Introduction to Solid State Physics (I)

Oct. 2, 4, 16, and 18, 2013

What holds a crystal together?

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Values of the cohesive energy of the crystalline elements are given in Table 1. Notice the wide variation in cohesive energy between different columns of the periodic table. The inert gas crystals are weakly bound, with cohesive energies less than a few percent of the cohesive energies of the elements in the C, Si, Ge . . . column. The alkali metal crystals have intermediate values of the cohesive energy. The transition element metals (in the middle columns) are quite strongly bound. The melting temperatures (Table 2) and bulk modulii (Table 3) vary roughly as the cohesive energies.

Forces holding a crystal together

- Electrostatic interaction between negative and positive charges
- Magnetic force
- Gravitational force

Magnetic forces have only a weak effect for the cohesion, and gravitational forces are negligible.

The attractive electrostatic interaction between negatively charged electrons and positively charged nuclei is entirely responsible for the cohesion of solids.

Classification of Solids based on Valence Electrons

- Classification of solids based on the **symmetry of crystal structures (**In the lectures 1-2**)**
  - – Where are the nuclei and electrons? – handled by **diffraction methods**: x-ray, electrons, and neutrons
  - – entirely on a single aspect of the solid: **geometrical symmetries**
  - – Blind to important structural aspects that affect its physical properties
    - Within each of the seven crystal systems one can find solids exhibiting the full range of **electrical, mechanical, magnetic, superconducting, and optical** properties

Diffraction studies of materials using x-rays, neutrons, and electrons

Unlike other types of radiation used in diffraction studies of materials, such as X-rays and neutrons, electrons are charged particles and interact with matter through the Coulomb forces.

This means that the incident electrons feel the influence of both the positively charged atomic nuclei and the surrounding electrons.

In comparison, X-rays interact with the spatial distribution of the valence electrons, while neutrons are scattered by the atomic nuclei through the strong nuclear forces.

In addition, the magnetic moment of neutrons is non-zero, and they are therefore also scattered by magnetic fields. Because of these different forms of interaction, the three types of radiation are suitable for different studies.

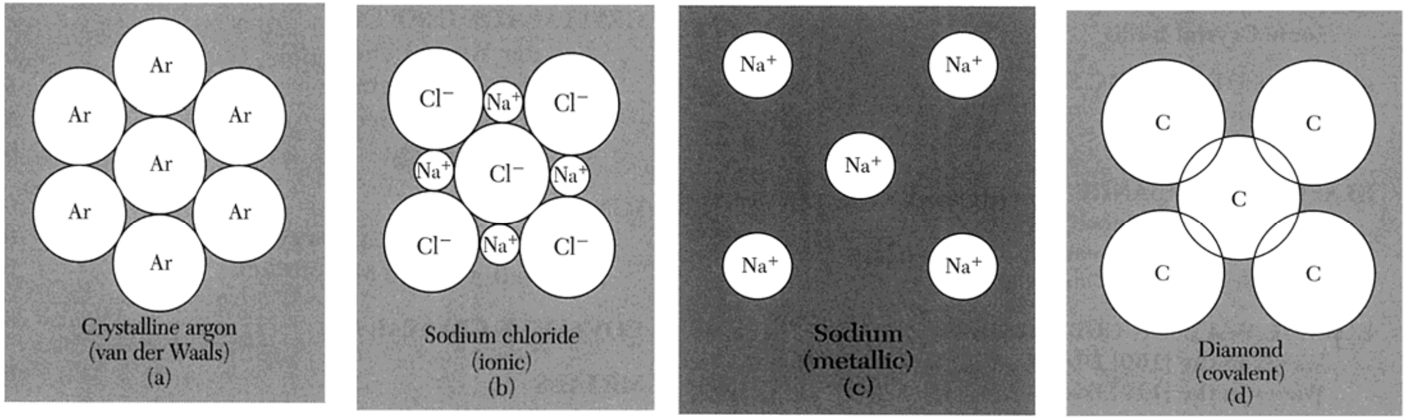
Classification of Solids based on Valence Electrons

- Classification of solids based on the configurations of the valence electrons
  - What holds a crystal together? The attractive electrostatic interaction between electrons (-) and nuclei (+) is entirely responsible for cohesion of solids. Magnetic forces: weak effect and gravitational forces: negligible.
    - Positive ion cores be kept apart to minimize the Coulomb repulsion
    - Valence electrons be kept apart to minimize the Coulomb repulsion
    - Valence electrons be kept close to positive ion cores to maximize the Coulomb attraction
    - Kinetic energy not much increased, e.g. localizing an electron in a region Δx; from the Heisenberg uncertainty principle, the related spread in momentum $\Delta(mv) \geq \hbar / \Delta x$, thus $\frac{1}{2} mv^2$ is at least $h^2/2m(2\pi \Delta x)^2$. If $\Delta x \approx 0.1$ nm~~, kinetic energy is $\approx 5 \times 10^{-12}$ erg $\approx$ 3 eV,~~ **$v \approx 10^8$ cm/sec, the same order as the Fermi velocity and 10 times higher than that derived from Maxwell-Boltzmann distribution in classical ideal gas at room temperature (Drude Theory)**
    - Pauli exclusion principle: two electrons cannot have all their quantum numbers equal.
  - Metals and insulators (partially filled energy bands) in perfect crystals at zero temperature: no semiconductors
  - Distribution of electrons, not in real space, but in wave vector space

Various types of crystal binding

- Crystals of inert gases
  - Van der Waals – London interaction
  - Repulsive interaction
  - Equilibrium lattice constants
  - Cohesive energy
- Ionic crystals
  - Electrostatic or Madelung energy
  - Evaluation of the Madelung constant
- Covalent crystals
- Metals
- Hydrogen bonds

In this chapter we are concerned with the question: What holds a crystal together? The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is entirely responsible for the cohesion of solids. Magnetic forces have only a weak effect on cohesion, and gravitational forces are negligible. Specialized terms categorize distinctive situations: exchange energy, van der Waals forces, and covalent bonds. The observed differences between the forms of condensed matter are caused in the final analysis by differences in the distribution of the outermost electrons and the ion cores (Fig. 1).



Crystalline argon
(van der Waals)
(a)

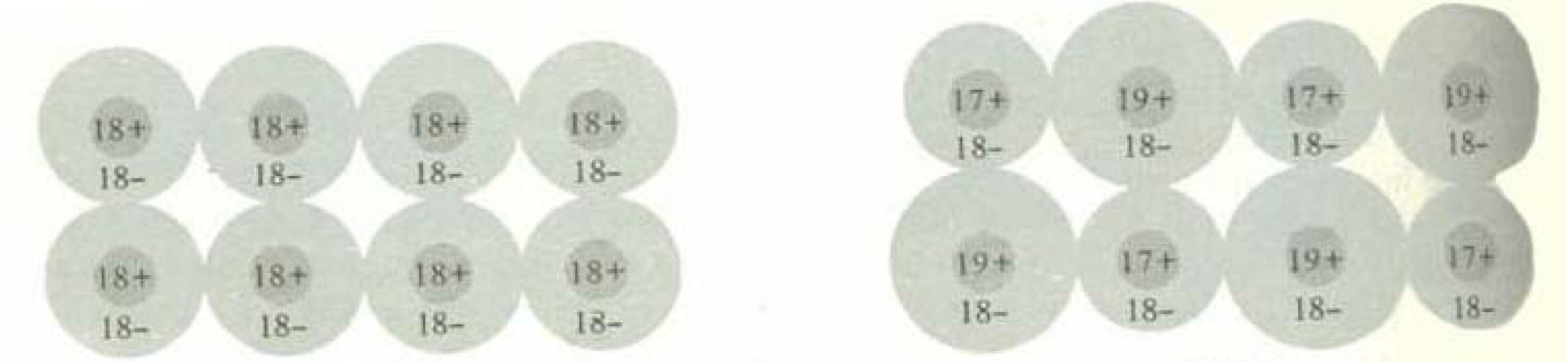
Sodium chloride
(ionic)
(b)

Sodium
(metallic)
(c)

Diamond
(covalent)
(d)

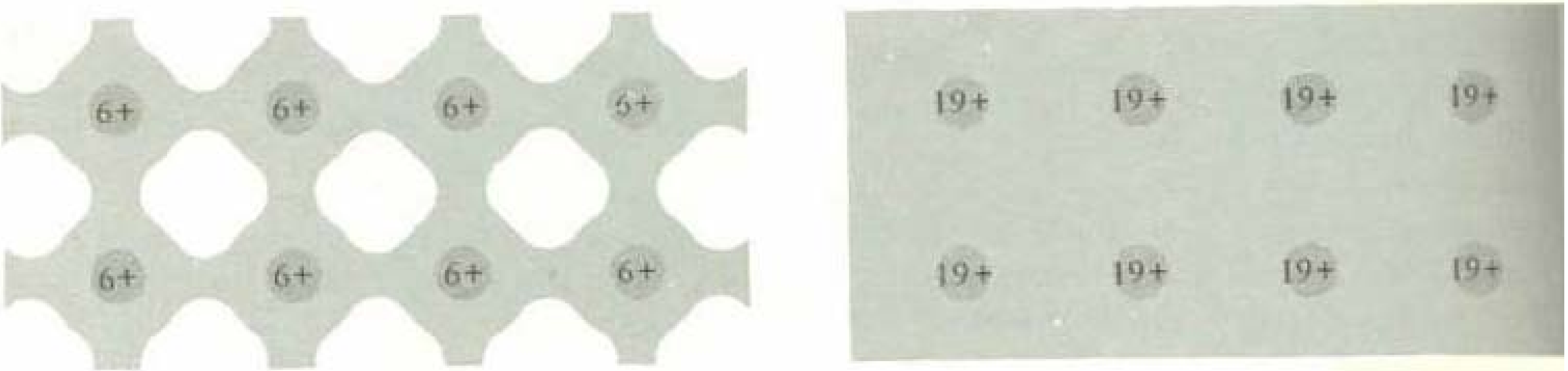
Figure 1 The principal types of crystalline binding. In (a) neutral atoms with closed electron shells are bound together weakly by the van der Waals forces associated with fluctuations in the charge distributions. In (b) electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by attractive electrostatic forces between the positive and negative ions. In (c) the valence electrons are taken away from each alkali atom to form a communal electron sea in which the positive ions are dispersed. In (d) the neutral atoms are bound together by the overlapping parts of their electron distributions.

Highly schematic two-dimensional representation of electronic charge distribution in the basic solid types



Molecular
(a)

Ionic
(b)



Covalent
(c)

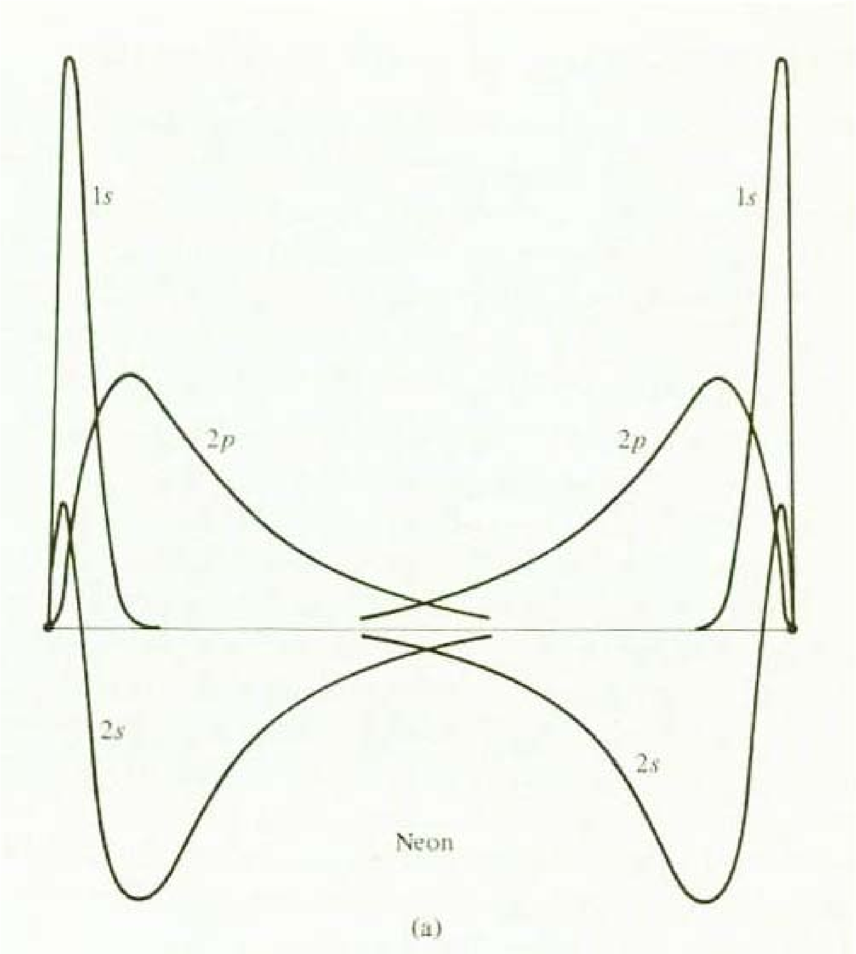
Metallic
(d)

- **Molecular crystal**
- **Ionic**
- **Covalent**
- **Metal**

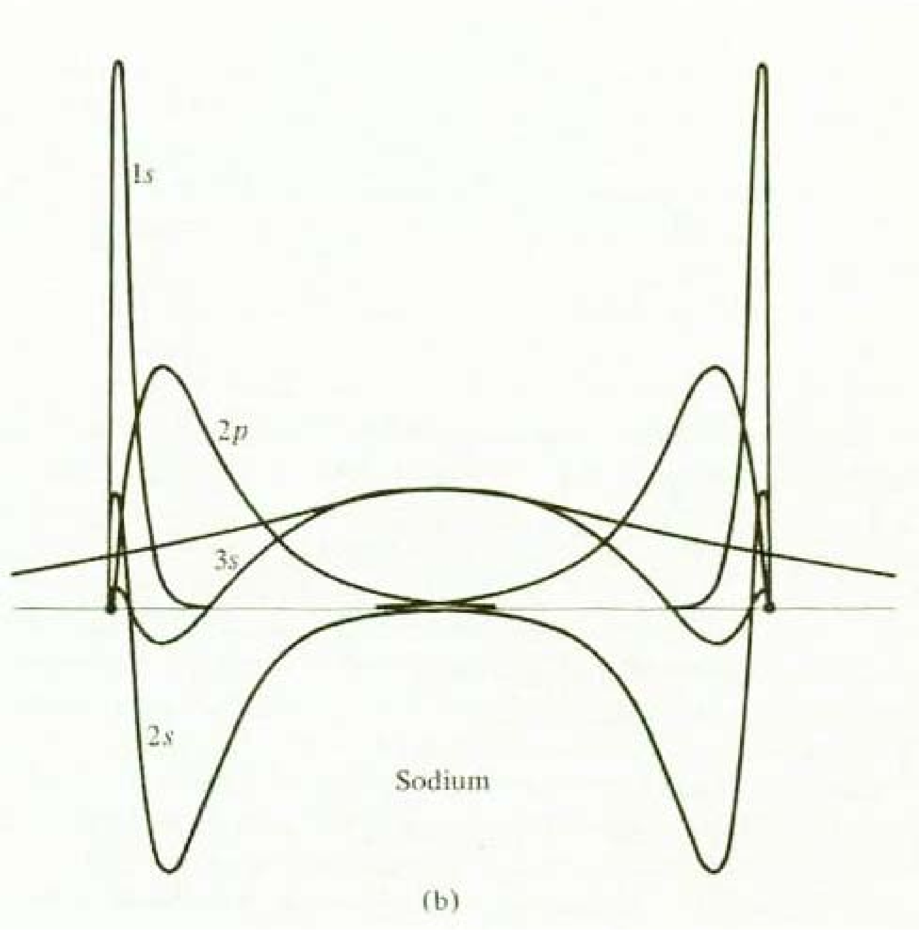
The observed differences between the forms of condensed matter are caused in the final analysis by differences in the **distribution of the outermost electrons and ion cores.**

At 0K, there are only conductors and insulators.

Calculated radial atomic wave functions for Neon



Calculated radial atomic wave functions for Sodium



Enormous overlap of 3s wave functions

Classification of Solids based on Valence Electrons - continued

- Insulators
  - **Covalent crystals**
    - Interstitial electronic distribution be localized in certain preferred directions, leading to what are known in the language of chemistry as "**bonds**".
    - Interstitial charge density: characteristic feature distinguishing covalent crystals from other two types of insulators
  - **Molecular crystals**
    - Solid noble gases: in atomic state they have completely filled electronic shells – a highly stable configuration which is only weakly perturbed in the solid.
    - Crystals of inert gas atoms are bound by the van der Waals interaction (including dipole-dipole interaction), and this varies with distance as $1/R^6$.

Classification of Solids based on Valence Electrons - continued

- Insulators
  - **Ionic crystals**
    - Compounds composed of a metallic and nonmetallic element
    - Like molecular crystals, ionic crystals have electronic charge distributions that are highly localized in the neighborhood of the ion cores
    - Some electrons have strayed so far from their parents as to the constituent of the opposite type – one might consider ionic crystal to be a molecular crystal in which the constituent molecules are not atoms but ions.
    - I-VII ionic crystals (Alkali Halides): ionic radii
    - II(A)-VI ionic crystals (II(B)-VI compound semiconductors)
    - III-V crystals (mixed ionic and covalent)

Classification of Solids based on Valence Electrons

- Metals
- Semiconductors (perfect crystals at T=0 all semiconductors are insulators)
    - IV or IV-IV, III-V, and II-VI
    - Are all covalent crystals (delocalization of charges in the covalent bond)
    - Sometimes with a small touch of ionic bonding as in III-V compounds
- Insulators
    - Covalent crystals
    - Molecular crystals
    - Ionic crystals
        - I-VII ionic crystals (Alkali Halides): ionic radii
        - II(A)-VI ionic crystals (II(B)-VI compound semiconductors)
        - III-V crystals (mixed ionic and covalent)

CRYSTALS OF INERT GASES

The inert gases form the simplest crystals. The electron distribution is very close to that of the free atoms. Their properties at absolute zero are summarized in Table 4. The crystals are transparent insulators, weakly bound, with low melting temperatures. The atoms have very high ionization energies (see Table 5). The outermost electron shells of the atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric. In the crystal the inert gas atoms pack together as closely as possible[1]: the crystal structures (Fig. 2) are all cubic close-packed (fcc), except He^3 and He^4.

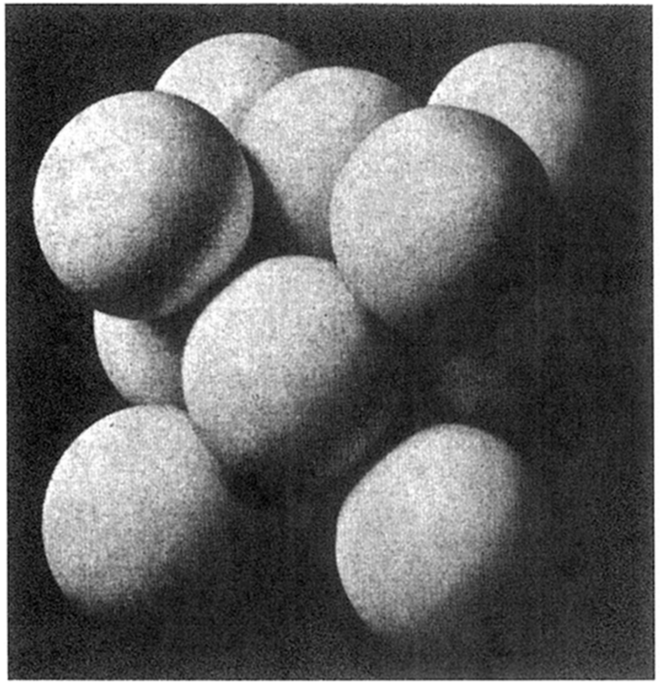


Figure 2 Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The lattice parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4 K.

