

1 Atomic Orbital Theory

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The detailed study of the structure of atoms (as distinguished from molecules) is largely the domain of the physicist. With respect to atomic structure, the interest of the chemist is usually confined to the behavior and properties of the three fundamental particles of atoms, namely the electron, the proton, and the neutron. In the model of the atom postulated by Niels Bohr (1885–1962), electrons surrounding the nucleus are placed in circular orbits. The electrons move in these orbits much as planets orbit the sun. In rationalizing atomic emission spectra of the hydrogen atom, Bohr assumed that the energy of the electron in different orbits was quantized, that is, the energy did not increase in a continuous manner as the orbits grew larger, but instead had discrete values for each orbit. Bohr's use of classical mechanics to describe the behavior of small particles such as electrons proved unsatisfactory, particularly because this model did not take into account the uncertainty principle. When it was demonstrated that the motion of electrons had properties of waves as well as of particles, the so-called dual nature of electronic behavior, the classical mechanical approach was replaced by the newer theory of quantum mechanics.

According to quantum mechanical theory the behavior of electrons is described by wave functions, commonly denoted by the Greek letter ψ . The physical significance of ψ resides in the fact that its square multiplied by the size of a volume element, $\psi^2 d\tau$, gives the probability of finding the electron in a particular element of space surrounding the nucleus of the atom. Thus, the Bohr model of the atom, which placed the electron in a fixed orbit around the nucleus, was replaced by the quantum mechanical model that defines a region in space surrounding the nucleus (an atomic orbital rather than an orbit) where the probability of finding the electron is high. It is, of course, the electrons in these orbitals that usually determine the chemical behavior of the atoms and so knowledge of the positions and energies of the electrons is of great importance. The correlation of the properties of atoms with their atomic structure expressed in the periodic law and the Periodic Table was a milestone in the development of chemical science.

Although most of organic chemistry deals with molecular orbitals rather than with isolated atomic orbitals, it is prudent to understand the concepts involved in atomic orbital theory and the electronic structure of atoms before moving on to

consider the behavior of electrons shared between atoms and the concepts of molecular orbital theory.

1.1 PHOTON (QUANTUM)

The most elemental unit or particle of electromagnetic radiation. Associated with each photon is a discrete quantity or quantum of energy.

1.2 BOHR OR PLANCK–EINSTEIN EQUATION

$$E = h\nu = hc/\lambda \quad (1.2)$$

This fundamental equation relates the energy of a photon E to its frequency ν (see Sect. 1.9) or wavelength λ (see Sect. 1.8). Bohr's model of the atom postulated that the electrons of an atom moved about its nucleus in circular orbits, or as later suggested by Arnold Sommerfeld (1868–1951), in elliptical orbits, each with a certain "allowed" energy. When subjected to appropriate electromagnetic radiation, the electron may absorb energy, resulting in its promotion (excitation) from one orbit to a higher (energy) orbit. The frequency of the photon absorbed must correspond to the energy difference between the orbits, that is, $\Delta E = h\nu$. Because Bohr's postulates were based in part on the work of Max Planck (1858–1947) and Albert Einstein (1879–1955), the Bohr equation is alternately called the Planck–Einstein equation.

1.3 PLANCK'S CONSTANT h

The proportionality constant $h = 6.6256 \times 10^{-27}$ erg seconds (6.6256×10^{-34} J s), which relates the energy of a photon E to its frequency ν (see Sect. 1.9) in the Bohr or Planck–Einstein equation. In order to simplify some equations involving Planck's constant h , a modified constant called \hbar , where $\hbar = h/2\pi$, is frequently used.

1.4 HEISENBERG UNCERTAINTY PRINCIPLE

This principle as formulated by Werner Heisenberg (1901–1976), states that the properties of small particles (electrons, protons, etc.) cannot be known precisely at any particular instant of time. Thus, for example, both the exact momentum p and the exact position x of an electron cannot both be measured simultaneously. The product of the uncertainties of these two properties of a particle must be on the order of Planck's constant: $\Delta p \cdot \Delta x = h/2\pi$, where Δp is the uncertainty in the momentum, Δx the uncertainty in the position, and h Planck's constant.

A corollary to the uncertainty principle is its application to very short periods of time. Thus, $\Delta E \cdot \Delta t = h/2\pi$, where ΔE is the uncertainty in the energy of the electron

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and Δt the uncertainty in the time that the electron spends in a particular energy state. Accordingly, if Δt is very small, the electron may have a wide range of energies. The uncertainty principle addresses the fact that the very act of performing a measurement of the properties of small particles perturbs the system. The uncertainty principle is at the heart of quantum mechanics; it tells us that the position of an electron is best expressed in terms of the *probability* of finding it in a particular region in space, and thus, eliminates the concept of a well-defined trajectory or orbit for the electron.

1.5 WAVE (QUANTUM) MECHANICS

The mathematical description of very small particles such as electrons in terms of their wave functions (see Sect. 1.15). The use of wave mechanics for the description of electrons follows from the experimental observation that electrons have both wave as well as particle properties. The wave character results in a probability interpretation of electronic behavior (see Sect. 1.20).

1.6 STANDING (OR STATIONARY) WAVES

The type of wave generated, for example, by plucking a string or wire stretched between two fixed points. If the string is oriented horizontally, say, along the x -axis, the waves moving toward the right fixed point will encounter the reflected waves moving in the opposite direction. If the forward wave and the reflected wave have the same amplitude at each point along the string, there will be a number of points along the string that will have no motion. These points, in addition to the fixed anchors at the ends, correspond to nodes where the amplitude is zero. Half-way between the nodes there will be points where the amplitude of the wave will be maximum. The variations of amplitude are thus a function of the distance along x . After the plucking, the resultant vibrating string will appear to be oscillating up and down between the fixed nodes, but there will be no motion along the length of the string—hence, the name standing or stationary wave.

Example. See Fig. 1.6.

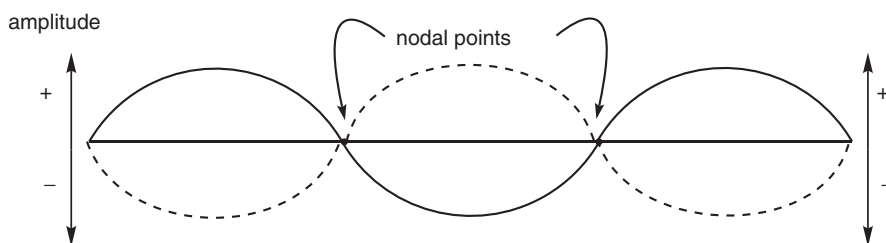


Figure 1.6. A standing wave; the two curves represent the time-dependent motion of a string vibrating in the third harmonic or second overtone with four nodes.

1.7 NODAL POINTS (PLANES)

The positions or points on a standing wave where the amplitude of the wave is zero (Fig. 1.6). In the description of orbitals, the node represent a point or plane where a change of sign occurs.

