Electronic Structure and the Properties of Solids	Cấu trúc điện tử và các tính chất của chất rắn	
THE PHYSICS OF THE CHEMICAL BOND	CÁC KIẾN THỨC VẬT LÝ VỀ LIÊN KẾT HÓA HỌC	
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Electronic Structure and the Properties of Solids	Cấu trúc điện tử và các tính chất của chất rắn	
ELECTRON STATES	CÁC TRẠNG THÁI ELECTRON (CÁC TRẠNG THÁI ĐIỆN TỬ)	
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	Trong phần này, chúng tôi sẽ cố gắng mô tả chất rắn bằng những ngôn từ đơn giản nhất. Chương 1 đề cập đến một phát biểu ngắn gọn về cơ sở cơ học lượng tử cho tất cả những phần thảo luận tiếp theo. Chương này nhằm trang bị cho độc giả một lượng kiến thức nhất định về cơ học lượng tử. Tuy nhiên, để người đọc có được cái nhìn toàn diện, chúng tôi sẽ trình bày một cách ngắn gọn những tiên đề làm cơ sở cho những phần tiếp theo. Tiếp theo đó, chúng tôi sẽ mô tả cấu trúc electron và liên kết trong các nguyên tử và phân tử nhỏ, những vấn đề mà chúng tôi đưa vào chỉ là những khía cạnh có liên quan trực tiếp đến thảo luận về chất rắn. Chương 2 sẽ nghiên cứu cấu trúc electron của chất rắn dựa trên việc mở rộng cơ sở được trình bày trong Chương 1. Vào cuối chương 2, chúng tôi giới thiệu giá trị của các số hạng và các phần tử của ma trận liên	

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.	nguyên tử. Chúng cũng được đề cập đến trong Bảng Các Nguyên Tố Trạng Thái Rắn ở phía sau sách. Những dữ liệu này được sử dụng rộng rãi để tính toán các tính chất của các chất rắn cộng hóa trị và ion.	
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.	Phần tóm tắt ở đầu mỗi chương nhằm giúp người đọc nhanh chóng có một cái nhìn toàn diện về các chủ đề được xét trong mỗi chương. Phần tóm tắt cũng giúp người đọc lựa chọn những phần nào mình cần đọc.	
CHAPTER I The Quantum- Mechanical Basis	CHƯƠNG I Cơ sở cơ học lượng tử	
SUMMARY	TÓM TẮT	
This chapter introduces the quantum mechanics required for the analyses in this text. The state of an electron is represented by a wave function t/i. Each observable is represented by an operator 0. Quantum theory asserts that the average of many measurements of an observable on electrons in a certain state is given in terms of these by …..	Chương này trình bày các kiến thức cơ học lượng tử cần thiết cho các phân tích trong tài liệu này. Trạng thái của một electron được biểu diễn bằng một hàm sóng….Mỗi quan sát được biểu diễn bằng một toán tử. Lý thuyết cơ học lượng tử khẳng định rằng giá trị trung bình trên nhiều lần đo của một quan sát trên các electron ở một trạng thái nào đó được biểu diễn theo những đại lượng này (ý nói đến hàm sóng và toán tử) là….Lượng tử hóa năng lượng cũng giống như xác định trạng thái từ ma trận Haminlton và nghiệm nhiễu loạn. Nguyên lý Pauli và sự phụ thuộc thời gian của trạng	
The quantization of energy follows, as does the determination of states from a Hamiltonian matrix and the perturbative solution. The Pauli principle and the time-		

dependence of the state are given as separate assertions.	thái được đưa ra dưới dạng những tiên đề riêng biệt.	
In the one-electron approximation, electron orbitals in atoms may be classified according to angular momentum. Orbitals with zero, one, two, and three units of angular momentum are called s, Pf d, and/orbitals, respectively. Electrons in the last unfilled shell of s and p electron orbitals are called valence electrons. The principal periods of the periodic table contain atoms with differing numbers of valence electrons in the same shell, and the properties of the atom depend mainly upon its valence, equal to the number of valence electrons. Transition elements, having different numbers of d orbitals or/orbitals filled, are found between the principal periods. When atoms are brought together to form molecules, the atomic states become combined (that is, mathematically, they are represented by linear combinations of atomic orbitals, or LCAO's) and their energies are shifted. The combinations of valence atomic orbitals with lowered energy are called bond orbitals, and their occupation	Trong phép gần đúng một electron, các orbital trong nguyên tử có thể được phân loại theo momen động lượng. Một cách tương ứng, các momen không, một, hai và ba đơn vị momen động lượng được gọi là các orbital s, p, d và f. Các electron ở phân lớp s và p ngoài cùng chưa đầy gọi là các electron hóa trị. Tính chất tuần hoàn cơ bản của bảng tuần hoàn chứa các nguyên tử có số electron hóa trị khác nhau trong cùng một lớp (phân lớp), và các tính chất của nguyên tử chủ yếu phụ thuộc vào hóa trị của nó, chính là số electron hóa trị. Các nguyên tố chuyển tiếp, có số orbital d khác nhau hoặc các orbital f được làm đầy xuất hiện giữa các chu kỳ cơ bản. Khi các nguyên tử đến gần nhau để hình thành các phân tử, các trạng thái nguyên tử trở thành kết hợp (tức là, về mặt toán học, chúng được biểu diễn bằng các tổ hợp tuyến tính của các orbital nguyên tử, hoặc LCAO) và năng lượng của chúng bị dịch chuyển. Sự kết hợp của các orbital nguyên tử hóa trị với năng lượng thấp hơn được gọi là các orbital liên kết, và chính việc các electron chiếm những orbital này đã liên kết các phân tử với nhau.	

by electrons bonds the molecules together. Bond orbitals are symmetric or nonpolar when identical atoms bond but become asymmetric or polar if the atoms are different. Simple calculations of the energy levels are made for a series of nonpolar diatomic molecules. 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 ij/(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 <f(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	Các orbital liên kết có tính chất đối xứng hoặc không có cực khi các nguyên tử giống hệt nhau liên kết nhưng sẽ bất đối xứng hoặc có cực nếu các nguyên tử khác nhau. Việc tính toán đơn giản các mức năng lượng được thực hiện cho một loạt các phân tử hai nguyên tử không có cực. [redacted] [redacted]	

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 position momentum where h 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, d/dt. 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	[redacted] [redacted] [redacted]	

multiplication by ỵ(r). Kinetic energy is represented by p2/2m = - (fi2/2m)v2. A particularly important observable is electron energy, which can be represented by a Hamiltonian operator: (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 0,for an electron with wave function Ip, is ……………………. (If lị/ depends on time, then so also will (0).) Even though the wave function describes an electron fully, different values can be obtained from a particular measurement of some observable. The average value of many measurements of the observable 0 for the same \Ị/ is written in Eq. (1-3) as <0>. The integral in the numerator on the right side of the equation is a special case of a matrix element; in general the wave function appearing to the left of the operator may be different from the wave function to the right of it. In such a case, the Dirac notation for the matrix element is	[redacted] [redacted] [redacted]	

……………………..

In a similar way the denominator on the right side of Eq. (1-3) can be shortened to (ip 11//). The angular brackets are also used separately. The bra (l I or {ỷị I means lAi(r)*; the ket 12) or I \jj2) means Il/2(r)- (These terms come from splitting the word “ bracket.”) When they are combined face to face, as in Eq. (1-4), an integration should be performed.

Eq. (1-3) is the principal assertion of the quantum mechanics needed in this book. Assertions (a) and (b) simply define wave functions and operators, but assertion (c) makes a connection with experiment. It follows from Eq. (1-3), for example, that the probability of finding an electron in a small region of space, d3r, is il/*(r)\jj(r)d3r. Thus is the probability density for the electron.

It follows also from Eq. (1-3) that there exist electron states having discrete or definite values for energy (or, states with discrete values for any other observable). This can be proved by construction. Since any measured quantity must be real, Eq. (1-3) suggests that the operator 0 is Hermitian. We know from mathematics that it is possible

[redacted]

[redacted]

[redacted]

to construct eigenstates of any Hermitian operator. However, for the Hamiltonian operator, which is a Hermitian operator, eigenstates are obtained as solutions of a differential equation, the time-independent Schroedinger equation, (1-5) where E is the eigenvalue. It is known also that the existence of boundary conditions (such as the condition that the wave functions vanish outside a given region of space) will restrict the solutions to a discrete set of eigenvalues E, and that these different eigenstates can be taken to be orthogonal to each other. It is important to recognize that eigenstates are wave functions which an electron may or may not have. If an electron has a certain eigenstate, it is said that the corresponding state is occupied by the electron. However, the various states exist whether or not they are occupied. We see immediately that a measurement of the energy of an electron represented by an eigenstate will always give the value E for that eigenstate, since the	[redacted] [redacted]	

average value of the mean-squared deviation from that value is zero: We have used the eigenvalue equation, Eq. (1-5), to write…..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 … for one electron in a diatomic molecule, we can make a linear combination of wave functions and i//2. where 1 and 2 designate energy eigenstates for electrons in the separate atoms that make up the molecule. Thus, ………………… (1-7) where Uị and u2 are	[redacted] [redacted]	

constants. The average energy, or energy expectation value, for such an electron is given by ………………………..(1-8) The states comprising the set (here, represented by \iĮ/ị) and IIĮ/2)) 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, (lAi|l/'i) = (.Ỷ2 I ^2) = 1-Moreover, we shall assume that the basis states are orthogonal: (ipị I iĮ/2) = 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 (ỷI IỶÌ)- 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 Hij = (lĮ/ị IHI then Eq. (1-8) becomes (Actually, by Hermiticity, H21 = H*2, but that fact is	[redacted] [redacted]	

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. Howeyer, 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 Uị and u2. In particular, setting the partial derivatives of that expression, with respect to uf and uf, equal to zero leads to the two equations ………………….	[redacted]	
(In taking these partial derivatives we have treated ul,uf,u2, and u\ 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£. The lower value is the energy expectation value of the lowest energy state, called the bonding state. It is ………………….	[redacted]	
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	[redacted]	

second solution to Eqs. (1-10) gives the energy of another state, also in the form of Eq. (1-7) but with different and u2. This second state is called the antibonding state. Its wave function is orthogonal to that of the bonding state; its energy is given by We may substitute either of these energies, Eb or £a, back into Eqs. (1-10) to obtain values for Uj and u2 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 H12 is much smaller than the magnitude of the difference I Hn — H221 - Then, Eq. (1-11) or Eq. (1-12) can be expanded in the perturbation Hl2 (and H2I) to obtain (1-13) for the energy of a state near Hill a similar expression may be obtained for an energy near H2 2 ■ These results are part of perturbation theory.	[redacted] [redacted] hững kết quả này là một phần của lý thuyết nhiễu loạn Các kết quả tương ứng với trường hợp nhiều số hạng rất cần thiết	

The corresponding result when many terms, rather than only two, are required in the expansion of the wave function is	trong khai triển hàm sóng có dạng [redacted]	
Similarly, for the state with energy near H1U the coefficient u2 obtained by solving Eq. (1-10) is ………………………	[redacted] trạng thái ứng với mức năng lượng [redacted] [redacted]	
The last step uses Eq. (1-13). When H2l is small, u2 is small, and the term «2 ệ2(r) in Eq. (1-7) is the correction to the unperturbed state, \ỳị{ĩ), obtained by perturbation theory. The wave function can be written to first order in the perturbation, divided by Hn - H22, and generalized to a coupling with many terms as……. (1-16)	Ở bước cuối cùng, chúng ta sẽ dùng phương trình [redacted] là hiệu chỉnh cho trạng thái [redacted] đại lượng thu được từ lý [redacted] Thế thì [redacted] dưới dạng nhiễu loạn bậc nhất [redacted] [redacted]	
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.	[redacted]	
All of the discussion to this point has concerned the spatial wave function ij/(r) of	[redacted]	

an electron. An electron also has spin. For any I^(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	[redacted] tiên đề [redacted] cùng [redacted] của nó [redacted] thường chỉ [redacted] [redacted] Từng trạng thái riêng biệt của electron [redacted] Trong những trường hợp khác, có thể chúng ta cần xét đến ảnh hưởng của những tương tác này [redacted] tiên đề [redacted] [redacted]	

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.	[redacted] rời rạc [redacted] một hệ có [redacted]	
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:	[redacted] như thế nào Tuy nhiên, đối với những trường hợp cần thông tin này, chúng ta phải áp dụng tiên đề thứ năm:	
(e) The time evolution of the wave function is given by the Schroedinger equation, (1-17)	Sự thay đổi theo thời gian của hàm sóng được biểu diễn bằng phương trình [redacted] [redacted]	
This assertion is not independent of assertion (c); nevertheless, it is convenient to separate them.	[redacted] việc xét riêng hai trường hợp sẽ thuận tiện hơn	
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	[redacted] hệ quả của năm tiên đề này đóng vai trò quan trọng nhưng không dễ thấy [redacted]	

explicitly in the context in which they arise. 1-B Electronic Structure of Atoms Because the potential energy K(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, L2, which takes on the discrete values L2 = /(/ + l)h2, (1-18) where / is an integer greater than or equal to 0. For each value of I there are 2/ + 1 different orthogonal eigenstates; that is, the component of angular momentum along any given direction can take on the values mh, with m = —/,—/ + 1, ..., I - 1, /ế The spatial wave functions representing these states are called orbitals since we can	[redacted] [redacted] các [redacted] [redacted] Vì vậy, sẽ rất thuận lợi nếu chúng ta phát biểu kết quả theo bình phương độ lớn momen động lượng, L2, đại lượng này nhận những giá trị rời rạc. [redacted] [redacted] trạng thái riêng trực giao [redacted] các thành phần của [redacted] dọc theo bất kỳ một hướng nào đó [redacted] nhận các [redacted] [redacted] các [redacted] chúng ta đang	

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.	liên tưởng đến các [redacted] tương ứng [redacted] trong đó năng lượng và momen động lượng không đổi quanh một trục nhất định [redacted] biểu diễn các liên kết hóa học trong đó quỹ đạo electron tương ứng không quá đơn giản	
The 21 4- 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	[redacted] trạng thái riêng trực giao với [redacted] giá trị [redacted] có tính chất [redacted]	

by means of two quantum numbers, the integers I and m.	[redacted]	
In the common terminology for states of small angular momentum, the first four—of smallest angular momentum—are	[redacted] [redacted] [redacted] [redacted] [redacted]	
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.”	[redacted]	
For any given value of I and m there are many different energy eigenstates; these are numbered by a third integer, ft, in order of increasing energy, starting with n = I + I. This starting point is chosen since, for the hydrogen atom, states of different I but the same n are degenerate; that is, E = (n, l,m\H\n,l, m) depends only on the quantum number n. Thus n is called the	[redacted]	

principal quantum number. Only for the hydrogen atom, where the potential is simply — e2/r, does the energy depend on n alone. However, the same numbering system is universally used for all other atoms too.	[redacted]	
In each state specified by n, I, 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.	[redacted]	
The s orbitals have vanishing angular momentum; I = 0 (and m = 0, since I m I < /). 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 Is state. Its wave function decreases monotonically with distance from the nucleus. The wave function of the next state, the	[redacted]	

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.)	[redacted]	
FIGURE 1-1 This depiction of an 5 orbital will be used frequently in this book.	[redacted]	
FIGURE 1-2 The three 5 states of lowest energy for atomic hydrogen. The orbitals, multiplied by r, are plotted as a function of distance from the nucleus.	[redacted]	
A plot of the first three s orbitals for a hydrogen atom is given in Fig. 1-2.	[redacted]	
The p orbitals have one unit of angular momentum, / = 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 YĨ, which are functions of angle only (this is explained in Schiff, 1968, p. 79): ……………………. (1-19)	[redacted]	

For a given I, the radial function is independent of m. For s orbitals, the spherical harmonic is Yq = (4n) 1/2. For p orbitals, the spherical harmonics are FIGURE 1-3 This p-orbital depiction will be used frequently in the book. ……………………. and ………………… 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 (1-20) These forms, used by Slater and Koster (1954), will be used extensively in this text. For each n when I = 1, there are three p orbitals oriented along the three Cartesian axes. Diagrams such as those	[redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted]	

shown in Fig. 1-4 illustrate the three angular forms.	[redacted]	
	[redacted]	
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. 1-5,c 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.	[redacted]	
	[redacted]	
The d orbitals have two units of angular momentum, I = 2, and therefore five m values: m = — 2, m = — 1, m = 0, m = 1, and m = 2. They can be conveniently	[redacted]	
FIGURE 1-4 Three p orbitals, each directed along a different Cartesian axis. (a) Fishnet plot	[redacted]	

(b) Contour plot

(c) Schematic representation

FIGURE 1-5

Three ways of representing atomic p orbitals.

represented in terms of Cartesian coordinates in the form

Fig. 1.6 corresponds to the third angular form listed in Eq. (1-21).

A very important feature of d orbitals is that they are concentrated much more closely at the nucleus than are s and p orbitals. The physical origin of this can be

FIGURE 1-6

The d orbiiai corresponding to the xy/r2 form in Eq. (1-21).

understood in terms of the n — 3 state of hydrogen. The 3s, 3p, and 3d states all have the same energy, but of these three, the d 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 p orbital. The s state, which Corresponds classically to an electron vibrating radially through the nucleus, stretches even further from the nucleus. Therefore, d states tend to be influenced much less by neighboring atoms than are s and p states of similar energy. We shall have little occasion to discuss /'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 F. rather than E. For hydrogen,

…………… (1'22)

where a0 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 Is 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 CO = AE/h, where AE 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, 5-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 Is, 2s, 2p, 3s, 3p, 3d, 45, and 4p orbitals as the		

atomic number (equal to the number of protons in the nucleus) increases. In lithium, atomic number 3, the Is level has dropped to a very low energy and is occupied by two electrons. The Is 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 FIGURE 1-7 Energy-level diagram for atomic hydrogen. The lines are branched at the right to show how many orbitals each line represents. continue to drop in energy and sp splitting (the difference in energy between levels, or Elp — £2s) 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 5 and p levels in each row (and sometimes those filling d levels) are traditionally called valence electrons and determine

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.

1- 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 a = 1, 2, 3run 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

where the ua are the coefficients that must be determined. The orbitals I a) representing the basis states are selected to be normalized, (a I a) = 1. We also take them (as in Section 1-A) to be orthogonal to each other; </?|a> = 0 if p =£ a.

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

In obtaining the second form, we allow the ua 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 uf be zero (as in Eq. 1-10), we obtain

or more simply,

with E — (ỷ IHI ệ)/(ệ I ệ). (Later, specific eigenvalues will be written as e’s with appropriate subscripts.) There is one such equation for each p corresponding to a basis state.

We have obtained a set of simultaneous linear algebraic equations with unknown coefficients Ma. 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 lowest electron state having a wave function orthogonal to that of the first, and so on. The solution of these equations gives the ua 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,

det(tf^ - Eȯp«) = 0, (1-27)

where “det ” means “determinant of” and ôpa is the unit matrix. We have made one further simplification of the notation in writing Hịla = (p\H\oc). 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, H2 • For the hydrogen molecule, we use two orbitals, 11) and 12), which represent Is states on atoms 1 and 2 respectively. Eq. (1-26) then becomes

where we have made the natural definition of the Is energy £s = (l|H|l) = (21H12). The energy Es 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 Is function slightly different from that of the free atom. We have defined a matrix element v2 = — #12 = —H21 to correspond to the notation we shall use later. The matrix element v2 is called a covalent energy, and is defined to be greater than zero; v2 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 as well as a high-energy solution, the antibonding state, with Substituting the eigenvalues given in Eqs. (1-29) and (1-30) back into Eq. (1-28) gives coefficients U1 and u2 . For the bonding state, Uị = u2 = 2~112, and for the antibonding state, Mj = —u2 = 2”1/2. The conventional depiction of these bond orbitals and antibond orbitals is illustrated in Fig. 1-10,a. Notice that the use of orthogonal eigenfunctions for the two atomic states (taking the overlap (112) = 0) is not consistent with Fig. 1-10,b, 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 v2 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 separated 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. Bonding orbital ca Antibonding energy level Kh Bonding energy level (a) Homopolar diatomic molecule Antibonding orbital Bonding orbital (b) Heteropolar diatomic molecule FIGURE 1-10 The formation of bonding and antibonding combinations of atomic orbitals in diatomic molecules, and the corresponding energy-level diagrams. 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 Is 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 Ss were the same. We shall often be interested in systems in which the diagonal energies ifn and H22 (that is, diagonal elements of

the Hamiltonian matrix) are different; such molecules are said to have a hetero- polar or simply polar bond. Let us use, as an example, the molecule LiH. We expect the linear combinations to be those of the hydrogen Is orbitals and lithium 2s orbitals, though as we indicated at the end of the preceding section, special con-siderations govern molecules involving hydrogen. In calculating the energy of heteropolar bonds, Eqs. (1-28) must be modified so that £s is replaced by two different energies, £* for the low-energy state (for the energy of the anion) and fij for the high-energy state (for the energy of the cation). The value of one half of the anion cation energy-difference is the polar energy: It is convenient to define the average of the cation and anion energy, written as Then Eqs. (1-31) become The solution of Eqs. (3-34) is trivial: £b and £a 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 and u2 values for the bonding state by substituting £b for the energy E in Eqs. (1-34), the first equation of which can then be rewritten as (1-36) Second, if the individual atomic wave functions do not overlap, the probability of finding the electron on atom 1 will be uị /(uỊ + uị) and the probability of finding it on atom 2 will be uị/ịuị + uị). 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 + 0Cp)/2 and the probability of finding it on atom 2 is (1 — ap)/2, where ap is the polarity defined by

We can expect the dipole of the bond to be proportional to u\ — u\ = bcp. 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

1- E Diatomic Molecules

In Section 1-C we noted that molecular hydrogen is unique in that a single atomic state, the Is 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 2, Be2, B2,

c2, N2, 02, and F2, 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 Py 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 Pz orbitals form bonding and antibonding combinations. The four resulting p-orbital combinations are called n states, by analogy with p		

states, because each has one unit of angular momentum around the molecular axis. The Tt states are also frequently distinguished by a g, for gemde (German for “ even ”), or

The coupling of atomic orbitals in lithium-row diatomic molecules, and the resultant bond designations (at right).

u, 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 % orbitals, the bonding combination is ungerade a n orbital that is gerade (ng) is zero on the plane bisecting the bond.