Crystals of inert gases

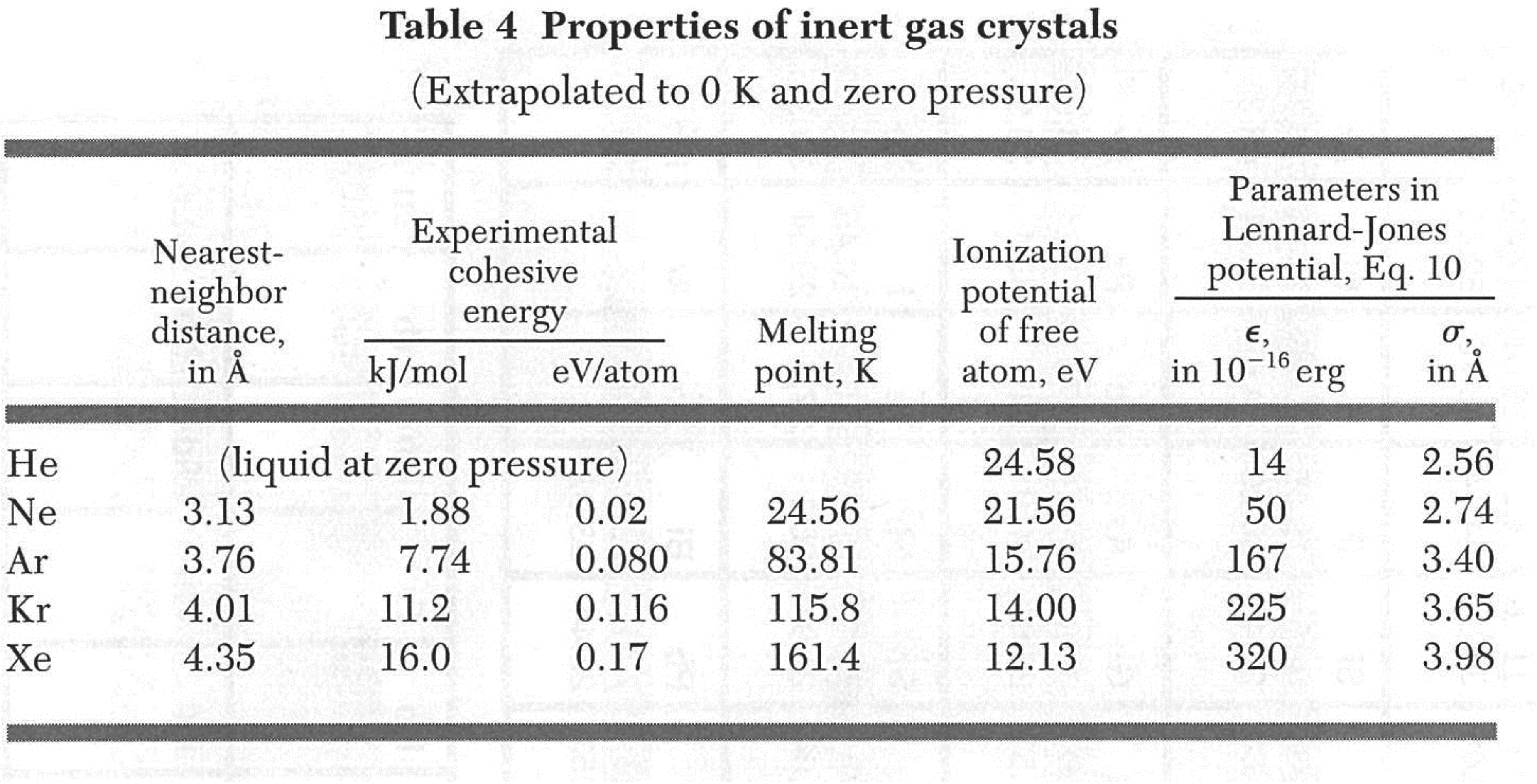


Table 4 Properties of inert gas crystals

(Extrapolated to 0 K and zero pressure)

	Nearest-neighbor distance, in Å	Experimental cohesive energy		Melting point, K	Ionization potential of free atom, eV	Parameters in Lennard-Jones potential, Eq. 10	
		kJ/mol	eV/atom			ϵ, in 10^{-16} erg	σ, in Å
He	(liquid at zero pressure)				24.58	14	2.56
Ne	3.13	1.88	0.02	24.56	21.56	50	2.74
Ar	3.76	7.74	0.080	83.81	15.76	167	3.40
Kr	4.01	11.2	0.116	115.8	14.00	225	3.65
Xe	4.35	16.0	0.17	161.4	12.13	320	3.98

What holds an inert gas crystal together? The electron distribution in the crystal is not significantly distorted from the electron distribution around the free atoms because not much energy is available to distort the free atom charge distributions. The cohesive energy of an atom in the crystal is only 1 percent or less of the ionization energy of an atomic electron. Part of this distortion gives the van der Waals interaction.

Van der Waals-London Interaction

Consider two identical inert gas atoms at a separation R large in comparison with the radii of the atoms. What interactions exist between the two neutral atoms? If the charge distributions on the atoms were rigid, the interaction between atoms would be zero, because the electrostatic potential of a spherical distribution of electronic charge is canceled outside a neutral atom by the electrostatic potential of the charge on the nucleus. Then the inert gas atoms could show no cohesion and could not condense. But the atoms induce dipole moments in each other, and the induced moments cause an attractive interaction between the atoms.

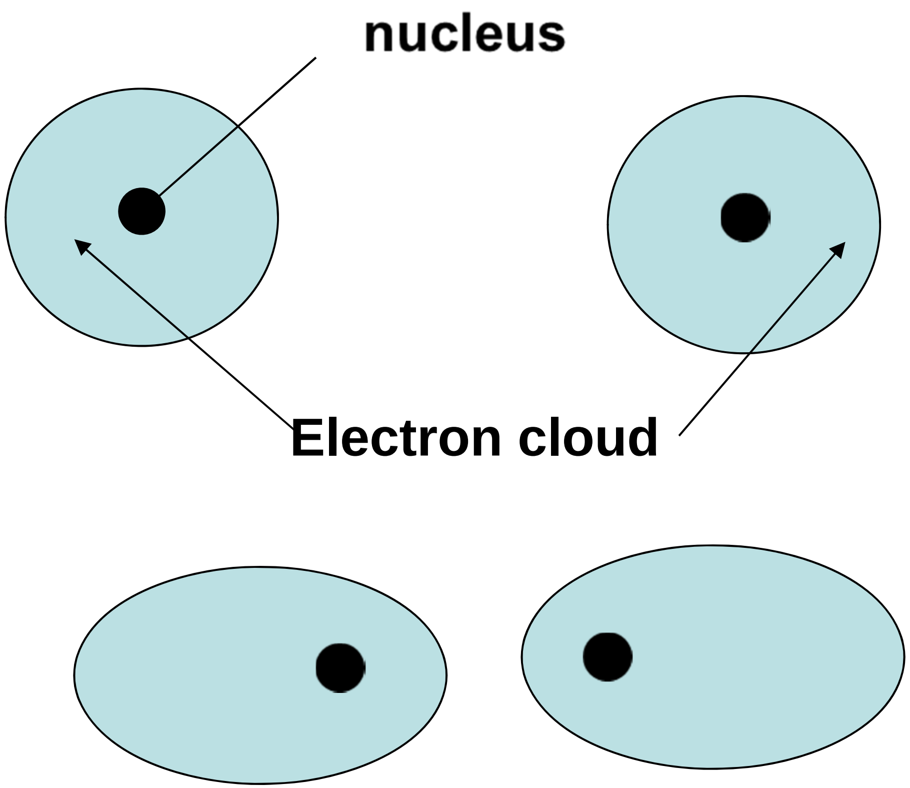
Crystals of inert gases

- The inert gases form the simplest crystals.
- The electron distribution in the crystal is very close to that of the free atoms.
- The crystals are transparent insulators, weakly bound, with low melting temperatures.
- The atoms have very high ionization energies.
- The outermost electron shells of the atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric.
- In the crystal the inert gas atoms packed as close as possible and the crystal structures are all cubic close-packed structure (fcc) except He^3 and He^4.
- The cohesive energy of an atom in the crystal is only 1 percent or less of the ionization energy of an atomic electron. Not much energy available to distort the free atom charge distributions.
- **Part of this distortion gives the van der Waals interaction.**

A crystal formed by van der Waals interaction

Attractive interaction between inert gases (Ar, He, Ne, Kr, and Xe) atoms is caused by an induced dipole-dipole moment, namely van der Waals interaction (called "London interaction")

Distortion of charge distribution



nucleus

Electron cloud

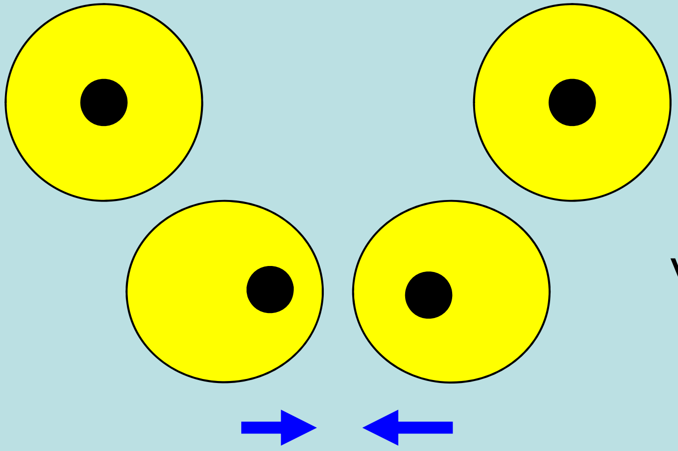
Distortion of charge distribution in the constituents (valence electrons and nuclei is significant in

1. **Ionic bond**
2. **metallic bond**
3. **covalent bond**

but it becomes insignificant in molecular crystal, in which the atoms are bonded via van der Waals interaction

Why? because 1, 2 and 3 involve strong electrostatic field, i.e. attraction between negatively charges and positively charges, and also among electrons (electron interaction)

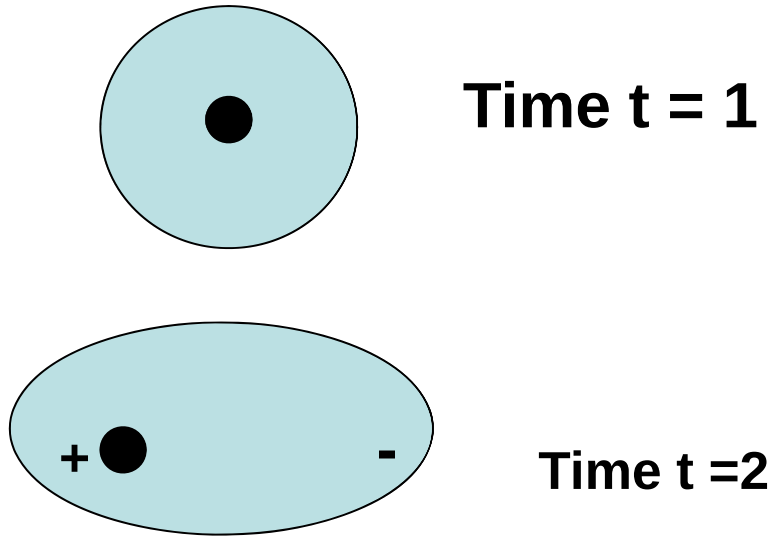
Why van der Waals interaction is less distorted when two atoms approaches? because atoms (e.g. Ar) are neutral-charged



Van der Waals interaction

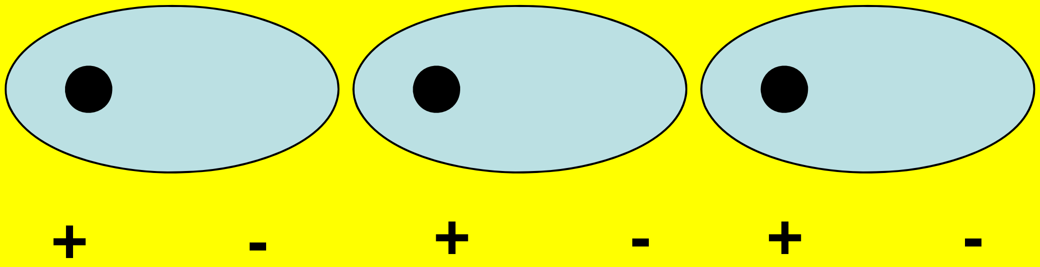
What is the induced dipole-dipole moments between atoms?

The average position of electrons in an atom does not always coincide with that of nucleus, meaning that the electron distribution may not be symmetric all the time.



The atoms induce dipole moments in each other, and the induced moments cause an attractive interaction between the atoms.

In this case an electric field is produced, which will interact with neighboring atoms



As a model, let us consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges +-e with separations x1 and x2.

It is true that the time-average electric moments are all zero.

But, the electrons are in motion around the nucleus even in the lowest electronic state, and at any instant of time there is likely to be a non-vanishing electric dipole moment from this motion.

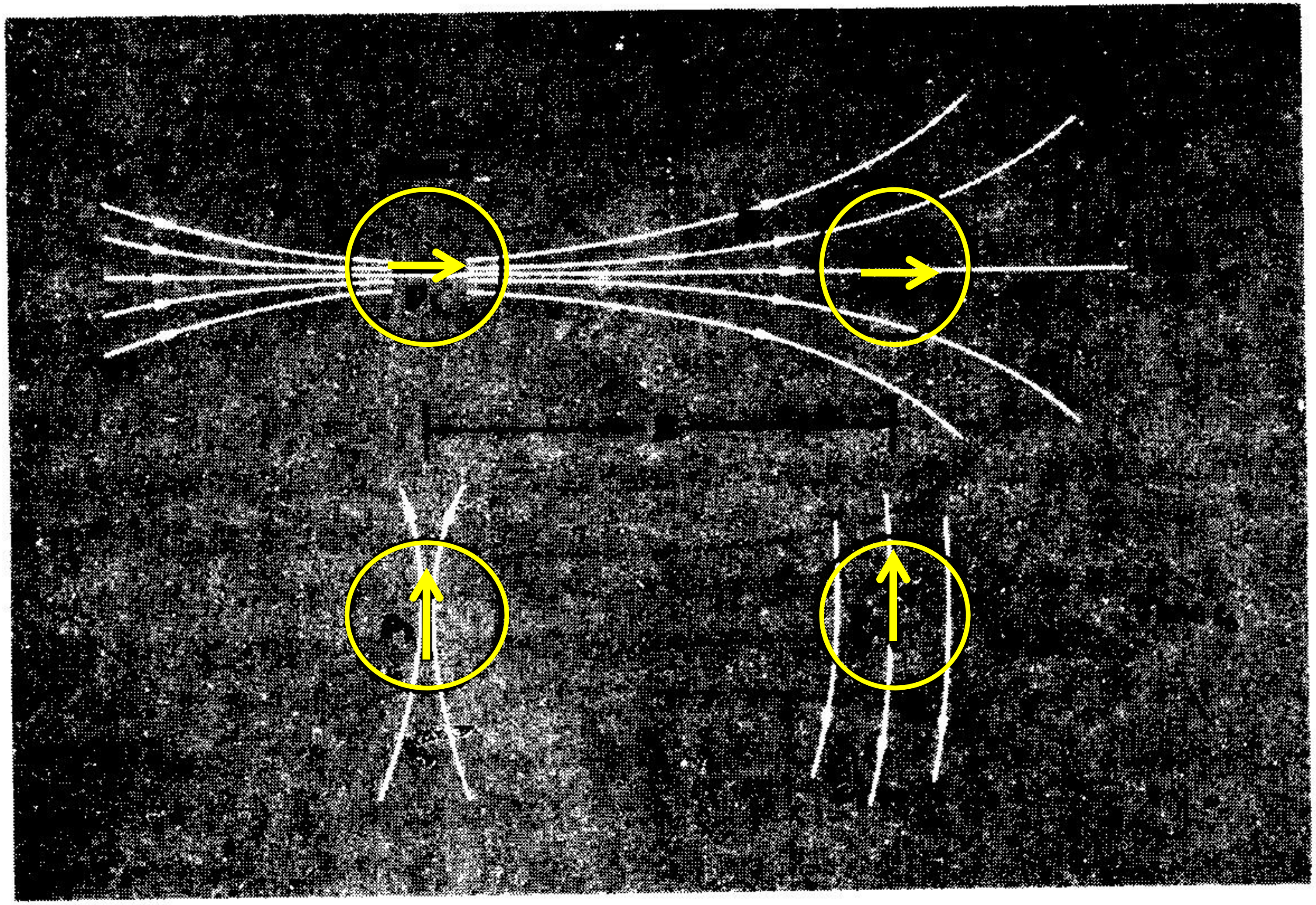


Figure 3 Origin of the van der Waals interaction, according to a classical argument. At one instant of time there is a dipole moment p_1 on atom 1. This produces an electric field E at atom 2, which acquires an induced dipole moment p_2. Diagrams are shown for two times, t_a and t_b. The interaction is always attractive: the closer the atoms, the tighter the binding.

motion around the nucleus even in the lowest electronic state, and at any instant of time there is likely to be a nonvanishing electric dipole moment from this motion.[3] An instantaneous dipole moment of magnitude p_1 on one atom (Fig. 3) produces an electric field E of magnitude $2p_1/R^3$ at the center of the second atom distant R from the first atom. This field will induce an instantaneous dipole moment $p_2 = \alpha E = 2\alpha p_1/R^3$ on the second atom; here α is the electronic polarizability, defined in Eq. (13.31) as the dipole moment per unit electric field.

