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Electronic Structure and the Properties of Solids

THE PHYSICS OF THE CHEMICAL BOND

Walter A. Harrison
STANFORD UNIVERSITY

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To my wife, Lucky,
and to my sons, Rick, John, Bill, and Bob
IT IS WITH GREAT PLEASURE that I greet the Dover edition of this book, which joins my Solid State Theory as affordable physics. It comes with some minor corrections to the last printing by W. H. Freeman and Company.

This text appeared in 1980, very early in the development of the simplified methods for calculating properties in the context of tight-binding theory. As mentioned in the original preface, the derivation of the basic formulae for interatomic couplings only arose during the production of the first edition. Fortunately, all the essentials of the theory were complete enough to be included. There have been a number of developments since the appearance of the book which both simplify the theory and make it more accurate. It has not been possible to incorporate these in this edition but it may be helpful to give references to the principal ones.

Perhaps the most significant was a redetermination of the parameters giving the coupling between atomic orbitals on neighboring atoms. By incorporating an additional atomic orbital in perturbation theory, as done for other reasons by Louie, it was possible to fit a larger set of energy-band values and the fitting was more stable. The resulting couplings were rather different (\(\eta_{\sigma\sigma} = -1.32, \eta_{\pi\sigma} = 1.42, \eta_{\sigma\pi} = 2.22, \text{ and } \eta_{\pi\pi} = -0.63\), rather than the adjusted values given in Table 2-1). The additional atomic orbital could then be discarded and with the new parameters it became possible to abandon the distinction between two types of covalent energies \(V_2\) and \(V_2^b\) and the
corresponding two types of polar energies \((V_1\) and \(V_2\)); one could use those based upon hybrids for dielectric as well as bonding properties. This was a very considerable simplification with no appreciable loss of accuracy. Since we were changing the couplings, we also changed over to the use of Hartree-Fock term values, from page 534, instead of the Herman-Skillman term values from the Solid State Table. The latter were appropriate when most of our comparisons were with band calculations which utilized similar approximations to those used in the Herman-Skillman tables. We tend now to compare more with experiment and the Hartree-Fock tables are closer to the experimental term values.

A second simplification was the introduction of overlap repulsions between atoms in covalent solids as a power-law variation, \(\eta_0 Z^2/\text{ehl}^2\), with the coefficient \(\eta_0\) adjusted to give the correct lattice spacing.\(^3\) A similar form varying as the inverse eighth power of spacing was introduced for ionic solids.\(^4\) This is not quite as accurate nor general as exponential forms but by using the algebraic form with the leading factor fit to obtain the known equilibrium spacing, it was possible to use all terms in the energy in terms of the parameters of the theory \((V_1, V_2, V_3)\) and thus to obtain elementary formulae for properties such as the bulk modulus. This does produce appreciable errors, however, and more accurate procedures have been developed by van Schilfgaarde and Sher.\(^5\)

Extended bond orbitals were introduced on page 83 of the text, but few of the corresponding corrections to the properties were calculated. Since publication corrections have been made to the total energy of semiconductors to obtain cohesion,\(^2\) heats of solution,\(^6\) and corrections to the dielectric properties.\(^7\) There have also been studies of Coulomb effects\(^8\) in semiconductors and insulators, including self-consistency and the "many-body" enhancement of the gap, in the same spirit as the analyses in this text.

We completed the evaluation of the effective interaction between ions in metals introduced on page 387, using the Fermi-Thomas dielectric function from page 378. This led to the remarkably simple form \(V(d) = Z^2 e^2 e^{-kd} \times \cosh^2 \kappa d/\lambda d\) and a good description of the bonding properties of simple metals.\(^9\) We also followed up the analysis of transition-metals given in Chapter 20 in a series of studies,\(^10\) and on the analysis of transition-metal compounds\(^1\) given in Chapter 19. As might be expected, we also made application of the elementary theory of electronic structure to the newly discovered high-temperature superconductors.\(^12\)

Recent studies by Zaanan, Sawatzky, and Allen\(^1\) have made it clear that the origin of the metal-insulator transition in transition-metal compounds, discussed in Section 19-B, is not associated with the s- to d-state promotion to which we attributed it and nothing from that section should be used without considering these more recent and complete studies.

There have been very dramatic developments in the understanding of semiconductor surface reconstructions discussed in Section 10-B. A number of theoretical studies showed that Coulomb effects will prevent the Jahn-Teller distortion proposed by Haneman and discussed in Section 10-B. Pandey\(^4\) proposed that the observed two-by-one reconstruction of the silicon (111) surface is instead due to a \(\pi\)-bonded chain configuration, which is now generally accepted. The two-by-one reconstruction on the silicon (100) surface, which we attributed to a "ridge" structure, is now generally recognized to be the Schlier-Farnsworth dimer formation, which we discussed but thought an unlikely structure. It is also established that the dimers are canted as proposed by Chadi.\(^13\) The adatom model of the seven-by-seven reconstruction on silicon (111) surfaces, which we proposed in Section 10-D, was spectacularly confirmed using the scanning tunneling microscope by Binnig, Rohrer, Gerber and Weibel,\(^16\) with almost exactly the Lander-Morrison pattern which we suggested. However, further studies by Takayanagi, Tanishiro, Takahashi, and Takahashi\(^17\) indicated a much more intricate structure including also stacking faults and dimers; that model is generally accepted. Finally the natural semiconductor band line-ups proposed in Section 10-F were brought into question by Tersoff,\(^18\) who suggested that there were "neutral points" in the energy bands which would align, fixing the band offsets at heterojunctions. In the context of the tight-binding theory of this text these neutral points are the average hybrid energies in each crystal.\(^19\) Any difference in the average hybrid energy on the two sides of a heterojunction will be reduced by a factor of the dielectric constant of the systems. The reason the natural band line-ups of Section 10-F worked as well as they did is that the average hybrid energies are frequently the same so no dielectric screening is necessary. The theory based upon matching average hybrids\(^19\) is just as simple and more general and accurate than that given here.

These more recent developments have strengthened and supported the methods discussed in this text. Except for the new choice of parameters, which eliminated the awkward use of two sets of covalent and polar energies, these developments do not modify the basic theory described, but simply add to it. I hope that the description given here can continue to be useful to the materials scientist and physicist.

Walter A. Harrison
April 1988

References:


In the past few years the understanding of the electronic structure of solids has become sufficient that it can now be used as the basis for direct prediction of the entire range of dielectric and bonding properties, that is, for the prediction of properties of solids in terms of their chemical composition. Before that, good theories of generic properties had been available (for example, the free-electron theory of metals), but these theories required adjustment of parameters for each material. It had also been possible to interpolate properties among similar materials (as with ionicity theory) or to make detailed prediction of isolated properties (such as the energy bands for perfect crystals). The newer predictions have ranged from Augmented Plane Wave (APW) or multiple-scattering techniques for calculating total energies in perfect crystals, possible with full-scale computers, to elementary calculations of defect structures, which can be done with linear combinations of atomic orbitals (LCAO theory) or pseudopotentials on hand-held calculators. The latter, simpler category is of such importance in the design of materials and in the interpretation of experiments that there is need for a comprehensive text on these methods. This book has been written to meet that need.

The Solid State Table of the Elements, folded into the book near the back cover, exemplifies the unified view of electronic structure which is sought, and its relation to the properties of solids. The table contains the parameters needed to calculate nearly any property of any solid, using a hand-held calculator; these are parameters such as the LCAO matrix elements and pseudopotential core radii, in terms of which elementary descriptions of the electronic structure can be given. The approach used throughout this book has been to simplify the description of
The text itself is designed for a senior or first-year graduate course. It grew out of a one-quarter course in solid state chemistry offered as a sequel to a one-quarter solid state physics course taught at the level of Kittel's *Introduction to Solid State Physics*. A single quarter is a very short time for either course. The two courses, though separate, were complementary, and were appropriate for students of physics, applied physics, chemistry, chemical engineering, materials science, and electrical engineering.

