

previously for a particle in a box. In the case of the hydrogen atom, the "box" is a sphere with sloping rather than vertical potential "walls." As with the particle-in-a-box solution, constraints or boundary conditions are imposed which make possible the solution of the wave equation. These conditions are:

1. The wave function must be single-valued.
2. The wave function and its first derivative must be continuous.
3. The wave function must go to zero at infinity. This is a necessary condition so that the atom be finite.
4. The probability of finding the electron summed over all space must be one, that is, the wave function must be normalized.

It is found that the solution for the hydrogen atom contains three quantum numbers n , l , and m_l (as expected for a three-dimensional system). The allowed values for these quantum numbers are discussed below. Each solution found for a different set of n , l , m_l is called an *eigenfunction* and represents an orbital in the hydrogen atom.

In order to plot the complete wave functions, one would in general require a four-dimensional graph with coordinates for each of the three spatial dimensions (x , y , z ; or r , θ , ϕ) and a fourth value of the wave function.

In order to circumvent this problem and also to make it easier to visualize the actual distribution of electrons within the atom, it is common to break down the wave function, Ψ , into three parts, each of which is a function of but a single variable. It is most convenient to use polar coordinates, so one obtains:

$$\Psi(r, \theta, \phi) = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi) \quad (2.9)$$

where $R(r)$ gives the dependence of Ψ upon distance from the nucleus and Θ and Φ give the angular dependence.

The radial wave function, R

The radial functions for the first three orbitals⁵ in the hydrogen atom are

$$n = 1, l = 0, m_l = 0 \quad R = 2 \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0} \quad 1s \text{ orbital}$$

$$n = 2, l = 0, m_l = 0 \quad R = \left(\frac{1}{2\sqrt{2}} \right) \left(\frac{Z}{a_0} \right)^{3/2} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0} \quad 2s \text{ orbital}$$

$$n = 2, l = 1, m_l = 0 \quad R = \left(\frac{1}{2\sqrt{6}} \right) \left(\frac{Z}{a_0} \right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \quad 2p \text{ orbital}$$

⁵ The general formulas for radial eigenfunctions in terms of the quantum numbers n and l are given by L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, and by D. J. Royer, "Bonding Theory," McGraw-Hill, New York, 1968. The complete wave functions including both the radial and angular parts through the n th level are given by Pauling ($n = 6$), Royer ($n = 3$), and F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed., Wiley, New York, 1966 ($n = 3$).

where Z is the nuclear charge, e is the base of natural logarithms, and a_0 is the radius of the first Bohr orbit. According to the Bohr theory, this was an immutable radius, but in wave mechanics it is simply the "most probable" radius for the electron to be at. Its value, 52.9 pm, is determined by $a_0 = h^2/4\pi^2 me^2$, where h is Planck's constant and m and e are the mass and charge of the electron, respectively. In hydrogen, $Z = 1$, but similar orbitals may be constructed where $Z > 1$ for other elements. For many-electron atoms, exact solutions of the wave equation are impossible to obtain, and these "hydrogen-like" orbitals are often used as a first approximation.⁶

Although the radial functions may appear formidable, the important aspects may be made apparent by grouping the constants. For a given atom, Z will be constant and may be combined with the other constants, resulting in considerable simplification:

$n = 1, l = 0, m_l = 0$	$R = K_{1s} e^{-Zr/a_0}$	1s orbital
$n = 2, l = 0, m_l = 0$	$R = K_{2s} \left(2 - \frac{Zr}{a_0} \right) e^{-Zr/2a_0}$	2s orbital
$n = 2, l = 1, m_l = 0$	$R = K_{2p} r e^{-Zr/2a_0}$	2p orbital

The most apparent feature of the radial wave functions is that they all represent an exponential "decay" (mathematically similar in form to the radioactive decay of radioactive isotopes), and that for $n = 2$ the decay is slower than for $n = 1$. This may be generalized for all radial functions: They decay as e^{-Zr/na_0} . For this reason, the radius of the various orbitals (actually, the most *probable* radius) increases with increasing n . A second feature is the presence of a *node* in the 2s radial function. At $r = 2a_0/Z$, $R = 0$ and the value of the radial function changes from positive to negative. Again, this may be generalized: s orbitals have $n - 1$ nodes, p orbitals have $n - 2$ nodes, etc. The radial functions for the hydrogen 1s, 2s, and 2p orbitals are shown in Fig. 2.3.

