Chapter 3

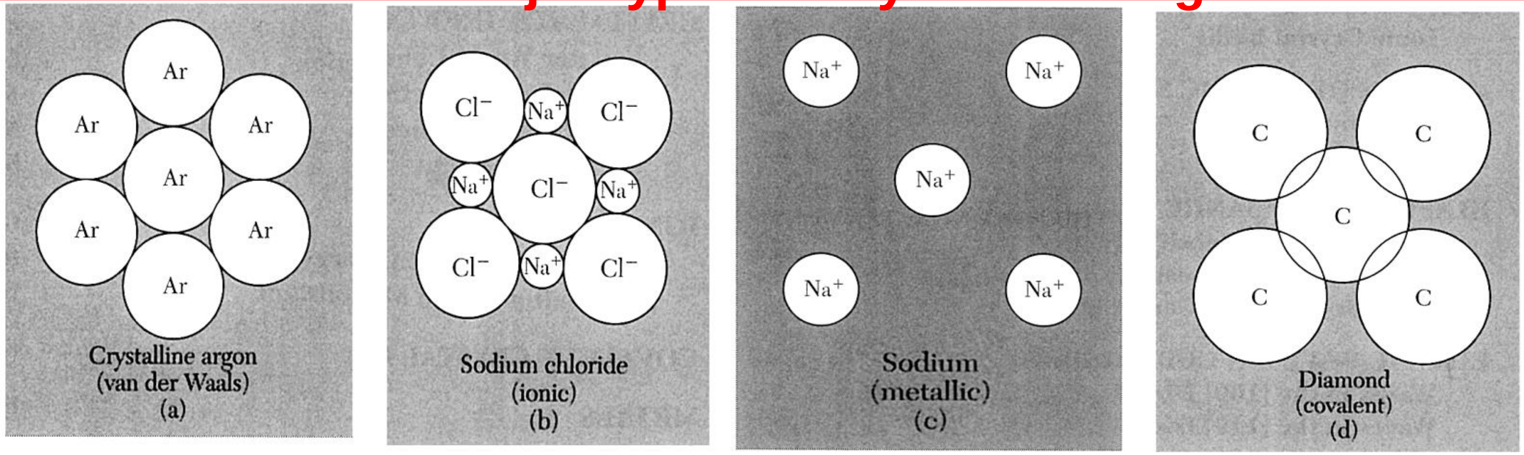
Crystal Binding and Elastic Constants

OUTLINES

1. Cohesive energy
2. Crystals of inert gases
3. Ionic crystals
4. Covalent crystals
5. Metals
6. Hydrogen bonds
7. Elastic strains
8. Elastic compliance
9. Elastic waves

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).

Four major types of crystal binding



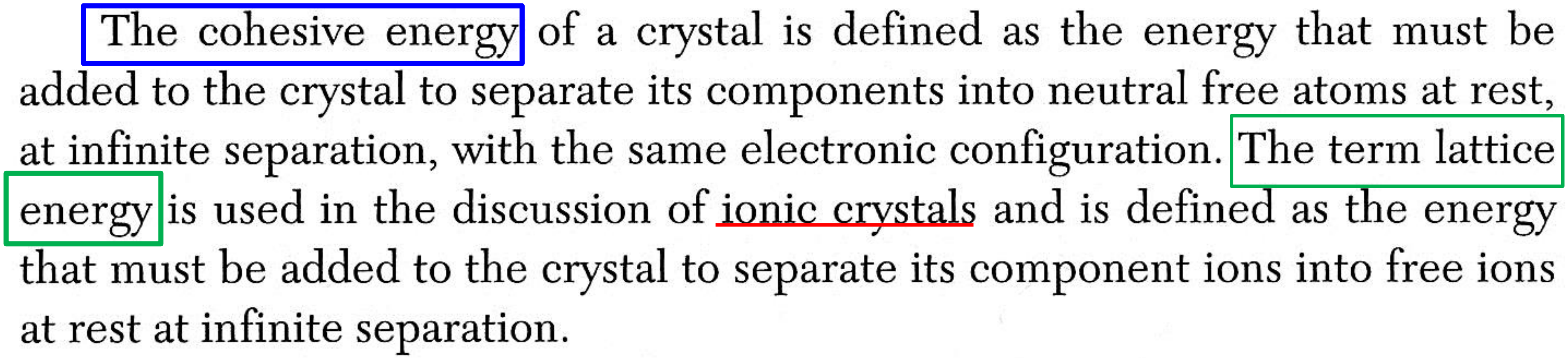
Crystalline argon (van der Waals) (a)