Serving so broad an audience has dictated a simplified analysis that depends on three approximations: a one-electron framework, simple approximate interatomic matrix elements, and empty-core pseudopotentials. Refinement of these methods is not difficult, and is in fact carried out in a series of appendices. The text begins with an introduction to the quantum mechanics needed in the text. An introductory course in quantum mechanics can be considered a prerequisite. What is reviewed here will not be adequate for a reader with no background in quantum theory, but should aid readers with limited background.

The problems at the ends of chapters are an important aspect of the book. They clearly show that the calculations for systems and properties of genuine and current interest are actually quite elementary. A set of problem solutions, and comments on teaching the material, are contained in a teacher's guide that can be obtained from the publisher.

I anticipate that some users will object that much of the material covered in this book is so recent it is not possible to feel as comfortable in teaching it as in teaching a more settled field such as solid state physics. I believe, however, that the subject dealt with here is so important, particularly now that techniques such as molecular beam epitaxy enable one to produce almost any material one designs, that no modern solid state scientist should be trained without a working knowledge of the kind of solid state chemistry described in this text.

Walter A. Harrison
June 1979
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Part I

Electron States

In this part of the book, we shall attempt to describe solids in the simplest meaningful framework. Chapter 1 contains a simple, brief statement of the quantum-mechanical framework needed for all subsequent discussions. Prior knowledge of quantum mechanics is desirable. However, for review, the premises upon which we will proceed are outlined here. This is followed by a brief description of electronic structure and bonding in atoms and small molecules, which includes only those aspects that will be directly relevant to discussions of solids.

Chapter 2 treats the electronic structure of solids by extending the framework established in Chapter 1. At the end of Chapter 2, values for the interatomic matrix elements and term values are introduced. These appear also in a Solid State Table of the Elements at the back of the book. These will be used extensively to calculate properties of covalent and ionic solids.

The summaries at the beginnings of all chapters are intended to give readers a concise overview of the topics dealt with in each chapter. The summaries will also enable readers to select between familiar and unfamiliar material.
1-A Quantum Mechanics

For the purpose of our discussion, let us assume that only electrons have important quantum-mechanical behavior. Five assertions about quantum mechanics will enable us to discuss properties of electrons. Along with these assertions, we shall make one or two clarifying remarks and state a few consequences.

Our first assertion is that

(a) Each electron is represented by a wave function, designated as \( \psi(r) \). A wave function can have both real and imaginary parts. A parallel statement for light would be that each photon can be represented by an electric field \( \mathbf{E}(r, t) \). To say that an electron is represented by a wave function means that specification of the wave function gives all the information that can exist for that electron except information about the electron spin, which will be explained later, before assertion (d). In a mathematical sense, representation of each electron in terms of its own wave function is called a one-electron approximation.

(b) Physical observables are represented by linear operators on the wave function. The operators corresponding to the two fundamental observables, position and momentum, are

\[
\begin{align*}
\text{position} & \leftrightarrow r, \\
\text{momentum} & \leftrightarrow \mathbf{p} = \frac{\hbar}{i} \frac{\partial}{\partial r}.
\end{align*}
\]

(1.1)

where \( \hbar \) is Planck’s constant. An analogous representation in the physics of light is of the observable, frequency of light; the operator representing the observable is proportional to the derivative (operating on the electric field) with respect to time, \( \frac{\partial}{\partial t} \). The operator \( r \) in Eq. (1.1) means simply multiplication (of the wave function) by position \( r \). Operators for other observables can be obtained from Eq. (1.1) by substituting these operators in the classical expressions for other observables. For example, potential energy is represented by a multiplication by \( V(r) \). Kinetic energy is represented by \( p^2/2m = -(\hbar^2/2m)V^2 \). A particularly important observable is electron energy, which can be represented by a Hamiltonian operator:

\[
H = -\frac{\hbar^2}{2m} \nabla^2 + V(r).
\]

(1.2)

The way we use a wave function of an electron and the operator representing an observable is stated in a third assertion:

(c) The average value of measurements of an observable \( O \) for an electron with wave function \( \psi \), is

\[
\langle O \rangle = \frac{\int \psi^*(r)O\psi(r)d^3r}{\int \psi^*(r)\psi(r)d^3r}.
\]

(1.3)
average value of the mean-squared deviation from that value is zero:

$$\langle (H - E)^2 \rangle = \frac{\langle \psi | H^2 - 2EH + E^2 | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \psi | E^2 - 2E + E^2 | \psi \rangle}{\langle \psi | \psi \rangle} = 0. \quad (1-6)$$

We have used the eigenvalue equation, Eq. (1-5), to write $H | \psi \rangle = E | \psi \rangle$. The electron energy eigenstates, or energy levels, will be fundamental in many of the discussions in the book. In most cases we shall discuss that state of some entire system which is of minimum energy, that is, the ground state, in which, therefore, each electron is represented by an energy eigenstate corresponding to the lowest available energy level.

In solving problems in this book, we shall not obtain wave functions by solving differential equations such as Eq. (1-5), but shall instead assume that the wave functions that interest us can be written in terms of a small number of known functions. For example, to obtain the wave function $\psi$ for one electron in a diatomic molecule, we can make a linear combination of wave functions $\psi_1$ and $\psi_2$, where 1 and 2 designate energy eigenstates for electrons in the separate atoms that make up the molecule. Thus,

$$\psi(r) = u_1 \psi_1(r) + u_2 \psi_2(r), \quad (1-7)$$

where $u_1$ and $u_2$ are constants. The average energy, or energy expectation value, for such an electron is given by

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{u_1^* u_1 \langle \psi_1 | H | \psi_1 \rangle + u_2^* u_2 \langle \psi_2 | H | \psi_2 \rangle}{u_1^* u_1 + u_2^* u_2} = \frac{u_1^* u_1 \langle \psi_1 | E_1 | \psi_1 \rangle + u_2^* u_2 \langle \psi_2 | E_2 | \psi_2 \rangle}{u_1^* u_1 + u_2^* u_2}, \quad (1-8)$$

The states comprising the set (here, represented by $| \psi_1 \rangle$ and $| \psi_2 \rangle$) in which the wave function is expanded are called basis states. It is customary to choose the scale of the basis states such that they are normalized; that is, $\langle \psi_1 | \psi_1 \rangle = \langle \psi_2 | \psi_2 \rangle = 1$. Moreover, we shall assume that the basis states are orthogonal: $\langle \psi_1 | \psi_2 \rangle = 0$. This may in fact not be true, and in Appendix B we carry out a derivation of the energy expectation value while retaining overlaps in $\langle \psi_1 | \psi_2 \rangle$. It will be seen in Appendix B that the corrections can largely be absorbed in the parameters of the theory. In the interests of conceptual simplicity, overlaps are omitted in the main text, though their effect is indicated at the few places where they are of consequence.
We can use the notation $H_{ij} = \langle \psi_i | H | \psi_j \rangle$; then Eq. (1-8) becomes

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{u_1^2 u_1 H_{11} + u_1^2 u_2 H_{12} + u_2^2 u_1 H_{21} + u_2^2 u_2 H_{22}}{u_1^2 u_1 + u_2^2 u_2}. \quad (1-9)$$

(Actually, by Hermiticity, $H_{24} = H_{42}^*$, but that fact is not needed here.)

Eq. (1-7) describes only an approximate energy eigenstate, since the two terms on the right side are ordinarily not adequate for exact description. However, within this approximation, the best estimate of the lowest energy eigenvalue can be obtained by minimizing the entire expression (which we call $E$) on the right in Eq. (1-9) with respect to $u_1$ and $u_2$. In particular, setting the partial derivatives of that expression, with respect to $u_1^2$ and $u_2^2$, equal to zero leads to the two equations

$$H_{11} u_1 + H_{12} u_2 = E u_1, \quad (1-10)$$

$$H_{21} u_1 + H_{22} u_2 = E u_2.$$  

(In taking these partial derivatives we have treated $u_1$, $u_1^2$, $u_2$, and $u_2^2$ as independent. It can be shown that this is valid, but the proof will not be given here.)

