$$\mathbf{r}_1 = \mathbf{R} + \frac{m}{m_1}\mathbf{r}, \quad \mathbf{r}_2 = \mathbf{R} - \frac{m}{m_2}\mathbf{r}, \quad (7-167)$$

in which

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

is the reduced mass. For the partial derivatives of  $\Psi$ , we find

$$\frac{\partial\Psi}{\partial x_1} = \frac{m_1}{m_1 + m_2} \frac{\partial\Psi}{\partial X} + \frac{\partial\Psi}{\partial x}, \quad \frac{\partial\Psi}{\partial x_2} = \frac{\partial\Psi}{\partial x} - \frac{m_2}{m_1 + m_2} \frac{\partial\Psi}{\partial X},$$

or

$$\nabla_1 = \frac{m}{m_2} \nabla_R + \nabla, \quad \nabla_2 = \frac{m}{m_1} \nabla_R - \nabla, \quad (7-168)$$

where

$$\nabla_R = \left[ \frac{\partial}{\partial X}, \frac{\partial}{\partial Y}, \frac{\partial}{\partial Z} \right], \quad \text{and} \quad \nabla = \left[ \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right].$$

By these substitutions, Eq. (7-164) becomes ( $r = |\mathbf{r}|$ )

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\Psi - \frac{\hbar^2}{2m}\nabla^2\Psi - \frac{e^2}{r}\Psi = E_i\Psi, \quad (7-169)$$

where  $\Psi$  is now to be regarded as a function of  $\mathbf{R}$  and  $\mathbf{r}$ . Equation (7-169) is separable; it has a solution in the form of a product function:

$$\Psi(\mathbf{R}, \mathbf{r}) = \phi(\mathbf{R})\psi(\mathbf{r}). \quad (7-170)$$

By the usual procedure, one finds that the functions  $\phi$  and  $\psi$  satisfy the equations

$$-\frac{\hbar^2}{2(m_1 + m_2)}\nabla_R^2\phi(\mathbf{R}) = E_c\phi(\mathbf{R}), \quad (7-171)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) - \frac{e^2}{r}\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (7-172)$$

where  $E_c + E = E_i$ .

The equation for  $\phi(\mathbf{R})$  has the general solution

$$\phi(\mathbf{R}) = \text{constant} \times e^{(i/\hbar)\mathbf{P}\cdot\mathbf{R}}, \quad (7-173)$$

where  $\mathbf{P}$  is a constant vector of arbitrary direction; the magnitude of  $\mathbf{P}$  is

$$|\mathbf{P}| = \sqrt{2(m_1 + m_2)E_c}. \quad (7-174)$$

The function  $\phi(\mathbf{R})$  represents the motion of the center of mass of the system as that of a single particle of mass  $m_1 + m_2$  and energy  $E_c = P^2/2(m_1 + m_2)$ . It describes a plane wave, indicating that the motion of the center of mass is that of a free particle. This corresponds to the classical result that the center of mass moves in a straight line with constant speed.

Equation (7-172) for the relative motion is the Schrödinger equation for an equivalent particle having the reduced mass and moving in a fixed central field,  $V(r) = -e^2/r$ . The energy of relative motion,  $E$ , is determined as the eigenvalue of this equivalent problem. In the treatment of Eq. (7-172), it is convenient to introduce "atomic" units, in which the energy is measured in multiples of the ionization energy of hydrogen,  $me^4/2\hbar^2$ , and the coordinate in terms of the Bohr radius  $\hbar^2/me^2$ . Expressed in these units, which are equivalent to writing  $\hbar = 1$ ,  $e^2 = 2$ ,  $m = \frac{1}{2}$ , Eq. (7-172) becomes

$$\nabla^2\psi + \left(E + \frac{2}{r}\right)\psi = 0. \quad (7-175)$$



The potential-energy function  $V(r) = 2/r$  is spherically symmetric, and the eigenfunctions are therefore  $(2l+1)$ -fold degenerate, having the form

$$\psi = R(r) Y_l^m(\theta, \phi). \quad (7-176)$$

The radial equation (7-64) is  $\psi_{\text{of } u \text{ show}}$

$$\frac{d^2 u}{dr^2} + \left[ E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] u = 0 \quad (u = rR). \quad (7-177)$$

Since  $R$  must be finite at  $r = 0$  and such that the integral

$$\int_0^\infty R^2 r^2 dr = \int_0^\infty u^2 dr$$

exists, the boundary conditions on the solutions of Eq. (7-177) are

$$u = 0 \quad \text{at} \quad r = 0 \quad \text{and} \quad u \rightarrow 0 \quad \text{as} \quad r \rightarrow \infty. \quad (7-178)$$

From the discussion of Section 5-4, we expect to find a continuum of solutions for  $E > 0$ , corresponding to the classical hyperbolic orbits, and a discrete spectrum of energy states for  $E < 0$ , corresponding to the elliptic orbits of the Bohr theory. Attention will be given to the bound states of negative energy. We proceed by the polynomial method, which is now familiar.

If  $r$  is large, Eq. (7-177) is approximated by

$$u'' - (-E)u = 0 \quad \left[ u' = \frac{du}{dr}, u'' = \frac{d^2 u}{dr^2} \right], \quad (7-179)$$

which has the solutions  $u = \exp(\pm \sqrt{-E} r)$ , and we are led to make the substitution

$$u = w \exp(-\sqrt{-E} r). \quad (7-180)$$

The differential equation for  $w$  is

$$w'' - 2\sqrt{-E} w' + \left( \frac{2}{r} - \frac{l(l+1)}{r^2} \right) w = 0. \quad (7-181)$$

Note that this substitution results in an equation which will yield a two-term recurrence relation for the coefficients in the series solution. Equation (7-177) would lead to a three-term recurrence relation.

Equation (7-181) can be solved formally by means of a power series in  $r$ , beginning with a term in  $r^\alpha$ . The exponent  $\alpha$  is determined by the

$$\alpha(\alpha-1)r^{\alpha-2} - 2\sqrt{-E}\alpha r^{\alpha-1} + \frac{2}{r}r^{\alpha-1} - \ell(\ell+1)r^{\alpha-2} = [\alpha(\alpha-1) - \ell(\ell+1)]r^{\alpha-2} \quad (7-7)$$

THE HYDROGEN ATOM  $\psi = R(r)Y_{\ell}^m(\theta, \phi)$

$$\alpha r \rightarrow 0 \text{ as } r \rightarrow \infty \text{ to get } \alpha(\alpha-1) - \ell(\ell+1) = 0, \quad (7-182)$$

which is obtained as the coefficient of  $r^{\alpha-2}$  if  $r^\alpha$  is substituted for  $w$  in Eq. (7-181). This gives

$$\alpha = \ell + 1 \quad \text{or} \quad \alpha = -\ell, \quad (7-183)$$

and since  $\ell$  is not negative, the first of the conditions (7-178) is satisfied only by the root  $\alpha = \ell + 1$ . Hence the power series is

$$w = \sum_{k=\ell+1}^{\infty} a_k r^k, \quad (7-184)$$

in which  $a_{\ell+1}$  is an arbitrary number and the remaining  $a_k$  are determined by the recurrence formula

$$a_{k+1} = 2 \frac{k\sqrt{-E} - 1}{k(k+1) - \ell(\ell+1)} a_k. \quad (7-185)$$

As  $k \rightarrow \infty$ , the ratio  $a_{k+1}/a_k$  approaches  $2\sqrt{-E}/k$ ; thus  $w$  behaves, for large  $r$ , like the function  $\exp(2\sqrt{-E}r)$ . Therefore  $u$  is not bounded as  $r \rightarrow \infty$  unless the series (7-184) is broken off at some value  $n$  of the index  $k$ . This happens, and  $w$  is a polynomial, if

$$E = E_n = -\frac{1}{n^2} \quad (n > \ell), \quad (7-186)$$

or, in conventional units,

$$E_n = -\frac{me^4}{2n^2\hbar^2} \quad (n = \ell + 1, \ell + 2, \dots). \quad (7-187)$$