Sodium chloride (ionic) (b)

Sodium (metallic) (c)

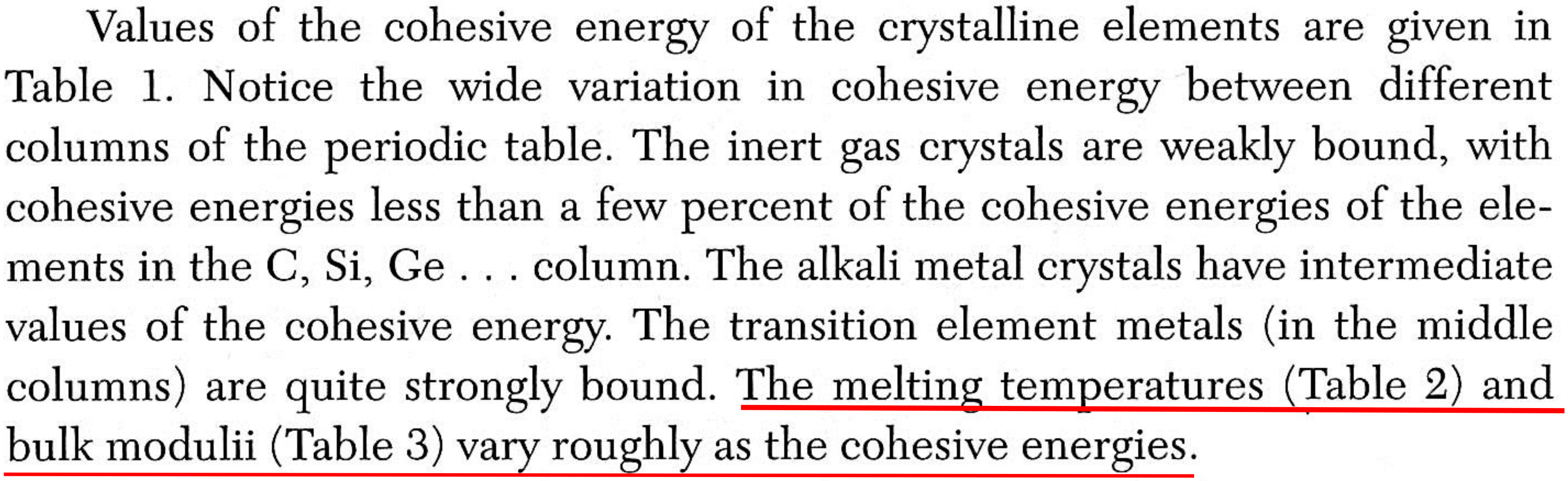
Diamond (covalent) (d)

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.



The cohesive energy of a crystal is defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration. The term lattice energy is used in the discussion of ionic crystals and is defined as the energy that must be added to the crystal to separate its component ions into free ions at rest at infinite separation.

See Tables 1, 2, and 3



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.

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.

