

# Concepts in Computational Materials Science

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stand-alone lecture course, but can be used as part of "Wahlpflichtfach" Theoretical Solid State Physics (3 CP)

## Chapter I - Introduction

Goal: Introduce concepts from theory of condensed matter

≡ electrons and nuclei in some form  
~  $10^{23}$  of them

that allow us to

- understand ~~a~~ given physical phenomena e.g. result of an experiment, but not just

- but also, to make predictions for the behavior of a given material, based only on "first principles" of theoretical physics

- possibly, given a reasonable computer

"Material Science" - not just fundamental idea, but possibly useful for some actual application!

- construction
- solar cell

- biophysics
- superconductivity
- etc MANY opportunities

Why can we do that?

Many-body Schrödinger Equation

$$\hat{H}(\bar{\Psi}_{\text{In}}(\{\underline{R}_{\text{I}}\}, \{\underline{r}_k\})) = E_{\text{In}} \bar{\Psi}_{\text{In}}(\{\underline{R}_{\text{I}}\}, \{\underline{r}_k\})$$

↓

Many-body Hamiltonian

M nuclei, N electrons

$\bar{\Psi}_{\text{In}}$  Many-body wave function  
(ground state or excited state)

function of all nuclear coordinates  $\{\underline{R}_{\text{I}}\}$   
all electron coordinates  $\{\underline{r}_k\}$

... but all the ingredients of  $\hat{H}$  are known!

$$\hat{H} = \hat{T}^e + \hat{T}^{\text{nuc}} + \hat{V}^{\text{ee}} + \hat{V}^{\text{nuc-euc}} + \hat{V}^{\text{e-nuc}}$$

$$1) \quad \hat{T}^e = \sum_{k=1}^N \frac{p_k^2}{2m} \quad p_k \rightarrow \frac{\hbar}{i} \nabla_k$$

$$2) \quad \hat{T}^{\text{nuc}} = \sum_{\text{I}=1}^M \frac{p_{\text{I}}^2}{2M_{\text{I}}}$$

$$3) \quad \hat{V}^{\text{ee}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{k, k' \\ k \neq k'}}^{NN} \frac{e^2}{|\underline{r}_k - \underline{r}_{k'}|}$$

$$4) \hat{V}^{\text{huc-nc}} = \frac{1}{2} \frac{1}{4\pi\epsilon_0} \sum_{\substack{I, J \\ I \neq J}}^{M, N} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

$$5) \hat{V}^{\text{huc-c}} = \frac{1}{4\pi\epsilon_0} \sum_{I=1}^M \sum_{k=1}^N \frac{Z_I e^2}{|R_I - r_k|}$$

Note : We left a few "details" :

- relativity
- spin (electrons & nuclei)
- electromagnetic fields (Lorentz invariance??)

Should really be looking at Dirac's Equ (1928)

- 4 component wave function
- matrix equation

For the purposes of this course will talk about Schrödinger's Equation, but note in principle, could do same material using Dirac's Equ.

Dirac (1929) : "becomes desirable that approximate practical methods of qm should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation"

Dirac was right - 80 years and ongoing!

## A) Develop explanations

- semiconductors
- superconductivity
- nature of chemical bond

## B) Make actual predictions

- Hartree 1927
- 1950s "quantum chemistry"  
(molecules, wave function output)
- ~1980 quantitative predictions (structure etc.)  
for simple solids - Si)

underlying theory formalized 1964  
"Density functional theory"  
(rigorous in principle)

## Plan for this course

### Part I - Systematic approximations to an exact theory

- full theory (already done.)
- Electrons and nuclei (Born-Oppenheimer approx.)
- Electronic structure theory
  - Hartree, Hartree-Fock  
outlook "quantum chemistry"
  - Density functional theory (principle)
  - Density functional theory (practice)
- Nuclei revisited: Molecular Dynamics

- Part II - First-principles accuracy for Model Hamiltonians
- molecular dynamics (force fields)
  - Ising-like models & first-principles statistical mechanics

Textbooks - see web site and script

## Chapter 2 Many-Body Schrödinger Equation

Discussion of the Many-Body Wave Function

$$\hat{H} \Psi_n = E_n \Psi_n$$

$$\bar{\Psi}_n \equiv \bar{\Psi}_n(\{\mathbf{R}_i\}, \{\mathbf{r}_k\})$$

Ground state :  $n = 0$   
 $E_0$  minimal

All excited states :  $n > 0$ .

A function of  $10^{23}$  particle coordinates

All mixed together!

We throw in  $10^{23}$  individual particles,  
but there is no reason why they should  
behave as such in  $\bar{\Psi}_n$  - could even look  
like 1 particle,  $10^{23}$  coordinates.

