

Crystal Binding

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Crystal Binding

Issues that are addressed in this chapter include:

- Inert gases
 - Ionic crystals
 - Covalent crystals
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1 Crystals of inert gases

☐ The cohesive energy

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 same electronic configuration.

☐ Inert gases

Inert gases form the simplest crystals for which:

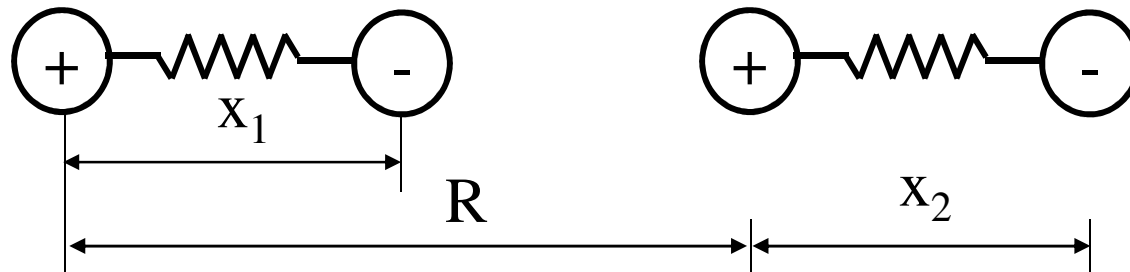
1. The electron distribution is very close to that of free atoms
 2. The outermost electron shells are completely filled and the charge distribution is spherically symmetric
 3. The electronic structure is FCC lattice
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- © The atoms of the inert gasses attract each other via the so-called Van Der Waals interaction (dipole-dipole interaction)
- © The unperturbed Hamiltonian of the system is the one of two independent oscillators and is given by:

$$H_0 = \frac{p_1^2}{2m} + \frac{1}{2}cx_1^2 + \frac{p_2^2}{2m} + \frac{1}{2}cx_2^2$$

- © The interaction energy of the oscillators is given by:

$$H_1 = \frac{1}{4\pi\epsilon} \left[\frac{e^2}{R} + \frac{e^2}{R+x_2-x_1} - \frac{e^2}{R+x_2} - \frac{e^2}{R-x_1} \right] \approx -2 \frac{e^2 x_1 x_2}{4\pi\epsilon R^3}$$



- © Now using center-of-mass and relative coordinates, the Hamiltonian H_1 can be diagonalized. The center of mass and relative coordinates are given by:

$$\begin{cases} x_s = \frac{1}{\sqrt{2}}(x_1 + x_2) \\ x_a = \frac{1}{\sqrt{2}}(x_1 - x_2) \end{cases} \rightarrow \begin{cases} x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \\ x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \end{cases}$$

- © Similar transformation is made for the momentum operators to get:

$$\begin{cases} p_s = \frac{1}{\sqrt{2}}(p_1 + p_2) \\ p_a = \frac{1}{\sqrt{2}}(p_1 - p_2) \end{cases} \rightarrow \begin{cases} p_1 = \frac{1}{\sqrt{2}}(p_s + p_a) \\ p_2 = \frac{1}{\sqrt{2}}(p_s - p_a) \end{cases}$$

- © With the above transformations, the Hamiltonian of the system becomes:

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

- © That means that the angular frequencies involved in the potential energy term are of the following form:

$$\omega_{s,a} = \sqrt{\frac{C}{m}} \sqrt{1 \mp \frac{e^2}{2\pi\epsilon C R^3}}$$

- © The zero point energy of the system is then given by:

$$E = \frac{1}{2} \hbar (\omega_s + \omega_a)$$

- © Using a well known Taylor series expansion of a square-root function, of the form:

$$f(x) = \sqrt{1 \pm x} \approx 1 \pm \frac{1}{2}x - \frac{1}{8}x^2 + \dots$$

one can arrive at the following final result for the total energy of the system:

$$E = \hbar \sqrt{\frac{C}{m}} \left[1 - \frac{1}{8} \left(\frac{e^2}{2\pi\epsilon C R^3} \right)^2 + \dots \right] = E_0 + \Delta U$$

where:

$$\Delta U = -\frac{\hbar}{8} \sqrt{\frac{C}{m}} \left(\frac{e^2}{2\pi\epsilon C R^3} \right)^2 = -\frac{A}{R^6}$$

Hence, the Van der Waals interaction varies as the minus the sixth power of the separation of the two oscillators.