Since we are principally interested in the *probability* of finding electrons at various points in space, we shall be more concerned with the *square* of the radial functions than with the functions themselves. A useful way of looking at the problem is to consider the atom to be composed of "layers" much like an onion and to examine the probability of finding the electron in the "layer" which extends from r to $r + dr$, as shown in Fig. 2.4. The volume of the thin shell may be considered to be dV . Now the volume of the sphere is:

$$V = \frac{4\pi r^3}{3} \quad (2.10)$$

$$dV = 4\pi r^2 dr \quad (2.11)$$

$$R^2 dV = 4\pi r^2 R^2 dr \quad (2.12)$$

⁶ The use of hydrogen-like orbitals for multielectron atoms neglects electron-electron repulsion, which may often cause serious problems (see pp. 27–29).

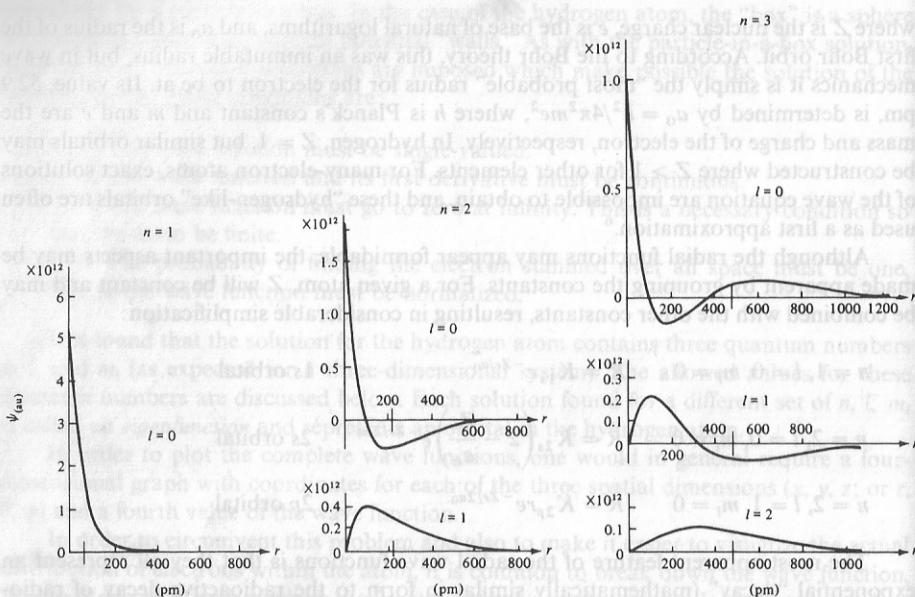


Fig. 2.3 Radial part of the hydrogen eigenfunctions for $n = 1, 2, 3$. [From "Atomic Spectra and Atomic Structure," by Gerhard Herzberg, Dover Publications, Inc., New York, 1944. Reprinted through permission of the publisher.]

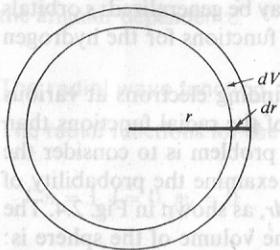


Fig. 2.4 Volume of shell of thickness dr .

Consider the radial portion of the wave function for the 1s orbital as plotted in Fig. 2.3. When it is squared and multiplied by $4\pi r^2$, we obtain the *probability function* shown in Fig. 2.5. The essential features of this function may be obtained qualitatively as follows:

1. At $r = 0$, $4\pi r^2 R^2 = 0$; hence the value at the nucleus must be zero.
2. At large values of r , R approaches zero rapidly and hence $4\pi r^2 R^2$ must approach zero.
3. In between, r and R both have finite values, so there is a maximum in the plot of probability ($4\pi r^2 R^2$) as a function of r . This maximum occurs at $r = a_0$, the value of the Bohr radius.

