

Quantum theory

of

Condensed Matter 1

Introduction to the course

Condensed matter theory aims at the comprehension of the physical properties of solids and liquids in and out of equilibrium.

In this course we will concentrate on solids and, in particular on crystalline solids, with long range order in the atomic position.

A solid is composed of atoms held together by the chemical bond.

A microscopic description of a solid is obtained with quantum mechanics but the elevated number of atoms composing the solid implies that technique of statistical physics must be adopted.

GOOD NEWS In principle, the Hamilton operator describing the solid is known. Of the 4 fundamental interactions (strong interaction, weak interaction, Coulomb interaction, gravitation) only Coulomb interaction plays a role, as for atomic and molecular physics. Moreover, typically also relativistic effects can be neglected (exception: solids with strong spin-orbit coupling).

BAD NEWS Due to the large number of involved particles AND of the interaction an exact evaluation of the statistical properties of solids is out of reach.

=> New methods, concepts and suitable approximations have to be developed

We shall deal primarily with crystalline solids. However many of the concepts to be developed can be applied also to:

- quasi-crystals, amorphous solids, liquids

- low dimensional materials:

2 dimensions: . 2DEG in semiconductor heterostructures
. graphene sheets

1 dimension: . semiconductor or metallic quantum wires
. "long" carbon nanotubes

0 dimensions: . quantum dots, molecules, fullerenes

One major effort of contemporary condensed matter physics is to understand equilibrium and non-equilibrium properties of meso and nanostructures ($1\text{nm} < L < 1\mu\text{m}$) composed of different materials for novel applications

- nano electronics, (molecular/organic electronics, topological electronics, spintronics)

- quantum information processing (quantum computing, magnetic memories)

Aim of the course is the understanding of

- 1) The electronic properties of solids (band structure, el-el interaction)
- 2) The role of the ionic motion (el-ph coupling, thermal transport)
- 3) The linear response to external perturbations (conductivity, magnetic susceptibility)
- 4) Special states of matter (magnetism, superconductivity)

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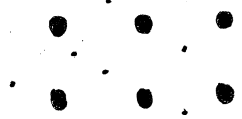
Literature : Czycholl, "Theoretische Festkörperphysik", Springer
Brum and Flensberg, "Many-Body Quantum Theory in Cond. Mat. Phys.", Oxford
Ashcroft and Mermin, "Solid State Physics", Sander College

CHAPTER 1: INTRODUCTION TO THE PHYSICS OF SOLIDS

1.1 Microscopic description

We consider crystalline solids with a long range order. Microscopically we identify a type of constituents:

