

A Pictorial Approach to Molecular Bonding

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Preface

With the development of accurate molecular calculations in recent years, useful predictions of molecular electronic properties are currently being made. It is therefore becoming increasingly important for the non-theoretically oriented chemist to appreciate the underlying principles governing molecular orbital formation and to distinguish them from the quantitative details associated with particular molecules. It seems highly desirable then that the non-theoretician be able to deduce results of general validity without esoteric mathematics. In this context, pictorial reasoning is particularly useful. Such an approach is virtually indispensable if bonding concepts are to be taught to chemistry students early in their careers.

Undergraduate chemistry majors typically find it difficult to formulate molecular orbital schemes, especially delocalized ones, for molecules more complicated than diatomics. The major reason for this regrettable situation is the general impracticability of teaching group theory before students take organic and inorganic courses, wherein the applications of these concepts are most beneficial. Consequently many students graduate with the misconception that the ground rules governing bonding in molecules such as NH_3 are somehow different from those which apply to aromatic systems such as C_6H_6 . Conversely, seniors and many graduate students are usually only vaguely, if at all, aware that sigma bonding (like extended pi bonding) can profitably be described in a delocalized manner when discussing the UV-photoelectron spectrum of CH_4 , for example. Moreover, many graduate students who have had group theory find it difficult to visualize pictorially the linear combinations of AOs which make up MOs and to picture the relative movements of the atoms in the normal vibrational modes of even very symmetrical polyatomic systems.

In 1968, Professor Klaus Ruedenberg and the author became aware of this

dilemma, and to remedy the situation we jointly developed a new course designed to teach the basic elements of chemical bonding to undergraduates. In order to do justice to the point of view of the theoretical as well as the experimental chemist, we team-taught the course for several years and, as a result of many hours of teaching and many more hours of discussion, a set of printed class notes came into existence. Using the nodal symmetries of atomic orbitals, Klaus outlined during one of these warmly acknowledged conversations how the intuitive reasoning associated with the “united atom model,” originally introduced by R. S. Mulliken in connection with correlation diagrams, can provide a tool for students to learn how to construct MOs in very simple systems of high symmetry. Further reflection along these lines led the author to determine with simple sketches whether the nodal properties of atomic orbitals placed at the center of more complicated and less symmetrical molecules could be effectively used as a device to generate their MOs as LCAOs. This “generator orbital” method appeared to be widely applicable and, after Klaus justified its generality on group theoretical grounds in 1973, we used this approach successfully ever since in a course on bonding taught mainly to undergraduate majors and interested graduate students. In 1975, Professor David K. Hoffman pointed out that the generator orbital approach can also be used for a pictorial deduction of localized MOs and of normal vibrational modes in molecules. Dave’s contributions of these ideas are also most warmly acknowledged and their development is included here.

Although the generator orbital concept can be presented in a mathematical and group theoretical framework, the concept and its applications lend themselves exceedingly well to a pictorial approach. The only prerequisites are high school level chemistry, geometry, physics, and trigonometry. Although integrals, vectors, and matrices are *briefly* touched upon, a working knowledge of these subjects is not necessary for understanding the generator orbital concept and its applications.

Some of the results of the fruitful collaborations with Klaus and David were published in article form.^a We believe that more widespread pedagogical benefit can be realized by developing a textbook containing the ideas and applications contained in these papers, as well as in the class notes which by 1977 had become quite voluminous. After the appearance of the articles in that year, the three of us completed a preliminary manuscript for such a book and made several serious attempts to bring it into publishable form. Because of the press of other commitments as well as philosophical differences (stemming from our respective scientific backgrounds) concerning the manner of presentation of the material, it devolved on the author, by mutual agreement,

^aSee D. K. Hoffman, K. Ruedenberg, and J. G. Verkade, “A Novel Pictorial Approach to Teaching MO Bonding Concepts in Polyatomic Molecules,” *J. Chem. Ed.*, 54, 590 (1977); and D. K. Hoffman, K. Ruedenberg, and J. G. Verkade, “Molecular Orbital Bonding Concepts in Polyatomic Molecules: A Novel Pictorial Approach,” *Structure and Bonding*, 33, 59 (1977).

to finish the project. The author, therefore, takes responsibility for errors and ambiguities which will undoubtedly be found, and it is hoped that these will be brought to his attention. The contents of essentially all of the first three chapters were adapted from more extensive class notes prepared by Klaus, and substantial portions of Chapters 4, 5, and 6 were developed in more extensive form by Klaus and David. David also made many helpful suggestions for the remaining chapters.

