# SOLID STATE PHYSICS

SECOND EDITION

J. S. Blakemore

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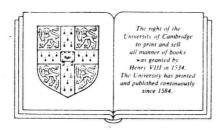
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### **PREFACE**

This book was written as the text for a one quarter, or one semester, introductory course on the physics of solids. For an undergraduate majoring in physics, the associated course will usually be taken during the last two undergraduate years. However, the book is designed also to meet needs of those with other degree majors: in chemistry, electrical engineering, materials science, etc., who may not encounter this requirement in their education until graduate school. Some topics discussed (band theory, for example) require familiarity with the language and concepts of quantum physics; and an assumed level of preparedness is one semester of "modern physics". A reader who has taken a formal quantum mechanics course will be well prepared, but it is recognized that this is often not possible. Thus Schrödinger's equation is seen from time to time, but formal quantum mechanical proofs are side-stepped.

The aim is thus a reasonably rigorous – but not obscure – first exposition of solid state physics. The emphasis is on crystalline solids, proceeding from lattice symmetries to the ideas of reciprocal space and Brillouin zones. These ideas are then developed: for lattice vibrations, the theory of metals, and crystalline semiconductors, in Chapters 2, 3, and 4 respectively. Aspects of the consequences of atomic periodicity comprise some 75% of the book's 500 pages. In order to keep the total exposition within reasonable bounds for a first solid state course, a number of *other* aspects of condensed matter physics have been included but at a relatively brief survey level. Those topics include lattice defects, amorphous solids, superconductivity, dielectric and magnetic phenomena, and magnetic resonance.

The text now offered is on many pages unchanged from that of the 1974 second edition published by Saunders. However, the present opportunity to offer this book through the auspices of Cambridge University Press has permitted me to correct some errors, add some needed lines of explanation (such as at the end of Section 1.5), revise some figures, and update the bibliographies following this preface and at the end of each chapter. The SI system of units, adopted for the second edition, is of course retained here. Two exceptions to the SI system should be noted: retention of the *Ångstrom unit* in describing interatomic distances, and use of the electron volt for discussions of energy per electron of per atom. There seems no sign that crystallographers are ready to quote lattice spacings in nanometers, and the  $10^{-10}$  conversion factor from Å to meters is an easy

one. Use of the eV rather than  $1.6 \times 10^{-19}$  J also simplifies many descriptions of energy transformation events. Questions of units are of course important for the numerical aspects of homework problems.

These problems are grouped at the end of each chapter, and there are 125 of them altogether. Many do include a numerical part, intended to draw the stude of attention to the relative magnitudes of quantities and influences more than to the importance of decimal place accuracy. The problems vary (intentionally) greatly in length and difficulty; and I have been told several times that some of these problems are too difficult for the level of the text. These can certainly provide a worthwhile challenge for one who has "graduated" from the present book to one of the advanced solid state texts cited in the General Reference list which follows this preface.

As in previous editions of this book, many more literature citation footnotes are given than are typical in an undergraduate text. These augment the bibliography at the end of each chapter in citing specific sources for *optional* additional reading. A paper so cited in a footnote may serve as the beginning of a literature search undertaken years after the owner's first exposure to this book, and the footnotes have been provided with this in mind.

The present book was written to be an account of *ideas* about the physics of solids rather than a compilation of facts and numbers. Accordingly, tables of numerically determined properties are relatively few in contrast, for example, to nearly 60 tables of data in the fifth edition of Kittel's well-known textbook. The reader needing quantitative physical data on solids has a variety of places to turn to, with extensive data in the *American Institute of Physics Handbook* (last revised in 1972) and in the *Handbook of Chemistry and Physics* (updated annually). As noted in the list of General References on page ix, new volumes have recently been appearing in the *Landolt–Börnstein Tables* series, including data compilation for some semiconductor materials. The work of consolidating numerical information concerning solids is indeed a continuous one.

Over the years of writing and rewriting material for successive editions of this book, I have been helped by many people who have made suggestions concerning the text, worked problems, and provided illustration material. To all of those individually acknowledged in the prefaces of the first and second editions, I am still grateful. In preparing this updated second edition for Cambridge University Press, my principal acknowledgement should go to L. E. Murr of the Oregon Graduate Center for the photographs that provide a number of attractive and informative new figures in Chapter 1, and to H. K. Henisch of Pennsylvania State University for the print used as Figure 1.2.