A feature of homopolar diatomic molecules is that s states and px states are also coupled, and all four states are required in the expansion of the corresponding molecular orbitals, called Ơ states. The bonding combination for a orbitals is gerade (Gg). The s and p states are hybridized in the molecule. (The ơ-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 (Vspa, - Vspa) 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 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 £s (one s		

orbital for each atom) and fip (three p orbitals for each atom, px, Py, and pz). 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 n orbitals oriented along the y-axis have the same energies as those oriented along the z-axis. The bonding and antibonding combinations for these are indicated by 1 nl§ and lng, 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 Ơ orbitals are, to a good approximation, a bonding combination of s states and an antibonding combination of s states, and a bonding combination of px states and an antibonding combination of px states, in order of increasing energy. The energies of the intermediate levels, indicated by 2ơ,, and 3 ơg 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<7,, is never greater than that of either of the two high-energy bonding states 3ơg and \nu. (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 loca-tion, 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 2ơg bonding state; the qualitative picture of electronic structure and binding of Li 2 is exactly the same for H2; the levels deriving from the valence p state of lithium may be disregarded. If the molecule were Be2, there would be four electrons in the molecule; two would occupy the 2ơg bonding state, and the other two would occupy the 2<r„ 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 Be2 is found in nature. As the atomic number of the constituents increases, bonding and antibonding states are filled in succession. F2 would have enough electrons to fill all but the highest antibonding state, 3σu. A pair of neon atoms would have enough electrons to fill all bonding and antibonding states and, like Be2, would not be bound at all. In 02, when the last levels to be filled are degenerate, a special situation occurs. Only two electrons occupy the lng state though there are states to accommodate four. There are different ways the state could be filled, and Hund's rule tells us which arrangement will have lowest energy. It states that when there is 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 exchange energy. It tends to be small enough that it is dominant only when there is orbital degeneracy, as in the case of 02, 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 Appendixes A and c.) In 02, the two degenerate lng states take one electron in a py state and one in a pz state. As a result, the charge density around the 02 molecule has cylindrical symmetry, though there is a net spin from the two electrons. In contrast, if both electrons were in py 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 H2 is like He (as mentioned at the end of Section 1-C), the molecule C2H4 is like 02, except that the two hydrogen protons are outside the carbon nucleus rather than inside. The number of electrons is the same in both C2H4 and 02 and essentially the same classification of electron levels can be made. However, if the protons in C2H4 are all placed in the same plane, the lnu 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 Py state and one pz 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. C2H4 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 C2H4. 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 vih = flip h2/(md2), where d is the internuclear distance and values for t]ijx are four universal constants for SSƠ, spa, ppơ, and ppn matrix elements, as given in the next chapter (Table 2-1). Furthermore, atomic term values (given in Table 2-2) can be used for Ep and fis. 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 major errors only for the ĩơg levels in 02 and F2. 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 n 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 I'D.

TABLE 1-1

One-electron energies in homopolar diatomic

molecules, as obtained by using solid state matrix elements. Values in parentheses are from accurate molecular orbital calculations. Shading denotes empty orbitals. Energies are in eV. SOURCES of data in parentheses: Li2, Be2, c2, Nj, and F2 from Ransil (1960); B2 from Padgett and Griffing (1959); 02 from Kotani, Mizuno, Kayama, and Ishiguro (1957); all reported in Slater (1968). There is, however, a complication in the treatment of the Ơ 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 a bonds, hybrid basis states can be made from s and p states, and these can be treated approximately as independent pairs, which reduces the prob-lem 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 ơ-bondeđ hetero- polar molecule.

PROBLEM 1-1 Elementary quantum mechanics

An electron in a hydrogen atom has a potential energy, — e2/V. The wave function for the lowest energy state is

\j/(r) = Ae~rla°

where a0 is the Bohr radius, a0 = h2/me2, and A is a real constant.

(a) Obtain A such that the wave function is normalized, (ệ I ệ} = 1.

(b) Obtain the expectation value of the potential energy, (ệ\ VịìỊ/).

(c) Calculation of the expectation value of the kinetic energy,

K.E.^I^Vl^X

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

Evaluate this expression to obtain K.E.

(d) Verify that the expectation value of the total energy, <|//| vịiị1} + K.E. is a minimum with respect to variation of 00. Thus a variational solution of the form e~',r would have given the correct wave function.

(e) Verify that this i//(r) is a solution of Eq. (1-5).

PROBLEM 1-2 Atomic orbitals

The hydrogen 2s and 2p orbitals can be written

and

(see Schiff, 1968, p. 94), and p orbitals can also be written with X replaced by V and by z. All four hydrogen orbitals have the same energy, — e2/(8flc).

Approximate the lithium 2,5 and 2p orbitals by the same functions and approximate the lithium potential by — e2/r + ucore(r), where

Calculate the expectation value of the energy of the 2s and 2p orbitals. The easiest way may be to calculate corrections to the — e2/(8a0) 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 c2, obtain the Ơ 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

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

Solutions will be even or odd, by symmetry, so there can be solutions with u2 = Uị and w4 = —u3, and the above reduce to two equations in two unknowns. Solve them for E. Then, solve again with If2 = — IIỊ and «4 = u3 .

Confirm the values of these energies as given in Table 1-1 for c2.

The lowest state contains comparable contributions from the s and p orbitals. What is the fraction of s character, that is, (uị + uịỵiuị + uị + uị + ul)1

CHAPTER 2

Electronic Structure of Solids

SUMMARY

In solids, atomic valence levels broaden into bands comprising as many states as there are atoms in the solid. Electrons in these band states are mobile, each electron state being characterized by a momentum p or wave number k = p/tt 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 bonds 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.

In this chapter we give a very brief description of solids, which is the principal subject of the book. The main goal is to fit solids into the context of atoms and molecules. In addition, we shall carefully formulate the energy band in the simplest possible case and study the behavior of electrons in energy bands.

2- A Energy Bands

When many atoms are brought together to form a solid, the number of electron states is conserved, just as in the formation of diatomic molecules. Likewise, as in diatomic molecules, the one-electron states for the solid can, to a reasonable approximation, be written as LCAO’s. However, in solids,

the number of basis states is great. A solid cube one centimeter on an edge may contain 1023 atoms, and for each, there is an atomic s orbital and three p orbitals. At first glance it might seem that such a problem, involving some 4 X 1023 equations, could not be attacked. However, the simplicity of the crystalline solid system allows us to proceed effectively and accurately. As the atoms are brought together, the atomic energy levels split into bands, which are analogous to the states illustrated for diatomic molecules in Fig. 1-12. The difference is that rather than splitting into a single bonding and a single antibonding state, the atomic levels split into an entire band of states distributed between extreme bonding and antibonding limits. To see how this occurs, let us consider the simplest interesting case, that of cesium chloride. The structure of CsCl is shown in Fig. 2-1,a. The chlorine atoms, represented by open circles, appear on the comers of a cube, and this cubic array is repeated throughout the entire crystal. At the center of each cube is a cesium atom		

(at the body-center position ill the cube). Cesium chloride is very polar, so the occupied orbitals lie almost entirely upon the chlorine atoms. As a first approximation we can say that the cesium atom has given up a valence electron to

(a) Crystal structure (b) Brillouin Zone

FIGURE 2-1

(a) A unit cube of the cesium chloride crystal structure, and (b) the corresponding Brillouin Zone in wave number space.

fill the shell of the chlorine atom, which becomes a charged atom, called an ion. Thus we take chlorine 3s orbitals and 3p orbitals as the basis states for describing the occupied states. Furthermore, the chlorine ions are spaced far enough apart that the s and p states can be considered separately, as was true at large inter- nuclear distance d in Fig. 1-12. Let us consider first the electron states in the crystal that are based upon the chlorine atomic 3s orbitals.

We define an index i that numbers all of the chlorine ions in the crystal. The chlorine atomic s state for each ion is written I Sị). We can approximate a crystalline state by

The variational calculation then leads immediately to a set of equations, in analogy to Eq. (1-26):

It is convenient at this stage to avoid the complications that arise from consideration of the crystalline surface, by introducing periodic boundary conditions. Imagine a crystal of chlorine ions that is Nị ions long in the x-direction, N2 long ill the ^-direction, and N3 long in the z-direction. The right surface of the crystal is connected to the left, the top to the bottom, and the front to the back. This is difficult to imagine in three dimensions, but in one dimension such a structure corresponds to a ring of ions rather than a straight segment with two ends. Closing the ring adds an Hịj matrix element coupling the states on the end ions. Periodic boundary conditions greatly simplify the problem mathematically; the only error that is introduced is the neglect of the effect of surfaces, which is beyond the scope of the discussion here.

The approximate description of the crystalline state, Eq. (2-1), contains a basis set of Np = N1N2 N3 states (for the Np pairs of ions), and there are Np solutions of Eq. (2-2).

These solutions can be written down directly and verified by substitution into Eq. (2-2). To do this we define a wave number that will be associated with each state: (2-3) where lĩị, n2, and n3 are integers such that —Nị/2 <nx< Nị/2, ..and X, y, and ….are units vectors in the three perpendicular directions, as indicated in Fig. 2-1,b. Then for each k allowed by Eq. (2-3), we can write the coefficient Uj in the form Here the r7- = (ml X + m2y + m3 z)a are the positions of the ions. We see immediately that there are as many values of k as there are chlorine ions; these correspond to the conservation of chlorine electron states. We also see that the wave functions for states of different k are orthogonal to each other. Values for k run almost continuously over a cubic region of wave number space, — n/a < kx < n/a, — n/a <ky < n/a, and — n/a < kz < %/a. This domain of k is called a Brillouin Zone. (The shape of the Brillouin Zone, here cubic, depends upon the crystal structure.) For a macroscopic crystal the Nị		

are very large, and the change in wave number for unit change in «j is very tiny. Eq. (2-4) is an exact solution of Eq. (2-2); however, we will show it for only the simplest approximation, namely, for the assumption that the |sf) are sufficiently localized that we can neglect the matrix element Hji = |S() unless (1) two states in question are the same (/' = j) or (2) they are from nearest-neighbor chlorine ions. For these two cases, the magnitudes of the matrix elements are, in analogy with the molecular case, In cesium chloride the main contribution to v2 comes from cesium ion states acting as intermediaries in a form that can be obtained from perturbation theory. We need not be further concerned here with the origin of v2 . (We shall discuss the ionic crystal matrix elements in Chapter 14.) For a particular value of j in Eq. (2-2), there are only seven values of i that contribute to the sum: i=j numbered as 0, and the six nearest-neighbor chlorine s states. The solution (valid for any i) is This energy varies with the wave number over the entire Brillouin Zone of Fig. 2-l,b.		

The results are customarily displayed graphically along certain lines within that Brillouin Zone. For example, Fig. 2-2,a shows a variation along the lines rx and TK of Fig. 2-l,b.

The calculation of bands based on p states proceeds in much the same way. In particular, if we make the simplest possible assumption—that each px orbital is coupled by a matrix element V'2 only to the px orbitals on the nearest neighbors in the x-direction and to no other p orbitals, and similarly for the py and pz orbitals— then the calculation can be separated for the three types of states. (Otherwise it would be necessary to solve three simultaneous equations together.) For the states based upon the px orbitals,

For py orbitals and pz orbitals, the second term is 2V2 COS kya and 1V'2 COS kza, respectively. The three corresponding p bands are also shown in Fig. 2-2,a. In later discussions we shall see that by the addition of matrix elements between orbitals that are more distant it is possible to obtain as accurate a description of the true bands as we like; for the present, crude approximations are sufficient to illustrate the method.

Can we construct other bands, for other orbitals, such as the cesium s orbital? It turns out that states that are not occupied in the ground state of the crystal are frequently not well described in the simplest LCÀO descriptions, but an approximate description can be made in the same way.

How would the simple bands change if we could somehow slowly eliminate the strong atomic potentials that give rise to the atomic states upon which the bands are based? The answer is given in Fig. 2-2,b. The gaps between bands decrease, including the gap between the cesium bands (not shown in Fig. 2-2,a) and the chlorine bands. The lowest bands have a recognizable similarity to each other in these two extreme limits. The limit shown in Fig. 2-2,b is in fact the limit as the electrons become completely free; the lowest band there is given by the equation for free-electron kinetic energy, E — tĩ2k2/2m. The other bands in Fig. 2-2,b are also free-electron bands but are centered at different wave

numbers (e.g., as E = h2(k — q)2/2m), in keeping with the choice to represent all states by wave numbers in the Brillouin Zone. Such free-electron descriptions will be appropriate later when we discuss metals; for cesium chloride, these descriptions are not so far from LCAO descriptions as one might have thought, and in fact the similarity will provide us, in Section 2-D, with approximate values for interatomic matrix elements such as v2 and V'l. Since there are as many states in each band as there are chlorine ions in the crystal, the four bands of Fig. 2-2,a, allowing both spins in each spatial state, can accommodate the seven chlorine electrons and one cesium electron. All states will be filled. This is the characteristic feature of an insulator; the state of the system cannot be changed without exciting an electron with several electron volts of energy, thus transferring it to one of the empty bands of greater energy. For that reason, light with frequency less than the difference between bands, divided by h, cannot be absorbed, and the crystal will be transparent.		

Similarly, currents cannot be induced by small applied voltages. This absence of electrical conductivity results from the full bands, not from any localization of the electrons at atoms or in bonds. It is important to recognize that bands exist in crystals and that the electrons are in states of the crystal just as, in the molecule 02, electrons form bonding and antibonding molecular states, rather than atomic states at the individual atoms. If, on the other hand, the bands of cesium chloride were as in Fig. 2-2,b, the eight electrons of each chlorine-cesium atom pair would fill the states only to the energy Ep shown in the figure; this is called the Fermi energy. Each band would only be partly filled, a feature that, as we shall see, is characteristic of a metal. 2- B Electron Dynamics In circumstances where the electron energy bands are neither completely full nor completely empty, the behavior of individual electrons in the bands will be of interest. This is not the principal area of concern in this text, but it is important to understand electron dynamics because this provides the link		

between the band properties and electronic properties of solids. Consider a Brillouin Zone, such as that defined for CsCl, and an energy band E(k), defined within that zone. Further, imagine a single electron within that band. If its wave function is an energy eigenstate, the time-dependent Schroedinger equation, Eq. (1-17), tells us that The magnitude of the wave function and therefore also the probability density at any point do not change with time. To discuss electron dynamics we must consider linear combinations of energy eigenstates of different energy. The convenient choice is a wave packet. In particular, we construct a packet, using states with wave numbers near k0 and parallel to it in the Brillouin Zone: Taking the form of \ị)h from Eqs. (2-1) and (2-3), and treating k - k0 as small, a little algebra shows that at t = 0, Eq. (2-8) corresponds to the state iỊ/ko modulated by a gaussian peak centered at r = 0. Furthermore, writing £(k) = E(k0) + (dE/dk) ■ (k - k0), we may see that the center of		

the gaussian moves with a velocity Thus it is natural to associate this velocity with an electron in the state Ijjko. Indeed, the relation is consistent with the expectation value of the current operator obtained for that state. We are also interested in the effects of small applied fields: imagine the electron wave packet described above, but now allow a weak, slowly varying potential F(r) to be present. The packet will work against this potential at the rate V • dv/dr. This energy can only come from the band energy of the electron, through a change, with time, of the central wave number k0 of the packet: This is consistent with the relation This can, in fact, be generalized to magnetic forces by replacing —dv/dx by the Lorenz force, — e[—¥<p + (v/c) X H], Eqs. (2-9) and (2-11) completely describe the dynamics of electrons in bands wherever it is possible to think in terms of wave packets; that is, whenever the fields are slowly varying relative to interatomic spacings. Notice that if we think of fik as the canonical		

momentum, then the band energy, written in terms of p = hk, plus the potential energy, F(r), play precisely the role of the classical Hamiltonian, since with these definitions, Eqs. (2-9) and (2-11), are precisely Hamilton’s equations. Thus, in terms of the energy bands E(k), we may proceed directly by using kinetic theory to examine the transport properties of solids, without thinking again of the microscopic theory that led to those bands. We may go even further and use this classical Hamiltonian to discuss a wave function for the packet itself, just as we constructed wave functions for electrons in Chapter 1. This enables us to treat band electrons bound to impurities in the solid with methods similar to those used to treat electrons bound to free atoms; however, it is imperative to keep in mind that the approximations are good only when the resulting wave functions vary slowly with position, and therefore their usefulness would be restricted to weakly bound impurity states. Let us note some qualitative aspects of electron dynamics. If the bands are narrow in energy, electron velocities		

will be small and electrons will behave like heavy particles. These qualities are observed in insulator valence bands and in transition-metal d bands. In simple metals and semiconductors the bands tend to be broader and the electrons are more mobile; in metals the electrons typically behave as free particles with masses near the true electron mass. One question that might be asked is: what happens when an electron is accelerated into the Brillouin Zone surface? The answer is that it jumps across the zone and appears on the opposite face. It is not difficult to see from Eq. (2-3) that if, for example, m; is changed by Nị (corresponding to going from a wave number on one zone face to a wave number on the opposite face) the phase factors change by e2”'; the states are therefore identical. In general, equivalent states are found on opposite zone faces, and an electron accelerated into one face will appear at the opposite face and continue to change its wave number according to Eq. (2-11). 2- C Characteristic Solid Types Before discussing in detail		

the various categories of solids, it is helpful to survey them in general terms. This is conveniently done by conceptually constructing the semiconductor silicon from free atoms. In the course of this, it will become apparent how the metallicity of a semiconductor varies with row number in the periodic table. With the general model as a basis we can also construct compounds of increasing polarity, starting with silicon or germanium and moving outward in the same row of the periodic table. Metallicity and polarity are the two principal trends shown by compounds and will provide a suitable framework for the main body of our discussions. Imagine silicon atoms arranged as in a diamond crystal structure but widely spaced. This structure will be discussed in the next chapter; a two-dimensional analogue of it is shown in Fig. 2-3. At large internuclear distance, two electrons are on each individual atom in s states and two are in p states. As the atoms are brought together, the atomic states broaden into bands, as we have indicated. (There are complications, unimportant here, if one goes		

beyond a one-electron picture.) The s bands are completely full, whereas the p bands can accommodate six electrons per atom and are only one third full. This partial filling of bands is characteristic of a metal. As the atoms are brought still closer together, the broadening bands finally reach each other, as shown in Fig. 2-3, and a new gap opens up with four bands below and four above. The bonding bands below (called valence bands) are completely full and the antibonding bands above (called con-duction bands) are completely empty; now the system is that of an insulator or, when the gap is small, of a semiconductor. In Chapter 1, it was noted that a crossing of bonding and antibonding states does not occur in the simple diatomic molecules, but that it can in larger molecules and in solids, as shown here.

The qualitative change in properties associated with such crossing is one of the most important concepts necessary for an understanding of chemical bonding, yet

FIGURE 2-3

The formation of bands in a homopolar tetrahedral

semiconductor as the atoms are brought together. Internuclear distance decreases to the right. it has not been widely examined until recently. Particular attention has been brought by Woodward and Hoffmann (1971) in their discussion of reactions between molecules. In that context, Woodward and Hoffmann found that when bonding and antibonding states are equally occupied, as in Be2, discussed earlier, no bonding energy is gained and the atoms repel each other. Only when the atoms are close enough that upper bonding levels can surpass or cross the energy of the lower antibonding levels above can bonding result. In some such cases (not Be2) a stably bonded system can be formed, but an energy barrier must be overcome in order to cause the atoms to bond. Reactions in which energy barriers must be overcome are called “symmetry forbidden reactions.” (See Woodward and Hoffmann, 1971, p. lOff, for a discussion of 2C2H4 -> C4H8.) The barrier remains, in fact, when there is no symmetry. In silicon, illustrated in Fig. 2-3, the crossing occurs because		

high symmetry is assumed to exist in the atomic arrangement. Because of this symmetry, the matrix elements of the Hamiltonian are zero between wave functions of states that are dropping in energy and those that are rising (ultimately to cross each other). If, instead, the silicon atoms were to come ■4 Increasing interatomic distance (d) FIGURE 2-4 The variation of energy of two levels which cross, as a function of atomic spacing d, in a symmetric situation, but do not cross when there is not sufficient symmetry. together as a distorted lattice with no symmetry, the corresponding matrix elements of the Hamiltonian would not be zero, and decreasing and increasing energy levels would not cross (see Fig. 2-4). In an arrangement of high symmetry, a plotting of total energy as a function of d may show a cusp in the region where electrons switch from bonding to antibonding states; a clear and abrupt qualitative change in behavior coincides with this cusp region. In an unsymmetric arrangement, change in total energy as a		

function of d is gradual but at small or at large internuclear distances, energies are indistinguishable from those observed in symmetric arrangements. Thus, though the crossing is artificial (and dependent on path), the qualitative difference, which we associate with covalent bottclinq, is not. For this reason, it is absolutely essential to know on which side of a diagram such as Fig. 2-3 or Fig. 2-4 a particular system lies. For example, in covalent silicon, bonding-antibonding splitting is the large term and the sp splitting is the small one. That statement explains why there is a gap between occupied states and unoccupied states, which makes covalent silicon a semiconductor, and knowing this guides us in numerical approximations. Similarly, in metals, bonding-antibonding splitting is the small term and the sp splitting the large term; this explains why it is a metal and guides our numerical approximations in metals. If we wished to make full, accurate machine calculations we would never need to make this distinction; we could simply look at the results of the full calculation to check		

for the presence of an energy gap. Instead, our methods are designed to result in intuitive understanding and approximate calculations of properties, which will allow us to guess trends without calculations in some cases, and which will allow us to treat complicated compounds that would otherwise be intractable by full, accurate calculation in other cases.

The diagram at the bottom of Fig. 2-3 was drawn to represent silicon but also, surprisingly, illustrates the homopolar series of semiconductors c, Si, Ge, and Sn. The internuclear distance is smallest in diamond, corresponding to the largest gap, far to the right in the figure. The internuclear distance becomes larger element by element down the series, corresponding to progression leftward in the figure to tin, for which the gap is zero. (Notice that in a plot of the bands, as in Fig. 2-2, the gap can vary with wave number. In tin it vanishes at only one wave number, as will be seen in Chapter 6, in Fig. 6-10.) Nonetheless we must regard each of these semiconductors—even tin—as a covalent solid in which the dominant energy is the

bonding-antibonding splitting. We can define a "metallicity" that increases from c to Sn, reflecting a decreasing ratio of bonding-antibonding splitting to sp splitting; nevertheless, if the structure is tetrahedral, the bonding-antibonding splitting has won the contest and the system is covalent. The discussion of Fig. 2-3 fits well with the LCAO description but the degree to which a solid is covalent or metallic is independent of which basis states are used in the calculation. Most of the analysis of covalent solids that will be made here will be based upon linear combinations of atomic orbitals, but we also wish to understand them in terms of free-electron-like behavior. (These two extreme approaches are illustrated for cesium chloride in Fig. 2-2.) Free-electron-like behavior is treated in Chapter 18, where two physical parameters will be designated, one of which dominates in the covalent solid and one of which dominates in the metallic solid. It can be useful here to see how these parameters correspond to the concepts discussed so far. In Fig. 2-2, the width of the		

bands, approximately Ep — Es, corresponds to the kinetic energy, £F, of the highest filled states. The bonding-antibonding splitting similarly corresponds to the residual splitting between bands which was suppressed completely in Fig. 2-2,b. For metals, this residual splitting is described by a pseudopotential. In metals, the small parameter is the pseudopotential divided by the Fermi energy (corresponding to the ratio of bonding-antibonding splitting to sp splitting, or the reciprocal of the metallicity). In the covalent solids, on the other hand, we would say that the pseudopotential is the dominant aspect of the problem and the kinetic energy can be treated as the small correction. In fact, in Chapter 18 the pseudopotential approach will be applied to simple tetrahedral solids; there, treating kinetic energies as small compared to the pseudopotential leads to a simple description of the covalent bond in which a one-to-one correspondence can be obtained between matrix elements of the pseudopotential (that is, between plane waves) and		

matrix elements of the Hamiltonian between atomic states. The correspondence between these two opposite approaches is even more remarkable than the similarity between the LCAO and free-electron bands in Fig. 2-2, though it is the latter similarity which will provide us with LCAO matrix elements.