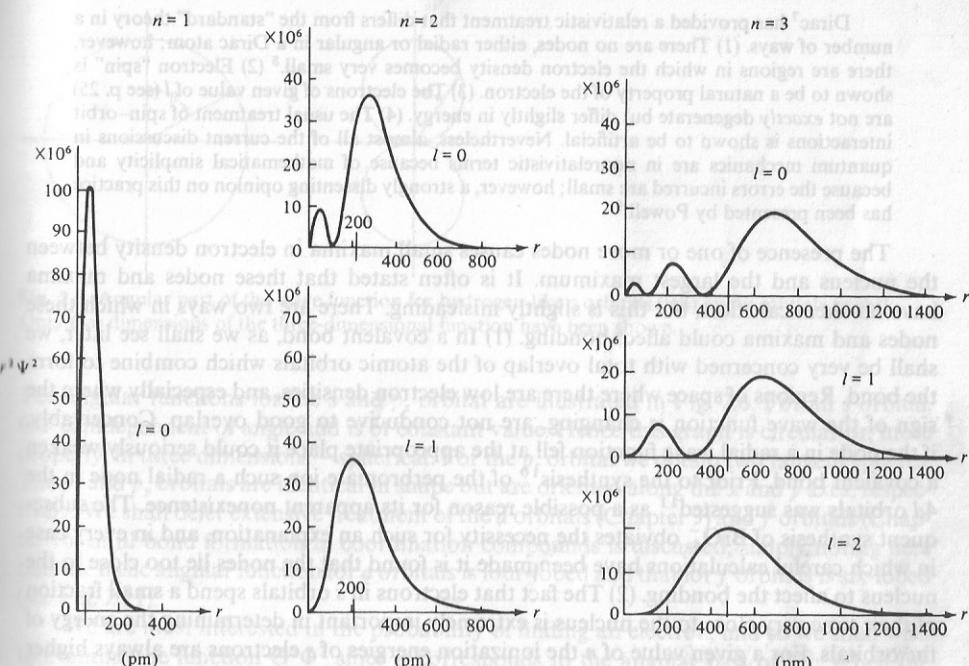


Fig. 2.5 Radial probability functions for $n = 1, 2, 3$ for the hydrogen atom. The function gives the probability of finding the electron in a spherical shell of thickness dr at a distance r from the nucleus. [From "Atomic Spectra and Atomic Structure," by Gerhard Herzberg, Dover Publications, Inc., New York, 1944. Reprinted through permission of the publisher.]

The meaning of Figs 2.6 and 2.7 is easily misunderstood. Neither one has any direct similarity to the probability function shown in Fig. 2.5. Similar probability functions (including the factor $4\pi r^2$) for the 2s, 2p, 3s, 3p, and 3d orbitals are also shown in Fig. 2.5. Note that although the radial function for the 2s orbital is both positive ($r < 2a_0/Z$) and negative ($r > 2a_0/Z$), the probability function is everywhere *positive* (as of course it must be to have any physical meaning) as a result of the squaring operation.

The presence of a node in the wave function indicates a point in space at which the probability of finding the electron has gone to zero. This raises the interesting question, "How does the electron get from one side of the node to the other if it can never be found exactly *at* the node?" This is not a valid question as posed, since it presupposes our macroscopically prejudiced view that the electron is a particle. If we consider the electron to be a standing wave, no problem arises because it simultaneously exists on both sides of a node. Consider a vibrating string on an instrument such as a guitar. If the string is fretted at the twelfth fret the note will go up one octave because the wavelength has been shortened by one-half. Although it is experimentally difficult (a finger is not an infinitesimally small point!), it is possible to sound the same note on either half of the octave-fretted string. This vibration can be continuous through the node at the fret. In fact, on the open string overtones occur at the higher harmonics such that nodes occur at various points along the string. Nodes are quite common to wave behavior, and conceptual problems arise only when we try to think of the electron as a "hard" particle with a definite position.

Dirac⁷ has provided a relativistic treatment that differs from the "standard" theory in a number of ways. (1) There are no nodes, either radial or angular in a Dirac atom; however, there are regions in which the electron density becomes very small.⁸ (2) Electron "spin" is shown to be a natural property of the electron. (3) The electrons of given value of l (see p. 25) are not *exactly* degenerate but differ slightly in energy. (4) The usual treatment of spin-orbit interactions is shown to be artificial. Nevertheless, almost all of the current discussions in quantum mechanics are in nonrelativistic terms because of mathematical simplicity and because the errors incurred are small; however, a strongly dissenting opinion on this practice has been presented by Powell.⁹

The presence of one or more nodes causes small maxima in electron density between the nucleus and the largest maximum. It is often stated that these nodes and maxima have no chemical effect, but this is slightly misleading. There are two ways in which these nodes and maxima could affect bonding. (1) In a covalent bond, as we shall see later, we shall be very concerned with total overlap of the atomic orbitals which combine to form the bond. Regions of space where there are low electron densities, and especially where the sign of the wave function is changing, are not conducive to good overlap. Conceivably, if the node in a radial wave function fell at the appropriate place it could seriously weaken a covalent bond. Prior to the synthesis¹⁰ of the perbromate ion such a radial node in the $4d$ orbitals was suggested¹¹ as a possible reason for its apparent nonexistence. The subsequent synthesis of BrO_4^- obviates the necessity for such an explanation, and in every case in which careful calculations have been made it is found that the nodes lie too close to the nucleus to affect the bonding. (2) The fact that electrons in s orbitals spend a small fraction of their time very close to the nucleus is extremely important in determining the energy of the orbitals. For a given value of n the ionization energies of s electrons are always higher than those of corresponding p electrons (and the trend continues to d and f electrons) because the s orbitals are more *penetrating*; i.e., they have considerable electron density in the region of the nucleus. This is the fundamental reason for the ordering of the energy levels: $1s, 2s, 2p, 3s, 3p$, etc. (see pp. 27 and 37).