ions = nuclei + closed electron shells
valence electrons

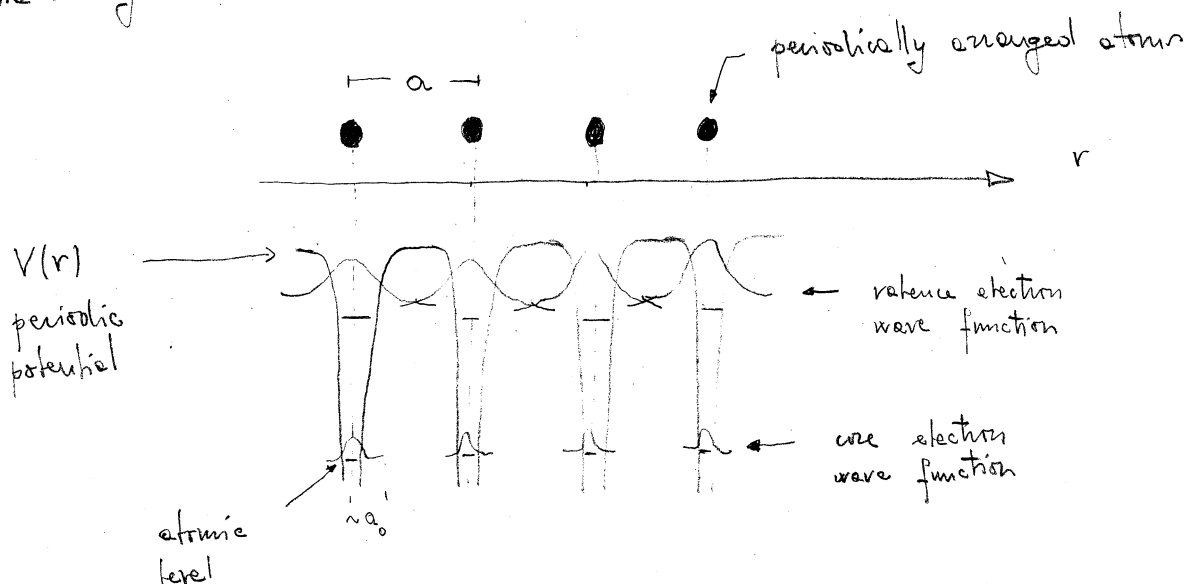


A more rigorous approach would start from nuclei and electrons i.e. all stable constituents of matter related by the electromagnetic interaction. Spatial extension of the electron wave functions in the different shells of the isolated atom shows that this is NOT necessary. To obtain an estimate we can use the formula for hydrogen (like) atoms:

$$E(n; Z) = -\frac{Z^2}{n^2} |E(1,1)| \quad \text{and} \quad E(1,1) = -\frac{\hbar^2}{2m\alpha_0^2} = 13.6 \text{ eV} = 1 \text{ Ry}$$

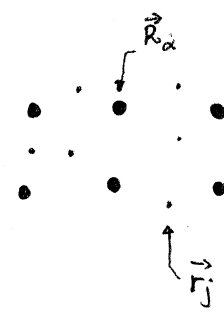
The wave functions of electrons in inner shells (core electrons) with binding energies of several tens of eV extend over a distance $\ll a_0$ ($a_0 \sim 0.5 \text{ \AA}$) much smaller than the lattice spacing of a solid (Au (fcc) $a = 4.08 \text{ \AA}$, Ag (fcc) $a = 4.09 \text{ \AA}$, Fe (bcc) $a = 2.87 \text{ \AA}$)

Schematically



1.2 Hamiltonian of a solid

The Hamiltonian of a solid is known. It contains the electrostatic interaction between the charged components of matter. With the further simplification introduced in 1.1:

$$\begin{aligned}
 \hat{H} &= \hat{T}_{el} + \hat{T}_{ion} + \hat{V}_{ee} + \hat{V}_{ei} + V_{ii} \\
 &= - \sum_{j=1}^N \frac{\hbar^2}{2m} \nabla_j^2 - \sum_{\alpha=1}^M \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + \sum_{j < k}^N \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_j - \vec{r}_k|} \\
 &\quad - \sum_{j, \alpha} \frac{z_{\alpha} e^2}{4\pi\epsilon_0} \frac{1}{|\vec{r}_j - \vec{R}_{\alpha}|} + \sum_{\alpha < \beta}^M \frac{z_{\alpha} z_{\beta} e^2}{4\pi\epsilon_0} \frac{1}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} \quad (1.1)
 \end{aligned}$$


• z_{α} is the charge of the ion: $z = N_{ce}$ when N_{ce} = number of core electrons

\Rightarrow for a neutral system $N = \sum_{\alpha} z_{\alpha}$

• \hat{H} can represent all kinds of materials, from steel to plastic, glass, diamond

If we would be able to solve the Schrödinger equation (SE)

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

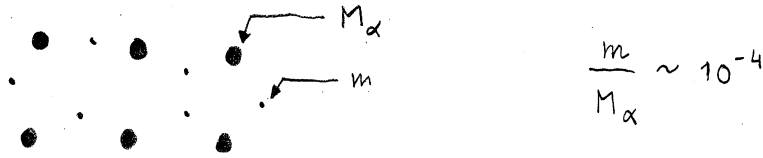
we could predict all properties of a given material (solid, molecule, glass..)

• It is hopeless to solve the Schrödinger equation for the N-body system. The dimension of the many-body space grows exponentially with the particle number!