Usual strategy: Attempt to separate the problem into suitably decoupled effective particles anyway, but why this worked so well puzzled early solid-state physicists.

Example: Superconductivity

above  $T = T_c$ : "normal" conductors (conventional) or even "bad" conductors (high  $T_c$  - oxides, pnictides)

Reason, qualitatively (conventional)

- 2 "electrons" form pairs ("Cooper pairs")
- "pair" is spin 0 / 1 entity - behaves like Boson can formally occupy same exact ground state
- need attraction (electrons repel each other)  
→ phonons (vibrations of the nuclei)

Wave function can really look anything but like individual electrons, nuclei.

Remember: What we are really interested in in practice is not necessarily the wave function.

Rather, observables of some kind:

- $E_n - E_0$  excitation energies
- magnetization of FM
- dipole moment of a molecule
- LOTS of examples

If we can somehow get around computing full  $\bar{\Psi}_n$ , our life would be simpler.

## 2.2 Separating Electrons and Nuclei

Born-Oppenheimer Approximation ("Adiabatic Approximation")

Qualitatively:  $\frac{m_{atom}}{m_{el}} \gg 1$  (e.g. 1836 for  $\frac{m_H}{m_e}$ )

electrons react much faster to perturbation than nuclei

First step: Define space of electron-only wave functions for fixed nuclear coordinates  $\{\underline{R}_I\}$

$$\{\bar{\Phi}_\nu(\{\underline{R}_I\}, \{\underline{r}_k\})\}$$

↑  
effectively, parameters.

Define by:  $(\hat{T}^e + \hat{V}^{e-nuc} + \hat{V}^{e-e}) \bar{\Phi}_\nu = E_\nu \bar{\Phi}_\nu$

but  $E_\nu \equiv E_\nu(\{\underline{R}_I\})$

Wouldn't it be good if we could find some separable form

$$\bar{\Psi}_n(\{\underline{R}_I\}, \{\underline{r}_k\}) \stackrel{?}{=} \sum_n(\{\underline{R}_I\}) \cdot \bar{\Phi}_n(\{\underline{R}_I\}, \{\underline{r}_k\})$$

More precisely, what we would like is

$$E_n \bar{\Psi}_n = E_n \Lambda_n \cdot \bar{\Phi}_n$$

$$\hat{T}(\bar{\Psi}_n) = \underbrace{(\hat{T}^{\text{nuc}} + \hat{V}^{\text{elec-nuc}})}_{\text{"H}_{\text{nuc}}"} + \underbrace{(\hat{T}^{\text{e}} + \hat{V}^{\text{e-nuc}} + \hat{V}^{\text{e-e}})}_{\text{"H}_{\text{e}}(\{\mathbf{R}_{\text{I}}\})} \Lambda_n \bar{\Phi}_n$$

$$\hat{T} \bar{\Phi}_n = \underbrace{(\hat{H}_{\text{nuc}} \Lambda_n)}_{\text{this works}} + \underbrace{\Lambda_n (\hat{H}^{\text{e}} \bar{\Phi}_n)}_{\text{this works}}$$

↳ but this does not (exactly)

because  $\hat{T}^{\text{nuc}} = \sum_{\text{I}}^M -\frac{\nabla_{\text{I}}^2}{2}$  acts also on  $\bar{\Phi}_n(\{\mathbf{R}_{\text{I}}, \{\mathbf{r}_n\})$

$$\hat{T}^{\text{nuc}} \Lambda_n \bar{\Phi}_n = \underbrace{(\hat{T}^{\text{nuc}} \Lambda_n)}_{\checkmark} \cdot \bar{\Phi}_n = \underbrace{-\sum_{\text{I}} \left(\frac{\nabla_{\text{I}}^2}{2} \Lambda\right)}_{-\left(\sum_{\text{I}} \frac{\nabla_{\text{I}}^2}{2} \Phi_n\right) \cdot \Lambda_n \{ \mathbf{R}_k \}} \left(\frac{\nabla_{\text{I}}}{2} \bar{\Phi}_n\right)$$

what we would have needed if BO approx. were exact (it's not!).

Note: Units

Initial MB S' Eq: Written in SI units.

More convenient:

$$\left. \begin{array}{l} \frac{1}{4\pi\epsilon_0} \rightarrow 1 \\ e \rightarrow 1 \\ \hbar \rightarrow 1 \end{array} \right\}$$

Then: • All lengths in Eq's automatically in units of

$$\text{"bohr"} = \frac{4\pi\epsilon_0 \hbar^2}{m e^2} = 0.0529177 \text{ nm}$$

• All energies automatically in



"Hartree" units

$$1 \text{ Ha} = 27.212 \text{ eV}$$

Note  $1 \text{ Ry} = \frac{1}{2} \text{ Ha}$