Angular wave functions

The angular part of the wave function determines the shape of the electron cloud and varies depending upon the type of orbital involved (s, p, d , or f) and its orientation in space. However, for a given type of orbital, such as s or p_z , the angular wave function is independent of the principal quantum number or energy level. Some typical angular functions are:

$$\begin{array}{ll} l = 0, m_l = 0 & \Theta\Phi = (1/4\pi)^{1/2} \quad s \text{ orbital} \\ l = 1, m_l = 0 & \Theta\Phi = (3/4\pi)^{1/2} \cos \theta \quad p_z \text{ orbital} \\ l = 2, m_l = 0 & \Theta\Phi = (5/16\pi)^{1/2}(3 \cos^2 \theta - 1) \quad d_{z^2} \text{ orbital} \end{array}$$

⁷ P. A. Dirac, *Proc. R. Soc. London, Ser. A*, **1928**, *117*, 610; **1928**, *118*, 351.

⁸ For contour diagrams of relativistic orbitals, see A. Szabo, *J. Chem. Educ.*, **1969**, *46*, 678.

⁹ R. E. Powell, *J. Chem. Educ.*, **1968**, *45*, 558.

¹⁰ E. H. Appelman, *J. Am. Chem. Soc.*, **1968**, *90*, 1900.

¹¹ D. S. Urch, *J. Inorg. Nucl. Chem.*, **1963**, *25*, 771.

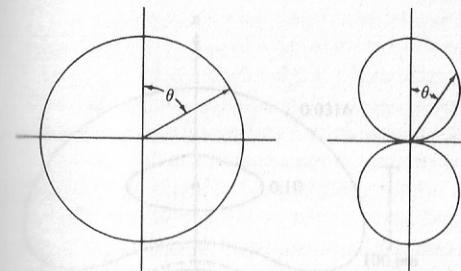


Fig. 2.6 Angular part of the wave function for hydrogen-like s orbitals (left) and p orbitals (right). Only two dimensions of the three-dimensional function have been shown.

The angular functions for the s and p_z orbital are illustrated in Fig. 2.6. For an s orbital, $\Theta\Phi$ is independent of angle and is of constant value. Hence this graph is circular or, more properly, in three dimensions—spherical. For the p_z orbital we obtain two tangent spheres. The p_x and p_y orbitals are identical in shape but are oriented along the x and y axes, respectively. We shall defer extensive treatment of the d orbitals (Chapter 9) and f orbitals (Chapter 16) until bond formation in coordination compounds is discussed, simply noting here that the basic angular function for d orbitals is four-lobed and that for f orbitals is six-lobed (see Fig. 2.11).

We are most interested in the probability of finding an electron, and so we shall wish to examine the function $\Theta^2\Phi^2$ since it corresponds to the angular part of Ψ^2 . When the angular functions are squared, different orbitals change in different ways. For an s orbital squaring causes no change in shape since the function is everywhere the same; thus another sphere is obtained. For both p and d orbitals, however, the plot tends to become more elongated (see Fig. 2.7).

The meaning of Figs. 2.6 and 2.7 is easily misinterpreted. Neither one has any direct physical meaning. Both are graphs of mathematical functions, just as Figs. 2.3 and 2.5 are. Both may be used to obtain information about the probable distribution of electrons, but

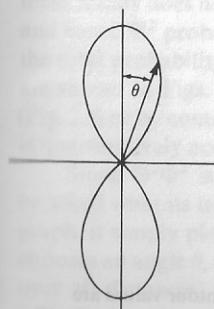


Fig. 2.7 Angular probability function for hydrogen-like p orbitals. Only two dimensions of the three-dimensional function have been shown.

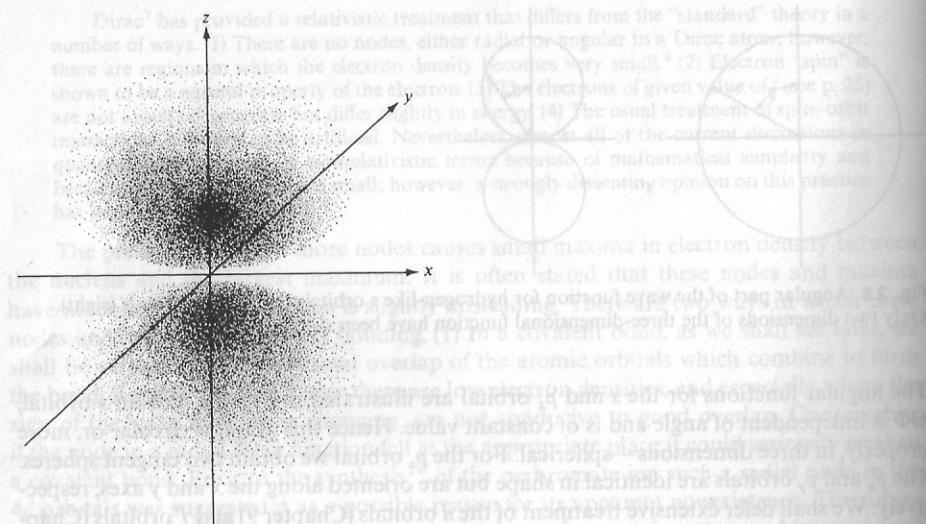


Fig. 2.8 Pictorial representation of electron density in a hydrogen-like $2p$ orbital.

