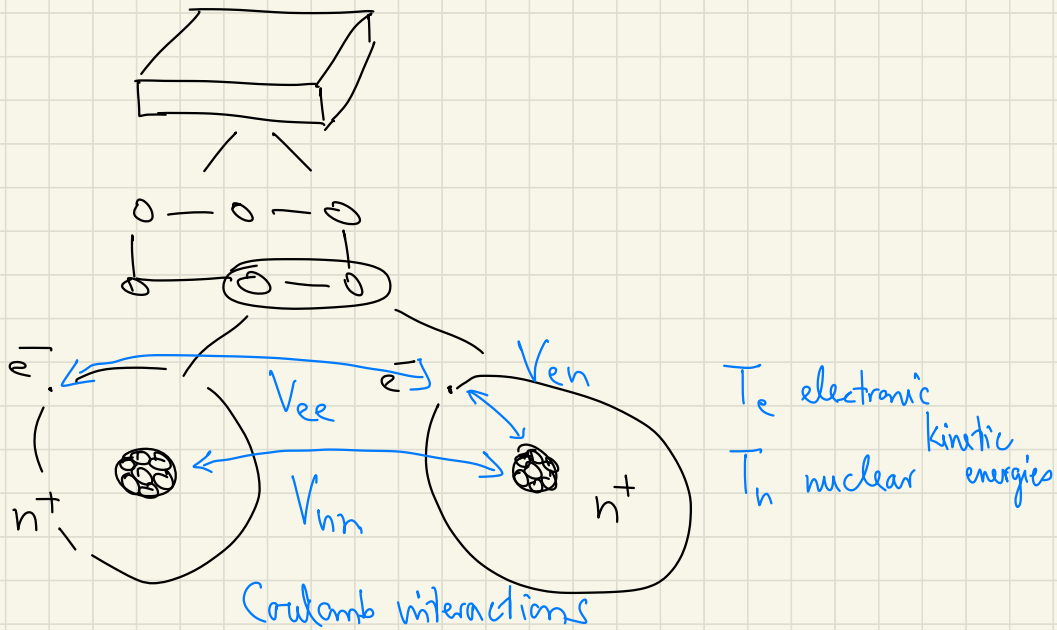


This week: Summary of  
first three theory lectures &  
outlook to Kohn-Sham theory

# 0) Motivation & Background

Central problem of condensed matter physics:



$$H = T_e + T_n + V_{ee} + V_{en} + V_{nn}$$

$$= \sum_i \frac{p_i^2}{2m_e} + \sum_i \frac{p_i^2}{2M_i} + \sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,j} \frac{Z^2 e^2}{|\vec{R}_i - \vec{R}_j|} + \sum_{i,j} \frac{-Ze^2}{|\vec{r}_i - \vec{R}_j|}$$

$\Rightarrow$  Need to solve the Schrödinger equation

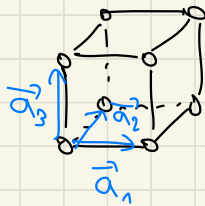
$$H\psi = E\psi$$

Goal of the course: Provide a theoretical background of DFT & do practical applications of calculations

# 1) Recap of basic properties of solids

1.1 What is a crystal?  $\rightarrow$  Periodic arrangement of unit cells containing one or more atoms

1.2 What is a unit cell?  $\rightarrow$  Fundamental building block that if repeated periodically, builds the entire crystal



Simple cubic

## 1.3 Symmetry operations

(reflections, rotations, translations)