Now, as an introduction to polar semiconductors, let us follow the variation of electronic structure, beginning with an elemental semiconductor and moving to more polar solids. For this, germanium is a better starting point than silicon, and in order of increasing polarity the series is Ge, GaAs, ZnSe, and CuBr. The total number of electrons in each of these solids is the same (they are isoelectronic) and the structure is the same for all; they differ in that the nuclear charge increases on one of the atoms (the anion) and decreases on the other (the cation). The qualita-

FIGURE 2-5

Change in the bands as a homopolar semiconductor is made increasingly polar, and then as the two atom types are made more alike without broadening the levels.

tive variation in electronic structure in this series is illustrated in Fig. 2-5,a. Bear in mind that even in nonpolar solids there are two types of atomic sites, one to the right and one to the left of the horizontal bonds in the figure. In polar solids the nuclear charge on the atom to the right is increased, compound by compound. This will tend to displace the bond charges (electron density) toward the atom with higher nuclear charge (center diagram in Fig. 2-5,a) and, in fact, the corresponding transfer of charge in most cases is even larger than the change in nuclear charge, so the atom with greater nuclear charge should be thought of as negative; hence, the term anion is used to denote the nonmetallic atom. At high polarities most of the electronic charge may be thought of as residing on the nonmetallic atom, as shown.

The most noticeable change in the energy bands of Fig. 2-5,b, as polarity increases, is the opening up of a gap between the valence bands as shown. There is also a widening of the gap between valence and conduction bands and some broadening of the valence band. In extremely polar solids, at the center of

the figure, the valence band, to a first approximation, has split into an anion s band and three narrow anion p bands. The conduction bands in this model—the unoccupied bands—also split into s bands and p bands, but in a real crystal of high polarity, the bands for unoccupied orbitals remain very broad and even free-electron-like. We can complete the sequence of changes in the model shown in Fig. 2-5 by pulling the atoms apart to obtain isolated free atom energies. Perhaps the simplest path is that shown on the right side of Fig. 2-5, where the metallic and nonmetallic atoms become more alike and where the individual energy bands remain narrow. Where the levels cross, electrons of the anion fill available orbitals of the cation; the crossing results in a reduction of the atomic charges to zero. By comparing Fig. 2-5 with Fig. 2-3, we can see that there is no discontinuous change in the qualitative nature of the electronic structure in going from homopo- lar to highly polar solids of the same crystal structure (Fig. 2-5), but that discontinuity is encountered in going from the atomic electronic		

structure to the covalent one (Fig. 2-3). Properties vary smoothly with polarity over the entire range. This feature has been apparent for a long time and led Pauling to define ionicity in terms of energies of formation in order to provide a scale for the trend (Pauling, 1960). Coulson et al. (1962) redefined ionicity in terms of an LCAO description much like the one we shall use in Chapter 3. Phillips (1970) gave still a third definition in terms of the dielectric constant. The formula for polarity of a simple bond, introduced in Eq. (1-37), is essentially equivalent to the ionicity defined by Coulson, but the ionicities defined by Pauling and by Phillips are to a first approximation proportional to the square of that polarity. We will use the term polarity to describe a variation in electronic structure in covalent solids, and the particular values defined by Eq. (1-37) will directly enter the calculation of some properties. We do not use polarity to interpolate properties from one material to another. However, such interpolative approaches are commonly used, and degree of ionicity or polarity is

frequently used to rationalize trends in properties. Therefore it is best to examine that approach briefly. The distinction between these two approaches is subtle but of fundamental importance. We have seen that there are trends with polarity and with metallicity among the tetrahedral solids. One of the trends is the decrease, with increasing metallicity and increasing polarity, of the angular rigidity that stabilizes the open tetrahedral structure. Thus, if either increases too far, the structure collapses to form a close- packed structure. When this happens, the new system has a qualitatively different electronic structure, and different concepts and approximations become appropriate. We may think of this as analogous to a phase diagram, as illustrated in Fig. 2-6. If a combination of atoms (e.g., lithium and flourine) is too polar, a close-packed rocksalt structure is formed. LiF is an ionic crystal and most frequently the best initial approximation to the electronic structure is based on independent ions, which we used in the discussion of the cesium		

chloride energy bands. Ionic solids can be distinguished from covalent solids by their characteristic crystalline structures, a topic that will be taken up later. When the metallicity is too great, a close-packed structure again becomes more Polarity FIGURE 2-6 A schematic phase diagram indicating the three qualitatively different types of solids discussed in the book. The phase boundaries are topologically correct but details of shape are only schematic. Stable. In this case the electronic structure ordinarily approximates that of a free-electron gas and may be analyzed with methods appropriate to free-electron gases. Again, the crystal structure is the determining feature for the classification. When tin has a tetrahedral structure it is a covalent solid; when it has a close- packed white-tin structure, it is a metal. Even silicon and germanium, when melted, become close-packed and liquid metals. To complete the “ phase diagram,” there must also be a line separating metallic and ionic systems. Materials near		

this line are called intermetallic compounds; they can lie on the metallic side (an example is Mg2Pb) or on the ionic side (for example, CsAu). Consideration of intermetallic compounds takes the trends far beyond the isoelectronic series that we have been discussing. The sharp distinction between ionic and covalent solids is maintained in a rearrangement of the periodic table of elements made by Pantelides and Harrison (1975). In this table, the alkali metals and some of their neighbors are transferred to the right (see Fig. 2-7). The elements of the carbon column (column 4) and compounds made from elements to either side of that column (such as GaAs or CdS) are covalent solids with tetrahedral structures. Compounds made from elements to either side of the helium column of rare gases (such as KC1 or CaO) are ionic compounds with characteristic ionic structures. A few ionic and covalent compounds do not fit this correlation; notably, MgO, AgF, AgCl, and AgBr are ionic compounds, and MgS and MgSe can occur in either		

ionic or covalent structures. (Notice that Mg is found both in column 2 and column 10). The interesting isoelectronic series for ionic compounds will be those such as Ar, KC1, CaS, and ScP, obtained from argon by transferring protons between argon nuclei. In this case the ion receiving the proton is the metallic ion and the electronic structure is thought of as a slightly distorted rare gas structure. This model leads to a theory of ionic-compound bonding that is even simpler than the bonding theory for covalent solids. The Pantiledes-Harrison rearrangement of the periodic table is used as the format for the Solid State Table, where the parameters needed for the calculation of properties have been gathered.

2- D Solid State Matrix Elements

Almost all of the discussion of covalent and ionic solids in this book is based upon descriptions of electron states as linear combinations of atomic orbitals. In order to obtain numerical estimates of properties we need numerical values for the matrix elements giving rise to the covalent and polar energies for the properties being considered. There is no best choice for these parameters since a trade-off must be made between simplicity (or universality) of the choice and accuracy of the predictions that result when they are used. Clearly if different values are used for each property of each material, exact values of the properties can be accommodated. We shall follow a procedure near the opposite extreme, by introducing four universal parameters in terms of which all interatomic matrix elements between s and p states for all systems can be estimated. We shall also use a single set of atomic s and p orbital energies throughout. These are the principal parameters needed for the entire range of properties, though the accuracy of the corresponding predictions is limited.

One might at first think that interatomic matrix elements could be calculated by using tabulated atomic wave functions and potentials estimated for the various solids. Such approaches have a long history of giving poor numerical results and have tended to discredit the LCAO method itself. However, the difficulty seems to be that though true atomic orbitals do not provide a good basis for describing electronic structure, there are atomiclike orbitals that can provide a very good description. One can therefore obtain a useful theory by using LCAO formalism but obtaining the necessary matrix elements by empirical or semiempirical methods.

One of the oldest and most familiar such approaches is the “Extended Hueckel Approximation” (Hoffman, 1963.) Let us take a moment to examine this approach, though later we shall choose an alternative scheme. Detailed rationalizations of the approach are given in Blyholder and Coulson (1968), and in Gilbert (1970, p. 244); a crude intuitive derivation will suffice for our purposes, as follows. We seek matrix elements of the Hamiltonian between atomic orbitals on adjacent atoms, (p\H\cc). If I a) were an eigenstate of the Hamiltonian, we could replace HI a) by Ea|a), where £a is the eigenvalue. Then if the overlap (,P\oc) is written

Spa, the matrix element becomes EaSpa. This, however, treats the two

orbitals differently, so we might use the average instead of Ea. Finding that this does not give good values, we introduce a scale factor G, to be adjusted to fit the properties of heavy molecules; this leads to the extended Hueckel formula: (.PịHịù) = GSpa(ep + ea)/2. (2-12) These matrix elements are substituted into the Hamiltonian matrix of Eq. (2-2) for a molecule, or a cluster of atoms, and the matrix is diagonalized. A value of G = 1.75 is usually taken; the difference from unity presumably, arises from the peculiar manner in which nonorthogonality is incorporated. The Extended Hueckel Approximation and a wide range of methods that may be considered as descendents of it (e.g., the CNDO method—Complete Neglect of Differential Overlap) have enjoyed considerable success in theoretical chemistry. Some machine calculation is required, first in determining the parameters s from tabulated wave functions or numerical approximations to them, and second in solving the resulting simultaneous equations, as at Eq. (2-2).		

This difficulty is exacerbated by the fact that s drops rather slowly with increasing distance between atoms, so a very large number of matrix elements are required. The computation required for any given system is very small, however, in comparison with what is required to obtain more accurate solutions. Once an Extended Hueckel Approximation has been made, direct machine computations of any property can be made and alternatives to the simplest approximations—e.g., Eq. (2-12)— can be made which improve agreement with the experimental values. Such improvements are described in detail by Pople and Beveridge (1970). Combining descriptions of electronic structure that are essentially correct, with the use of high-speed computers, and the results of a number of years of trial and error in correcting the simplest approximations, probably provide the most accurate predictions of the diverse properties of complex systems that are presently available. For isolated properties, such as the energy bands of solids, other computer methods are much more reliable and accurate.		

The approach that will be used in this text is different, in that the description of electronic structures is greatly simplified to provide a more vivid understanding of the properties; numerical estimates of properties will be obtained with calculations that can be carried through by hand rather than machine. We shall concentrate on the “physics” of the problem. In this context a semiempirical determination of matrix elements is appropriate. The first attempt at this (Harrison, 1973c) followed Phillips (1970) in obtaining the principal matrix element v2 from the measured dielectric constant. A second attempt (Harrison and Ciraci,1974) used the principal peak in the optical reflectivity of the covalent solids, which we shall come to later, as the basis for the principal matrix element; this led to the remarkable finding that v2 scaled from material to material quite accurately as the inverse square of the interatomic distance, the bond length d, between atoms. A subsequent study of the detailed form of valence bands (Pantelides and Harrison, 1975), combined with v2 determined from the		

peak in optical reflectivity, gave a complete set of interatomic matrix elements for covalent solids with the finding that all of them varied approximately as d~2 from material to material. The reason for this dependence recently became very clear in a study of the bands of covalent solids by Froyen and Harrison (1979). They took advantage of the similarity of the LCAO bands and free-electron bands, noted in Fig. 2-2. By equating selected energy differences obtained in the two limits, they derived formulae that had this dependence for all of the interatomic matrix elements. We may in fact see in detail how this occurs by considering Fig. 2-2. The lowest band, labelled s in Fig. 2-2,a, was given by Eq. (2-5). For k in an x-direction, it becomes E(k) = es — 4V2 — 2V2 cos ka, varying by 4VZ from r (where k = 0) to X (where k = %/a). The free-electron energy in Fig. 2-2,b varies by (h2/2m)(n/a)2 over the same region of wave number space for the lowest band. Thus, if both limiting models are to be appropriate, and therefore consistent with each other, it must follow that v2 = t]h2/{ma2) with rj =		

7t2/8 = 1.23. This predicts the dependence upon the inverse square of interatomic distance and a coefficient that depends only upon crystal structure. A similar comparison of the second band gives the same form with a different coefficient for the matrix element v'2 between p states. This simplest model is not so relevant, but it illustrates the point nicely. Before going to more relevant systems we must define more precisely the notation to be used for general interatomic matrix elements.

These matrix elements will be important throughout the text; they are specified here following the conventions used by Slater and Koster (1954) and used earlier while discussing the diatomic molecule. In general, for a matrix element <a|//|/j> between orbitals on different atoms we construct the vector d, from the nucleus of the atom of which I a) is an orbital (the “ left ” atom) to that of the atom of which I/?) is an orbital (the “right” atom). Then spherical coordinate systems are constructed with the z-axes parallel to d, and with origins at each atom; the angular form of the orbitals can be taken as Y?(9, ệ) for the left orbital and VỊ! (O', Ộ) for the right orbital. The angular factors depending upon ệ combine to (Notice that the wave function (a I is the complex conjugate of I a).) The integration over ậ gives zero unless m' = m. Then all matrix elements (a|H||S) vanish unless rri = m, and these are labelled by Ớ, n, or Ỏ (in analogy with s, p, d) for m — I). 1, and 2 respectively. Thus, for example, the matrix element Vspa corresponds to 1 = 0, I = 1, m = 0. Slater and Koster (1954) designated matrix elements by enclosing the indices within parentheses; thus, the element VWm used in this book and their (Wm) are the same.

We saw how formulae for the matrix elements can be obtained by equating band energies from LCAO theory and from free-electron theory in Fig. 2-2. Froye.1 and Harrison (1979) made the corresponding treatment of the tetrahedral solids, again including only matrix elements between nearest-neighbor atoms. The form of their results is just as found for the simple cubic case

Notice that the subscript m is a quantum number but the m in the denominator

Dimensionless coefficients in Eq. (2-13) determining approximate interatomic matrix elements. Theoretical values Coefficient Simple cubic structure Tetrahedral structure Adjusted value* NOTE: Theoretical values (Froyen and Harrison, 1979) were obtained by equating band energies from I (\0 and free-eiectron theory, as described in the text. Adjusted values (Harrison, 1976b, 1977a) were obtained by fitting tile energy bands of silicon and germanium; the adjusted values appear in the Solid State Table. is the electron mass. The length d is the internuclear distance, equal to a in the simple cubic structure. If d is given in angstroms, this form is easily evaluated, using h2/m = 7.62 eV-Å2. In Table 2-1 we give the values of the dimensionless cnefficients obtained by Froyen and Harrison for both the simple cubic and Id rahedral structures. The calculation is closely related to that just carried through for the bands of Fig. 2-2, and in fact, the VSS<J matrix element for the simple cubic case is just the negative of the v2 value evaluated there, leading to the		

t]ssa = — 7t2/8. wv shall see in Section 18-A exactly how the other theoretical coefficients listed were obtained.

Motice that the coefficients obtained for the tetrahedral structure differ from those obtained for the simple cubic structure and indeed the coefficients for any mu; structure depend somewhat upon which band energies are used. However, the differences are not great and we shall neglect them. The coefficients we shall use are close to those given by Froyen and Harrison (1979) for the tetrahedral structure, but were obtained somewhat earlier by Harrison (1976b), who adjusted tliL'm to give the interatomic matrix elements found by Chadi and Cohen (1975) in fitting the known energy bands of silicon and germanium. The average of the coefficients so obtained for silicon and germanium is listed in Table 2-1 in the column headed “Adjusted,” and these are the values listed in the Solid State Table and used throughout this text. Also listed in the Solid State Table are forms lor predicting matrix elements involving atomic d states, formulae which will be developed in Chapter 20.

The coefficients in Table 2-1 have been obtained entirely in the context of nearest-neighbor coupling between states. They would have been different if a

*For recent developments, see the Preface to the Dover Edition.

TABLE 2-2

Atomic term values from Herman and Skillman (196.Í). or extrapolated from their values.

Atomic term value (eV)

second-neighbor LCAO fit had been used, for example, and it would not therefore be appropriate to use them if the description of the bands were to be extended to second-neighbor interactions.

It will ordinarily be more convenient in solids to use the forms for angular dependence, x/r, y/r, and z/r, as in Eq. (1-20), rather than the forms Y”i(0, <p). Then in order to obtain matrix elements involving these orbitals, we need to expand the

NOTE: These values appear also in the Solid State Table.

p orbital in question in terms of 17, which are defined with respect to the coordinate system discussed above. For p orbitals this is quite simple.

For the simplest geometries it leads to the identification of matrix elements shown in the upper four diagrams of Fig. 2-8. For arbitrary geometries the result depends upon the direction cosines giving the vector d in the coordinate system of X, y, and z; this is illustrated at the bottom in Fig. 2-8. The corresponding transformations for d

FIGURE 2-8

The four types of interatomic matrix elements entering the study of s- and p-bonded systems are chosen as for diatomic molecules as shown in Fig. 1-11. Approximate values for each are obtained from the bond length, or internuclear distance, í/, by Vfj — riijtS/md2, with tiij taking values given in Table 2-1 and in the Solid State Table at the back of the book. When p orbitals are not oriented simply as shown ill the upper diagrams, they may be decomposed geometrically as vectors in order to evaluate matrix elements as illustrated in the bottom diagrams. It can be seen that the interatomic matrix element at the bottom right consists of cancelling the contributions that lead to a vanishing matrix element.

orbitals as well as p orbitals will be given in detail in

Table 20-1, but for s and p orbitals the simple vector transformations illustrated in Fig. 2-8 should be sufficient; the results can be checked with Table 20-1. When we give the Froyen-Harrison analysis in Chapter 18-A, we shall see that the same procedure can give an estimate of the energy difference Ep — £s. It is of the correct general magnitude but fails to describe the important trend in the energy bands among the covalent solids c, Si, Ge, and Sn. Furthermore, it does not provide a means of estimating term-value differences such as scp — e“ in polar solids. Thus, for these intra-atomic parameters we shall use calculated atomic term values, which are listed in Table 2-2. A comparison shows them to be roughly consistent with term values obtained in the fit to known bands done by Chadi and Cohen (1975) for the polar semiconductors as well as for silicon and germanium. This particular set of calculated values (by Herman and Skillman, 1963) was chosen since the approximations used in the calculation were very similar to those used in determining		

the energy bands that led to the parameters in Table 2-1. The values would not have differed greatly if they were taken from Hartree-Fock calculations (such values are tabulated in Appendix A). Values based on Hartree-Fock calculations have the advantage of giving good values for d states. Therefore, though the calculations in this book are based upon the Herman-Skillman values, for some applications the Hartree-Fock values may be better suited. Notice that as absolute numbers the atomic energy values have only limited meaning in any case. Imagine, for example, that the value Ep for oxygen correctly gives the energy required to remove an electron from an isolated oxygen atom in space. If this atom is brought close to the surface of a metal (or, almost equivalently, to the surface of a covalent solid with a large dielectric constant) but not close enough for any chemical bonding to take place, how much energy is now required to remove the electron from the oxygen? One way to calculate this is to move the neutral atom to infinity, with no work required, remove the		

electron requiring £p, and then return the oxygen ion to its initial position; as it returns it gains an energy e2/4d from the image field, where d is the final distance from the surface. The resultant correction of fip, with d equal to 2 Â, is 1.8 eV, far from negligible. The precise value is uncertain because of the dielectric approximation, the uncertainty in the d used, and other effects, but we may expect that significant corrections of the absolute energies are needed relative to the values in vacuum. The reason that the values are nevertheless useful as parameters is that in solids such corrections are similar for all atoms involved and the relative values are meaningful. How do the values obtained from Tables 2-1 and 2-2 compare with the values obtained directly by fitting energy bands? This comparison is made in Table 2-3 for the covalent systems studied by Chadi and Cohen. Agreement is semiquantitative throughout and all trends are reproduced except the splitting of values for VsptT in the compounds. The discrepancies are comparable		

to the differences between different fits (the most recent fits are used here), thus justifying the use of the simple forms in our studies. Significantly different values are obtained if one includes a greater number of matrix elements in the fit (Pandey, 1976) and would be appropriate if we were to include these matrix elements in the calculation of properties other than the bands themselves. Significantly different values have also been given by Levin (1974).

The coefficients from Table 2-1 and atomic term values from Table 2-2 will suffice for calculation of an extraordinarily wide range of properties of covalent and ionic solids using only a standard hand-held calculator. This is impressive testimony to the simplicity of the electronic structure and bonding in these systems. Indeed the same parameters gave a semiquantitative prediction of the one-electron energy levels of diatomic molecules in Table 1-1. However, that theory is intrinsically approximate and not always subject to successive correc-

TABLE 2-3

Matrix elements from the Solid State Table, compared with values (in parentheses) from fits to individual bands. All values are in eV. SOURCES of data in parentheses: c from Chadi and Martin (1976); Si and Ge from Chadi and Cohen (1975); GaAs and ZnSe from Chadi and Martin (1976). NOTE: Where two values of Vspr are given for compounds, the first vaiue is for an s state in the nonmetallic atom and p state in the metallic atom. States are reversed for the second value. Where two values of («p — cs)/4 are listed, the first value is for the metallic atom, the second for the nonmetallic atom. tions and improvements. In most cases our predictions of properties will be accurate on a scale reflected in Table 2-3, and though the introduction of further parameters allows a more accurate fit to the data, it may be that improvements at a more fundamental level are required for a more realistic treatment and that these improvements cannot be made without sacrificing the conceptual and computational simplicity of the picture that will be constructed in the course of		

this book. Before proceeding to quantitative studies of the covalent solids it is appropriate to comment on the concept of “electronegativity,” introduced by Pauling to denote the tendency of atoms to attract electrons to themselves (discussed recently, for example, by Phillips, 1973b, p. 32). It may be an unfortunate term since the positive terminal of a battery has greater electronegativity than the negative terminal. Furthermore, it was defined to be dimensionless rather than to have more natural values in electron volts. It would be tempting to take the hybrid energy values of Table 2-2 as the definition of electronegativity, but it will be seen that in some properties the energy Ep is a more appropriate measure. Therefore it will be a wiser choice to use the term only qualitatively. Then from Table 2-2 (or from Fig. 1-8) we see that the principal trend is an increase in electronegativity with increasing atomic number proceeding horizontally from one inert gas to the next (e.g., from neon, Na, Mg, Al, Si, p,		

s, and Cl to argon). In addition, the elements between helium and neon have greater electronegativity than the heavier elements. It is useful to retain " electronegativity " to describe these two qualitative trends.

2- E Calculation of Spectra

We have seen that in solids, bands of electron energies exist rather than the discrete levels of atoms or molecules. Similarly there are bands of vibration frequencies rather than discrete modes. Thus, to show electron eigenvalues, a curve was given in Fig. 2-2 rather than a table of values. However, a complete specification of the energies within the bands for a three-dimensional solid requires a three-dimensional plot and that cannot be made; even in two dimensions an attempt is of limited use. Instead, a convenient representation of electronic structure can be made by plotting the number of states, per unit energy, as a function of energy. This loses the information about, for example, electron velocity, since that requires a knowledge of energy as a function of wave number. However, it is all that is needed to sum the energies of

the electrons for given atomic arrangements. Calculation of such a spectrum might seem straightforward, but if done by sampling, it requires an inordinate amount of calculation. For example, to produce a plot we might divide the energy region of interest into one thousand intervals and then evaluate the energies (as we did in Section 2-A) over a closely spaced grid in the Brillouin Zone, keeping track of the number of eigenvalues obtained in each interval. A great increase in efficiency can be obtained by noting that the energy bands have the full symmetry of the Brillouin Zone—in the case of CsCl, a cube—so that the entire Brillouin Zone need not be sampled. One could sample one half the zone and multiply the results by two, one eighth and multiply by eight, or in fact, for a cube, one forty-eighth suffices. However, even in a sample of thousands of values, the resulting histogram shows large statistical fluctuations. Therefore an alternative approach is required. The approach most commonly used, and used extensively in the curves in		

this book, is the Gilat-Raubenheimer scheme (Raubenheimer and Gilat, 1966). In this scheme, the idea is to replace the true bands by approximate bands, but then to calculate the density of levels for that spectrum accurately. This is done by dividing up the Brillouin Zone, or a forty-eighth of the zone for cubic symmetry, into cells; of the order of fifty may be appropriate; Raubenheimer and Gilat used cells in the shape of cubes. They then fit each band in each cell by a linear expression, $Ek = E0 + A1 kx + A2ky + A3kz$, with k measured from the center of the cell. Then the energy region of interest for the system is divided into some 1000 energy intervals and the contribution to each of these intervals is accurately and analytically obtained from the linear values of the bands in each cell. This is illustrated for one dimension in Fig. 2-9. We see that the distribution of the approximate bands is obtained exactly. This turns out to eliminate most of the statistical error and to give very good results.