Because of the small size of the atomic nucleus, the electron density is very large near the nucleus and drops off rapidly as the distance from the nucleus increases. This is true for all atoms, but the effect is most pronounced in the lightest elements. For example, the radius of the $1s$ orbital of hydrogen is about 52 pm, while that of the $1s$ orbital of cesium is about 150 pm. The radius of the $2p$ orbital of hydrogen is about 100 pm, while that of the $2p$ orbital of cesium is about 150 pm. The radius of the $3p$ orbital of hydrogen is about 150 pm, while that of the $3p$ orbital of cesium is about 200 pm.

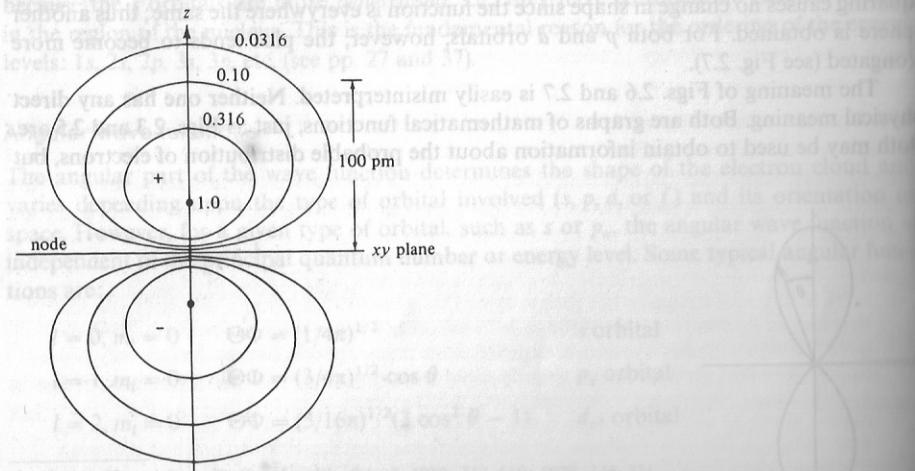


Fig. 2.9 Electron density contours for hydrogen-like $2p_z$ orbital of carbon. Contour values are relative to the electron density maximum. The xy plane is a nodal surface. The signs (+ and -) refer to the original wave function, Ψ . [From E. A. Ogryzlo and G. B. Porter, *J. Chem. Educ.*, 1963, 40, 258. Reproduced with permission.]

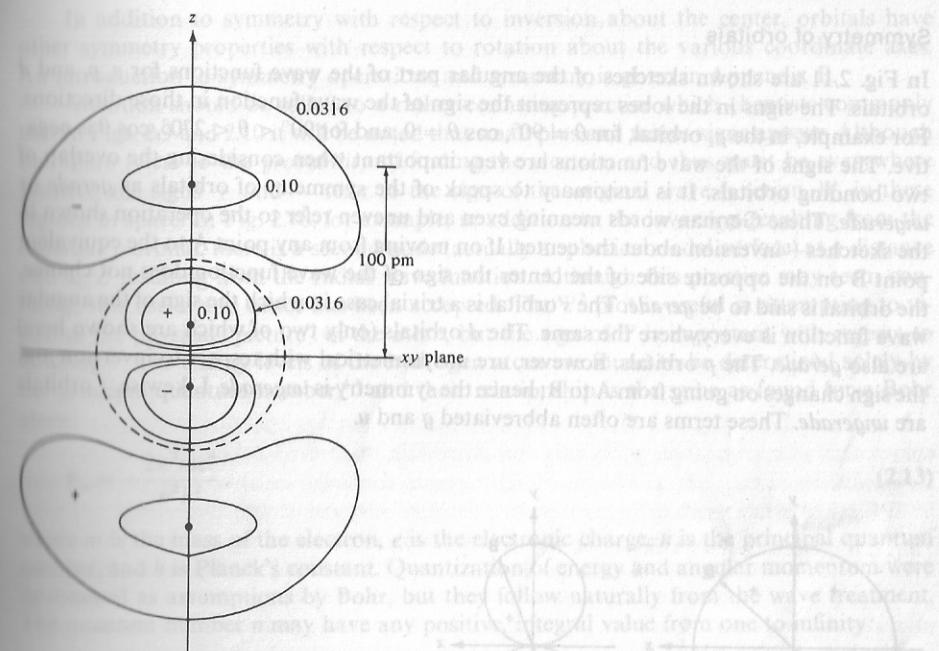


Fig. 2.10 Electron density contours for hydrogen-like $3p_z$ orbital of chlorine. Contour values are relative to the electron density maximum. The xy plane and a sphere of radius 52 pm (dashed line) are nodal surfaces. The signs (+ and -) refer to the original wave function, Ψ . [From E. A. Ogryzlo and G. B. Porter, *J. Chem. Educ.*, 1963, 40, 258. Reproduced with permission.]

