Charles Kittel

INTRODUCTION TO SOLID STATE PHYSICS

FIFTH EDITION

JOHN WILEY & SONS, INC.
NEW YORK / LONDON / SYDNEY / TORONTO

About the Author

CHARLES KITTEL has taught solid state physics at the University of California at Berkeley since 1951, having previously been at the Bell Laboratories. His undergraduate work in physics was done at M.I.T. and at the Cavendish Laboratory of Cambridge University. His Ph.D. research was in theoretical nuclear physics with Professor Gregory Breit at the University of Wisconsin. He has been awarded three Guggenheim fellowships, the Oliver Buckley Prize for Solid State Physics, and the Distinguished Teaching Award at Berkeley. He is a member of the National Academy of Science and of the American Academy of Arts and Sciences. The first edition of *ISSP* appeared in 1953 as the first textbook to integrate the elementary parts of solid state physics for use by seniors and beginning graduate students; now in the fifth edition, *ISSP* is one of the most widely translated science textbooks. His recent research is in the field of electron-hole condensation in semiconductors.

IONIC CRYSTALS

Ionic crystals are made up of positive and negative ions. The **ionic bond** results from the electrostatic interaction of oppositely charged ions. Two common crystal structures found for ionic crystals, the sodium chloride and the cesium chloride structures, were shown in Chapter 1.

The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells, as in the inert gas atoms. In lithium fluoride the configuration of the neutral atoms are, according to the periodic table in the front endpapers of this book, Li: $1s^2 2s$, F: $1s^2 2s^2 2p^5$. The singly charged ions have the configurations Li^+: $1s^2$, F^-: $1s^2 2s^2 2p^6$, as for helium and neon, respectively. Inert gas atoms have closed shells, and the charge distributions are spherically symmetric. We expect that the charge distributions on each ion in an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms. This picture is confirmed by x-ray studies of electron distributions (Fig. 7).

A quick estimate suggests that we are not misguided in looking to electrostatic interactions for a large part of the binding energy of an ionic crystal. The distance between a positive ion and the nearest negative ion in crystalline sodium chloride is 2.81×10^{-8} cm, and the attractive coulomb part of the potential energy of the two ions by themselves is 5.1 eV. This value may be compared (Fig. 8) with the experimental value of 7.9 eV per molecule unit for the cohesive energy of crystalline NaCl with respect to separated Na^+ and Cl^- ions. We now calculate the lattice energy more closely.

Electrostatic or Madelung Energy

The long range interaction between ions with charge $\pm q$ is the electrostatic interaction $\pm q^2/r$ attractive between ions of opposite charge and repulsive between ions of the same charge. The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction at short distances between ion cores. The repulsive interactions between ions with inert gas configurations are similar to those between inert gas atoms. The van der Waals part of the attractive interaction in ionic crystals makes a relatively small contribution to the cohesive energy in ionic crystals, of the order of 1 or 2 percent. The main contribution to the binding energy of ionic crystals is electrostatic and is called the **Madelung energy.**

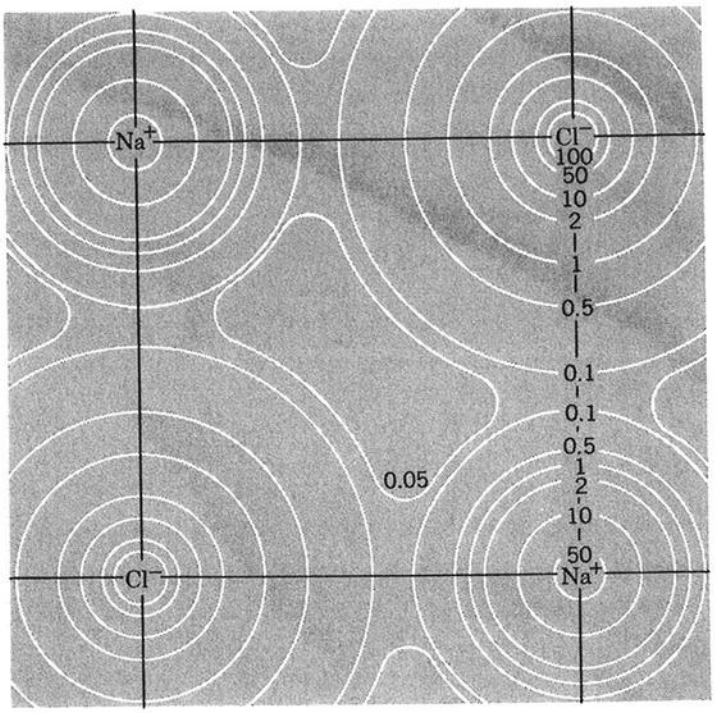

Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht, Z. Naturforschg. **12a**, 983 (1957).