• New concepts and new mathematical tools need to be developed.

1.3 Structural reducibility (Following G. Czycholl "Theoretische Festkörperphysik", Springer, Ch. 2)

Not all components of \hat{H} need to be treated simultaneously. In particular one can decouple the motion of electrons and ions.



This decoupling (Born-Oppenheimer approx., 1927) is based on the observation that, due to their large masses M_α , the ions move much slower than the electrons of mass m . \Rightarrow electrons adapt instantaneously to the actual ion configuration.

Classical proof:

Assume thermal equilibrium of the whole system \Rightarrow electrons and ions have the same average thermal energy per degree of freedom:

$$\left\langle \frac{m v_i^2}{2} \right\rangle = \left\langle \frac{M_\alpha v_\alpha^2}{2} \right\rangle = \frac{3}{2} k_B T \quad (1.2)$$

mass ratio $m/M_\alpha \sim 10^{-4} \Rightarrow v_i/v_\alpha \sim 10^2$

Quantum mech. proof:

1) The total wave function $\Psi = \Psi(\{\vec{r}_j\}, \{\vec{R}_\alpha\})$. Motivated by the previous observation we consider $\{\vec{R}_\alpha\}$ as parameters and write:

$$\underbrace{\left(\hat{T}_{el} + \hat{V}_{ee} + \hat{V}_{ei} + \hat{V}_{ii} \right)}_{\hat{H}_{el}} \Phi_k = \sum_{\alpha} \hat{R}_\alpha \Phi_k(\{\vec{r}_j\}; \{\vec{R}_\alpha\}) \quad (1.3)$$

\forall ionic configuration $\{\vec{R}_\alpha\}$ we find the solution of the SE $\hat{H}_{el} \phi = \epsilon \phi$.

ii) For a given configuration $\{\vec{R}_\alpha\}$, the Φ_k form a complete set and can thus be used to expand the total wave function:

$$\Psi(\{\vec{r}_j\}; \{\vec{R}_\alpha\}) = \sum_k \Phi_k(\{\vec{r}_j\}; \{\vec{R}_\alpha\}) \chi_k(\{\vec{R}_\alpha\}) \quad (1.4)$$

$$\Rightarrow \hat{H}\Psi = \sum_k (\hat{H}_{el} + \hat{T}_{ion}) \Phi_k(\{\vec{r}_j\}; \{\vec{R}_\alpha\}) \chi_k(\{\vec{R}_\alpha\}) = E \sum_k \Phi_k \chi_k \quad (1.5)$$

$$\begin{aligned} \Sigma_k(\{\vec{R}_\alpha\}) \downarrow &= \sum_{\alpha=1}^M \sum_{l=x,y,z} \frac{\hat{P}_{\alpha l}^2}{2M_\alpha} & \hat{P}_{\alpha l} &= -i\hbar \frac{\partial}{\partial R_{\alpha l}} \end{aligned}$$

iii) Use the orthogonality of $\{\Phi_k\}$ to eliminate the electronic coordinates by multiplying with Φ_s^* and integrating over $\{\vec{r}_j\}$:

$$\sum_k \int d\{\vec{r}_j\} \Phi_s^* \Phi_k (\Sigma_k + \hat{T}_{ion}) \chi_k + \sum_k \sum_{\alpha=1}^M \int d\{\vec{r}_j\} \Phi_s^* \left[\left(\sum_l \frac{\hat{P}_{\alpha l}^2}{2M_\alpha} \Phi_k \right) \chi_k + 2 \sum_l \frac{(\hat{P}_{\alpha l} \Phi_k)(\hat{P}_{\alpha l} \chi_k)}{2M_\alpha} \right] = E \sum_k \int d\{\vec{r}_j\} \Phi_s^* \Phi_k \chi_k$$

to obtain the equation above we used the product form

$$\begin{aligned} &\frac{\partial^2}{\partial R_{\alpha l}^2} \left[\Phi_k(\{\vec{r}_j\}; \{\vec{R}_\alpha\}) \chi_k(\{\vec{R}_\alpha\}) \right] = \\ &= \chi_k \frac{\partial^2}{\partial R_{\alpha l}^2} \Phi_k + 2 \left(\frac{\partial}{\partial R_{\alpha l}} \chi_k \right) \left(\frac{\partial}{\partial R_{\alpha l}} \Phi_k \right) + \Phi_k \frac{\partial^2}{\partial R_{\alpha l}^2} \chi_k \end{aligned}$$

