

Computational Modelling of Quantum Materials

Lectures: Mondays 1pm - 4pm

Office hours: Tuesdays 1-3pm

dijurashchuk@tanex.tau.ac.il

Exam dates: TBD

Exercises: Login to a workstation

Performed on the cluster

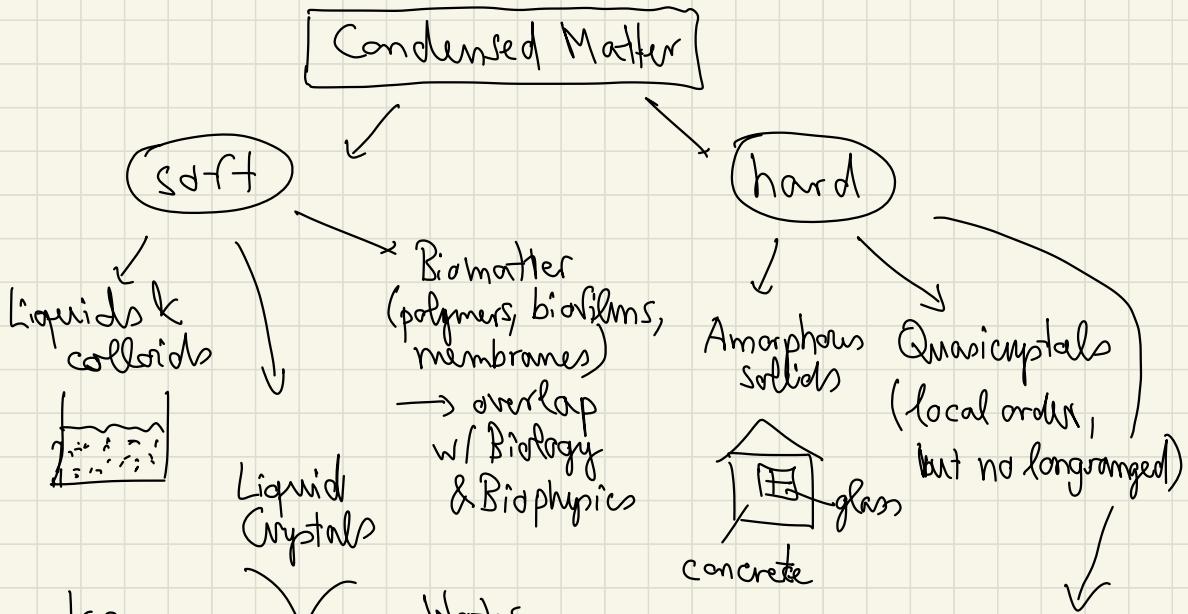
Until 1st exercise: bash scripting

Literature: Feliciano Giustino Materials Modeling with Density Functional Theory

Richard Martin Electronic Structure

Jorge Kohanoff Electronic structure calculations for solids and molecules

O. Overview & Motivation

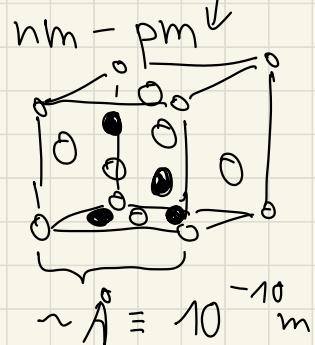


length scales: mm - nm

Methods: Statistical physics, physics of complex systems, continuum mechanics

→ Condensed Matter Theory 2

Diamond
(cubic unit cell)



Many-body quantum mechanics

Analytical approach

Condensed Matter Theory 1

Computational methods

This course

Quantum materials : Crystals in which the quantum-mechanical nature of the atoms

realizes in an intriguing way :

"emergence" : novel phenomena arising from
collective interactions that cannot be
described by the qm. of the individual atoms

→ quasiparticles, superconductivity, etc.

Phil Anderson "More is different" Science 177, 4047
(1972)

From: Since 2000, 8/23 Nobel prizes were given for condensed matter phenomena

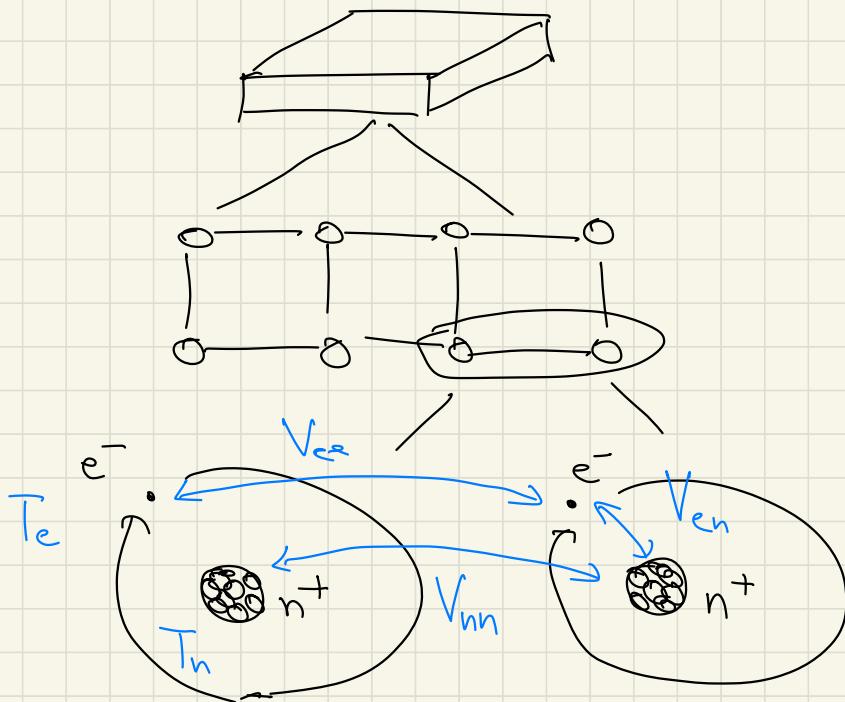
Ideas: • Room-temperature, ambient pressure superconductor → $T_c \sim 290\text{ K}$