Beaverton, Oregon March 1985

J. S. BLAKEMORE

## **GENERAL REFERENCES**

#### Solid State Physics (Introductory/Intermediate Level)

- R. H. Bube, Electrons in Solids: An Introductory, Survey (Academic Press, 1981).
- R. H. Bube, Electronic Properties of Crystalline Solids (Academic Press, 1973).
- A. J. Dekker, Solid State Physics (Prentice-Hall, 1957). [Was never revised and is now out of print, but includes interesting discussion of several topics others omit.]
- H. J. Goldsmid (ed.), Problems in Solid State Physics (Pion, 1968).
- W. A. Harrison, Electronic Structure and the Properties of Solids (Freeman, 1980).
- C. Kittel, Introduction to Solid State Physics (Wiley, 5th ed., 1976).
- J. P. McKelvey, Solid-State and Semiconductor Physics (Krieger, 1982).
- H. M. Rosenberg, The Solid State (Oxford Univ. Press, 2nd ed., 1979).

#### Solid State Physics (Advanced Level)

- N. W. Ashcroft and N. D. Mermin, Solid State Physics (Holt, 1976).
- J. Callaway, Quantum Theory of the Solid State (Academic Press, 1974), 2 vols.
- D. L. Goodstein, States of Matter (Prentice-Hall, 1975).
- W. A. Harrison, Solid State Theory (Dover, 1980).
- A. Haug, Theoretical Solid State Physics (Pergamon Press, 1972), 2 vols.
- W. Jones and N. H. March, Theoretical Solid State Physics (Wiley, 1973), 2 vols.
- C. Kittel, Quantum Theory of Solids (Wiley, 1963).
- R. Kubo and T. Nagamiya (eds.), Solid State Physics (McGraw-Hill, 1969).
- P. T. Landsberg (ed.), Solid State Theory, Methods & Applications (Wiley, 1969).
- R. E. Peierls, Quantum Theory of Solids (Oxford, 1965). [Out of print, but a classic.]
- F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940). [Another out-of-print classic still of great value.]
- J. Ziman, Principles of the Theory of Solids (Cambridge Univ. Press, 2nd ed., 1972).

#### **Solid State Electronics**

- A. Bar-Lev, Semiconductors and Electronic Devices (Prentice-Hall, 1979).
- N. G. Einspruch (ed.), VLSI Electronics: Microstructure Science (Academic Press, Vol. 1, 1981, through vol. 8, 1984, and continuing).
- R. J. Elliott and A. F. Gibson, An Introduction to Solid State Physics and its Applications (Barnes and Noble, 1974).
- A. S. Grove, Physics and Technology of Semiconductor Devices (Wiley, 1967).
- A. G. Milnes, Semiconductor Devices and Integrated Circuits (Van Nostrand, 1980).
- T. S. Moss, G. J. Barrett and B. Ellis, Semiconductor Optoelectronics (Butterworths, 1973).
- B. G. Streetman, Solid State Electronic Devices (Prentice-Hall, 2nd ed., 1980).
- S. M. Sze, Physics of Semiconductor Devices (Wiley, 2nd ed., 1981).
- F. F. Y. Wang, Introduction to Solid State Electronics (North-Holland, 1980).

#### GENERAL REFERENCES

X

#### Quantum Phenomena

- F. J. Bockhoff, Elements of Quantum Theory (Addison-Wesley, 2nd ed., 1976).
- A. P. French and E. F. Taylor, An Introduction to Quantum Physics (Norton, 1978).
- B. K. Ridley, Quantum Processes in Semiconductors (Oxford Univ. Press, 1981).
- D. ter Haar (ed.), Problems in Quantum Mechanics (Pion, 3rd ed., 1975).

#### Statistical Physics

- S. Fujitta, Statistical and Thermal Physics (Krieger, 1984).
- C. Kittel, Elementary Statistical Physics (Wiley, 1958).
- C. Kittel and H. Kroemer, Thermal Physics (Freeman, 2nd ed., 1980).
- F. Mohling, Statistical Mechanics (Wiley-Halsted, 1982).
- L. E. Reichl, A Modern Course in Statistical Physics (Univ. Texas, 1980).
- R. C. Tolman, The Principles of Statistical Mechanics (Dover, 1979).