neither may in any way be regarded as a “picture” of an orbital. It is an unfortunate fact that fuzzy drawings of Figs. 2.6 or 2.7 are often presented as “orbitals.” Now one can define an orbital in any way one wishes, corresponding to Ψ , Ψ^2 , R , R^2 , $\Theta\Phi$, or $\Theta^2\Phi^2$, but it should be realized that Figs. 2.3, 2.5, 2.6, and 2.7 are mathematical functions and drawing them fuzzily does not represent an atom. Chemists tend to think in terms of electron clouds, and hence Ψ^2 probably gives the best intuitive “picture” of an orbital. Methods of showing the total probability of finding an electron including both radial and angular probabilities are shown in Figs. 2.8–2.10. Although electron density may be shown either by shading (Fig. 2.8) or by contours of equal electron density (Figs. 2.9 and 2.10), only the latter method is quantitatively accurate.¹²

Since $\Theta^2\Phi^2$ is termed an angular probability function, the question may properly be asked what its true meaning is, if not a “picture” of electron distribution. Like any other graph, it simply plots the value of a function ($\Theta^2\Phi^2$) versus the variable (θ or θ , ϕ). If one chooses an angle θ , the probability that the electron will be found in that direction (summed over all distances) is proportional to the magnitude of the vector connecting the origin with the functional plot at that angle.

¹² For further discussion of this point, see B. Perlmutter-Hayman, *J. Chem. Educ.*, 1969, 46, 428.

Symmetry of orbitals

In Fig. 2.11 are shown sketches of the angular part of the wave functions for *s*, *p*, and *d* orbitals. The signs in the lobes represent the sign of the wave function in those directions. For example, in the *p*_{*z*} orbital, for $\theta = 90^\circ$, $\cos \theta = 0$, and for $90^\circ < \theta < 270^\circ$, $\cos \theta$ is negative. The signs of the wave functions are very important when considering the overlap of two bonding orbitals. It is customary to speak of the symmetry of orbitals as *gerade* or *ungerade*. These German words meaning even and uneven refer to the operation shown in the sketches—inversion about the center. If on moving from any point A to the equivalent point B on the opposite side of the center the sign of the wave function does not change, the orbital is said to be *gerade*. The *s* orbital is a trivial case in which the sign of the angular wave function is everywhere the same. The *d* orbitals (only two of which are shown here) are also *gerade*. The *p* orbitals, however, are unsymmetrical with respect to inversion and the sign changes on going from A to B; hence the symmetry is *ungerade*. Likewise, *f* orbitals are *ungerade*. These terms are often abbreviated *g* and *u*.

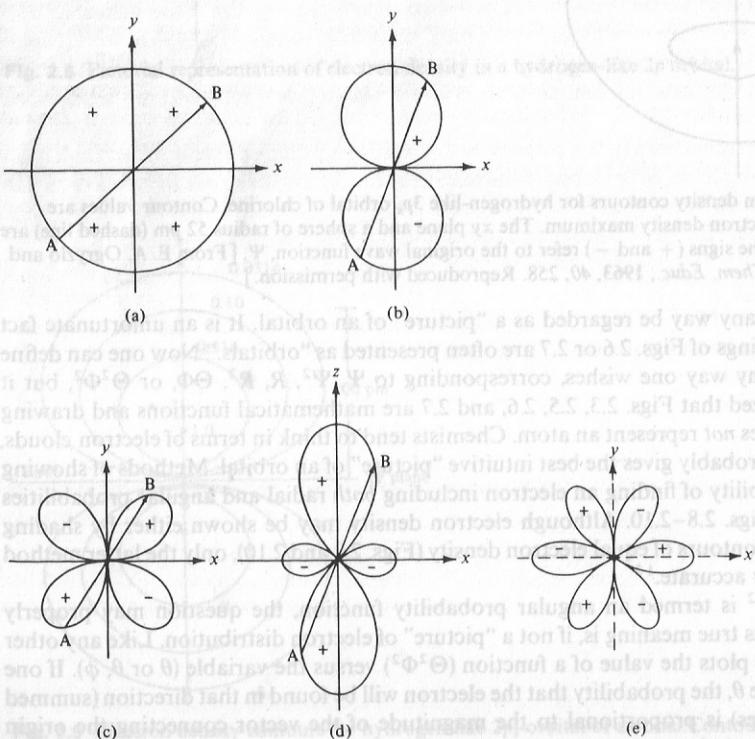


Fig. 2.11 Angular wave functions of *s*, *p*, *d*, and *f* orbitals illustrating *gerade* and *ungerade* symmetry: (a) *s* orbital, *gerade*; (b) *p* orbital, *ungerade*; (c) *d*_{*xy*} orbital and (d) *d*_{*z*²} orbital, both *gerade*; (e) *f*_{*z*³} orbital, *ungerade*.