For the SE we obtain

$$\left[\hat{T}_{ion} + \Sigma_k(\{\vec{R}_\alpha\}) \right] \chi_s(\{\vec{R}_\alpha\}) + \sum_k \hat{A}_{sk}(\{\vec{R}_\alpha\}) \chi_k = E \chi_s \quad (1.6)$$

where the operator \hat{A}_{sk} reads:

$$\begin{aligned} \hat{A}_{sk}(\{\vec{R}_\alpha\}) &= - \sum_{\alpha=1}^M \sum_l \frac{\hbar^2}{2M_\alpha} \int d\{\vec{r}_j\} \Phi_s^* \left[\left(\frac{\partial^2}{\partial R_{\alpha l}^2} \Phi_k \right) + 2 \left(\frac{\partial}{\partial R_{\alpha l}} \Phi_k \right) \frac{\partial}{\partial R_{\alpha l}} \right] \chi_k \quad (1.7) \\ &\equiv \hat{A}_{sk,1} + \hat{A}_{sk,2} \end{aligned}$$

Neglecting the contributions from \hat{A}_{sk} : i.e.

$s=k$ correction to the electronic energy of the s state } due to MOTION
 $s \neq k$ transition between electronic states } of the ions.

one gets:

$$\left[\hat{T}_{ion} + \varepsilon_s(\{\vec{R}_\alpha\}) \right] \chi_s(\{\vec{R}_\alpha\}) = E \chi_s(\{\vec{R}_\alpha\}) \quad (1.8)$$

In other words $s \in$ for the ions in the effective potential $\varepsilon_s(\{\vec{R}_\alpha\})$.

The solutions of (1.8) are labelled $\chi_{s,m}(\{\vec{R}_\alpha\})$ with corresponding eigenenergy $E_{s,m}$. s is the electronic and m the ionic quantum number.

notes

- The effects of the chemical bonding are captured in $\varepsilon_s(\{\vec{R}_\alpha\})$
- The equilibrium configuration of the lattice corresponds to minima of $\varepsilon_s(\{\vec{R}_\alpha\})$ (When they exist. They always exist for $\varepsilon_0(\{\vec{R}_\alpha\})$ the electronic ground state) The corresponding configuration $\{\vec{R}_{0,\alpha}\}$ gives the crystalline structure of a solid.

• We define $E_{ion} = \langle E_{s,m+1} - E_{s,m} \rangle$ $E_{el} = \langle \bar{E}_{s+1,m} - E_{s,m} \rangle$

$$E_{ion} \sim \hbar \sqrt{\frac{k}{M}}$$

$$k = \frac{\partial^2 \varepsilon}{\partial R^2} \sim \frac{E_{el}}{a_0^2}$$

where a_0 is the Bohr radius

$$E_{el} \sim \frac{\hbar^2}{m a_0^2}$$

$$\Rightarrow E_{ion}^2 \sim \frac{\hbar^2 \bar{E}_{el}}{M a_0^2} = \frac{m}{M} \bar{E}_{el}^2 \Rightarrow \boxed{\frac{E_{ion}}{E_{el}} \sim \sqrt{\frac{m}{M}}} \quad (1)$$

Validity of Born-Oppenheimer

$$A_{sk,1} = \sum_{\alpha=1}^M \sum_l \frac{\hbar^2}{2M_\alpha} \int d\{\vec{r}_j\} \phi_s^* \frac{\partial^2}{\partial R_{\alpha l}^2} \phi_k$$