#### Wave Phenomena

- L. Brillouin, Wave Properties and Group Velocity (Academic Press, 1960).
- L. Brillouin, Wave Propagation in Periodic Structures (Dover, 1972).
- I. G. Main, Vibrations and Waves in Physics (Cambridge Univ. Press, 1978).
- C. F. Squire, Waves in Physical Systems (Prentice-Hall, 1971).

#### **Numerical Data**

American Institute of Physics Handbook (McGraw-Hill, 3rd ed., 1972). Handbook of Chemistry and Physics (CRC Press, 66th ed., 1985). Handbuch der Physik (S. Flügge, general editor for 54 volume series) (Springer-Verlag, 1956 through 1974).

Landolt-Börnstein Tables (Springer-Verlag). [Volumes date from the 1950s and earlier, but new ones are now appearing on solid state topics.]

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## CRYSTALLINITY AND THE FORM OF SOLIDS

Solid materials can be classified according to a variety of criteria. Among the more significant of these is the description of a solid as being either *crystalline* or *amorphous*. The solid state physics community has tended during the period from the mid-1940's to the late 1960's to concentrate a much larger effort on crystalline solids than on the less tractable amorphous ones.

An amorphous solid exhibits a considerable degree of short range order in its nearest-neighbor bonds, but not the long range order of a periodic atomic lattice; examples include randomly polymerized plastics, carbon blacks, allotropic forms of elements such as selenium and antimony, and glasses. A glass may alternatively be thought of as a supercooled liquid in which the viscosity is too large to permit atomic rearrangement towards a more ordered form. Since the degree of ordering of an amorphous solid depends so much on the conditions of its preparation, it is perhaps not inappropriate to suggest that the preparation and study of amorphous solids has owed rather less to science and rather more to art than the study of crystalline materials. Intense study since the 1960s on glassy solids such as amorphous silicon (of interest for its electronic properties) is likely to create a more nearly quantitative basis for interpreting both electronic and structural features of noncrystalline materials.

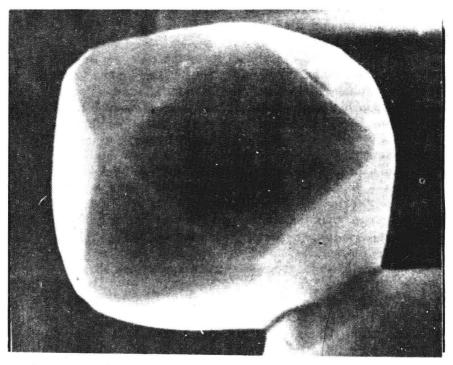
In the basic theory of the solid state, it is a common practice to start with models of single crystals of complete perfection and infinite size. The effects of impurities, defects, surfaces, and grain boundaries are then added as perturbations. Such a procedure often works quite well even when the solid under study has grains of microscopic or submicroscopic size, provided that long range order extends over distances which are very large compared with the interatomic spacing. However,

it is particularly convenient to carry out experimental measurements on large single crystals when they are available, whether they are of natural origin or synthetically prepared. Figures 1-1 and 1-2 show examples of microscopic and macroscopic synthetic crystals.

Large natural crystals of a variety of solids have been known to man for thousands of years. Typical examples are quartz (SiO<sub>2</sub>), rocksalt (NaCl), the sulphides of metals such as lead and zinc, and of course gemstones such as ruby (Al<sub>2</sub>O<sub>3</sub>) and diamond (C). Some of these natural crystals exhibit a surprising degree of purity and crystalline perfection, which has been matched in the laboratory only during the past few years.<sup>2</sup> For many centuries the word "crystal" was applied specifically to quartz; it is based on the Greek word implying a form similar to that of ice. In current usage, a *crystalline solid* is one in which the atomic arrangement is regularly repeated, and which is likely to exhibit an external morphology of planes making characteristic angles with each other *if* the sample being studied happens to be a *single* crystal.

When two single crystals of the same solid are compared, it will usually be found that the sizes of the characteristic plane "faces" are

<sup>&</sup>lt;sup>2</sup> Indeed, synthetically created diamonds still do not compare in quality with the finest natural diamonds. For most other gemstones, man seems to have been able to do at least as well as nature.



**Figure 1-1** Scanning electron microscope view of small NiO crystal, with well developed facets. (Photo courtesy of L. E. Murr, Oregon Graduate Center.) At room temperature, antiferromagnetic ordering provides for NiO a trigonal distortion of the (basically rocksalt) atomic arrangement.