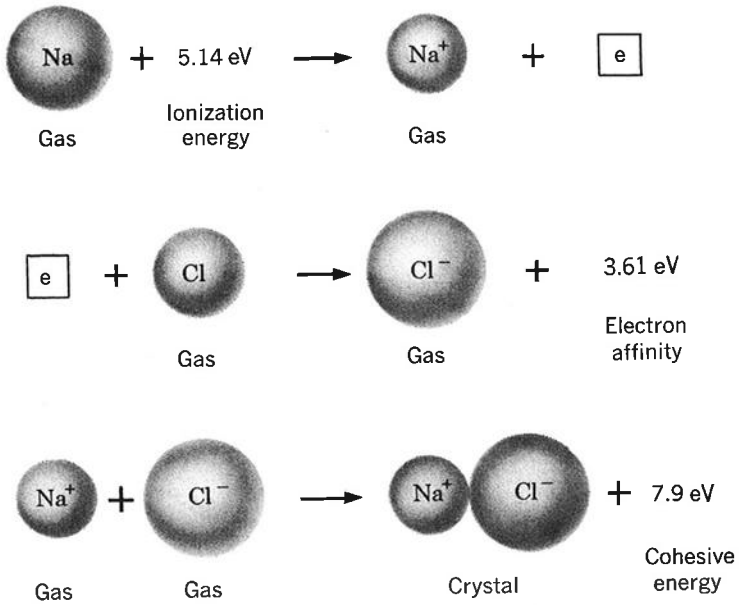

Figure 8 The energy per molecule unit of a crystal of sodium chloride is $(7.9 - 5.1 + 3.6) = 6.4$ eV lower than the energy of separated neutral atoms. The cohesive energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 3, and values of the electron affinity are given in Table 5.

If U_{ij} is the interaction energy between ions i and j, we define a sum U_i which includes all interactions involving the ion i:

$$U_i = \sum_j{}' U_{ij} \ , \tag{22}$$

where the summation includes all ions except $j = i$. We suppose that U_{ij} may be written as the sum of a central field repulsive potential of the form $\lambda \exp(-r/\rho)$, where λ and ρ are empirical parameters, and a coulomb potential $\pm q^2/r$. Thus

$$\text{(CGS)} \qquad U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm q^2/r_{ij} \ , \tag{23}$$

where the + sign is taken for the like charges and the − sign for unlike charges. The repulsive term describes the fact that each ion resists overlap with the electron distributions of neighboring ions. We treat the strength λ and range ρ as constants to be determined from observed values of the lattice constant and compressibility; we have used the exponential form of the empirical repulsive potential rather than the R^{-12} form used for the inert gases. The change is made because it may give a better representation of the repulsive interaction. For the ions, we do not have gas-phase data available to permit the independent determination of λ and ρ. We note that ρ is a measure of the range of the repulsive interaction: when $r = \rho$, the repulsive interaction is reduced to e^{-1} of the value at $r = 0$. In SI units the coulomb interaction is $\pm q^2/4\pi\epsilon_0 r$; we write this section in CGS units in which the coulomb interaction is $\pm q^2/r$.

In the NaCl structure (Fig. 1.20) the value of U_i does not depend on whether the reference ion i is a positive or a negative ion. The sum (22) can be arranged to converge rapidly, so that its value will not depend on the site of the reference ion in the crystal, as long as it is not near the surface. Neglecting surface effects, we may write the total lattice energy U_{tot} of a crystal composed of N molecules or $2N$ ions as $U_{\text{tot}} = NU_i$. Here N, rather than $2N$, occurs because we must count each *pair* of interactions only once or each bond only once. The total lattice energy is the energy required to separate the crystal into individual ions at an infinite distance apart.

It is convenient again to introduce quantities p_{ij} such that $r_{ij} \equiv p_{ij}R$, where R is the nearest-neighbor separation in the crystal. If we include the repulsive interaction only among nearest neighbors, we have

$$\text{(CGS)} \qquad U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \dfrac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \dfrac{1}{p_{ij}} \dfrac{q^2}{R} & \text{(otherwise).} \end{cases} \tag{24}$$

Thus

$$\text{(CGS)} \qquad U_{\text{tot}} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R}\right) . \tag{25}$$

TABLE 5 Electron Affinities of Negative Ions (Recommended Values)

The electron affinity is positive for a stable negative ion. Source: H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).

Atom	Electron Affinity Energy, in eV
H	0.7542
Li	0.62
C	1.27
O	1.46
F	3.40
Na	0.55
Al	0.46
Si	1.39
P	0.74
S	2.08
Cl	3.61
Br	3.36
I	3.06
K	0.50

where z is the number of nearest neighbors of any ion and

$$\boxed{\alpha \equiv \sum_j \frac{(\pm)}{p_{ij}} \equiv \textbf{Madelung constant} .} \tag{26}$$

The sum should include the nearest-neighbor contribution, which is just z. The $(\pm)$ sign is discussed just before (30). The value of the Madelung constant is of central importance in the theory of an ionic crystal. Methods for its calculation are discussed below.