The energy levels for hydrogen are therefore exactly the same as those obtained from the Bohr theory described in Chapter 1. The principal quantum number  $n$  determines the energy, and for each level  $E_n$ ,  $\ell$  can have any non-negative value smaller than  $n$ . The energy diagram is shown in Fig. 7-5, in which the fundamental degeneracy  $(2\ell+1)$  of each  $(n, \ell)$  state is indicated by the small numeral. The coincidence of the energies of states belonging to different  $\ell$  is accidental and is removed by a perturbation whose  $r$ -dependence is not  $1/r$ . The total degeneracy of the states of energy  $E_n$  is

$$\sum_{\ell=0}^{n-1} (2\ell+1) = 1 + 3 + 5 + \dots + (2n-1) = n^2. \quad (7-188)$$

The radial eigenfunctions  $u = u_{n,\ell}$  are of the form

$$u_{n,\ell} = e^{-r/a_n} r^{\ell+1} v, \quad (7-189)$$

see Born QM p. 175. Another conf. of the motion.  $\mathcal{H} \psi = E \psi$



$$\omega'' - 2\sqrt{-E}\omega' + \left(\frac{2}{r} - \frac{l(l+1)}{r^2}\right)\omega = 0$$

$$\omega = \sum_{k=l+1}^{\infty} a_k r^k$$

$$\omega' = \sum_{k=l+1}^{\infty} k a_k r^{k-1}$$

$$\omega'' = \sum_{k=l+1}^{\infty} k(k-1) a_k r^{k-2}$$

$$\text{Then } \sum_{k=l+1}^{\infty} \left\{ k(k-1) a_k r^{k-2} - 2\sqrt{-E} k a_k r^{k-1} + \left(\frac{2}{r} - \frac{l(l+1)}{r^2}\right) a_k r^k \right\}$$

$$= \sum_{k=l+1}^{\infty} \left\{ [k(k-1) - l(l+1)] a_k r^{k-2} + (-2k\sqrt{-E} + 2) a_k r^{k-1} \right\} = 0$$

set, in the 1st term  $k \rightarrow k+1$  so that we can match the  $r^{k-1}$  power of the second term —

$$[(k+1)k - l(l+1)] a_{k+1} r^{k-1} + (-2k\sqrt{-E} + 2) a_k r^{k-1} = 0$$

$$\Rightarrow k(k+1) - l(l+1) a_{k+1} + (-2k\sqrt{-E} + 2) a_k = 0$$

$$a_{k+1} = 2 \frac{k\sqrt{-E} - 1}{k(k+1) - l(l+1)} a_k$$

For large  $r$ , need to look at large  $k$   
 For large  $k$ ,  $a_{k+1}/a_k \sim 2\sqrt{-E}/k$   
 Compare to  $e^{2\sqrt{-E}r} = 1 + \frac{2\sqrt{-E}r}{1!} + \dots$   
 $+ \frac{(2\sqrt{-E})^k}{k!} r^k + \dots$   
 successive terms  $\frac{2\sqrt{-E}}{k} \Rightarrow \omega \sim e^{2\sqrt{-E}r}$

$$\text{for } r \rightarrow \infty \quad \omega'' - 2\sqrt{-E}\omega' \sim 0$$

$$\omega = e^{2\sqrt{-E}r} \quad \omega' - 2\sqrt{-E}\omega' = (2\sqrt{-E})(2\sqrt{-E})e^{2\sqrt{-E}r} - (2\sqrt{-E})(2\sqrt{-E})e^{2\sqrt{-E}r} = 0$$

$$\omega = \omega e^{-\sqrt{-E}r} \sim e^{2\sqrt{-E}r - \sqrt{-E}r} = e^{\sqrt{-E}r} \rightarrow \infty$$

So break off series at some value of  $k$ , call it  $n$   
 $F = -1/n^2 \quad a_{n+1} = 2 \frac{n\sqrt{-1/n^2} - 1}{n(n+1) - l(l+1)} a_n = 0 \quad \text{So } \omega = \sum_{k=0}^n a_k r^k$



$$\omega = \sum_{k=l+1}^n a_k r^k$$

$$n=1 \quad l=0$$

$$n=2 \quad l=0, 1$$

$$n=3 \quad l=0, 1, 2$$

$$n = l + j$$

That is  $0 \leq l \leq n-1$ ,  $l=0, 1, \dots, n-1$

Recall  $-l \leq m \leq l$ .

For  $n=1$ , we have  $l=0$ ,  $m=0$  so nondegenerate.

For  $n=2, \dots$  degenerate.

For given  $l$ ,  $(2l+1)$ -fold degeneracy from  $m$ .

For given  $n$

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

But  ~~$1+2+\dots+k$~~   $1+2+\dots+k = \frac{1}{2} k(k+1)$

$$S = 2 \cdot \frac{1}{2} (n-1)n + n = n^2$$



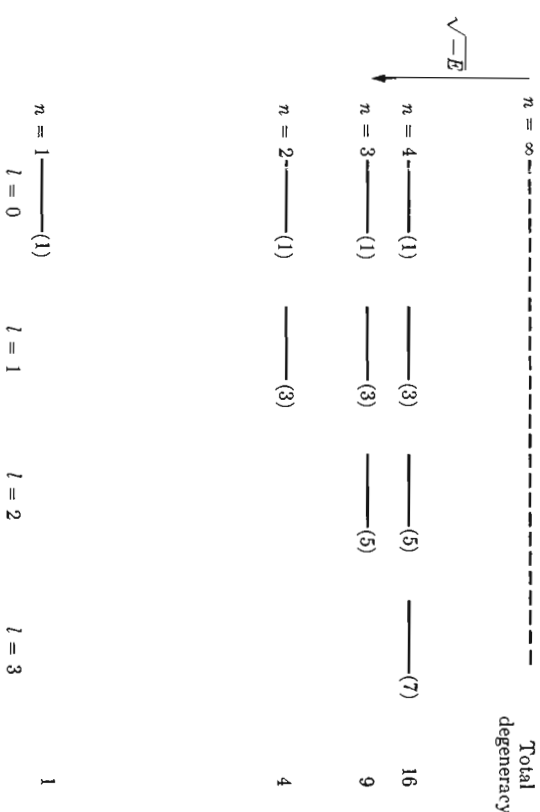


Fig. 7-5. Energy level diagram for the hydrogen atom. The  $(2l+1)$ -fold degeneracy of each state is indicated in parentheses, and the total degeneracy for all states with a given principal quantum number  $n$  has been entered on the right.

where  $v$  is a polynomial solution of the differential equation

$$t \frac{d^2 v}{dt^2} + (2l+2-t) \frac{dv}{dt} + (n-l-1)v = 0, \quad (7-190)$$

where  $t = 2r/n$ . This equation defines the Laguerre polynomial  $L_{n-l-1}^{2l+1}(t)$ , whence

$$u_{n,l} = N e^{-r/n} r^{l+1} L_{n-l-1}^{2l+1} \left( \frac{2r}{n} \right), \quad (7-191)$$

in which the normalization constant  $N$  is determined by

$$\int_0^\infty |u|^2 dr = |N|^2 \int_0^\infty e^{-2r/n} r^{2l+2} \left[ L_{n-l-1}^{2l+1} \left( \frac{2r}{n} \right) \right]^2 dr = 1, \quad (7-192)$$

or

$$\left( \frac{n}{2} \right)^{2l+3} |N|^2 \int_0^\infty e^{-t} t^{\alpha+1} [L_k^\alpha(t)]^2 dt = 1$$

$$(\alpha = 2l+1, \quad k = n-l-1). \quad (7-193)$$

This normalization integral differs from (7-144) in that the integrand contains the factor  $t^{\alpha+1}$  rather than  $t^\alpha$ . However, by the recurrence relation (7-131), we have

$$tL_k^\alpha = (2k + \alpha + 1)L_k^\alpha - (k+1)L_{k+1}^\alpha - (k+\alpha)L_{k-1}^\alpha; \quad (7-194)$$

multiplying by  $e^{-t} t^\alpha L_k^\alpha(t)$  and integrating, we obtain from Eq. (7-141)

$$\int_0^\infty e^{-t} t^{\alpha+1} [L_k^\alpha]^2 dt = (2k + \alpha + 1) \int_0^\infty e^{-t} t^\alpha [L_k^\alpha]^2 dt$$

$$= (2k + \alpha + 1) \Gamma(\alpha + 1) \binom{k + \alpha}{k}. \quad (7-195)$$

Combining Eqs. (7-195), (7-193), and (7-191), and using Eq. (7-145), we have

$$u_{n,l} = \sqrt{\frac{2\pi}{n^3}} \frac{\Lambda_{n-l-1}^{2l+1}}{\Lambda_{n-l-1}^{2l+1}} \left( \frac{2r}{n} \right), \quad (7-196)$$

and the orthonormal wave functions for the bound states of hydrogen are

$$\psi_{n,l,m} = \frac{1}{r} u_{n,l}(r) Y_l^m(\theta, \phi). \quad (7-197)$$

The functions  $u_{n,l}$  for  $n = 1, 2, 3$  are<sup>11</sup>

$$\begin{aligned} u_{10} &= 2re^{-r} & l_{10} &\sim r^2 e^{-2r/a_0} & \text{no limit at } r=a_0 \\ u_{20} &= \frac{1}{\sqrt{8}} e^{-r/2} (2-r), & u_{21} &= \frac{1}{\sqrt{24}} e^{-r/2} r^2 \\ u_{30} &= \frac{2}{81\sqrt{3}} e^{-r/3} (27-18r+2r^2), & & & \\ u_{31} &= \frac{4}{81\sqrt{6}} e^{-r/3} r^2 (6-r), & u_{32} &= \frac{4}{81\sqrt{30}} e^{-r/3} r^3. \end{aligned} \quad (7-198)$$

The functions  $u_{n,l}$  are shown in Fig. 7-6.