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¹ For discussions of single growth techniques, see the bibliography at the end of Chapter I.

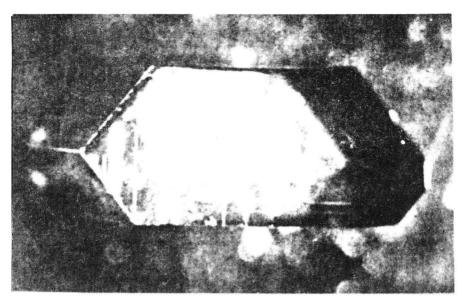


Figure 1-2 The growing surface of a calcium tartrate crystal, during growth in a tartrate gel infused with calcium chloride solution. From *Crystal Growth in Gels* by H. K. Henisch (Penn. State Univ. Press, 1970).

not in the same proportion (the "habit" varies from crystal to crystal). On the other hand the interfacial angles are always the same for crystals of a given material; this was noted in the sixteenth century and formed the basis of the crystallography of the next three centuries. These observations had to await the development of the atomic concept for an explanation, and it was not until Friedrich, Knipping, and Laue demonstrated in 1912 that crystals could act as three-dimensional diffraction gratings for X-rays that the concept of a regular and periodic atomic arrangement received a sound experimental foundation. More recently, the periodic arrangement of atoms has been made directly visible by field-emission microscopy.<sup>3</sup>

Whether we wish to study mechanical, thermal, optical, electronic, or magnetic properties of crystals—be they natural ones, synthetic single crystals (such as Ge, Si, Al<sub>2</sub>O<sub>3</sub>, KBr, Cu, Al), or polycrystalline aggregates—most of the results obtained will be strongly influenced by the periodic arrangement of atomic cores or by the accompanying periodic electrostatic potential. The consequences of periodicity take up a major fraction of this book, for a periodic potential has many consequences, and exact or approximate solutions are possible in many situations.

In this first chapter we shall consider how atoms are bonded together and how symmetry requirements result in the existence of a limited variety of crystal classes. There is no optimum order for consideration of the two topics of bonding and crystal symmetry, since each depends on the other for illumination; it is recommended that the

<sup>&</sup>lt;sup>3</sup> See, for example, Figure 1-56(a) on page 79, for an ion-microscope view of atoms at the surface of an iridium crystal.

#### 4 CRYSTALLINITY AND THE FORM OF SOLIDS

reader skim through the next two sections completely before embarking upon a detailed study of either.

The chapter continues (in Section 1.3) with an account of some of the simpler lattices in which real solids crystallize. The emphasis of the section is on the structures of elements and of the more familiar inorganic binary compounds.

Sections 1.4 (Crystal Diffraction) and 1.5 (Reciprocal Space) are closely connected, and once again it is recommended that both sections be read through before a detailed study of either is undertaken. An understanding of the reciprocal lattice helps one to see what diffraction of a wave in a crystal is all about, and *vice versa*.

Section 1.6 does little more than mention the principal types of point and line imperfection in a crystal. Bibliographic sources are cited for the reader who wishes to know more about dislocations, or about the chemical thermodynamics of defect interactions in solids.

### Forms of Interatomic Binding

1.1

All of the mechanisms which cause bonding between atoms derive from electrical attraction and repulsion. The differing strengths and differing types of bond are determined by the particular electronic structures of the atoms involved. The weak van der Waals (or residual) bond provides a universal weak attraction between closely spaced atoms and its influence is overridden when the conditions necessary for ionic, covalent, or metallic bonding are also present.

The existence of a stable bonding arrangement (whether between a pair of otherwise isolated atoms, or throughout a large, three-dimensional crystalline array) implies that the spatial configuration of positive ion cores and outer electrons has less total energy than any other configuration (including infinite separation of the respective atoms). The energy deficit of the configuration compared with isolated atoms is known as the *cohesive energy*, and ranges in value from 0.1 eV/atom for solids which can muster only the weak van der Waals bond to 7 eV/atom or more in some covalent and ionic compounds and some metals. The cohesive energy constitutes the reduction in potential energy of the bonded system (compared with separate atoms) *minus* the additional kinetic energy which the Heisenberg uncertainty principle tells us must result from localization of the nuclei and outer shell electrons.