At the equilibrium separation $dU_{\text{tot}}/dR = 0$, so that

$$\text{(CGS)} \qquad N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho}\exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0 , \tag{27}$$

or

$$\text{(CGS)} \qquad R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2/z\lambda . \tag{28}$$

This determines the equilibrium separation R_0 if the parameters ρ, λ of the repulsive interaction are known. For SI, replace q^2 by $q^2/4\pi\epsilon_0$.

The total lattice energy of the crystal of $2N$ ions at their equilibrium separation R_0 may be written, using (25) and (28), as

$$\text{(CGS)} \qquad U_{\text{tot}} = -\frac{N\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right) . \tag{29}$$

The term $-N\alpha q^2/R_0$ is the Madelung energy. We shall find that ρ is of the order of $0.1R_0$, so that the repulsive interaction has a very short range.

Evaluation of the Madelung Constant[8]

The first calculation of the coulomb energy constant α was made by Madelung.[9] A powerful general method for lattice sum calculations was developed by Ewald,[10] and Evjen and Frank[11] have given simple methods that arrange the counting in rapidly convergent ways. Electronic computers are widely used.

The definition of the Madelung constant α is

$$\alpha = \sum_j{}' \frac{(\pm)}{p_{ij}} .$$

If we take the reference ion as a negative charge the plus sign will be used for positive ions and the minus sign for negative ions. An equivalent definition is

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{r_j} , \tag{30}$$

where r_j is the distance of the jth ion from the reference ion and R is the nearest-neighbor distance. It must be emphasized that the value given for α will depend on whether it is defined in terms of the nearest-neighbor distance R or in terms of the lattice parameter a or in terms of some other relevant length.

As an example, we compute the Madelung constant for the infinite line of ions of alternating sign in Fig. 9. Pick a negative ion as reference ion, and let R denote the distance between adjacent ions. Then

$$\frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \cdots\right] ,$$

or

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right] ;$$

the factor 2 occurs because there are two ions, one to the right and one to the left, at equal distances r_j. We sum this series by the expansion

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \cdots .$$

Thus the Madelung constant for the one-dimensional chain is $\alpha = 2 \ln 2$. In three dimensions the series presents greater difficulty. It is not possible to write down the successive terms by a casual inspection. More important, the series will not converge unless the successive terms in the series are arranged so that the contributions from the positive and negative terms nearly cancel.

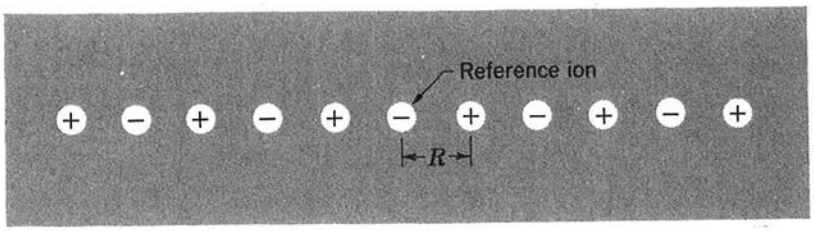

Figure 9 Line of ions of alternating signs, with distance R between ions.

Typical values of the Madelung constant are listed below, based on unit charges and *referred to the nearest-neighbor distance:*

Structure	α
Sodium chloride, NaCl	1.747565
Cesium chloride, CsCl	1.762675
Zinc blende, cubic ZnS	1.6381

The cesium chloride structure is shown in Fig. 1.23. Each ion is at the center of a cube formed by eight ions of the opposite charge. For the same nearest-neighbor distance the cesium chloride structure has a slightly (~ 1 percent) higher Madelung contribution to the cohesive energy than in the sodium chloride structure. But there are more nearest neighbors in CsCl, so that the repulsive energy is higher. Each ion has eight nearest neighbors contributing to the repulsive energy, whereas there are only six in sodium chloride. The repulsive energy is about 10 percent of the total energy of sodium chloride; roughly, we might expect the repulsive energy to be perhaps $\frac{8}{6} \times 10$ percent $\approx$ 13 percent of the total energy in cesium chloride. This increase outweighs the Madelung energy difference and may favor the sodium chloride structure by a small amount. Many more ionic crystals are known with the sodium chloride structure than with the cesium chloride structure, but the differences in binding energy are small. We can decide which structure will be stable for a particular salt only by a consideration of higher-order contributions to the energy. The Madelung and repulsive contributions to the binding of a KCl crystal are shown in Fig. 10. Properties of alkali halide crystals having the sodium chloride structure are given in Table 6. The calculated values of the cohesive energy are in exceedingly good agreement with the observed values.