1.8 WAVELENGTH λ

The minimum distance between nearest-neighbor peaks, troughs, nodes or equivalent points of the wave.

Example. The values of λ , as shown in Fig. 1.8.

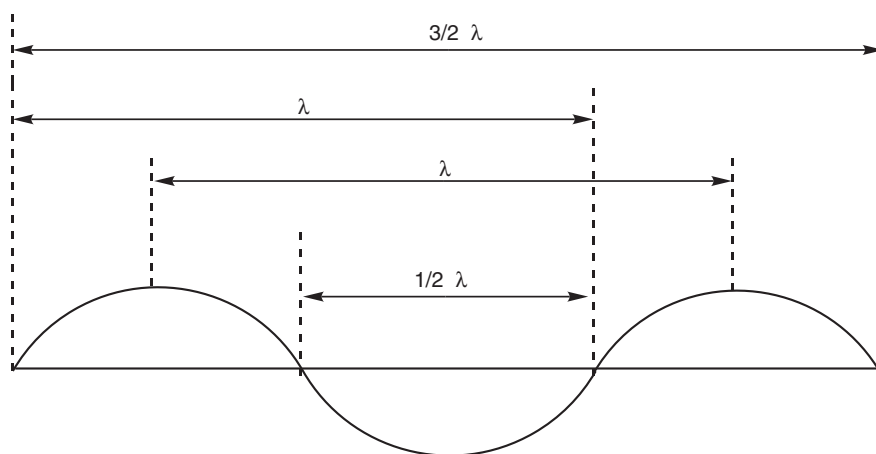


Figure 1.8. Determination of the wavelength λ of a wave.

1.9 FREQUENCY ν

The number of wavelengths (or cycles) in a light wave that pass a particular point per unit time. Time is usually measured in seconds; hence, the frequency is expressed in s^{-1} . The unit of frequency, equal to cycles per second, is called the Hertz (Hz). Frequency is inversely proportional to wavelength; the proportionality factor is the speed of light c ($3 \times 10^{10} \text{ cm s}^{-1}$). Hence, $\nu = c/\lambda$.

Example. For light with λ equal to 300 nm ($300 \times 10^{-7} \text{ cm}$), the frequency $\nu = (3 \times 10^{10} \text{ cm s}^{-1}) / (300 \times 10^{-7} \text{ cm}) = 1 \times 10^{15} \text{ s}^{-1}$.

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1.10 FUNDAMENTAL WAVE (OR FIRST HARMONIC)

The stationary wave with no nodal point other than the fixed ends. It is the wave from which the frequency ν' of all other waves in a set is generated by multiplying the fundamental frequency ν by an integer n :

$$\nu' = n\nu \quad (1.10)$$

Example. In the fundamental wave, $\lambda/2$ in Fig. 1.10, the amplitude may be considered to be oriented upward and to continuously increase from either fixed end, reaching a maximum at the midpoint. In this “well-behaved” wave, the amplitude is zero at each end and a maximum at the center.

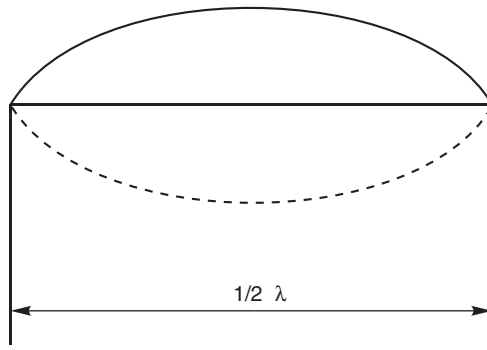


Figure 1.10. The fundamental wave.

1.11 FIRST OVERTONE (OR SECOND HARMONIC)

The stationary wave with one nodal point located at the midpoint ($n = 2$ in the equation given in Sect. 1.10). It has half the wavelength and twice the frequency of the first harmonic.

Example. In the first overtone (Fig. 1.11), the nodes are located at the ends and at the point half-way between the ends, at which point the amplitude changes direction. The two equal segments of the wave are portions of a single wave; they are not independent. The two maximum amplitudes come at exactly equal distances from the ends but are of opposite signs.

1.12 MOMENTUM (P)

This is the vectorial property (i.e., having both magnitude and direction) of a moving particle; it is equal to the mass m of the particle times its velocity \mathbf{v} :

$$\mathbf{p} = m\mathbf{v} \quad (1.12)$$

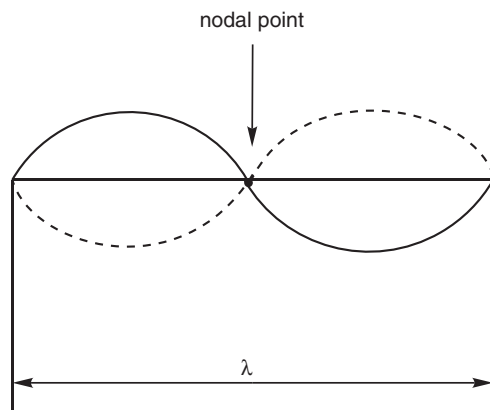


Figure 1.11. The first overtone (or second harmonic) of the fundamental wave.

1.13 DUALITY OF ELECTRONIC BEHAVIOR

Particles of small mass such as electrons may exhibit properties of either particles (they have momentum) or waves (they can be defracted like light waves). A single experiment may demonstrate either particle properties or wave properties of electrons, but not both simultaneously.

1.14 DE BROGLIE RELATIONSHIP

The wavelength of a particle (an electron) is determined by the equation formulated by Louis de Broglie (1892–1960):

$$\lambda = h/p = h/mv \quad (1.14)$$

where h is Planck's constant, m the mass of the particle, and v its velocity. This relationship makes it possible to relate the momentum p of the electron, a particle property, with its wavelength λ , a wave property.

1.15 ORBITAL (ATOMIC ORBITAL)

A wave description of the size, shape, and orientation of the region in space available to an electron; each orbital has a specific energy. The position (actually the probability amplitude) of the electron is defined by its coordinates in space, which in Cartesian coordinates is indicated by $\psi(x, y, z)$. ψ cannot be measured directly; it is a mathematical tool. In terms of spherical coordinates, frequently used in calculations, the wave function is indicated by $\psi(r, \theta, \varphi)$, where r (Fig. 1.15) is the radial distance of a point from the origin, θ is the angle between the radial line and the

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z -axis, and ϕ is the angle between the x -axis and the projection of the radial line on the xy -plane. The relationship between the two coordinate systems is shown in Fig. 1.15. An orbital centered on a single atom (an *atomic orbital*) is frequently denoted as ϕ (phi) rather than ψ (psi) to distinguish it from an orbital centered on more than one atom (a molecular orbital) that is almost always designated ψ .