Many teachers of inorganic chemistry are currently seeking ways to reintroduce more descriptive chemistry at both the undergraduate and graduate levels. Part of the motivation in writing this book was to provide students with some simple tools for rationalizing the bonding in a very wide variety of molecules in a highly unified theoretically sound manner. By utilizing the generator orbital approach, the total time spent in teaching bonding concepts in inorganic, organic, and physical chemistry courses can actually be significantly reduced.

My loving thanks go to my wife, Sue, whose support and patience were truly wonderful in helping me finish this project. I also thank Mrs. Joyce Gilbert and Mrs. Peggy Biskner for their excellent deciphering and typing skills in bringing my handwritten manuscript into readable form. My thanks also go to Professor Walter Struve and the members of my 1984 and 1985 Structure and Bonding classes for reading the final manuscript and making many helpful suggestions.

Ames, Iowa
July 1986

John Verkade



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CHAPTER 1

The Orbital Picture for Bound Electrons

The primary purpose of this book is to develop for the non-theoretically oriented chemist a pictorial approach to molecular orbitals. To accomplish this goal we consider in this chapter and Chapter 2 the fundamental properties of electrons and orbitals which are required for the introduction of “generator orbitals.” Generator orbitals (which will be defined later) constitute the tool with which the three-dimensional visualization of molecular orbitals is achieved in subsequent chapters. We will see that the vibrational modes of molecules are also easily visualized with this approach. After we apply the generator orbital concept in Chapter 3 to bonding and to vibrational motion in diatomics, we will apply this concept for the same purposes to more complex polyatomic molecules possessing a variety of geometrical shapes.

1.1. Traveling and Standing Waves

Since we will soon appreciate that electrons can behave as either traveling or standing waves, it is important to understand some properties of waves. When a guitar string is plucked, the magnitude of the string displacement is called its *amplitude*. The louder the instrument is played, the greater the amplitude. It is interesting, however, that the amplitude of a plucked string varies over its length, and it also changes with time. Thus *the amplitude for such a one-dimensional wave is a function of both position and time: $f(x, t)$* . As we will see shortly, the standing wave pattern in a plucked string fixed at both ends is composed of two traveling waves. In a traveling wave, an observer sees a sinusoidal pattern moving with constant velocity along the x direction (i.e., the length) of the string. The amplitude or displacement function for the wave is given by Equation 1-1; alternatively the sine function may be substituted by

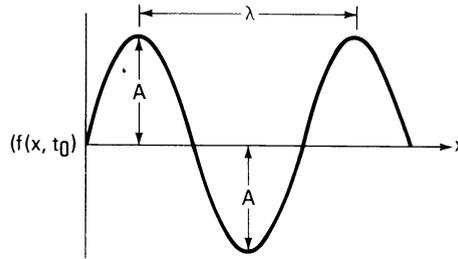


Figure 1-1. A “snapshot” of a sinusoidal wave traveling in the x direction with wavelength λ .

the cosine function:

$$f(x, t) = A \sin 2\pi \left(\frac{x}{\lambda} - \frac{t}{\tau} \right). \quad (1-1)$$

Here x measures the distance along the string, t is the time, A is the maximum amplitude, and λ and τ are constants having the same units as x and t , respectively. The dimension of f is that of A , which in the case of the string would be in units of length.

To see the meaning of λ , suppose the wave is frozen at a fixed time $t = t_0$. The amplitude is now a sinusoidal function of space only (see Figure 1-1). *The distance at which the entire pattern repeats itself is called the wavelength, λ .* The reciprocal of λ is called the *wave number*, $\bar{\nu}$, and it represents the number of full waves per centimeter.

In order to appreciate the meaning of τ , suppose an observer views the wave at a fixed point $x = x_0$. The observer will then see an amplitude which oscillates from a positive value to an equal but negative value with time (Figure 1-2). The time it takes for the amplitude to return to its initial value is called the *period*, τ . The number of times this phenomenon occurs per second

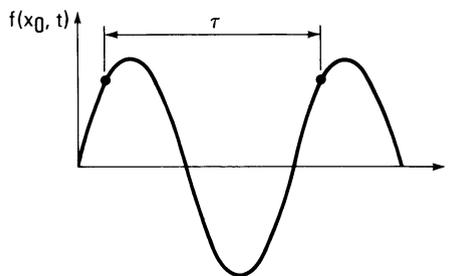


Figure 1-2. The behavior of the amplitude of a traveling wave as viewed at a fixed point $x = x_0$, where τ is the period.

is given by $1/\tau$, and this quantity is called the *frequency*, ν . The speed v of an advancing crest in a traveling wave is given by $v = \lambda\nu$.

