2. Solid as a quantum system

In general, a solid consists of ions, i.e. nuclei and the tightly bound electrons of the inner shells, and valence electrons.

Note: The separation of core and valence electrons is not unique and depends on the material, context, etc.

The Hamilton operator of this many-particle system encompasses the following contributions

$$\mathcal{H} = \mathcal{H}_{ee} + \mathcal{H}_{ion} + \mathcal{H}_{ee-ion}$$

with

$$\mathcal{H}_{ee} = \sum_i \frac{p_i^2}{2m} + \sum_{i<j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \text{spin-orbit correction} \qquad \text{electron mass } m$$

$$\mathcal{H}_{ion} = \sum_n \frac{P_n^2}{2M_n} + \sum_{n<m} V_{ion}(\vec{R}_n - \vec{R}_m) \qquad \text{ion mass } M_n$$

$$V_{ion}(\vec{r}) = \frac{Z^2e^2}{|\vec{r}|} + \text{correction from core electrons}$$

$$\mathcal{H}_{el-ion} = -\sum_{i,n} \frac{Ze^2}{|\vec{r}_i - \vec{R}_n|} \qquad Ze \mathrel{\hat{=}} \text{charge of an ion}$$

where we have not explicitly included any relativistic effects such as spin-orbit coupling (which, however, turn out to be essential for the descriptions of some solids such as topological insulators → later)

This Hamiltonian is quite well-known and establishes the fundamental microscopic description of a solid. However, it is by far too complicated to be solved exactly. Numerically, even on a supercomputer only a few particles can be treated but not 10^{23}!

We thus need approximations, for which an understanding of the fundamental degrees of freedom is essential!

But how can we identify the relevant degrees of freedom ?

Consider the Hamiltonian in atomic units : (CGS units $4\pi\varepsilon_0 \to 1$)

- measure length in units of Bohr radius $a_0 = \frac{\hbar^2}{me^2} \approx 0.5\ \text{Å}$
- and energies in units of 2× Rydberg (energies) $2R_y = \frac{me^4}{\hbar^2} = \frac{e^2}{a} = 2 \cdot 13{,}6\,\text{eV}$

to obtain (using $\vec{p} \to -i\hbar\vec{\nabla}$)

$$\mathcal{H} = \underbrace{\sum_i -\frac{\nabla_i^2}{2} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}}_{\mathcal{H}_{ee}} + \underbrace{\sum_n \frac{m}{M_n} \cdot \left(-\frac{\nabla_n^2}{2}\right) + \sum_{n<m} \frac{Z_n Z_m}{|\vec{R}_n - \vec{R}_m|}}_{\mathcal{H}_{ion}} + \underbrace{\sum_{i,n} -\frac{Z_n}{|\vec{r}_i - \vec{R}_n|}}_{\mathcal{H}_{el\text{-}ion}}$$

Apart from the atomic numbers Z_n the Hamiltonian involves only a single parameter, i.e. the mass ratio between the masses of electrons and ions

$$\boxed{\frac{m}{M_n} \cong 10^{-3} \sim 10^{-5}}$$

Strategy: Develop a systematic expansion in this small parameter $\frac{m}{M_n}$ by treating the kinetic part of the ions, T_{ion}, as a perturbation

$$\mathcal{H} = \mathcal{H}_0 + T_{ion} \quad \text{with} \quad T_{ion} = \sum_n \frac{m}{M_n} \cdot \left(-\frac{\nabla_n^2}{2}\right)$$

2.1 Adiabatic approximation (Born - Oppenheimer)

Definition : adiabatic / diabatic

etymology : greek, unable / able to be crossed

usage in thermodynamics:

adiabatic process $\hat{=}$ transfer of work without transfer of heat (at constant entropy)

usage in quantum mechanics:

adiabatic process $\hat{=}$ gradually, slowly changing conditions allow the system to adapt as a function of time. If the system starts in an eigenstate of the initial Hamiltonian, it will end in the corresponding eigenstate of the final Hamiltonian. (cf. also "adiabatic theorem" of quantum mechanics and Landau - Zener problem)