Solving Eqs. (1-10) gives two values of $E$. The lower value is the energy expectation value of the lowest energy state, called the bonding state. It is

$$E_n = \frac{H_{11} + H_{22}}{2} - \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12} H_{21}}. \quad (1-11)$$

An electron in a bonding state has energy lowered by the proximity of the two atoms of a diatomic molecule; the lowered energy helps hold the atoms together in a bond. The second solution to Eqs. (1-10) gives the energy of another state, also in the form of Eq. (1-7) but with different $u_1$ and $u_2$. This second state is called the antibonding state. Its wave function is orthogonal to that of the bonding state; its energy is given by

$$E_n = \frac{H_{11} + H_{22}}{2} + \sqrt{\left(\frac{H_{11} - H_{22}}{2}\right)^2 + H_{12} H_{21}}. \quad (1-12)$$

We may substitute either of these energies, $E_n$ or $E_N$, back into Eqs. (1-10) to obtain values for $u_1$ and $u_2$ for each of the two states, and therefore, also the form of the wave function for an electron in either state.

A particularly significant, simple approximation can be made in Eqs. (1-11) or (1-12) when the matrix element $H_{11}$ is much smaller than the magnitude of the difference $|H_{11} - H_{22}|$. Then, Eq. (1-11) or Eq. (1-12) can be expanded in the perturbation $H_{12}$ (and $H_{21}$) to obtain

$$E' \approx H_{11} + \frac{H_{12} H_{21}}{H_{11} - H_{22}}, \quad (1-13)$$

for the energy of a state near $H_{11}$; a similar expression may be obtained for an energy near $H_{22}$. These results are part of perturbation theory. The corresponding result when many terms, rather than only two, are required in the expansion of the wave function is

$$E' \approx H_0 + \sum_j \frac{H_{ij} H_{ji}}{H_{jj} - H_{ij}}. \quad (1-14)$$

Similarly, for the state with energy near $H_{11}$, the coefficient $u_2$ obtained by solving Eq. (1-10) is

$$u_2 = \frac{E - H_{11} u_1}{H_{12}} \approx \frac{H_{21} u_1}{H_{11} - H_{22}}. \quad (1-15)$$

The last step uses Eq. (1-13). When $H_{12}$ is small, $u_2$ is small, and the term $u_2 \psi_2(r)$ in Eq. (1-7) is the correction to the unperturbed state, $\psi_1(r)$, obtained by perturbation theory. The wave function can be written to first order in the perturbation, divided by $H_{11} - H_{22}$, and generalized to a coupling with many terms as

$$\psi(r) = \psi_1(r) + \sum_j \frac{\psi_j(r) H_{ji}}{H_{jj} - H_{ij}}. \quad (1-16)$$

The perturbation-theoretic expressions for the electron energy, Eq. (1-14), and wave function, Eq. (1-16), will be useful at many places in this text.

All of the discussion to this point has concerned the spatial wave function $\psi(r)$ of an electron. An electron also has spin. For any $\psi(r)$ there are two possible spin states. Thus, assertion (a) set forth earlier should be amended to say that an electron is described by its spatial wave function and its spin state. The term "state" is commonly used to refer to only the spatial wave function, when electron spin is not of interest. It is also frequently used to encompass both wave function and electron spin.

In almost all systems discussed in this book, there will be more than one electron. The individual electron states in the systems and the occupation of those states by electrons will be treated separately. The two aspects cannot be entirely separated because the electrons interact with each other. At various points we shall need to discuss the effects of these interactions.

In discussing electron occupation of states we shall require an additional assertion—the Pauli principle:

(d) Only two electrons can occupy a single spatial state; these electrons must be of opposite spin. Because of the discreteness of the energy eigenstates discussed above, we can use the Pauli principle to specify how states are filled with electrons to attain a system of lowest energy.

Because we shall discuss states of minimum energy, we shall not ordinarily be interested in how the wave function changes with time. For the few cases in which that information is wanted, a fifth assertion applies:
(c) The time evolution of the wave function is given by the Schroedinger equation,

$$ih \frac{\partial \psi}{\partial t} = H \psi.$$  \hspace{1cm} (1-17)

This assertion is not independent of assertion (c); nevertheless, it is convenient to separate them.

At some places, particularly in the discussion of angular momentum in the next section, consequences of these five assertions will be needed which are not immediately obvious. These consequences will be stated explicitly in the context in which they arise.

1-B Electronic Structure of Atoms

Because the potential energy $V(r)$ of an electron in a free atom is spherically symmetric (or at least we assume it to be), we can expect the angular momentum of an orbiting electron not to change with time. In the quantum-mechanical context this means that electron energy eigenstates can also be chosen to be angular momentum eigenstates. It is convenient to state the result in terms of the square of the magnitude of the angular momentum, $I^2$, which takes on the discrete values

$$I^2 = l(l+1)\hbar^2,$$  \hspace{1cm} (1-18)

where $l$ is an integer greater than or equal to 0. For each value of $l$ there are $2l+1$ different orthogonal eigenstates; that is, the component of angular momentum along any given direction can take on the values $m \hbar$, with $m = -l, -l+1, \ldots, l-1, l$.

The spatial wave functions representing these states are called orbitals since we can imagine the corresponding classical (that is, not quantum-mechanical) electron orbits as having fixed energy and fixed angular momentum around a given axis. The term orbital will be used to refer specifically to the spatial wave function of an electron in an atom or molecule. We will also use the term orbital for electron wave functions representing chemical bonds where the corresponding electron orbits would not be so simple.

The $2l+1$ orthogonal eigenstates with different $m$ values all have the same energy, because the potential $V(r)$ is spherically symmetric and the energy does not depend upon the orientation of the angular momentum. States of the same energy are said to be degenerate. The angular momentum properties follow from assertions (a), (b), and (c) in Section 1-A but are not derived here. The concept of angular momentum is convenient since it makes it possible to classify all energy eigenstates by means of two quantum numbers, the integers $l$ and $m$.

In the common terminology for states of small angular momentum, the first four—of smallest angular momentum—are

- $l = 0$: $s$ state,
- $l = 1$: $p$ state,
- $l = 2$: $d$ state,
- $l = 3$: $f$ state.

The first three letters, $s$, $p$, and $d$, were first used nearly a century ago to describe characteristic features of spectroscopic lines and stand for “sharp,” “principal,” and “diffuse.”

For any given value of $l$ and $m$ there are many different energy eigenstates; these are numbered by a third integer, $n$, in order of increasing energy, starting with $n = l + 1$. This starting point is chosen since, for the hydrogen atom, states of different $l$ but the same $n$ are degenerate; that is, $E = \langle n, l, m | H | n, l, m \rangle$ depends only on the quantum number $n$. Thus $n$ is called the principal quantum number. Only for the hydrogen atom, where the potential is simply $-e^2/r$, does the energy depend on $n$ alone. However, the same numbering system is universally used for all other atoms too.

In each state specified by $n$, $l$, and $m$, two electrons can be accommodated, with opposite spins, according to the Pauli principle. These atomic states are the building blocks for description of the electron energies in small molecules, and in solids, as well as in individual atoms.

The $s$ orbitals have vanishing angular momentum; $l = 0$ (and $m = 0$, since $|m| \leq l$). The wave function for an $s$ orbital is spherically symmetric, and it is depicted in diagrams as a circle with a dot representing the nucleus at the center (Fig. 1-1). The lowest energy state, $n = 1$, is called a $1s$ state. Its wave function decreases monotonically with distance from the nucleus. The wave function of the next state, the $2s$ state, drops to zero, becomes negative, and then decays upward to zero. Each subsequent $s$ orbital has an additional node. (Such forms are in fact necessary if the orbitals are to be orthogonal to each other.)

**FIGURE 1-1**

This depiction of an $s$ orbital will be used frequently in this book.
The three s states of lowest energy for atomic hydrogen. The orbitals, multiplied by \( r \), are plotted as a function of distance from the nucleus.