The surface of a wave coming in on a beach is a two-dimensional traveling wave (Figure 1-3) since it has troughs and crests possessing length along y . The amplitude function is again given by Equation 1-1 and is a constant along the y direction. To visualize a three-dimensional traveling wave, consider what happens when a sound wave is produced. The air, which was of constant density before the sound, now possesses regions of higher and lower density which are depicted in Figure 1-4, wherein only the x and z dimensions are shown for clarity. The density in any given yz plane is constant. The propagation of such a plane wave is characterized by positive and negative deviations from the average density of air. The magnitude of these deviations is the amplitude.

To understand *standing* waves, it helps to examine the traveling waves we have considered for points, lines, or planes where the amplitude is zero and where it is maximum. Zero-amplitude regions are called *nodes*, and *antinodes* refer to places of maximum amplitude. In a traveling wave, nodes and antinodes move at the same velocity as the whole pattern. In a standing wave, the nodes and antinodes are fixed in space. The amplitude of a standing wave is given by any one of the expressions in Equation 1-2:

$$\begin{aligned}
 &A \left(\sin 2\pi \frac{t}{\tau} \right) \left(\sin 2\pi \frac{x}{\lambda} \right) \\
 &A \left(\sin 2\pi \frac{t}{\tau} \right) \left(\cos 2\pi \frac{x}{\lambda} \right) \\
 &A \left(\cos 2\pi \frac{t}{\tau} \right) \left(\sin 2\pi \frac{x}{\lambda} \right) \\
 &A \left(\cos 2\pi \frac{t}{\tau} \right) \left(\cos 2\pi \frac{x}{\lambda} \right).
 \end{aligned}
 \tag{1-2}$$

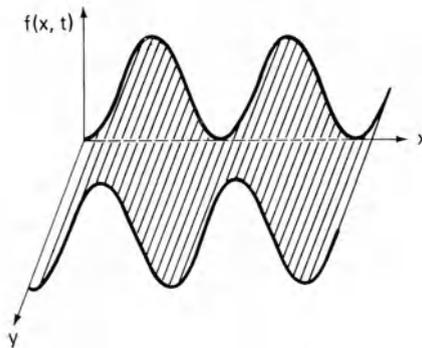


Figure 1-3. A two-dimensional traveling wave represented by the surface of an ocean.

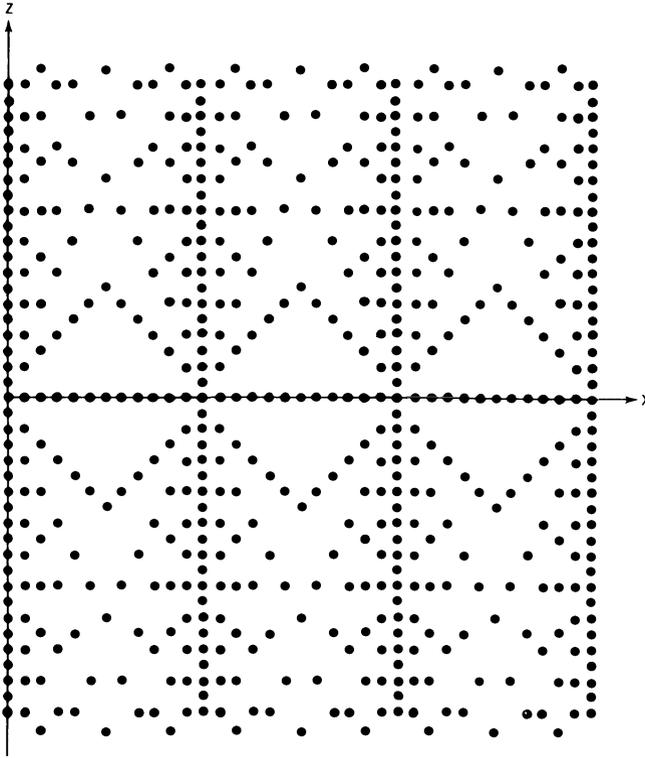


Figure 1-4. A two-dimensional cross section of a traveling sound wave caused by the yz surface vibrating back and forth across $x = 0$, thereby causing compressions and rarefactions among the air molecules to move along the x direction.