In covalent bonding the angular placement of bonds is very important, while in some other types of bonding a premium is placed upon securing the largest possible coordination number (number of nearest neighbors). Such factors are clearly important in controlling the most favorable three-dimensional structure. For some solids, two or more quite different structures would result in nearly the same energy, and a change in temperature or hydrostatic pressure can then provoke a change from one allotropic form of the solid to another, as envisaged in Figure 1-3. As discussed further under the heading of the Covalent Bond, an allotropic transition to an energetically more favorable structure can sometimes be postponed, depending on the rate of conditions of cooling or warming.

 $<sup>^4</sup>$  The joule is a rather large energy unit for discussion of events involving a single atom. Thus energies in this book will often be quoted in terms of electron volts per particle or per microscopic system. (It is hoped that the context will leave no doubt as to whether an energy change in eV refers to a molecule, an atom, or a single electron.) One elementary charge moved through a potential difference of one volt involves a potential energy change of  $1.6022\times 10^{-19}$  joule (see the table of useful constants inside the cover). Chemists tend to cite bond energies and cohesive energies in calories per mole.  $^{\circ}1$  eV/molecule is equivalent to 23,000 calories per mole, or  $9.65\times 10^4$  joule/mole.

#### CRYSTALLINITY AND THE FORM OF SOLIDS

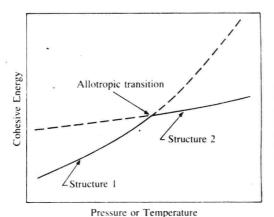


Figure 1-3 Cohesive energy versus temperature or pressure for a solid in which two different atomic arrangements are possible. An allotropic transition *may* occur at the pressure or temperature at which one structure replaces the other as having minimum energy.

#### THE VAN DER WAALS BOND

As previously noted, van der Waals bonding occurs universally between closely spaced atoms, but is important only when the conditions for stronger bonding mechanisms fail. It is a weak bond, with a typical strength of 0.2 eV/atom, and occurs between neutral atoms and between molecules. The name van der Waals is associated with this form of bond since it was he who suggested that weak attractive forces between molecules in a gas lead to an equation of state which represents the properties of real gases rather better than the ideal gas law does. However, an explanation of this general attractive force had to await the theoretical attentions of London (1930).

London noted that a neutral atom has zero permanent electric dipole moment, as do many molecules; yet such atoms and molecules are attracted to others by electrical forces. He pointed out that the zero-point motion, which is a consequence of the Heisenberg uncertainty principle, gives any neutral atom a fluctuating dipole moment whose amplitude and orientation vary rapidly. The field induced by a dipole falls off as the cube of the distance. Thus if the nuclei of two atoms are separated by a distance r, the instantaneous dipole of each atom creates an instantaneous field proportional to  $(1/r)^3$  at the other. The potential energy of the coupling between the dipoles (which is attractive) is then

$$E_{attr} = -\left(\frac{A}{r^6}\right) \tag{1-1}$$

A quantum-mechanical calculation of the strength of this dipole-dipole attraction suggests that  $E_{\rm attr}$  would reach 10 eV if r could be as small as 1Å. However, a spacing this small is impossible because of overlap repulsion.

As the interatomic distance decreases, the attractive tendency begins to be offset by a repulsive mechanism when the electron clouds of the atoms begin to overlap. This can be understood in terms of the Pauli exclusion principle, that two or more electrons may not occupy the same quantum state. Thus overlap of electron clouds from two atoms with quasi-closed-shell configurations is possible only by promotion of some of the electrons to higher quantum states, which requires more energy.

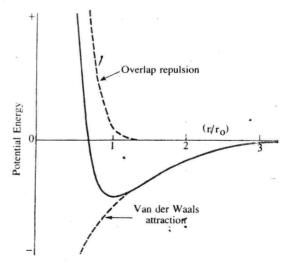
The variation of repulsive energy with interatomic spacing can be simulated either by a power law expression (a dependence as strong as  $r^{-11}$  or  $r^{-12}$  being necessary) or in terms of a characteristic length. The latter form is usually found to be the most satisfactory, and the total energy can then be written as

$$E = -\left(\frac{A}{r^6}\right) + B \exp\left(-\frac{r}{\rho}\right) \tag{1-2}$$

which is drawn as the solid curve in Figure 1-4. The strength of the bond formed and the equilibrium distance  $r_0$  between the atoms so bonded depend on the magnitudes of the parameters A, B, and  $\rho$ . Since the characteristic length  $\rho$  is small compared with the interatomic spacing, the equilibrium arrangement of minimum E occurs with the repulsive term making a rather small reduction in the binding energy.<sup>5</sup>