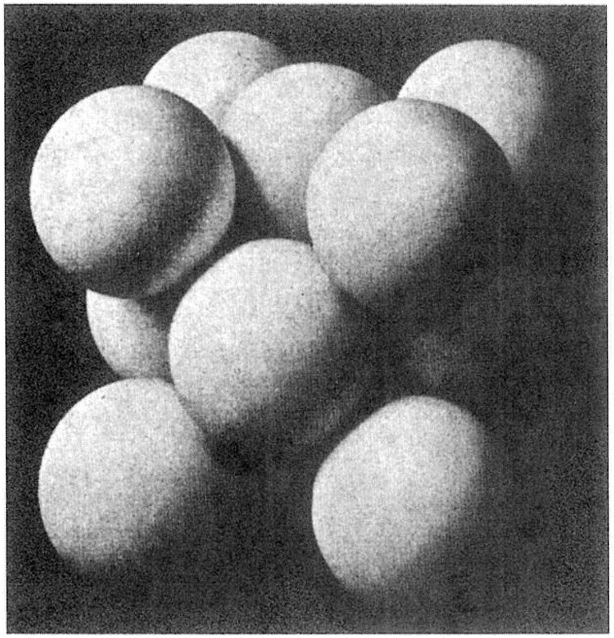


Figure 2 Cubic close-packed (fcc) crystal structure of the inert gases Ne, Ar, Kr, and Xe. The lattice parameters of the cubic cells are 4.46, 5.31, 5.64, and 6.13 Å, respectively, at 4 K.