Cubic



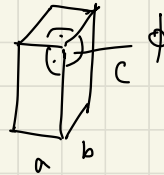
Tetragonal



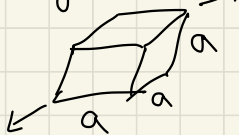
Orthorhombic



Monoclinic



Trigonal

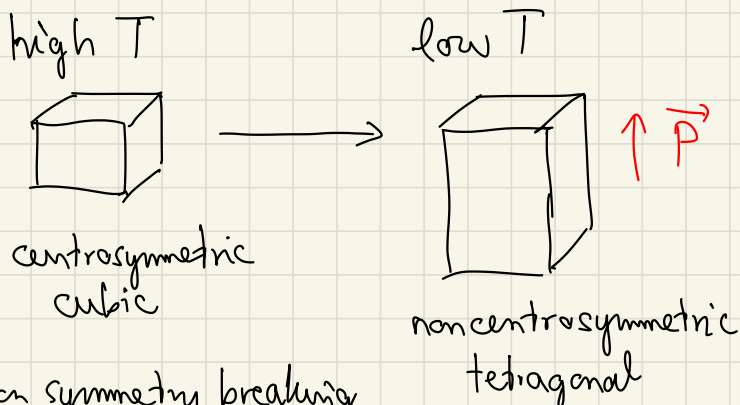


Hexagonal



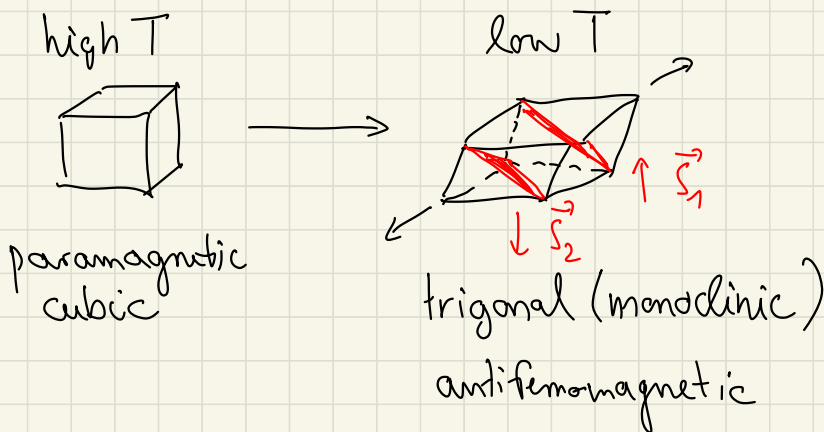
Crystal symmetry is directly connected to the electronic properties of the material.

Example 1:  $\text{BaTiO}_3$



The inversion symmetry breaking upon cooling allows  $\text{BaTiO}_3$  to obtain a ferroelectric polarization,  $\vec{P}$

Example 2:  $\text{NiO}$



1.4 What is the reciprocal lattice?  $\rightarrow$  Fourier transform of the direct (real-space) lattice, where we convert space  $\rightarrow$  momentum  
 $\vec{r} \rightarrow \vec{k}$

1.5 Bloch theorem:  $e^-$  wavefunctions obey periodicity of the crystal

2) Introduction to density functional theory (DFT)

$$H \psi(\vec{r}, \vec{R}) = E \psi(\vec{r}, \vec{R})$$

$$H = T_e + \underbrace{T_n + V_{ee} + V_{en} + V_{nn}}_{H_B}$$

2.1 BO Approximation

Assumption: Nuclei are much heavier than the electrons

$$M \gg m_e, \quad \frac{M_{\text{Hydrogen}}}{m_e} \approx 1836$$

$$\Rightarrow T_n \ll T_e$$

Ansatz: Adiabatically decoupling  $e^-$  &  $n^+$  degrees of freedom

$$\psi(\vec{r}, \vec{R}, t) = \sum_n \underbrace{\chi_n(\vec{R}, t)}_{n^+ \text{ wavefunction}} \psi_n^{\vec{R}}(\vec{r}) \quad \text{feel the nuclear potential on a background}$$

$$\Rightarrow H_{BO} \psi(\vec{r}, \vec{R}, t) = \sum_n \chi_n(\vec{R}, t) \underbrace{H_{BO} \psi_n^{\vec{R}}(\vec{r})}_{= E_n^{BO} \psi_n^{\vec{R}}(\vec{r})} = \sum_n E_n^{BO} \chi_n(\vec{R}, t) \psi_n^{\vec{R}}(\vec{r})$$

For the  $e^-$  system:  $T_n = 0$ ,  $V_{nn} = \text{const.}$

↳ add it to energy eigenvalue

⇒ left to solve:

$e^-e^-$  Coulomb  
interaction

static periodic background  
treated as external  
single-particle potential

$$\left[ \frac{-\hbar^2}{2m_e} \sum_i \vec{\nabla}_i^2 + \frac{e^2}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e^2 \sum_{i\alpha} \frac{Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} \right] \psi(\vec{r})$$

↑  
 $e^-$  kinetic energy

$$= (\varepsilon - V_{nn}) \psi(\vec{r})$$

↑  
only relevant when comparing  
energies between different structural  
configurations

Still many-body problem with more variables than we can solve.