A plot of the first three s orbitals for a hydrogen atom is given in Fig. 1-2.

The \( p \) orbitals have one unit of angular momentum, \( l = 1 \); there are three orbitals corresponding to \( m = -1, m = 0, \) and \( m = 1 \). (See Fig. 1-3.) Any orbital, including those of the \( p \) series, can be written as a product of a function of radial distance from the nucleus and one of the spherical harmonics \( Y_l^m \), which are functions of angle only (this is explained in Schiff, 1968, p. 79):

\[
\psi_{nlm}(r) = R_{nl}(r) Y_l^m(\theta, \phi) 
\]

(1-19)

For a given \( l \), the radial function is independent of \( m \). For s orbitals, the spherical

\[
\begin{align*}
Y_{1}^{1} &= (3/8\pi)^{1/2} \sin \theta e^{-i\phi}, \\
Y_{1}^{0} &= (3/4\pi)^{1/2} \cos \theta,
\end{align*}
\]

and

\[
Y_{1}^{-1} = (3/8\pi)^{1/2} \sin \theta e^{i\phi}.
\]

In solid state physics it is frequently more convenient to take linear combinations of the spherical harmonics to obtain angular dependences proportional to the component of radial distance from the nucleus along one of the three orthogonal axes \( x, y, \) or \( z \). In this way, the three independent \( p \) orbitals may be written

\[
\psi_{s1m}(r) = \left( \frac{3}{4\pi} \right)^{1/2} R_{nl}(r) \begin{vmatrix} x/r \\ y/r \\ z/r \end{vmatrix}
\]

(1-20)

These forms, used by Slater and Koster (1954), will be used extensively in this text. For each \( n \) when \( l = 1 \), there are three \( p \) orbitals oriented along the three Cartesian axes. Diagrams such as those shown in Fig. 1-4 illustrate the three angular forms.

Except for the different orientations, the orbitals look the same. The wave function is zero in an entire plane perpendicular to the axis of orientation and, at a given radius, the wave function is positive on one side and negative on the other. There are various other ways to visualize such orbitals. Three are compared in Fig. 1-5; Fig. 1-5c is simplest and most common and, except for the sign of the wave function, is the same as the orbital shown at the left in Fig. 1-4.

The \( d \) orbitals have two units of angular momentum, \( l = 2 \), and therefore five \( m \) values: \( m = -2, -1, 0, 1, \) and \( 2 \). They can be conveniently

\[
\begin{align*}
X_{\text{p}_{1}} & \quad \text{orbital} \\
X_{\text{p}_{2}} & \quad \text{orbital} \\
X_{\text{p}_{3}} & \quad \text{orbital}
\end{align*}
\]

(1-4)

Three \( p \) orbitals, each directed along a different Cartesian axis.
understood in terms of the \( n = 3 \) state of hydrogen. The 3s, 3\( p \), and 3d states all have the same energy, but of these three, the 3d state corresponds classically to an orbit that is circular. At lesser angular momentum, a classical orbit of the same energy reaches further into space; this corresponds to the great spatial extent of the 3\( p \) orbital. The 3s state, which corresponds classically to an electron vibrating radially through the nucleus, stretches even further from the nucleus. Therefore, 3\( d \) states tend to be influenced much less by neighboring atoms than are 3s and 3\( p \) states of similar energy.

We shall have little occasion to discuss \( f \) orbitals, though they are important in studying properties of the rare-earth metals. The \( f \) orbitals are even more strongly concentrated near the nucleus and isolated from neighboring atoms than are \( d \) orbitals.

Let us now discuss the electronic states in the hydrogen atom. As indicated, the energy of an electronic state for hydrogen depends only upon the principal quantum number \( n \). In this book, atomic energy eigenvalues, or other eigenvalues measured from the same zero of energy, will be designated by \( \varepsilon \) rather than \( E \). For hydrogen,

\[
\varepsilon_n = -\frac{m_e^2}{2\hbar^2 n^2} = -\frac{1}{n^2} \times 13.6 \text{ eV},
\]

where \( a_0 \) is the Bohr radius, 0.529 Å, \( e \) is the magnitude of the electron charge, \( m \) is the electron mass, \( n \) is the principal quantum number, and the unit of energy is the electron volt (eV).

A sketch of the energies of the states of hydrogen, the energy levels, is given in Fig. 1-7. In the ground state of the hydrogen atom, a single electron occupies the 1s orbital. All of the other states, having higher energies, represent excited states of the system. The electron can be transferred from the ground state to an excited state by exposing it to light of angular frequency \( \omega = \Delta E / \hbar \), where \( \Delta E \) is the energy difference between the two levels. Indeed, the most direct experimental study of energy levels of atoms (also called term values) in excited states is based upon spectroscopic analysis of the corresponding light absorption and emission lines.

To understand the electron states systematically in elements other than hydrogen, imagine that the charge of the hydrogen nucleus is increased element by element and, thereby, the atomic number, \( Z \), is steadily increased. At the same time, imagine that an electron is added each time the nuclear charge is increased by one unit \( e \). As the nuclear charge increases, the entire set of states drops in energy, relative to hydrogen. In all atoms but hydrogen, s-state energies are lower than p-state energies of the same principal quantum number. In Fig. 1-8 is shown the relative variation in energy of occupied 1s, 2s, 2\( p \), 3s, 3\( p \), 3d, 4s, and 4\( p \) orbitals as the atomic number (equal to the number of protons in the nucleus) increases.

In lithium, atomic number 3, the 1s level has dropped to a very low energy and is occupied by two electrons. The 1s orbital is considered part of the atomic core of lithium; a single electron occupies a 2s orbital. In the lithium row, all elements, to neon, \( Z = 10 \), have a "lithium core"; the energy levels in successive atoms.
continue to drop in energy and \( sp \) splitting (the difference in energy between levels, or \( \varepsilon_{3p} - \varepsilon_{3s} \)) increases. At neon, both \( 2s \) and \( 2p \) orbitals have become filled; starting with the next element, sodium, they become part of the atomic core, since, at sodium, filling of the \( 3s \) orbital begins, to be followed by filling of the \( 3p \) orbitals. The filling of successive levels is the essence of periodic variation in the properties of elements as the atomic number increases. The levels are filled in each subsequent row of the periodic table the same way they are filled in the lithium row, but the number of states in the atomic core is larger in lower rows of the table.

In the potassium row, the unoccupied \( 3d \) level begins to be filled; its energy has dropped more slowly than that of the \( 3s \) and \( 3p \) levels, but it becomes filled before the \( 4p \) level begins to fill; then in the ground state of scandium the \( 3d \) level becomes occupied with one electron. Elements in which some \( d \) states are occupied are called transition metals. The \( 3d \) states have become completely filled when copper, atomic number 29, is reached. The \( 3d \) states become part of the atomic core as \( Z \) increases further, and the series Cu, Zn, Ga, ..., gains electrons in an order similar to that of the series Na, Mg, Al, ....

Almost all of the properties of elements are determined by the occupied levels of highest energy; the electrons filling the \( s \) and \( p \) levels in each row (and sometimes those filling \( d \) levels) are traditionally called valence electrons and determine

---

FIGURE 1-8
Trends in the variation of atomic term values, in electron volts (data from Herman and Skillman, 1963). The \( \varepsilon_s \) and \( \varepsilon_p \) values are the same as those listed also in the Solid State Table at the back of the book. The \( 3d \) and \( 4s \) energy plots were made smooth in the middle of the transition series for clarity.

---

FIGURE 1-9
Periodic chart of the elements.
chemical properties. They also have excited states available to them within a few electron volts. Since these energy differences correspond to electromagnetic frequencies in the optical range, the valence electrons determine the optical properties of the elements. The periodic table (Fig. 1-9) summarizes the successive filling of electronic levels as the atomic number increases.