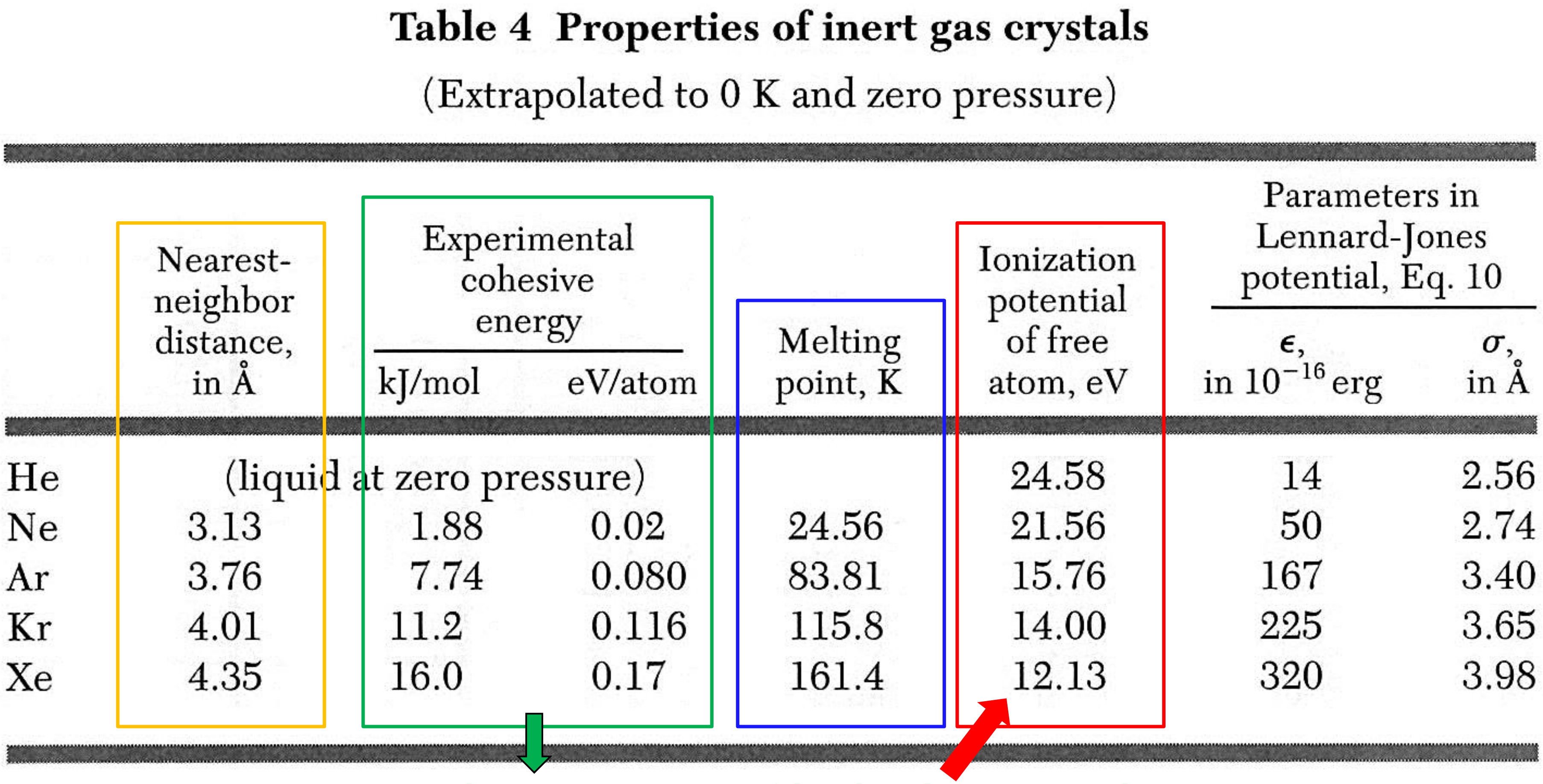


Table 4 Properties of inert gas crystals

(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

R_o

~ about only 1 % of ionization potential

σ

$R_o/\sigma \sim 1.09$

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.

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

Same m, C, and W_o

$$\mathcal{H}_0 = \frac{1}{2m} p_1^2 + \tfrac{1}{2} C x_1^2 + \frac{1}{2m} p_2^2 + \tfrac{1}{2} C x_2^2 \quad . \qquad (1)$$

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

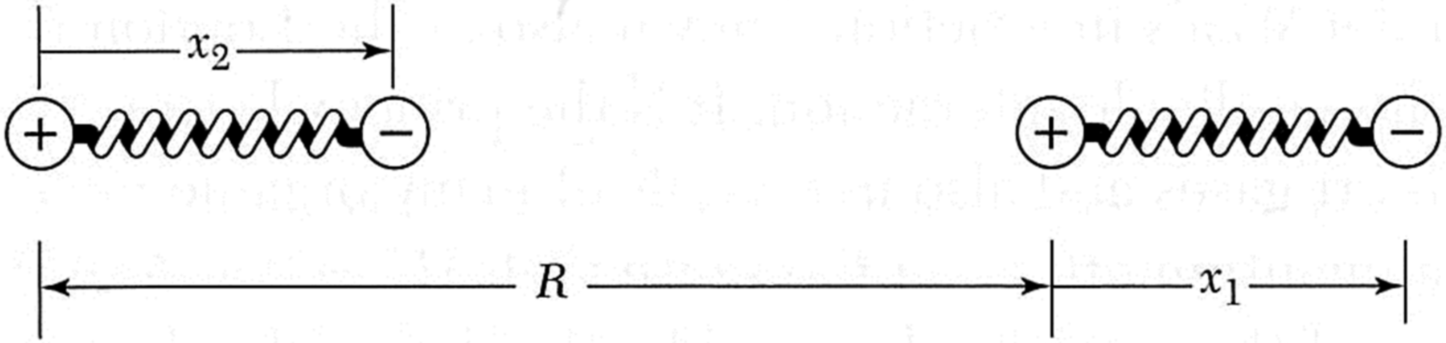


Figure 3 Coordinates of the two oscillators.

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

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

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

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

The total hamiltonian with the approximate form (3) for $\mathcal{H}_1$ 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

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

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

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

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

$E_n = (n + ½)\, h\omega_o$

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

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

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 $\Delta U \rightarrow 0$ as $\hbar \rightarrow 0$. 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.