⇒ Two approaches: a) Wavefunction methods  
↳ solve for many-body wavefct.

b) DFT

## 2.2 Wavefunction methods

Idea: Use the variational principle to minimize the energy

$$\frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \geq E_0 \text{ ground state energy}$$

Assumption: Minimizing this will give us a good approximation of the ground-state wavefunction

Ansatz:

$$\begin{aligned} \text{a) Hartree approximation } \psi(\vec{r} = \{\vec{r}_i\}) &= \prod_{i=1}^N \phi_i(\vec{r}_i) = \\ &= \phi_1(\vec{r}_1) \dots \phi_N(\vec{r}_N) \end{aligned}$$

b) Hartree-Fock approximation

$$\psi(\vec{r} = \{\vec{r}_i\}, \sigma = \{\sigma_i\}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1)\chi_1(\sigma_1) & \dots & \phi_N(\vec{r}_1)\chi_N(\sigma_1) \\ \vdots & \ddots & \vdots \\ \phi_1(\vec{r}_N)\chi_1(\sigma_N) & \dots & \phi_N(\vec{r}_N)\chi_N(\sigma_N) \end{vmatrix}$$

↑      ↑  
Spatial   Spin  
parts

If two states are the same:  $(\vec{r}_i, \sigma_i) = (\vec{r}_j, \sigma_j) \Rightarrow |\cdot| = 0$

We now need to minimize the energy:

$$\langle \psi_{H(F)} | H | \psi_{H(F)} \rangle \equiv \varepsilon_{H(F)} [\phi_i]$$

$$\Rightarrow \frac{\delta \varepsilon_{H(F)} [\phi_i]}{\delta \phi_i(\vec{r})} = 0$$

This minimization yields a new set of equations:

Hartree (-Fock) equations

$$\left[ \frac{-\hbar^2}{2m_e} \nabla^2 + V_{\text{ext}}(\vec{r}) + V_H(\vec{r}) \right] \phi_i(\vec{r})$$

(contains  $V_{\text{ex}}$ ) Hartree potential

$\equiv$  classical electrostatic contribution to the Coulomb interaction

$$- \frac{e^2}{2} \sum_j S_{\chi_i \chi_j} \int d\vec{r}' \frac{\phi_j^*(\vec{r}') \phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \phi_i(\vec{r})$$

exchange potential

acting nonlocally on

all positions  $\vec{r}'$

$$= \varepsilon_i \phi_i(\vec{r})$$

result

Overall reduces the energy of the system w/ respect to the classical



Still, we have  $N$  coupled integro-differential equations and need to solve them iteratively:

- (i) Initializing the  $\phi_i$  (educated guess, e.g. atomic orbitals)
- (ii) Compute potential energies (external, Hartree, exchange)
- (iii) Compute a new set of  $\phi_i$  from HF equation
- (iv) Recompute potential energies w/ new  $\phi_i$
- (v) Iterate until convergence

To date: Systems of 10-100  $e^-$  are feasible

## 2.3 Hohenberg - Kohn theorems

(Nobel prize 1998  
in Chemistry  
for Walter Kohn)

Theorem 1:  $V_{\text{ext}} \Leftrightarrow n_0(\vec{r})$  (up to additive constant)

$(V_{\text{en}})$

external potential      ground-state particle density

Corollary 1: With  $V_{\text{ext}}$ ,  $H$  is completely determined  
 $\Rightarrow$  all properties of the system are determined by  $n_0(\vec{r})$

Theorem 2: For any  $V_{\text{ext}} \exists E[n]$ , where global minimum of  $E[n]$  gives us  $\epsilon_0$  (gs energy)  
AND  $E[n] = \epsilon_0 \Leftrightarrow n = n_0$

Corollary 2:  $E[n]$  is sufficient to determine  $\epsilon_0$  and  $n_0$

$$\epsilon_0 = \min_{\Psi} [\langle \Psi | T_e + V_{ee} + V_{\text{ext}} | \Psi \rangle]$$

2-step minimization

$$= \min_n \min_{\Psi \rightarrow n} [\langle \Psi | T_e + V_{ee} | \Psi \rangle + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r})]$$