[8]A detailed review and bibliography is given by M. P. Tosi, *Solid state physics* **16,** 1 (1964).
[9]E. Madelung, Physik. Z. **19,** 524 (1918).
[10]P. P. Ewald, Ann. Physik **64,** 253 (1921); see also Appendix A to the second edition of this book.
[11]H. M. Evjen, Phys. Rev. **39,** 675 (1932); F. C. Frank, Phil. Mag. **41,** 1287 (1950).

TABLE 6 Properties of Alkali Halide Crystals with the NaCl Structure

All values (except those in brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-Neighbor Separation R_0, in Å	Bulk Modulus B, in 10^{11} dyn/cm^2	Repulsive Energy Parameter $z\lambda$, in 10^{-8} erg	Repulsive Range Parameter ρ, in Å	Cohesive Energy Compared to Free Ions, in kcal/mol	
					Experimental	Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, *Solid state physics* **16**, 1 (1964).

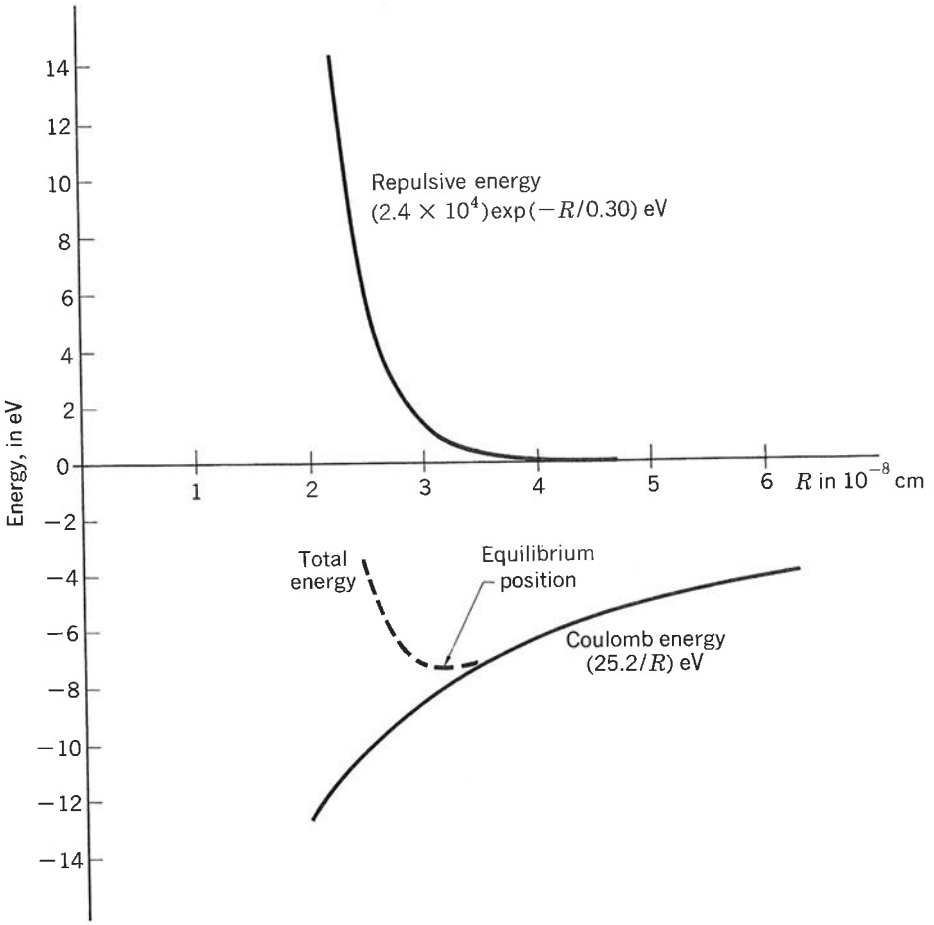

Figure 10 Energy per molecule of KCl crystal, showing Madelung and repulsive contributions.

COVALENT CRYSTALS

The covalent bond is the classical electron pair or homopolar bond of chemistry, particularly of organic chemistry. It is a strong bond: the bond between two carbon atoms in diamond has a cohesive energy of 7.3 eV with respect to separated neutral atoms. This is comparable with the bond strength in ionic crystals, although the covalent bond acts between neutral atoms. The covalent bond has strong directional properties. Thus carbon, silicon, and germanium have the diamond structure, with atoms joined to four nearest neighbors at tetrahedral angles, even though this arrangement gives a low filling of space, 0.34 of the available space, compared with 0.74 for a close-packed structure. The tetrahedral bond allows only four nearest neighbors, whereas a close-packed structure has 12. We should not overemphasize the similarity of the bonding of carbon and silicon. Carbon gives biology, but silicon gives geology.

