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BONDING AND COHESION IN SOLIDS

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1 Cohesion and Bonding

1.1 Model of Atoms in a Solid

The atoms in a solid are divided into **Ion Cores** which consists of the nuclei together with the strongly bound **Core Electrons** and the **Valence Electrons**. This latter provides the **bonding glue**.

- **Na** : $\left(1s^2, 2s2, 2p^6\right) \;+\; \left(3s^1\right)$
- **Si** : $\left(1s^2, 2s2, 2p^6\right) \;+\; \left(3s^2, 3p^2\right)$
- **A** : $\left(1s^2, 2s2, 2p^6\right) \;+\; \left(3s^1, 3p^6\right)$

1.2 The Born Oppenheimer Approximation

The full hamiltonian of the model of our system is given by :

$$
\begin{aligned}
H \;=\; \sum_n \left(P_n^2/2M\right) \;+\; \sum_i \left(p_i^2/2m\right) \;+\; \sum_{nm} V(R_n - R_m) \\
+\; \sum_{ij} \left(e^2/r_{ij}\right) \;+\; \sum_{ni} V(r_i - R_n)
\end{aligned}
$$

As in many time evolution problems, the two constituents : the ion cores and the electrons have very different time scales associates with their motion : $\tau_{ions} >> \tau_{el}$. In such cases we can always dissociate the two motions. We can assume that while the fast constituent evolves, the slower constituents are frozen in time. The motion of the slower constituent is then modified by the contribution of the fast moving part. This is the **Adiabatic Approximation** .

We assume that the full wave function can be broken up as follows :

$$
\Psi(\{R_n\},\{r_i\}) \;=\; \Phi(\{R_n\})\, \phi_{\{R_n\}}(\{r_i\})
$$

Assuming that the ions are frozen in time during the motion of the electrons :

$$\begin{aligned}\left\{\sum_i (p_i^2/2m) + \sum_{ij} (e^2/r_{ij}) + \sum_{ni} V(r_i - R_n)\right\} \phi_{\{R_n\}}(\{r_i\}) \\ = E(\{R_n\})\phi_{\{R_n\}}(\{r_i\})\end{aligned}$$

If we now neglect the derivatives of the electronic wave functions with respect to the ion coordinates, we get :

$$\left\{\sum_n \left(P_n^2/2M\right) + V_{II} + E(\{R_n\})\right\}\Phi = E\Phi$$

Thus the motion of the ions is modified from the free ionic motion by the motion of the electronic glue which surrounds it. The net potential is :

$$V(\{R_n\}) = V_{II} + E_{elec}$$

The ion-ion potential is repulsive. The electronic contribution, for some value of $\{R_n\}$ must be attractive and just balancing the Coulomb repulsion between ions. This $\{R_n^0\}$ is the equilibrium distribution of the ions in the solid.

Note Under specific circumstances the Born-Oppenheimer approximation may break down. A classic example is the case of almost localized electrons (sluggish electrons) in dirty alloys. Here the localization of the electrons in regions of the solid mean that the time scale associated with the electron being in the vicinity of a moving ion-core is of the same order as the time scale associated with the motion of the ion-core itself. Here the BO approximation breaks down. The direct consequence of this is that at very low temperatures we get a resistance minima (very like a Kondo minimum) but not of magnetic origin.

Conditions to be fulfilled for bonding in a solid

1. Ions must be kept apart to minimize effects of their mutual Coulomb repulsion.
2. For the same reason the electrons should be kept apart. This automatically leads to exchange-correlation holes in the charge cloud of valence electrons.
3. Valence electrons should come together with ions to provide the attractive interaction.
4. In doing all this, if we localize electrons in space, we must do it in such a way that the kinetic energy does not increase. This would mean an effective repulsion.

   If electrons are localized in a range Δx then by the uncertainty principle $\Delta p \geq (\hbar/\Delta x)$ which implies $\Delta E \geq (\hbar^2/2m\Delta x)$ e.g. if $\Delta x \simeq 10^{-8} cm$ then $\Delta E \geq 3eV$

The stability of the atom is then a subtle combination of all four conditions.

1.3 Van der Waals Interaction

The charge distribution in a inert gas atom is not rigidly spherical. During its evolution instantaneously the gas may have regions of greater density. This would mean that the atom has an instantaneous dipole associated with it. This dipole produces an electric field : $\mathbf{E} = (2\mathrm{p}_1/\mathrm{R}^3)\,\hat{\mathrm{e}}$. If another atom sits in this field and if α is the electronic polarizability of its electron cloud, then this field induces a dipole in it $\mathbf{p}_2 = (2\alpha\mathrm{p}_1/\mathrm{R}^3)\hat{\mathrm{e}}$. The consequent potential is always attractive :

$$V(R) = \frac{4\alpha p_1^2}{R^6}$$

If we take two charged oscillators :

$$H_0 = (p_1^2/2m) + (p_2^2/2m) + (\beta x_1^2/2) + (\beta x_2^2/2)$$

$$H_1 = \frac{e^2}{R} + \frac{e^2}{R + x_1 - x_2} - \frac{e^2}{R + x_1} - \frac{e^2}{R - x_2}$$