The differential equation (7-177) for the radial functions  $u_{n,l}$ , i.e.,

$$\frac{d^2 u}{dr^2} + \left[ E + \frac{2}{r} - \frac{l(l+1)}{r^2} \right] u = 0, \quad (7-199)$$

is, for  $l \neq 0$ , exactly of the form (5-47), in which the equivalent potential

<sup>11</sup> E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*. Cambridge: Cambridge University Press, 1935, p. 117.



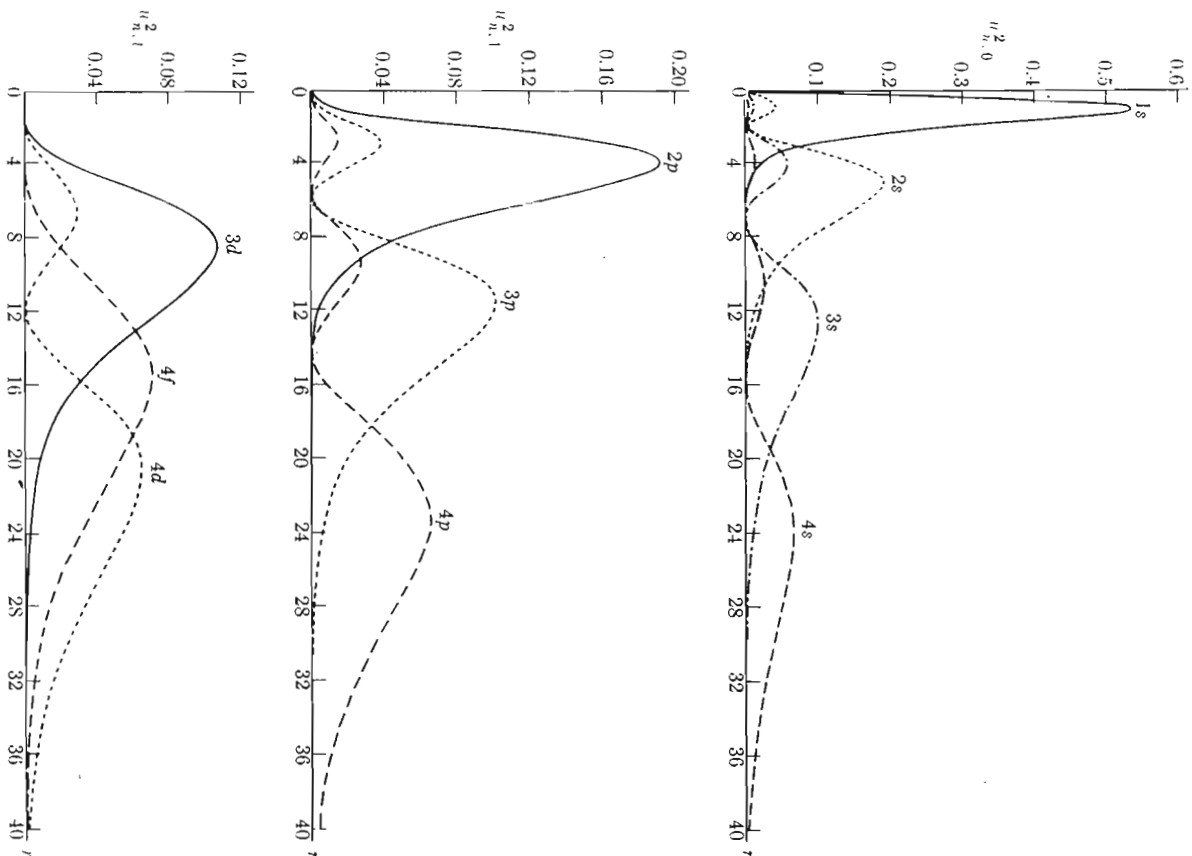


FIG. 7-6. The radial probability distribution function  $w_{n,l}^2$  for several values of the quantum numbers  $n, l$ . (From E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1953, by permission.)

FIG. 7-7. Equivalent potential  $V'$  for the hydrogen atom [Eq. (7-200)] in the state  $n = 2, l = 1$ .

energy (Fig. 7-7)

$$V' = -\frac{2}{r} + \frac{l(l+1)}{r^2} \quad (7-200)$$

As  $l$  increases  $V'$  is pushed out from origin is infinite at  $r = 0$ . Hence, the restriction  $r \geq 0$  (which was, of course, not imposed upon  $x$  in Chapter 5) does not matter since the admissible solutions of Eq. (7-199) for  $r < 0$  would vanish identically in any case. The general theory of Sections 5-4 ff. is therefore directly applicable. The eigenfunction of lowest energy corresponds, as we have seen, to  $n = l + 1$ . This function has zeros only at  $r = 0$  and  $r = \infty$  [cf. Eq. (7-198)]; the total number of distinct zeros is, in general,  $n - l + 1$ . The classical turning points are the values of  $r$  for which

$$E - V' = -\frac{1}{n^2} + \frac{2}{r} - \frac{l(l+1)}{r^2} = 0, \quad (7-201)$$

giving

$$r_1, r_2 = n^2 \mp \sqrt{n^2 - l(l+1)}. \quad (7-202)$$

These points correspond closely to the extrema of the Bohr orbit. The classical energy equation (cf. Section 1-13) is

$$E = \frac{1}{2m} \left( p_r^2 + \frac{p_\theta^2}{r^2} \right) - \frac{e^2}{r}, \quad (7-203)$$



and the maximum and minimum values of  $r$  occur when the radial momentum  $p_r$  vanishes. Since  $p_\phi = \hbar k$  and  $E = -me^4/2n^2\hbar^2$ , Eq. (7-203), in units  $\hbar^2/me^2$  and with  $p_r = 0$ , is

$$-\frac{1}{n^2} = \frac{k^2}{r^2} - \frac{2}{r}. \quad (7-204)$$

This result becomes the same as Eq. (7-201) if the quantity  $k^2$  is replaced by  $l(l+1)$ , showing once more the approximate validity of the Bohr theory.

Because of the exponential character of the wave function outside the classical region, the quantity  $|u|^2$  has its largest values within the region of the Bohr orbit. The case  $l = n - 1$ , which corresponds to the circular orbit, has just one maximum in this region, and as  $n$  becomes large, the position of this maximum can be shown to approach the corresponding classical radius. This is an example of the correspondence principle. Further similarities to the Bohr orbits are made evident by the calculation of certain expectations. For example,

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty u_{n,l}^2 \frac{dr}{r} = \frac{2}{n^3} \int_0^\infty \left[ \Lambda_{n-l-1}^{2l+1} \left( \frac{2r}{n} \right) \right]^2 dr = \frac{1}{n^2}. \quad (7-205)$$

The time average of this quantity in the Bohr-Sommerfeld theory is

$$\overline{\left( \frac{1}{r} \right)} = \frac{1}{P} \int_0^P \frac{1}{r} dt = \frac{m}{p_\phi P} \frac{p_\phi^2}{me^2} \int_0^{2\pi} \frac{d\phi}{1 - \epsilon \cos \phi} = \frac{1}{n^2 a_0}, \quad (7-206)$$

in which the integration variable has been changed from  $t$  to  $\phi$  by means of

$$p_\phi = m r^2 \dot{\phi} = \text{constant}, \quad (7-207)$$

and the expression (1-45) has been substituted. The quantities

$$a_0 = \frac{\hbar^2}{me^2} \quad \text{and} \quad P = \frac{p_\phi^3}{me^4} \frac{2\pi}{(1 - \epsilon^2)^{3/2}} \quad (7-208)$$

are the Bohr radius and the period of the classical motion, respectively. The expectation of the kinetic energy,  $T = p^2/2m$ , can be obtained directly from Eq. (7-205) and the Schrödinger equation

$$\text{Thus,} \quad \frac{p^2}{2m} \psi - \frac{e^2}{r} \psi = E\psi. \quad (7-209)$$

*(e^{-2/r} is the radial wave)*

$$\langle T \rangle = \langle \psi, T\psi \rangle = \langle E \rangle + \left\langle \frac{2}{r} \right\rangle = E + \frac{2}{n^2} = -\frac{1}{n^2} \langle V \rangle, \quad (7-210)$$

which is referred to as the *virial theorem* (cf. Section 1-9).<sup>11</sup> Further examples of this kind are described in Problem 7-40.