The standard result of electrostatics for the energy of interaction of two dipoles of moment $\mathbf{p}_1$ and $\mathbf{p}_2$ separated by $\mathbf{R}$ is

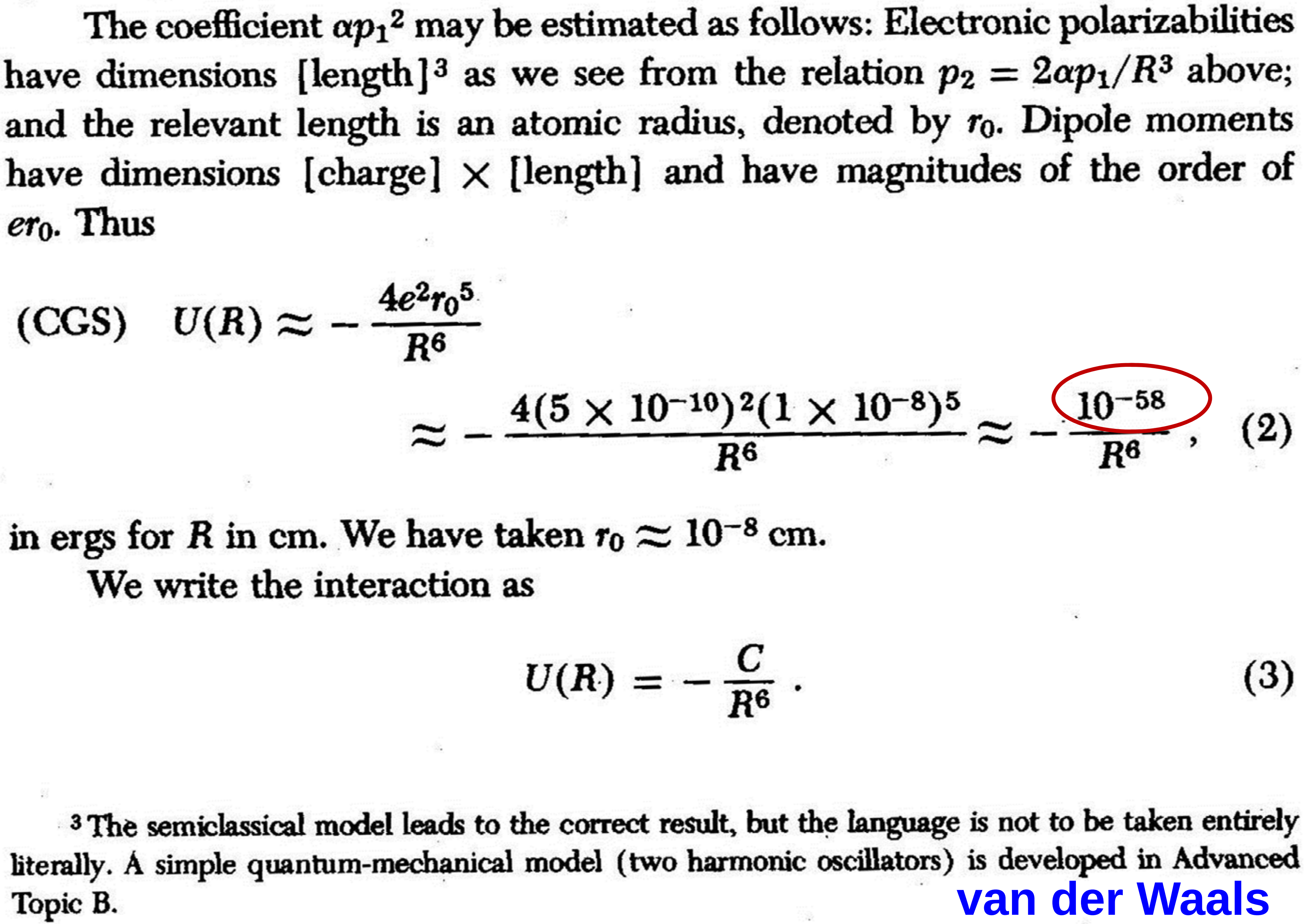
$$\text{(CGS)} \qquad U(R) = \frac{\mathbf{p}_1 \cdot \mathbf{p}_2}{R^3} - \frac{3(\mathbf{p}_1 \cdot \mathbf{R})(\mathbf{p}_2 \cdot \mathbf{R})}{R^5} \; . \tag{1a}$$

Because the induced moments in the van der Waals interaction are parallel, we have for the potential energy of the dipole moments

$$\text{(CGS)} \qquad U(R) \approx -\frac{2p_1p_2}{R^3} = -\frac{4\alpha {p_1}^2}{R^6} \; . \tag{1b}$$

The interaction is attractive. To obtain (1) in SI, multiply the right-hand side by $1/4\pi\epsilon_0$.

van der Waals interaction -I



The coefficient $\alpha p_1{}^2$ may be estimated as follows: Electronic polarizabilities have dimensions [length]^3 as we see from the relation $p_2 = 2\alpha p_1/R^3$ above; and the relevant length is an atomic radius, denoted by r_0. Dipole moments have dimensions [charge] × [length] and have magnitudes of the order of er_0. Thus

$$(\text{CGS}) \quad U(R) \approx -\frac{4e^2r_0{}^5}{R^6}$$
$$\approx -\frac{4(5\times10^{-10})^2(1\times10^{-8})^5}{R^6} \approx -\frac{10^{-58}}{R^6}\,, \qquad (2)$$

in ergs for R in cm. We have taken $r_0 \approx 10^{-8}$ cm.

We write the interaction as

$$U(R) = -\frac{C}{R^6}\,. \qquad (3)$$

[3] The semiclassical model leads to the correct result, but the language is not to be taken entirely literally. A simple quantum-mechanical model (two harmonic oscillators) is developed in Advanced Topic B.

van der Waals interaction -I

This is known variously as the van der Waals interaction,[4] the London interaction, or the induced dipole-dipole interaction. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules. Taking $C \approx 10^{-58}$ erg-cm^6, the interaction[5] at a separation $R = 4$ Å as for krypton has the value $U \approx 2 \times 10^{-14}$ erg, whence in temperature units $U/k_B \approx 100°$K, of the order of magnitude of the melting temperature of inert gas crystals.

Because of the R^{-6} dependence the interaction increases rapidly at shorter distances. For example, at the interatomic separation of metallic copper, 2.55 Å, the van der Waals interaction between the Cu^+ ion cores is $\approx 2 \times 10^{-13}$ ergs for the above value of C. A better value of C may be as much as ten times greater, which would account for a substantial part of the high cohesive energy of copper (Table 1).

[4] The quantum-mechanical theory is discussed by H. Margenau, Revs. Mod. Phys. 11, 1 (1939); see also *Advances in chemical physics* 12: *Intermolecular forces,* J. O. Hirschfelder, ed., Interscience, 1967, and S. Doniach, Phil. Mag. 8, 129 (1963).

[5] It is easier to grasp the magnitude of an interaction energy U if it is expressed in terms of an effective temperature which we define by the relation $k_BT = U$, where k_B is the Boltzmann constant.

As a model, we consider two identical linear harmonic oscillators 1 and 2 separated by R. Each oscillator bears charges $\pm e$ with separations x_1 and x_2, as in Fig. 3. The particles oscillate along the x axis. Let p_1 and p_2 denote the momenta. The force constant is C. Then the hamiltonian of the unperturbed system is

$$\mathcal{H}_0 = \frac{1}{2m}p_1^2 + \tfrac{1}{2}Cx_1^2 + \frac{1}{2m}p_2^2 + \tfrac{1}{2}Cx_2^2 \ . \tag{1}$$

Each uncoupled oscillator is assumed to have the frequency ω_0 of the strongest optical absorption line of the atom. Thus $C = m\omega_0^2$.

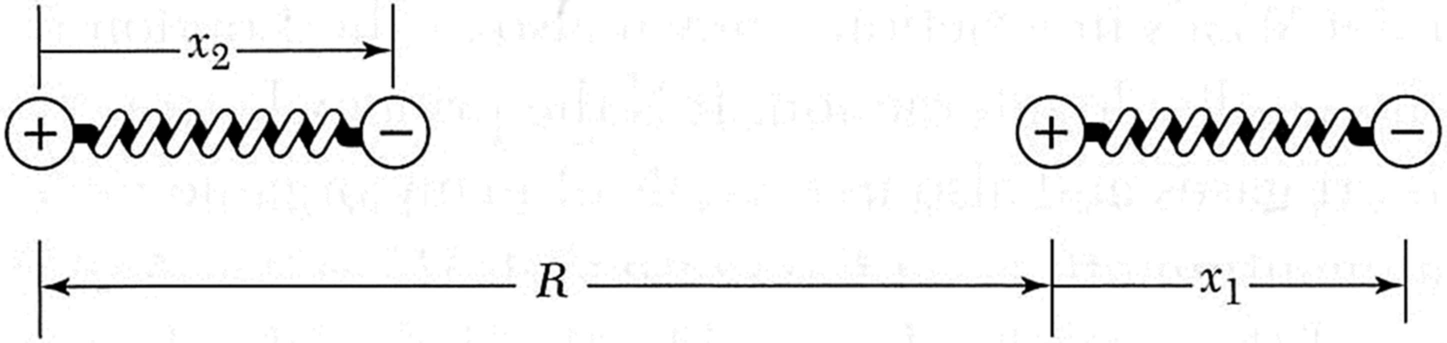


Figure 3 Coordinates of the two oscillators.

van der Waals interaction - II

Let $\mathscr{H}_1$ be the coulomb interaction energy of the two oscillators. The geometry is shown in the figure. The internuclear coordinate is R. Then

$$\text{(CGS)} \qquad \mathscr{H}_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2} \ ; \tag{2}$$

in the approximation $|x_1|, |x_2| \ll R$ we expand (2) to obtain in lowest order:

$$\mathscr{H}_1 \cong -\frac{2e^2 x_1 x_2}{R^3} \ . \tag{3}$$

The total hamiltonian with the approximate form (3) for $\mathscr{H}_1$ can be diagonalized by the normal mode transformation

$$x_s \equiv \frac{1}{\sqrt{2}}(x_1 + x_2) \ ; \qquad x_a \equiv \frac{1}{\sqrt{2}}(x_1 - x_2) \ , \tag{4}$$

or, on solving for x_1 and x_2,

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \ ; \qquad x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \ . \tag{5}$$

The subscripts s and a denote symmetric and antisymmetric modes of motion. Further, we have the momenta p_s, p_a associated with the two modes:

$$p_1 \equiv \frac{1}{\sqrt{2}}(p_s + p_a) \ ; \qquad p_2 \equiv \frac{1}{\sqrt{2}}(p_s - p_a) \ . \tag{6}$$

The total hamiltonian $\mathcal{H}_0 + \mathcal{H}_1$ after the transformations (5) and (6) is

$$\mathcal{H} = \left[\frac{1}{2m}p_s^2 + \frac{1}{2}\left(C - \frac{2e^2}{R^3}\right)x_s^2\right] + \left[\frac{1}{2m}p_a^2 + \frac{1}{2}\left(C + \frac{2e^2}{R^3}\right)x_a^2\right] . \tag{7}$$

The two frequencies of the coupled oscillators are found by inspection of (7) to be

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3}\right)\Big/ m\right]^{1/2} = \omega_0\left[1 \pm \frac{1}{2}\left(\frac{2e^2}{CR^3}\right) - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 + \cdots\right] , \tag{8}$$

with ω_0 given by $(C/m)^{1/2}$. In (8) we have expanded the square root.

The zero point energy of the system is $\frac{1}{2}\hbar(\omega_s + \omega_a)$; because of the interaction the sum is lowered from the uncoupled value $2 \cdot \frac{1}{2}\hbar\omega_0$ by

$$\Delta U = \tfrac{1}{2}\hbar(\Delta\omega_s + \Delta\omega_a) = -\hbar\omega_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = -\frac{A}{R^6} . \tag{9}$$

This attractive interaction varies as the minus sixth power of the separation of the two oscillators.

This is called the van der Waals interaction, known also as the London interaction or the induced dipole-dipole interaction. It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules. The interaction is a quantum effect, in the sense that $\Delta U \to 0$ as $\hbar \to 0$. Thus the zero point energy of the system is lowered by the dipole-dipole coupling of Eq. (3). The van der Waals interaction does not depend for its existence on any overlap of the charge densities of the two atoms.

An approximate value of the constant A in (9) for identical atoms is given by $\hbar\omega_0\alpha^2$, where $\hbar\omega_0$ is the energy of the strongest optical absorption line and α is the electronic polarizability (Chapter 15).

Repulsive Interaction

As the two atoms are brought together, their charge distributions gradually overlap (Fig. 4), thereby changing the electrostatic energy of the system. At sufficiently close separations the overlap energy is repulsive, in large part because of the **Pauli exclusion principle**. The elementary statement of the principle is that two electrons cannot have all their quantum numbers equal. When the charge distributions of two atoms overlap, there is a tendency for electrons from atom *B* to occupy in part states of atom *A* already occupied by electrons of atom *A*, and vice versa.

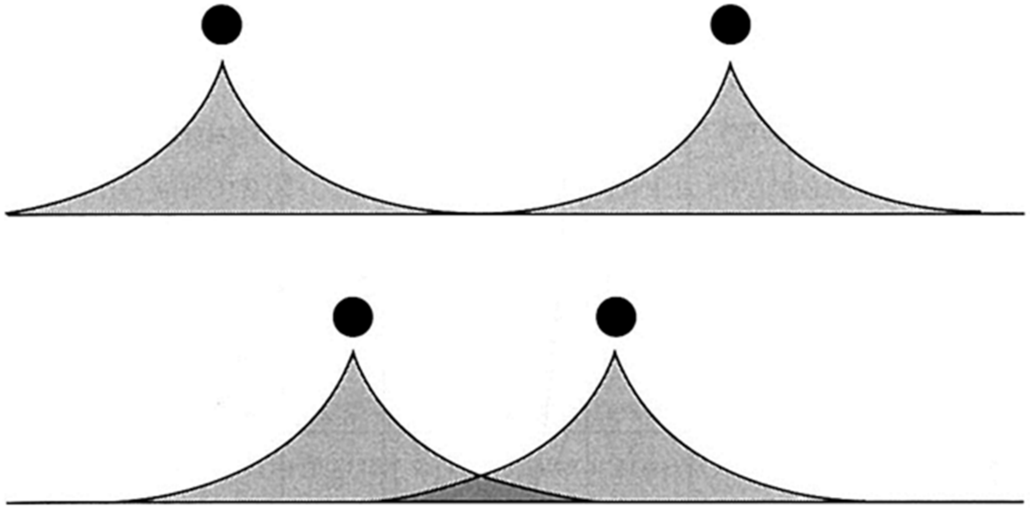
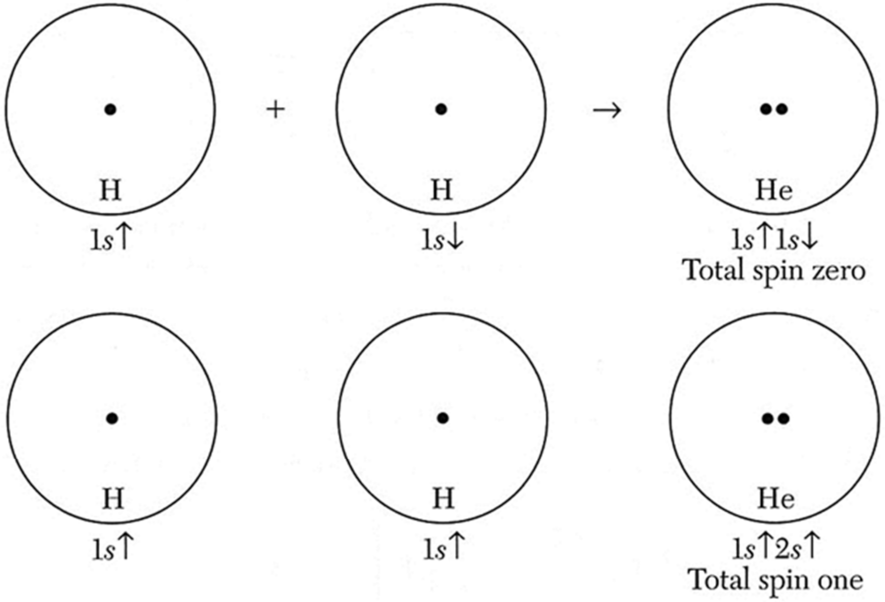


Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.

The Pauli principle prevents multiple occupancy, and electron distributions of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied high energy states of the atoms. Thus the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction. An extreme example in which the overlap is complete is shown in Fig. 5.



(a)
Total electron
energy: −78.98 eV

(b)
Total electron
energy: −59.38 eV

Figure 5 The effect of Pauli principle on the repulsive energy: in an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. In (a) the electrons have antiparallel spins and the Pauli principle has no effect: the electrons are bound by −78.98 eV. In (b) the spins are parallel: the Pauli principle forces the promotion of an electron from a 1s ↑ orbital of H to a 2s ↑ orbital of He. The electrons now are bound by -59.38 eV, less than (a) by 19.60 eV. This is the amount by which the Pauli principle has increased the repulsion. We have omitted the repulsive coulomb energy of the two protons, which is the same in both (a) and (b).

We make no attempt here to evaluate the repulsive interaction[2] from first principles. Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form B/R^{12}, where B is a positive constant, when used together with a long-range attractive potential of the form of (9). The constants A and B are empirical parameters determined from independent measurements made in the gas phase; the data used include the virial coefficients and the viscosity. It is usual to write the total potential energy of two atoms at separation R as

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right] , \qquad (10)$$

where ϵ and σ are the new parameters, with $4\epsilon\sigma^6 = A$ and $4\epsilon\sigma^{12} = B$. The potential (10) is known as the Lennard-Jones potential, Fig. 6. The force between the two atoms is given by $-dU/dR$. Values of ϵ and σ given in Table 4 can be obtained from gas-phase data, so that calculations on properties of the solid do not involve disposable parameters.

Other empirical forms for the repulsive interaction are widely used, in particular the exponential form $\lambda \exp(-R/\rho)$, where ρ is a measure of the range of the interaction. This is generally as easy to handle analytically as the inverse power law form.

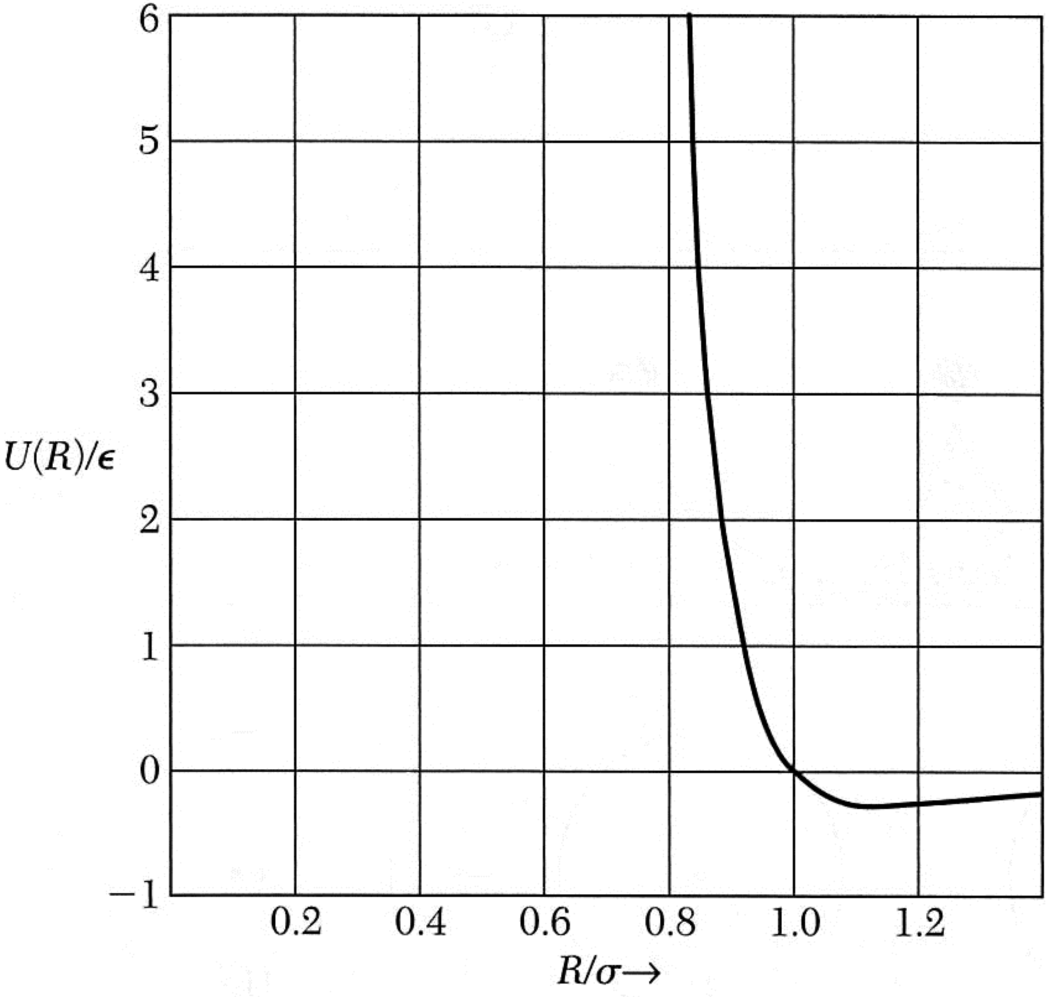


Figure 6 Form of the Lennard-Jones potential (10) which describes the interaction of two inert gas atoms. The minimum occurs at $R/\sigma = 2^{1/6} \cong 1.12$. Notice how steep the curve is inside the minimum, and how flat it is outside the minimum. The value of U at the minimum is $-\epsilon$; and $U = 0$ at $R = \sigma$.