$\downarrow$   
 $F[n]$  Levy-Lieb functional

$$= \min_n \left[ \underbrace{F[n] + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r})}_{E[n]} \right]$$

Remarks:

a)  $E[n] = F[n] + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r})$

$\min_{\psi \rightarrow n} [\langle \psi | T_e + V_{ee} | \psi \rangle]$

depends only on the type of particle

interaction w/  
external potential

b) The exact functional  $F[n]$  requires constrained search for  $N$ -particle wavefunctions  $\rightarrow$  impractical

"Constrained search is for understanding, not computation"  
Perdew

c)  $F[n]$  still contains  $V_{ee}$ , which still needs approximation  
Practically, approximations on explicit functionals of the density are too crude.

d) Are the HK theorems trivial?

Yes! Density  $n$  is a highly integrated quantity

$$n(\vec{r}_1) = N \int d\vec{r}_2 \dots \int d\vec{r}_N \Psi^*(\vec{r}_1 \dots \vec{r}_N) \Psi(\vec{r}_1 \dots \vec{r}_N)$$

Example of a simple density functional: Thomas-Fermi-Dirac theory

Idea: Approximate  $E[n]$  locally by the energy of a homogeneous electron gas with  $n(\vec{r})$ :

$$E[n] = \int d\vec{r} n(\vec{r}) \varepsilon[n(\vec{r})]$$

↑ energy density of the homogeneous electron gas

Remember/Assume: Energy of homog.  $e^-$  gas from Jellium model

$$\varepsilon_{\vec{k}} = \underbrace{\varepsilon_{\vec{k}}^0}_{\frac{\hbar^2 k^2}{2m_e} \propto n^{2/3}} - \underbrace{\frac{2e^2 k_F}{\pi}}_{\propto k \propto n^{1/3}} \underbrace{F\left(\frac{k}{k_F}\right)}_{F(x) = \frac{-1}{2} - \frac{1-x}{4x} \ln \left| \frac{1+x}{1-x} \right|} + \text{Hartree energy}$$

positive charges  
 $e^- \quad e^- \quad e^-$

explicitly dependent on  $n$

take average

$$F[n] = C_{\text{kin}} \int d\vec{r} n^{5/3}(\vec{r}) + \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} - C_{\text{ex}} \int d\vec{r} n^{4/3}(\vec{r})$$

$F[n]$  is now an explicit functional of the  $e^-$  density  $n(\vec{r})$

Variation of  $F[n]$  w/ respect to  $n(\vec{r})$

$$\frac{\delta}{\delta n(\vec{r})} \left\{ F[n] + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r}) - \mu \left[ \int d\vec{r} n(\vec{r}) - N \right] \right\} = 0$$

Variation yields:

$$\underbrace{\mu}_{\substack{\uparrow \\ \downarrow \\ E_F}} = \frac{5}{3} C_{\text{kin}} n^{2/3}(\vec{r}) + V_{\text{ext}}(\vec{r}) + e^2 \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} - \frac{4}{3} C_{\text{ex}} n^{1/3}(\vec{r})$$

Appeal: Singular equation for the  $e^-$  density  $n(\vec{r})$   
instead of  $3N$ -particle Schrödinger equation

Problem: Very crude approximation & a lot of physics missing,  
such as atomic shell structure.

$\Rightarrow$  Not useful for meaningful calculations

## 2.4 Kohn-Sham theory

Kohn & Sham Physical Review **140**  
(1965)  
"Self-consistent equations including exchange and correlation effects"

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi | T_e + V_{ee} | \Psi \rangle$$

$$= \min_{\Psi \rightarrow n} \langle \Psi | \frac{\hbar^2}{2m} \sum_i \vec{\nabla}_i^2 | \Psi \rangle$$

Kinetic energy, unknown as a functional of  $n$  & contains nonlocal operator  $\vec{\nabla}$

$$+ \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

Hartree energy  $E_H[n]$   
known exactly as a functional of  $n$ , largest part of the interaction

$$+ \tilde{E}_{xc}[n]$$

Exchange - correlation energy  
contains all interactions beyond classical  $E_H[n]$   
unknown & small

correlation  $\equiv$  everything beyond exchange in HF approximation