In the first expression the amplitude vanishes for $x = 0$ and at every half-wavelength [i.e., $x = (1/2)\lambda, \lambda, (3/2)\lambda, 2\lambda$, etc.]. The antinodes are seen from this expression to appear halfway between the nodes. In the remaining expressions, nodes and antinodes appear at different x values. In all the expressions, however, the nodes and antinodes are at fixed values of x and are independent of time. There is an important difference between nodes and antinodes in a standing wave. Nodes are time-independent points, lines, or planes while antinodes oscillate with time. In a one-dimensional wave the amplitude points oscillate between positive and negative values of z (Figure 1-5) and in a two-dimensional wave the amplitude line does the same. In a three-dimensional plane wave, a density oscillates in the yz plane.

Standing waves occur when *boundary conditions* are imposed. Clamps at both ends of a vibrating string impose the important boundary condition that there be nodes at these endpoint positions. The wave, therefore, *must* be a standing wave and in fact the length (L) of the domain between the endpoints

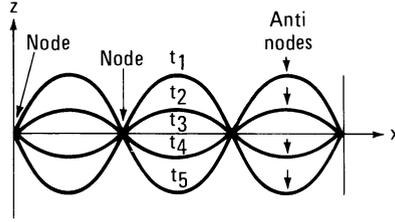


Figure 1-5. A standing wave bounded at the extreme ends, showing the time-independent nodes and time-dependent antinodes.

must be a multiple of the length between any *two* nodes ($\frac{1}{2}\lambda$). Thus the only wavelengths permitted are $\lambda_n = 2L/n$, with $n = 1, 2, 3, 4$, etc. In other words, λ is *quantized* to particular values and the λ_n are the *characteristic* or “*eigen*” values of the wavelength.

It is an interesting observation that two identical traveling waves propagating in opposite directions form a standing wave when superposed. Thus, for example, even though neither one of two superposed traveling one-dimensional waves contains points at which the amplitude vanishes *at all times*, such points (the nodes) do exist in the standing wave.

1.2. Wave Energy and Interference

All waves contain energy. Such energy can be kinetic and potential energy of matter (as for water or sound waves) or it can be electromagnetic (as in light waves). In all cases, the *amount of wave energy per unit volume* (i.e., the energy density or intensity) *is proportional to the square of the amplitude* (e.g., f^2 in Equation 1-1). In a traveling wave, energy flows along the direction of propagation. In a standing wave the energy is *localized* in the regions between the nodes and the nodes always have zero energy density.

If two or more sound waves having different frequencies encounter each other, their amplitudes superpose to form a new wave $f(x, y, z, t) = f_1(x, y, z, t) + f_2(x, y, z, t) + \cdots + f_n(x, y, z, t)$. Because the amplitudes of the constituent waves enhance one another at some points and cancel each other at others, a new set of oscillations is created. This has important consequences for the composite wave. Thus the energy density at most points in the new wave [i.e., $f^2 = (f_1 + f_2 + f_3 + \cdots + f_n)^2$] is not the same as the sum of the energy densities of the constituent waves [i.e., $f_1^2 + f_2^2 + \cdots + f_n^2$]. The difference of these two sums plotted along the direction of propagation gives an *interference* pattern. Such interference of two frequencies (Figure 1-6a) gives rise to the “beat” (Figure 1-6b) of fluctuating sound intensity heard when two identical or different instruments are playing slightly different pitches (frequencies) at the same intensity.