Equilibrium Lattice Constants

If we neglect the kinetic energy of the inert gas atoms, the cohesive energy of an inert gas crystal is given by summing the Lennard-Jones potential (10) over all pairs of atoms in the crystal. If there are N atoms in the crystal, the total potential energy is

$$U_{\mathrm{tot}} = \tfrac{1}{2}N(4\epsilon)\left[\sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{12} - \sum_j{}' \left(\frac{\sigma}{p_{ij}R}\right)^{6}\right] , \tag{11}$$

where $p_{ij}R$ is the distance between reference atom i and any other atom j, expressed in terms of the nearest-neighbor distance R. The factor $\frac{1}{2}$ occurs with the N to compensate for counting twice each pair of atoms.

The summations in (11) have been evaluated, and for the fcc structure

$$\sum_j{}' p_{ij}^{-12} = 12.13188 ; \qquad \sum_j{}' p_{ij}^{-6} = 14.45392 . \tag{12}$$

There are 12 nearest-neighbor sites in the fcc structure; we see that the series are rapidly converging and have values not far from 12. The nearest neighbors contribute most of the interaction energy of inert gas crystals. The corresponding sums for the hcp structure are 12.13229 and 14.45489.

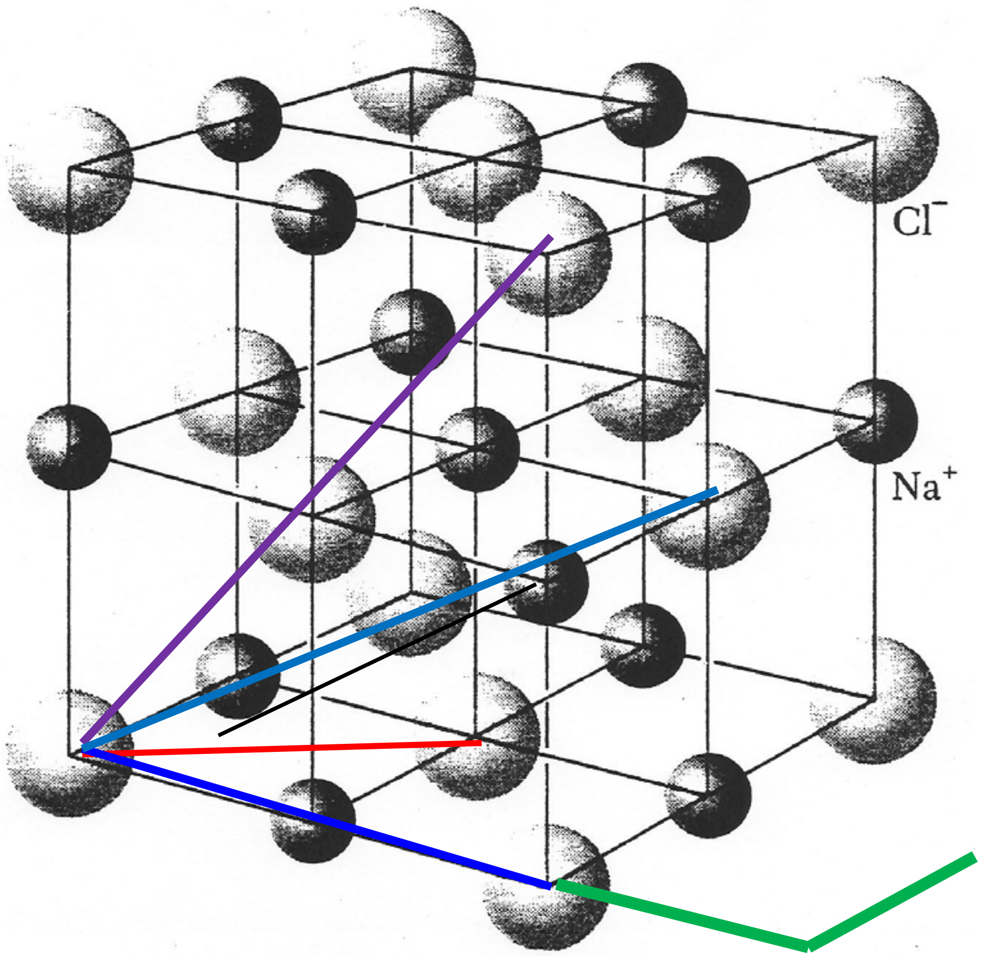


Figure 15 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

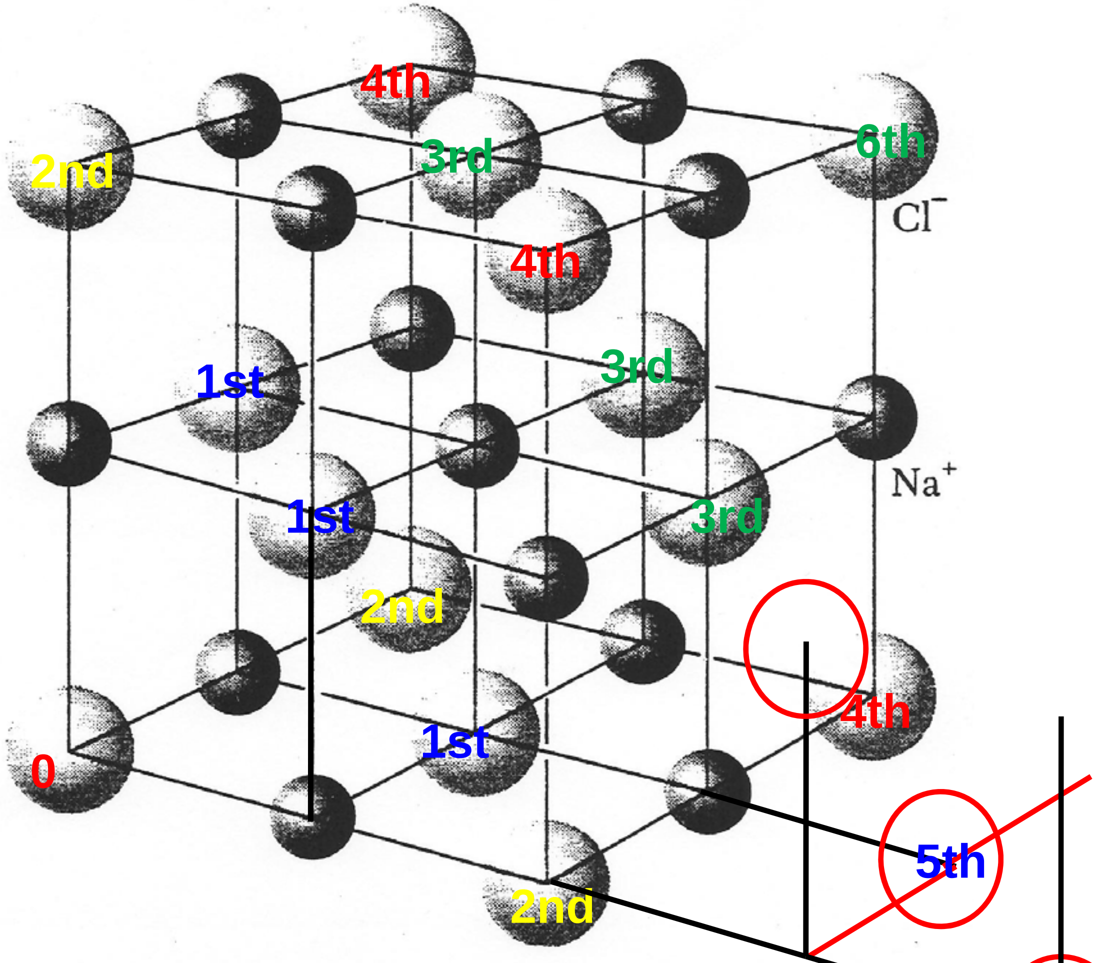


Figure 15 We may construct the sodium chloride crystal structure by arranging Na$^+$ and Cl$^-$ ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl$^-$ ion at 000 and one Na$^+$ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

- <½ ½ 0> $R_1 = \frac{\sqrt{1}}{\sqrt{2}} * 12 \rightarrow (1/R_1)^{12}\ 12$
- <1 0 0> $R_2 = \frac{\sqrt{2}}{\sqrt{2}} \text{ x } 6 \rightarrow (1/R_1)^{12}\ (1/\sqrt{2}\,)^{12}\ \text{ x } 6 = 0.0938$
- <1 ½ ½> $R_3 = \frac{\sqrt{3}}{\sqrt{2}} \text{ x } 24 \rightarrow (1/R_1)^{12}\ (1/\sqrt{3}\,)^{12}\ \text{ x } 24 = 0.0329$
- <1 1 0> $R_4 = \frac{\sqrt{4}}{\sqrt{2}} \text{ x } 12 \rightarrow (1/R_1)^{12}\ (1/\sqrt{4}\,)^{12}\ \text{ x } 12 = 0.0029$
- <3/2 ½ 0> $R_5 = \frac{\sqrt{5}}{\sqrt{2}} \text{ x } 24 \rightarrow (1/R_1)^{12}\ (1/\sqrt{5}\,)^{12}\ \text{ x } 24 = 0.0015$
- <1 1 1> $R_6 = \frac{\sqrt{6}}{\sqrt{2}} \text{ x } 8 \rightarrow (1/R_1)^{12}\ (1/\sqrt{6}\,)^{12}\ \text{ x } 8 = 0.0002$
- <3/2 ½ 1> $R_7 = \frac{\sqrt{7}}{\sqrt{2}} \text{ x } 24 \rightarrow (1/R_1)^{12}\ (1/\sqrt{7}\,)^{12}\ \text{ x } 24 = 0.0002$
- <2 0 0> $R_8 = \frac{\sqrt{8}}{\sqrt{2}} \text{ x } 6 \rightarrow (1/R_1)^{12}\ (1/\sqrt{8}\,)^{12}\ \text{ x } 6 = 0.00002289$

If we take U_{tot} in (11) as the total energy of the crystal, the equilibrium value R_0 is given by requiring that U_{tot} be a minimum with respect to variations in the nearest-neighbor distance R:

$$\frac{dU_{\text{tot}}}{dR} = 0 = -2N\epsilon\left[(12)(12.13)\frac{\sigma^{12}}{R^{13}} - (6)(14.45)\frac{\sigma^{6}}{R^{7}}\right] , \tag{13}$$

whence

$$R_0/\sigma = 1.09 \ , \tag{14}$$

the same for all elements with an fcc structure. The observed values of R_0/σ, using the independently determined values of σ given in Table 4, are:

	Ne	Ar	Kr	Xe
R_0/σ	1.14	1.11	1.10	1.09 .

The agreement with (14) is remarkable. The slight departure of R_0/σ for the lighter atoms from the universal value 1.09 predicted for inert gases can be explained by zero-point quantum effects. From measurements on the gas phase we have predicted the lattice constant of the crystal.

Cohesive Energy

The cohesive energy of inert gas crystals at absolute zero and at zero pressure is obtained by substituting (12) and (14) in (11):

$$U_{\mathrm{tot}}(R) = 2N\epsilon\left[(12.13)\left(\frac{\sigma}{R}\right)^{12} - (14.45)\left(\frac{\sigma}{R}\right)^{6}\right] , \qquad (15)$$

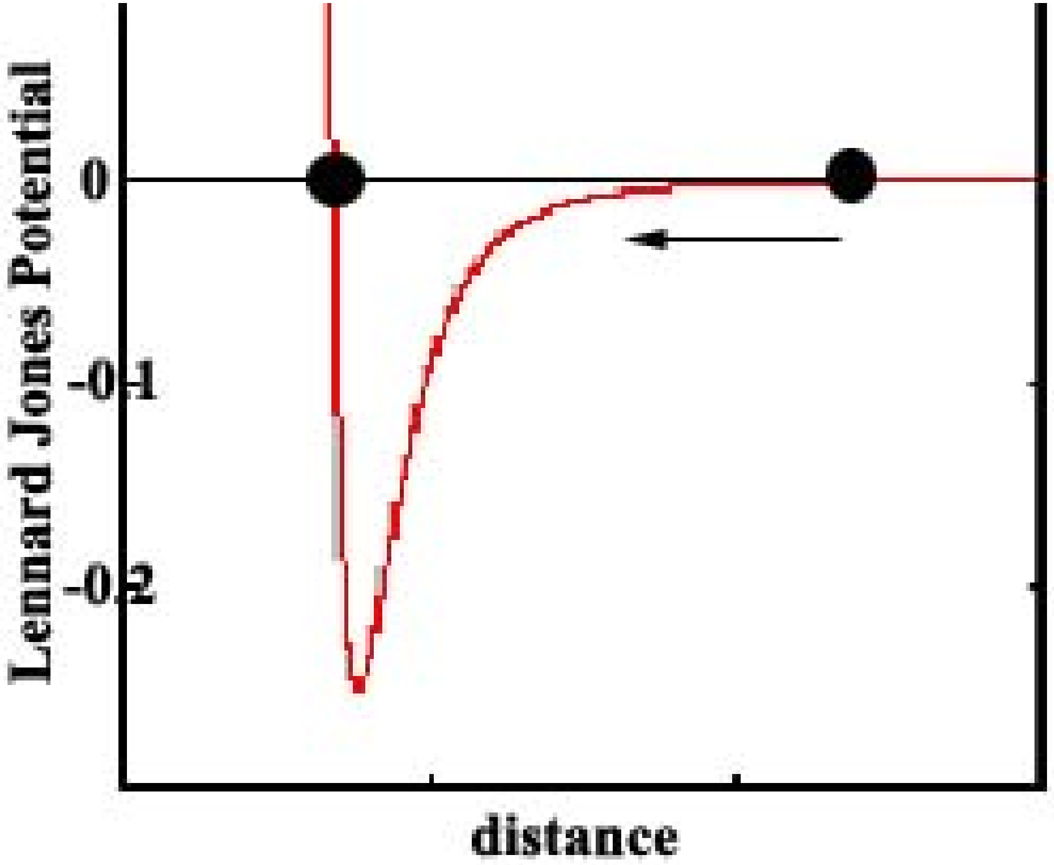
and, at $R = R_0$,

$$U_{\mathrm{tot}}(R_0) = -(2.15)(4N\epsilon) , \qquad (16)$$

the same for all inert gases. This is the calculated cohesive energy when the atoms are at rest. Quantum-mechanical corrections act to reduce the binding by 28, 10, 6, and 4 percent of Eq. (16) for Ne, Ar, Kr, and Xe, respectively.

The heavier the atom, the smaller the quantum correction. We can understand the origin of the quantum correction by consideration of a simple model in which an atom is confined by fixed boundaries. If the particle has the quantum wavelength λ, where λ is determined by the boundaries, then the particle has kinetic energy $p^2/2M = (h/\lambda)^2/2M$ with the de Broglie relation $p = h/\lambda$ for the connection between the momentum and the wavelength of a particle. On this model the quantum zero-point correction to the energy is inversely proportional to the mass. The final calculated cohesive energies agree with the experimental values of Table 4 within 1 to 7 percent.

One consequence of the quantum kinetic energy is that a crystal of the isotope Ne^{20} is observed to have a larger lattice constant than a crystal of Ne^{22}. The higher quantum kinetic energy of the lighter isotope expands the lattice because the kinetic energy is reduced by expansion. The observed lattice constants (extrapolated to absolute zero from 2.5 K) are Ne^{20}, 4.4644 Å; Ne^{22}, 4.4559 Å.



When two atoms are brought closer the potential energy (Lennard Jones potential) vary with the distance. The attractive interaction (negative sign) occurs while one atom approaching the other. If atoms are too close the repulsive force begins to emerge (positive sign).

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).

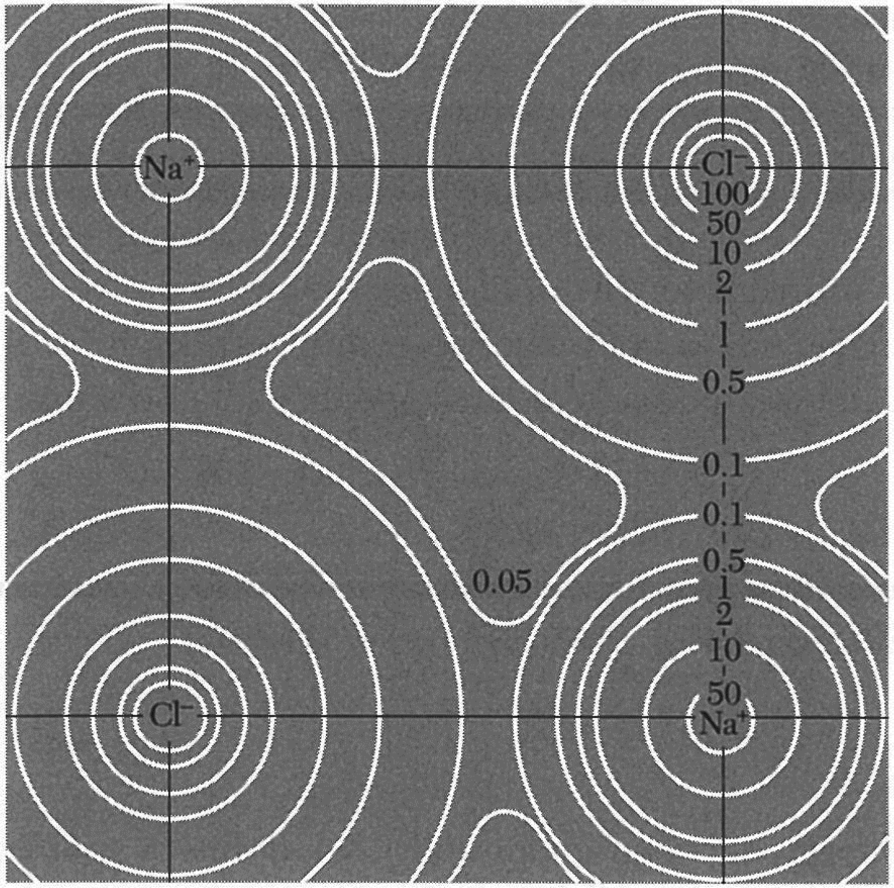
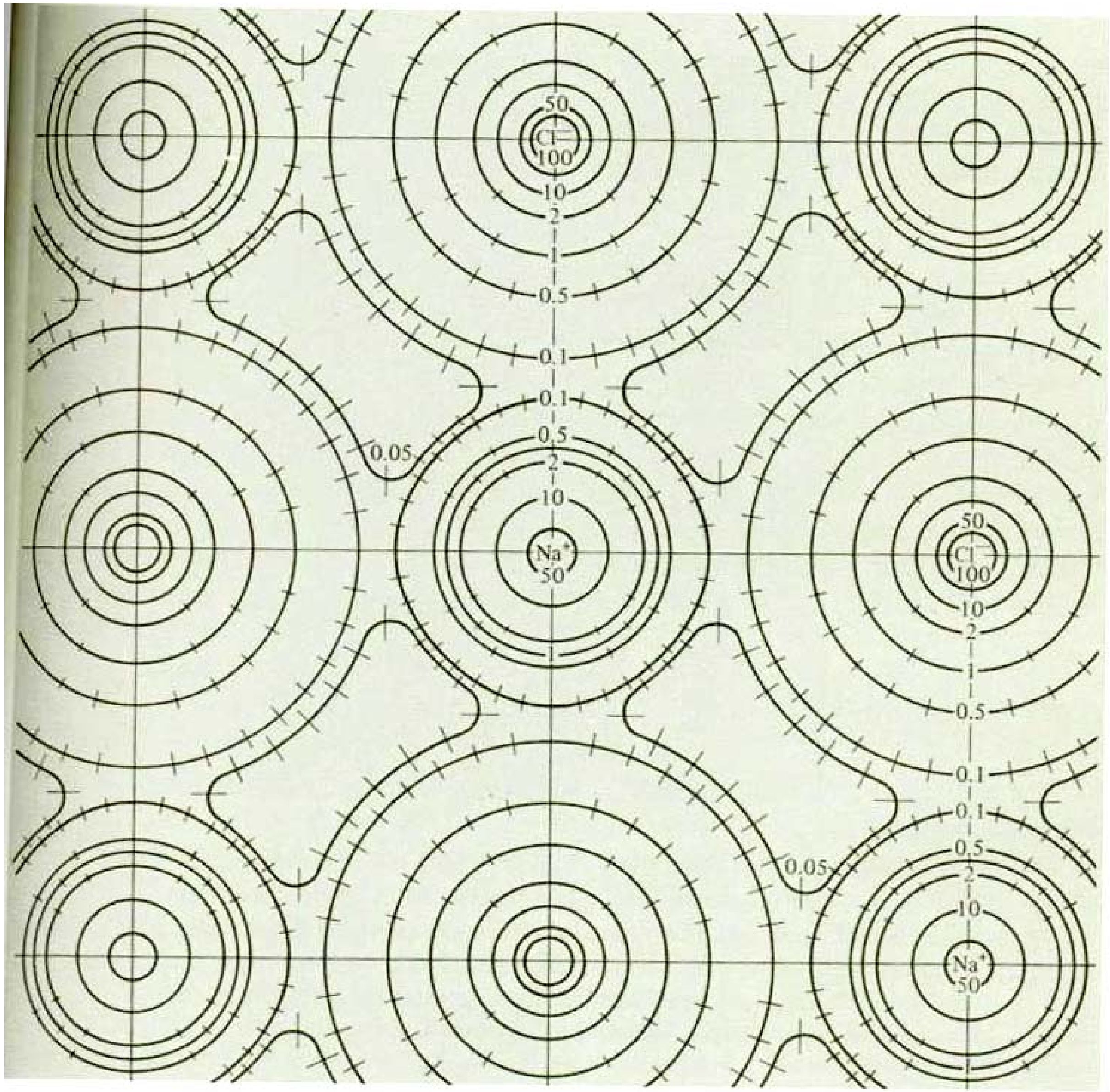


Figure 7 Electron density distribution in the base plane of NaCl, after x-ray studies by G. Schoknecht. The numbers on the contours give the relative electron concentration.