In addition to symmetry with respect to inversion about the center, orbitals have other symmetry properties with respect to rotation about the various coordinate axes. An introduction to symmetry operations and symmetry is given in Appendix B.

Attention should be called to a rather confusing practice which chemists commonly use. In Figs. 2.9 and 2.10 it will be noted that small plus and minus signs appear. Although the figure refers to the *probability* of finding the electron and thus must be everywhere positive, the signs + and - refer to the sign of the original wave function, Ψ , in these regions of space. In Fig. 2.10, for example, in addition to the inversion resulting from the *ungerade* *p* orbital, there is a second node (actually a spherical nodal surface) at a distance of $6 a_0/Z$ resulting from the radial wave function. Although this practice may seem confusing, it is useful and hence has been accepted. The Ψ^2 plot is useful in attempting to visualize the physical "picture" of the atom, but the sign of Ψ is important with respect to bonding.¹³ The energy levels of the hydrogen atom are found to be determined solely by the principal quantum number,¹⁴ and their relationship is the same as found for a Bohr atom:

$$E_n = -\frac{2\pi^2 me^4}{n^2 h^2} \quad (2.13)$$

where m is the mass of the electron, e is the electronic charge, n is the principal quantum number, and h is Planck's constant. Quantization of energy and angular momentum were introduced as assumptions by Bohr, but they follow naturally from the wave treatment. The quantum number n may have any positive, integral value from one to infinity:

$$n = 1, 2, 3, 4, \dots, \infty$$

The lowest (most negative) energy corresponds to the minimum value of n ($n = 1$) and the energies increase (become less negative) with increasing n until the *continuum* is reached ($n = \infty$). Here the electron is no longer bound to the atom and thus is no longer quantized, but may have any amount of kinetic energy.

The allowed values of l range from zero to $n - 1$:

$$l = 0, 1, 2, 3, \dots, n - 1$$

The quantum number l is a measure of the orbital angular momentum of the electron and determines the "shape" of the orbital. The types of orbitals are designated by the letters *s*, *p*, *d*, *f*, *g*, ..., corresponding to the values of $l = 0, 1, 2, 3, 4, \dots$. The first four letters originate in spectroscopic notation (see p. 32) and the remainder follow alphabetically. In the previous section we have seen the various angular wave functions and the resulting distribution of electrons. The nature of the angular wave function is determined by the value of the quantum number l .

¹³ See M. Orchin and H. H. Jaffé, "The Importance of Antibonding Orbitals," Houghton Mifflin, Boston, 1967, pp. 5, 6, 9, for a good discussion of this point.

¹⁴ This statement is true only for the nonrelativistic treatment. If relativity effects are included, a small dependence on l is also found. This should not be confused with the much larger differences in orbital energies that result from electron-electron interactions in *polyelectronic atoms*.

For orbitals with $l > 0$, there are a number $(2l + 1)$ of equivalent ways in which the orbitals may be oriented in space. In the absence of an electric or magnetic field these orientations are *degenerate*; i.e., they are identical in energy. Consider, for example, the p orbital. It is possible to have a p orbital in which the maximum electron density lies on the z axis and the xy plane is a nodal plane. Equivalent orientations have the maximum electron density along the x or y axis. Application of a magnetic field splits the degeneracy of the set of three p orbitals. The *magnetic quantum number*, m_l , is related to the component of angular momentum along a chosen axis—for example, the z axis—and determines the orientation of the orbital in space. Values of m_l range from $-l$ to $+l$:

$$m_l = -l, -l+1, \dots, -1, 0, +1, +2, \dots, +l$$

Thus for $l = 1$, $m_l = -1, 0, +1$, and there are three p orbitals possible, p_x , p_y , and p_z . Similarly, for $l = 2$ (d orbitals), $m_l = -2, -1, 0, +1, +2$, and for $l = 3$ (f orbitals), $m_l = -3, -2, -1, 0, +1, +2, +3$.¹⁵

It is an interesting fact that just as the single s orbital is spherically symmetric, the summation of a set of three p orbitals, five d orbitals, or seven f orbitals is also spherical (Unsöld's theorem). Thus, although it might appear as though an atom such as neon with a filled set of s and p orbitals would have a "lumpy" electron cloud, the total probability distribution is perfectly spherical (see Problem 2.16).