I-C Electronic Structure of Small Molecules

We have seen how to enumerate the electron states of single atoms. If we consider several isolated atoms as a system, the composite list of electron states for the system would simply be the collection of all states from all atoms. If the atoms are brought together closely enough that the wave functions of one atom overlap the wave functions of another, the energies of the states will change, but in all cases the number of states will be conserved. No states disappear or are created. If the sum of the energies of the occupied states decreases as the atoms are brought together, a molecule is said to be bound. An additional energy must be supplied to separate the atoms. (It should be noted that other terms influence the total energy of a system, and all influences must be considered in evaluating bonding energy. We shall return to this later.)

It turns out that the energy of occupied electronic states in small molecules, and indeed in solids, which have large numbers of atoms, can be rather well approximated with linear combinations of atomic orbitals (or LCAO's). Making such an approximation constitutes a very great simplification in the problem of determining molecular energies since, instead of unknown functions, only unknown coefficients appear in the linear combination. The LCAO description of the occupied molecular orbitals is much more accurate if the atomic orbitals upon which the approximation is based differ somewhat from those of the isolated constituent atoms; this complication will not arise in this book since ultimately our calculations will be in terms of matrix elements, not in terms of the orbitals themselves. The smaller the number of atomic orbitals used, the greater will be the simplification, but the poorer will be the accuracy. For our discussion of solids, a set of orbitals will be chosen that is small enough to enable calculation of a wide range of properties simply. For calculations of properties depending only upon occupied states, the accuracy will be quite good, but for excited states—those electron states which are unoccupied in the ground state of the system—the properties are not accurately calculated. We can make the same choice of orbitals in diatomic molecules that will turn out to be appropriate for solids.

In describing states of the small molecule (as well as the solid) the first step is to enumerate each of the electronic states in the atom that will be used in the mathematical expansion of the electron states in the molecule. These become our basis states. We let the index \( \alpha = 1, 2, 3, \ldots, n \) run from one up to the number of states that are used. Then the molecular state may be written (with the notation discussed in Section 1-A) as

\[
| \psi \rangle = \sum_{\alpha} u_{\alpha} | \alpha \rangle.
\]  

(1-23)

where the \( u_{\alpha} \) are the coefficients that must be determined. The orbitals \( | \alpha \rangle \) representing the basis states are selected to be orthogonal to each other; \( \langle \beta | \alpha \rangle = 0 \) if \( \beta \neq \alpha \).

Next, we must find the coefficients \( u_{\alpha} \) of Eq. (1-23) for the electron states of lowest energy, by doing a variational calculation as indicated in Section 1-A. That is, we evaluate the variation

\[
\delta \left( \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \right) = \sum_{\alpha} \frac{u_{\alpha}^* u_{\beta} \langle \beta | H | \alpha \rangle}{\sum_{\alpha} u_{\alpha}^* u_{\alpha}} = 0.
\]  

(1-24)

In obtaining the second form, we allow the \( u_{\alpha} \) to be complex, though ordinarily for our purposes this would not be essential. We also make use of the linearity of the Hamiltonian operator to separate the various terms in the expectation value of the Hamiltonian. In particular, if we require that variations with respect to a particular \( u_{\beta}^\alpha \) be zero (as in Eq. 1-10), we obtain

\[
\sum_{\alpha} \frac{u_{\alpha}^* \langle \beta | H | \alpha \rangle}{\sum_{\alpha} u_{\alpha}^* u_{\alpha}} - \frac{u_{\beta}^* u_{\beta} \langle \beta | H | \beta \rangle u_{\beta}}{\left( \sum_{\alpha} u_{\alpha}^* u_{\alpha} \right)^2} = 0,
\]  

(1-25)

or more simply,

\[
\sum_{\alpha} \langle \beta | H | \alpha \rangle u_{\alpha} - E u_{\beta} = 0,
\]  

(1-26)

with \( E = \langle \psi | H | \psi \rangle /\langle \psi | \psi \rangle \). (Later, specific eigenvalues will be written as \( \varepsilon \), with appropriate subscripts.) There is one such equation for each \( \beta \) corresponding to a basis state.

We have obtained a set of simultaneous linear algebraic equations with unknown coefficients \( u_{\alpha} \). Their solution gives as many eigenvalues \( E \) as there are equations. The lowest \( E \) corresponds to the lowest electron state; the next lowest, to the next electron state having a wave function orthogonal to that of the first, and so on. The solution of these equations gives the \( u_{\alpha} \), which, with Eq. (1-23), give wave functions for the one-electron energy eigenstates directly. The eigenvalues themselves can also be obtained directly from the secular equation, familiar from ordinary algebra. The secular determinant vanishes,

\[
\text{det}(H_{\beta \beta} - E \delta_{\beta \beta}) = 0,
\]  

(1-27)

where "det" means "determinant of" and \( \delta_{\beta \beta} \) is the unit matrix. We have made one further simplification of the notation in writing \( H_{\beta \beta} = \langle \beta | H | \beta \rangle \). We shall see in Section 2-D how simple estimates of these matrix elements can be made. Then, from Eqs. (1-26) and (1-27), we can obtain the energies and the states themselves.
Let us use the foregoing method to describe the states in a small molecule. The hydrogen molecule, with two electrons, is a simple case and is more closely related to the systems we shall be considering than the simpler hydrogen molecular ion, $H_2^+$. For the hydrogen molecule, we use two orbitals, $|1\rangle$ and $|2\rangle$, which represent 1s states on atoms 1 and 2 respectively. Eq. (1-26) then becomes
\[
(E - E)u_1 - V_2 u_2 = 0; \]
\[-V_2 u_1 + (E - E)u_2 = 0; \]
(1-28)
where we have made the natural definition of the 1s energy $\epsilon = \langle 1 | H | 1 \rangle = \langle 2 | H | 2 \rangle$. The energy $\epsilon$ is slightly different from what it would be in a free atom, first, because an electron associated with atom 1 has a potential energy lowered by the presence of the second atom, and second, because the energy may be lowered as a result of the choice of a 1s function slightly different from that of the free atom. We have defined a matrix element $V_2 = -H_{12} = -H_{21}$ to correspond to the notation we shall use later. The matrix element $V_2$ is called a *covalent energy*, and is defined to be greater than zero; $V_2$ will generally be used for interatomic matrix elements, in this case between $s$ orbitals. All the wave function coefficients are taken to be real in this case; we may always choose real coefficients but in solids will find it convenient to use complex coefficients. Eq. (1-28) is easily solved to obtain a low-energy solution, the *bonding state*, with energy
\[
\epsilon_b = \epsilon_1 - V_2, \quad (1-29)
\]
as well as a high-energy solution, the *antibonding state*, with
\[
\epsilon_a = \epsilon_1 + V_2. \quad (1-30)
\]

Substituting the eigenvalues given in Eqs. (1-29) and (1-30) back into Eq. (1-28) gives coefficients $u_1$ and $u_2$. For the bonding state, $u_1 = u_2 = 2^{-1/2}$, and for the antibonding state, $u_1 = -u_2 = 2^{1/2}$. The conventional depiction of these *bond orbitals* and *antibond orbitals* is illustrated in Fig. 1-10a.

Notice that the use of orthogonal eigenfunctions for the two atomic states (taking the overlap $\langle 1 | 2 \rangle = 0$) is not consistent with Fig. 1-10b, in which a clear nonzero overlap is shown. The derivation made in Appendix B allows for a nonzero overlap and shows that part of its effect can be absorbed by a modification of the value of $V_2$ and the other part can be absorbed in a central-force overlap interaction between the atoms, which is discussed in Chapter 7. Here, for the hydrogen molecule, the lowering of the energy of the molecule, in comparison to isolated atoms, is only approximately accounted for by Eq. (1-29).