V_{ii} enters Eq. (13) as an additive constant \Rightarrow $\{\vec{R}_\alpha\}$ dependence of $\phi_k(\{\vec{r}_j\}, \{\vec{R}_\alpha\})$ comes primarily from $\hat{V}_{ei} \Rightarrow$ one expects a dependence from the relative positions $|\vec{r}_j - \vec{R}_\alpha|$

$$A_{sk,1} \sim \sum_{\alpha=1}^M \sum_l \frac{\hbar^2}{2M_\alpha} \int d\{\vec{r}_j\} \phi_s^* \frac{\partial^2}{\partial r_{jl}^2} \phi_k = \sum_{\alpha=1}^M \frac{m}{M_\alpha} \langle \phi_s | \hat{T}_{el} | \phi_k \rangle$$

$\frac{m}{M_\alpha}$ smaller than the electronic energy E_{el}

$\left(\frac{m}{M_\alpha}\right)^{1/2}$ smaller than the ionic energy E_{ion}

$$A_{sk,2} \chi_k = -2 \frac{\hbar^2}{2M_\alpha} \int d\{\vec{r}_j\} \phi_s^* \left(\frac{\partial}{\partial R_{\alpha l}} \phi_k \right) \frac{\partial}{\partial R_{\alpha l}} \chi_k$$

$$\sim \frac{1}{M_\alpha} \langle \hat{P}_{el} \rangle \langle \hat{P}_{ion} \rangle \sim \frac{1}{M_\alpha} \sqrt{m E_{el}} \sqrt{M_\alpha E_{ion}} \stackrel{(1.9)}{=} \sqrt{\frac{m}{M_\alpha} \left(\frac{m}{M_\alpha}\right)^{1/2} E_{el}^2} = \left(\frac{m}{M_\alpha}\right)^{3/4} E_e$$

\Rightarrow a factor $\left(\frac{m}{M_\alpha}\right)^{3/4}$ smaller than the ionic energy E_{ion} .

- The Born-Oppenheimer approx. is also called adiabatic approx.

- $A_{sk,2}$ is only $10^{-1} - 10^{-2}$ smaller than E_{ion} . It gives rise to the non-adiabatic el-phonon coupling, usually handled within perturbation theory.

iv) If the diabatic term A_{sk} is neglected one finds:

$$\left\{ \begin{array}{l} (\hat{T}_{ion} + \Sigma_{el,k}) \chi_{k,m} = E_{k,m} \chi_{k,m} \quad \text{ions} \quad (1.10a) \\ (\hat{T}_{el} + \hat{V}_{ee} + \hat{V}_{ei} + \hat{V}_{ii}) \phi_k = \Sigma_{el,k} \phi_k \quad \text{electrons} \quad (1.10b) \end{array} \right.$$

Notice that, de facto one very often considers only the electronic ground state associated to a specific nuclear configuration \Rightarrow obtaining only one adiabatic potential, $\Sigma_{el,0}(\{\vec{R}_\alpha\})$.

1.4 Universality

The focus of our analysis is NOT the entire energy profile but the the dynamics associated to the LOW ENERGY STATES.

This is due to the universal behaviour of the "low temperature" limit of system with different microscopic structure.

For example: temperature dependence of the specific heat due to phonons.

\Rightarrow Consequently we can employ simple model Hamiltonians and discard the details of the microscopic interaction potentials.

1.5 Methods

- The large number of particles involved in the description of a solid implies that statistical concepts need to be used
- The large number of interacting particles is efficiently treated in Ψ quantization which automatically deals with the fermionic/bosonic character of the particles. In practice: the symmetrization/antisymmetrization of the bosonic/fermionic wavefunction
- Equilibrium properties are captured by
 - Equilibrium density matrices \Rightarrow distribution functions
 - Equilibrium Green's functions + Feynman diagrams
- Non-equilibrium properties are captured by
 - Kubo linear response theory (in presence of weak perturbations the non-eq. problem is transferred to the equilibrium one)
 - Non-equilibrium (Keldish) Green's functions
 - Boltzmann transport equation
 - Liouville eq. for the density matrix.