In the Gilat-Raubenheimer scheme it is inconvenient to obtain the necessary values of the gradient of the energy with respect to wave number in each cell, and the cubes do not fit the Brillouin Zone section exactly, so there are problems in calculating the energy at the surface of the section. For this reason Jepsen and Andersen (1971) and later, independently, Lehman and Taut (1972) replaced cubes by tetrahedra and wrote the distribution of energies in terms of the values at the four comers. A clear description of this much simpler approach is given by Rath and Freeman (1975), who include the necessary formulae. It is also helpful to see one manner in which the Brillouin Zone can be divided into cells. This is shown in Fig. 2-10, This procedure has been discussed also by Gilat and Bharatiya (1975). Another scheme,

(c) Number of states contributed in each interval

FIGURE 2-9

A schematic representation of the Gilat-Raubenheimer scheme for calculating densities of states. The energy bands (a) are replaced by linear bands (b) in each cell. The contribution by each cell to each of a set of small energy intervals (c) is then obtained analytically.

utilizing a more accurate approximation to the bands, has been considered recently by Chen (1976).

In some sense this is a computational detail, but the resulting curves are so essential to solid state properties that the detail is important. Once a program has been written for a given Brillouin Zone, any of the spectra for the corresponding structure can be efficiently and accurately obtained from the bands themselves.

PROBLEM 2-1 Calculating one-dimensional energy bands

Let us make an elementary calculation of energy bands, using the notation of LCAO theory. For many readers the procedure will be familiar. Consider a ring of N atoms, each with an s orbital. We seek an electronic state in the form of an LCAO,

where the integers a number the atoms. We can evaluate the expectation value of the energy, considering all atoms to be identical, so (a I HI a) = R is the same for all a. We can also neglect all matrix elements (a\H\p'), except if a and /? differ by one; we write that

FIGURE 2-10

(a) The body-centered-

cubic Brillouin Zone is divided into 48 equivalent pyramidal segments. (Two such pyramids are required for face-centered cubic zones.) (b) The pyramid is cut by equally spaced planes parallel to the base, (c) Most of the slab may be subdivided into triangular prisms. An edge is left over on the right which can be divided into triangular prisms with one tetrahedron left over. Each triangular prism (d) may finally be divided into three tetrahedra, (e). This divides the Brillouin Zone entirely into tetrahedra of equal volume. The bands are taken to be linear in wave number within each tetrahedron. We shall treat the uj as independent of ua and minimize the expression with respect to UĨ, giving a linear algebraic equation for each a. (a) Show that for any integer it there is a solution for all of these equations of the form (b) Give the energy as a function of n, and sketch it as a function of n/N for large N. Include positive and negative n. (c) Obtain the value of A that normalizes the electron state.		

(d) Show that for an n outside the range — N/2 <n< N/2, the electron state obtained is identical to that for some n within this range (within the Brillouin Zone). It suffices to prove that for given n the ua are unchanged by the addition of N to n. PROBLEM 2-2 Electron dynamics Consider an electron in a one-dimensional energy band given by E(k) = — y2 COS ka in a Brillouin Zone, —n/a < k < n/a. At time t = 0, with the electron having wave number k = 0, apply an electric field ê. Obtain the energy, the speed, and the position of the electron as a function of time. The behavior will be oscillatory. It can be thought of as acceleration of the electron followed by gradual diffraction caused by the lattice. How many lattice distances (each distance a = 2 Å) does the electron go if v2 = 2 eV and the field is 100 volts per centimeter?		

FIGURE 1-4	[redacted]	
Three p orbitals, each directed along a different Cartesian axis.	[redacted]	
(a) Fishnet plot (b) Contour plot (c) Schematic representation	[redacted] [redacted] [redacted]	
FIGURE 1-5	[redacted]	
Three ways of representing atomic p orbitals.	[redacted]	
represented in terms of Cartesian coordinates in the form	[redacted]	
Fig. 1.6 corresponds to the third angular form listed in Eq. (1-21).	[redacted]	
A very important feature of d orbitals is that they are concentrated much more closely at the nucleus than are s and p orbitals. The physical origin of this can be	[redacted]	
FIGURE 1-6	[redacted]	
The d orbiiai corresponding to the xy/r2 form in Eq. (1-21).	[redacted]	
understood in terms of the n — 3 state of hydrogen. The 3s, 3p, and 3d states all have the same energy, but of these	[redacted]	

three, the d 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 p orbital.

The s state, which Corresponds classically to an electron vibrating radially through the nucleus, stretches even further from the nucleus. Therefore, d states tend to be influenced much less by neighboring atoms than are s and p states of similar energy. We shall have little occasion to discuss /'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

[redacted]

[redacted]

eigenvalues, or other eigenvalues measured from the same zero of energy, will be designated by F. rather than E. For hydrogen, …………… (1'22)	[redacted] [redacted]	
where a0 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).	[redacted]	
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 Is 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 CO = AE/h, where AE 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.	[redacted]	

	[redacted]	
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, 5-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 Is, 2s, 2p, 3s, 3p, 3d, 45, and 4p orbitals as the atomic number (equal to the number of protons in the nucleus) increases.	[redacted]	
In Litium, atomic number 3, the Is level has dropped to a very low energy and is occupied by two electrons. The Is orbital is considered part of the atomic core of Litium; a single electron occupies a 2s orbital. In the Litium row, all elements, to	[redacted]	

neon, z= 10, have a “Litium core”; the energy levels in successive atoms FIGURE 1-7 Energy-level diagram for atomic hydrogen. The lines are branched at the right to show how many orbitals each line represents. continue to drop in energy and sp splitting (the difference in energy between levels, or Elp — £2s) 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 Litium row, but the number of states in the atomic core is larger in lower rows of the table.	[redacted] [redacted] [redacted] [redacted]	

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 5 and p levels in each row (and sometimes those filling d levels) are traditionally called valence electrons and determine

FIGURE 1-9
Periodic chart of the elements.

chemical properties. They also have excited states available to them within a

[redacted]

[redacted]

[redacted]

[redacted]

[redacted]

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.	[redacted]	
1- C Electronic Structure of Small Molecules	[redacted]	
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.	[redacted]	

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

[redacted]

[redacted]

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.	[redacted]	
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.	[redacted]	

<table>
<tr><td>We let the index a = 1, 2, 3run 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</td><td>[redacted]</td><td></td></tr>
<tr><td>where the ua are the coefficients that must be determined. The orbitals I a) representing the basis states are selected to be normalized, (a I a) = 1. We also take them (as in Section 1-A) to be orthogonal to each other; </?|a> = 0 if p =£ a.</td><td>[redacted]</td><td></td></tr>
<tr><td>Next, we must find the coefficients ua of Eq. (1-23) for the electron state of lowest energy, by doing a variational calculation as indicated in Section 1-A. That is, we evaluate the variation</td><td>[redacted]</td><td></td></tr>
<tr><td>~~In obtaining the second form, we allow the ua 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</td><td>[redacted]</td><td></td></tr>
</table>

with respect to a particular uf be zero (as in Eq. 1-10), we obtain or more simply, with E — (ỷ IHI ệ)/(ệ I ệ). (Later, specific eigenvalues will be written as e’s with appropriate subscripts.) There is one such equation for each p corresponding to a basis state. We have obtained a set of simultaneous linear algebraic equations with unknown coefficients Ma. 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 lowest electron state having a wave function orthogonal to that of the first, and so on. The solution of these equations gives the ua 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,	[redacted]	

det(tf^ - Eỏp«) = 0, (1-27)	[redacted]	
	[redacted]	
where “det ” means “determinant of” and ôpa is the unit matrix. We have made one further simplification of the notation in writing Hịla = (p\H\oc). 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.	[redacted]	
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, H2 • For the hydrogen molecule, we use two orbitals, 11) and 12), which represent Is states on atoms 1 and 2 respectively. Eq. (1-26) then becomes	[redacted]	
where we have made the natural definition of the Is	[redacted]	

energy £s = (l|H|l) = (21H12). The energy Es 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 Is function slightly different from that of the free atom. We have defined a matrix element v2 = — #12 = —H21 to correspond to the notation we shall use later. The matrix element v2 is called a covalent energy, and is defined to be greater than zero; v2 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 as well as a high-energy solution, the antibonding state, with	[redacted]	

Substituting the eigenvalues given in Eqs. (1-29) and (1-30) back into Eq. (1-28) gives coefficients U1 and u2 . For the bonding state, Uị = u2 = 2~112, and for the antibonding state, Mj = —u2 = 2”1/2. The conventional depiction of these bond orbitals and antibond orbitals is illustrated in Fig. 1-10,a. Notice that the use of orthogonal eigenfunctions for the two atomic states (taking the overlap (112) = 0) is not consistent with Fig. 1-10,b, 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 v2 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	[redacted] [redacted] [redacted]	

molecule, the lowering of the energy of the molecule, in comparison to separated 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.	[redacted]	
Bonding orbital ca	[redacted]	
Antibonding energy level	[redacted]	
Kh Bonding energy level	[redacted]	
(a) Homopolar diatomic molecule	[redacted]	
Antibonding orbital	[redacted]	
Bonding orbital	[redacted]	
(b) Heteropolar diatomic molecule	[redacted]	
FIGURE 1-10	[redacted]	
The formation of bonding and antibonding combinations of atomic orbitals in diatomic molecules, and the corresponding energy-level	[redacted]	

diagrams. 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.	[redacted]	

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.	[redacted]	
We found that hydrogen Is 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.	[redacted]	
Hydrogen is a very special case also when it is a part of other molecules. We saw that in the Litium 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	[redacted]	

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, CH_4, as “ neon ” with four protons split off from the nucleus, just as we can think of H_2 as “helium” with a split nucleus. 1- D The Simple Polar Bond In the H_2 molecule just discussed, the two hydrogen atoms brought together were identical, and their two energies Ss were the same. We shall often be interested in systems in which the diagonal energies ifn and H_{22} (that is, diagonal elements of the Hamiltonian matrix) are different; such molecules are said to have a hetero- polar or simply polar bond. Let us use, as an example, the molecule	[redacted]	

LiH. We expect the linear combinations to be those of the hydrogen Is orbitals and Litium 2s orbitals, though as we indicated at the end of the preceding section, special con-siderations govern molecules involving hydrogen.	[redacted]	
In calculating the energy of heteropolar bonds, Eqs. (1-28) must be modified so that £s is replaced by two different energies, £* for the low-energy state (for the energy of the anion) and fij for the high-energy state (for the energy of the cation).	[redacted]	
The value of one half of the anion cation energy-difference is the polar energy:	[redacted]	
It is convenient to define the average of the cation and anion energy, written as	[redacted]	
Then Eqs. (1-31) become	[redacted]	
The solution of Eqs. (3-34) is trivial:	[redacted]	

£b and £a 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 and u2 values for the bonding state by substituting £b for the energy E in Eqs. (1-34), the first equation of which can then be rewritten as	[redacted] [redacted]	

(1-36)	[redacted]	
Second, if the individual atomic wave functions do not overlap, the probability of finding the electron on atom 1 will be uị /(uḬ + uị) and the probability of finding it on atom 2 will be uị/ịuị + uị). 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 + 0Cp)/2 and the probability of finding it on atom 2 is (1 — ap)/2, where ap is the polarity defined by	[redacted]	
We can expect the dipole of the bond to be proportional to u\ — u\ = bcp. The polarity of the bond and the resulting dipole are central to an understanding of partially covalent solids.	[redacted]	
Another useful concept is the complementary quantity, covalency, defined by	[redacted]	
1- E Diatomic Molecules	[redacted]	

In Section 1-C we noted that molecular hydrogen is unique in that a single atomic state, the Is 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 2, Be2, B2, c2, N2, 02, and F2, 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

[redacted]

[redacted]

[redacted]

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 Py 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 Pz orbitals form bonding and antibonding combinations. The four resulting p-orbital combinations are called n states, by analogy with p states, because each has one unit of angular momentum around the molecular axis. The Tt states are also frequently distinguished by a g, for gemde (German for “ even ”), or	[redacted] [redacted]	

The coupling of atomic orbitals in Litium-row diatomic molecules, and the resultant bond designations (at right). u, 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 % orbitals, the bonding combination is ungerade a n orbital that is gerade (ng) is zero on the plane bisecting the bond. A feature of homopolar diatomic molecules is that s states and px states are also coupled, and all four states are required in the expansion of the corresponding molecular orbitals, called Ơ states. The bonding combination for a orbitals is gerade (Gg). The s and p states are hybridized in the molecule. (The ơ-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	[redacted]	

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 (Vspa, - Vspa) 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.	[redacted]	
FIGURE 1-12	[redacted]	
The development of molecular energy levels as a pair of Litium-row atoms is brought together (that is, internuclear distance d decreases from left to right).	[redacted]	
Let us trace the changes in energy that occur as a pair of identical atoms from the Litium 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 £s (one s orbital for each atom) and fip	[redacted]	

(three p orbitals for each atom, px, Py, and pz). 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 n orbitals oriented along the y-axis have the same energies as those oriented along the z-axis. The bonding and antibonding combinations for these are indicated by 1 nl§ and lng, 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 Ơ orbitals are, to a good approximation, a bonding combination of s states and an antibonding combination of s states, and a bonding combination of px states and an antibonding combination of px states, in order of increasing energy. The energies of the intermediate levels, indicated by 2ơ,, and 3 ơg in the figure, become comparable and should be thought of as

[redacted]

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 Litium row (Slater, 1968, pp. 451 and 452).	[redacted]	
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<7,, is never greater than that of either of the two high-energy bonding states 3ơg and \nu.	[redacted]	
(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	[redacted]	
As indicated in Section 1-A, the energy of electron states and their occupation by electrons are quite separate topics. For example, it is	[redacted]	

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 loca-tion, 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	[redacted] [redacted]	

diatomic molecule are both Litium, there are only two valence electrons, which would be put in the 2ơg bonding state; the qualitative picture of electronic structure and binding of Li 2 is exactly the same for H2; the levels deriving from the valence p state of Litium may be disregarded. If the molecule were Be2, there would be four electrons in the molecule; two would occupy the 2ơg bonding state, and the other two would occupy the 2<r„ 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 Be2 is found in nature. As the atomic number of the constituents increases, bonding and antibonding states are filled in succession. F2 would have enough electrons to fill all but the highest antibonding state, 3ơu. A pair of neon atoms would have enough electrons to fill all bonding and antibonding states and, like Be2, would not be bound at all.	[redacted]	

	[redacted]	
In 02, when the last levels to be filled are degenerate, a special situation occurs. Only two electrons occupy the lng state though there are states to accommodate four. There are different ways the state could be filled, and Hund’s rule tells us which arrangement will have lowest energy. It states that when there is 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	[redacted]	

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 exchange energy. It tends to be small enough that it is dominant only when there is orbital degeneracy, as in the case of 02, 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 Appendixes A and c.) In 02, the two degenerate lng states take one electron in a py state and one in a pz state. As a result, the charge density around the 02 molecule has cylindrical symmetry, though there is a net spin from the two electrons. In contrast, if both electrons were in py 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.	[redacted]	

In the same sense that H2 is like He (as mentioned at the end of Section 1-C), the molecule C2H4 is like 02, except that the two hydrogen protons are outside the carbon nucleus rather than inside. The number of electrons is the same in both C2H4 and 02 and essentially the same classification of electron levels can be made. However, if the protons in C2H4 are all placed in the same plane, the lnu 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 Py state and one pz state of parallel spin. Then the electron density would be	[redacted] [redacted]	

cylindrically symmetric as in oxygen, and the protons would rotate into perpendicular planes in order to attain lower Coulomb interaction energy. C_2H_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 C_2H_4. Furthermore, that conception can be quite different from solid to solid, depending on which stable configuration of atoms is present.	[redacted]	

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 vih = flip h2/(md2), where d is the internuclear distance and values for t]ijx are four universal constants for SSƠ, spa, ppơ, and ppn matrix elements, as given in the next chapter (Table 2-1). Furthermore, atomic term values (given in Table 2-2) can be used for Ep and fis. 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	[redacted] [redacted]	

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 major errors only for the ĩơg levels in 02 and F2. 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.

[redacted]

	[redacted]	
Heteropolar Bonds	[redacted]	
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 n 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 I'D.	[redacted]	
TABLE 1-1	[redacted]	
One-electron energies in homopolar diatomic molecules, as obtained by using solid state matrix elements. Values in parentheses are from accurate molecular orbital calculations. Shading denotes empty orbitals. Energies are in eV.	[redacted]	
SOURCES of data in parentheses: Li2, Be2, c2, Nj,	[redacted]	

and F2 from Ransil (1960); B2 from Padgett and Griffing (1959); 02 from Kotani, Mizuno, Kayama, and Ishiguro (1957); all reported in Slater (1968). There is, however, a complication in the treatment of the Ơ 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 a bonds, hybrid basis states can be made from s and p states, and these can be treated approximately as independent pairs, which reduces the prob-lem 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.	[redacted]	

Therefore, we will not discuss the special case of ơ-bondeđ hetero- polar molecule. PROBLEM 1-1 Elementary quantum mechanics An electron in a hydrogen atom has a potential energy, — e2/V. The wave function for the lowest energy state is \j/(r) = Ae~rla° where a0 is the Bohr radius, a0 = h2/me2, and A is a real constant. (a) Obtain A such that the wave function is normalized, (ệ I ệ} = 1. (b) Obtain the expectation value of the potential energy, (ệ\ VịiỊ/). (c) Calculation of the expectation value of the kinetic energy, K.E.^I^Vl^X is trickier because of the infinite curvature at /• = 0. By partial integration in Eq. (1-3), an equivalent form is obtained: Evaluate this expression to obtain K.E. (d) Verify that the expectation value of the total energy, <|//| vịiị1} + K.E. is a	[redacted]	

minimum with respect to variation of 00. Thus a variational solution of the form e~',r would have given the correct wave function. (e) Verify that this i//(r) is a solution of Eq. (1-5). PROBLEM 1-2 Atomic orbitals The hydrogen 2s and 2p orbitals can be written and (see Schiff, 1968, p. 94), and p orbitals can also be written with X replaced by V and by z. All four hydrogen orbitals have the same energy, — e2/(8flc). Approximate the Litium 2,5 and 2p orbitals by the same functions and approximate the Litium potential by — e2/r + ucore(r), where Calculate the expectation value of the energy of the 2s and 2p orbitals. The easiest way may be to calculate corrections to the — e2/(8a0) value. This gives the correct qualitative picture of the Litium 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 c2, obtain the Ơ 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

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

Solutions will be even or odd, by symmetry, so there can be solutions with u2 = Uị and w4 = —u3, and the above reduce to two equations in two unknowns. Solve them for E. Then, solve again with If2 = — IIỊ and «4 = u3 .

Confirm the values of these energies as given in Table 1-1 for c2.

The lowest state contains comparable contributions from the s and p orbitals. What is the fraction of s character, that is, (uị + uịỵiuị + uị + uị + ul)1

CHAPTER 2

Electronic Structure of Solids

SUMMARY

In solids, atomic valence levels broaden into bands comprising as many states as there are atoms in the solid. Electrons in these band states are mobile, each electron state being characterized by a momentum p or wave number

k = p/tt 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 bonds 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.

In this chapter we give a very brief description of solids, which is the principal subject of the book. The main goal is to fit solids into the context of atoms and molecules. In addition, we shall carefully formulate the energy band in the simplest possible case and study the behavior of electrons in energy bands.

2- A Energy Bands

When many atoms are brought together to form a solid, the number of electron states is conserved, just as in the formation of diatomic molecules. Likewise, as in diatomic molecules, the one-electron states for the solid

can, to a reasonable approximation, be written as LCAO’s. However, in solids, the number of basis states is great. A solid cube one centimeter on an edge may contain 1023 atoms, and for each, there is an atomic s orbital and three p orbitals. At first glance it might seem that such a problem, involving some 4 X 1023 equations, could not be attacked. However, the simplicity of the crystalline solid system allows us to proceed effectively and accurately. As the atoms are brought together, the atomic energy levels split into bands, which are analogous to the states illustrated for diatomic molecules in Fig. 1-12. The difference is that rather than splitting into a single bonding and a single antibonding state, the atomic levels split into an entire band of states distributed between extreme bonding and antibonding limits. To see how this occurs, let us consider the simplest interesting case, that of cesium chloride. The structure of CsCl is shown in Fig. 2-1,a. The chlorine atoms, represented by open circles, appear on the comers of a cube, and this cubic array		

is repeated throughout the entire crystal. At the center of each cube is a cesium atom (at the body-center position ill the cube). Cesium chloride is very polar, so the occupied orbitals lie almost entirely upon the chlorine atoms. As a first approximation we can say that the cesium atom has given up a valence electron to

(a) Crystal structure (b) Brillouin Zone

FIGURE 2-1

(a) A unit cube of the cesium chloride crystal structure, and (b) the corresponding Brillouin Zone in wave number space.

fill the shell of the chlorine atom, which becomes a charged atom, called an ion. Thus we take chlorine 3s orbitals and 3p orbitals as the basis states for describing the occupied states. Furthermore, the chlorine ions are spaced far enough apart that the s and p states can be considered separately, as was true at large inter- nuclear distance d in Fig. 1-12. Let us consider first the electron states in the crystal that are based upon the chlorine atomic 3s orbitals.

We define an index i that numbers all of the chlorine ions in the crystal. The chlorine atomic s state for each ion is written I Sị). We can approximate a crystalline state by

The variational calculation then leads immediately to a set of equations, in analogy to Eq. (1-26):

It is convenient at this stage to avoid the complications that arise from consideration of the crystalline surface, by introducing periodic boundary conditions. Imagine a crystal of chlorine ions that is Nị ions long in the x-direction, N2 long ill the ^-direction, and N3 long in the z-direction. The right surface of the crystal is connected to the left, the top to the bottom, and the front to the back. This is difficult to imagine in three dimensions, but in one dimension such a structure corresponds to a ring of ions rather than a straight segment with two ends. Closing the ring adds an Hịj matrix element coupling the states on the end ions. Periodic boundary conditions greatly simplify the problem mathematically; the only error that is introduced is the neglect of the effect of surfaces, which is beyond the scope of the discussion here.

The approximate description of the crystalline state, Eq. (2-1), contains a basis set of Np

= N1N2 N3 states (for the Np pairs of ions), and there are Np solutions of Eq. (2-2). These solutions can be written down directly and verified by substitution into Eq. (2-2). To do this we define a wave number that will be associated with each state: (2-3) where lĩị, n2, and n3 are integers such that —Nị/2 <nx< Nị/2, ..and X, y, and ….are units vectors in the three perpendicular directions, as indicated in Fig. 2-1,b. Then for each k allowed by Eq. (2-3), we can write the coefficient Uj in the form Here the r7- = (ml X + m2y + m3 z)a are the positions of the ions. We see immediately that there are as many values of k as there are chlorine ions; these correspond to the conservation of chlorine electron states. We also see that the wave functions for states of different k are orthogonal to each other. Values for k run almost continuously over a cubic region of wave number space, — n/a < kx < n/a, — n/a <ky < n/a, and — n/a < kz < %/a. This domain of k is called a Brillouin Zone. (The shape of the Brillouin Zone, here		

cubic, depends upon the crystal structure.) For a macroscopic crystal the Nị are very large, and the change in wave number for unit change in «j is very tiny. Eq. (2-4) is an exact solution of Eq. (2-2); however, we will show it for only the simplest approximation, namely, for the assumption that the |sf) are sufficiently localized that we can neglect the matrix element Hji = |S() unless (1) two states in question are the same (/' = j) or (2) they are from nearest-neighbor chlorine ions. For these two cases, the magnitudes of the matrix elements are, in analogy with the molecular case, In cesium chloride the main contribution to v2 comes from cesium ion states acting as intermediaries in a form that can be obtained from perturbation theory. We need not be further concerned here with the origin of v2 . (We shall discuss the ionic crystal matrix elements in Chapter 14.) For a particular value of j in Eq. (2-2), there are only seven values of i that contribute to the sum: i=j numbered as 0, and the six nearest-neighbor chlorine s states. The solution (valid for any i) is		

This energy varies with the wave number over the entire Brillouin Zone of Fig. 2-l,b. The results are customarily displayed graphically along certain lines within that Brillouin Zone. For example, Fig. 2-2,a shows a variation along the lines rx and TK of Fig. 2-l,b.