Electron density distribution in the base plane of NaCl by x-ray diffraction

It is expected that the charge distribution on each ion in an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms.



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 molecular unit for the lattice energy of crystalline NaCl with respect to separated Na^+ and Cl^- ions. We now calculate the energy more closely.

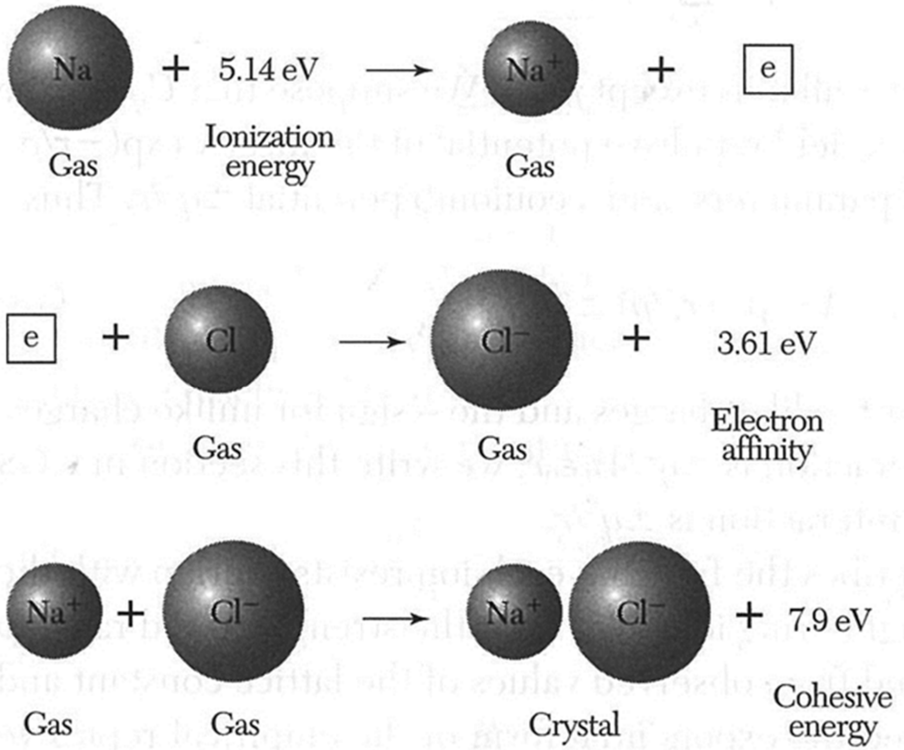


Figure 8 The energy per molecule unit of a crystal of sodium chloride is (7.9 − 5.1 + 3.6) = 6.4 eV lower than the energy of separated neutral atoms. The lattice energy with respect to separated ions is 7.9 eV per molecule unit. All values on the figure are experimental. Values of the ionization energy are given in Table 5, and values of the electron affinity are given in Table 6.

Electrostatic or Madelung Energy

The long-range interaction between ions with charge ±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**.

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:

$$U_i = \sum_j{}' U_{ij} \ , \tag{17}$$

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

(CGS)
$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm q^2/r_{ij} \ , \tag{18}$$

where the + sign is taken for the like charges and the – sign for unlike charges. 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 $\pm q^2/r$.

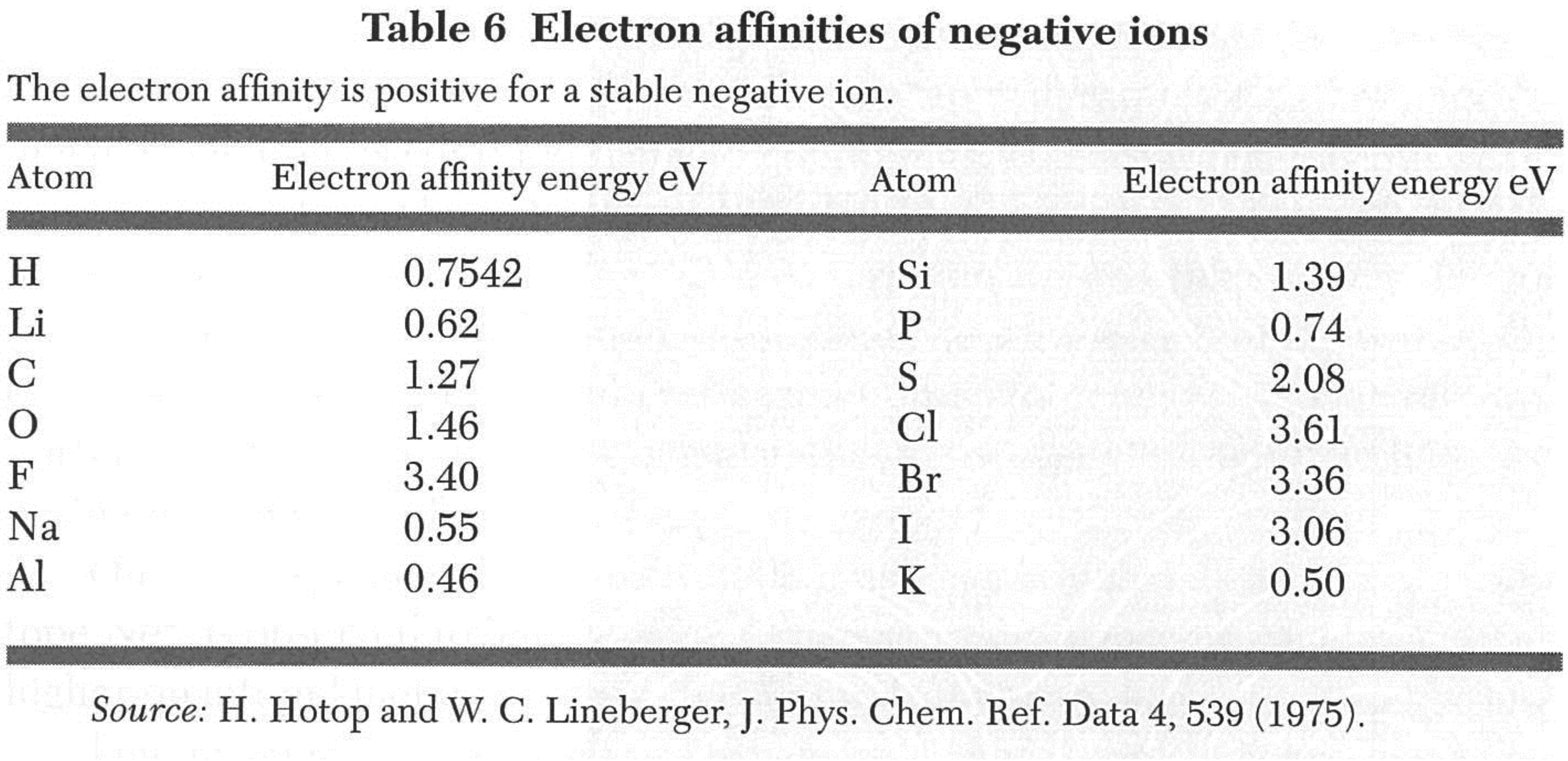


Table 6 Electron affinities of negative ions

The electron affinity is positive for a stable negative ion.

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

Source: H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data 4, 539 (1975).

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 the NaCl structure the value of U_i does not depend on whether the reference ion i is a positive or a negative ion. The sum in (17) 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. We neglect surface effects and 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 defined as 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

$$\text{(CGS)} \qquad U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \dfrac{q^2}{R} & \text{(nearest neighbors)} \\ \pm \dfrac{1}{p_{ij}} \dfrac{q^2}{R} & \text{(otherwise).} \end{cases} \tag{19}$$

Thus

$$\text{(CGS)} \qquad U_{tot} = NU_i = N\left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right) , \tag{20}$$

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

$$\boxed{\alpha \equiv \sum_j{}' \frac{(\pm)}{p_{ij}} \equiv \textbf{Madelung constant} \ .} \tag{21}$$

The sum should include the nearest-neighbor contribution, which is just z. The (±) sign is discussed just before (25). The value of the Madelung constant is of central importance in the theory of an ionic crystal. Methods for its calculation are discussed next.

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

$$\text{(CGS)} \qquad N\frac{dU_i}{dR} = -\frac{Nz\lambda}{\rho}\exp(-R/\rho) + \frac{N\alpha q^2}{R^2} = 0 \ , \tag{22}$$

or

$$\text{(CGS)} \qquad R_0^2 \exp(-R_0/\rho) = \rho\alpha q^2/z\lambda \ . \tag{23}$$

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 (20) and (23), as

$$\text{(CGS)} \qquad U_{tot} = -\frac{N\alpha q^2}{R_0}\left(1 - \frac{\rho}{R_0}\right) \ . \tag{24}$$

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.

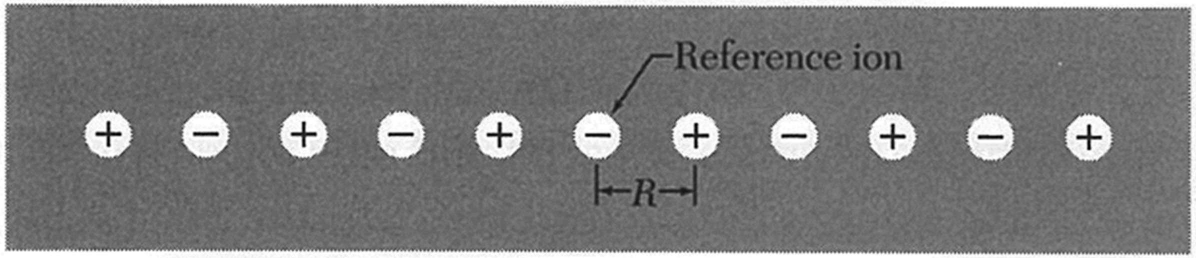
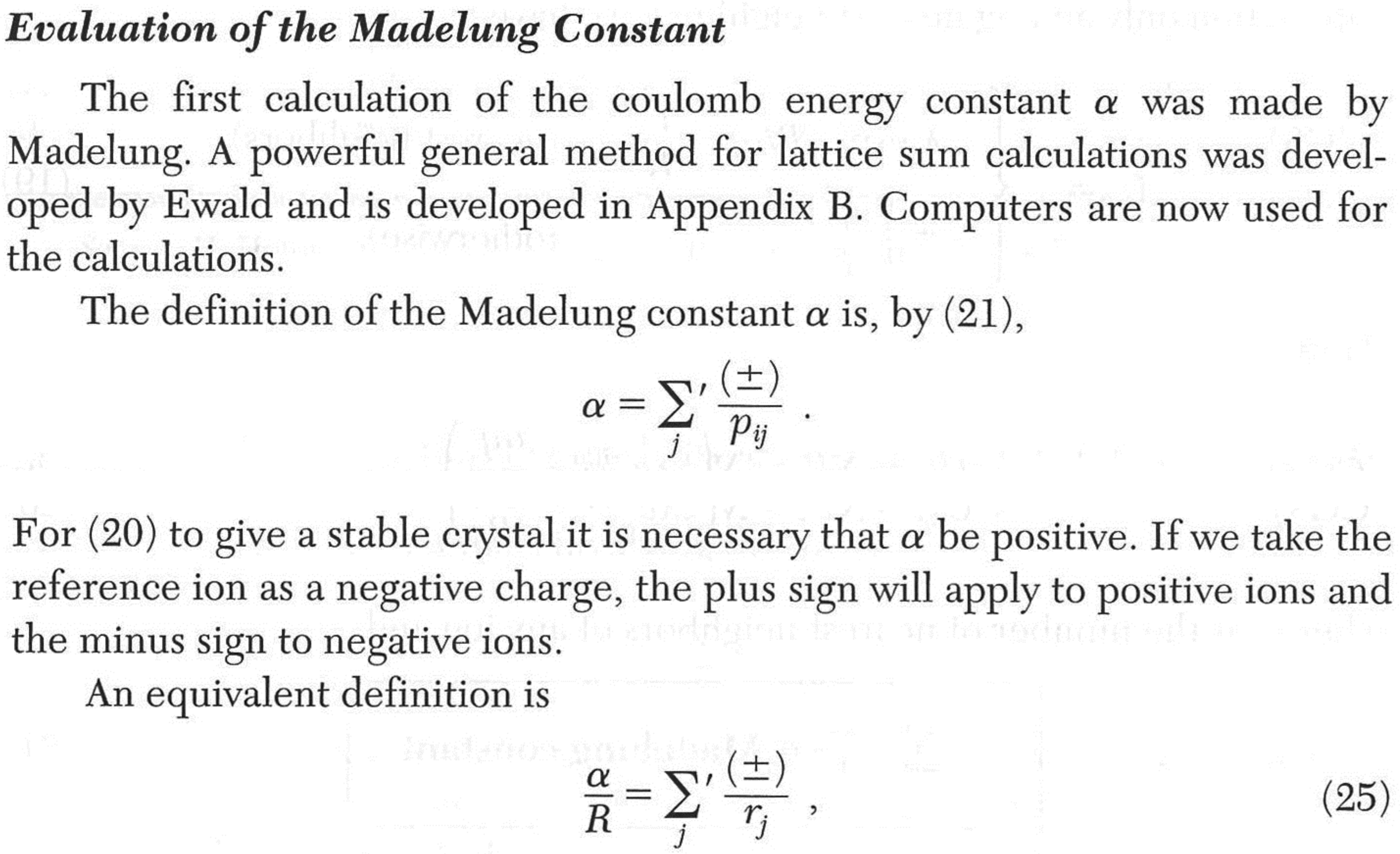


Figure 9 Line of ions of alternating signs, with distance R between ions.



Evaluation of the Madelung Constant

The first calculation of the coulomb energy constant α was made by Madelung. A powerful general method for lattice sum calculations was developed by Ewald and is developed in Appendix B. Computers are now used for the calculations.

The definition of the Madelung constant α is, by (21),

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

For (20) to give a stable crystal it is necessary that α be positive. If we take the reference ion as a negative charge, the plus sign will apply to positive ions and the minus sign to negative ions.

An equivalent definition is

$$\frac{\alpha}{R} = \sum_j{}' \frac{(\pm)}{r_j} \; , \tag{25}$$

where r_j is the distance of the jth ion from the reference ion and R is the nearest-neighbor distance. 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

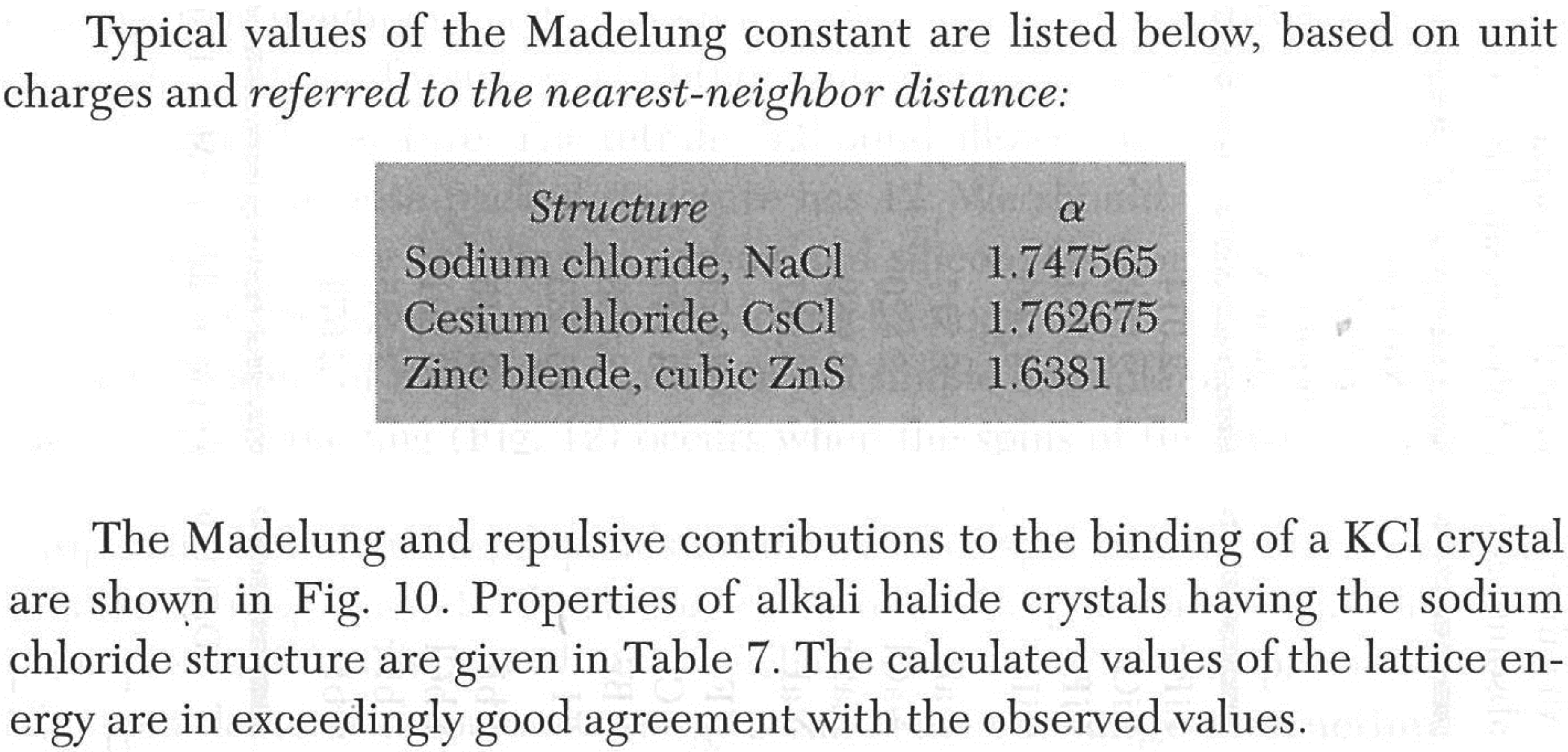
$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \cdots\right];$$

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.