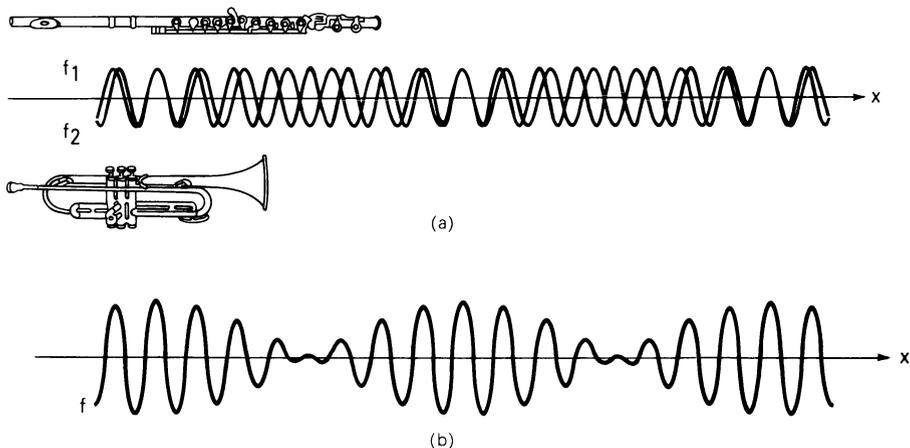


Figure 1-6. Superposition of two traveling waves of different frequency (a) to give a composite traveling wave (b) having “beats” of intensity. The closer the two frequencies are to each other, the closer together the “beats” are heard.

1.3. Electron Orbitals

Under many conditions, electrons behave as waves while under others they possess the characteristics of particles. This should not be disconcerting. The fundamental mathematical theory actually encompasses both the classical (particle) and the quantum mechanical (wave) descriptions harmoniously. It is only because of our limited ability of visualization that these approaches appear to be so different. Free electrons (i.e., in the absence of external forces and thus moving with constant velocity in a straight line) are found to act like three-dimensional traveling plane waves. In certain types of planar molecules such as butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) electrons behave like plane waves enclosed in a box. In a molecule in which double bonds alternate with single bonds (i.e., *conjugated* π bond systems), the π electrons (of which there are four in butadiene) move across *all the carbon atoms and also spend part of their time between the central two carbons*, even though the way we normally write the formula does not indicate this. In many respects the behavior and properties of these π electrons can be described in terms of a free electron wave constrained to move along the carbon-carbon bond skeleton. Although we will not detail such a description here, these boundary conditions (as in the case of the string clamped at both ends) lead to quantized wavelengths $\lambda_k = 2L/k$, where L is related to the length of the carbon skeleton and $k = 1, 2, 3$, etc. The kinetic energy in ergs of a free electron (which is the only kind of energy it has, even when constrained to remain in a confined space) is given by Equation 1-3 (which we do not derive), where m = the mass of the electron and h is Planck's constant (6.6×10^{-27} erg-sec). This energy quantization is

$$\varepsilon_k = \left(\frac{h^2}{8mL^2} \right) k^2 \quad (1-3)$$

characteristic of *all* electrons in atoms as well as molecules. Such electrons are all restricted to certain regions of space by electrostatic nuclear attractions and are said to be *bound* electrons. *All bound electrons (atomic and molecular) have wave character and possess quantized energy levels.* Although unbound electrons also have wave properties, their energies are not quantized. Quantization is the result of imposing boundaries on a wave. The energy levels of bound electron waves are spaced differently from one atom or molecule to another.

What does an amplitude function of an electron wave signify? For a string it is displacement of a point along z , for a water wave it is a similar displacement of a line parallel to y , and for a sound wave it is a deviation of air density from the average. For electron waves the amplitude function is related to the *distribution of the electron density* and is denoted by $\psi(x, y, z, t)$. How we reconcile the ideas of electrons as particles and as clouds having density will be made more clear shortly. For a free electron, ψ has the mathematical features described earlier for traveling waves, but for a bound electron (i.e., a localized electron wave with boundary conditions on its length) the properties of ψ are those of standing waves. In accord with Equation 1-2, a *three-dimensional* standing electron wave is a product of a space function ϕ_n and a time function f_n , i.e.,

$$\psi_n(x, y, z, t) = \phi_n(x, y, z) f_n(t). \quad (1-4)$$

For a one-dimensional standing wave this space factor has the sinusoidal form

$$\phi_n(x) = A \sin \frac{2\pi x}{\lambda_n}. \quad (1-5)$$

It contains the quantized wavelength λ_n discussed earlier which, in turn, is related to the orbital energy ε_n given by Equation 1-3. The *space* amplitudes ϕ_n associated with the first four ε_n values (i.e., $n = 1, 2, 3, 4$) are shown in Figure 1-7. The time factors of Equation 1-4 for different bound electrons are given by $f_n = \exp(-i\varepsilon_n t/\hbar)$. Their functional form is thus the same for all states and it is only the value of the energy ε_n which differentiates between different states and different systems. *However, the spatial amplitudes for bound electrons differ markedly, and it is these functions that characterize the individual natures of various states.* In general (i.e., for electrons under the influence of forces) these space amplitudes are three-dimensional in nature [$\phi_n(x, y, z)$] and their shapes are not sinusoidal. One important feature of the electron waves shown in Figure 1-7 which carries over into *all* standing electron waves is that they too possess *nodes*, *positive lobes* (amplitudes), and *negative lobes*.