If one wishes to describe the total energy as a function of the separation between atoms, one cannot simply add the energy of the two electrons in the bonding state. The central-force corrections required by this overlap, as well as other terms, must all be included.
Although it is possible to understand the hydrogen molecule in terms of the ideas we have discussed, hydrogen has only limited relevance to the problems we will be considering. In fact, it is not the most satisfactory way to describe the hydrogen molecule itself. In the equilibrium configuration for hydrogen, the two protons are so close together that a much better model is one in which the two protons are thought of as being superimposed; that is, we consider the nucleus to be that of the helium atom. Once this is understood, one can make corrections for the fact that in hydrogen the two protons are actually separated. Such an approach is more in tune with the spirit of this text: we will always seek the simplest description appropriate to the system we are interested in, and make corrections afterward. It has been argued that this united atom approach, treating H₂ as a correction applied to He, is inappropriate when the protons are far apart. That is indeed true, but we are ultimately interested in H₂ at equilibrium spacing. We will therefore simply restate our results for H₂ in the terminology to be used later and move on.

We found that hydrogen 1s levels are split into bonding and antibonding levels when the two atoms form the molecule. The separation of those two levels is 2V₂, where V₂ is the covalent energy. To find the total energy of this system it is necessary to add a number of corrections to the simple sum of energies of the electrons. It will be convenient to postpone consideration of such corrections until systematic treatment in Chapter 7.

Hydrogen is a very special case also when it is a part of other molecules. We saw that in the lithium row and in the sodium row of the periodic table both a valence s state and a valence p state are present. We will see that when these atoms form molecules, the bond orbitals are mixtures of both s and p orbitals. There is no valence p state in hydrogen, and its behavior is quite different. In many ways the hydrogen proton may be regarded as a loose positive charge that keeps a molecule neutral rather than as an atom that forms a bond in the same sense that heavier atoms do. Thus we can think of methane, CH₄, as “neon” with four protons split off from the nucleus, just as we can think of H₂ as “helium” with a split nucleus.

### 1-D The Simple Polar Bond

In the H₂ molecule just discussed, the two hydrogen atoms brought together were identical, and their two energies εᵣ were the same. We shall often be interested in systems in which the diagonal energies H₁₁ and H₁₂ (that is, diagonal elements of the Hamiltonian matrix) are different; such molecules are said to have a heteropolar or simply polar bond. Let us use, as an example, the molecule LiH. We expect the linear combinations to be those of the hydrogen 1s orbitals and lithium 2s orbitals, though as we indicated at the end of the preceding section, special considerations govern molecules involving hydrogen.

In calculating the energy of heteropolar bonds, Eqs. (1-28) must be modified so that εᵣ is replaced by two different energies, εᵣ for the low-energy state (for the energy of the anion) and εᵣ for the high-energy state (for the energy of the cation). Eqs. (1-28) then become

\[
\begin{align*}
\left( \epsilon_s - E \right) u_1 - V_2 u_2 &= 0; \\
- V_2 u_1 + \left( \epsilon_r - E \right) u_2 &= 0.
\end{align*}
\]  

(1-31)

The value of one half of the anion–cation energy-difference is the polar energy:

\[
V_3 = \frac{\epsilon_r - \epsilon_s}{2}.
\]

(1-32)

It is convenient to define the average of the cation and anion energy, written as

\[
\bar{\epsilon} = \frac{\epsilon_s + \epsilon_r}{2}.
\]

(1-33)

Then Eqs. (1-31) become

\[
\begin{align*}
\left( \bar{\epsilon} - V_3 - E \right) u_1 - V_2 u_2 &= 0; \\
- V_2 u_1 + \left( \bar{\epsilon} + V_3 - E \right) u_2 &= 0.
\end{align*}
\]  

(1-34)

The solution of Eqs. (3-34) is trivial:

\[
\begin{align*}
e_{\bar{\epsilon}} &= \bar{\epsilon} - \left( V_2^2 + V_3^2 \right)^{1/2}; \\
e_u &= \bar{\epsilon} + \left( V_2^2 + V_3^2 \right)^{1/2}.
\end{align*}
\]  

(1-35)

ε₀ and εₜ are bonding and antibonding energies, respectively. The splitting of these levels is shown in Fig. 1-10,b. In looking at the energy-level diagram of that figure, imagine that the interaction between the two atomic levels, represented by V₂, pushes the levels apart. This is the qualitative result that follows also from the perturbation-theoretic expression, Eq. (1-14).

It is also shown in the figure that the charge density associated with the bonding state shifts to the low-energy side of the molecule (the direction of the anion). This means that the molecule has an electric dipole; the molecule is said to have a polar bond. Polarity of bonding is an important concept in solids and it is desirable to introduce the notion here briefly; it will be examined later, more fully, in discussion of solids. To describe polarity mathematically, first we obtain u₁ and u₂ values for the bonding state by substituting ε₀ for the energy E in Eqs. (1-34), the first equation of which can then be rewritten as

\[
u_1 = \frac{V_2}{\sqrt{V_2^2 + V_3^2 - V_3^2} - V_3} u_2.
\]  

(1-36)

Second, if the individual atomic wave functions do not overlap, the probability of
finding the electron on atom 1 will be \( u_1^2 / (u_1^2 + u_2^2) \) and the probability of finding it on atom 2 will be \( u_2^2 / (u_1^2 + u_2^2) \). This follows from the average-value theorem, Eq. (1-3). Manipulation of Eq. (1-36) leads to the result that the probability of the electron appearing on atom 1 is \((1 + \alpha_{y})/2\) and the probability of finding it on atom 2 is \((1 - \alpha_{y})/2\), where \(\alpha_{y}\) is the **polarity** defined by

\[
\alpha_{y} = V_{3} / (V_{2} + V_{3})^{1/2}.
\]  

(1-37)

We can expect the dipole of the bond to be proportional to \(u_{1}^2 - u_{2}^2 = \alpha_{y}\). The polarity of the bond and the resulting dipole are central to an understanding of partially covalent solids.

Another useful concept is the complementary quantity, **covalency**, defined by

\[
\alpha_{c} = V_{2} / (V_{2} + V_{3})^{1/2}.
\]  

(1-38)

### 1-E Diatomic Molecules

In Section 1-C we noted that molecular hydrogen is unique in that a single atomic state, the 1s state, dominates its bonding properties. In the bonding of other diatomic molecules, valence s states and p states are important, and this will be true also in solids. Only aspects of diatomic molecules that have direct relevance to solids will be taken up here. A more complete discussion can be found in Slater (1968) or Coulson (1970).

**Homopolar Bonds**

Specific examples of homopolar diatomic molecules are Li, Be, B, C, N, O, F, and H, though, as seen in Fig. 1-8, variation in energy of the s and p electron states is very much the same in other series of the periodic table as it is for these elements. Four valence states for each atom must be considered—a single s state and three p states. It might seem at first that the mathematical expansion of each molecular electronic state would require a linear combination of all of these valence states; however, the matrix elements between some sets of orbitals can be seen by symmetry to vanish, and the problem of determining the states separates into two simpler problems. Fig. 1-11 indicates schematically which orbitals are coupled. The matrix elements between other orbitals than those indicated by a connecting line are zero.

The \( p_x \) orbitals of atoms 1 and 2 are coupled only to each other. They form simple bonding and antibonding combinations just as in the hydrogen molecule. In a similar way, the \( p_y \) orbitals form bonding and antibonding combinations. The four resulting \( p \)-orbital combinations are called \( \pi \) states, by analogy with \( p \) states, because each has one unit of angular momentum around the molecular axis. The \( \pi \) states are also frequently distinguished by a \( g \), for *gerade* (German for "even"), or

**FIGURE 1-11**
The coupling of atomic orbitals in lithium-row diatomic molecules, and the resultant bond designations (at right).
For ungerade ("odd"), depending on whether the wave function of the orbital is even or odd when inverted through a point midway between the atoms. For π orbitals, the bonding combination is ungerade (\(\pi_u\)); a π orbital that is gerade (\(\pi_g\)) is zero on the plane bisecting the bond.