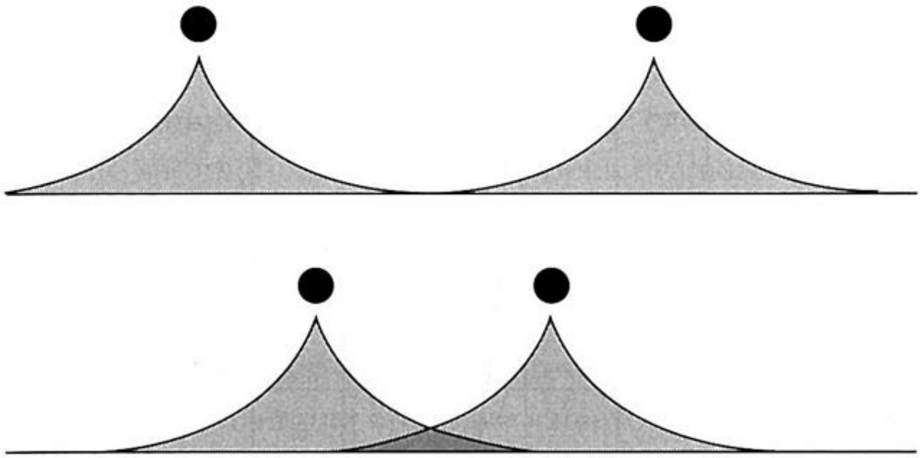


Figure 4 Electronic charge distributions overlap as atoms approach. The solid circles denote the nuclei.

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.

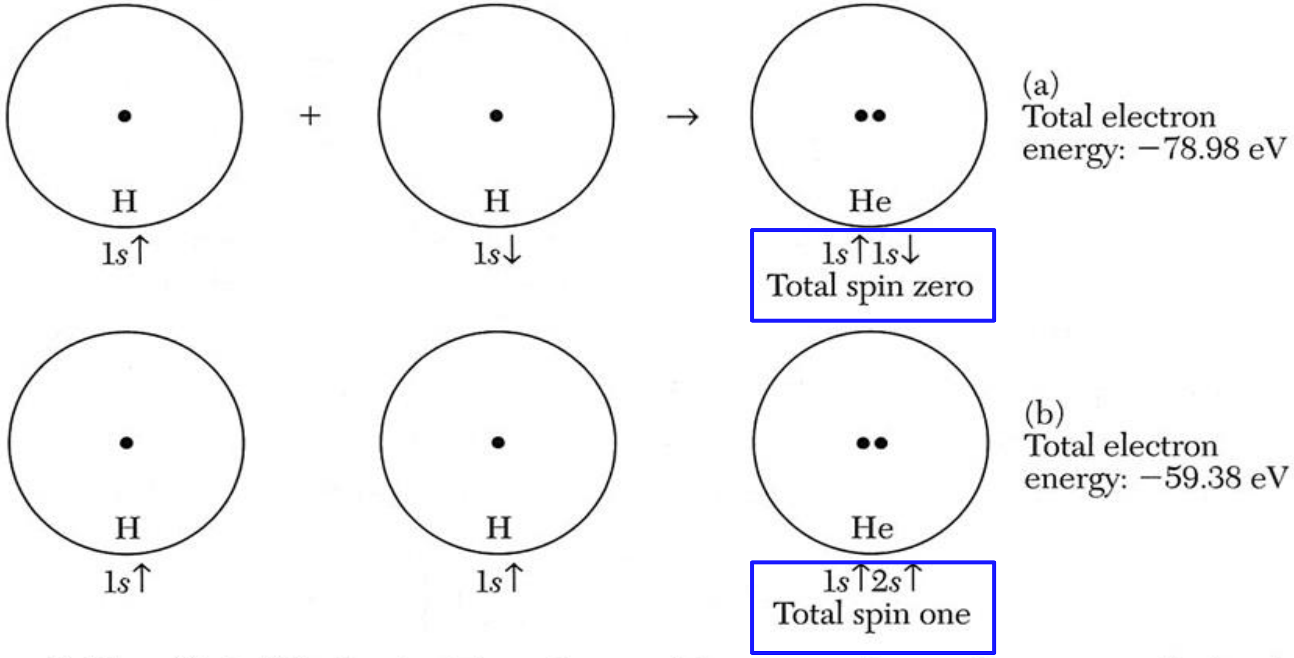


Figure 5 The effect of Pauli principle on the repulsive energy: in an extreme example, two hydrogen atoms are pushed together until the protons are almost in contact. The energy of the electron system alone can be taken from observations on atomic He, which has two electrons. In (a) the electrons have 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

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

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.