The covalent bond is usually formed from two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. The spins of the two electrons in the bond are antiparallel.

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter. Compare the bond length (2 Å) of Cl_2 with the interatomic distance (3.76 Å) of Ar in solid Ar; also compare the cohesive energies given in Table 1. The difference between Cl_2 and Ar_2 is that the Cl atom has five electrons in the 3p shell and the Ar atom has six, filling the shell, so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si, and Ge lack four electrons with respect to filled shells, and thus these elements (for example) can have an attractive interaction associated with charge overlap. The electron configuration of carbon is $1s^2 2s^2 2p^2$. Further details can be found in works on quantum chemistry, where it is shown that to form a tetrahedral system of covalent bonds the carbon atom must first be promoted to the electronic configuration $1s^2 2s 2p^3$. This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed. The strength of the covalent bond is indicated in Table 7.

There is a continuous range of crystals between the ionic and the covalent limits. It is often important to estimate the extent a given bond is ionic or covalent. A semiempirical theory of the fractional ionic or covalent character of a bond in a dielectric crystal has been developed with considerable success by J. C. Phillips; some of his conclusions are given in Table 8. We think of NaCl as an ionic crystal and of SiC and GaAs as largely covalent. Atoms with nearly filled shells (Na, Cl) tend to be ionic, whereas atoms in columns III, IV, and V of the periodic table tend to be covalent (In, C, Ge, Si, As).

TABLE 7 Energy Values for Single Covalent Bonds

Bond	Bond Energy		Bond	Bond Energy	
	eV	kJ/mol		eV	kJ/mol
H—H	4.5	435	P—P	2.2	213
C—C	3.6	347	O—O	1.4	138
Si—Si	1.8	176	Te—Te	1.4	138
Ge—Ge	1.6	159	Cl—Cl	2.5	243

After L. Pauling.

TABLE 8 Fractional Ionic Character of Bonds in Binary Crystals

Crystal	Fractional Ionic Character	Crystal	Fractional Ionic Character
Si	0.00		
SiC	0.18	CuCl	0.75
Ge	0.00	CuBr	0.74
ZnO	0.62	AgCl	0.86
ZnS	0.62	AgBr	0.85
ZnSe	0.63	AgI	0.77
ZnTe	0.61		
		MgO	0.84
CdO	0.79	MgS	0.79
CdS	0.69	MgSe	0.79
CdSe	0.70		
CdTe	0.67	LiF	0.92
		NaCl	0.94
InP	0.42	RbF	0.96
InAs	0.36		
InSb	0.32		
GaAs	0.31		
GaSb	0.26		

After J. C. Phillips, *Bonds and bands in semiconductors*, Academic Press, 1973, Chap. 2.

The binding of molecular hydrogen is a simple example of a covalent bond.[12] The strongest binding (Fig. 11) occurs when the spins of the two electrons are antiparallel. The binding depends on the relative spin orientation not because there are strong magnetic dipole forces between the spins, but because the Pauli principle modifies the distribution of charge according to the spin orientation. This spin-dependent coulomb energy is called the **exchange interaction.**

What is the origin of the difference in chemical behavior between He, with a filled $1s^2$ shell and other atoms with filled s^2 outer shells, including Be($2s^2$), Mg($3s^2$), Ca($4s^2$), and Sr($5s^2$)? With respect to the possibility of ionic bonding in the divalent state, we see from Table 2 that the energy required to remove two electrons is much greater in He (79 eV) than in Be (28 eV), Mg (23 eV), Ca (18 eV), or Sr (17 eV). With respect to covalent bonding involving the promotion of one electron in an s orbital to the lowest available p orbital, the energy required is an order of magnitude higher in He (21 eV) than in Be (2.73 eV), Mg (2.71 eV), Ca (1.88 eV), and Sr (1.80 eV). These elements will not act like inert gases or like ionic crystals; for them the real competition is between the metallic state and the covalent state.

[12]L. Pauling and E. B. Wilson, *Introduction to quantum mechanics*, McGraw-Hill, 1935.