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 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 7. The calculated values of the lattice energy are in exceedingly good agreement with the observed values.

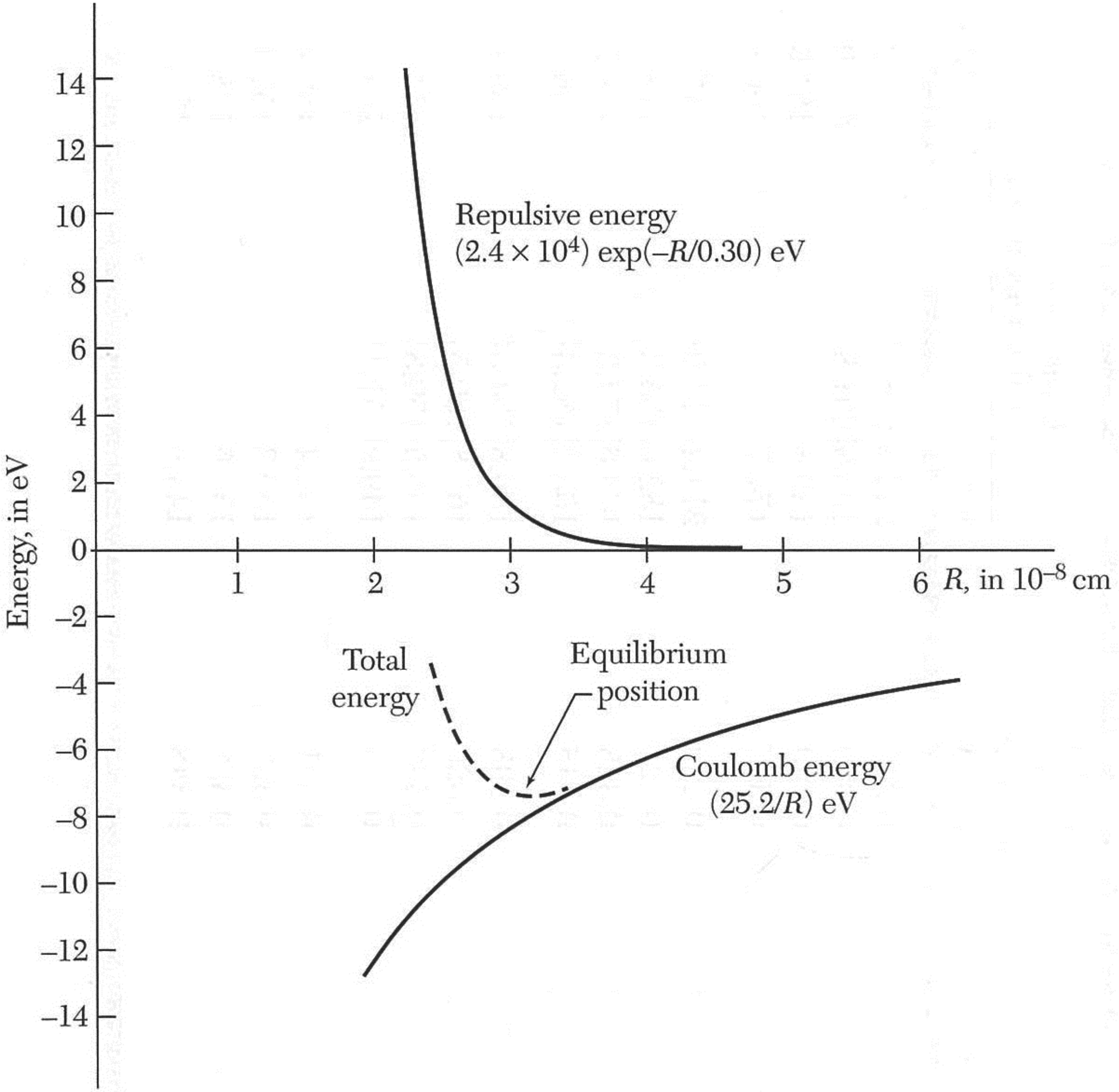


Figure 10 Energy per molecule of KCl crystal, showing Madelung (coulomb) and repulsive contributions.

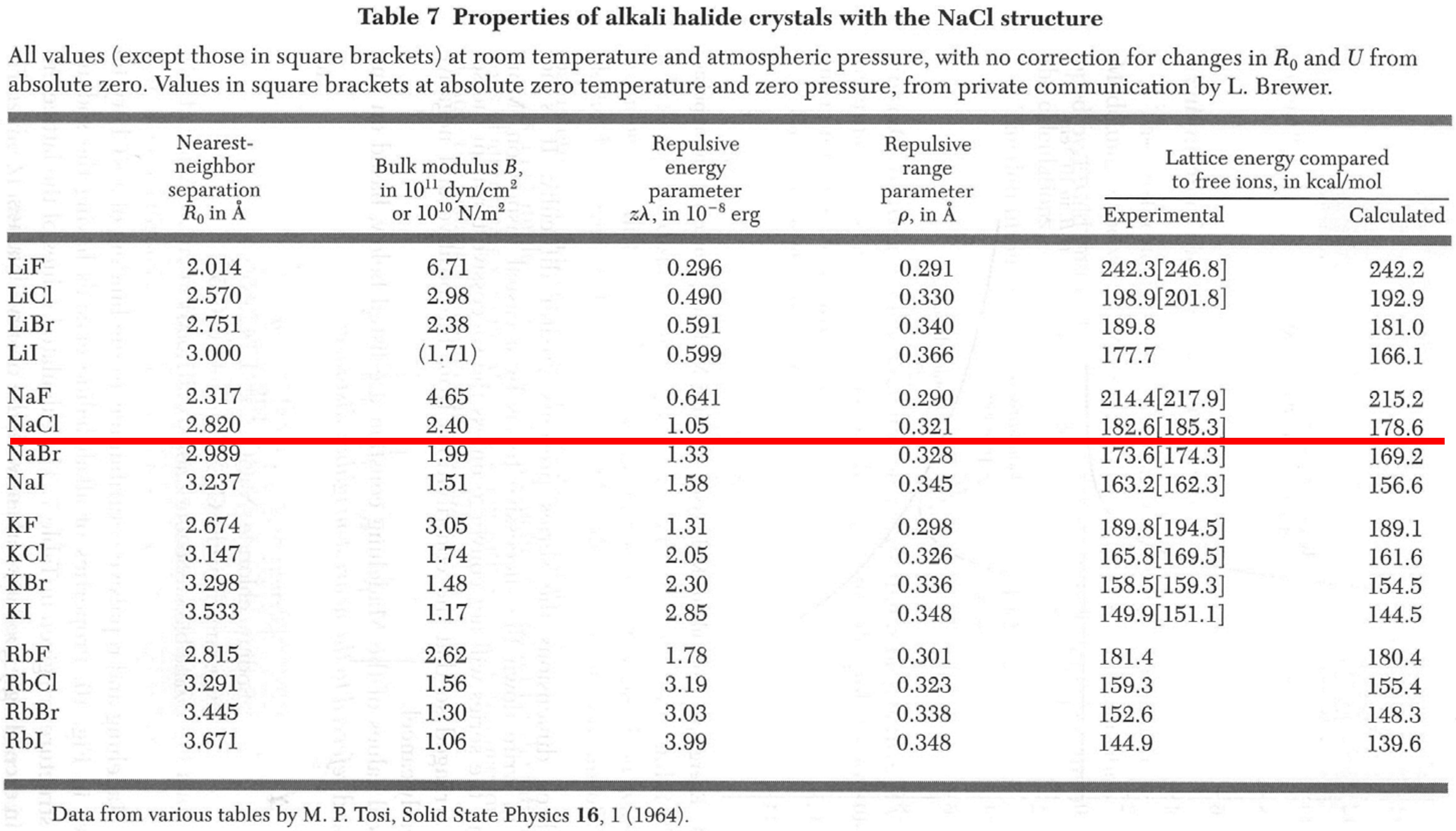


Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square 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 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol: Experimental	Lattice energy compared to free ions, in kcal/mol: 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).

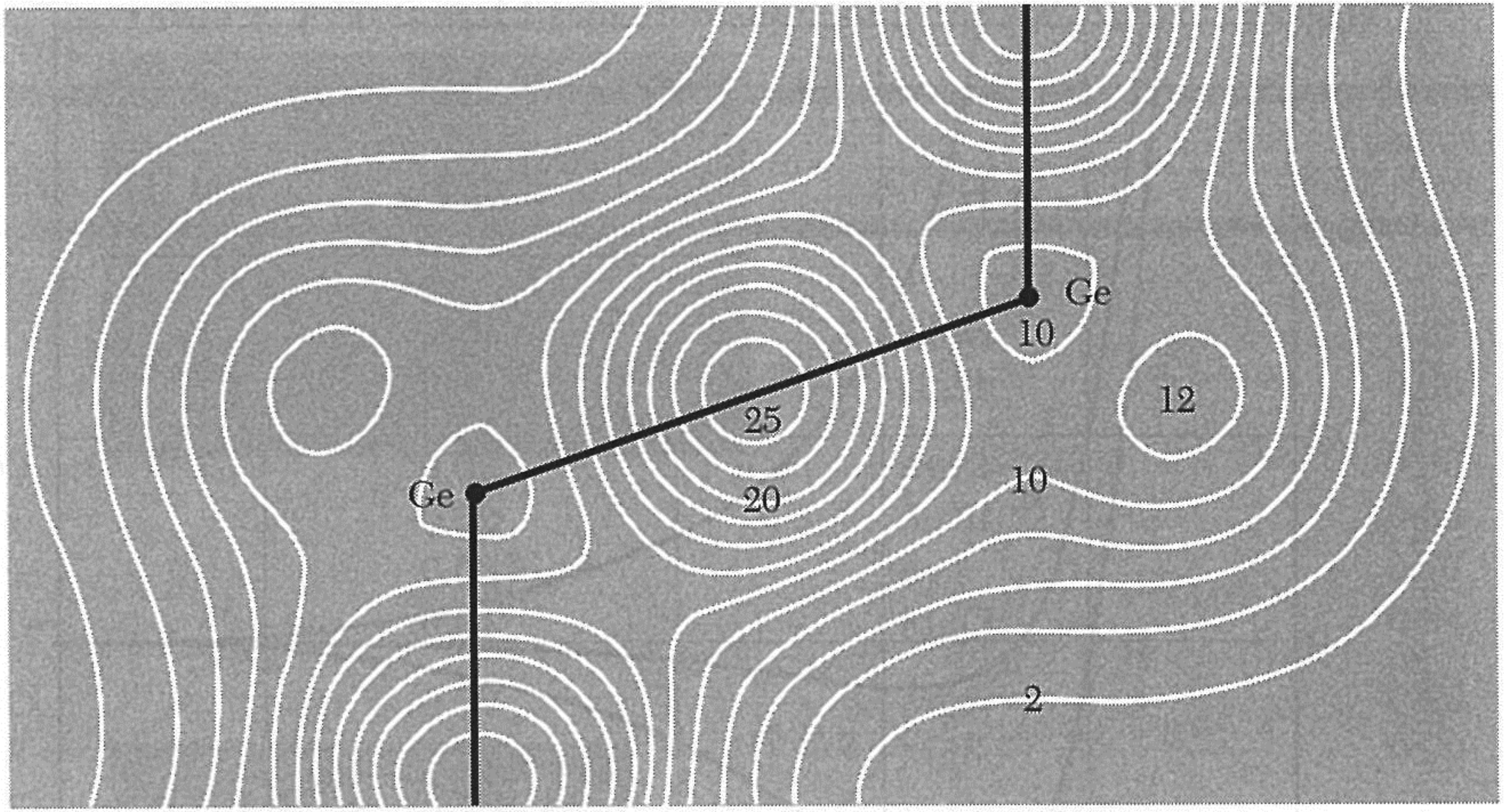
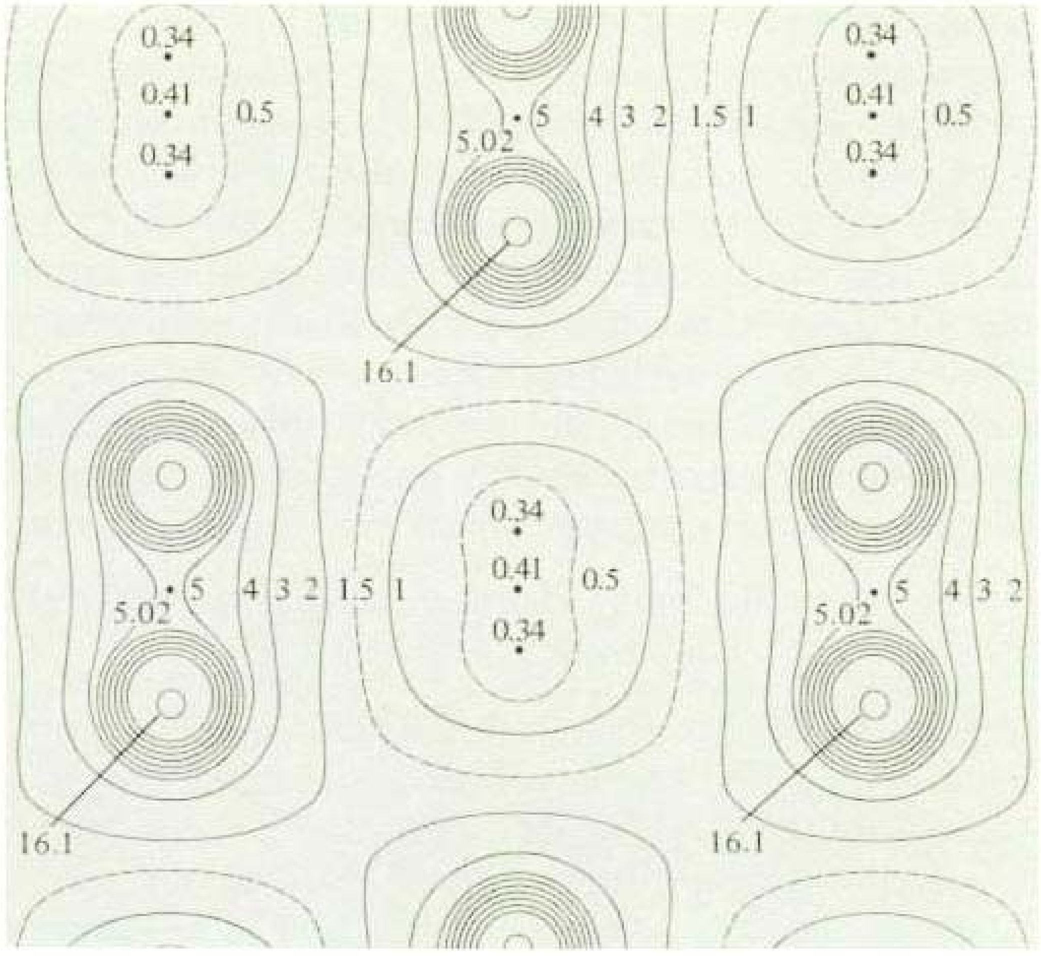
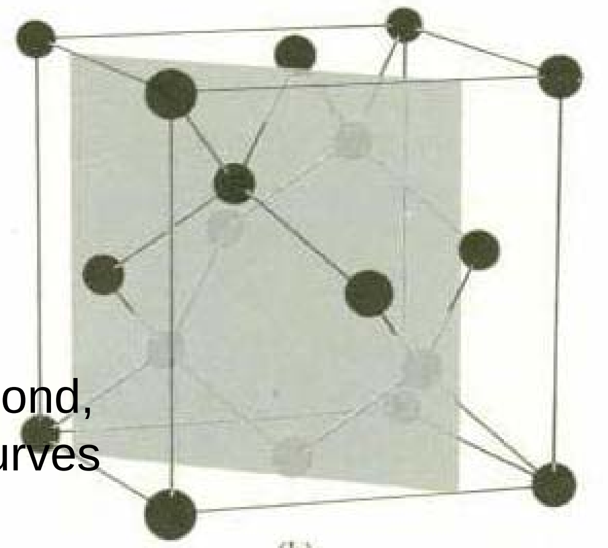


Figure 11 Calculated valence electron concentration in germanium. The numbers on the contours give the electron concentration per primitive cell, with four valence electrons per atom (eight electrons per primitive cell). Note the high concentration midway along the Ge-Ge bond, as we expect for covalent bonding. (After J. R. Chelikowsky and M. L. Cohen.)

Characteristic of covalent crystal



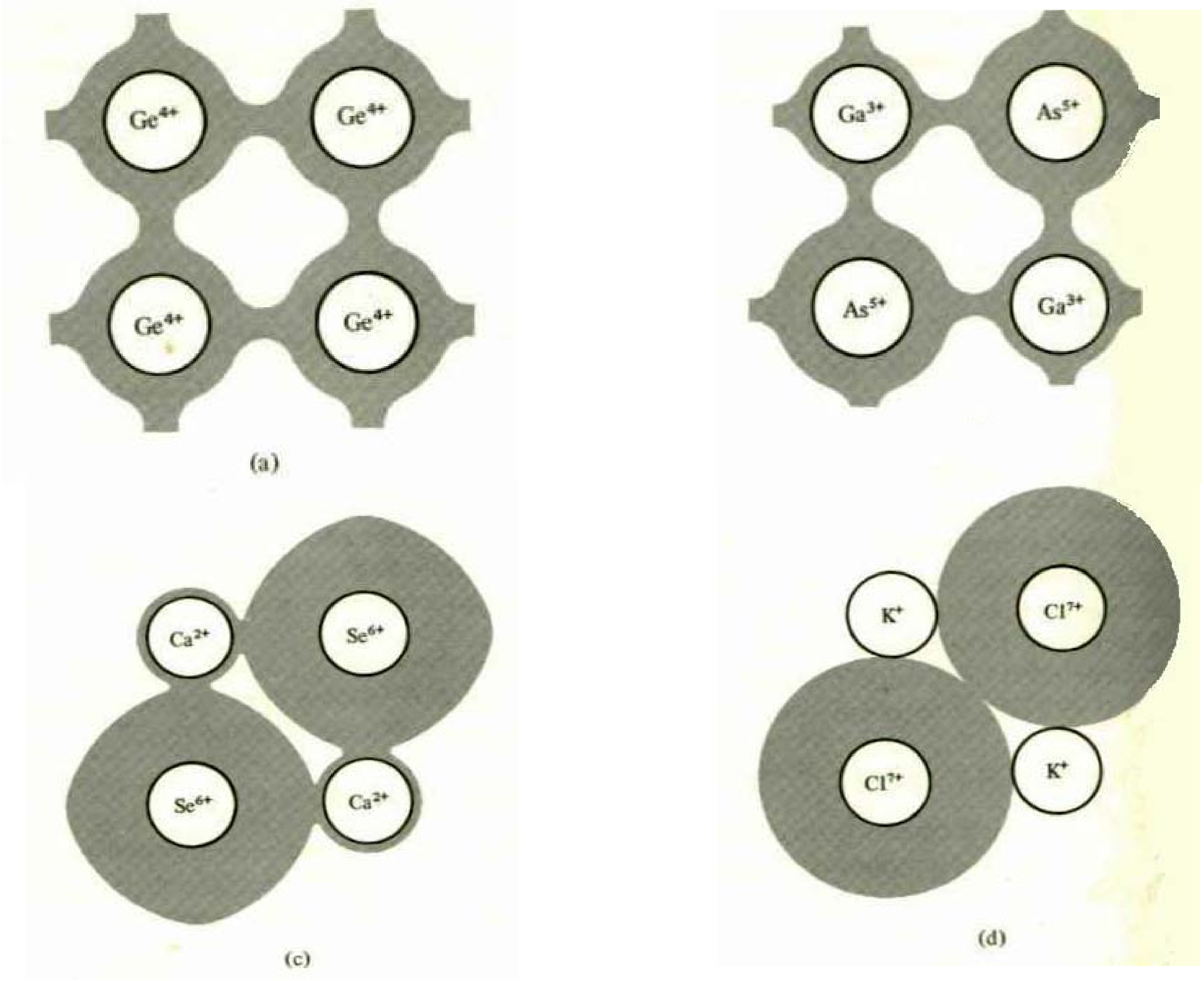
(a)



(b)

Electronic charge distribution on a plane section of diamond, as suggested by x-ray diffraction. Numbers along the curves indicate electrons per cubic Å.