Here : electrons possess a smaller mass and are thus much faster than the ions; the electrons practically follow instantaneously the movement of ions

→ dynamics of electrons and ions decouple

→ adiabatic approximation systematic in the small parameter m/M_n

Step I: zeroth order in $\frac{m}{M_n}$ (electronic Schrödinger equation)

Consider electronic subsystem in the presence of a fixed ion configuration $\{\vec{R}_1, \vec{R}_2, \dots, \vec{R}_M\}$.

Described by the electronic many-particle wavefunction

$\psi = \psi(\{r_1, r_2, \dots, r_N\}; \{R_1, R_2, \dots, R_M\})$

which is the solution to the eigenvalue problem for the adiabatic motion of electrons

$$\boxed{\mathcal{H}_0 \psi_{\underline{\underline{\alpha}}} = \mathcal{E}_\alpha(R_1, \dots, R_M)\, \psi_{\underline{\underline{\alpha}}}} \quad (\mathrm{I})$$

electronic quantum numbers

where $\mathcal{H}_0 = \mathcal{H}_{el} + \mathcal{H}_{el-ion} + V_{ion}$

The exact solution of (I) is in general not possible
→ further approximations are necessary (later)

With the help of the (approximate) ground-state energy $\mathcal{E}_0(\{R_n\})$ one obtains the crystal structure $\{R_n^0\}$ by minimizing with respect to the ion configuration

$$E_0 = \min_{\{R_n\}} \mathcal{E}_0(\{R_n\}) = \mathcal{E}_0(\{R_n^0\})$$

Step II: adiabatic correction

represent the full wavefunction in the eigenbasis of (I)

$$\underbrace{\Phi(\{r_i\},\{R_n\})}_{\text{full electron-ion wavefunction}} = \sum_\alpha \underbrace{\varphi_\alpha(\{R_n\})}_{\text{expansion coefficient}} \underbrace{\psi_\alpha(\{r_i\},\{R_n\})}_{\text{electronic many-particle wavefct for } \underline{\text{fixed}} \text{ ions } \{R_n\}}$$

orthogonal basis:

$$\int d^3\vec{r}\ \psi_\beta^*(\dots)\,\psi_\alpha(\dots) = \delta_{\alpha\beta}$$

The full stationary Schrödinger equation then reads

$$E\phi = \mathcal{H}\phi = (\mathcal{H}_0 + T)\phi = \sum_\alpha \big(\varepsilon_\alpha(\{R_n\}) + T\big)\,\varphi_\alpha(\{R_n\})\,\psi_\alpha(\{r\},\{R\})$$

idea: Derive an effective Hamiltonian for "expansion parameters" φ_α by using orthogonality of ψ_α. To this end, apply a projection by multiplying $\int d^3\vec{r}\ \psi_\beta^+(\{\vec{r}\},\{R\}) \times$ (from left)

This gives

$$E\,\varphi_\beta(\{R\}) = \varepsilon_\beta(\{R\})\,\varphi_\beta(\{R\}) + \sum_\alpha \int d^3\vec{r}\ \psi_\beta^+(\{r\},\{R\})\,T\,\varphi_\alpha(\{R\})\,\psi_\alpha(\{r\},\{R\})$$

with
$$T\,\varphi_\alpha \psi_\alpha = \sum_n \frac{m}{2M_n}\left(-\nabla_n^2\right)\varphi_\alpha\psi_\alpha$$
$$= -\sum_n \frac{m}{2M_n}\left[(\nabla_n^2\varphi_\alpha)\psi_\alpha + \varphi_\alpha(\nabla_n^2\psi_\alpha) + 2(\nabla_n\varphi_\alpha)(\nabla_n\psi_\alpha)\right]$$