#### REFERENCES

CONDON, E. U. and SHORTLEY, G. H., *The Theory of Atomic Spectra*. Cambridge: Cambridge University Press, 1953. The definitions of the spherical harmonics (Chapter III, §4) have become generally accepted as standard. Chapter V contains a complete discussion of hydrogen and its relation to the general theory of one-electron systems.

KRAMERS, H. A., *The Foundations of Quantum Theory*. Amsterdam: North-Holland Publishing Company, 1957. Chapter III contains a thorough discussion of the quantum mechanics of many-particle systems. The central-field problem and the hydrogen atom are the subject matter of §46.

ROJANSKY, V., *Introductory Quantum Mechanics*. New York: Prentice-Hall, Inc., 1946. Chapter XII presents tables of the spherical harmonics and a discussion of their theory, based upon the eigenvalue problems for the operators  $L_x$  and  $L^2$ . The appendix contains a useful collection of formulae relating to the functions  $Y_l^m(\theta, \phi)$ .

SCHRIF, L. I., *Quantum Mechanics*. 2nd ed., New York: McGraw-Hill Book Co., Inc., 1955. The subject matter of the present chapter is treated in Sections 14, 15, and 16. Section 15 contains a discussion of the three-dimensional square well potential. The solution of the hydrogen problem in parabolic coordinates is given in Section 16.

<sup>11</sup> H. Goldstein, *Classical Mechanics*. Reading, Mass.: Addison-Wesley Publishing Co., Inc., 1950, p. 71.



**Solution.** The Schrödinger equation may be factorized so that its solutions become

$$u(r, \vartheta, \varphi) = \frac{1}{r} \chi_l(r) Y_{l,m}(\vartheta, \varphi) \quad (62.1)$$

with radial equations

$$\chi_l'' + \left[ k^2 - \frac{l(l+1)}{r^2} \right] \chi_l = 0; \quad k^2 = \frac{2mE}{\hbar^2} \quad (62.2)$$

in  $0 \leq r \leq R$ , and zero outside. This differential equation can, by using  $z = kr$  as variable and splitting off a factor  $z^{\frac{1}{2}}$ ,

$$\chi_l = z^{\frac{1}{2}} \varphi(z),$$

be reduced to

$$\varphi'' + \frac{1}{z} \varphi' + \left\{ 1 - \frac{(l + \frac{1}{2})^2}{z^2} \right\} \varphi = 0,$$

i.e. to the Bessel equation whose solutions are  $J_{\pm(l+\frac{1}{2})}(z)$ . We therefore may write the complete solution of (62.2)

$$\chi_l(r) = \sqrt{\frac{\pi k r}{2}} \{ C_1 J_{l+\frac{1}{2}}(kr) + C_2 J_{-(l+\frac{1}{2})}(kr) \}. \quad (62.3)$$

It has become usual to introduce the so-called spherical Bessel functions

$$\left. \begin{aligned} j_l(z) &= \sqrt{\frac{\pi z}{2}} J_{l+\frac{1}{2}}(z), \\ n_l(z) &= (-1)^{l+1} \sqrt{\frac{\pi z}{2}} J_{-(l+\frac{1}{2})}(z) \end{aligned} \right\} \quad (62.4)$$

with the asymptotic behaviour for large positive values of  $z$ :

$$j_l(z) \rightarrow \sin\left(z - \frac{l\pi}{2}\right); \quad n_l(z) \rightarrow -\cos\left(z - \frac{l\pi}{2}\right) \quad (62.5)$$

and with the power series around the origin, approximated for  $|z| \ll l + \frac{1}{2}$  each by its first term,

$$j_l = \frac{2^l l!}{(2l+1)!} z^{l+1}; \quad n_l(z) = -\frac{(2l)!}{2^l l!} z^{-l}. \quad (62.6)$$

The second term of the solution (62.3) leads, at  $r=0$ , to  $\chi_l \propto r^{-l}$  and  $u \propto r^{-l-1}$ . The normalization integral,

$$\int d\tau |u|^2 = \int_0^\infty dr |\chi_l|^2 = 1, \quad (62.7)$$

therefore does not exist unless  $C_2 = 0$  in (62.3). This does, however, not hold in the case  $l=0$  where the singularity of  $u$  is not pronounced enough to let the integral diverge at  $r=0$ . Even in this case the singular solution must be excluded, because it would make the energy integral<sup>12</sup>

$$E = \frac{\hbar^2}{2m} \int d\tau (\nabla u)^2 \quad (62.8)$$

diverge at the origin (cf. also Problem 65). Hence, normalizable solutions are restricted to

$$\chi_l(r) = C j_l(kr). \quad (62.9)$$

From this set of solutions we select the eigenfunctions by the condition

$$j_l(kR) = 0 \quad (62.10a)$$

or

$$J_{l+\frac{1}{2}}(kR) = 0. \quad (62.10b)$$

Since, for each given value of  $l + \frac{1}{2}$ , the Bessel function has an infinite number of zeros, we find an infinite number of values  $k_{n,l}$  and of energy levels

$$E_{n,l} = \frac{\hbar^2}{2m} k_{n,l}^2 \quad (62.11)$$

for each  $l$ , with  $n, l = 1, 2, 3, \dots$  the radial quantum number counting the zeros.

For the lowest  $l$  values, the spherical Bessel functions are

$$\left. \begin{aligned} j_0(z) &= \sin z; & j_1(z) &= \frac{\sin z}{z} - \cos z; \\ j_2(z) &= -3 \frac{\cos z}{z} + \left( \frac{3}{z^2} - 1 \right) \sin z, \end{aligned} \right\} \quad (62.12)$$

<sup>12</sup> For  $l=0$  and small  $r$ , this solution would become  $u \sim \frac{1}{r}$  and the kinetic energy integral  $E \sim \int dr/r^2$ .



and for higher values of  $l$  they may easily be constructed from the recurrence relation

$$j_l(z) = \frac{l}{z} j_{l-1}(z) - j'_{l-1}(z). \quad (62.13)$$

Their zeros may be determined from simple transcendental equations:

$$\left. \begin{aligned} j_0(z) &= 0 & \text{if } \sin z = 0 & \text{ or } z = n_r \pi; \\ j_1(z) &= 0 & \text{if } \tan z = z; \\ j_2(z) &= 0 & \text{if } \tan z = \frac{3z}{3-z^2} \text{ etc.} \end{aligned} \right\} \quad (62.14)$$

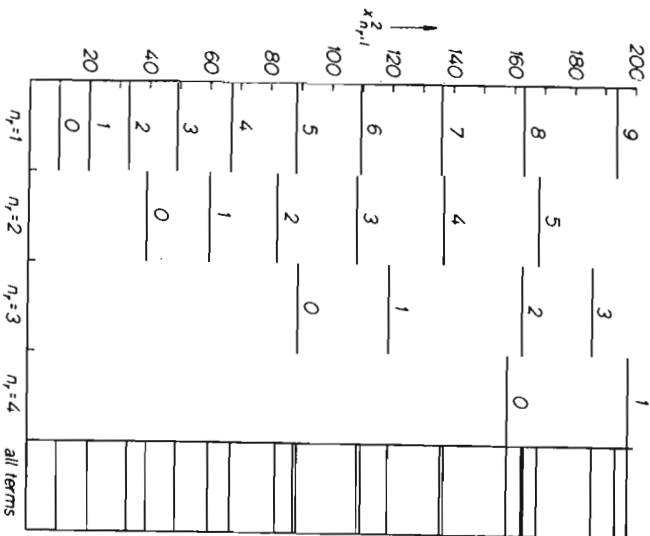


Fig. 35. Energy levels for a particle enclosed in a sphere

They all tend towards either  $n\pi$  for even, or  $(n+\frac{1}{2})\pi$  for odd  $l$ . In Fig. 35, the lowest energy values have been represented in multiples of  $\hbar^2/2mR^2$ , and the parameter

$$x_{n_r, l} = k_{n_r, l} R \quad (62.15)$$

has been tabulated completely up to 15.