The projection of r on the z -axis is $z = OB$, and OBA is a right angle. Hence, $\cos \theta = z/r$, and thus, $z = r \cos \theta$. $\cos \phi = x/OC$, but $OC = AB = r \sin \theta$. Hence, $x = r \sin \theta \cos \phi$. Similarly, $\sin \phi = y/AB$; therefore, $y = AB \sin \phi = r \sin \theta \sin \phi$. Accordingly, a point (x, y, z) in Cartesian coordinates is transformed to the spherical coordinate system by the following relationships:

$$\begin{aligned}z &= r \cos \theta \\y &= r \sin \theta \sin \phi \\x &= r \sin \theta \cos \phi\end{aligned}$$

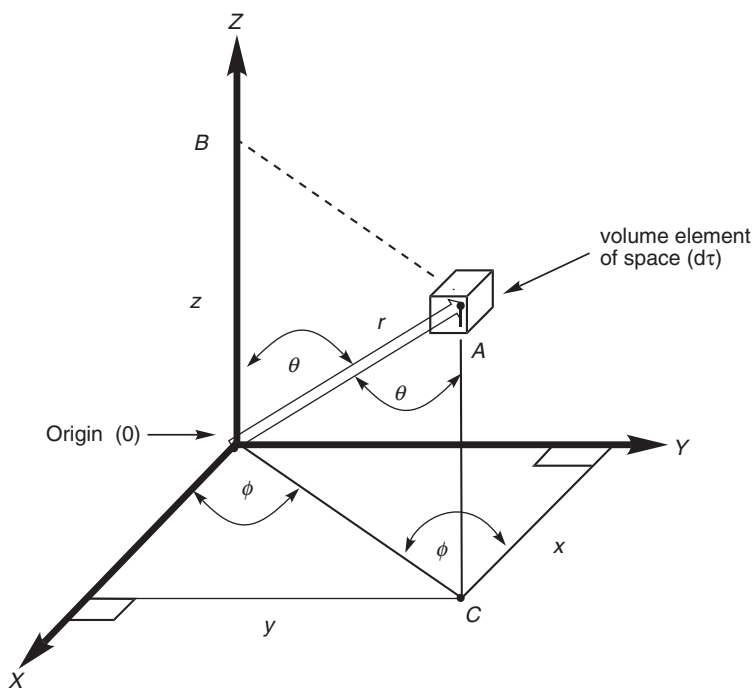


Figure 1.15. The relationship between Cartesian and polar coordinate systems.

1.16 WAVE FUNCTION

In quantum mechanics, the wave function is synonymous with an orbital.

1.17 WAVE EQUATION IN ONE DIMENSION

The mathematical description of an orbital involving the amplitude behavior of a wave. In the case of a one-dimensional standing wave, this is a second-order differential equation with respect to the amplitude:

$$d^2f(x)/dx^2 + (4\pi^2/\lambda^2) f(x) = 0 \quad (1.17)$$

where λ is the wavelength and the amplitude function is $f(x)$.

1.18 WAVE EQUATION IN THREE DIMENSIONS

The function $f(x, y, z)$ for the wave equation in three dimensions, analogous to $f(x)$, which describes the amplitude behavior of the one-dimensional wave. Thus, $f(x, y, z)$ satisfies the equation

$$\partial^2f(x)/\partial x^2 + \partial^2f(y)/\partial y^2 + \partial^2f(z)/\partial z^2 + (4\pi^2/\lambda^2) f(x, y, z) = 0 \quad (1.18)$$

In the expression $\partial^2f(x)/\partial x^2$, the portion $\partial^2/\partial x^2$ is an operator that says “partially differentiate twice with respect to x that which follows.”

1.19 LAPLACIAN OPERATOR

The sum of the second-order differential operators with respect to the three Cartesian coordinates in Eq. 1.18 is called the Laplacian operator (after Pierre S. Laplace, 1749–1827), and it is denoted as ∇^2 (del squared):

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \quad (1.19a)$$

which then simplifies Eq. 1.18 to

$$\nabla^2f(x, y, z) + (4\pi^2/\lambda^2) f(x, y, z) = 0 \quad (1.19b)$$

1.20 PROBABILITY INTERPRETATION OF THE WAVE FUNCTION

The wave function (or orbital) $\psi(r)$, because it is related to the amplitude of a wave that determines the location of the electron, can have either negative or positive values. However, a *probability*, by definition, must always be positive, and in the present case this can be achieved by squaring the amplitude. Accordingly, the probability of finding an electron in a specific volume element of space $d\tau$ at a distance r from the nucleus is $\psi(r)^2 d\tau$. Although ψ , the orbital, has mathematical significance (in

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that it can have negative and positive values), ψ^2 has physical significance and is always positive.

1.21 SCHRÖDINGER EQUATION

This is a differential equation, formulated by Erwin Schrödinger (1887–1961), whose solution is the wave function for the system under consideration. This equation takes the same form as an equation for a standing wave. It is from this form of the equation that the term *wave mechanics* is derived. The similarity of the Schrödinger equation to a wave equation (Sect. 1.18) is demonstrated by first substituting the de Broglie equation (1.14) into Eq. 1.19b and replacing f by ϕ :

$$\nabla^2\phi + (4\pi^2m^2v^2/h^2)\phi = 0 \quad (1.21a)$$

To incorporate the total energy E of an electron into this equation, use is made of the fact that the total energy is the sum of the potential energy V , plus the kinetic energy, $1/2 mv^2$, or

$$v^2 = 2(E - V)/m \quad (1.21b)$$

Substituting Eq. 1.21b into Eq. 1.21a gives Eq. 1.21c:

$$\nabla^2\phi + (8\pi^2m/h^2)(E - V)\phi = 0 \quad (1.21c)$$

which is the Schrödinger equation.

1.22 EIGENFUNCTION

This is a hybrid German-English word that in English might be translated as “characteristic function”; it is an acceptable solution of the wave equation, which can be an orbital. There are certain conditions that must be fulfilled to obtain “acceptable” solutions of the wave equation, Eq. 1.17 [e.g., $f(x)$ must be zero at each end, as in the case of the vibrating string fixed at both ends; this is the so-called boundary condition]. In general, whenever some mathematical operation is done on a function and the same function is regenerated multiplied by a constant, the function is an eigenfunction, and the constant is an eigenvalue. Thus, wave Eq. 1.17 may be written as

$$d^2f(x)/dx^2 = -(4\pi^2/\lambda^2) f(x) \quad (1.22)$$

This equation is an eigenvalue equation of the form:

$$(\text{Operator}) (\text{eigenfunction}) = (\text{eigenvalue}) (\text{eigenfunction})$$

where the operator is (d^2/dx^2) , the eigenfunction is $f(x)$, and the eigenvalue is $(4\pi^2/\lambda^2)$. Generally, it is implied that wave functions, hence orbitals, are eigenfunctions.