Single-electron standing waves are called *orbitals* and this term applies to the total wave function $\psi_n(x, y, z, t)$ as well as to only its spatial amplitude $\phi_n(x, y, z)$. An electron described by ψ_n is said to occupy the orbital ψ_n or ϕ_n .

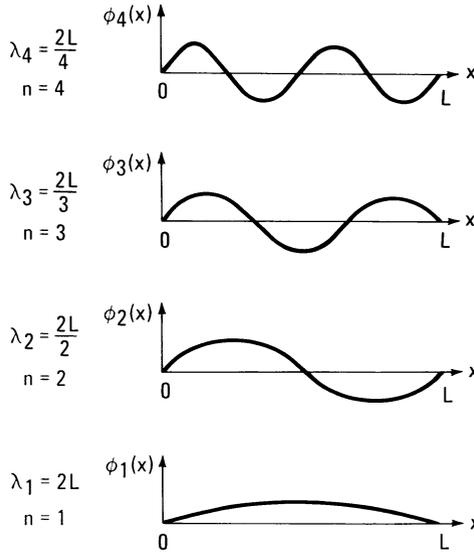


Figure 1-7. A series of space amplitudes ϕ_n for four values of ϵ_n ($n = 1$ to 4).

1.4. Normalization and Orthogonality

These formidable words denote rather simple concepts which can be developed after we consider how the electron density is related to the electron wave function. Earlier it was stated that the amplitude function ψ “describes the distribution of an electron.” How can this be if ψ can have negative values? The answer is that *the fraction of the electron cloud which is found at the time t in the infinitesimally small volume element $dV = dx dy dz$ enclosing the point x, y, z is given by $|\psi(x, y, z, t)|^2 dV$, and this quantity is always positive.* (Recall that the letter d in dx , etc., simply means an infinitesimally small increment.) This means that at time t the volume element dV makes a contribution of $m|\psi|^2 dV$ to the total electron mass and a contribution $-e|\psi|^2 dV$ to the total electron charge. The quantity $|\psi|^2$ is called the *orbital density*. More rigorously it describes the *probability* of finding the electron in dV .

Because the time factor in Equation 1-4 is of the form $\exp(i\alpha)$ with α being real, one finds $|\psi|^2 = \phi^2 |f|^2 = \phi^2(x, y, z)$. This shows that bound orbital densities do not change with time and that they can be calculated. Since ϕ^2 tells us the essential characteristics of a given system, we will deal mainly with the *spatial orbitals* $\phi(x, y, z)$ rather than total functions $\psi(x, y, z, t)$.

Since ϕ^2 describes one whole electron in the entire space and $\phi^2 dV$ represents the fraction of this electron in the volume dV , we can add up all the $\phi^2 dV$ in the space and say that it is equal to one electron. The mathematical procedure for such addition is called *integration* and its notation is shown in Equation 1-6.

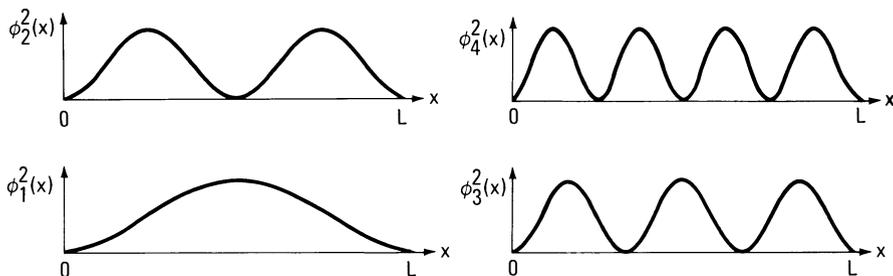


Figure 1-8. The ϕ_n of Figure 1-7 are squared to show their probability densities $\phi_n^2(x)$.

$$\int dV \phi^2(x, y, z) = 1 \quad (1-6)$$

This requirement is called the *normalization* of the orbital ϕ and it says that the single electron is contained in the space defined by adding up all the infinitesimally small volume elements dV which contain electron density.