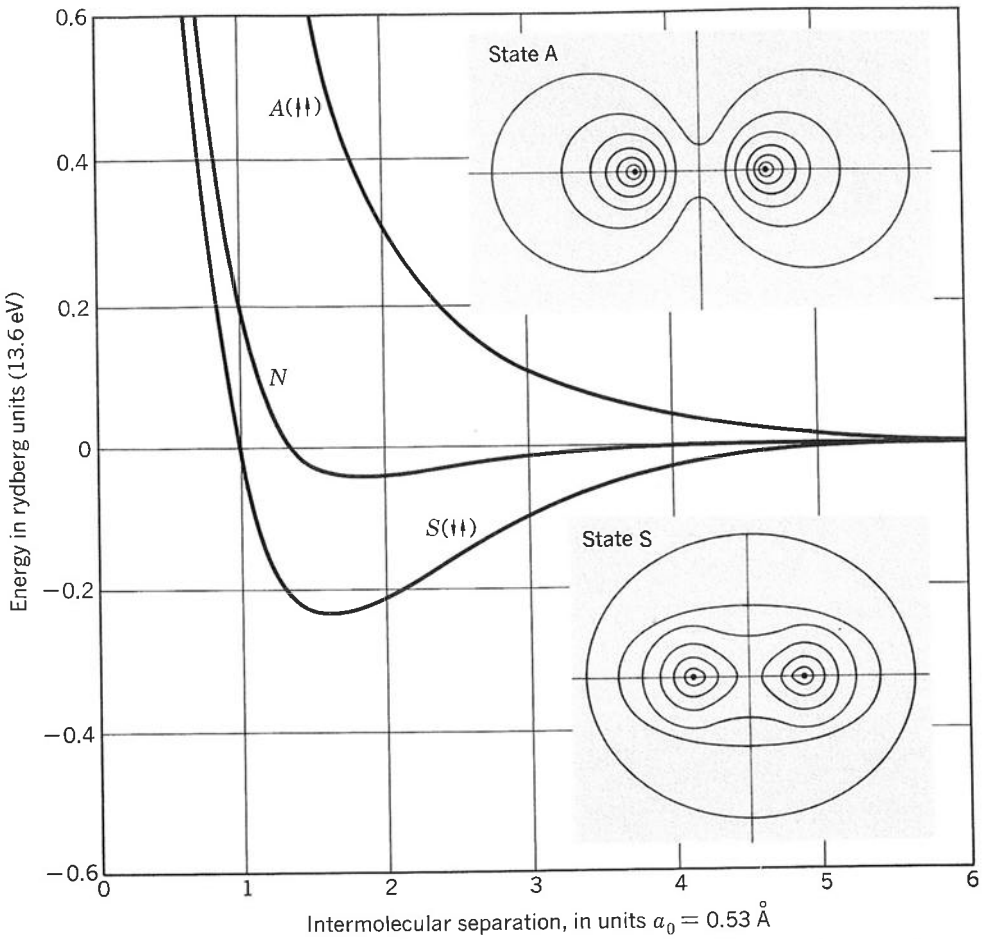

Figure 11 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve N refers to a classical calculation with free atom charge densities; A is the result for parallel electron spins, taking the Pauli exclusion principle into account, and S (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states A and S.

METAL CRYSTALS

Metals are characterized by high electrical conductivity, and a large number of the electrons in a metal must be free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy, but, as compared with the free atom, the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal. The valence electrons of the atom become the conduction electrons of the metal.

We may think of an alkali metal crystal as an array of positive charges embedded in a nearly uniform sea of negative charge. In the transition metals there may be additional binding from inner electron shells. Transition metals and the metals immediately following them in the periodic table have large *d*-electron shells and are characterized by high binding

energy (Table 1). This may be caused in part by covalent bonding and in part by the van der Waals interaction of the cores. In iron and tungsten, for example, the *d*-electrons make a substantial contribution to the binding energy.

The binding energy of an alkali metal crystal is considerably less than that of an alkali halide crystal: the bond formed by a conduction electron is not very strong. The interatomic distances are relatively large in the alkali metals because the kinetic energy of the conduction electrons is lower at large interatomic distances. This leads to weak binding. Metals tend to crystallize in relatively close-packed structures: hcp, fcc, bcc, and some other closely related structures, and not in loosely-packed structures such as diamond.

HYDROGEN-BONDED CRYSTALS

Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. It is known, however, that under certain conditions an atom of hydrogen is attracted by rather strong forces to two atoms, thus forming what is called a **hydrogen bond**[13] between them, with a bond energy of the order of 0.1 eV. It is believed that the hydrogen bond is largely ionic in character, being formed only between the most electronegative atoms, particularly F, O, and N. In the extreme ionic form of the hydrogen bond, the hydrogen atom loses its electron to another atom in the molecule; the bare proton forms the hydrogen bond. The small size of the proton permits only two nearest-neighbor atoms, because the atoms adjacent to the proton are so close that more than two of them would get in each other's way; thus the hydrogen bond connects only two atoms (Fig. 12).

The hydrogen bond is an important part of the interaction between H_2O molecules and is responsible together with the electrostatic attraction of the electric dipole moments for the striking physical properties of water and ice. The hydrogen bond restrains protein molecules to their normal geometrical arrangements. It is also responsible for the polymerization of hydrogen fluoride and formic acid, for example. It is important in certain ferroelectric crystals, such as potassium dihydrogen phosphate.