A feature of homopolar diatomic molecules is that s states and p states are also coupled, and all four states are required in the expansion of the corresponding molecular orbitals, called a states. The bonding combination for s orbitals is gerade (\(\sigma_g\)). The s and p states are hybridized in the molecule. (The \(\sigma\)-orbital combinations have no angular momentum around the molecular axis.) However, it is not necessary to solve four simultaneous equations; instead, construct gerade and ungerade combinations of s states and of p states. There are no matrix elements of the Hamiltonian between the gerade and ungerade combinations, so the calculation of states again reduces to the solution of quadratic equations, as in the case of the hydrogen molecule. Notice that the two pairs of coupled s and p states have matrix elements of opposite sign (\(V_{sp} = -V_{ps}\)) because of the difference in the sign of the p lobe in the two cases. The general convention for signs will be specified in Section 2-D.

![Figure 1-12](image)

The development of molecular energy levels as a pair of lithium-row atoms is brought together (that is, internuclear distance \(d\) decreases from left to right).

Let us trace the changes in energy that occur as a pair of identical atoms from the lithium row come together. Qualitatively these changes are the same for any of the elements and they are illustrated schematically in Fig. 1-12. On the left, corresponding to large separations of the atoms, the energy levels have simply the atomic energies \(e_s\) (one s orbital for each atom) and \(e_p\) (three p orbitals for each atom, \(p_x\), \(p_y\), and \(p_z\)). As the atoms are brought together, the electron levels split (one energy going down and the other, up) and bonding and antibonding pairs are formed. The \(\pi\) orbitals oriented along the y-axis have the same energies as those oriented along the x-axis. The bonding and antibonding combinations for these are indicated by \(1\sigma_g\) and \(1\pi_g\), respectively. The number one indicates the first combination of that symmetry in order of increasing energy. Each corresponds to two orbitals and is drawn with double lines. At large separation the \(\sigma\) orbitals are, to a good approximation, a bonding combination of s states and an antibonding combination of s states, and a bonding combination of p states and an antibonding combination of p states, in order of increasing energy. The energies of the intermediate levels, indicated by \(2\sigma_g\) and \(3\sigma_g\) in the figure, become comparable and should be thought of as bonding and antibonding combinations of sp-hybrids, mixtures of \(s\) states and \(p\) states. Their ordering is as shown, and is the same for all the diatomic molecules of the lithium row (Slater, 1968, pp. 451 and 452).

A particularly significant aspect of the energy levels seems to apply to all of these simple diatomic molecules: the energy of the low-lying antibonding state \(2\sigma_u\) is never greater than that of either of the two high-energy bonding states \(3\sigma_g\) and \(1\pi_u\). (The latter two can occur in either order, as suggested in the figure.) Such crossings of bonding and antibonding levels do occur in solids and are an essential feature of the electronic structure of what are called covalent solids.

The Occupation of Levels

As indicated in Section 1-A, the energy of electron states and their occupation by electrons are quite separate topics. For example, it is possible to specify the energy values at an observed spacing, as in Fig. 1-12, and then to assign to them, in order of increasing energy, whatever electrons are available, ignoring any effect that an electron in one level may have on an electron in another level. More precisely, the energy of a state in any system is defined to be the negative of the energy required to move a single electron from the designated state to an infinitely distant location, without changing the number of electrons in the other states. Most theoretical calculations of energy levels determine what that energy is for each state, since this information is closely related to a wide variety of properties. When we calculate the total energy of solids, we will consider corrections to the sum of these energies; for the present, it is satisfactory to think of these energy levels as remaining fixed in energy as electrons are added to them.

If two atoms forming a diatomic molecule are both lithium, there are only two valence electrons, which would be put in the \(2\sigma_g\) bonding state; the qualitative picture of electronic structure and binding of \(\text{Li}_2\) is exactly the same for \(\text{H}_2\); the
levels deriving from the valence \( p \) state of lithium may be disregarded. If the molecule were \( \text{Be}_2 \), there would be four electrons in the molecule; two would occupy the \( 2\sigma_g \) bonding state, and the other two would occupy the \( 2\sigma_u \) antibonding state. The greater energy of the antibonding electrons (in comparison to the atomic levels) would tend to cancel the energy of the bonding electrons, and hence, bonding would be expected to be weak, though \( \text{Be}_2 \) is found in nature. As the atomic number of the constituents increases, bonding and antibonding states are filled in succession. \( \text{F}_2 \) would have enough electrons to fill all but the highest antibonding state, \( 3\sigma_u \). A pair of neon atoms would have enough electrons to fill all bonding and antibonding states and, like \( \text{Be}_2 \), would not be bound at all.

In \( \text{O}_2 \), when the last levels to be filled are degenerate, a special situation occurs. Only two electrons occupy the \( 1\pi_g \) state though there are states to accommodate four. There are different ways the state could be filled, and \textit{Hund's rule} tells us which arrangement will have lowest energy. It states that when there is \textbf{orbital degeneracy}, the electrons will be arranged to maximize the total spin. This means that each electron added to a set of degenerate levels will have the same (parallel) spin, if possible, as the electron which preceded it. The physical origin of this rule is the fact that two electrons of the same spin can never be found at precisely the same place, for basically the same reason that leads to the Pauli principle. Thus electrons of the same spin avoid each other, and the repulsive Coulomb interaction energy between them is smaller than for electrons of opposite spin. The corresponding lowering in energy per electron for parallel-spin electrons, compared to antiparallel-spin electrons, is called \textit{exchange energy}. It tends to be small enough that it is dominant only when there is orbital degeneracy, as in the case of \( \text{O}_2 \), or very near orbital-degeneracy. The dominance of exchange energy is the origin of the spin alignment in ferromagnetic metals. (A more complete discussion of exchange energy appears in Appendices A and C.)

In \( \text{O}_2 \), the two degenerate \( 1\pi_g \) states take one electron in a \( p_z \) state and one in a \( p_x \) state. As a result, the charge density around the \( \text{O}_2 \) molecule has cylindrical symmetry, though there is a net spin from the two electrons. In contrast, if both electrons were in \( p_z \) states, they would necessarily also have opposite spin. This would lead to a flattened charge distribution around the molecule. Hund's rule tells us that the former arrangement has lower energy because of the exchange energy.

In the same sense that \( \text{H}_2 \) is like \( \text{He} \) (as mentioned at the end of Section 1-C), the molecule \( \text{C}_2\text{H}_4 \) is like \( \text{O}_2 \), except that the two hydrogen protons are outside the carbon nucleus rather than inside. The number of electrons is the same in both \( \text{C}_2\text{H}_4 \) and \( \text{O}_2 \) and essentially the same classification of electron levels can be made. However, if the protons in \( \text{C}_2\text{H}_4 \) are all placed in the same plane, the \( 1\pi_g \) state oriented in that plane will have lower energy than that oriented perpendicular to the plane. The orbital energy will then be lowered if the first orbital is occupied with electrons with both spins. This planar form in fact gives the stable ground-state arrangement of nuclei and electrons in ethylene. If it were possible to increase the exchange energy it would eventually become energetically favorable to occupy one \( p_z \) state and one \( p_x \) state of parallel spin. Then the electron density would be cylindrically symmetric as in oxygen, and the protons would rotate into perpendicular planes in order to attain lower Coulomb interaction energy. \( \text{C}_2\text{H}_4 \) illustrates several points of interest. First, any elimination of orbital degeneracy will tend to override the influence of exchange energy. Second, atoms (in this case, protons) can arrange themselves in such a way as to eliminate degeneracy; this creates an asymmetric electron density that stabilizes the new arrangement. Through this self-consistent, cooperative arrangement, electrons and atoms minimize their mutual energy. This same cooperative action is often responsible for the spatial arrangement of atoms in solids. Once that arrangement is specified in solids, a particular conception of the electronic structure becomes appropriate, just as in the case of \( \text{C}_2\text{H}_4 \). Furthermore, that conception can be quite different from solid to solid, depending on which stable configuration of atoms is present.