Table of the values of  $x_{n_r, l}$

$\begin{matrix} n_r \\ l \end{matrix}$	1	2	3	4
0	3.142	6.283	9.425	12.566
1	4.493	7.725	10.904	14.066
2	5.764	9.095	12.323	15.511
3	6.988	10.417	13.698	16.972
4	8.183	11.705		
5	9.356	12.967		
6	10.513	14.207		
7	11.657			
8	12.791			
9	13.916			

**NB.** This problem is closely related to the simpler, one-dimensional one dealt with in Problem 18. The solutions for  $l=0$  exactly correspond to the antisymmetric wave functions of the one-dimensional problem.

### Problem 63. Square well of finite depth

To determine the eigenvalues of bound states in the square well potential

$$V(r) = \begin{cases} -V_0 & \text{for } r < R, \\ 0 & \text{for } r > R, \end{cases} \quad (63.1)$$

for  $l=0, 1, 2$ . Numerical results shall then be determined for the "well size"  $2mV_0R^2/\hbar^2 = 100$ .

**Solution.** With the abbreviations

$$\frac{2m|E|}{\hbar^2} = \kappa^2; \quad \frac{2mV_0}{\hbar^2} = k_0^2; \quad \frac{2m(V_0 - |E|)}{\hbar^2} = k^2 \quad (63.2)$$

the radial part of the Schrödinger equation becomes

$$\chi_l'' + \left( k^2 - \frac{l(l+1)}{r^2} \right) \chi_l = 0 \quad (63.3a)$$

inside, and

$$\chi_l'' + \left( -\kappa^2 - \frac{l(l+1)}{r^2} \right) \chi_l = 0 \quad (63.3b)$$



compensate each other, and as a result the *density of states* is the same for the case of periodic boundary conditions and the box. In either case the eigenfunctions constitute a complete set, in terms of which an arbitrary wave packet can be expanded by Fourier series within the basic cube.

2.  $V = 0$  as a *Central Force Problem*. The free particle problem can also be regarded as a *central force* problem, since  $V = 0$  is a special, if trivial, case of a potential that depends only on the radial coordinate  $r$ . From the point of view of Chapter 9, the eigenfunctions must be separable in spherical polar coordinates, and the angular momentum must be a constant of the motion. We therefore assume the eigenfunctions in the form (9.27) or

$$\psi(r, \theta, \varphi) = R(r) Y_l^m(\theta, \varphi) \quad (10.15)$$

and for  $V = 0$  these must satisfy the radial equation

$$\left[ -\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right) + \frac{l(l+1)\hbar^2}{2\mu r^2} \right] R(r) = ER(r) \quad (10.16)$$

The differential equation (10.16) can be solved by standard power series techniques, but it is more economical to observe that a closely related equation has already been encountered earlier in discussing the WKB method. If we substitute

$$\rho = \sqrt{\frac{2\mu E}{\hbar^2}} r = kr, \quad v(\rho) = rR(r) \quad (10.17)$$

and

$$\lambda = l + 1 \quad \text{or} \quad -l \quad (10.18)$$

(10.16) becomes

$$\frac{d^2 v}{d\rho^2} + \left[ 1 - \frac{\lambda(\lambda-1)}{\rho^2} \right] v = 0 \quad (10.19)$$

This equation was discussed in detail in Section 7.5. The solution of (10.19) which vanishes at  $\rho = 0$  is given by (7.60) and (7.65) as

$$v(\rho) = \rho^{l+1} \int_{-i}^{+i} e^{\rho t} (1 + t^2)^l dt \quad (10.20)$$

This solution is closely related to the *spherical Bessel function*  $j_l$ , defined by<sup>2</sup>

$$j_l(z) = \frac{z^l}{2^{l+1} \cdot l!} \int_{-1}^{+1} e^{izs} (1 - s^2)^l ds \quad (10.21)$$

for a complex variable  $z$ . The first term in the series expansion of (10.21) in <sup>2</sup> Since  $\rho$  is positive by definition, the variable  $z$  will be used in this chapter in all formulas which are also valid outside of the real positive axis of the complex plane.

powers of  $z$  is

$$j_l(z) = \frac{2^l \cdot l!}{(2l+1)!} z^l + O(z^{l+2}) \quad (10.22)$$

We thus see that the spherical Bessel function  $j_l(kr)$  is the solution of the radial equation

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dR}{dr} \right) + \frac{l(l+1)}{r^2} R = k^2 R \quad (10.23)$$

which is finite at the origin and is said to be *regular*. The radial eigenfunction of the Schrödinger equation for the free particle is thus

$$R(r) = C j_l(kr) \quad (10.24)$$

A useful formula is obtained by integrating (10.21) by parts  $l$  times and using the definition (9.50) of the Legendre polynomials:

$$j_l(z) = \frac{1}{2^l i!} \int_{-1}^{+1} e^{izs} P_l(s) ds \quad (10.25)$$

The asymptotic form of the spherical Bessel functions can be derived from this expression by further integration by parts, and the leading term is

$$j_l(\rho) \sim \frac{\cos[\rho - (l+1)\pi/2]}{\rho} \quad (|\rho| \gg 1 \quad \text{and} \quad |\rho| \gg l) \quad (10.26)$$

We also note the relation between the *spherical* and the *ordinary Bessel functions*:

$$j_l(z) = \sqrt{\frac{\pi}{2z}} J_{l+1/2}(z) \quad (10.27)$$

All other solutions of (10.23) are singular at the origin and are not admissible as energy eigenfunctions for the free particle. Nevertheless they have important uses and will be introduced here.<sup>3</sup>

Two particularly useful singular solutions of the equation

$$-\frac{1}{z^2} \frac{d}{dz} \left( z^2 \frac{dR}{dz} \right) + \frac{l(l+1)}{z^2} R = R$$

are the *spherical Hankel functions* of the *first* and *second kind*, defined for  $0 \leq \arg z \leq \pi/2$  by the relations

$$h_l^{(1)}(z) = \frac{z^l}{i 2^l \cdot l!} \int_{-\infty}^i e^{z t} (1 + t^2)^l dt \quad (10.28a)$$

<sup>3</sup> Some of the related mathematical work is found in Section 7.5. For details see P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill Book Company, 1953, Chapter 5.



and

$$h_i^{(2)}(z) = \frac{z^l}{i2^l \cdot l!} \int_{-i}^{\infty e^{i\pi}} e^{zt}(1+t^2)^l dt \quad (10.28b)$$

where  $\pi/2 < \alpha < \pi$ . The Hankel functions diverge as  $z^{-l-1}$  near the origin:

$$h_i^{(1,2)}(z) = \pm \frac{(2l)!}{i2^l \cdot l!} z^{-l-1} + O^{(1,2)}(z^{-l}) \quad (10.29)$$

**Exercise 10.1.** Prove (10.29) by substituting  $x = zt$  in (10.28a) and (10.28b).

The asymptotic behavior of the Hankel functions for large positive  $\rho$  can be inferred from (7.64) by an appropriate change of symbols:

$$h_i^{(1)}(\rho) \sim \frac{1}{\rho} \exp \left\{ i \left[ \rho - \frac{\pi}{2} (l+1) \right] \right\} \quad (10.30)$$

$$h_i^{(2)}(\rho) \sim \frac{1}{\rho} \exp \left\{ -i \left[ \rho - \frac{\pi}{2} (l+1) \right] \right\} \quad (10.31)$$