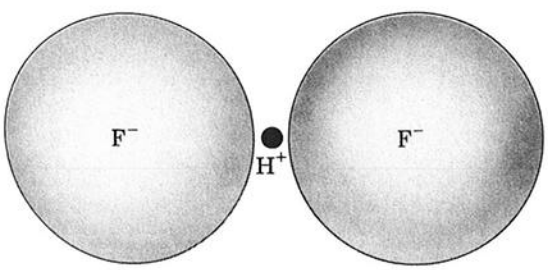

Figure 12 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.

[13]M. D. Joesten and L. Schaad, *Hydrogen bonding*, Dekker, 1974.

ATOMIC RADII

Distances between atoms in crystals can be measured very accurately by x-ray diffraction methods, often to 1 part in 10^5. Can we say that the observed distance between atoms or ions may be assigned, so much to atom A, and so much to atom B? Can a definite meaning be assigned to the radius of an atom or ion, irrespective of the nature and composition of the crystal?

Strictly, the answer is no. The charge distribution around an atom is not limited by a rigid spherical boundary. The size of a sodium atom depends on whether it is free, or in a metal, or in an ionic crystal. The radius of a sodium atom in metallic sodium might be taken as 1.86 Å, which is one-half the nearest-neighbor distance of 3.72 Å. Electron diffraction study of gaseous F_2 gives a F-F internuclear distance of 1.44 Å, one-half of which is 0.72 Å. Adding 1.86 Å and 0.72 Å gives 2.58 Å as an estimate of the Na-F bond length. The actual Na-F distance in crystalline sodium fluoride is rather smaller, 2.32 Å, so that taking the mean of the atomic radii is not very accurate here. The values of the ionic radii of Na^+ and F^- given in Table 9 are 1.24 Å and 1.16 Å, respectively. The sum of the ionic radii is 2.40 Å. The close agreement with the observed value of 2.32 Å for the crystal is not surprising: values of ionic radii in tables are usually selected so that their sums represent on the average the internuclear distances in crystals at room temperature.

But used with care and in the proper context, the concept of atomic radius can be useful and fruitful. The interatomic distance between C atoms in diamond is 1.54 Å; one-half of this is 0.77 Å. In silicon, which has the same crystal structure, one-half the interatomic distance is 1.17 Å. Now SiC crystallizes in two forms, in both of which each atom is surrounded by four atoms of the opposite kind. If we add the C and Si radii just given, we predict 1.94 Å for the length of the C-Si bond, in fair agreement with the 1.89 Å observed for the bond length. This is the kind of agreement (a few percent) that we shall find in using tables of atomic radii.[14]

TABLE 9 Average Crystal Radii of the Alkali and Halogen Ions in the NaCl-Type Alkali Halides (Å)

	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
Huggins–Mayer form[a]	0.94	1.24	1.54	1.68	1.83	1.16	1.62	1.76	1.97

[a] M. P. Tosi and F. G. Fumi, J. Phys. Chem. Solids **25**, 31, 45 (1964).

Tetrahedral Covalent Radii

Pauling has proposed the set of empirical tetrahedral covalent atomic radii included in Table 10 for atoms in crystals with coordination number four, such as the diamond, cubic ZnS, and hexagonal ZnS structures. A large number of observed interatomic distances in appropriate compounds agree closely with the sums of the tetrahedral radii.

Ionic Crystal Radii

In Table 10 we include a set of ionic crystal radii in inert gas configurations, after Zachariasen. The ionic radii are to be used in conjunction with Table 11. Let us consider $BaTiO_3$, with a lattice constant of 4.004 Å at room temperature. Each Ba^{++} ion has 12 nearest O^{--} ions, so that the coordination number is 12 and the correction Δ_{12} of Table 11 applies. If we suppose that the structure is determined by the Ba-O contacts, we have $D_{12} = 1.29 + 1.46 + 0.19 = 2.94$ Å, or $a = 4.16$ Å; if the Ti-O contact determines the structure, we have $D_6 = 0.60 + 1.46 = 2.06$, or $a = 4.12$ Å. The actual lattice constant is somewhat smaller than the estimates and may perhaps suggest that the bonding is not purely ionic, but is partly covalent.

[14]For references on atomic and ionic radii, see L. Pauling, *The nature of the chemical bond,* 3rd ed., Cornell, 1960, Chap. 7, 11, 13; Landolt-Börnstein, *Tabellen* 1:4 (1950), p. 521 et seq; J. C. Slater, J. Chem. Phys. **41,** 3199 (1964); B. J. Austin and V. Heine, J. Chem. Phys. **45,** 928 (1966); R. G. Parsons and V. F. Weisskopf, Zeits. f. Physik **202,** 492 (1967); S. Geller, Z. Kristallographie **125,** 1 (1967); see Table 2 of H. G. F. Winkler, *Struktur und Eigenschaften der Kristalle,* 2nd ed., Springer, 1955. A detailed analysis of ionic radii in oxides and fluorides has been made by R. D. Shannon and C. T. Prewitt, Acta Cryst. **B25,** 925 (1969). A critical revision of the ionic radii in alkali halides has been proposed by M. P. Tosi and F. G. Fumi, Table 9.