The calculation of bands based on p states proceeds in much the same way. In particular, if we make the simplest possible assumption—that each px orbital is coupled by a matrix element V'2 only to the px orbitals on the nearest neighbors in the x-direction and to no other p orbitals, and similarly for the py and pz orbitals— then the calculation can be separated for the three types of states. (Otherwise it would be necessary to solve three simultaneous equations together.) For the states based upon the px orbitals,

For py orbitals and pz orbitals, the second term is 2V2 COS kya and 1V'2 COS kza, respectively. The three corresponding p bands are also shown in Fig. 2-2,a. In later discussions we shall see that by the addition of matrix elements between orbitals that are more distant it is

possible to obtain as accurate a description of the true bands as we like; for the present, crude approximations are sufficient to illustrate the method. Can we construct other bands, for other orbitals, such as the cesium s orbital? It turns out that states that are not occupied in the ground state of the crystal are frequently not well described in the simplest LCÀO descriptions, but an approximate description can be made in the same way. How would the simple bands change if we could somehow slowly eliminate the strong atomic potentials that give rise to the atomic states upon which the bands are based? The answer is given in Fig. 2-2,b. The gaps between bands decrease, including the gap between the cesium bands (not shown in Fig. 2-2,a) and the chlorine bands. The lowest bands have a recognizable similarity to each other in these two extreme limits. The limit shown in Fig. 2-2,b is in fact the limit as the electrons become completely free; the lowest band there is given by the equation for free-electron kinetic energy, E — tĩ2k2/2m. The other bands in		

Fig. 2-2,b are also free-electron bands but are centered at different wave numbers (e.g., as E = h2(k — q)2/2m), in keeping with the choice to represent all states by wave numbers in the Brillouin Zone. Such free-electron descriptions will be appropriate later when we discuss metals; for cesium chloride, these descriptions are not so far from LCAO descriptions as one might have thought, and in fact the similarity will provide us, in Section 2-D, with approximate values for interatomic matrix elements such as v2 and V'l. Since there are as many states in each band as there are chlorine ions in the crystal, the four bands of Fig. 2-2,a, allowing both spins in each spatial state, can accommodate the seven chlorine electrons and one cesium electron. All states will be filled. This is the characteristic feature of an insulator; the state of the system cannot be changed without exciting an electron with several electron volts of energy, thus transferring it to one of the empty bands of greater energy. For that reason, light with frequency less than the difference		

between bands, divided by h, cannot be absorbed, and the crystal will be transparent. Similarly, currents cannot be induced by small applied voltages. This absence of electrical conductivity results from the full bands, not from any localization of the electrons at atoms or in bonds. It is important to recognize that bands exist in crystals and that the electrons are in states of the crystal just as, in the molecule 02, electrons form bonding and antibonding molecular states, rather than atomic states at the individual atoms. If, on the other hand, the bands of cesium chloride were as in Fig. 2-2,b, the eight electrons of each chlorine-cesium atom pair would fill the states only to the energy Ep shown in the figure; this is called the Fermi energy. Each band would only be partly filled, a feature that, as we shall see, is characteristic of a metal. 2- B Electron Dynamics In circumstances where the electron energy bands are neither completely full nor completely empty, the behavior of individual electrons in the bands will be of interest. This is not the principal area of concern in		

this text, but it is important to understand electron dynamics because this provides the link between the band properties and electronic properties of solids. Consider a Brillouin Zone, such as that defined for CsCl, and an energy band E(k), defined within that zone. Further, imagine a single electron within that band. If its wave function is an energy eigenstate, the time-dependent Schroedinger equation, Eq. (1-17), tells us that The magnitude of the wave function and therefore also the probability density at any point do not change with time. To discuss electron dynamics we must consider linear combinations of energy eigenstates of different energy. The convenient choice is a wave packet. In particular, we construct a packet, using states with wave numbers near k0 and parallel to it in the Brillouin Zone: Taking the form of \ị)h from Eqs. (2-1) and (2-3), and treating k - k0 as small, a little algebra shows that at t = 0, Eq. (2-8) corresponds to the state iḶ/ko modulated by a gaussian peak centered at r =		

0. Furthermore, writing £(k) = E(k0) + (dE/dk) ■ (k - k0), we may see that the center of the gaussian moves with a velocity

Thus it is natural to associate this velocity with an electron in the state Ijjko. Indeed, the relation is consistent with the expectation value of the current operator obtained for that state.

We are also interested in the effects of small applied fields: imagine the electron wave packet described above, but now allow a weak, slowly varying potential F(r) to be present. The packet will work against this potential at the rate V • dv/dr. This energy can only come from the band energy of the electron, through a change, with time, of the central wave number k0 of the packet:

This is consistent with the relation

This can, in fact, be generalized to magnetic forces by replacing —dv/dx by the Lorenz force, — e[—¥<p + (v/c) X H],

Eqs. (2-9) and (2-11) completely describe the dynamics of electrons in bands wherever it is possible to think in terms of wave packets; that is, whenever the fields are slowly varying relative to interatomic spacings. Notice that if we think of fik as the canonical momentum, then the band energy, written in terms of p = hk, plus the potential energy, F(r), play precisely the role of the classical Hamiltonian, since with these definitions, Eqs. (2-9) and (2-11), are precisely Hamilton's equations. Thus, in terms of the energy bands E(k), we may proceed directly by using kinetic theory to examine the transport properties of solids, without thinking again of the microscopic theory that led to those bands. We may go even further and use this classical Hamiltonian to discuss a wave function for the packet itself, just as we constructed wave functions for electrons in Chapter 1. This enables us to treat band electrons bound to impurities in the solid with methods similar to those used to treat electrons bound to free atoms; however, it is imperative to keep in mind that the approximations are good only when the resulting wave functions vary slowly with position, and therefore their usefulness would be restricted to weakly bound impurity states.

Let us note some qualitative

aspects of electron dynamics. If the bands are narrow in energy, electron velocities will be small and electrons will behave like heavy particles. These qualities are observed in insulator valence bands and in transition-metal d bands. In simple metals and semiconductors the bands tend to be broader and the electrons are more mobile; in metals the electrons typically behave as free particles with masses near the true electron mass. One question that might be asked is: what happens when an electron is accelerated into the Brillouin Zone surface? The answer is that it jumps across the zone and appears on the opposite face. It is not difficult to see from Eq. (2-3) that if, for example, m; is changed by Nị (corresponding to going from a wave number on one zone face to a wave number on the opposite face) the phase factors change by e2”'; the states are therefore identical. In general, equivalent states are found on opposite zone faces, and an electron accelerated into one face will appear at the opposite face and continue to change its wave number according to Eq. (2-11).		

2- C Characteristic Solid Types

Before discussing in detail the various categories of solids, it is helpful to survey them in general terms. This is conveniently done by conceptually constructing the semiconductor silicon from free atoms. In the course of this, it will become apparent how the metallicity of a semiconductor varies with row number in the periodic table. With the general model as a basis we can also construct compounds of increasing polarity, starting with silicon or germanium and moving outward in the same row of the periodic table. Metallicity and polarity are the two principal trends shown by compounds and will provide a suitable framework for the main body of our discussions.

Imagine silicon atoms arranged as in a diamond crystal structure but widely spaced. This structure will be discussed in the next chapter; a two-dimensional analogue of it is shown in Fig. 2-3. At large internuclear distance, two electrons are on each individual atom in s states and two are in p states. As the atoms are brought together, the atomic states broaden into

bands, as we have indicated. (There are complications, unimportant here, if one goes beyond a one-electron picture.) The s bands are completely full, whereas the p bands can accommodate six electrons per atom and are only one third full. This partial filling of bands is characteristic of a metal. As the atoms are brought still closer together, the broadening bands finally reach each other, as shown in Fig. 2-3, and a new gap opens up with four bands below and four above. The bonding bands below (called valence bands) are completely full and the antibonding bands above (called con-duction bands) are completely empty; now the system is that of an insulator or, when the gap is small, of a semiconductor. In Chapter 1, it was noted that a crossing of bonding and antibonding states does not occur in the simple diatomic molecules, but that it can in larger molecules and in solids, as shown here. The qualitative change in properties associated with such crossing is one of the most important concepts necessary for an understanding of chemical bonding, yet		

FIGURE 2-3 The formation of bands in a homopolar tetrahedral semiconductor as the atoms are brought together. Internuclear distance decreases to the right. it has not been widely examined until recently. Particular attention has been brought by Woodward and Hoffmann (1971) in their discussion of reactions between molecules. In that context, Woodward and Hoffmann found that when bonding and antibonding states are equally occupied, as in Be_2, discussed earlier, no bonding energy is gained and the atoms repel each other. Only when the atoms are close enough that upper bonding levels can surpass or cross the energy of the lower antibonding levels above can bonding result. In some such cases (not Be_2) a stably bonded system can be formed, but an energy barrier must be overcome in order to cause the atoms to bond. Reactions in which energy barriers must be overcome are called “symmetry forbidden reactions.” (See Woodward and Hoffmann, 1971, p. lOff, for a discussion of $2C_2H_4 \rightarrow C_4H_8$.) The barrier remains, in fact, when		

there is no symmetry. In silicon, illustrated in Fig. 2-3, the crossing occurs because high symmetry is assumed to exist in the atomic arrangement. Because of this symmetry, the matrix elements of the Hamiltonian are zero between wave functions of states that are dropping in energy and those that are rising (ultimately to cross each other). If, instead, the silicon atoms were to come together as a distorted lattice with no symmetry, the corresponding matrix elements of the Hamiltonian would not be zero, and decreasing and increasing energy levels would not cross (see Fig. 2-4).

■4 Increasing interatomic distance (d)

FIGURE 2-4

The variation of energy of two levels which cross, as a function of atomic spacing d, in a symmetric situation, but do not cross when there is not sufficient symmetry.

In an arrangement of high symmetry, a plotting of total energy as a function of d may show a cusp in the region where electrons switch from bonding to antibonding states; a clear and abrupt qualitative change in behavior coincides

with this cusp region. In an unsymmetric arrangement, change in total energy as a function of d is gradual but at small or at large internuclear distances, energies are indistinguishable from those observed in symmetric arrangements. Thus, though the crossing is artificial (and dependent on path), the qualitative difference, which we associate with covalent bottclinq, is not. For this reason, it is absolutely essential to know on which side of a diagram such as Fig. 2-3 or Fig. 2-4 a particular system lies. For example, in covalent silicon, bonding-antibonding splitting is the large term and the sp splitting is the small one. That statement explains why there is a gap between occupied states and unoccupied states, which makes covalent silicon a semiconductor, and knowing this guides us in numerical approximations. Similarly, in metals, bonding-antibonding splitting is the small term and the sp splitting the large term; this explains why it is a metal and guides our numerical approximations in metals. If we wished to make full, accurate machine calculations we would never need to make		

this distinction; we could simply look at the results of the full calculation to check for the presence of an energy gap. Instead, our methods are designed to result in intuitive understanding and approximate calculations of properties, which will allow us to guess trends without calculations in some cases, and which will allow us to treat complicated compounds that would otherwise be intractable by full, accurate calculation in other cases.

The diagram at the bottom of Fig. 2-3 was drawn to represent silicon but also, surprisingly, illustrates the homopolar series of semiconductors c, Si, Ge, and Sn. The internuclear distance is smallest in diamond, corresponding to the largest gap, far to the right in the figure. The internuclear distance becomes larger element by element down the series, corresponding to progression leftward in the figure to tin, for which the gap is zero. (Notice that in a plot of the bands, as in Fig. 2-2, the gap can vary with wave number. In tin it vanishes at only one wave number, as will be seen in Chapter 6, in Fig. 6-10.) Nonetheless we must regard each of these

semiconductors—even tin—as a covalent solid in which the dominant energy is the bonding-antibonding splitting. We can define a “metallicity” that increases from c to Sn, reflecting a decreasing ratio of bonding-antibonding splitting to sp splitting; nevertheless, if the structure is tetrahedral, the bonding-antibonding splitting has won the contest and the system is covalent. The discussion of Fig. 2-3 fits well with the LCAO description but the degree to which a solid is covalent or metallic is independent of which basis states are used in the calculation. Most of the analysis of covalent solids that will be made here will be based upon linear combinations of atomic orbitals, but we also wish to understand them in terms of free-electron-like behavior. (These two extreme approaches are illustrated for cesium chloride in Fig. 2-2.) Free-electron-like behavior is treated in Chapter 18, where two physical parameters will be designated, one of which dominates in the covalent solid and one of which dominates in the metallic solid. It can be useful here to see how these parameters		

correspond to the concepts discussed so far. In Fig. 2-2, the width of the bands, approximately Ep — Es, corresponds to the kinetic energy, £F, of the highest filled states. The bonding-antibonding splitting similarly corresponds to the residual splitting between bands which was suppressed completely in Fig. 2-2,b. For metals, this residual splitting is described by a pseudopotential. In metals, the small parameter is the pseudopotential divided by the Fermi energy (corresponding to the ratio of bonding-antibonding splitting to sp splitting, or the reciprocal of the metallicity). In the covalent solids, on the other hand, we would say that the pseudopotential is the dominant aspect of the problem and the kinetic energy can be treated as the small correction. In fact, in Chapter 18 the pseudopotential approach will be applied to simple tetrahedral solids; there, treating kinetic energies as small compared to the pseudopotential leads to a simple description of the covalent bond in which a one-to-one correspondence can be obtained between matrix		

elements of the pseudopotential (that is, between plane waves) and matrix elements of the Hamiltonian between atomic states. The correspondence between these two opposite approaches is even more remarkable than the similarity between the LCAO and free-electron bands in Fig. 2-2, though it is the latter similarity which will provide us with LCAO matrix elements.

Now, as an introduction to polar semiconductors, let us follow the variation of electronic structure, beginning with an elemental semiconductor and moving to more polar solids. For this, germanium is a better starting point than silicon, and in order of increasing polarity the series is Ge, GaAs, ZnSe, and CuBr. The total number of electrons in each of these solids is the same (they are isoelectronic) and the structure is the same for all; they differ in that the nuclear charge increases on one of the atoms (the anion) and decreases on the other (the cation). The qualita-

FIGURE 2-5

Change in the bands as a homopolar semiconductor is made increasingly polar, and

then as the two atom types are made more alike without broadening the levels. tive variation in electronic structure in this series is illustrated in Fig. 2-5,a. Bear in mind that even in nonpolar solids there are two types of atomic sites, one to the right and one to the left of the horizontal bonds in the figure. In polar solids the nuclear charge on the atom to the right is increased, compound by compound. This will tend to displace the bond charges (electron density) toward the atom with higher nuclear charge (center diagram in Fig. 2-5,a) and, in fact, the corresponding transfer of charge in most cases is even larger than the change in nuclear charge, so the atom with greater nuclear charge should be thought of as negative; hence, the term anion is used to denote the nonmetallic atom. At high polarities most of the electronic charge may be thought of as residing on the nonmetallic atom, as shown. The most noticeable change in the energy bands of Fig. 2-5,b, as polarity increases, is the opening up of a gap between the valence bands as shown. There is also a widening of the gap between valence and conduction bands		

and some broadening of the valence band. In extremely polar solids, at the center of the figure, the valence band, to a first approximation, has split into an anion s band and three narrow anion p bands. The conduction bands in this model—the unoccupied bands—also split into s bands and p bands, but in a real crystal of high polarity, the bands for unoccupied orbitals remain very broad and even free-electron-like.

We can complete the sequence of changes in the model shown in Fig. 2-5 by pulling the atoms apart to obtain isolated free atom energies. Perhaps the simplest path is that shown on the right side of Fig. 2-5, where the metallic and nonmetallic atoms become more alike and where the individual energy bands remain narrow. Where the levels cross, electrons of the anion fill available orbitals of the cation; the crossing results in a reduction of the atomic charges to zero.

By comparing Fig. 2-5 with Fig. 2-3, we can see that there is no discontinuous change in the qualitative nature of the electronic structure in going from homopolar to highly polar solids of the same crystal structure (Fig. 2-5),

but that discontinuity is encountered in going from the atomic electronic structure to the covalent one (Fig. 2-3). Properties vary smoothly with polarity over the entire range. This feature has been apparent for a long time and led Pauling to define ionicity in terms of energies of formation in order to provide a scale for the trend (Pauling, 1960). Coulson et al. (1962) redefined ionicity in terms of an LCAO description much like the one we shall use in Chapter 3. Phillips (1970) gave still a third definition in terms of the dielectric constant. The formula for polarity of a simple bond, introduced in Eq. (1-37), is essentially equivalent to the ionicity defined by Coulson, but the ionicities defined by Pauling and by Phillips are to a first approximation proportional to the square of that polarity. We will use the term polarity to describe a variation in electronic structure in covalent solids, and the particular values defined by Eq. (1-37) will directly enter the calculation of some properties. We do not use polarity to interpolate properties from one material to another. However, such		

interpolative approaches are commonly used, and degree of ionicity or polarity is frequently used to rationalize trends in properties. Therefore it is best to examine that approach briefly. The distinction between these two approaches is subtle but of fundamental importance. We have seen that there are trends with polarity and with metallicity among the tetrahedral solids. One of the trends is the decrease, with increasing metallicity and increasing polarity, of the angular rigidity that stabilizes the open tetrahedral structure. Thus, if either increases too far, the structure collapses to form a close-packed structure. When this happens, the new system has a qualitatively different electronic structure, and different concepts and approximations become appropriate. We may think of this as analogous to a phase diagram, as illustrated in Fig. 2-6. If a combination of atoms (e.g., Litium and flourine) is too polar, a close-packed rocksalt structure is formed. LiF is an ionic crystal and most frequently the best initial approximation to the electronic structure is		

based on independent ions, which we used in the discussion of the cesium chloride energy bands. Ionic solids can be distinguished from covalent solids by their characteristic crystalline structures, a topic that will be taken up later.

When the metallicity is too great, a close-packed structure again becomes more

Polarity

FIGURE 2-6

A schematic phase diagram indicating the three qualitatively different types of solids discussed in the book. The phase boundaries are topologically correct but details of shape are only schematic.

Stable. In this case the electronic structure ordinarily approximates that of a free-electron gas and may be analyzed with methods appropriate to free-electron gases. Again, the crystal structure is the determining feature for the classification. When tin has a tetrahedral structure it is a covalent solid; when it has a close- packed white-tin structure, it is a metal. Even silicon and germanium, when melted, become close-packed and liquid metals.

To complete the “ phase

diagram," there must also be a line separating metallic and ionic systems. Materials near this line are called intermetallic compounds; they can lie on the metallic side (an example is Mg2Pb) or on the ionic side (for example, CsAu). Consideration of intermetallic compounds takes the trends far beyond the isoelectronic series that we have been discussing. The sharp distinction between ionic and covalent solids is maintained in a rearrangement of the periodic table of elements made by Pantelides and Harrison (1975). In this table, the alkali metals and some of their neighbors are transferred to the right (see Fig. 2-7). The elements of the carbon column (column 4) and compounds made from elements to either side of that column (such as GaAs or CdS) are covalent solids with tetrahedral structures. Compounds made from elements to either side of the helium column of rare gases (such as KC1 or CaO) are ionic compounds with characteristic ionic structures. A few ionic and covalent compounds do not fit this correlation; notably, MgO,		

AgF, AgCl, and AgBr are ionic compounds, and MgS and MgSe can occur in either ionic or covalent structures. (Notice that Mg is found both in column 2 and column 10). The interesting isoelectronic series for ionic compounds will be those such as Ar, KC1, CaS, and ScP, obtained from argon by transferring protons between argon nuclei. In this case the ion receiving the proton is the metallic ion and the electronic structure is thought of as a slightly distorted rare gas structure. This model leads to a theory of ionic-compound bonding that is even simpler than the bonding theory for covalent solids. The Pantiledes-Harrison rearrangement of the periodic table is used as the format for the Solid State Table, where the parameters needed for the calculation of properties have been gathered.

2- D Solid State Matrix Elements

Almost all of the discussion of covalent and ionic solids in this book is based upon descriptions of electron states as linear combinations of atomic orbitals. In order to obtain numerical estimates of properties we need numerical values for the matrix

elements giving rise to the covalent and polar energies for the properties being considered. There is no best choice for these parameters since a trade-off must be made between simplicity (or universality) of the choice and accuracy of the predictions that result when they are used. Clearly if different values are used for each property of each material, exact values of the properties can be accommodated. We shall follow a procedure near the opposite extreme, by introducing four universal parameters in terms of which all interatomic matrix elements between s and p states for all systems can be estimated. We shall also use a single set of atomic s and p orbital energies throughout. These are the principal parameters needed for the entire range of properties, though the accuracy of the corresponding predictions is limited. One might at first think that interatomic matrix elements could be calculated by using tabulated atomic wave functions and potentials estimated for the various solids. Such approaches have a long history of giving poor		

numerical results and have tended to discredit the LCAO method itself. However, the difficulty seems to be that though true atomic orbitals do not provide a good basis for describing electronic structure, there are atomiclike orbitals that can provide a very good description. One can therefore obtain a useful theory by using LCAO formalism but obtaining the necessary matrix elements by empirical or semiempirical methods.