To make the discussion of the electronic structure of diatomic molecules quantitative, it is necessary to have values for the various matrix elements. It will be found that for solids, a reasonably good approximation of the interatomic matrix elements can be obtained from the formula \( V_{mn} = \eta_{mn} \hbar^2/(nd^4) \), where \( d \) is the internuclear distance and values for \( \eta_{mn} \) are four universal constants for \( s\sigma, s\pi, p\sigma, \) and \( p\pi \) matrix elements, as given in the next chapter (Table 2-1). Furthermore, atomic term values (given in Table 2-2) can be used for \( \varepsilon_s \) and \( \varepsilon_p \). Applying such an approximation to the well-understood diatomic molecules will not reveal anything about those molecules, but can tell something about the reliability of the approximations that will be used in the study of solids. The necessary quadratic equations can be solved to obtain the molecular orbital energies in terms of the matrix elements and values for all matrix elements can be obtained from Tables 2-1 and 2-2. This gives the one-electron energies listed in Table 1-1, where the bond lengths (distance between the two nuclei) are also listed. For comparison with these values, results of full-scale self-consistent molecular orbital calculations are listed in parentheses. The solid state matrix elements give a very good semi-quantitative account of the occupied states (which lie below the shaded area) for the entire range of homopolar molecules; there are large errors only for the \( 3\sigma_g \) levels in \( \text{O}_2 \) and \( \text{F}_2 \). The empty levels above (shaded) are not well given. Neither will the empty levels be as well given as the occupied ones in the description of solids in terms of simple LCAO theory. This degree of success in applying solid state matrix elements outside the realm of solids, to diatomic molecules, gives confidence in their application in a wide range of solid state problems.

Heteropolar Bonds

Bonding of diatomic molecules in which the constituent atoms are different can be analyzed very directly, and only one or two points need be made. The \( \pi \) states in heteropolar diatomic bonding are calculated just as the simple polar bond was. In each case only one orbital on each atom is involved. A polarity can be assigned to these bonds, just as it was in Section 1-D.
There is, however, a complication in the treatment of the $\sigma$ bonds. Because the states are no longer purely gerade and ungerade, the four simultaneous equations cannot be reduced to two sets of two. In a diatomic molecule this would not be much of a complication, but it is very serious in solids. Fortunately, for many solids containing $\sigma$ bonds, hybrid basis states can be made from $s$ and $p$ states, and these can be treated approximately as independent pairs, which reduces the problem to that of finding two unknowns for each bond. In other cases, solutions can be approximated by use of perturbation theory. The approximations that are appropriate in solids will often be very different from those appropriate for diatomic molecules. Therefore, we will not discuss the special case of $\sigma$-bonded heteroatomic molecule.

**Problem 1-1 Elementary quantum mechanics**

An electron in a hydrogen atom has a potential energy, $-e^2/r$. The wave function for the lowest energy state is

$$\psi(r) = Ae^{-r/a_0}$$

where $a_0$ is the Bohr radius, $a_0 = h^2/m\epsilon^2$, and $A$ is a real constant.

(a) Obtain $A$ such that the wave function is normalized, $\langle \psi | \psi \rangle = 1$.

(b) Obtain the expectation value of the potential energy, $\langle \psi | V | \psi \rangle$.

(c) Calculate the expectation value of the kinetic energy, $K.E. = \langle \psi | -\frac{h^2}{2m} \nabla^2 | \psi \rangle$.

is trickier because of the infinite curvature at $r = 0$. By partial integration in Eq. (1-3), an equivalent form is obtained:

$$K.E. = \frac{\hbar^2}{2m} \left( \int \phi^* \nabla \phi \, dr \right)$$

Evaluate this expression to obtain K.E.

(d) Verify that the expectation value of the total energy, $\langle \psi | V + K.E. | \psi \rangle$ is a minimum with respect to variation of $a_0$. Thus a variational solution of the form $e^{-\phi r}$ would have given the correct wave function.

(e) Verify that this $\psi(r)$ is a solution of Eq. (1-5).

**Problem 1-2 Atomic orbitals**

The hydrogen 2s and 2p orbitals can be written

$$\psi_s(r) = \left( \frac{1}{32\pi a_0^3} \right)^{1/2} \left( 2 - \frac{r}{a_0} \right) e^{-r/2a_0},$$

and

$$\psi_p(r) = \left( \frac{1}{32\pi a_0^3} \right)^{1/2} X \frac{r}{a_0} e^{-r/2a_0}$$

(see Schiff, 1968, p. 94), and $p$ orbitals can also be written with $x$ replaced by $y$ and by $z$. All four hydrogen orbitals have the same energy, $-e^2/(8a_0)$.

Approximate the lithium 2s and 2p orbitals by the same functions and approximate the lithium potential by $-e^2/r + v_{core}(r)$, where

$$v_{core} = \begin{cases} -2e^2/a_0 & \text{for } r \leq a_0 \\ 0 & \text{for } r > a_0 \end{cases}$$

Calculate the expectation value of the energy of the 2s and 2p orbitals. The easiest way may be to calculate corrections to the $-e^2/(8a_0)$ value. This gives the correct qualitative picture of the lithium valence states but is quantitatively inaccurate. Good quantitative results can be obtained by using forms such as are shown above and varying the parameters in the exponents. Such variational forms are called "Slater orbitals."
PROBLEM 1-3  Diatomic molecules

For \( \text{C}_2 \), obtain the \( \sigma \) states for the homopolar diatomic molecule (see Fig. 1-11), by using the matrix elements from the Solid State Table, at the back of the book, or from Tables 2-1 and 2-2, in Chapter 2. Writing

\[ |\phi\rangle = u_1 |s_1\rangle + u_2 |s_2\rangle + u_3 |p_{1s}\rangle + u_4 |p_{2s}\rangle. \]

the equations analogous to Eq. (2-2) become

\[
\begin{align*}
(e_s - E)u_1 + V_{ss} u_2 + 0 + V_{sp} u_3 &= 0; \\
V_{ss} u_2 + (e_p - E)u_3 - V_{sp} u_4 &= 0; \\
0 - V_{pp} u_3 + (e_p - E)u_4 + V_{pp} u_4 &= 0; \\
V_{sp} u_4 &= 0.
\end{align*}
\]

Solutions will be even or odd, by symmetry, so there can be solutions with \( u_2 = u_4 \) and \( u_3 = -u_3 \), and the above reduce to two equations in two unknowns. Solve them for \( E \).

Then, solve again with \( u_2 = -u_3 \) and \( u_3 = u_1 \).

Confirm the values of these energies as given in Table 1-1 for \( \text{C}_2 \).

The lowest state contains comparable contributions from the \( s \) and \( p \) orbitals. What is the fraction of \( s \) character, that is, \( (u_1^2 + u_2^2)/(u_1^2 + u_2^2 + u_3^2 + u_4^2) \)?

SUMMARY

In solids, atomic valence levels broaden into bands comprising as many states as there are atoms in the solid. Electronic states in these bands are mobile, each electron state being characterized by a momentum \( \mathbf{p} \) or wave number \( k = \mathbf{p}/\hbar \) that is restricted to a Brillouin Zone. If each atom in the solid has only four neighboring atoms, the atomic valence orbitals can be combined to form bond orbitals between each set of neighbors, and two electrons per bond can stabilize such an arrangement of atoms. In such covalent structures, bands of states based upon the bond orbitals will be fully occupied by electrons but other bands will be empty. The bands may be symmetric or polar. The covalent structure will not be stable if there are not two electrons per bond, if the bond energy is too small, or if the bond is too polar. Under these circumstances the lattice will tend to collapse to a denser structure. It may be an ionic crystal, which is a particularly stable arrangement, if by redistributing the electrons it can leave every atomic shell full or empty. Otherwise it will be metallic, having bands of states that are only partially occupied.

If the electron states are represented by linear combinations of atomic orbitals, the electron energy bands are found to depend on a set of orbital energies and interatomic matrix elements. Fitting these to accurate bands suggests that atomic term values suffice for the orbital energies and that nearest-neighbor interatomic matrix elements scale with bond-length \( d \) from system to system as \( d^{-2} \). This form, and approximate coefficients, all follow from the observation that the bands are also approximately given by a free-electron approximation. Atomic term values and coefficients determining interatomic matrix elements are listed in the Solid State Table and will be used in the study of covalent and ionic solids.