A highly schematic representation of the continuity from perfect covalent to perfect ionic crystals



(a)

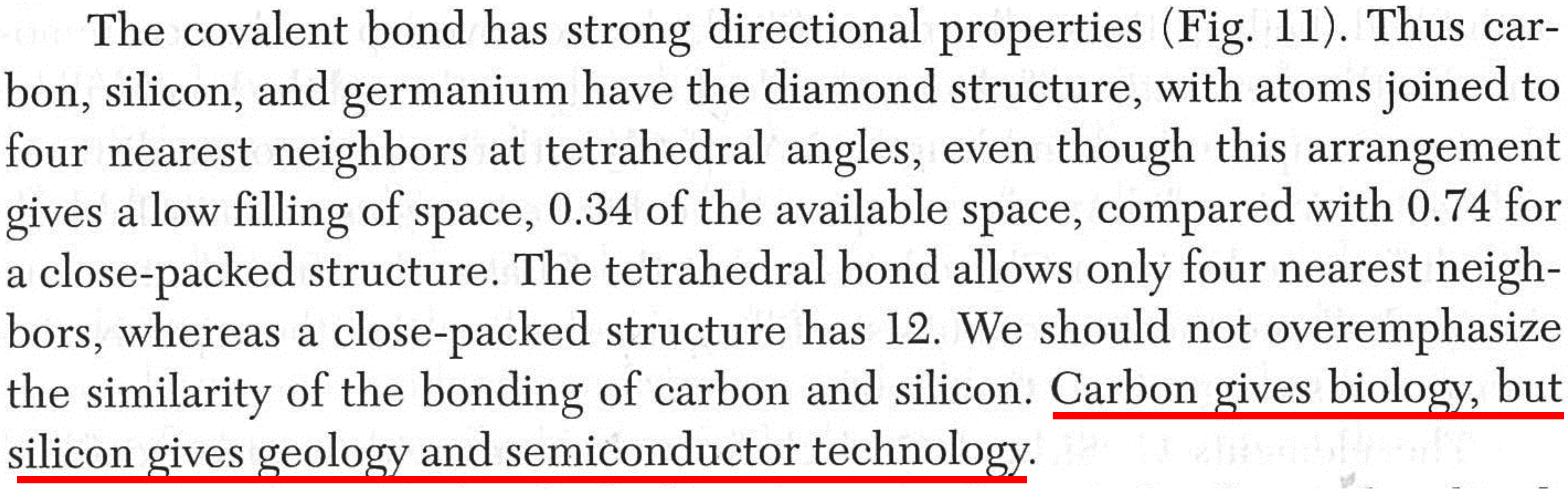
(c)

(d)

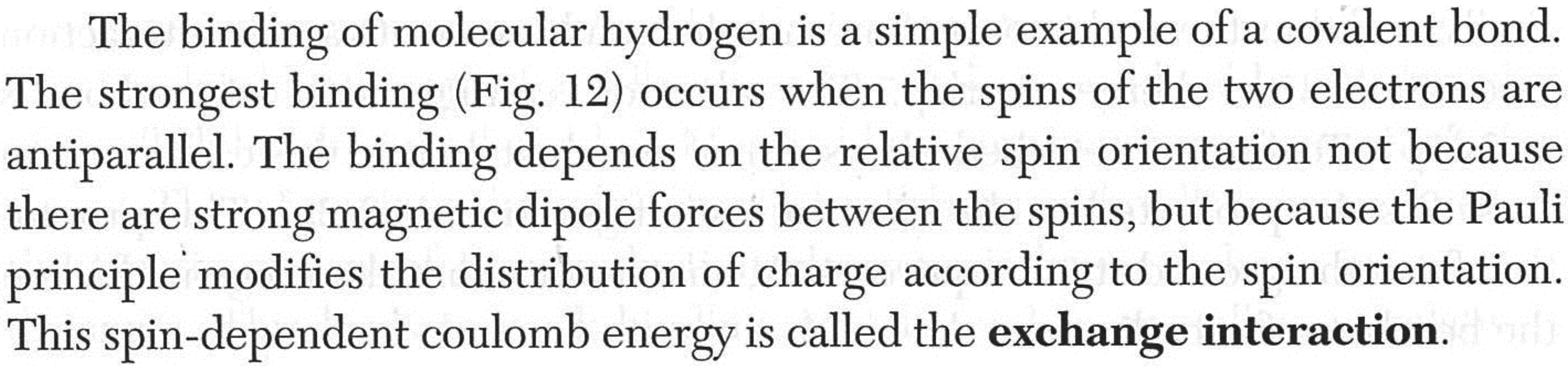
COVALENT CRYSTALS

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 with respect to separated neutral atoms is comparable with the bond strength in ionic crystals.

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 covalent bond has strong directional properties (Fig. 11). 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 and semiconductor technology.



The binding of molecular hydrogen is a simple example of a covalent bond. The strongest binding (Fig. 12) 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**.

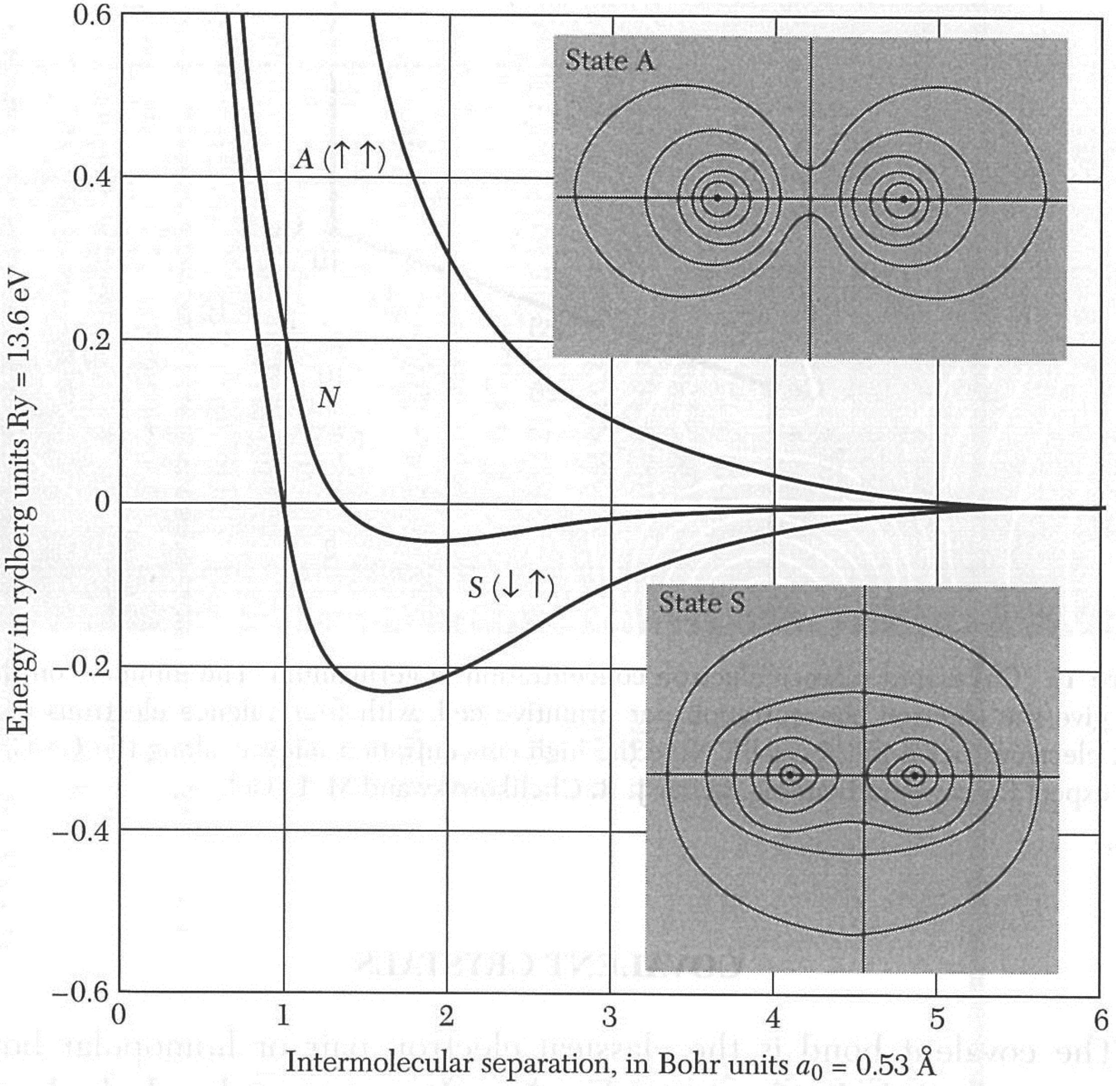


Figure 12 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve N refers to a classical calculation with free atom charge densities; A is the result for parallel electron spins, taking the Pauli exclusion principle into account, and S (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states A and S.

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 $1s^2 2s^2 2p^2$. 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.

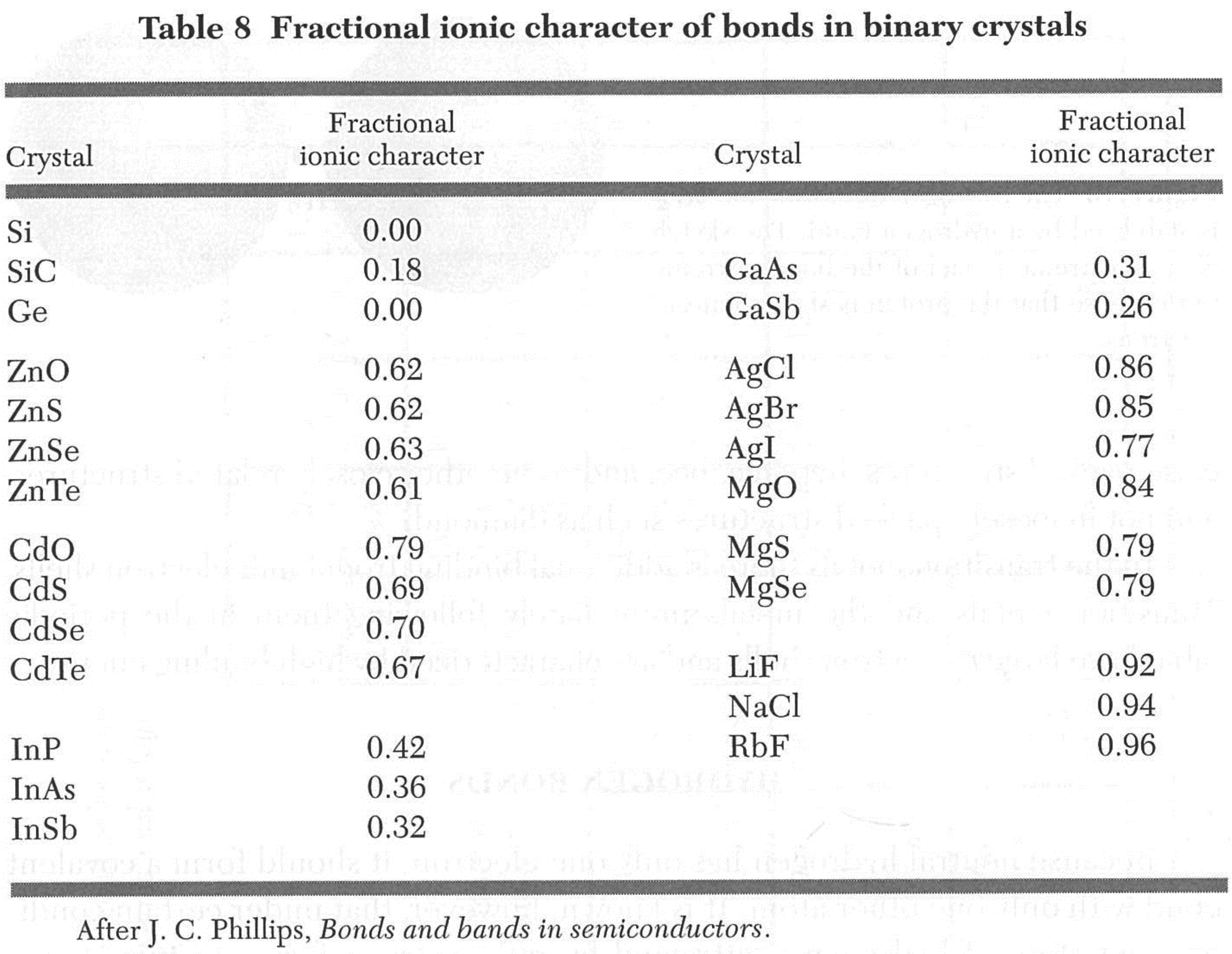
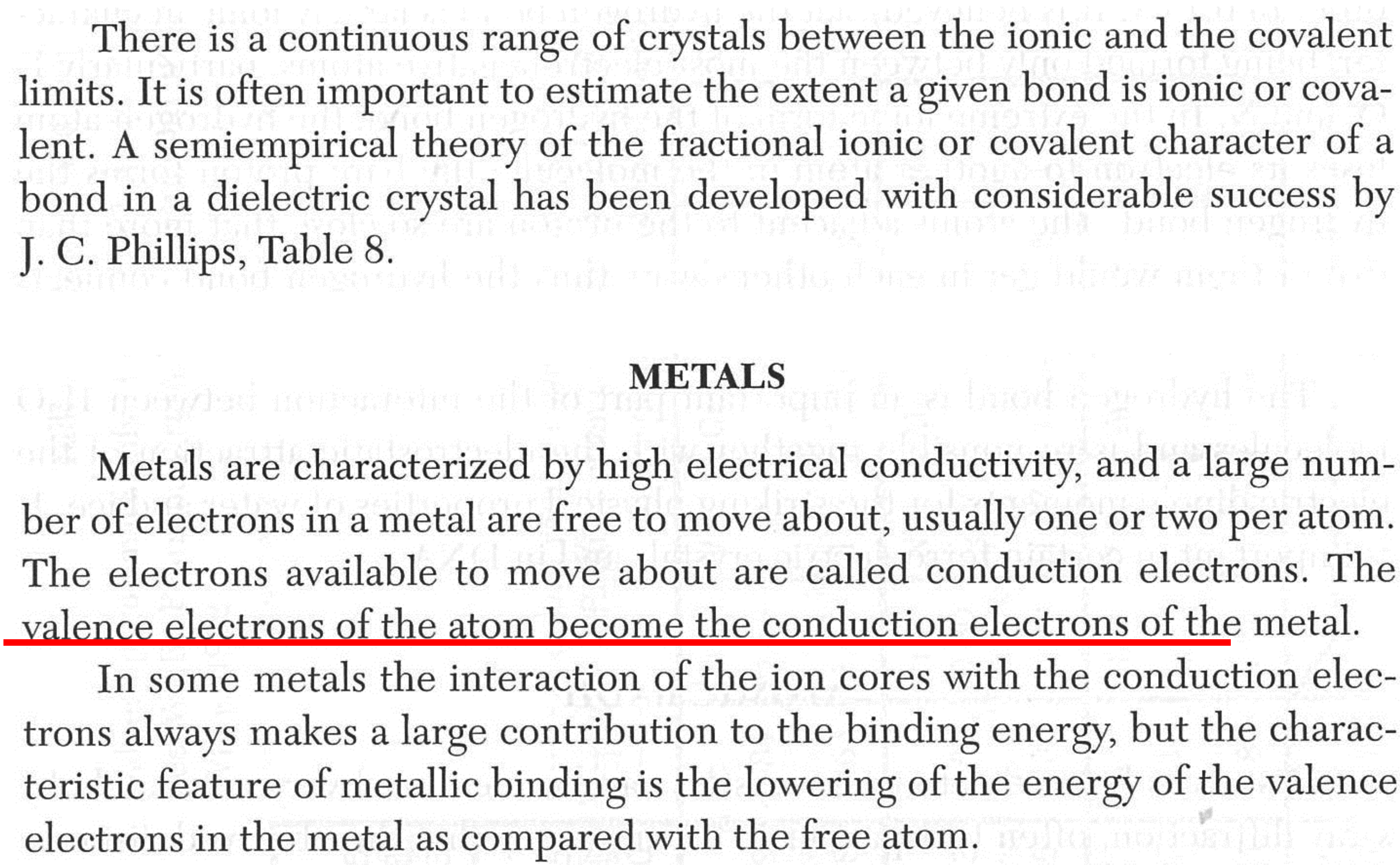


Table 8 Fractional ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00		
SiC	0.18	GaAs	0.31
Ge	0.00	GaSb	0.26
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		

After J. C. Phillips, *Bonds and bands in semiconductors*.



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, Table 8.

METALS

Metals are characterized by high electrical conductivity, and a large number of electrons in a metal are free to move about, usually one or two per atom. The electrons available to move about are called conduction electrons. The valence electrons of the atom become the conduction electrons of the metal.

In some metals the interaction of the ion cores with the conduction electrons always makes a large contribution to the binding energy, but the characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

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.

In the transition metals there is 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.