The Schrödinger equation thereby becomes
$$E\,\varphi_\beta(\{R\}) = \left(\varepsilon_\beta(\{R\}) + T\right)\varphi_\beta(\{R\}) + \sum_\alpha \hat{C}_{\beta\alpha}(\{R\})\,\varphi_\alpha(\{R\})$$

with the operator
$$\hat{C}_{\beta\alpha}(\{R\}) = -\int d^3\vec{r}\,\sum_n \frac{m}{2M_n}\left[\psi_\beta^+\nabla_n^2\psi_\alpha + 2(\psi_\beta^+\vec{\nabla}_n\psi_\alpha)\vec{\nabla}_n\right]$$

The off-diagonal parts of this operator, in particular, induce translations i.e. diabatic processes between electronic states. To lowest order this operator can be neglected.

In total one arrives at an effective eigenvalue problem for the ions only
$$\boxed{E\,\varphi_\beta(\{R\}) = \left(T + \varepsilon_\beta(\{R\})\right)\varphi_\beta(\{R\})} \qquad (\mathrm{II})$$

In particular, for the electronic ground state this reads
$$E\,\varphi_0\{R\} = \left(T + \varepsilon_0(\{R\})\right)\varphi_0(\{R\})$$

The potential $\varepsilon_0(\{R\})$ is thus minimized by the particular crystal structure of the material.

Summary Born-Oppenheimer approximation (adiabatic approximation)

1. Solve electronic Schrödinger eq. (I) for fixed positions of the ions $\{\vec{R}\}$
   → this gives the eigenenergies $\varepsilon_\alpha(\{R\})$
2. Solve the ionic Schrödinger eq. (II) with the effective potential given by $\varepsilon_\alpha(\{R\})$ for all α
   → this gives the crystal structure of the material

In order to estimate the correction to the ground-state energy attributed to the kinetic term T, let us consider a small derivation from the equilibrium configuration

$$\delta R_n = R_n - R_n^{(0)}$$

and Taylor-expand the potential in δR

2nd derivatives $\frac{\partial}{\partial R_n}\frac{\partial}{\partial R_m}\mathcal{E}_0(\{R\})$

$$\mathcal{E}_0(\{R\}) = \mathcal{E}_0(\{R^{(0)}\}) + \frac{1}{2}\,\delta R_n\, D_{nm}\,\delta R_m$$

no first-order term since we are at a minimum of potential!

One arrives at

$$E\,\varphi_0 = \left(\mathcal{E}_0(\{R^{(0)}\}) + \mathcal{H}_{\text{eff}}\right)\varphi_0$$

with the effective Hamiltonian (with $\vec{P}_n = -i\vec{\nabla}_n$)

$$\mathcal{H}_{\text{eff}} = \sum_n \frac{1}{2}\frac{m}{M_n}\vec{P}_n^{\,2} + \sum_{n,m}\frac{1}{2}\,\delta R_n\, D_{nm}\,\delta R_m$$

corresponding to a higher-dimensional <u>harmonic oscillator</u>.

The kinetic and the potential term in $\mathcal{H}_{\text{eff}}$ are of equal importance, which becomes manifest by rescaling

$$\delta R_n = \left(\frac{m}{M_n}\right)^{1/4} u_n$$

$$P_n = \left(\frac{m}{M_n}\right)^{-1/4} p_n$$

so that we get for a monatomic crystal ($M_n = M$)

$$\mathcal{H}_{\text{eff}} = \left(\frac{m}{M}\right)^{1/2}\left[\sum_n \frac{1}{2}\vec{p}_n^{\,2} + \sum_{n,m}\frac{1}{2}\,u_n\, D_{nm}\, u_m\right]$$

The <u>zero-point motion</u> leads to an adiabatic correction to the ground-state energy of the order

$$\boxed{\delta E = E - \mathcal{E}_0(\{R^{(0)}\}) = \mathcal{O}\left(\sqrt{\frac{m}{M}}\right)}$$