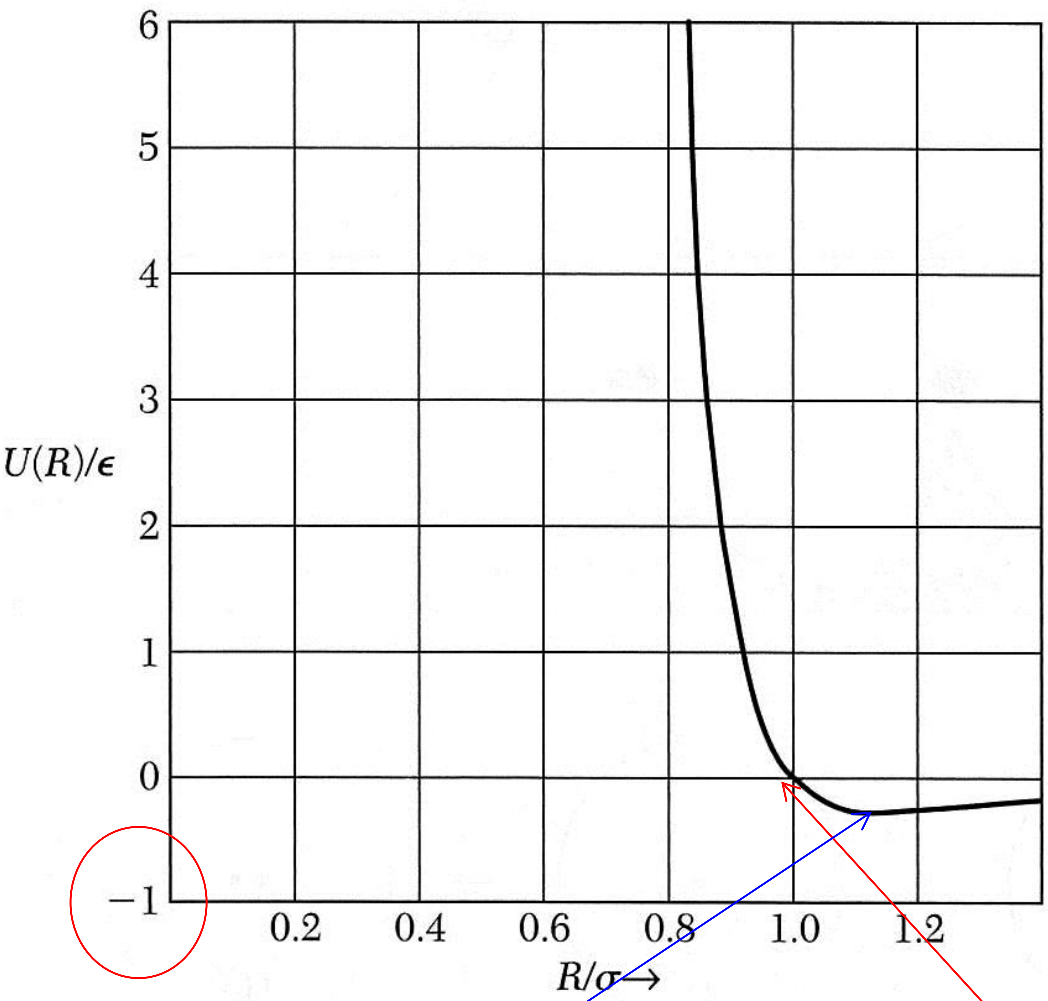


Figure 6 Form of the Lennard-Jones potential (10) which describes the interaction of two inert gas atoms. The minimum occurs at $R/\sigma = 2^{1/6} \cong 1.12$. Notice how steep the curve is inside the minimum, and how flat it is outside the minimum. The value of U at the minimum is $-\epsilon$; and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

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

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

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

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.

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:

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

whence

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

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):

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

and, at $R = R_0$,

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

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.

$$L = n\,(\lambda/2)$$

$$\lambda \propto L$$