1.23 EIGENVALUES

The values of λ calculated from the wave equation, Eq. 1.17. If the eigenfunction is an orbital, then the eigenvalue is related to the orbital energy.

1.24 THE SCHRÖDINGER EQUATION FOR THE HYDROGEN ATOM

An (eigenvalue) equation, the solutions of which in spherical coordinates are

$$\phi(r, \theta, \varphi) = R(r) \Theta(\theta) \Phi(\varphi) \quad (1.24)$$

The eigenfunctions ϕ , also called orbitals, are functions of the three variables shown, where r is the distance of a point from the origin, and θ and φ are the two angles required to locate the point (see Fig. 1.15). For some purposes, the *spatial* or radial part and the *angular* part of the Schrödinger equation are separated and treated independently. Associated with each eigenfunction (orbital) is an eigenvalue (orbital energy). An exact solution of the Schrödinger equation is possible only for the hydrogen atom, or any one-electron system. In many-electron systems wave functions are generally approximated as products of modified one-electron functions (orbitals). Each solution of the Schrödinger equation may be distinguished by a set of three quantum numbers, n , l , and m , that arise from the boundary conditions.

1.25 PRINCIPAL QUANTUM NUMBER n

An integer 1, 2, 3, . . . , that governs the size of the orbital (wave function) and determines the energy of the orbital. The value of n corresponds to the number of the shell in the Bohr atomic theory and the larger the n , the higher the energy of the orbital and the farther it extends from the nucleus.

1.26 AZIMUTHAL (ANGULAR MOMENTUM) QUANTUM NUMBER l

The quantum number with values of $l = 0, 1, 2, \dots, (n - 1)$ that determines the shape of the orbital. The value of l implies particular angular momenta of the electron resulting from the shape of the orbital. Orbitals with the azimuthal quantum numbers $l = 0, 1, 2$, and 3 are called *s*, *p*, *d*, and *f* orbitals, respectively. These orbital designations are taken from atomic spectroscopy where the words “sharp”, “principal”, “diffuse”, and “fundamental” describe lines in atomic spectra. This quantum number does not enter into the expression for the energy of an orbital. However, when

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electrons are placed in orbitals, the energy of the orbitals (and hence the energy of the electrons in them) is affected so that orbitals with the same principal quantum number n may vary in energy.

Example. An electron in an orbital with a principal quantum number of $n = 2$ can take on l values of 0 and 1, corresponding to $2s$ and $2p$ orbitals, respectively. Although these orbitals have the same principal quantum number and, therefore, the same energy when calculated for the single electron hydrogen atom, for the many-electron atoms, where electron–electron interactions become important, the $2p$ orbitals are higher in energy than the $2s$ orbitals.

1.27 MAGNETIC QUANTUM NUMBER m_l

This is the quantum number having values of the azimuthal quantum number from $+l$ to $-l$ that determines the orientation in space of the orbital angular momentum; it is represented by m_l .

Example. When $n = 2$ and $l = 1$ (the p orbitals), m_l may thus have values of $+1$, 0 , -1 , corresponding to three $2p$ orbitals (see Sect. 1.35). When $n = 3$ and $l = 2$, m_l has the values of $+2$, $+1$, 0 , -1 , -2 that describe the five $3d$ orbitals (see Sect. 1.36).

1.28 DEGENERATE ORBITALS

Orbitals having equal energies, for example, the three $2p$ orbitals.

1.29 ELECTRON SPIN QUANTUM NUMBER m_s

This is a measure of the intrinsic angular momentum of the electron due to the fact that the electron itself is spinning; it is usually designated by m_s and may only have the value of $1/2$ or $-1/2$.

1.30 s ORBITALS

Spherically symmetrical orbitals; that is, ϕ is a function of $R(r)$ only. For s orbitals, $l = 0$ and, therefore, electrons in such orbitals have an orbital magnetic quantum number m_l equal to zero.

1.31 $1s$ ORBITAL

The lowest-energy orbital of any atom, characterized by $n = 1$, $l = m_l = 0$. It corresponds to the fundamental wave and is characterized by spherical symmetry and no

nodes. It is represented by a projection of a sphere (a circle) surrounding the nucleus, within which there is a specified probability of finding the electron.

Example. The numerical probability of finding the hydrogen electron within spheres of various radii from the nucleus is shown in Fig. 1.31a. The circles represent contours of probability on a plane that bisects the sphere. If the contour circle of 0.95 probability is chosen, the electron is 19 times as likely to be inside the corresponding sphere with a radius of 1.7 Å as it is to be outside that sphere. The circle that is usually drawn, Fig. 1.31b, to represent the 1s orbital is meant to imply that there is a high, but unspecified, probability of finding the electron in a sphere, of which the circle is a cross-sectional cut or projection.

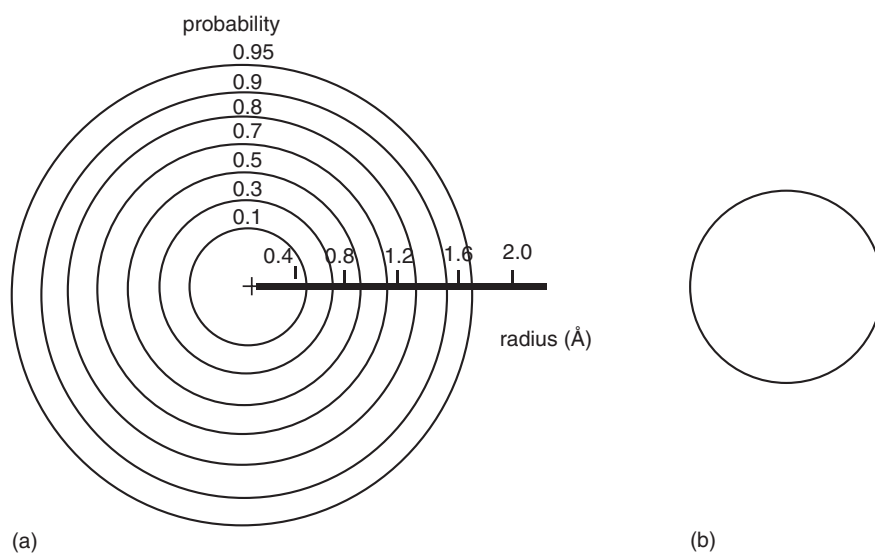


Figure 1.31. (a) The probability contours and radii for the hydrogen atom, the probability at the nucleus is zero. (b) Representation of the 1s orbital.

1.32 2s ORBITAL

The spherically symmetrical orbital having one spherical nodal surface, that is, a surface on which the probability of finding an electron is zero. Electrons in this orbital have the principal quantum number $n = 2$, but have no angular momentum, that is, $l = 0$, $m_l = 0$.