Comparing (10.28a) and (10.28b) with (10.21), we can express the regular solution in terms of the Hankel functions:

$$j_l(z) = \frac{1}{2} [h_i^{(1)}(z) + h_i^{(2)}(z)] \quad (10.32)$$

It is useful to define also the *spherical Neumann function*  $n_l(z)$  as

$$n_l(z) = \frac{1}{2i} [h_i^{(1)}(z) - h_i^{(2)}(z)] \quad (10.33)$$

Hence,

$$h_i^{(1)}(z) = j_l(z) + in_l(z) \quad \text{and} \quad h_i^{(2)}(z) = j_l(z) - in_l(z)$$

For  $z \approx 0$ ,

$$n_l(z) = -\frac{(2l)!}{2^l \cdot l!} z^{-l-1} + O(z^{-l+1}) \quad (10.34)$$

and for large positive  $\rho$ ,

$$n_l(\rho) \sim \frac{\sin [\rho - (l+1)\pi/2]}{\rho} \quad (10.35)$$

This particular singular solution of the radial equation, being asymptotically out of phase by  $\pi/2$  compared to the regular solution (10.25), is sometimes distinguished as "the" irregular solution, although any linear combination of  $j_l$  and  $n_l$  that contains a nonvanishing portion of  $n_l$  is singular at the origin.

define  $j_l$ , then  $n_l$ 's (give explicit)  
Then from lin combos  $h_0^{(1)}, h_0^{(2)}, h_1^{(1)}, h_1^{(2)}$ , deduce  $\cos \theta + i \sin \theta = e^{i\theta}$

The explicit forms of the spherical Bessel, Hankel, and Neumann functions for  $l = 0, 1$ , and  $2$ , are given below

$$j_0(z) = \frac{\sin z}{z}$$

$$j_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z} \quad (10.36)$$

$$j_2(z) = \left( \frac{3}{z^3} - \frac{1}{z} \right) \sin z - \frac{3}{z^2} \cos z$$

$$n_0(z) = -\frac{\cos z}{z}$$

$$n_1(z) = -\frac{\cos z}{z^2} - \frac{\sin z}{z} \quad (10.37)$$

$$n_2(z) = -\left( \frac{3}{z^3} - \frac{1}{z} \right) \cos z - \frac{3}{z^2} \sin z$$

$$h_0^{(1)}(z) = -i \frac{e^{iz}}{z}$$

$$h_1^{(1)}(z) = \left( -\frac{i}{z^2} - \frac{1}{z} \right) e^{iz} \quad (10.38)$$

$$h_2^{(1)}(z) = \left( -\frac{3i}{z^3} - \frac{3}{z^2} + \frac{i}{z} \right) e^{iz}$$

$$h_0^{(2)}(z) = i \frac{e^{-iz}}{z}$$

$$h_1^{(2)}(z) = \left( \frac{i}{z^2} - \frac{1}{z} \right) e^{-iz} \quad (10.39)$$

$$h_2^{(2)}(z) = \left( \frac{3i}{z^3} - \frac{3}{z^2} - \frac{i}{z} \right) e^{-iz}$$

**3. Spherical Harmonic Expansion of Plane Waves.** The regular radial eigenfunctions of the Schrödinger equation for  $V = 0$  constitute a complete set, as a consequence of a fundamental theorem concerning Sturm-Liouville differential equations<sup>4</sup> of which (10.19) is an example. Hence, we have before us two alternative complete sets of eigenfunctions of the free particle

<sup>4</sup> P. M. Morse and H. Feshbach, *Methods of Theoretical Physics*, McGraw-Hill Book Company, New York, 1953, p. 738.

$$\sin(x-y) = \sin x \cos y - \cos x \sin y$$



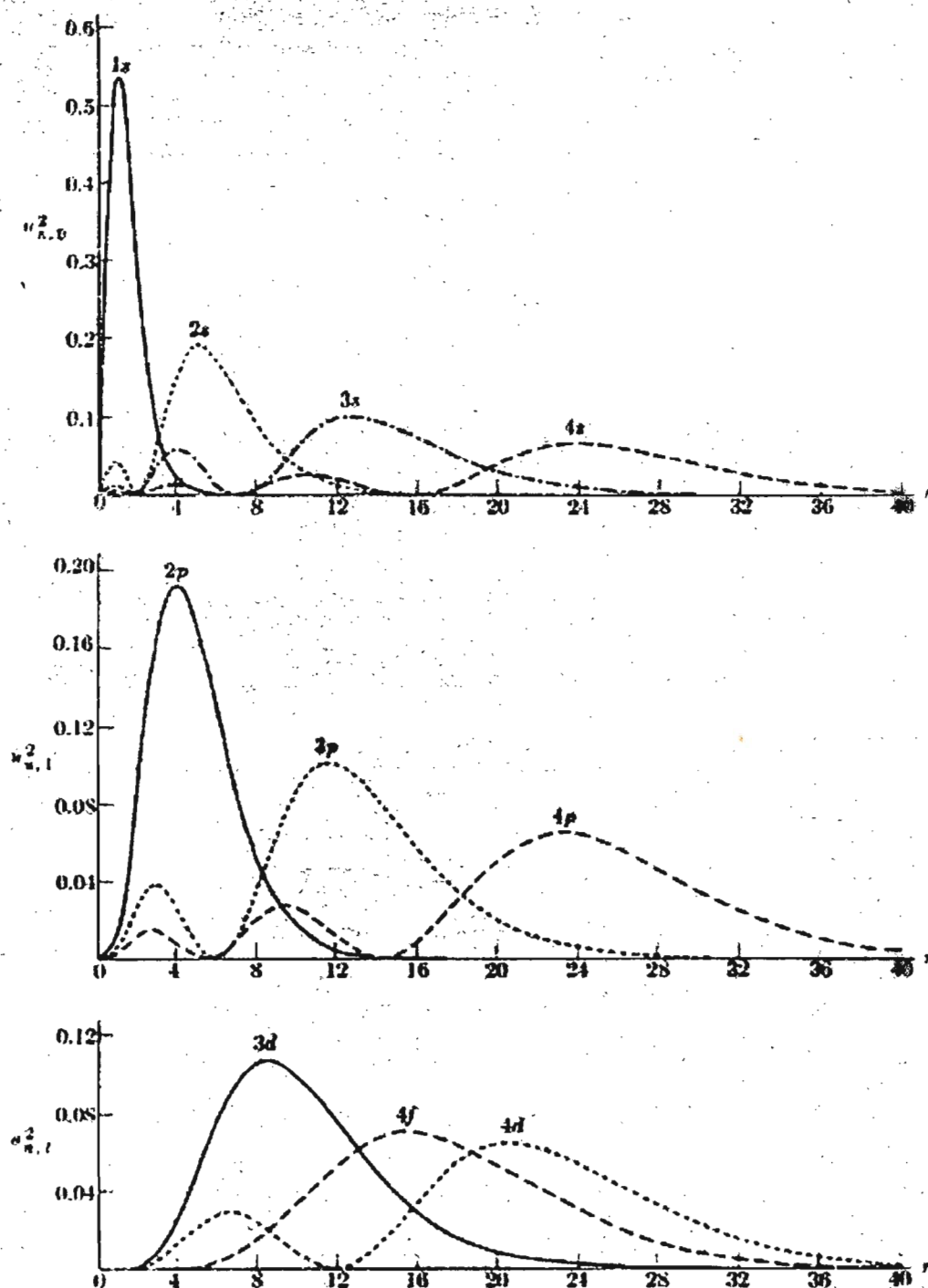


FIG. 7-6. The radial probability distribution function  $w_{n,l}^2$  for several values of the quantum numbers  $n, l$ . (From E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1933, by permission.)