One of the oldest and most familiar such approaches is the “Extended Hueckel Approximation” (Hoffman, 1963.) Let us take a moment to examine this approach, though later we shall choose an alternative scheme. Detailed rationalizations of the approach are given in Blyholder and Coulson (1968), and in Gilbert (1970, p. 244); a crude intuitive derivation will suffice for our purposes, as follows. We seek matrix elements of the Hamiltonian between atomic orbitals on adjacent atoms, (p\H\cc). If I a) were an eigenstate of the Hamiltonian, we could replace HI a) by Ea|a), where £a is the eigenvalue. Then if the overlap (,P\oc) is written

Spa, the matrix element becomes EaSpa. This, however, treats the two orbitals differently, so we might use the average instead of Ea. Finding that this does not give good values, we introduce a scale factor G, to be adjusted to fit the properties of heavy molecules; this leads to the extended Hueckel formula: (.PịHịù) = GSpa(ep + ea)/2. (2-12) These matrix elements are substituted into the Hamiltonian matrix of Eq. (2-2) for a molecule, or a cluster of atoms, and the matrix is diagonalized. A value of G = 1.75 is usually taken; the difference from unity presumably, arises from the peculiar manner in which nonorthogonality is incorporated. The Extended Hueckel Approximation and a wide range of methods that may be considered as descendents of it (e.g., the CNDO method—Complete Neglect of Differential Overlap) have enjoyed considerable success in theoretical chemistry. Some machine calculation is required, first in determining the parameters s from tabulated wave functions or numerical approximations to		

them, and second in solving the resulting simultaneous equations, as at Eq. (2-2). This difficulty is exacerbated by the fact that s drops rather slowly with increasing distance between atoms, so a very large number of matrix elements are required. The computation required for any given system is very small, however, in comparison with what is required to obtain more accurate solutions. Once an Extended Hueckel Approximation has been made, direct machine computations of any property can be made and alternatives to the simplest approximations—e.g., Eq. (2-12)— can be made which improve agreement with the experimental values. Such improvements are described in detail by Pople and Beveridge (1970). Combining descriptions of electronic structure that are essentially correct, with the use of high-speed computers, and the results of a number of years of trial and error in correcting the simplest approximations, probably provide the most accurate predictions of the diverse properties of complex systems that are presently available. For isolated properties, such as the energy		

bands of solids, other computer methods are much more reliable and accurate. The approach that will be used in this text is different, in that the description of electronic structures is greatly simplified to provide a more vivid understanding of the properties; numerical estimates of properties will be obtained with calculations that can be carried through by hand rather than machine. We shall concentrate on the “physics” of the problem. In this context a semiempirical determination of matrix elements is appropriate. The first attempt at this (Harrison, 1973c) followed Phillips (1970) in obtaining the principal matrix element v2 from the measured dielectric constant. A second attempt (Harrison and Ciraci,1974) used the principal peak in the optical reflectivity of the covalent solids, which we shall come to later, as the basis for the principal matrix element; this led to the remarkable finding that v2 scaled from material to material quite accurately as the inverse square of the interatomic distance, the bond length d, between atoms. A subsequent study of the detailed form of valence		

bands (Pantelides and Harrison, 1975), combined with v2 determined from the peak in optical reflectivity, gave a complete set of interatomic matrix elements for covalent solids with the finding that all of them varied approximately as d~2 from material to material. The reason for this dependence recently became very clear in a study of the bands of covalent solids by Froyen and Harrison (1979). They took advantage of the similarity of the LCAO bands and free-electron bands, noted in Fig. 2-2. By equating selected energy differences obtained in the two limits, they derived formulae that had this dependence for all of the interatomic matrix elements. We may in fact see in detail how this occurs by considering Fig. 2-2. The lowest band, labelled s in Fig. 2-2,a, was given by Eq. (2-5). For k in an x-direction, it becomes E(k) = es — 4V2 — 2V2 cos ka, varying by 4VZ from r (where k = 0) to X (where k = %/a). The free-electron energy in Fig. 2-2,b varies by (h2/2m)(n/a)2 over the same region of wave number space for the lowest band. Thus, if both limiting models are to be appropriate,		

and therefore consistent with each other, it must follow that v2 = t]h2/{ma2) with rj = 7t2/8 = 1.23. This predicts the dependence upon the inverse square of interatomic distance and a coefficient that depends only upon crystal structure. A similar comparison of the second band gives the same form with a different coefficient for the matrix element v'2 between p states. This simplest model is not so relevant, but it illustrates the point nicely. Before going to more relevant systems we must define more precisely the notation to be used for general interatomic matrix elements.

These matrix elements will be important throughout the text; they are specified here following the conventions used by Slater and Koster (1954) and used earlier while discussing the diatomic molecule. In general, for a matrix element <a|//|/j> between orbitals on different atoms we construct the vector d, from the nucleus of the atom of which I a) is an orbital (the “ left ” atom) to that of the atom of which I/?) is an orbital (the “right” atom). Then spherical coordinate systems are constructed with the z-axes

parallel to d, and with origins at each atom; the angular form of the orbitals can be taken as Y?(9, ệ) for the left orbital and VỊ! (O', Ộ) for the right orbital. The angular factors depending upon ệ combine to (Notice that the wave function (a I is the complex conjugate of I a).) The integration over ậ gives zero unless m' = m. Then all matrix elements (a|H||S) vanish unless rri = m, and these are labelled by Ớ, n, or Ỏ (in analogy with s, p, d) for m — I). 1, and 2 respectively. Thus, for example, the matrix element Vspa corresponds to 1 = 0, I = 1, m = 0. Slater and Koster (1954) designated matrix elements by enclosing the indices within parentheses; thus, the element VWm used in this book and their (Wm) are the same. We saw how formulae for the matrix elements can be obtained by equating band energies from LCAO theory and from free-electron theory in Fig. 2-2. Froye.1 and Harrison (1979) made the corresponding treatment of the tetrahedral solids, again including only matrix elements between nearest-neighbor atoms. The form of their results is just as found for the simple cubic case		

Notice that the subscript m is a quantum number but the m in the denominator Dimensionless coefficients in Eq. (2-13) determining approximate interatomic matrix elements. Theoretical values Coefficient Simple cubic structure Tetrahedral structure Adjusted value* NOTE: Theoretical values (Froyen and Harrison, 1979) were obtained by equating band energies from I (\0 and free-eiectron theory, as described in the text. Adjusted values (Harrison, 1976b, 1977a) were obtained by fitting tile energy bands of silicon and germanium; the adjusted values appear in the Solid State Table. is the electron mass. The length d is the internuclear distance, equal to a in the simple cubic structure. If d is given in angstroms, this form is easily evaluated, using h2/m = 7.62 eV-Å2. In Table 2-1 we give the values of the dimensionless cnefficients obtained by Froyen and Harrison for both the simple cubic and Id rahedral structures. The calculation is closely related to that just carried through for the bands of Fig. 2-2, and in fact, the VSS<J matrix element for the		

simple cubic case is just the negative of the v2 value evaluated there, leading to the t]ssa = — 7t2/8. wv shall see in Section 18-A exactly how the other theoretical coefficients listed were obtained.

Motice that the coefficients obtained for the tetrahedral structure differ from those obtained for the simple cubic structure and indeed the coefficients for any mu; structure depend somewhat upon which band energies are used. However, the differences are not great and we shall neglect them. The coefficients we shall use are close to those given by Froyen and Harrison (1979) for the tetrahedral structure, but were obtained somewhat earlier by Harrison (1976b), who adjusted tliL'm to give the interatomic matrix elements found by Chadi and Cohen (1975) in fitting the known energy bands of silicon and germanium. The average of the coefficients so obtained for silicon and germanium is listed in Table 2-1 in the column headed “Adjusted,” and these are the values listed in the Solid State Table and used throughout this text. Also listed in the Solid State Table are forms lor predicting matrix elements involving atomic d states, formulae which will be developed in Chapter 20.

The coefficients in Table 2-1 have been obtained entirely in the context of nearest-neighbor coupling between states. They would have been different if a

*For recent developments, see the Preface to the Dover Edition.

TABLE 2-2

Atomic term values from Herman and Skillman (196.Í). or extrapolated from their values.

Atomic term value (eV)

second-neighbor LCAO fit had been used, for example, and it would not therefore be appropriate to use them if the description of the bands were to be extended to second-neighbor interactions.

It will ordinarily be more convenient in solids to use the forms for angular dependence, x/r, y/r, and z/r, as in Eq. (1-20), rather than the forms Y”i(0, <p). Then in order to obtain matrix elements involving these orbitals, we need to expand the

NOTE: These values appear also in the Solid State Table.

p orbital in question in terms of 17, which are defined with respect to the coordinate system discussed above. For p orbitals this is quite simple. For the simplest geometries it leads to the identification of matrix elements shown in the upper four diagrams of Fig. 2-8. For arbitrary geometries the result depends upon the direction cosines giving the vector d in the coordinate system of X, y, and z; this is illustrated at the bottom in Fig. 2-8. The corresponding transformations for d

FIGURE 2-8

The four types of interatomic matrix elements entering the study of s- and p-bonded systems are chosen as for diatomic molecules as shown in Fig. 1-11. Approximate values for each are obtained from the bond length, or internuclear distance, í/, by Vfj — riijtS/md2, with tiij taking values given in Table 2-1 and in the Solid State Table at the back of the book. When p orbitals are not oriented simply as shown ill the upper diagrams, they may be decomposed geometrically as vectors in order to evaluate matrix elements as illustrated in the bottom diagrams. It can be seen that the interatomic matrix element at the bottom right consists of cancelling the contributions that lead to a vanishing matrix element.

orbitals as well as p orbitals will be given in detail in Table 20-1, but for s and p orbitals the simple vector transformations illustrated in Fig. 2-8 should be sufficient; the results can be checked with Table 20-1.

When we give the Froyen-Harrison analysis in Chapter 18-A, we shall see that the same procedure can give an estimate of the energy difference Ep — £s. It is of the correct general magnitude but fails to describe the important trend in the energy bands among the covalent solids c, Si, Ge, and Sn. Furthermore, it does not provide a means of estimating term-value differences such as scp — e“ in polar solids. Thus, for these intra-atomic parameters we shall use calculated atomic term values, which are listed in Table 2-2. A comparison shows them to be roughly consistent with term values obtained in the fit to known bands done by Chadi and Cohen (1975) for the polar semiconductors as well as for silicon and germanium.

This particular set of calculated values (by Herman and Skillman, 1963) was chosen since the approximations used in the calculation were very similar to those used in determining the energy bands that led to the parameters in Table 2-1. The values would not have differed greatly if they were taken from Hartree-Fock calculations (such values are tabulated in Appendix A). Values based on Hartree-Fock calculations have the advantage of giving good values for d states. Therefore, though the calculations in this book are based upon the Herman-Skillman values, for some applications the Hartree-Fock values may be better suited.

Notice that as absolute numbers the atomic energy values have only limited meaning in any case. Imagine, for example, that the value Ep for oxygen correctly gives the energy required to remove an electron from an isolated oxygen atom in space. If this atom is brought close to the surface of a metal (or, almost equivalently, to the surface of a covalent solid with a large dielectric constant) but not close enough for any chemical bonding to take place, how much energy is now required to remove the electron from the oxygen? One way to

calculate this is to move the neutral atom to infinity, with no work required, remove the electron requiring £p, and then return the oxygen ion to its initial position; as it returns it gains an energy e2/4d from the image field, where d is the final distance from the surface. The resultant correction of fip, with d equal to 2 Â, is 1.8 eV, far from negligible. The precise value is uncertain because of the dielectric approximation, the uncertainty in the d used, and other effects, but we may expect that significant corrections of the absolute energies are needed relative to the values in vacuum. The reason that the values are nevertheless useful as parameters is that in solids such corrections are similar for all atoms involved and the relative values are meaningful. How do the values obtained from Tables 2-1 and 2-2 compare with the values obtained directly by fitting energy bands? This comparison is made in Table 2-3 for the covalent systems studied by Chadi and Cohen. Agreement is semiquantitative throughout and all trends are reproduced except the		

splitting of values for VsptT in the compounds. The discrepancies are comparable to the differences between different fits (the most recent fits are used here), thus justifying the use of the simple forms in our studies. Significantly different values are obtained if one includes a greater number of matrix elements in the fit (Pandey, 1976) and would be appropriate if we were to include these matrix elements in the calculation of properties other than the bands themselves. Significantly different values have also been given by Levin (1974). The coefficients from Table 2-1 and atomic term values from Table 2-2 will suffice for calculation of an extraordinarily wide range of properties of covalent and ionic solids using only a standard hand-held calculator. This is impressive testimony to the simplicity of the electronic structure and bonding in these systems. Indeed the same parameters gave a semiquantitative prediction of the one-electron energy levels of diatomic molecules in Table 1-1. However, that theory is intrinsically approximate and		

not always subject to successive corrections and improvements. In most cases our predictions of properties will be accurate on a scale reflected in Table 2-3, and though the introduction of further parameters allows a more accurate fit to the data, it may be that improvements at a more fundamental level are required for a more realistic treatment and that these improvements cannot be made without sacrificing the conceptual and

TABLE 2-3

Matrix elements from the Solid State Table, compared with values (in parentheses) from fits to individual bands. All values are in eV.

SOURCES of data in parentheses: c from Chadi and Martin (1976); Si and Ge from Chadi and Cohen (1975); GaAs and ZnSe from Chadi and Martin (1976).

NOTE: Where two values of Vspr are given for compounds, the first vaiue is for an s state in the nonmetallic atom and p state in the metallic atom. States are reversed for the second value. Where two values of («p — cs)/4 are listed, the first value is for the metallic atom, the second for the nonmetallic atom.

computational simplicity of the picture that will be constructed in the course of this book. Before proceeding to quantitative studies of the covalent solids it is appropriate to comment on the concept of “electronegativity,” introduced by Pauling to denote the tendency of atoms to attract electrons to themselves (discussed recently, for example, by Phillips, 1973b, p. 32). It may be an unfortunate term since the positive terminal of a battery has greater electronegativity than the negative terminal. Furthermore, it was defined to be dimensionless rather than to have more natural values in electron volts. It would be tempting to take the hybrid energy values of Table 2-2 as the definition of electronegativity, but it will be seen that in some properties the energy Ep is a more appropriate measure. Therefore it will be a wiser choice to use the term only qualitatively. Then from Table 2-2 (or from Fig. 1-8) we see that the principal trend is an increase in electronegativity with increasing atomic number		

proceeding horizontally from one inert gas to the next (e.g., from neon, Na, Mg, Al, Si, p, s, and Cl to argon). In addition, the elements between helium and neon have greater electronegativity than the heavier elements. It is useful to retain “ electronegativity ” to describe these two qualitative trends.

2- E Calculation of Spectra

We have seen that in solids, bands of electron energies exist rather than the discrete levels of atoms or molecules. Similarly there are bands of vibration frequencies rather than discrete modes. Thus, to show electron eigenvalues, a curve was given in Fig. 2-2 rather than a table of values. However, a complete specification of the energies within the bands for a three-dimensional solid requires a three-dimensional plot and that cannot be made; even in two dimensions an attempt is of limited use. Instead, a convenient representation of electronic structure can be made by plotting the number of states, per unit energy, as a function of energy. This loses the information about, for example, electron velocity, since that requires a knowledge of energy as a

function of wave number. However, it is all that is needed to sum the energies of the electrons for given atomic arrangements. Calculation of such a spectrum might seem straightforward, but if done by sampling, it requires an inordinate amount of calculation. For example, to produce a plot we might divide the energy region of interest into one thousand intervals and then evaluate the energies (as we did in Section 2-A) over a closely spaced grid in the Brillouin Zone, keeping track of the number of eigenvalues obtained in each interval. A great increase in efficiency can be obtained by noting that the energy bands have the full symmetry of the Brillouin Zone—in the case of CsCl, a cube—so that the entire Brillouin Zone need not be sampled. One could sample one half the zone and multiply the results by two, one eighth and multiply by eight, or in fact, for a cube, one forty-eighth suffices. However, even in a sample of thousands of values, the resulting histogram shows large statistical fluctuations. Therefore an alternative approach is required.		

The approach most commonly used, and used extensively in the curves in this book, is the Gilat-Raubenheimer scheme (Raubenheimer and Gilat, 1966). In this scheme, the idea is to replace the true bands by approximate bands, but then to calculate the density of levels for that spectrum accurately. This is done by dividing up the Brillouin Zone, or a forty-eighth of the zone for cubic symmetry, into cells; of the order of fifty may be appropriate; Raubenheimer and Gilat used cells in the shape of cubes. They then fit each band in each cell by a linear expression, $Ek = E0 + A1\ kx + A2ky + A3kz$, with k measured from the center of the cell. Then the energy region of interest for the system is divided into some 1000 energy intervals and the contribution to each of these intervals is accurately and analytically obtained from the linear values of the bands in each cell. This is illustrated for one dimension in Fig. 2-9. We see that the distribution of the approximate bands is obtained exactly. This turns out to eliminate most of the statistical error and to give very good results.		

In the Gilat-Raubenheimer scheme it is inconvenient to obtain the necessary values of the gradient of the energy with respect to wave number in each cell, and the cubes do not fit the Brillouin Zone section exactly, so there are problems in calculating the energy at the surface of the section. For this reason Jepsen and Andersen (1971) and later, independently, Lehman and Taut (1972) replaced

(c) Number of states
contributed in each interval

FIGURE 2-9

A schematic representation of the Gilat-Raubenheimer scheme for calculating densities of states. The energy bands (a) are replaced by linear bands (b) in each cell. The contribution by each cell to each of a set of small energy intervals (c) is then obtained analytically.

cubes by tetrahedra and wrote the distribution of energies in terms of the values at the four comers. A clear description of this much simpler approach is given by Rath and Freeman (1975), who include the necessary formulae. It is also helpful to see one manner in which the Brillouin Zone can be divided into cells. This is shown in Fig. 2-10, This procedure has been discussed also by Gilat and Bharatiya (1975). Another scheme, utilizing a more accurate approximation to the bands, has been considered recently by Chen (1976).

In some sense this is a computational detail, but the resulting curves are so essential to solid state properties that the detail is important. Once a program has been written for a given Brillouin Zone, any of the spectra for the corresponding structure can be efficiently and accurately obtained from the bands themselves.

PROBLEM 2-1 Calculating one-dimensional energy bands

Let us make an elementary calculation of energy bands, using the notation of LCAO theory. For many readers the procedure will be familiar. Consider a ring of N atoms, each with an s orbital. We seek an electronic state in the form of an LCAO,

where the integers a number the atoms. We can evaluate the expectation value of the energy, considering all atoms to be identical, so (a I HI a) = R is the same for all a. We can also neglect all matrix elements (a\H\p'), except if a and /? differ by one; we write that

FIGURE 2-10

(a) The body-centered-cubic Brillouin Zone is divided into 48 equivalent pyramidal segments. (Two such pyramids are required for face-centered cubic zones.) (b) The pyramid is cut by equally spaced planes parallel to the base, (c) Most of the slab may be subdivided into triangular prisms. An edge is left over on the right which can be divided into triangular prisms with one tetrahedron left over. Each triangular prism

(d) may finally be divided into three tetrahedra, (e). This divides the Brillouin Zone entirely into tetrahedra of equal volume. The bands are taken to be linear in wave number within each tetrahedron.

We shall treat the uj as independent of ua and minimize the expression with respect to UĨ, giving a linear algebraic equation for each a.

(a) Show that for any integer it there is a solution for all of these equations of the form

(b) Give the energy as a function of n, and sketch it as a function of n/N for large N. Include positive and negative n.

(c) Obtain the value of A that normalizes the electron state. (d) Show that for an n outside the range — N/2 <n< N/2, the electron state obtained is identical to that for some n within this range (within the Brillouin Zone). It suffices to prove that for given n the ua are unchanged by the addition of N to n. PROBLEM 2-2 Electron dynamics Consider an electron in a one-dimensional energy band given by E(k) = — y2 COS ka in a Brillouin Zone, —n/a < k < n/a. At time t = 0, with the electron having wave number k = 0, apply an electric field ê. Obtain the energy, the speed, and the position of the electron as a function of time. The behavior will be oscillatory. It can be thought of as acceleration of the electron followed by gradual diffraction caused by the lattice. How many lattice distances (each distance a = 2 Å) does the electron go if v2 = 2 eV and the field is 100 volts per centimeter?		

PROBLEM 1-1 Elementary quantum mechanics An electron in a hydrogen atom has a potential energy, — e2/V. The wave function for the lowest energy state is \j/(r) = Ae~rla° where a0 is the Bohr radius, a0 = h2/me2, and A is a real constant. (a) Obtain A such that the wave function is normalized, (ệ I ệ} = 1. (b) Obtain the expectation value of the potential energy, (ệ\ VịìỊ/). (c) Calculation of the expectation value of the kinetic energy, K.E.^I^Vl^X is trickier because of the infinite curvature at /• = 0. By partial integration in Eq. (1-3), an equivalent form is obtained: Evaluate this expression to obtain K.E. (d) Verify that the expectation value of the total energy, <|//| vịiị1} + K.E. is a minimum with respect to variation of 00. Thus a variational solution of the	[redacted]	

form e~',r would have given the correct wave function.	[redacted]	
(e) Verify that this i//(r) is a solution of Eq. (1-5).	[redacted]	
PROBLEM 1-2 Atomic orbitals	[redacted]	
The hydrogen 2s and 2p orbitals can be written and	[redacted]	
(see Schiff, 1968, p. 94), and p orbitals can also be written with X replaced by V and by z. All four hydrogen orbitals have the same energy, — e2/(8flc).	[redacted]	
Approximate the Litium 2,5 and 2p orbitals by the same functions and approximate the Litium potential by — e2/r + ucore(r), where	[redacted]	
Calculate the expectation value of the energy of the 2s and 2p orbitals. The easiest way may be to calculate corrections to the — e2/(8a0) value.	[redacted]	
This gives the correct qualitative picture of the Litium valence states but is quantitatively inaccurate.	[redacted]	

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 c2, obtain the Ơ 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 ~~the equations analogous to Eq. (2-2) become~~ ~~Solutions will be even or odd, by symmetry, so there can be solutions with u2 = Uị and w4 = u3, and the above reduce to two equations in two unknowns. Solve them for E. Then, solve again with If2 = IIị a~~nd «4 = u3 . Confirm the values of these energies as given in Table 1-1 for c2.	[redacted] [redacted] [redacted] [redacted] [redacted] [redacted]	

The lowest state contains comparable contributions from the s and p orbitals. What is the fraction of s character, that is, (uị + uịỵiuị + uị + uị + ul)1 CHAPTER 2 Electronic Structure of Solids SUMMARY In solids, atomic valence levels broaden into bands comprising as many states as there are atoms in the solid. Electrons in these band states are mobile, each electron state being characterized by a momentum p or wave number k = p/tt 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	[redacted] [redacted] [redacted] [redacted] [redacted]	

other bands will be empty. The bonds 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.	[redacted] [redacted]	

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.

[redacted]

In this chapter we give a very brief description of solids, which is the principal subject of the book. The main goal is to fit solids into the context of atoms and molecules. In addition, we shall carefully formulate the energy band in the simplest possible case and study the behavior of electrons in energy bands.