Electronic velocity

- Kinetic energy not much increased, e.g. localizing an electron in a region Δx; from the **Heisenberg uncertainty principle**, the related spread in momentum $\Delta(mv) \geq \hbar/\Delta x$, thus ½ mv^2 is at least $h^2/2m(2\pi\,\Delta x)^2$. If $\Delta x \approx 0.1$ nm, kinetic energy is $\approx 5 \times 10^{-12}$ erg ≈ 3 eV
  - **Fermi velocity** $v_F = \frac{p_F}{m} = \frac{4.20}{r_s/a_0} \times 10^8 \text{cm/sec}$
    - The Fermi velocity plays a role in the theory of metals comparable to the thermal velocity, $v = (3k_BT/m)^{1/2}$, in a classical gas.
- Estimate v_0 (**In Drude's time of ~1900 it was natural to estimate v_0 from classical equi-partition of energy**)

$$\frac{1}{2}mv_0^2 = \frac{3}{2}k_BT$$

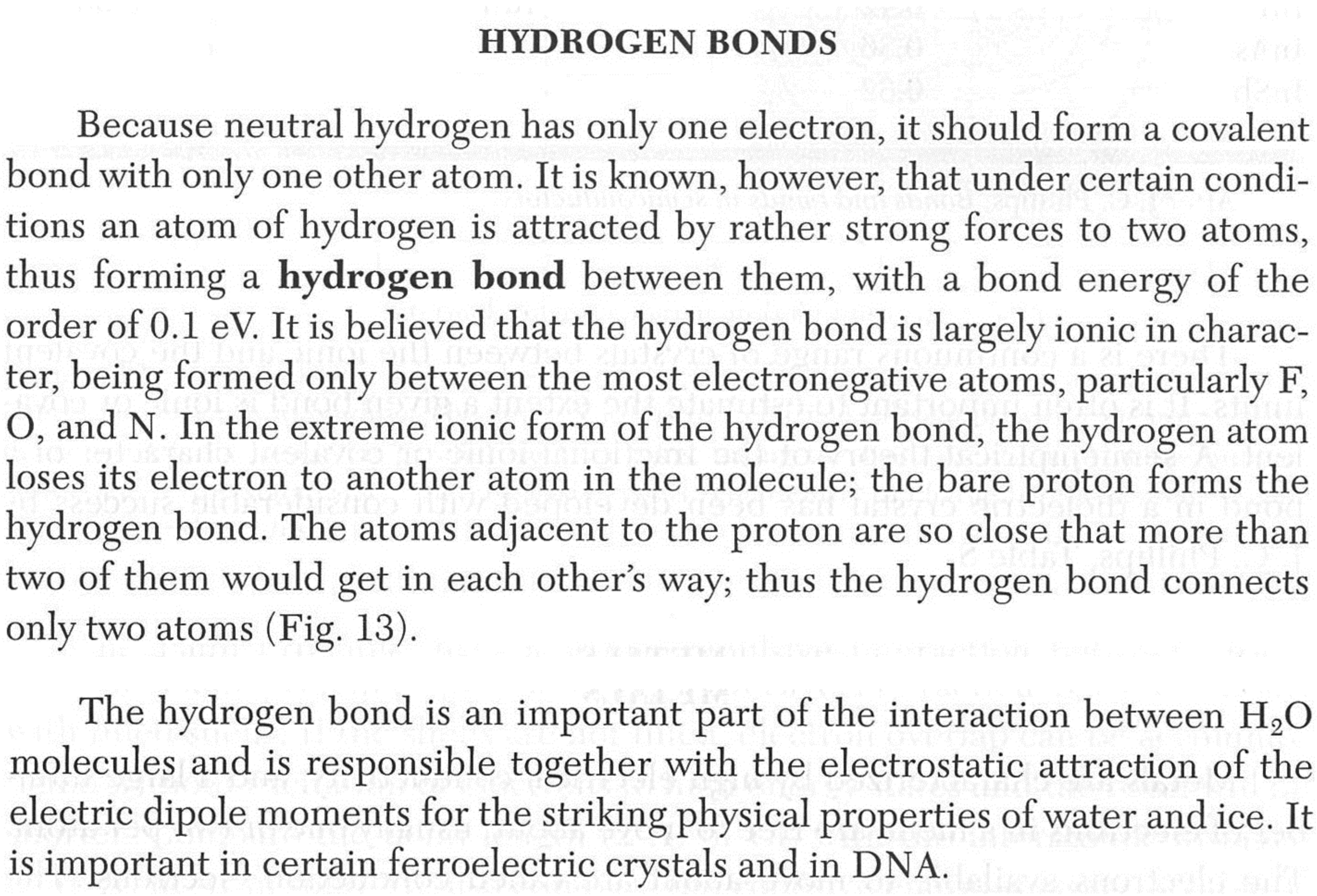
v_0 is of order $10^7\ cm/s$

Valence vs Core Electrons

- The aspects of the atomic electronic configuration that are significantly altered when the atoms are assembled together into solid
- In simple metals, only conduction electrons are valence electrons, and all others in the rigid ion core
- In transition metals, electrons in the highest d-shells as valence rather than core electrons

Metals vs Insulators (electron distribution)

K- space or r-space



HYDROGEN BONDS

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 a **hydrogen bond** 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 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. 13).

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. It is important in certain ferroelectric crystals and in DNA.

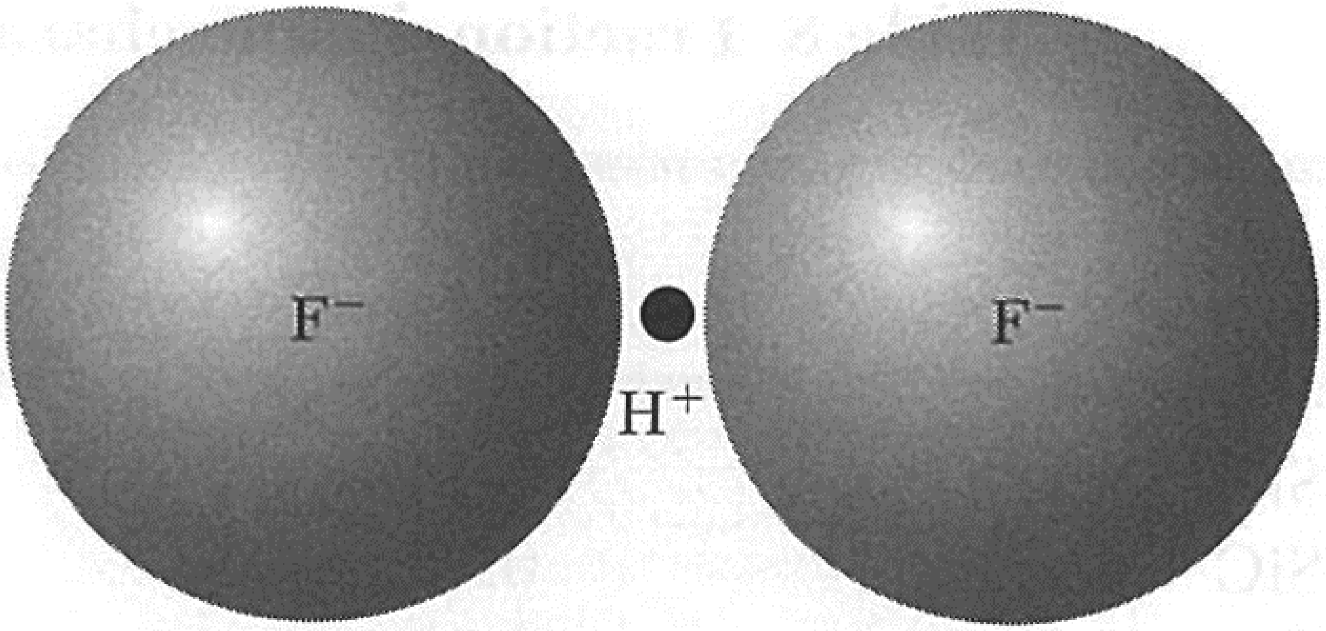


Figure 13 The hydrogen difluoride ion HF_2^- is stabilized by a hydrogen bond. The sketch is of an extreme model of the bond, extreme in the sense that the proton is shown bare of electrons.

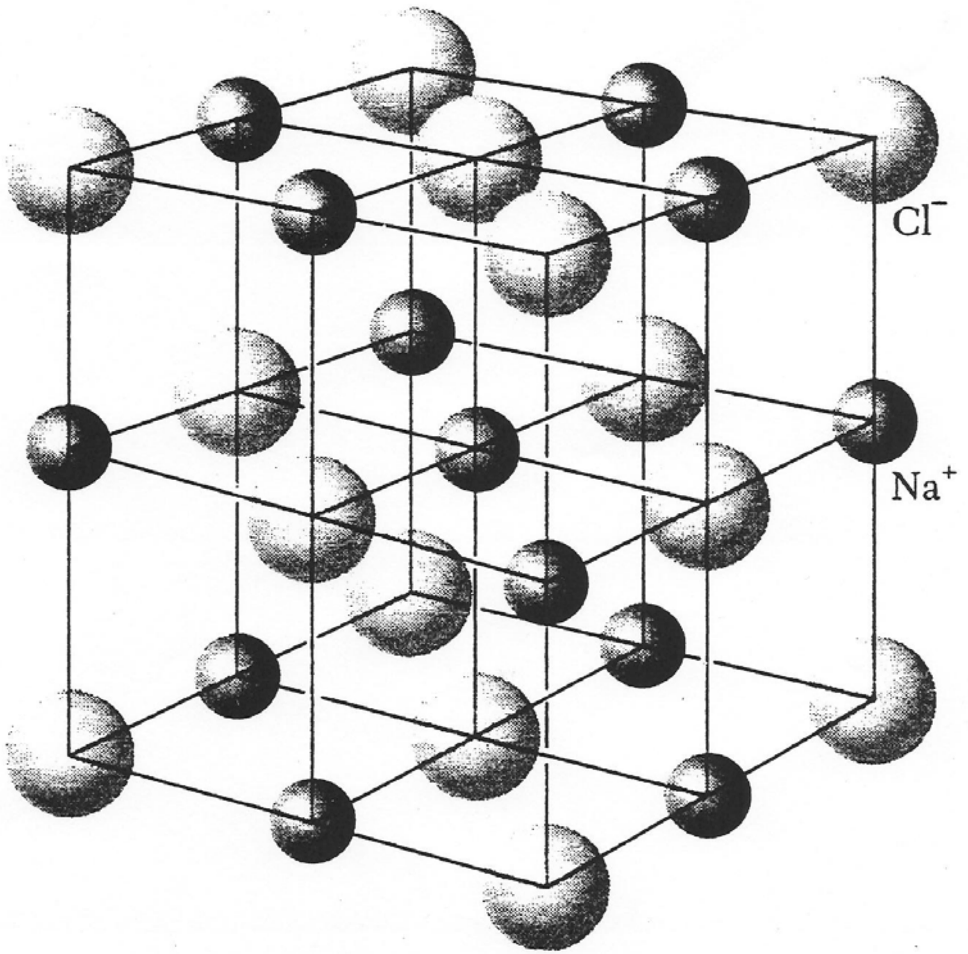


Figure 15 We may construct the sodium chloride crystal structure by arranging Na^+ and Cl^- ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl^- ion at 000 and one Na^+ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

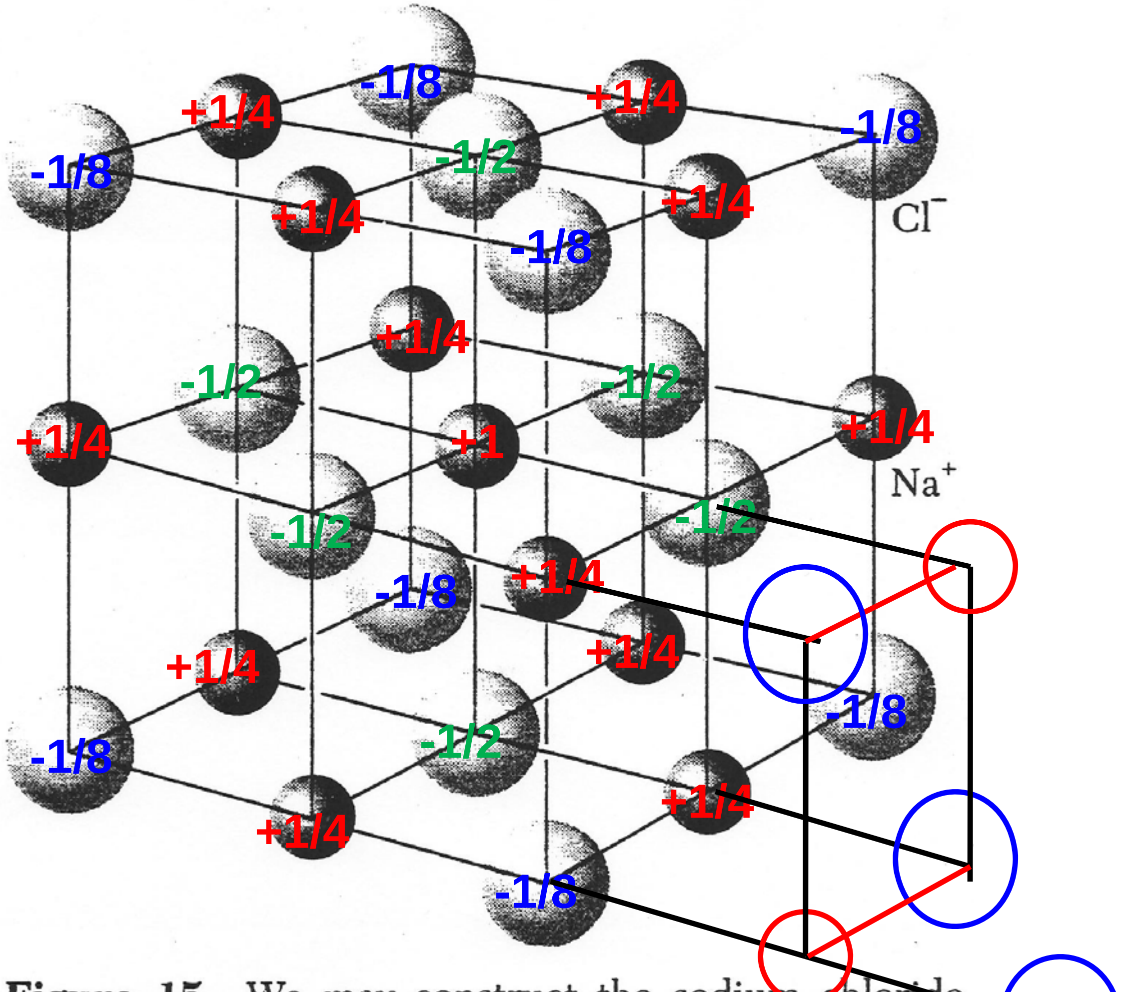


Figure 15 We may construct the sodium chloride crystal structure by arranging Na$^+$ and Cl$^-$ ions alternately at the lattice points of a simple cubic lattice. In the crystal each ion is surrounded by six nearest neighbors of the opposite charge. The space lattice is fcc, and the basis has one Cl$^-$ ion at 000 and one Na$^+$ ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The figure shows one conventional cubic cell. The ionic diameters here are reduced in relation to the cell in order to clarify the spatial arrangement.

Table 5 Ionization energies

The total energy required to remove the first two electrons is the sum of the first and second ionization potentials. (*Source:* National Bureau of Standards Circular 467.)

← Energy to remove one electron, in eV →
← Energy to remove two electrons, in eV →

H 13.595																	**He** 24.58 78.98
Li 5.39 81.01	**Be** 9.32 27.53											**B** 8.30 33.45	**C** 11.26 35.64	**N** 14.54 44.14	**O** 13.61 48.76	**F** 17.42 52.40	**Ne** 21.56 62.63
Na 5.14 52.43	**Mg** 7.64 22.67											**Al** 5.98 24.80	**Si** 8.15 24.49	**P** 10.55 30.20	**S** 10.36 34.0	**Cl** 13.01 36.81	**Ar** 15.76 43.38
K 4.34 36.15	**Ca** 6.11 17.98	**Sc** 6.56 19.45	**Ti** 6.83 20.46	**V** 6.74 21.39	**Cr** 6.76 23.25	**Mn** 7.43 23.07	**Fe** 7.90 24.08	**Co** 7.86 24.91	**Ni** 7.63 25.78	**Cu** 7.72 27.93	**Zn** 9.39 27.35	**Ga** 6.00 26.51	**Ge** 7.88 23.81	**As** 9.81 30.0	**Se** 9.75 31.2	**Br** 11.84 33.4	**Kr** 14.00 38.56
Rb 4.18 31.7	**Sr** 5.69 16.72	**Y** 6.5 18.9	**Zr** 6.95 20.98	**Nb** 6.77 21.22	**Mo** 7.18 23.25	**Tc** 7.28 22.54	**Ru** 7.36 24.12	**Rh** 7.46 25.53	**Pd** 8.33 27.75	**Ag** 7.57 29.05	**Cd** 8.99 25.89	**In** 5.78 24.64	**Sn** 7.34 21.97	**Sb** 8.64 25.1	**Te** 9.01 27.6	**I** 10.45 29.54	**Xe** 12.13 33.3
Cs 3.89 29.0	**Ba** 5.21 15.21	**La** 5.61 17.04	**Hf** 7. 22.	**Ta** 7.88 24.1	**W** 7.98 25.7	**Re** 7.87 24.5	**Os** 8.7 26.	**Ir** 9.	**Pt** 8.96 27.52	**Au** 9.22 29.7	**Hg** 10.43 29.18	**Tl** 6.11 26.53	**Pb** 7.41 22.44	**Bi** 7.29 23.97	**Po** 8.43	**At**	**Rn** 10.74
Fr	**Ra** 5.28 15.42	**Ac** 6.9 19.0															
			Ce 6.91	**Pr** 5.76	**Nd** 6.31	**Pm**	**Sm** 5.6	**Eu** 5.67	**Gd** 6.16	**Tb** 6.74	**Dy** 6.82	**Ho**	**Er**	**Tm**	**Yb** 6.2	**Lu** 5.0	
			Th	**Pa**	**U** 4.	**Np**	**Pu**	**Am**	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**	

Table 9 Atomic and ionic radii

Values approximate only. Units are 1 Å $=10^{-10}$ m. For original references see W. B. Pearson, *Crystal chemistry and physics of metals and alloys*, Wiley, 1972.

← Standard radii for ions in inert gas (filled shell) configuration →
← Radii of atoms when in tetrahedral covalent bonds →
← Radii of ions in 12-coordinated metals →

H 2.08																	He
Li 0.68 1.56	Be 0.35 1.06 1.13											B 0.23 0.88 0.98	C 0.15 0.77 0.92	N 1.71 0.70	O 1.40 0.66	F 1.36 0.64	Ne 1.58
Na 0.97 1.91	Mg 0.65 1.40 1.60											Al 0.50 1.26 1.43	Si 0.41 1.17 1.32	P 2.12 1.10	S 1.84 1.04	Cl 1.81 0.99	Ar 1.88
K 1.33 2.38	Ca 0.99 1.98	Sc 0.81 1.64	Ti 0.68 1.46	V 1.35	Cr 1.28	Mn 1.26	Fe 1.27	Co 1.25	Ni 1.25	Cu 1.35 1.28	Zn 0.74 1.31 1.39	Ga 0.62 1.26 1.41	Ge 0.53 1.22 1.37	As 2.22 1.18 1.39	Se 1.98 1.14	Br 1.95 1.11	Kr 2.00
Rb 1.48 2.55	Sr 1.13 2.15	Y 0.93 1.80	Zr 0.80 1.60	Nb 0.67 1.47	Mo 1.40	Tc 1.36	Ru 1.34	Rh 1.35	Pd 1.38	Ag 1.26 1.52 1.45	Cd 0.97 1.48 1.57	In 0.81 1.44 1.66	Sn 0.71 1.40 1.55	Sb 2.45 1.36 1.59	Te 2.21 1.32	I 2.16 1.28	Xe 2.17
Cs 1.67 2.73	Ba 1.35 2.24	La 1.15 1.88	Hf 1.58	Ta 1.47	W 1.41	Re 1.38	Os 1.35	Ir 1.36	Pt 1.39	Au 1.37 1.44	Hg 1.10 1.48 1.57	Tl 0.95 1.72	Pb 0.84 1.75	Bi 1.70	Po 1.76	At	Rn
Fr 1.75	Ra 1.37	Ac 1.11															

Ce 1.01 1.71– 1.82	Pr 1.83	Nd 1.82	Pm 1.81	Sm 1.80	Eu 2.04^{2+}– 1.80^{3+}	Gd 1.80	Tb 1.78	Dy 1.77	Ho 1.77	Er 1.76	Tm 1.75	Yb 1.94^{2+}– 1.74^{3+}	Lu
Th 0.99 1.80	Pa 0.90 1.63	U 0.83 1.56	Np 1.56	Pu 1.58– 1.64	Am 1.81	Cm	Bk	Cf	Es	Fm	Md	No	Lr