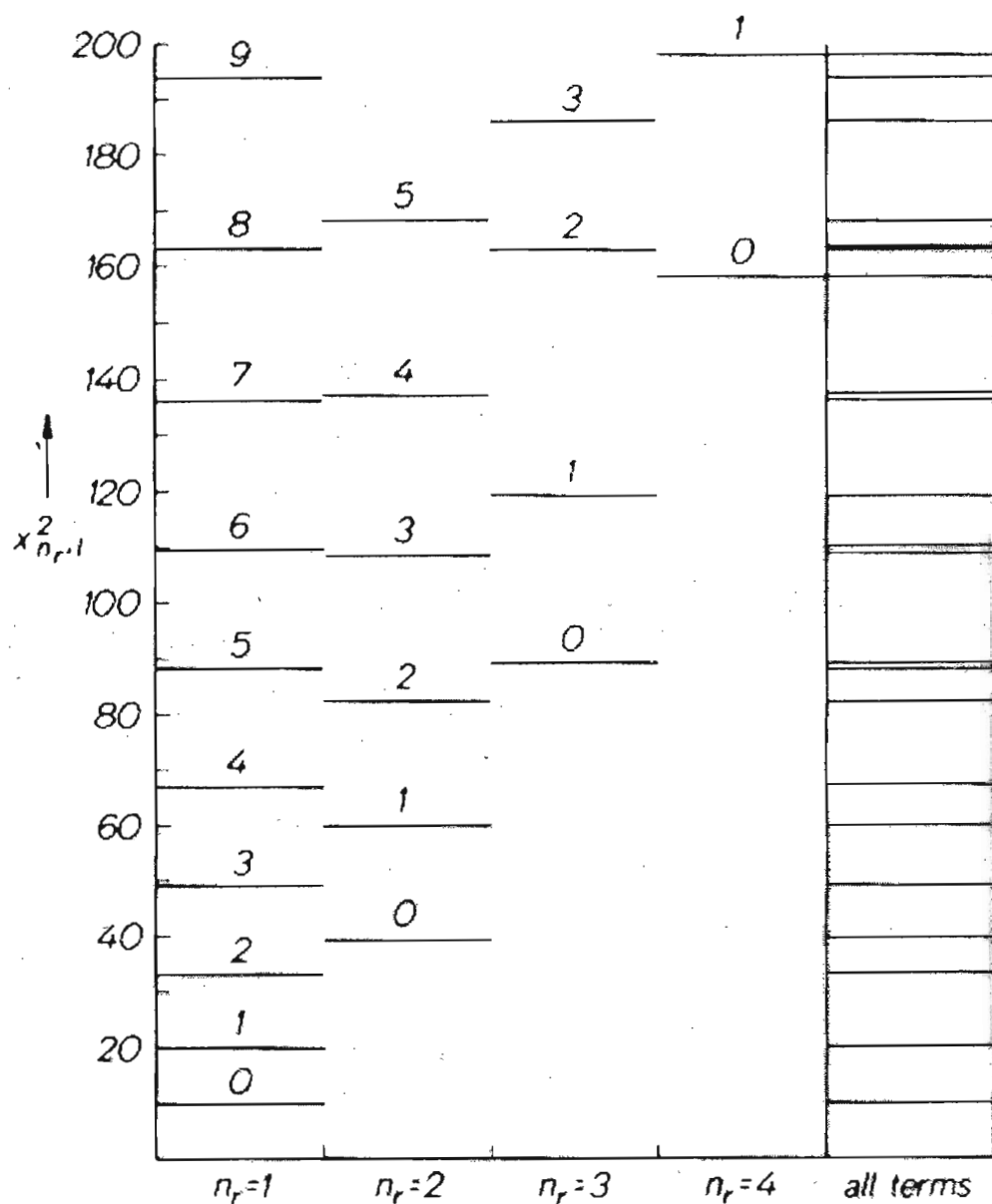



Fig. 35. Energy levels for a particle enclosed in a sphere



Table of the values of  $x_{n,l}$

		1	2	3	4
0		3.142	6.283	9.425	12.566
1		4.493	7.725	10.904	14.066
2		5.764	9.095	12.323	
3		6.988	10.417	13.698	
4		8.183	11.705		
5		9.356	12.967		
6		10.513	14.207		
7		11.657			
8		12.791			
9		13.916			



# The kinetic energy operator in 3D

Classically,  $K = \frac{1}{2m} p_r^2 + \frac{1}{2mr^2} L^2$   
 $p_r$  is radial component of the momentum.

What is  $\hat{p}_r$ ?

$$(\underline{A} \times \underline{B}) \cdot (\underline{C} \times \underline{D}) = (\underline{A} \cdot \underline{C})(\underline{B} \cdot \underline{D}) - (\underline{A} \cdot \underline{D})(\underline{B} \cdot \underline{C})$$

(just write out in Cartesian components)

If we want to deal w ops, need to keep order straight.

$$[r_\alpha, p_\beta] = i\hbar \delta_{\alpha\beta}, \text{ so } p_\beta r_\alpha = r_\alpha p_\beta - i\hbar \delta_{\alpha\beta}$$

$$RHS = \sum_{\alpha} \sum_{\beta} A_{\alpha} C_{\alpha} B_{\beta} D_{\beta} - \sum_{\alpha} \sum_{\beta} A_{\alpha} D_{\alpha} B_{\beta} C_{\beta} \quad \text{dot products.}$$

$$= \sum_{\alpha} \sum_{\beta} \{ A_{\alpha} B_{\beta} C_{\alpha} D_{\beta} - A_{\alpha} B_{\beta} C_{\beta} D_{\alpha} \} \quad \text{keep original order}$$

$$L^2 = \underline{L} \cdot \underline{L} = (\underline{r} \times \underline{p}) \cdot (\underline{r} \times \underline{p})$$

$$= \sum_{\alpha} \sum_{\beta} \{ r_{\alpha} p_{\beta} r_{\alpha} p_{\beta} - r_{\alpha} p_{\beta} r_{\beta} p_{\alpha} \}$$

$$\begin{aligned} p_{\beta} r_{\alpha} - r_{\alpha} p_{\beta} &= -i\hbar \delta_{\alpha\beta} \\ p_{\beta} r_{\beta} &= i\hbar \delta_{\alpha\beta} \end{aligned}$$

$$= \sum_{\alpha} \sum_{\beta} \{ (r_{\alpha} r_{\alpha} p_{\beta} p_{\beta} - i\hbar \delta_{\alpha\beta} r_{\alpha} p_{\beta}) - (p_{\beta} r_{\alpha} r_{\beta} p_{\alpha} + i\hbar \delta_{\alpha\beta} r_{\beta} p_{\alpha}) \}$$

$$= r^2 p^2 - 2i\hbar \underline{r} \cdot \underline{p} - \sum_{\alpha} \sum_{\beta} (r_{\beta} p_{\beta} r_{\alpha} p_{\alpha} - i\hbar \delta_{\beta\beta} r_{\alpha} p_{\alpha})$$

$$= r^2 p^2 - 2i\hbar \underline{r} \cdot \underline{p} - (\underline{r} \cdot \underline{p})(\underline{r} \cdot \underline{p}) + i\hbar 3 \underline{r} \cdot \underline{p}$$

$$L^2 = r^2 p^2 + i\hbar \underline{r} \cdot \underline{p} - (\underline{r} \cdot \underline{p})(\underline{r} \cdot \underline{p})$$



Solve for  $p^2$

$$r^2 p^2 = L^2 - i\hbar (\underline{r} \cdot \underline{p}) + (\underline{r} \cdot \underline{p})^2$$

$$p^2 = \frac{1}{r^2} (\underline{r} \cdot \underline{p})^2 - \frac{i\hbar}{r^2} \underline{r} \cdot \underline{p} + \frac{L^2}{r^2} \quad \text{(put in 'box') (X)}$$

Define a new operator  $p_r$  - the radial component of the momentum -

$$p_r = \frac{1}{2} \left( \frac{1}{r} \underline{r} \cdot \underline{p} + \underline{p} \cdot \underline{r} \frac{1}{r} \right) = \frac{1}{2} (\hat{r} \cdot \underline{p} + \underline{p} \cdot \hat{r})$$

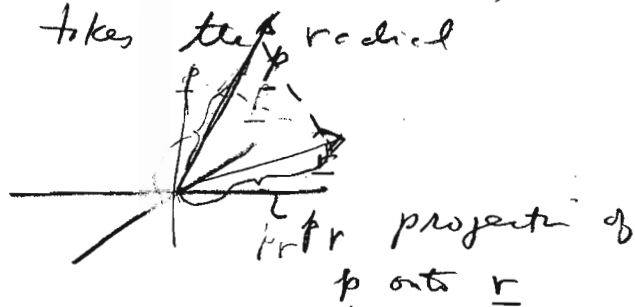
$\hat{r} \equiv \underline{r}/|\underline{r}| = \underline{r}/r$  a unit ~~vec~~ vectn. [N.B.  $\hat{\cdot}$  indicates unit vectors conventionally (nothing to do w/  $\Phi(r)$ )]

$$\hat{r} \cdot \hat{r} = \frac{\underline{r}}{r} \cdot \frac{\underline{r}}{r} = \frac{r^2}{r^2} = 1.$$

Comparing this with the classical version of  $p_r$ ,

$$p_r \equiv \hat{r} \cdot \underline{p} \quad \text{is} \quad \hat{r} \text{ takes the radial}$$

Component of the momentum.