The next-to leading order correction derives from the $\hat{C}_{\beta\alpha}$ operator

$$\hat{C}_{\beta\alpha} \cong \int d^3\vec{r} \sum_n \frac{m}{2M_n} 2 \left(\psi_\beta^+ \vec{\nabla}_n \psi_\alpha \right) \vec{P}_n$$

$$= \int d^3\vec{r} \sum_n \left(\frac{m}{M_n} \right)^{3/4} \left(\psi_\beta^+ \vec{\nabla}_n \psi_\alpha \right) \vec{P}_n$$

so that $$\frac{C_{\beta\alpha}}{\delta E} \sim \mathcal{O}\left(\left(\frac{m}{M_n} \right)^{1/4} \right)$$

$\Rightarrow$ the adiabatic approximation is controlled in the parameter

$$\varkappa = \left(\frac{m}{M} \right)^{1/4}$$

with $\left(\frac{m}{M}\right) \sim 10^{-5} - 10^{-3}$ follows $\varkappa \sim 10^{-2} - 10^{-1}$.

If $\varkappa$ is too large, the crystal structure will melt due to zero-point fluctuations $\longrightarrow$ superfluid ^{3}He and ^{4}He.

2.2 Cohesive energy of crystals

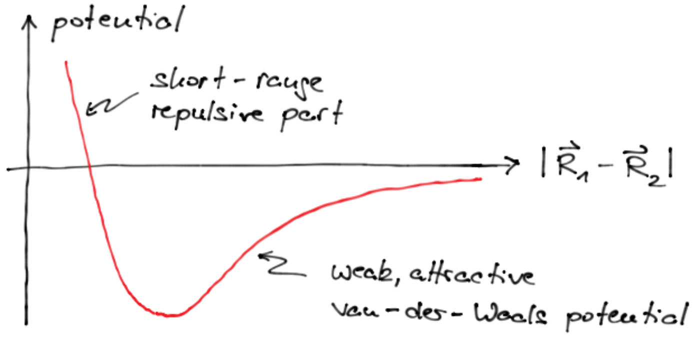
The crystal structure is obtained by minimizing the electronic ground state energy $\mathcal{E}_0(\{\vec{R}\})$ with respect to the ion configuration $\{\vec{R}\}$. The energy of the equilibrium configuration $\{\vec{R}^{(0)}\}$, i.e. $\mathcal{E}_0(\{\vec{R}^{(0)}\})$, carries information about the cohesive energy or binding energy of the crystal, i.e. the amount of energy required to disassemble it into its constituents.

The function $\mathcal{E}_0(\{\vec{R}\})$ is in general unknown. However, there are certain limits where the origin of the cohesive energy can be identified.

Phenomenological classification of bonding in crystals

- van-der-Waals bonding

Molecular crystals consisting of the noble gases with fully-filled electronic shells (no valence electrons) like Ne, Ar, Kr, ...
The atoms interact pair-wise via the weak, attractive van-der-Waals interaction arising from fluctuating dipole moments



$$\sim -\frac{1}{|\vec{R}_1 - \vec{R}_2|^6}$$

often modeled by Lennard-Jones potential

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

- ionic binding

Ionic crystals consisting of oppositely charged ions.
Ions attract each other pair-wise by means of the strong Coulomb interaction. Crystal structures with a large coordination number z preferred.
Examples: NaCl, CsCl, ZnS

- covalent bonding

Covalent crystals are characterized by a distribution of valence electrons that substantially differs from the one found in the isolated atoms/ions.
Similar to the chemical bonding in molecules like H_2 (Heitler-London th.)
The bonding is spacially oriented. For example, in the crystal structure of C, Si, Ge along the links of the diamond lattice.

- metallic bonding

Mediated by valence electrons, which become delocalized from the ion cores (→ conduction electrons). No spatial orientation (in contrast to covalent case).