We have spoken of van der Waals bonding so far as occurring between a pair of otherwise isolated atoms. Within a three-dimensional solid, the dipole-dipole attractive and overlap repulsive effects with respect to the various neighbor atoms add to give an overall cohesive energy still in accord with Equation 1-2. There are no restrictions on bond angles, and solids bound by van der Waals forces tend to form in the (close-packed) crystal structures for which an atom has the largest possible number of nearest neighbors. (This is the case, for example, in the crystals of the inert gases Ne, Ar, Kr, and Xe, all face-centered-cubic structures, in which each atom has twelve nearest neighbors.) The rapid decrease of van der Waals attraction with distance makes atoms beyond the nearest neighbors of very little importance.

Figure 1-4 Total potential energy in a van der Waals bond (solid curve), showing the attractive and repulsive terms which combine to give a stable bond at an internuclear distance r<sub>0</sub>.



<sup>&</sup>lt;sup>5</sup> See Problem 1.1 for an exercise of this principle.

The solid inert gases<sup>6</sup> are fine examples of solids which are bound solely by van der Waals forces, because the closed-shell configurations of the atoms eliminate the possibility of other, stronger bonding mechanisms. Far more typically do we find solids in which van der Waals forces bind saturated molecules together, molecules within which much stronger mechanisms are at work. This is the case with crystals of many saturated organic compounds and also for solid H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>. The example of Cl<sub>2</sub>, with a sublimation energy of 0.2 eV/molecule but a dissociation energy of 2.5 eV/molecule, shows how the van der Waals bond between diatomic molecules can be broken much more readily than the covalent Cl-Cl bond.

#### THE COVALENT BOND

The covalent bond, sometimes referred to as a valence or homopolar bond, is an electron-pair bond in which two atoms share two electrons. The result of this sharing is that the electron charge density is high in the region between the two atoms. An atom is limited in the number of covalent bonds it can make (depending on how much the number of outer electrons differs from a closed-shell configuration), and there is a marked directionality in the bonding. Thus carbon can be involved in four bonds at tetrahedral angles (109.5°), and the characteristic tetrahedral arrangement is seen in crystalline diamond and in innumerable organic compounds. Other examples of characteristic angles between adjacent covalent bonds are 105° in plastic sulphur and 102.6° in tellurium.

The hydrogen molecule,  $H_2$ , serves as a simple example of the covalent bond. Two isolated hydrogen atoms have separate 1s states for their respective electrons. When they are brought together, the interaction between the atoms splits the 1s state into two states of differing energy, as sketched in Figure 1-5. When the two nuclei are very close together, the total energy is increased for both kinds of states by internuclear electrostatic repulsion; but for the 1s state marked<sup>8</sup>  $\sigma_g$ , which has an even (symmetric) orbital wave-function, the energy is lowered (i.e., there is an attractive tendency) for a moderate spacing.<sup>9</sup>

<sup>&</sup>lt;sup>6</sup> For helium, the zero-point motion is so violent that solidification even at absolute zero can be accomplished only by applying an external pressure of 30 atmospheres.

<sup>&</sup>lt;sup>7</sup> Remember that in quantum mechanics we cannot describe a specific orbit for a bound electron but only a wave-function  $\psi$  whose square is proportional to the probability of finding an electron at a location on a time-averaged basis. Then if  $\psi$  is a normalized wave-function (such that  $\psi^2$  integrated over all space is unity), the average charge density at any location is the value of  $-e\psi^2$ .

<sup>&</sup>quot;The designation of the two orbital wave-functions as  $\sigma_k$  and  $\sigma_u$  comes from the German terms "gerade" and "ungerade" for even and odd.

<sup>&</sup>lt;sup>9</sup> A principal feature of the bonding attraction is the resonance energy corresponding to the exchange of the two electrons between the two atomic orbitals, as first discussed by W. Heitler and F. London, Z. Physik 44, 455 (1927). For a recent account of this in English, see E. E. Anderson, *Modern Physics and Quantum Mechanics* (W. B. Saunders, 1971), p. 390.