From the above rules we may obtain the allowed values of n , l , and m_l . We have seen previously (p. 16) that a set of particular values for these three quantum numbers determines an eigenfunction or orbital for the hydrogen atom. The possible orbitals are therefore

$n = 1$	$l = 0$	$m_l = 0$	1s orbital
$n = 2$	$l = 0$	$m_l = 0$	2s orbital
$n = 2$	$l = 1$	$m_l = -1, 0, +1$	$2p_{(x,y,z)}$ orbitals
$n = 3$	$l = 0$	$m_l = 0$	3s orbital
$n = 3$	$l = 1$	$m_l = -1, 0, +1$	$3p_{(x,y,z)}$ orbitals
$n = 3$	$l = 2$	$m_l = -2, -1, 0, +1, +2$	$3d_{(z^2, x^2 - y^2, xy, xz, yz)}$ orbitals ¹⁶
$n = 4$	$l = 0$	$m_l = 0$	4s orbital

We can now summarize the relation between the quantum numbers n , l , and m_l and the physical pictures of electron distribution in orbitals by a few simple rules. It should be emphasized that these rules are no substitute for a thorough understanding of the previous discussion, but merely serve as handy guides to recall some of the relations.

1. Within a given atom, the lower the value of n , the more stable (lower in energy) will be the orbital.

¹⁵ Although the p_z and d_{z^2} orbitals correspond to $m = 0$, there is no similar one-to-one correspondence for the other orbitals and other values of m . See J. C. Davis, Jr., "Advanced Physical Chemistry," Ronald, New York, 1965, pp. 170–171, or B. N. Figgis, "Introduction to Ligand Fields," Wiley, New York, 1966, pp. 9–15.

¹⁶ These orbitals are sketched and discussed further in Chapter 9.

2. There are n types of orbitals in the n th energy level (e.g., the third energy level has s , p , and d orbitals).
3. There are $2l + 1$ orbitals of each type (e.g., one s , three p , five d , and seven f). This is also equal to the number of values which m_l may assume for a given l value.
4. There are $n - l - 1$ nodes in the radial distribution functions of all orbitals (e.g., the $3s$ orbital has two nodes, the $4d$ orbitals each have one).
5. There are l nodal surfaces in the angular distribution function of all orbitals (e.g., s orbitals have none, d orbitals have two).

THE POLYELECTRONIC ATOM

With the exception of Unsöld's theorem, above, *everything discussed thus far has dealt only with the hydrogen atom, the only atom for which the Schrödinger wave equation has been solved exactly*. This treatment can be extended readily to one-electron ions isoelectronic with hydrogen, such as He^+ , Li^{+2} , and Be^{+3} , by using the appropriate value of the nuclear charge, Z . The next simplest atom, helium, consists of a nucleus and two electrons. We thus have three interactions: the attraction of electron 1 for the nucleus, the attraction of electron 2 for the nucleus, and the repulsion between electrons 1 and 2. This is an example of the classic three-body problem in physics and cannot be solved exactly. We can, however, approximate a solution to a high degree of accuracy using successive approximations. For simple atoms such as helium this is not too difficult, but for heavier atoms the number of interactions which must be considered rises at an alarming rate and the calculations become extremely laborious. A number of methods of approximation have been used, but we shall not explore them here beyond describing in conceptual terms one of the more accurate methods. It is referred to as the Hartree-Fock method, after the men who developed it, or as the *self-consistent field* (SCF) method. It consists of (1) assuming a reasonable wave function for each of the electrons in an atom except one, (2) calculating the effect which the field of the nucleus and the remainder of the electrons exert on the chosen electron, and (3) calculating a wave function for the last electron, including the effects of the field of the other electrons. A different electron is then chosen, and using the field resulting from the other electrons (including the contribution from the improved wave function of the formerly chosen electron), an improved wave function for the second electron is calculated. This process is continued until the wave functions for all of the electrons have been improved, and the cycle is then started over to improve further the wave function of the first electron in terms of the field resulting from the improved wave functions of the other electrons. The cycle is repeated as many times as necessary until a negligible change takes place in improving the wave functions. At this point it may be said that the wave functions are self-consistent and are a reasonably accurate description of the atom.

Such calculations indicate that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals previously discussed. The principal difference lies in the consequence of the increased nuclear charge—all the orbitals are somewhat contracted. It is common to call such orbitals which have been adjusted by an appropriate nuclear charge *hydrogen-like orbitals*. Within a given major energy level it is found that the energy of these orbitals increases in the order $s < p < d < f$. For the higher energy levels