[redacted]

[redacted]

2- A Energy Bands

When many atoms are brought together to form a solid, the number of electron states is conserved, just as in the formation of diatomic molecules. Likewise, as in diatomic molecules, the one-electron states for the solid

[redacted]

can, to a reasonable approximation, be written as LCAO’s. However, in solids, the number of basis states is great. A solid cube one centimeter on an edge may contain 1023 atoms, and for each, there is an atomic s orbital and three p orbitals. At first glance it might seem that such a problem, involving some 4 X 1023 equations, could not be attacked. However, the simplicity of the crystalline solid system allows us to proceed effectively and accurately. As the atoms are brought together, the atomic energy levels split into bands, which are analogous to the states illustrated for diatomic molecules in Fig. 1-12. The difference is that rather than splitting into a single bonding and a single antibonding state, the atomic levels split into an entire band of states distributed between extreme bonding and antibonding limits. To see how this occurs, let us	[redacted]	

consider the simplest interesting case, that of cesium chloride. The structure of CsCl is shown in Fig. 2-1,a. The chlorine atoms, represented by open circles, appear on the comers of a cube, and this cubic array is repeated throughout the entire crystal. At the center of each cube is a cesium atom (at the body-center position ill the cube). Cesium chloride is very polar, so the occupied orbitals lie almost entirely upon the chlorine atoms. As a first approximation we can say that the cesium atom has given up a valence electron to (a) Crystal structure (b) Brillouin Zone FIGURE 2-1 (a) A unit cube of the cesium chloride crystal structure, and (b) the corresponding Brillouin Zone in wave number space. fill the shell of the chlorine atom, which becomes a charged atom, called an ion. Thus we take chlorine 3s orbitals and 3p orbitals as the basis states for describing the	[redacted]	

occupied states. Furthermore, the chlorine ions are spaced far enough apart that the s and p states can be considered separately, as was true at large internuclear distance d in Fig. 1-12. Let us consider first the electron states in the crystal that are based upon the chlorine atomic 3s orbitals.	[redacted]	
We define an index i that numbers all of the chlorine ions in the crystal. The chlorine atomic s state for each ion is written I Sị). We can approximate a crystalline state by	[redacted]	
The variational calculation then leads immediately to a set of equations, in analogy to Eq. (1-26):	[redacted]	
	[redacted]	
It is convenient at this stage to avoid the complications that arise from consideration of the crystalline surface, by introducing periodic boundary conditions. Imagine a crystal of chlorine ions that is Nị ions long in the x-	[redacted]	

direction, N2 long ill the ^-direction, and N3 long in the z-direction. The right surface of the crystal is connected to the left, the top to the bottom, and the front to the back. This is difficult to imagine in three dimensions, but in one dimension such a structure corresponds to a ring of ions rather than a straight segment with two ends. Closing the ring adds an Hij matrix element coupling the states on the end ions. Periodic boundary conditions greatly simplify the problem mathematically; the only error that is introduced is the neglect of the effect of surfaces, which is beyond the scope of the discussion here.	[redacted]	
The approximate description of the crystalline state, Eq. (2-1), contains a basis set of Np = N1N2 N3 states (for the Np pairs of ions), and there are Np solutions of Eq. (2-2). These solutions can be written down directly and verified by substitution into Eq. (2-2). To do this we define a wave number that will be associated with each state:	[redacted]	

(2-3) where lĩị, n2, and n3 are integers such that —Nị/2 <nx< Nị/2, ..and X, y, and ….are units vectors in the three perpendicular directions, as indicated in Fig. 2-1,b. Then for each k allowed by Eq. (2-3), we can write the coefficient Uj in the form Here the r7- = (ml X + m2y + m3 z)a are the positions of the ions. We see immediately that there are as many values of k as there are chlorine ions; these correspond to the conservation of chlorine electron states. We also see that the wave functions for states of different k are orthogonal to each other. Values for k run almost continuously over a cubic region of wave number space, — n/a < kx < n/a, — n/a <ky < n/a, and — n/a < kz < %/a. This domain of k is called a Brillouin Zone. (The shape of the Brillouin Zone, here cubic, depends upon the crystal structure.) ~~For a macroscopic crystal the~~ Nị are very large, and the change in wave number for unit change in «j is very tiny. Eq. (2-4) is an exact solution of Eq. (2-2); however, we will	[redacted] [redacted] [redacted]	

show it for only the simplest approximation, namely, for the assumption that the |sf) are sufficiently localized that we can neglect the matrix element Hji = |S() unless (1) two states in question are the same (/' = j) or (2) they are from nearest-neighbor chlorine ions. For these two cases, the magnitudes of the matrix elements are, in analogy with the molecular case,	[redacted]	
In cesium chloride the main contribution to v2 comes from cesium ion states acting as intermediaries in a form that can be obtained from perturbation theory. We need not be further concerned here with the origin of v2 . (We shall discuss the ionic crystal matrix elements in Chapter 14.) For a particular value of j in Eq. (2-2), there are only seven values of i that contribute to the sum: i=j numbered as 0, and the six nearest-neighbor chlorine s states. The solution (valid for any i) is	[redacted]	
This energy varies with the wave number over the entire	[redacted]	

Brillouin Zone of Fig. 2-l,b. The results are customarily displayed graphically along certain lines within that Brillouin Zone. For example, Fig. 2-2,a shows a variation along the lines rx and TK of Fig. 2-l,b. The calculation of bands based on p states proceeds in much the same way. In particular, if we make the simplest possible assumption—that each px orbital is coupled by a matrix element V'2 only to the px orbitals on the nearest neighbors in the x-direction and to no other p orbitals, and similarly for the py and pz orbitals— then the calculation can be separated for the three types of states. (Otherwise it would be necessary to solve three simultaneous equations together.) For the states based upon the px orbitals, For py orbitals and pz orbitals, the second term is 2V2 COS kya and 1V'2 COS kza, respectively. The three corresponding p bands are also shown in Fig. 2-2,a. In later discussions we shall see that by the addition of matrix elements between orbitals	[redacted] [redacted] [redacted]	

that are more distant it is possible to obtain as accurate a description of the true bands as we like; for the present, crude approximations are sufficient to illustrate the method.	[redacted]	
Can we construct other bands, for other orbitals, such as the cesium s orbital? It turns out that states that are not occupied in the ground state of the crystal are frequently not well described in the simplest LCÀO descriptions, but an approximate description can be made in the same way.	[redacted]	
How would the simple bands change if we could somehow slowly eliminate the strong atomic potentials that give rise to the atomic states upon which the bands are based? The answer is given in Fig. 2-2,b. The gaps between bands decrease, including the gap between the cesium bands (not shown in Fig. 2-2,a) and the chlorine bands. The lowest bands have a recognizable similarity to each other in these two extreme limits. The limit shown in Fig. 2-2,b is in fact the limit as the electrons	[redacted]	

become completely free; the lowest band there is given by the equation for free-electron kinetic energy, E — tĩ2k2/2m. The other bands in Fig. 2-2,b are also free-electron bands but are centered at different wave numbers (e.g., as E = h2(k — q)2/2m), in keeping with the choice to represent all states by wave numbers in the Brillouin Zone. Such free-electron descriptions will be appropriate later when we discuss metals; for cesium chloride, these descriptions are not so far from LCAO descriptions as one might have thought, and in fact the similarity will provide us, in Section 2-D, with approximate values for interatomic matrix elements such as v2 and V'l. Since there are as many states in each band as there are chlorine ions in the crystal, the four bands of Fig. 2-2,a, allowing both spins in each spatial state, can accommodate the seven chlorine electrons and one cesium electron. All states	[redacted] [redacted]	

will be filled. This is the characteristic feature of an insulator; the state of the system cannot be changed without exciting an electron with several electron volts of energy, thus transferring it to one of the empty bands of greater energy. For that reason, light with frequency less than the difference between bands, divided by h, cannot be absorbed, and the crystal will be transparent. Similarly, currents cannot be induced by small applied voltages. This absence of electrical conductivity results from the full bands, not from any localization of the electrons at atoms or in bonds. It is important to recognize that bands exist in crystals and that the electrons are in states of the crystal just as, in the molecule 02, electrons form bonding and antibonding molecular states, rather than atomic states at the individual atoms. If, on the other hand, the bands of cesium chloride were as in Fig. 2-2,b, the	[redacted] [redacted]	

eight electrons of each chlorine-cesium atom pair would fill the states only to the energy Ep shown in the figure; this is called the Fermi energy. Each band would only be partly filled, a feature that, as we shall see, is characteristic of a metal. 2- B Electron Dynamics In circumstances where the electron energy bands are neither completely full nor completely empty, the behavior of individual electrons in the bands will be of interest. This is not the principal area of concern in this text, but it is important to understand electron dynamics because this provides the link between the band properties and electronic properties of solids. Consider a Brillouin Zone, such as that defined for CsCl, and an energy band E(k), defined within that zone. Further, imagine a single electron within that band. If its wave function is an energy eigenstate, the time-dependent Schroedinger equation, Eq. (1-17), tells us that	[redacted] [redacted] [redacted] [redacted]	

	[redacted]	
The magnitude of the wave function and therefore also the probability density at any point do not change with time. To discuss electron dynamics we must consider linear combinations of energy eigenstates of different energy. The convenient choice is a wave packet. In particular, we construct a packet, using states with wave numbers near k0 and parallel to it in the Brillouin Zone:	[redacted]	
Taking the form of \į)h from Eqs. (2-1) and (2-3), and treating k - k0 as small, a little algebra shows that at t = 0, Eq. (2-8) corresponds to the state iĮ/ko modulated by a gaussian peak centered at r = 0. Furthermore, writing £(k) = E(k0) + (dE/dk) ■ (k - k0), we may see that the center of the gaussian moves with a velocity	[redacted]	
Thus it is natural to associate this velocity with an electron in the state Ijjko. Indeed, the relation is consistent with the expectation value of the current operator obtained for that state.	[redacted]	

We are also interested in the effects of small applied fields: imagine the electron wave packet described above, but now allow a weak, slowly varying potential F(r) to be present. The packet will work against this potential at the rate V • dv/dr. This energy can only come from the band energy of the electron, through a change, with time, of the central wave number k0 of the packet:	[redacted]	
This is consistent with the relation	[redacted]	
This can, in fact, be generalized to magnetic forces by replacing —dv/dx by the Lorenz force, — e[—¥<p + (v/c) X H],	[redacted]	
Eqs. (2-9) and (2-11) completely describe the dynamics of electrons in bands wherever it is possible to think in terms of wave packets; that is, whenever the fields are slowly varying relative to interatomic spacings. Notice that if we think of fik as the canonical momentum, then the band energy, written in terms of p = hk, plus the potential energy, F(r), play precisely the role of the classical Hamiltonian, since with these	[redacted]	

definitions, Eqs. (2-9) and (2-11), are precisely Hamilton’s equations. Thus, in terms of the energy bands E(k), we may proceed directly by using kinetic theory to examine the transport properties of solids, without thinking again of the microscopic theory that led to those bands. We may go even further and use this classical Hamiltonian to discuss a wave function for the packet itself, just as we constructed wave functions for electrons in Chapter 1. This enables us to treat band electrons bound to impurities in the solid with methods similar to those used to treat electrons bound to free atoms; however, it is imperative to keep in mind that the approximations are good only when the resulting wave functions vary slowly with position, and therefore their usefulness would be restricted to weakly bound impurity states. Let us note some qualitative aspects of electron dynamics. If the bands are narrow in energy, electron velocities will be small and electrons	[redacted] [redacted]	

will behave like heavy particles. These qualities are observed in insulator valence bands and in transition-metal d bands. In simple metals and semiconductors the bands tend to be broader and the electrons are more mobile; in metals the electrons typically behave as free particles with masses near the true electron mass. One question that might be asked is: what happens when an electron is accelerated into the Brillouin Zone surface? The answer is that it jumps across the zone and appears on the opposite face. It is not difficult to see from Eq. (2-3) that if, for example, m; is changed by Nị (corresponding to going from a wave number on one zone face to a wave number on the opposite face) the phase factors change by e2”'; the states are therefore identical. In general, equivalent states are found on opposite zone faces, and an electron accelerated into one face will appear at the opposite face and continue to change its	[redacted] [redacted]	

wave number according to Eq. (2-11).	[redacted]	
2-C Characteristic Solid Types	[redacted]	
Before discussing in detail the various categories of solids, it is helpful to survey them in general terms. This is conveniently done by conceptually constructing the semiconductor silicon from free atoms. In the course of this, it will become apparent how the metallicity of a semiconductor varies with row number in the periodic table. With the general model as a basis we can also construct compounds of increasing polarity, starting with silicon or germanium and moving outward in the same row of the periodic table. Metallicity and polarity are the two principal trends shown by compounds and will provide a suitable framework for the main body of our discussions.	[redacted]	
Imagine silicon atoms arranged as in a diamond crystal structure but widely spaced. This structure will be discussed in the next chapter; a two-dimensional analogue	[redacted]	

of it is shown in Fig. 2-3.

At large internuclear distance, two electrons are on each individual atom in s states and two are in p states. As the atoms are brought together, the atomic states broaden into bands, as we have indicated. (There are complications, unimportant here, if one goes beyond a one-electron picture.) The s bands are completely full, whereas the p bands can accommodate six electrons per atom and are only one third full. This partial filling of bands is characteristic of a metal. As the atoms are brought still closer together, the broadening bands finally reach each other, as shown in Fig. 2-3, and a new gap opens up with four bands below and four above. The bonding bands below (called valence bands) are completely full and the antibonding bands above (called con-duction bands) are completely empty; now the system is that of an insulator or, when the gap is small, of a semiconductor. In Chapter 1, it was noted that a

[redacted]

crossing of bonding and antibonding states does not occur in the simple diatomic molecules, but that it can in larger molecules and in solids, as shown here.	[redacted]	
The qualitative change in properties associated with such crossing is one of the most important concepts necessary for an understanding of chemical bonding, yet	[redacted]	
	[redacted]	
FIGURE 2-3 The formation of bands in a homopolar tetrahedral semiconductor as the atoms are brought together. Internuclear distance decreases to the right.	[redacted]	
it has not been widely examined until recently. Particular attention has been brought by Woodward and Hoffmann (1971) in their discussion of reactions between molecules. In that context, Woodward and Hoffmann found that when bonding and antibonding states are equally occupied, as in Be2, discussed earlier, no bonding energy is gained and	[redacted]	

the atoms repel each other. Only when the atoms are close enough that upper bonding levels can surpass or cross the energy of the lower antibonding levels above can bonding result. In some such cases (not Be2) a stably bonded system can be formed, but an energy barrier must be overcome in order to cause the atoms to bond. Reactions in which energy barriers must be overcome are called “symmetry forbidden reactions.” (See Woodward and Hoffmann, 1971, p. lOff, for a discussion of 2C2H4 -> C4H8.) The barrier remains, in fact, when there is no symmetry. In silicon, illustrated in Fig. 2-3, the crossing occurs because high symmetry is assumed to exist in the atomic arrangement. Because of this symmetry, the matrix elements of the Hamiltonian are zero between wave functions of states that are dropping in energy and those that are rising (ultimately to cross each other). If, instead, the silicon atoms were to	[redacted]	

come ■4 Increasing interatomic distance (d) FIGURE 2-4 The variation of energy of two levels which cross, as a function of atomic spacing d, in a symmetric situation, but do not cross when there is not sufficient symmetry. together as a distorted lattice with no symmetry, the corresponding matrix elements of the Hamiltonian would not be zero, and decreasing and increasing energy levels would not cross (see Fig. 2-4). In an arrangement of high symmetry, a plotting of total energy as a function of d may show a cusp in the region where electrons switch from bonding to antibonding states; a clear and abrupt qualitative change in behavior coincides with this cusp region. In an unsymmetric arrangement, change in total energy as a function of d is gradual but at small or at	[redacted]	

large internuclear distances, energies are indistinguishable from those observed in symmetric arrangements. Thus, though the crossing is artificial (and dependent on path), the qualitative difference, which we associate with covalent bottclinq, is not. For this reason, it is absolutely essential to know on which side of a diagram such as Fig. 2-3 or Fig. 2-4 a particular system lies. For example, in covalent silicon, bonding-antibonding splitting is the large term and the sp splitting is the small one. That statement explains why there is a gap between occupied states and unoccupied states, which makes covalent silicon a semiconductor, and knowing this guides us in numerical approximations. Similarly, in metals, bonding-antibonding splitting is the small term and the sp splitting the large term; this explains why it is a metal and guides our numerical approximations in metals. If we wished to make full, accurate machine calculations we would never need to make this distinction; we could simply look at the results of the full calculation to check	[redacted] [redacted]	

for the presence of an energy gap. Instead, our methods are designed to result in intuitive understanding and approximate calculations of properties, which will allow us to guess trends without calculations in some cases, and which will allow us to treat complicated compounds that would otherwise be intractable by full, accurate calculation in other cases. The diagram at the bottom of Fig. 2-3 was drawn to represent silicon but also, surprisingly, illustrates the homopolar series of semiconductors c, Si, Ge, and Sn. The internuclear distance is smallest in diamond, corresponding to the largest gap, far to the right in the figure. The internuclear distance becomes larger element by element down the series, corresponding to progression leftward in the figure to tin, for which the gap is zero. (Notice that in a plot of the bands, as in Fig. 2-2, the gap	[redacted] [redacted]	

can vary with wave number. In tin it vanishes at only one wave number, as will be seen in Chapter 6, in Fig. 6-10.) Nonetheless we must regard each of these semiconductors—even tin—as a covalent solid in which the dominant energy is the bonding-antibonding splitting. We can define a "metallicity" that increases from c to Sn, reflecting a decreasing ratio of bonding-antibonding splitting to sp splitting; nevertheless, if the structure is tetrahedral, the bonding-antibonding splitting has won the contest and the system is covalent.	[redacted]	
The discussion of Fig. 2-3 fits well with the LCAO description but the degree to which a solid is covalent or metallic is independent of which basis states are used in the calculation. Most of the analysis of covalent solids that will be made here will be based upon linear combinations of atomic orbitals, but we also wish to understand them in terms of free-electron-like behavior. (These two extreme	[redacted]	

approaches are illustrated for cesium chloride in Fig. 2-2.) Free-electron-like behavior is treated in Chapter 18, where two physical parameters will be designated, one of which dominates in the covalent solid and one of which dominates in the metallic solid. It can be useful here to see how these parameters correspond to the concepts discussed so far. In Fig. 2-2, the width of the bands, approximately Ep — Es, corresponds to the kinetic energy, £F, of the highest filled states. The bonding-antibonding splitting similarly corresponds to the residual splitting between bands which was suppressed completely in Fig. 2-2,b. For metals, this residual splitting is described by a pseudopotential. In metals, the small parameter is the pseudopotential divided by the Fermi energy (corresponding to the ratio of bonding-antibonding splitting to sp splitting, or the reciprocal of the metallicity). In the covalent solids, on the other hand, we would say that	[redacted] [redacted]	

the pseudopotential is the dominant aspect of the problem and the kinetic energy can be treated as the small correction. In fact, in Chapter 18 the pseudopotential approach will be applied to simple tetrahedral solids; there, treating kinetic energies as small compared to the pseudopotential leads to a simple description of the covalent bond in which a one-to-one correspondence can be obtained between matrix elements of the pseudopotential (that is, between plane waves) and matrix elements of the Hamiltonian between atomic states. The correspondence between these two opposite approaches is even more remarkable than the similarity between the LCAO and free-electron bands in Fig. 2-2, though it is the latter similarity which will provide us with LCAO matrix elements. Now, as an introduction to polar semiconductors, let us follow the variation of electronic structure, beginning with an elemental semiconductor and moving to more polar solids. For this, germanium is a better starting	[redacted] [redacted] [redacted] [redacted]	

point than silicon, and in order of increasing polarity the series is Ge, GaAs, ZnSe, and CuBr.

The total number of electrons in each of these solids is the same (they are isoelectronic) and the structure is the same for all; they differ in that the nuclear charge increases on one of the atoms (the anion) and decreases on the other (the cation). The qualitative variation in electronic structure in this series is illustrated in Fig. 2-5,a. Bear in mind that even in nonpolar solids there are two types of atomic sites, one to the right and one to the left of the horizontal bonds in the figure. In polar solids the nuclear charge on the atom to the right is increased, compound by compound. This will tend to displace the bond charges (electron density) toward the atom with higher nuclear

FIGURE 2-5
Change in the bands as a homopolar semiconductor is made increasingly polar, and then as the two atom types are made more alike without broadening the levels.

[redacted]

[redacted]

[redacted]

[redacted]

charge (center diagram in Fig. 2-5,a) and, in fact, the corresponding transfer of charge in most cases is even larger than the change in nuclear charge, so the atom with greater nuclear charge should be thought of as negative; hence, the term anion is used to denote the nonmetallic atom. At high polarities most of the electronic charge may be thought of as residing on the nonmetallic atom, as shown.	[redacted]	
The most noticeable change in the energy bands of Fig. 2-5,b, as polarity increases, is the opening up of a gap between the valence bands as shown. There is also a widening of the gap between valence and conduction bands and some broadening of the valence band. In extremely polar solids, at the center of the figure, the valence band, to a first approximation, has split into an anion s band and three narrow anion p bands. The conduction bands in this model—the unoccupied bands—also split into s bands and p bands, but in a real crystal of high polarity, the bands for unoccupied orbitals remain very broad and even	[redacted]	

free-electron-like.	[redacted]	
We can complete the sequence of changes in the model shown in Fig. 2-5 by pulling the atoms apart to obtain isolated free atom energies. Perhaps the simplest path is that shown on the right side of Fig. 2-5, where the metallic and nonmetallic atoms become more alike and where the individual energy bands remain narrow. Where the levels cross, electrons of the anion fill available orbitals of the cation; the crossing results in a reduction of the atomic charges to zero.	[redacted]	
By comparing Fig. 2-5 with Fig. 2-3, we can see that there is no discontinuous change in the qualitative nature of the electronic structure in going from homopo- lar to highly polar solids of the same crystal structure (Fig. 2-5), but that discontinuity is encountered in going from the atomic electronic structure to the covalent one (Fig. 2-3). Properties vary smoothly with polarity over the entire range. This feature	[redacted]	

has been apparent for a long time and led Pauling to define ionicity in terms of energies of formation in order to provide a scale for the trend (Pauling, 1960). Coulson et al. (1962) redefined ionicity in terms of an LCAO description much like the one we shall use in Chapter 3. Phillips (1970) gave still a third definition in terms of the dielectric constant. The formula for polarity of a simple bond, introduced in Eq. (1-37), is essentially equivalent to the ionicity defined by Coulson, but the ionicities defined by Pauling and by Phillips are to a first approximation proportional to the square of that polarity. We will use the term polarity to describe a variation in electronic structure in covalent solids, and the particular values defined by Eq. (1-37) will directly enter the calculation of some properties. We do not use polarity to interpolate properties from one material to another. However, such interpolative approaches are commonly used, and degree of ionicity or polarity is frequently used to rationalize	[redacted]	

trends in properties. Therefore it is best to examine that approach briefly. The distinction between these two approaches is subtle but of fundamental importance. We have seen that there are trends with polarity and with metallicity among the tetrahedral solids. One of the trends is the decrease, with increasing metallicity and increasing polarity, of the angular rigidity that stabilizes the open tetrahedral structure. Thus, if either increases too far, the structure collapses to form a close- packed structure. When this happens, the new system has a qualitatively different electronic structure, and different concepts and approximations become appropriate. We may think of this as analogous to a phase diagram, as illustrated in Fig. 2-6. If a combination of atoms (e.g.,	[redacted] [redacted]	

Litium and flourine) is too polar, a close-packed rocksalt structure is formed. LiF is an ionic crystal and most frequently the best initial approximation to the electronic structure is based on independent ions, which we used in the discussion of the cesium chloride energy bands. Ionic solids can be distinguished from covalent solids by their characteristic crystalline structures, a topic that will be taken up later.	[redacted]	
When the metallicity is too great, a close-packed structure again becomes more	[redacted]	
Polarity	[redacted]	
FIGURE 2-6 A schematic phase diagram indicating the three qualitatively different types of solids discussed in the book. The phase boundaries are topologically correct but details of shape are only schematic.	[redacted]	
Stable. In this case the electronic structure ordinarily approximates that of a free-electron gas and may be analyzed with methods appropriate to free-electron	[redacted]	

gases.

Again, the crystal structure is the determining feature for the classification. When tin has a tetrahedral structure it is a covalent solid; when it has a close- packed white-tin structure, it is a metal. Even silicon and germanium, when melted, become close-packed and liquid metals.