Example. Figure 1.32 shows the probability distribution of the 2s electron as a cross section of the spherical 2s orbital. The 2s orbital is usually drawn as a simple circle of arbitrary diameter, and in the absence of a drawing for the 1s orbital for comparison,

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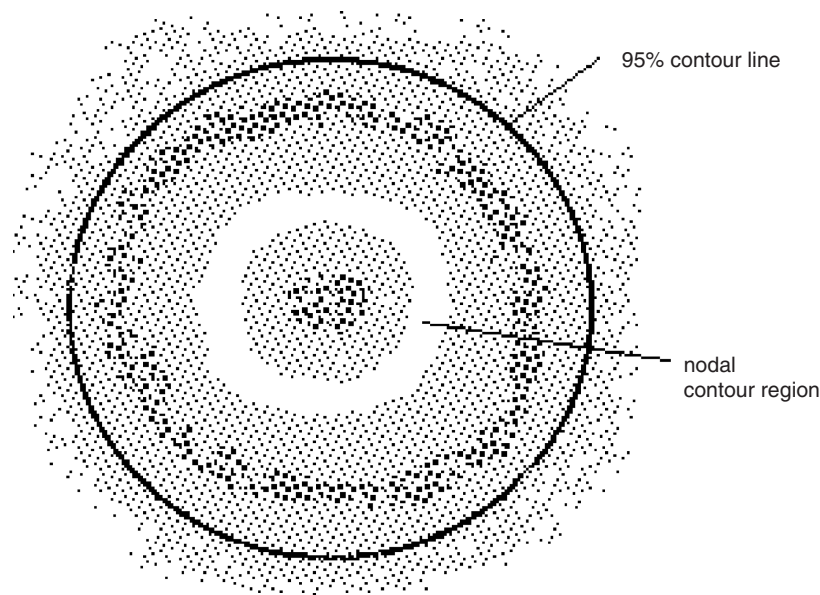


Figure 1.32. Probability distribution ψ^2 for the 2s orbital.

the two would be indistinguishable despite the larger size of the 2s orbital and the fact that there is a nodal surface within the 2s sphere that is not shown in the simple circular representation.

1.33 *p* ORBITALS

These are orbitals with an angular momentum l equal to 1; for each value of the principal quantum number n (except for $n = 1$), there will be three *p* orbitals corresponding to $m_l = +1, 0, -1$. In a useful convention, these three orbitals, which are mutually perpendicular to each other, are oriented along the three Cartesian coordinate axes and are therefore designated as $p_x, p_y,$ and p_z . They are characterized by having one nodal plane.

1.34 NODAL PLANE OR SURFACE

A plane or surface associated with an orbital that defines the locus of points for which the probability of finding an electron is zero. It has the same meaning in three dimensions that the nodal point has in the two-dimensional standing wave (see Sect. 1.7) and is associated with a change in sign of the wave function.

1.35 2p ORBITALS

The set of three degenerate (equal energy) atomic orbitals having the principal quantum number (n) of 2, an azimuthal quantum number (l) of 1, and magnetic quantum numbers (m_l) of +1, 0, or -1 . Each of these orbitals has a nodal plane.

Example. The $2p$ orbitals are usually depicted so as to emphasize their angular dependence, that is, $R(r)$ is assumed constant, and hence are drawn for convenience as a planar cross section through a three-dimensional representation of $\Theta(\theta)\Phi(\varphi)$. The planar cross section of the $2p_z$ orbital, $\varphi = 0$, then becomes a pair of circles touching at the origin (Fig. 1.35a). In this figure the wave function (without proof) is $\phi = \Theta(\theta) = (\sqrt{6}/2)\cos\theta$. Since $\cos\theta$, in the region $90^\circ < \theta < 270^\circ$, is negative, the top circle is positive and the bottom circle negative. However, the physically significant property of an orbital ϕ is its square, ϕ^2 ; the plot of $\phi^2 = \Theta^2(\theta) = 3/2 \cos^2\theta$ for the p_z orbital is shown in Fig. 1.35b, which represents the volume of space in which there is a high probability of finding the electron associated with the p_z orbital. The shape of this orbital is the familiar elongated dumbbell with both lobes having a positive sign. In most common drawings of the p orbitals, the shape of ϕ^2 , the physically significant function, is retained, but the plus and minus signs are placed in the lobes to emphasize the nodal property, (Fig. 1.35c). If the function $R(r)$ is included, the oval-shaped contour representation that results is shown in Fig. 1.35d, where $\phi^2(p_z)$ is shown as a cut in the yz -plane.

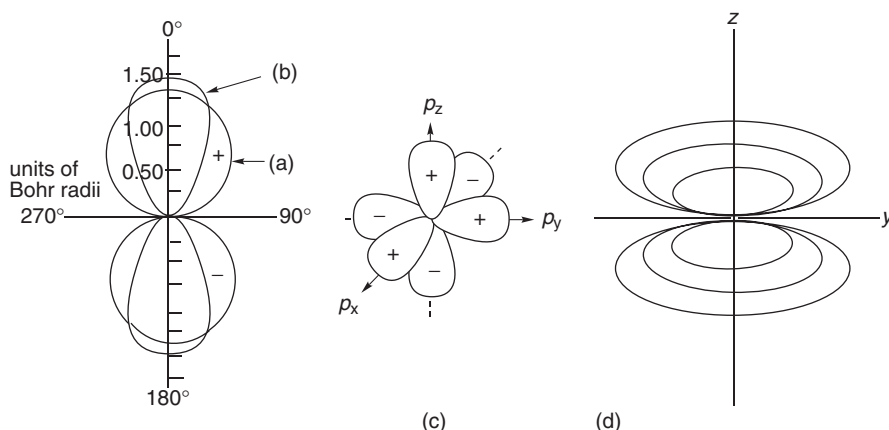


Figure 1.35. (a) The angular dependence of the p_z orbital; (b) the square of (a); (c) the common depiction of the three $2p$ orbitals; and (d) contour diagram including the radial dependence of ϕ .

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1.36 *d* ORBITALS

Orbitals having an angular momentum l equal to 2 and, therefore, magnetic quantum numbers, (m_l) of $+2$, $+1$, 0 , -1 , -2 . These five magnetic quantum numbers describe the five degenerate *d* orbitals. In the Cartesian coordinate system, these orbitals are designated as d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{xz} , and d_{yz} ; the last four of these *d* orbitals are characterized by two nodal planes, while the d_{z^2} has surfaces of revolution.

Example. The five *d* orbitals are depicted in Fig. 1.36. The d_{z^2} orbital that by convention is the sum of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ and, hence, really $d_{2z^2-x^2-y^2}$ is strongly directed along the z -axis with a negative “doughnut” in the xy -plane. The $d_{x^2-y^2}$ orbital has lobes pointed along the x - and y -axes, while the d_{xy} , d_{xz} , and d_{yz} orbitals have lobes that are pointed half-way between the axes and in the planes designated by the subscripts.