TABLE 10 Atomic and Ionic Radii

Values approximate only: see Table 11 for use of the standard radii of ions; for alkali and halogen ions, see Table 9.
Units are 1 Å = 10^{-10} m.

H																	He
Li 0.68	Be 0.30 1.06											B 0.16 0.88	C 0.77	N 0.70	O 1.46 0.66	F 1.33 0.64	Ne 1.58
Na 0.98	Mg 0.65 1.40	← Standard radii for ions in inert gas (filled shell) configuration →										Al 0.45 1.26	Si 0.38 1.17	P 1.10	S 1.90 1.04	Cl 1.81 0.99	Ar 1.88
		← Radii of atoms when in tetrahedral covalent bonds →															
		← Radii of ions in valence state indicated in superscript →															
K 1.33	Ca 0.94	Sc 0.68	Ti 0.60 $^{2+}$0.90	V $^{2+}$0.88	Cr $^{2+}$0.84	Mn $^{2+}$0.80	Fe $^{2+}$0.76	Co $^{2+}$0.74	Ni $^{2+}$0.72	Cu 1.35 $^{+}$0.96	Zn 1.31 $^{2+}$0.83	Ga 1.26 $^{3+}$0.62	Ge 1.22 $^{4+}$0.44	As 1.18 $^{3+}$0.69	Se 1.14	Br 1.95 1.11	Kr 2.00
Rb 1.48	Sr 1.10	Y 0.88	Zr 0.77	Nb 0.67	Mo	Tc	Ru	Rh	Pd $^{2+}$0.86	Ag 1.52 $^{+}$1.13	Cd 1.48 $^{2+}$1.03	In 1.44 $^{3+}$0.92	Sn 1.40 $^{4+}$0.74	Sb 1.36 $^{3+}$0.90	Te 1.32	I 2.16 1.28	Xe 2.17
Cs 1.67	Ba 1.29	La 1.04	Hf	Ta	W	Re	Os	Ir	Pt	Au $^{+}$1.37	Hg 1.48 $^{2+}$1.12	Tl $^{3+}$1.05	Pb $^{4+}$0.84	Bi	Po	At	Rn
Fr 1.75	Ra 1.37	Ac 1.11															

Ce 0.92 $^{3+}$1.11	Pr	Nd $^{3+}$1.08	Pm	Sm $^{3+}$1.04	Eu	Gd $^{3+}$1.02	Tb	Dy $^{3+}$0.99	Ho	Er $^{3+}$0.96	Tm	Yb $^{3+}$0.94	Lu
Th 0.99	Pa 0.90	U 0.83 $^{4+}$1.05	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

TABLE 11 Use of the Standard Radii of Ions Given in Table 10

The interionic distance D is represented by $D_N = R_C + R_A + \Delta_N$, for ionic crystals, where N is the coordination number of the cation (positive ion), R_C and R_A are the standard radii of the cation and anion, and Δ_N is a correction for coordination number. Room temperature.

N	Δ_N(Å)	N	Δ_N(Å)	N	Δ_N(Å)
1	−0.50	5	−0.05	9	+0.11
2	−0.31	6	0	10	+0.14
3	−0.19	7	+0.04	11	+0.17
4	−0.11	8	+0.08	12	+0.19

SUMMARY

1. Crystals of inert gas atoms are bound by the van der Waals interaction (induced dipole-dipole interaction), and this varies with distance as $1/R^6$.

2. The repulsive interaction between atoms arises generally from the electrostatic repulsion of overlapping charge distributions, and the Pauli principle, which compels overlapping electrons of parallel spin to enter orbitals of higher energy.

3. Ionic crystals are bound by the electrostatic attraction of charged ions of opposite sign. The electrostatic energy of a structure of $2N$ ions of charge $\pm q$ is

(CGS) $$U = -N\alpha \frac{q^2}{R} = -N \sum \frac{(\pm)q^2}{r_{ij}} ,$$

where α is the Madelung constant and R is the distance between nearest neighbors.

4. Metals are bound in large measure by the reduction in the kinetic energy of the valence electrons in the metal as compared with the free atom.

5. A covalent bond is characterized by the overlap of charge distributions of antiparallel electron spin. The Pauli contribution to the repulsion is reduced for antiparallel spins, and this makes possible a greater degree of overlap. The overlapping electrons bind their associated ion cores by electrostatic attraction.