If the distances x_1 and x_2 are much smaller than R then,

$$H_1 \simeq -\frac{2e^2 x_1 x_2}{R^3}$$

We can diagonalize the hamiltonian by changing to symmetric and antisymmetric combinations of the variables :

$$\omega_{s/a} = \omega_0 \left[1 \pm (e^2/\beta R^3) - \left(e^4/(2\beta^2 R^6)\right)\right]$$

$$E = (\hbar/2)(\omega_s + \omega_a) = -\frac{\hbar\omega_0}{8}\left(\frac{2e^2}{\beta R^3}\right)^2$$

Note that this is a quantum effect, in the sense that as $\hbar \to 0$, E→ 0.

This is an attractive effective interaction

As we bring the ion cores together with their own charge clouds following them, because of the conditions 1,2 and 4 mentioned before, the repulsion increases. Eventually it overtakes the attractive force. This **very short ranged** repulsion coming from various sources is usually modeled by a R^{-12} type energy. The model energy is then :

$$V(R) = 4A\left[\left(\frac{R_0}{R}\right)^{12} - \left(\frac{R_0}{R}\right)^{6}\right]$$

If the lattice points are given in terms of the nearest neighbour distance R by $R_{nm} = Rp_{nm}$, then

$$V_{tot} = 2AN\left[\left(\sum_{nm}\frac{1}{p_{nm}^6}\right)\left(\frac{R_o}{R}\right)^6 - \left(\sum_{nm}\frac{1}{p_{nm}^{12}}\right)\left(\frac{R_0}{R}\right)^{12}\right]$$

This energy can now be minimised with respect to R to obtain the equilibrium lattice distance and the cohesive energy : which is the energy at this minimum.

1.4 Bonding by the Electron Glue

The **Ionic, Covalent and Metallic Bondings** come under this common title. The main ingredient of this bonding is the valence electron charge cloud. How that charge cloud is distributed provides the different kind of bonding. In ionic bonding the charge clouds are dense near one type of atom and rare near others. This produces local charge excesses over and above the neutral background and the Coulomb attraction of these pseudo-charges binds the solid together. In covalent bonding the charge cloud is concentrated near the centre between two atoms, providing them with an indirect attraction to each other through it. In metallic bonding the charge cloud is reasonably distributed evenly and binds the atoms together in this uniform glue.

Example : Let us take a diatomic solid and build up the wavefunction of the valence elecrions as a linear combination of the atomic orbitals. The electron-

electron interaction may either be explicitly considered or an effective one-electron potential formed from, say, the LDA.

$$\Psi \;=\; \sum c_k \phi_k$$

If we consider the minimization of the functional

$$F(\{c_k\}) \;=\; E\langle\Psi|\Psi\rangle \;-\; \langle\Psi|H|\Psi\rangle$$

with respect to the variables $\{c_k\}$ we get :

$$\sum_m \left[E\langle\phi_k|\phi_m\rangle \;-\; \phi_k|H|\phi_m\rangle\right] c_m \;=\; 0$$

The above equations have a solution provided :

$$\det\left[ES_{km} \;-\; H_{km}\right] \;=\; 0$$

This is the **Secular Equation** and its solutions will give is both the spectrum as well as the charge density of the valence cloud.

1. if $c_1 = c_2$ the charge distribution is symmetric and builds up at the centre between the two atoms and we have a covalent bonding.
2. if $c_1 \neq c_2$ the charge distribution is asymmetric. There is more charge towards one of the atoms. This is **Charge Transfer** *Note that the concept of charge transfer in a solid is a difficult one, as it is not possible to assign charges to ions uniquely.* Such asymmetry leads to **ionicity** and ionic bonding.

In ionic solids the electronic contribution to the energy is dominated by the

Madelung Energy arising out of the Coulomb energy of attraction between these domains of excess negative and positive charges.

REQUIRED TO CALCULATE

We would preferably like to carry out first principles calculations (based, for example, on the local density functional approach) of the following quantity :

$$V(R) \;=\; V_{II} \;+\; V_{el}(R)$$

The second part is the electronic contribution which consists of several parts :

The single energy band part $V_B \;=\; \sum_{i \epsilon occ} E_i$

Hartree Part $V_H(\rho(r))$ which is obtained from a Poisson equation from the charge density produced in the band structure calculation : $\rho(r) \;=\; \sum_{i \epsilon occ} |\Psi_i|^2$ and $\nabla^2 V_H \;=\; -\rho(r)$

An Exchange-Correlation part, using a suitable LDA form.

A Madelung part coming from ionic charge distributions.

This energy is calculated as a function of lattice separation R. The repulsive part the should come automatically.