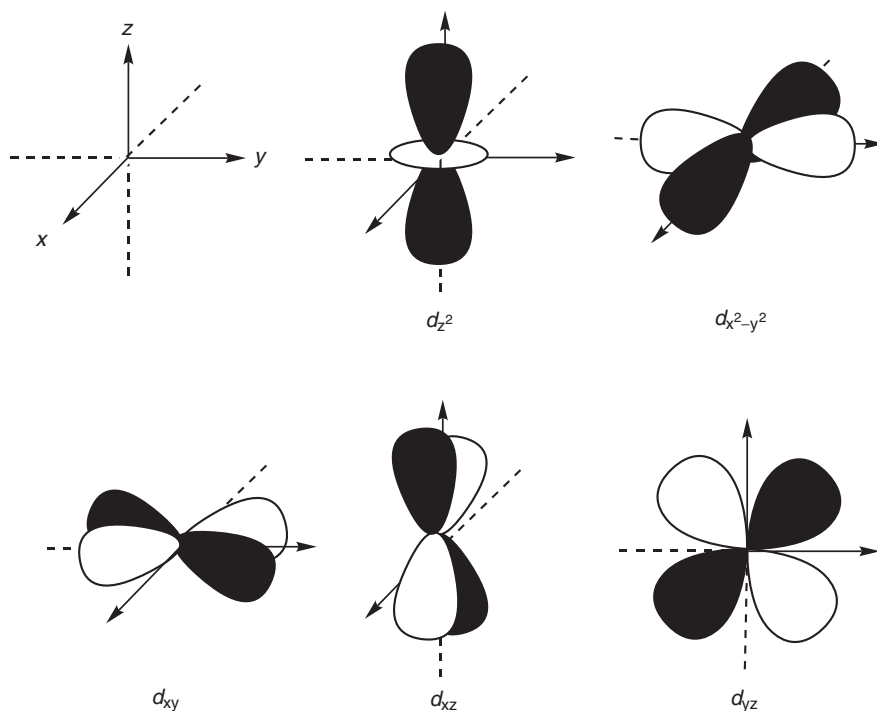


Figure 1.36. The five *d* orbitals. The shaded and unshaded areas represent lobes of different signs.

1.37 *f* ORBITALS

Orbitals having an angular momentum l equal to 3 and, therefore, magnetic quantum numbers, m_l of $+3$, $+2$, $+1$, 0 , -1 , -2 , -3 . These seven magnetic quantum numbers

describe the seven degenerate f orbitals. The f orbitals are characterized by three nodal planes. They become important in the chemistry of inner transition metals (Sect. 1.44).

1.38 ATOMIC ORBITALS FOR MANY-ELECTRON ATOMS

Modified hydrogenlike orbitals that are used to describe the electron distribution in many-electron atoms. The names of the orbitals, s , p , and so on, are taken from the corresponding hydrogen orbitals. The presence of more than one electron in a many-electron atom can break the degeneracy of orbitals with the same n value. Thus, the $2p$ orbitals are higher in energy than the $2s$ orbitals when electrons are present in them. For a given n , the orbital energies increase in the order $s < p < d < f < \dots$

1.39 PAULI EXCLUSION PRINCIPLE

According to this principle, as formulated by Wolfgang Pauli (1900–1958), a maximum of two electrons can occupy an orbital, and then, only if the spins of the electrons are opposite (paired), that is, if one electron has $m_s = +1/2$, the other must have $m_s = -1/2$. Stated alternatively, no two electrons in the same atom can have the same values of n , l , m_l , and m_s .

1.40 HUND'S RULE

According to this rule, as formulated by Friedrich Hund (1896–1997), a single electron is placed in all orbitals of equal energy (degenerate orbitals) before a second electron is placed in any one of the degenerate set. Furthermore, each of these electrons in the degenerate orbitals has the same (unpaired) spin. This arrangement means that these electrons repel each other as little as possible because any particular electron is prohibited from entering the orbital space of any other electron in the degenerate set.

1.41 AUFBAU (GER. BUILDING UP) PRINCIPLE

The building up of the electronic structure of the atoms in the Periodic Table. Orbitals are indicated in order of increasing energy and the electrons of the atom in question are placed in the unfilled orbital of lowest energy, filling this orbital before proceeding to place electrons in the next higher-energy orbital. The sequential placement of electrons must also be consistent with the Pauli exclusion principle and Hund's rule.

Example. The placement of electrons in the orbitals of the nitrogen atom (atomic number of 7) is shown in Fig. 1.41. Note that the $2p$ orbitals are higher in energy than the $2s$ orbital and that each p orbital in the degenerate $2p$ set has a single electron of the same spin as the others in this set.

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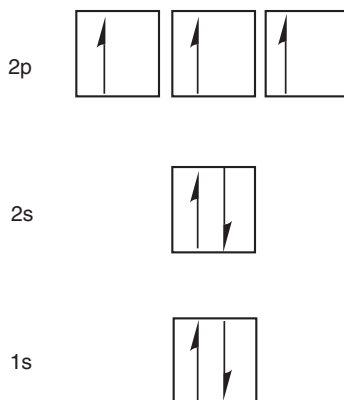


Figure 1.41. The placement of electrons in the orbitals of the nitrogen atom.

1.42 ELECTRONIC CONFIGURATION

The orbital occupation of the electrons of an atom written in a notation that consists of listing the principal quantum number, followed by the azimuthal quantum number designation (s , p , d , f), followed in each case by a superscript indicating the number of electrons in the particular orbitals. The listing is given in the order of increasing energy of the orbitals.

Example. The total number of electrons to be placed in orbitals is equal to the *atomic number* of the atom, which is also equal to the number of protons in the nucleus of the atom. The electronic configuration of the nitrogen atom, atomic number 7 (Fig. 1.41), is $1s^2 2s^2 2p^3$; for Ne, atomic number 10, it is $1s^2 2s^2 2p^6$; for Ar, atomic number 18, it is $1s^2 2s^2 2p^6 3s^2 3p^6$; and for Sc, atomic number 21, it is $[\text{Ar}]4s^2 3d^1$, where $[\text{Ar}]$ represents the rare gas, 18-electron electronic configuration of Ar in which all s and p orbitals with $n = 1$ to 3, are filled with electrons. The energies of orbitals are approximately as follows: $1s < 2s < 2p < 3s < 3p < 4s \approx 3d < 4p < 5s \approx 4d$.

1.43 SHELL DESIGNATION

The letters K, L, M, N, and O are used to designate the principal quantum number n .