To complete the “ phase diagram,” there must also be a line separating metallic and ionic systems. Materials near this line are called intermetallic compounds; they can lie on the metallic side (an example is Mg2Pb) or on the ionic side (for example, CsAu). Consideration of intermetallic compounds takes the trends far beyond the isoelectronic series that we have been discussing.
The sharp distinction between ionic and covalent solids is maintained in a rearrangement of the periodic table of elements made by Pantelides and Harrison (1975). In this table, the alkali metals and some of their neighbors are transferred to the right (see Fig. 2-7). The

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[redacted]

[redacted]

elements of the carbon column (column 4) and compounds made from elements to either side of that column (such as GaAs or CdS) are covalent solids with tetrahedral structures. Compounds made from elements to either side of the helium column of rare gases (such as KC1 or CaO) are ionic compounds with characteristic ionic structures. A few ionic and covalent compounds do not fit this correlation; notably, MgO, AgF, AgCl, and AgBr are ionic compounds, and MgS and MgSe can occur in either ionic or covalent structures. (Notice that Mg is found both in column 2 and column 10). The interesting isoelectronic series for ionic compounds will be those such as Ar, KC1, CaS, and ScP, obtained from argon by transferring protons between argon nuclei. In this case the ion receiving the proton is the metallic ion and the electronic structure is thought of as a slightly distorted rare gas structure. This model leads to a theory of ionic-compound bonding that is even simpler than the bonding theory for covalent solids. The Pantiledes-Harrison rearrangement of the periodic table is used as the	[redacted]	

format for the Solid State Table, where the parameters needed for the calculation of properties have been gathered.	[redacted]	
2- D Solid State Matrix Elements	[redacted]	
Almost all of the discussion of covalent and ionic solids in this book is based upon descriptions of electron states as linear combinations of atomic orbitals. In order to obtain numerical estimates of properties we need numerical values for the matrix elements giving rise to the covalent and polar energies for the properties being considered. There is no best choice for these parameters since a trade-off must be made between simplicity (or universality) of the choice and accuracy of the predictions that result when they are used. Clearly if different values are used for each property of each material, exact values of the properties can be accommodated. We shall follow a procedure near the opposite extreme, by	[redacted]	

introducing four universal parameters in terms of which all interatomic matrix elements between s and p states for all systems can be estimated. We shall also use a single set of atomic s and p orbital energies throughout. These are the principal parameters needed for the entire range of properties, though the accuracy of the corresponding predictions is limited. One might at first think that interatomic matrix elements could be calculated by using tabulated atomic wave functions and potentials estimated for the various solids. Such approaches have a long history of giving poor numerical results and have tended to discredit the LCAO method itself. However, the difficulty seems to be that though true atomic orbitals do not provide a good basis for describing electronic structure, there are atomiclike orbitals that can provide a very good description. One	[redacted] [redacted]	

<table>
<tr><td>can therefore obtain a useful theory by using LCAO formalism but obtaining the necessary matrix elements by empirical or semiempirical methods.
One of the oldest and most familiar such approaches is the “Extended Hueckel Approximation” (Hoffman, 1963.) Let us take a moment to examine this approach, though later we shall choose an alternative scheme. Detailed rationalizations of the approach are given in Blyholder and Coulson (1968), and in Gilbert (1970, p. 244);
a crude intuitive derivation will suffice for our purposes, as follows. We seek matrix elements of the Hamiltonian between atomic orbitals on adjacent atoms, (p\H\cc). If I a) were an eigenstate of the Hamiltonian, we could replace HI a) by Ea|a), where £a is the eigenvalue. Then if the overlap (,P\oc) is written Spa, the matrix element becomes EaSpa.</td><td>[redacted]
[redacted]</td><td></td></tr>
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This, however, treats the two orbitals differently, so we might use the average instead of Ea. Finding that this does not give good values, we introduce a scale factor G, to be adjusted to fit the properties of heavy molecules; this leads to the extended Hueckel formula: (.PịHịù) = GSpa(ep + ea)/2. (2-12)	[redacted] [redacted]	
These matrix elements are substituted into the Hamiltonian matrix of Eq. (2-2) for a molecule, or a cluster of atoms, and the matrix is diagonalized. A value of G = 1.75 is usually taken; the difference from unity presumably, arises from the peculiar manner in which nonorthogonality is incorporated.	[redacted]	
The Extended Hueckel Approximation and a wide range of methods that may be considered as descendents of it (e.g., the CNDO method—Complete Neglect of Differential Overlap) have enjoyed considerable success	[redacted]	

in theoretical chemistry. Some machine calculation is required, first in determining the parameters s from tabulated wave functions or numerical approximations to them, and second in solving the resulting simultaneous equations, as at Eq. (2-2). This difficulty is exacerbated by the fact that s drops rather slowly with increasing distance between atoms, so a very large number of matrix elements are required. The computation required for any given system is very small, however, in comparison with what is required to obtain more accurate solutions. Once an Extended Hueckel Approximation has been made, direct machine computations of any property can be made and alternatives to the simplest approximations—e.g., Eq. (2-12)— can be made which improve agreement with the experimental values. Such improvements are described in detail by Pople and Beveridge (1970). Combining descriptions of electronic structure that are essentially correct, with the use of high-speed computers, and the results of a number of years of trial and error in correcting the simplest approximations,	[redacted]	

probably provide the most accurate predictions of the diverse properties of complex systems that are presently available. For isolated properties, such as the energy bands of solids, other computer methods are much more reliable and accurate. The approach that will be used in this text is different, in that the description of electronic structures is greatly simplified to provide a more vivid understanding of the properties; numerical estimates of properties will be obtained with calculations that can be carried through by hand rather than machine. We shall concentrate on the “physics” of the problem. In this context a semiempirical determination of matrix elements is appropriate. The first attempt at this (Harrison, 1973c) followed Phillips (1970) in obtaining the principal matrix element v2 from the measured dielectric constant. A second attempt (Harrison and Ciraci,1974) used the	[redacted] [redacted]	

principal peak in the optical reflectivity of the covalent solids, which we shall come to later, as the basis for the principal matrix element; this led to the remarkable finding that v2 scaled from material to material quite accurately as the inverse square of the interatomic distance, the bond length d, between atoms. A subsequent study of the detailed form of valence bands (Pantelides and Harrison, 1975), combined with v2 determined from the peak in optical reflectivity, gave a complete set of interatomic matrix elements for covalent solids with the finding that all of them varied approximately as d~2 from material to material. The reason for this dependence recently became very clear in a study of the bands of covalent solids by Froyen and Harrison (1979). They took advantage of the similarity of the LCAO bands and free-electron bands, noted in Fig. 2-2. By equating	[redacted] [redacted]	

selected energy differences obtained in the two limits, they derived formulae that had this dependence for all of the interatomic matrix elements. We may in fact see in detail how this occurs by considering Fig. 2-2. The lowest band, labelled s in Fig. 2-2,a, was given by Eq. (2-5). For k in an x-direction, it becomes E(k) = es — 4V2 — 2V2 cos ka, varying by 4VZ from r (where k = 0) to X (where k = %/a). The free-electron energy in Fig. 2-2,b varies by (h2/2m)(n/a)2 over the same region of wave number space for the lowest band. Thus, if both limiting models are to be appropriate, and therefore consistent with each other, it must follow that v2 = t]h2/{ma2) with rj = 7t2/8 = 1.23. This predicts the dependence upon the inverse square of interatomic distance and a coefficient that depends only upon crystal structure. A similar comparison of the second band gives the same form with a different coefficient for the matrix element v'2 between p states.	[redacted]	

This simplest model is not so relevant, but it illustrates the point nicely. Before going to more relevant systems we must define more precisely the notation to be used for general interatomic matrix elements.	[redacted]	
These matrix elements will be important throughout the text; they are specified here following the conventions used by Slater and Koster (1954) and used earlier while discussing the diatomic molecule. In general, for a matrix element <a|//|/j> between orbitals on different atoms we construct the vector d, from the nucleus of the atom of which I a) is an orbital (the “ left ” atom) to that of the atom of which I/?) is an orbital (the “right” atom). Then spherical coordinate systems are constructed with the z-axes parallel to d, and with origins at each atom; the angular form of the orbitals can be taken as Y?(9, ệ) for the left orbital and VỊ! (O', Ộ) for the right orbital. The angular factors depending upon ệ	[redacted]	

combine to (Notice that the wave function (a I is the complex conjugate of I a).) The integration over ậ gives zero unless m' = m. Then all matrix elements (a|H||S) vanish unless rri = m, and these are labelled by Ơ, n, or Ỏ (in analogy with s, p, d) for m — I). 1, and 2 respectively. Thus, for example, the matrix element Vspa corresponds to 1 = 0, I = 1, m = 0. Slater and Koster (1954) designated matrix elements by enclosing the indices within parentheses; thus, the element VWm used in this book and their (Wm) are the same.	[redacted]	
We saw how formulae for the matrix elements can be obtained by equating band energies from LCAO theory and from free-electron theory in Fig. 2-2. Froye.1 and Harrison (1979) made the corresponding treatment of the tetrahedral solids, again including only matrix elements between nearest-neighbor atoms. The form of their results is just as found for the simple cubic case	[redacted]	

Notice that the subscript m is a quantum number but the m in the denominator Dimensionless coefficients in Eq. (2-13) determining approximate interatomic matrix elements. Theoretical values Coefficient Simple cubic structure Tetrahedral structure Adjusted value* NOTE: Theoretical values (Froyen and Harrison, 1979) were obtained by equating band energies from I (\0 and free-electron theory, as described in the text. Adjusted values (Harrison, 1976b, 1977a) were obtained by fitting the energy bands of silicon and germanium; the adjusted values appear in the Solid State Table. is the electron mass. The length d is the internuclear distance, equal to a in the simple cubic structure. If d is given in angstroms, this form is easily evaluated, using h2/m = 7.62 eV-Å2. In Table 2-1 we give the values of the dimensionless coefficients obtained by Froyen and	[redacted] [redacted] [redacted] [redacted] [redacted] [redacted] [redacted]	

Harrison for both the simple cubic and Id rahedral structures.

The calculation is closely related to that just carried through for the bands of Fig. 2-2, and in fact, the VSS<J matrix element for the simple cubic case is just the negative of the v2 value evaluated there, leading to the t]ssa = — 7t2/8. wv shall see in Section 18-A exactly how the other theoretical coefficients listed were obtained.

Motice that the coefficients obtained for the tetrahedral structure differ from those obtained for the simple cubic structure and indeed the coefficients for any one structure depend somewhat upon which band energies are used. However, the differences are not great and we shall neglect them. The coefficients we shall use are close to those given by Froyen and Harrison (1979) for the tetrahedral structure, but were obtained somewhat earlier by Harrison (1976b), who adjusted tliL'm to give the interatomic matrix

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[redacted]

elements found by Chadi and Cohen (1975) in fitting the known energy bands of silicon and germanium. The average of the coefficients so obtained for silicon and germanium is listed in Table 2-1 in the column headed “Adjusted,” and these are the values listed in the Solid State Table and used throughout this text. Also listed in the Solid State Table are forms lor predicting matrix elements involving atomic d states, formulae which will be developed in Chapter 20. The coefficients in Table 2-1 have been obtained entirely in the context of nearest-neighbor coupling between states. They would have been different if a *For recent developments, see the Preface to the Dover Edition. TABLE 2-2 Atomic term values from Herman and Skillman (196.Í). or extrapolated from their values.	[redacted]	

Atomic term value (eV) second-neighbor LCAO fit had been used, for example, and it would not therefore be appropriate to use them if the description of the bands were to be extended to second-neighbor interactions. It will ordinarily be more convenient in solids to use the forms for angular dependence, x/r, y/r, and z/r, as in Eq. (1-20), rather than the forms Y”i(0, <p). Then in order to obtain matrix elements involving these orbitals, we need to expand the NOTE: These values appear also in the Solid State Table. p orbital in question in terms of 17, which are defined with respect to the coordinate system discussed above. For p orbitals this is quite simple. For the simplest geometries it leads to the identification of matrix elements shown in the upper four diagrams of Fig. 2-8. For arbitrary geometries the result depends upon the direction cosines giving the vector d in the coordinate system of X, y, and z; this is illustrated at the bottom in	[redacted]	

Fig. 2-8. The corresponding transformations for d FIGURE 2-8 The four types of interatomic matrix elements entering the study of s- and p-bonded systems are chosen as for diatomic molecules as shown in Fig. 1-11. Approximate values for each are obtained from the bond length, or internuclear distance, í/, by Vfj — riijtS/md2, with tiij taking values given in Table 2-1 and in the Solid State Table at the back of the book. When p orbitals are not oriented simply as shown ill the upper diagrams, they may be decomposed geometrically as vectors in order to evaluate matrix elements as illustrated in the bottom diagrams. It can be seen that the interatomic matrix element at the bottom right consists of cancelling the contributions that lead to a vanishing matrix element. orbitals as well as p orbitals will be given in detail in Table 20-1, but for s and p	[redacted] [redacted] [redacted] [redacted]	

orbitals the simple vector transformations illustrated in Fig. 2-8 should be sufficient; the results can be checked with Table 20-1. When we give the Froyen-Harrison analysis in Chapter 18-A, we shall see that the same procedure can give an estimate of the energy difference Ep — £s. It is of the correct general magnitude but fails to describe the important trend in the energy bands among the covalent solids c, Si, Ge, and Sn. Furthermore, it does not provide a means of estimating term-value differences such as scp — e“ in polar solids. Thus, for these intra-atomic parameters we shall use calculated atomic term values, which are listed in Table 2-2. A comparison shows them to be roughly consistent with term values obtained in the fit to known bands done by Chadi and Cohen (1975) for the polar semiconductors as well as for silicon and germanium.	[redacted] [redacted]	

This particular set of calculated values (by Herman and Skillman, 1963) was chosen since the approximations used in the calculation were very similar to those used in determining the energy bands that led to the parameters in Table 2-1. The values would not have differed greatly if they were taken from Hartree-Fock calculations (such values are tabulated in Appendix A). Values based on Hartree-Fock calculations have the advantage of giving good values for d states. Therefore, though the calculations in this book are based upon the Herman-Skillman values, for some applications the Hartree-Fock values may be better suited. Notice that as absolute numbers the atomic energy values have only limited meaning in any case. Imagine, for example, that the value Ep for oxygen correctly gives the energy required to remove an electron from an isolated oxygen atom in space. If this atom is brought close to the surface of a metal	[redacted] [redacted] [redacted]	

(or, almost equivalently, to the surface of a covalent solid with a large dielectric constant) but not close enough for any chemical bonding to take place, how much energy is now required to remove the electron from the oxygen? One way to calculate this is to move the neutral atom to infinity, with no work required, remove the electron requiring £p, and then return the oxygen ion to its initial position; as it returns it gains an energy e2/4d from the image field, where d is the final distance from the surface. The resultant correction of fip, with d equal to 2 Â, is 1.8 eV, far from negligible. The precise value is uncertain because of the dielectric approximation, the uncertainty in the d used, and other effects, but we may expect that significant corrections of the absolute energies are needed relative to the values in vacuum. The reason that the values are nevertheless useful as parameters is that in solids such corrections are similar for all atoms involved and the	[redacted]	

relative values are meaningful. How do the values obtained from Tables 2-1 and 2-2 compare with the values obtained directly by fitting energy bands? This comparison is made in Table 2-3 for the covalent systems studied by Chadi and Cohen. Agreement is semiquantitative throughout and all trends are reproduced except the splitting of values for VsptT in the compounds. The discrepancies are comparable to the differences between different fits (the most recent fits are used here), thus justifying the use of the simple forms in our studies. Significantly different values are obtained if one includes a greater number of matrix elements in the fit (Pandey, 1976) and would be appropriate if we were to include these matrix elements in the calculation of properties other than the bands themselves.	[redacted] [redacted]	

Significantly different values have also been given by Levin (1974). The coefficients from Table 2-1 and atomic term values from Table 2-2 will suffice for calculation of an extraordinarily wide range of properties of covalent and ionic solids using only a standard hand-held calculator. This is impressive testimony to the simplicity of the electronic structure and bonding in these systems. Indeed the same parameters gave a semiquantitative prediction of the one-electron energy levels of diatomic molecules in Table 1-1. However, that theory is intrinsically approximate and not always subject to successive correc- TABLE 2-3 Matrix elements from the Solid State Table, compared with values (in parentheses) from fits to individual bands. All values are in eV. SOURCES of data in parentheses: c from Chadi and Martin (1976); Si and Ge from Chadi and Cohen (1975); GaAs and ZnSe from	[redacted]	

Chadi and Martin (1976).	[redacted]	
NOTE: Where two values of Vspr are given for compounds, the first vaiue is for an s state in the nonmetallic atom and p state in the metallic atom. States are reversed for the second value. Where two values of («p — cs)/4 are listed, the first value is for the metallic atom, the second for the nonmetallic atom.	[redacted]	
tions and improvements. In most cases our predictions of properties will be accurate on a scale reflected in Table 2-3, and though the introduction of further parameters allows a more accurate fit to the data, it may be that improvements at a more fundamental level are required for a more realistic treatment and that these improvements cannot be made without sacrificing the conceptual and computational simplicity of the picture that will be constructed in the course of this book.	[redacted]	
Before proceeding to quantitative studies of the	[redacted]	

covalent solids it is appropriate to comment on the concept of “electronegativity,” introduced by Pauling to denote the tendency of atoms to attract electrons to themselves (discussed recently, for example, by Phillips, 1973b, p. 32). It may be an unfortunate term since the positive terminal of a battery has greater electronegativity than the negative terminal. Furthermore, it was defined to be dimensionless rather than to have more natural values in electron volts. It would be tempting to take the hybrid energy values of Table 2-2 as the definition of electronegativity, but it will be seen that in some properties the energy Ep is a more appropriate measure. Therefore it will be a wiser choice to use the term only qualitatively. Then from Table 2-2 (or from Fig. 1-8) we see that the principal trend is an increase in electronegativity with increasing atomic number proceeding horizontally from one inert gas to the next (e.g., from neon, Na, Mg, Al, Si, p, s, and Cl to argon). In addition, the elements between helium and neon	[redacted]	

have greater electronegativity than the heavier elements. It is useful to retain “ electronegativity ” to describe these two qualitative trends.	[redacted]	
2-E Calculation of Spectra	[redacted]	
We have seen that in solids, bands of electron energies exist rather than the discrete levels of atoms or molecules. Similarly there are bands of vibration frequencies rather than discrete modes. Thus, to show electron eigenvalues, a curve was given in Fig. 2-2 rather than a table of values. However, a complete specification of the energies within the bands for a three-dimensional solid requires a three-dimensional plot and that cannot be made; even in two dimensions an attempt is of limited use. Instead, a convenient representation of electronic structure can be made by plotting the number of states, per unit energy, as a function of energy. This loses the information about, for example, electron velocity, since that requires a knowledge of energy as a function of wave number.	[redacted]	

However, it is all that is needed to sum the energies of the electrons for given atomic arrangements. Calculation of such a spectrum might seem straightforward, but if done by sampling, it requires an inordinate amount of calculation. For example, to produce a plot we might divide the energy region of interest into one thousand intervals and then evaluate the energies (as we did in Section 2-A) over a closely spaced grid in the Brillouin Zone, keeping track of the number of eigenvalues obtained in each interval. A great increase in efficiency can be obtained by noting that the energy bands have the full symmetry of the Brillouin Zone—in the case of CsCl, a cube—so that the entire Brillouin Zone need not be sampled. One could sample one half the zone and multiply the results by two, one eighth and multiply by eight, or in fact, for a cube, one forty-eighth suffices. However, even in a sample of thousands of values, the	[redacted] [redacted]	

resulting histogram shows large statistical fluctuations. Therefore an alternative approach is required. The approach most commonly used, and used extensively in the curves in this book, is the Gilat-Raubenheimer scheme (Raubenheimer and Gilat, 1966). In this scheme, the idea is to replace the true bands by approximate bands, but then to calculate the density of levels for that spectrum accurately. This is done by dividing up the Brillouin Zone, or a forty-eighth of the zone for cubic symmetry, into cells; of the order of fifty may be appropriate; Raubenheimer and Gilat used cells in the shape of cubes. They then fit each band in each cell by a linear expression, Ek = E0 + A1 kx + A2ky + A3kz, with k measured from the center of the cell. Then the energy region of interest for the system is divided into some 1000 energy intervals and the contribution to each of these intervals is accurately and	[redacted] [redacted]	

analytically obtained from the linear values of the bands in each cell. This is illustrated for one dimension in Fig. 2-9. We see that the distribution of the approximate bands is obtained exactly. This turns out to eliminate most of the statistical error and to give very good results.	[redacted]	
In the Gilat-Raubenheimer scheme it is inconvenient to obtain the necessary values of the gradient of the energy with respect to wave number in each cell, and the cubes do not fit the Brillouin Zone section exactly, so there are problems in calculating the energy at the surface of the section. For this reason Jepsen and Andersen (1971) and later, independently, Lehman and Taut (1972) replaced	[redacted]	
(c) Number of states contributed in each interval	[redacted]	
FIGURE 2-9 A schematic representation of the Gilat-Raubenheimer scheme for calculating densities of states. The energy	[redacted] [redacted]	

bands (a) are replaced by linear bands (b) in each cell. The contribution by each cell to each of a set of small energy intervals (c) is then obtained analytically. cubes by tetrahedra and wrote the distribution of energies in terms of the values at the four comers. A clear description of this much simpler approach is given by Rath and Freeman (1975), who include the necessary formulae. It is also helpful to see one manner in which the Brillouin Zone can be divided into cells. This is shown in Fig. 2-10, This procedure has been discussed also by Gilat and Bharatiya (1975). Another scheme, utilizing a more accurate approximation to the bands, has been considered recently by Chen (1976). In some sense this is a computational detail, but the resulting curves are so essential to solid state properties that the detail is important. Once a program has been written for a given Brillouin Zone, any of the spectra for the corresponding structure can be efficiently and accurately obtained from the bands themselves.	[redacted]	

	[redacted]	
PROBLEM 2-1 Calculating one-dimensional energy bands Let us make an elementary calculation of energy bands, using the notation of LCAO theory. For many readers the procedure will be familiar. Consider a ring of N atoms, each with an s orbital. We seek an electronic state in the form of an LCAO,	[redacted] [redacted]	
where the integers a number the atoms. We can evaluate the expectation value of the energy, considering all atoms to be identical, so (a I HI a) = R is the same for all a. We can also neglect all matrix elements (a\H\p'), except if a and /? differ by one; we write that	[redacted]	
FIGURE 2-10 (a) The body-centered-cubic Brillouin Zone is divided into 48 equivalent pyramidal segments. (Two such pyramids are required for face-centered cubic zones.) (b) The pyramid is cut	[redacted] [redacted]	

by equally spaced planes parallel to the base, (c) Most of the slab may be subdivided into triangular prisms. An edge is left over on the right which can be divided into triangular prisms with one tetrahedron left over. Each triangular prism (d) may finally be divided into three tetrahedra, (e). This divides the Brillouin Zone entirely into tetrahedra of equal volume. The bands are taken to be linear in wave number within each tetrahedron.	[redacted]	
We shall treat the uj as independent of ua and minimize the expression with respect to UĨ, giving a linear algebraic equation for each a.	[redacted]	
(a) Show that for any integer it there is a solution for all of these equations of the form	[redacted]	
(b) Give the energy as a function of n, and sketch it as a function of n/N for large N. Include positive and negative n.	[redacted]	
(c) Obtain the value of A that normalizes the electron state.	[redacted]	

(d) Show that for an n outside the range — N/2 <n< N/2, the electron state obtained is identical to that for some n within this range (within the Brillouin Zone). It suffices to prove that for given n the ua are unchanged by the addition of N to n. PROBLEM 2-2 Electron dynamics Consider an electron in a one-dimensional energy band given by E(k) = — y2 COS ka in a Brillouin Zone, —n/a < k < n/a. At time t = 0, with the electron having wave number k = 0, apply an electric field ê. Obtain the energy, the speed, and the position of the electron as a function of time. The behavior will be oscillatory. It can be thought of as acceleration of the electron followed by gradual diffraction caused by the lattice. How many lattice distances (each distance a = 2 Å) does the electron go if v2 = 2 eV and the field is 100 volts per centimeter?	[redacted] [redacted] [redacted] [redacted] [redacted]	

	[redacted]	