In the case of a one-dimensional standing electron wave (Figure 1-7) $\phi_n^2(x)dx$ is the fraction of an electron in ϕ_n which lies between x and $(x + dx)$. The probability densities $\phi_n^2(x)$ have the forms shown in Figure 1-8.

To help us understand orbital occupancies of ground and excited states of a system, it is very helpful to relate the geometrical shapes of different orbitals to their energies. Much information of this kind is contained in the nodes and antinodes (lobes) of orbitals. For example for our one-dimensional electron wave, the energies of the orbitals ϕ_n , as given by Equation 1-3 rise monotonically with n . Note that the number of nodes *inside* the box is given by $n - 1$. To help us generalize this observation to other systems, the concept of *orbital orthogonality* is important. To appreciate this concept consider what happens when we generalize the normalization integral (Equation 1-6) to *two* different spatial orbitals ϕ and ψ as shown in Equation 1-7. Since the time factor is no longer necessary for us, ψ will be used to denote another spatial orbital. The

$$\int dV \phi(x, y, z)\psi(x, y, z) = \langle \phi | \psi \rangle \quad (1-7)$$

integral in Equation 1-7 (for which we will use the shorthand notation $\langle \phi | \psi \rangle$) is called the *overlap integral* between ϕ and ψ . This integral is zero for two normalized orbitals on the same atom. Orbitals for which the overlap integral is zero are said to be *orthogonal* to each other. Strictly speaking this applies only to nondegenerate orbitals. Degenerate orbitals such as $2px$, $2py$, $2pz$ are indeed orthogonal to one another, but as we shall see later, linear combinations of these orbitals need not be. Orthogonality does not imply that the two orbitals are at right angles to each other in space. It means only that their overlap is zero.

The relation between orbital orthogonality and orbital nodal character can

be seen by examining the one-dimensional electron wave. For example, are ϕ_1 and ϕ_2 orthogonal, i.e., is $\langle \phi_1 | \phi_2 \rangle = 0$? The product of the two orbitals is plotted in Figure 1-9. If we integrate over the distance 0 to L , the contributions of the positive and negative lobes cancel by symmetry. Thus the integral $\langle \phi_1 | \phi_2 \rangle$ is equal to 0 and the orbitals are orthogonal. *The pivotal point here is that one of the orbitals (ϕ_2) has a node where the other (ϕ_1) does not.* Similar reasoning applies to three-dimensional orbitals. Each orbital of an atom or molecule has a characteristic nodal structure which renders all the nondegenerate orbitals orthogonal to each other in the same way that ϕ_1 and ϕ_2 in Figure 1-9 are. As a general rule the number of nodes of an orbital in a given system increases with the orbital energy.

It is important to note that observations on mass or charge density of the electron tell us only about $|\psi|^2$ but not directly about ψ . In fact, there is no observable property of the electron which allows us to observe ψ directly. To calculate any electronic property, however, we must in general have the amplitude ψ . Thus an important area of research is the development of more accurate wave functions which describe electron behavior in atoms and molecules. It should be noted that the calculation of any observable property always involves the wave function ψ multiplied either by itself or by some derivative of ψ . Consequently, the wave function ψ yields the same value for any property as the wave function $-\psi$. The sign of ψ is therefore arbitrary. In other words, ψ and $-\psi$ are two equivalent alternative mathematical descriptions of the same physical orbital.

1.5. Systems with Many Electrons

In atoms and molecules with many electrons, electrons occupy various orbitals, and quantum states of the total system differ by their occupation patterns. The possible occupation patterns are restricted by the *Pauli exclusion principle*, which specifies that each orbital cannot be occupied by more than two electrons. Moreover, if any orbital contains two electrons, they must have opposite spin rotations. The concept of an electron as a particle spinning on its axis seems incongruous when we are describing the wave nature of an electron in a confined space. Recall that particle and wave descriptions

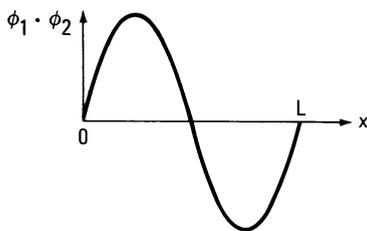


Figure 1-9. Plot of $\phi_1 \cdot \phi_2$ showing the total area under the curve to be zero.