Example. The $1s$ orbital which has the lowest principal quantum number, $n = 1$, is designated the K shell; the shell when $n = 2$ is the L shell, made up of the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals; and the shell when $n = 3$ is the M shell consisting of the $3s$, the three $3p$ orbitals, and the five $3d$ orbitals. Although the origin of the use of the letters K, L, M, and so on, for shell designation is not clearly documented, it has been suggested that these letters were abstracted from the name of physicist Charles Barkla (1877–1944, who received the Nobel Prize, in 1917). He along with collaborators had noted that two rays were characteristically emitted from the inner shells of an element after

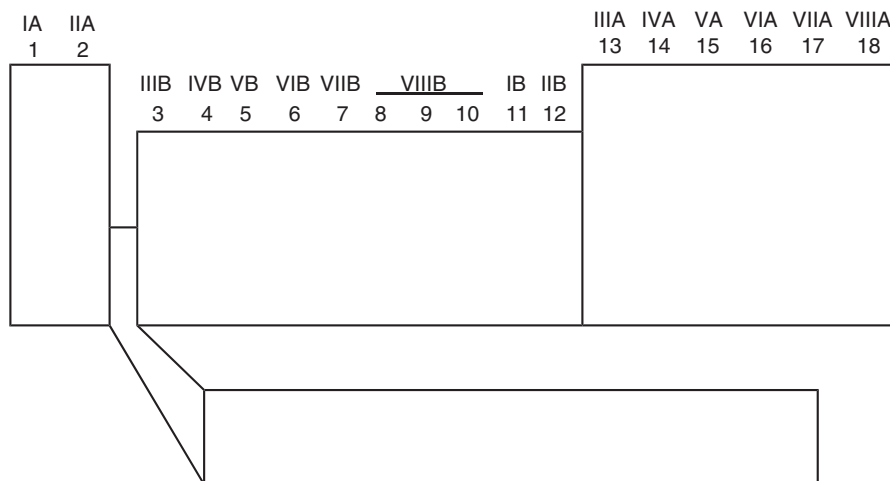
X-ray bombardment and these were designated K and L. He chose these mid-alphabet letters from his name because he anticipated the discovery of other rays, and wished to leave alphabetical space on either side for future labeling of these rays.

1.44 THE PERIODIC TABLE

An arrangement in tabular form of all the known elements in rows and columns in sequentially increasing order of their atomic numbers. The Periodic Table is an expression of the periodic law that states many of the properties of the elements (ionization energies, electron affinities, electronegativities, etc.) are a periodic function of their atomic numbers. By some estimates there may be as many as 700 different versions of the Periodic Table. A common display of this table, Fig. 1.44a, consists of boxes placed in rows and columns. Each box shown in the table contains the symbol of the element, its atomic number, and a number at the bottom that is the average atomic weight of the element determined from the natural abundance of its various isotopes. There are seven rows of the elements corresponding to the increasing values of the principal quantum number n , from 1 to 7. Each of these rows begins with an element having one electron in the ns orbital and terminates with an element having the number of electrons corresponding to the completely filled K, L, M, N, and O shell containing 2, 8, 18, 32, and 32 electrons, respectively. Row 1 consists of the elements H and He only; row 2 runs from Li to Ne; row 3 from Na to Ar, and so on. It is in the numbering of the columns, often called groups or families, where there is substantial disagreement among interested chemists and historians.

The table shown in Fig. 1.44a is a popular version (sometimes denoted as the American ABA scheme) of the Periodic Table. In the ABA version the elements in a column are classified as belonging to a group, numbered with Roman numerals I through VIII. The elements are further classified as belonging to either an A group or a B group. The A group elements are called *representative* or *main group elements*. The last column is sometimes designated as Group 0 or Group VIIIA. These are the rare gases; they are characterized by having completely filled outer shells; they occur in monoatomic form; and they are relatively chemically inert. The B group elements are the *transition metal elements*; these are the elements with electrons in partially filled $(n-1)d$ or $(n-2)f$ orbitals. The 4th and 5th row transition metals are called *outer transition metals*, and the elements shown in the 6th and 7th row at the bottom of Fig. 1.44a are the *inner transition metals*.

Although there is no precise chemical definition of *metals*, they are classified as such if they possess the following group characteristics: high electrical conductivity that decreases with increasing temperature; high thermal conductivity; high *ductility* (easily stretched, not brittle); and *malleability* (can be hammered and formed without breaking). Those elements in Fig. 1.44a that are considered metals are shaded either lightly (A group) or more darkly (B group); those that are not shaded are *non-metals*; those having properties intermediate between metals and nonmetals are cross-hatched. The members of this last group are sometimes called *metalloids* or *semimetals*; these include boron, silicon, germanium, arsenic, antimony, and tellurium. The elements in the A group have one to eight electrons in their outermost



(b)

Figure 1.44. (b) A block outline showing the Roman numeral American ABA designation and the corresponding Arabic numeral IUPAC designation for families of elements in the Periodic Table.

shell and their group Roman number corresponds to the number of electrons in this shell, for example, Ca(IIA), Al(IIIA), C(IVA), and so on. Elements in Group IA are called *alkali metals* and those in Group IIA are called *alkaline earth metals*.

Recently, the International Union of Pure and Applied Chemistry (IUPAC) recommended a version of the Periodic Table in which the A and B designations are eliminated, the Roman numerals of the columns are replaced with Arabic numerals, and the columns are numbered from 1 to 18. These column numbers make it possible to assign each of the outer transition metals to a separate group number, thus, for example, the *triads of Group VIII B transition metals*: Fe, Co, Ni; Ru, Rh, Pd; and Os, Ir, Pt in Fig. 1.44a become, respectively, members of Groups 8, 9, and 10 in the IUPAC version. This version has many advantages; for example, it eliminates the ambiguity of the definition of transition metals as well as the group assignments of H and He. It does not, however, indicate a group number assignment to any of the two rows of inner transition metals consisting of 14 elements each (which would require 32 instead of 18 groups), nor does it provide the chemical information, for example, the number of valence electrons in each group, that is provided by the older labels. Thus, the valuable advantage of correlating the B group with the same number A group inherent in the ABA system is lost, for instance, the fact that there are five valence electrons in the structure of both nitrogen (Group VA) and vanadium (Group VB). Nevertheless the IUPAC version is gaining increasing acceptance.

1.45 VALENCE ORBITALS

The orbitals of an atom that may be involved in bonding to other atoms. For the main group or representative elements, these are the ns or $ns + np$ orbitals, where n is the

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quantum number of the highest occupied orbital; for the outer transition metals, these are the $(n - 1)d + ns$ orbitals; and for the inner transition metals, these are the $(n - 2)f + ns$ orbitals. Electrons in these orbitals are *valence electrons*.

Example. The valence orbitals occupied by the four valence electrons of the carbon atom are the $2s + 2p$ orbitals. For a 3rd row element such as Si (atomic number 14) with the electronic configuration $[1s^2 2s^2 2p^6] 3s^2 3p^2$, shortened to $[\text{Ne}] 3s^2 3p^2$, the $3s$ and $3p$ orbitals are the valence orbitals. For a 4th row ($n = 4$) element such as Sc (atomic number 21) with the electronic configuration $[\text{Ar}] 3d^1 4s^2$, the valence orbitals are $3d$ and $4s$, and these are occupied by the three valence electrons. In the formation of coordination complexes, use is made of lowest-energy vacant orbitals, and because these are involved in bond formation, they may be considered vacant valence orbitals. Coordination complexes are common in transition metals chemistry.