If we tried to use  $\hat{r} \cdot \underline{p}$  as operator in QM it is not Hermitian. But, you know that  $AB + BA$  is Hermitian, even if  $AB$  is not.  $(AB)^\dagger = B^\dagger A^\dagger$   
 $(AB + BA)^\dagger = (AB)^\dagger + (BA)^\dagger = B^\dagger A^\dagger + A^\dagger B^\dagger = A^\dagger B^\dagger + B^\dagger A^\dagger$   
 when  $A + B$  are Hermitian.  $= AB + BA$  Q.E.D.



You show that  $[r, p_r] = i\hbar$  where  $p_r = \hat{r} \cdot \underline{p}$   
 First show that  $[r, \underline{p}] = i\hbar \underline{r}/|\underline{r}| = i\hbar \hat{r}$ , then  $\hat{r} \cdot [r, \underline{p}]$   
 $= r \hat{r} \cdot \underline{p} - \hat{r} \cdot \underline{p} r = r p_r - p_r r = [r, p_r]$   
 Want to write  $p^2$  in terms of  $p_r$ .

Remember  $[p_x, f] = \frac{\hbar}{i} \frac{\partial f}{\partial x}$

$$[\underline{p}, f] = \frac{\hbar}{i} \left( \frac{\partial f}{\partial x} \hat{i} + \frac{\partial f}{\partial y} \hat{j} + \frac{\partial f}{\partial z} \hat{k} \right) = \frac{\hbar}{i} \underline{\nabla} f$$

$$f = r/r \quad \underline{p} \cdot \underline{r}/r = \underline{p} \cdot \underline{p}/r + \frac{\hbar}{i} \underline{\nabla} \cdot \underline{r}/r$$

$$p_r = \frac{1}{2} \left( \frac{1}{r} \underline{r} \cdot \underline{p} + \underline{p} \cdot \underline{r} \frac{1}{r} \right) = \frac{1}{2} \left( \frac{1}{r} \underline{r} \cdot \underline{p} + \underline{p} \cdot \underline{r} \frac{1}{r} + \frac{\hbar}{i} \underline{\nabla} \cdot \underline{r} \frac{1}{r} \right)$$

$$p_r = \frac{1}{r} \underline{r} \cdot \underline{p} - \frac{i\hbar}{r}$$

$$\begin{aligned} \underline{\nabla} \cdot \frac{\underline{r}}{r} &= \sum_{\alpha} \left( \frac{\partial_x r_{\alpha}}{r} + r_{\alpha} \partial_x \frac{1}{r} \right) \\ &= \left( \sum_{\alpha} \frac{1}{r} \right) + \sum_{\alpha} r_{\alpha} \partial_x \frac{1}{\sqrt{x^2 + y^2 + z^2}} \\ &= \frac{3}{r} + -\frac{1}{2} \sum_{\alpha} r_{\alpha} \frac{2 r_{\alpha}}{r^3} \\ &= \frac{3}{r} - \sum_{\alpha} \frac{r_{\alpha}^2}{r^3} = \frac{3}{r} - \frac{r^2}{r^3} = \frac{2}{r} \end{aligned}$$

So

$$\underline{r} \cdot \underline{p} = r p_r + i\hbar$$

Then (see pg 2 X)

$$\frac{1}{r^2} (\underline{r} \cdot \underline{p})^2 - \frac{i\hbar}{r^2} (\underline{r} \cdot \underline{p}) = \frac{1}{r^2} (\underline{r} \cdot \underline{p} - i\hbar) (\underline{r} \cdot \underline{p})$$

$$= \frac{1}{r^2} (r p_r + i\hbar - i\hbar) (\underline{r} \cdot \underline{p}) = \frac{1}{r^2} p_r (\underline{r} \cdot \underline{p}) = \frac{1}{r^2} p_r (r p_r + i\hbar)$$

$$= \frac{1}{r^2} (\overbrace{p_r r p_r}^{= r p_r - i\hbar} + i\hbar p_r) = \frac{1}{r^2} (r p_r p_r - i\hbar p_r + i\hbar p_r) = p_r^2$$

$$p^2 = p_r^2 + \frac{L^2}{r^2}$$

$$K = \frac{1}{2m} p_r^2 + \frac{1}{2m r^2} L^2$$

from  $r p_r - p_r r = i\hbar$




Return to the  $S$  equation. Let us set  $V=0$  to do the 3D free particle problem.

$$H = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$= \frac{1}{2m} p_r^2 + \frac{1}{2mr^2} L^2$$

Look for eigenvalues of  $H, L^2, L_z$ .

Useful for theory of scattering,

incident plane wave  $k$   ← scattered waves (spherical)

Far from material the waves are free particle (3D)

The  $S$  eq is

$$\left[ \frac{1}{2m} p_r^2 + \frac{1}{2mr^2} l(l+1)\hbar^2 \right] \psi_{klm}(r, \theta, \phi) = \frac{\hbar^2 k^2}{2m} \psi_{klm}(r, \theta, \phi)$$

where  $E = \hbar^2 k^2 / 2m$  is free particle energy

The radial momentum operator is

$$p_r = \frac{1}{r} \underline{r} \cdot \underline{p} - \frac{i\hbar}{r}$$

now,  $\underline{p} = \frac{\hbar}{i} \left( \frac{d}{dr} \hat{r} + \frac{d}{d\theta} \hat{\theta} + \frac{d}{d\phi} \hat{\phi} \right)$  in sph. coords, so

$$\underline{r} \cdot \underline{p} = \frac{\hbar}{i} r \frac{d}{dr}$$

$$\underline{r} \cdot \underline{p} = r \hat{r} \cdot \underline{p} = r \frac{\hbar}{i} \frac{d}{dr} \quad \left( \frac{\hat{r} \cdot \hat{r}}{1} \right)$$

$$p_r = \frac{\hbar}{i} \left( \frac{d}{dr} + \frac{1}{r} \right)$$



And, we may write this as

$$p_r = \frac{\hbar}{i} \frac{1}{r} \frac{d}{dr} r \quad \text{since}$$

$$\frac{\hbar}{i} \frac{1}{r} \frac{d}{dr} r f = \frac{\hbar}{i} \left( r \frac{df}{dr} + f \right) = \frac{\hbar}{i} \left( r \frac{d}{dr} + 1 \right) f$$

$$p_r p_r f = -\hbar^2 \frac{1}{r} \frac{d}{dr} \left( r \frac{1}{r} \frac{d}{dr} r f \right) = -\hbar^2 \frac{1}{r} \frac{d^2}{dr^2} r f$$

Then the eq. is for radial part

$$\textcircled{*} \quad \left[ -\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} r + \frac{\hbar^2}{2mr^2} l(l+1) \right] R(r) = E R(r)$$

This diff. eq. can be solved by standard power series solution method (Essentially same method as we did for Legendre).

Another way: set  $\rho = \sqrt{\frac{2mE}{\hbar^2}} r \equiv kr$      $v(\rho) = r R(r)$

and  $\lambda = l+1$  or  $\lambda = -l$  (Rename Legendre)

Then diff. eq. becomes

$$\frac{d^2 v}{d\rho^2} + \left[ 1 - \frac{\lambda(\lambda-1)}{\rho^2} \right] v = 0$$

$$* \quad \frac{1}{r} \frac{d^2}{dr^2} r f = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{df}{dr} \right)$$

$$\text{both} = \frac{2f'}{r} + f''$$



The solution of this equation defines, for the solution that vanishes at  $\rho=0$ , are the spherical Bessel function of the first kind. (Regular soln).

$$R(r) = C j_l(kr)$$

They are related to the ordinary Bessel functions as

$$j_l(z) = \sqrt{\frac{\pi}{2z}} J_{l+\frac{1}{2}}(z).$$

$$j_0(kr) = \sin kr / kr$$

$$j_1(kr) = \frac{\sin kr}{(kr)^2} - \frac{\cos kr}{kr}$$

$$j_l(\rho) = \rho^l \left( -\frac{1}{\rho} \frac{d}{d\rho} \right)^l j_0(\rho)$$

Show plots.



Fig. 8.6 Plots of the spherical Bessel functions  $j_0$ ,  $j_1$ , and  $j_2$ .