- © Besides the Van der Waals interaction, when two atoms are brought together, their charge distribution begins to overlap, giving rise to the exchange interaction due to the Pauli exclusion principle.
- © Since this interaction is difficult to be evaluated from first principles, it is usually parametrized with a term that goes as $1/R^{12}$, which then when added to the Van der Waals term gives rise to the famous Lennard-Jones potential that is of the following form:

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

In here, σ and ε are parameters that are evaluated in the following manner:

1. One first re-writes the Lennard-Jones potential as a sum of all pairs of atoms in the crystal as:

$$U_{TOT}(R) = \frac{1}{2} N(4\epsilon) \left[\sum_j \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j \left(\frac{\sigma}{p_{ij}R} \right)^6 \right]$$

where $p_{ij}R$ is the distance between the reference atom i and any other atom j . For FCC structure with 12 nearest neighbors, we have:

$$\sum_j \left(\frac{1}{p_{ij}} \right)^{12} = 12.13188, \quad \sum_j \left(\frac{1}{p_{ij}} \right)^6 = 14.45392$$

2. The condition that the net force on the atom is zero then gives $R_0/s = 1.09$, and the cohesive energy is:

$$U_{TOT}(R) = -2.15(4N\epsilon)$$

2 Ionic Crystals

□ There are two major differences between inert gas solids and ionic solids:

1. In ionic solids, the Coulomb attraction force is much larger than the Van der Waals. As a result, the interatomic spacing is much smaller.
2. The binding of ions is orders of magnitude stronger in ionic solids. The electrostatic energy of the interacting ions solely dominates the properties of ionic solids.

□ There are several types of crystal structures for simple ionic solids:

1. Rocksalt and cesium chloride structures
 2. Structure of ionic crystals that are made up of equal numbers of oppositely charged ions - fluorite structure
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- © The electrostatic energy of an ionic crystal is defined relative to the energy of ions at infinite separation. Let's specify that the interaction between ions i and j is given by:

$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm \frac{q^2}{4\pi\epsilon r_{ij}}$$

Repulsive interaction

Repulsive or attractive interaction

- © The total interaction is then:

$$U_i = \sum_j U_{ij}$$

- © For better understanding, we can define:

$$U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \frac{q^2}{4\pi\epsilon R} & , \text{ for nearest-neighbors} \\ \pm \frac{1}{\rho_{ij}} \frac{q^2}{4\pi\epsilon R} & , \text{ otherwise} \end{cases}$$

© The total interaction energy is then:

$$U = NU_i = N \left[\lambda \exp(-R/\rho) - \alpha \frac{q^2}{4\pi\epsilon R} \right]$$

where α is the Madelung constant, that appears in the above expression, and is of the following form:

$$\alpha = 1 \mp \sum_j' \frac{1}{\rho_{ij}}$$

© As an example for the evaluation of the Madelung constant we consider a 1D chain of atoms separated by R , that has alternating charge density. In this case:

$$\alpha = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} + \dots \right] = 2 \ln 2$$

© The cohesive energy is then given by:

$$U_{TOT} = -N \frac{\alpha q^2}{4\pi\epsilon R_0} \left[1 - \frac{\rho}{R_0} \right], \text{ where } \exp(-R_0/\rho) = \frac{\rho}{\lambda} \frac{\alpha q^2}{4\pi\epsilon R_0^2}$$