1.46 ATOMIC CORE (OR KERNEL)

The electronic structure of an atom after the removal of its valence electrons.

Example. The atomic core structure consists of the electrons making up the noble gas or *pseudo-noble gas* structure immediately preceding the atom in the Periodic Table. A pseudo-noble gas configuration is one having all the electrons of the noble gas, plus, for the outer transition metals, the 10 electrons in completely filled $(n - 1)d$ orbitals; and for the inner transition metals, the noble gas configuration plus the $(n - 2)f^{14}$, or the noble gas plus $(n - 1)d^{10}(n - 2)f^{14}$. Electrons in these orbitals are not considered valence electrons. The core structure of Sc, atomic number 21, is that corresponding to the preceding rare gas, which in this case is the Ar core. For Ga, atomic number 31, with valence electrons $4s^2 4p^1$, the core structure consists of the pseudo-rare gas structure $\{[\text{Ar}] 3d^{10}\}$.

1.47 HYBRIDIZATION OF ATOMIC ORBITALS

The mathematical mixing of two or more different orbitals on a given atom to give the same number of new orbitals, each of which has some of the character of the original component orbitals. Hybridization requires that the atomic orbitals to be mixed are similar in energy. The resulting hybrid orbitals have directional character, and when used to bond with atomic orbitals of other atoms, they help to determine the shape of the molecule formed.

Example. In much of organic (carbon) chemistry, the $2s$ orbital of carbon is mixed with: (a) one p orbital to give two hybrid sp orbitals (digonal linear); (b) two p orbitals to give three sp^2 orbitals (trigonal planar); or (c) three p orbitals to give four sp^3 orbitals (tetrahedral). The mixing of the $2s$ orbital of carbon with its $2p_y$ to give two carbon sp orbitals is shown pictorially in Fig. 1.47. These two hybrid atomic orbitals have the form $\phi_1 = (s + p_y)$ and $\phi_2 = (s - p_y)$.

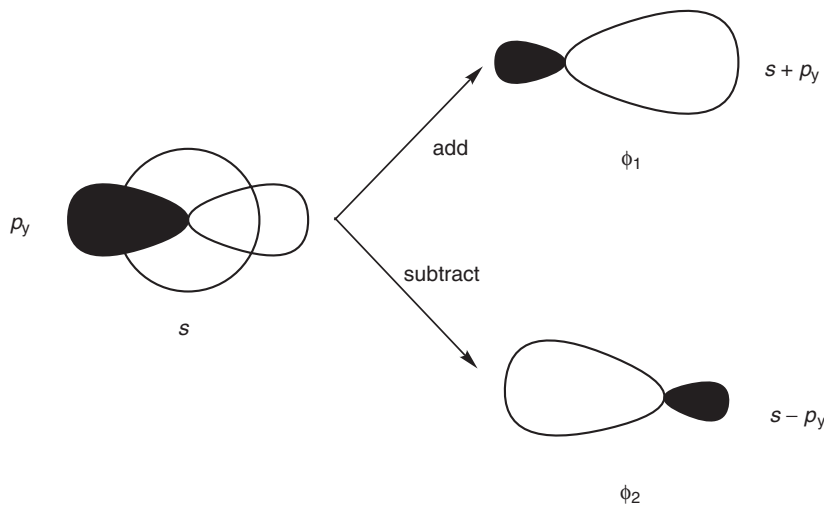


Figure 1.47. The two hybrid sp atomic orbitals, ϕ_1 and ϕ_2 . The shaded and unshaded areas represent lobes of different mathematical signs.

1.48 HYBRIDIZATION INDEX

This is the superscript x on the p in an sp^x hybrid orbital; such an orbital possesses $[x/(1+x)]$ (100) percent p character and $[1/(1+x)]$ (100) percent s character.

Example. The hybridization index of an sp^3 orbital is 3 (75% p -character); for an $sp^{0.894}$ orbital, it is 0.894 (47.2% p -character).

1.49 EQUIVALENT HYBRID ATOMIC ORBITALS

A set of hybridized orbitals, each member of which possesses precisely the same value for its hybridization index.

Example. If the atomic orbitals $2s$ and $2p_z$ are distributed equally in two hybrid orbitals, each resulting orbital will have an equal amount of s and p character; that is, each orbital will be sp ($s^{1.00}p^{1.00}$) (Fig. 1.47). If the $2s$ and two of the $2p$ orbitals are distributed equally among three hybrid orbitals, each of the three equivalent orbitals will be sp^2 ($s^{1.00}p^{2.00}$) (Fig. 1.49). Combining a $2s$ orbital equally with three $2p$ orbitals gives four equivalent hybrid orbitals, $s^{1.00}p^{3.00}$ (sp^3); that is, each of the four sp^3 orbitals has an equal amount of s character, $[1/(1+3)] \times 100\% = 25\%$, and an equal amount of p character, $[3/(1+3)] \times 100\% = 75\%$.

1.50 NONEQUIVALENT HYBRID ATOMIC ORBITALS

The hybridized orbitals that result when the constituent atomic orbitals are not equally distributed among a set of hybrid orbitals.

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Example. In hybridizing a $2s$ with a $2p$ orbital to form two hybrids, it is possible to put more p character and less s character into one hybrid and less p and more s into the other. Thus, in hybridizing an s and a p_z orbital, it is possible to generate one hybrid that has 52.8% p ($sp^{1.11}$) character. The second hybrid must be 47.2% p and is therefore $sp^{0.89}$ ($[x/(1+x)] \times 100\% = 47.2\%$; $x = 0.89$). Such nonequivalent carbon orbitals are found in CO, where the sp carbon hybrid orbital used in bonding to oxygen has more p character than the other carbon sp hybrid orbital, which contains a lone pair of electrons. If dissimilar atoms are bonded to a carbon atom, the sp hybrid orbitals will always be nonequivalent.

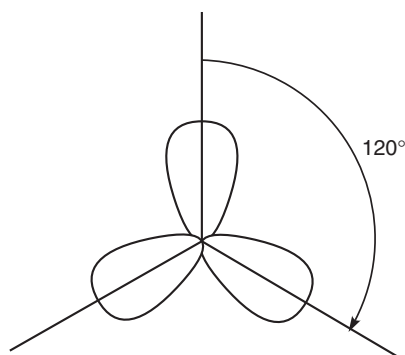


Figure 1.49. The three hybrid sp^2 atomic orbitals (all in the same plane).

Acknowledgment. The authors thank Prof. Thomas Beck and Prof. William Jensen for helpful comments.

SUGGESTED READING

See, for example,

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