• Room-T & single-phase multiferroic
(magnetic & electric dipole)
w/ strong coupling

Money: Semiconductor industry
 Quantum technology sector

Central problem of condensed matter physics & quantum materials

Electronic Correlation



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

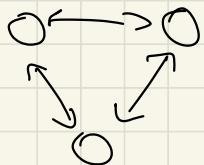
$$= \sum_i \frac{p_i^2}{2m_e} + \sum_i \frac{P_i^2}{2M_n} + \sum_{i < j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i < j} \frac{Z^2 e^2}{|\vec{R}_i - \vec{R}_j|} + \sum_{i < j} \frac{-Ze^2}{|\vec{r}_i - \vec{r}_j|}$$

Nonrelativistic Hamiltonian (not considering e^-/h^+ spins)

\Rightarrow Need to solve the Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle$$

Problem: Even the classical 3-body problem is not solvable analytically



e.g. 3 celestial bodies
coupled by gravity

In our case: $0(10^{23})$ particles in a solid

Complexity of the system of equations
scales exponentially with the particle number.

\Rightarrow unsolvable exactly { analytically
numerically

CMP tries to find intelligent approximations & models
to describe solid-state properties.

Condensed matter theory: Model systems w/
qualitative predictions

e.g. superconductivity
quantum Hall effect

Computational condensed matter physics / materials science:

First-principles (ab-initio) calculations
for quantitative predictions & high accuracy

In our many-body problem: Approximations around
the $e^- - e^-$ interaction, V_{ee} with a background of
classical & static nuclei $T_n = 0$

$$V_{nn} = \text{const.}$$

→ Framework: Density functional theory (DFT)

Goal of the course

Theoretical background & practical application
of ab-initio calculations based on DFT.

Overview of the semester

- Week : 1 Introduction & recap of periodic solids
2 Introduction to DFT
3 Exercise I
4 Repetition class
5 Computational aspects of DFT
6 Exercise II
7 Comput. aspects of DFT
8 Exercise III
9 Advanced methods for the xc-energy
10 Exercise IV
11 Adv. meth. for the xc-energy

1. Crystals & symmetries

1.1 Definition What is a crystal?

A periodic arrangement of unit cells, each containing one or multiple atoms or molecules

What is a crystal lattice?

An infinite set of points that can be constructed from a set of linearly independent lattice vectors with integer coefficients.

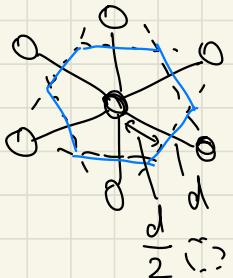
⇒ "Bravais lattice"

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

$n_i \in \mathbb{Z}$ and \vec{a}_i are noncollinear

1.2 Unit cells

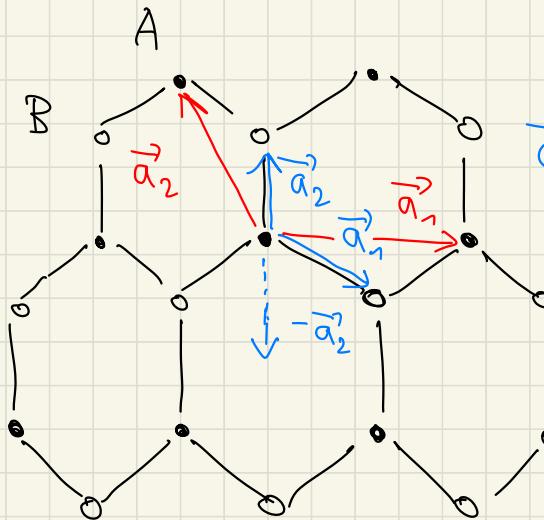
Example for a primitive unit cell:



Wigner - Seitz cell

Primitive unit cell:
Unit cell with smallest possible volume

Graphene :

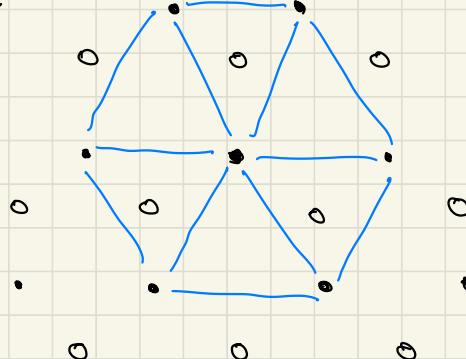


A and B sites have different environments

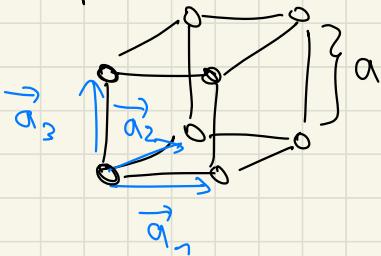
\vec{a}_1 & \vec{a}_2 : primitive lattice vectors build the entire lattice, but lead to inequivalent sites.

\vec{a}_1 & \vec{a}_2 : nonprimitive, but connect equivalent sites

⇒ Bravais lattice
is hexagonal



Examples of unit cells in 3D: cubic



Simple cubic

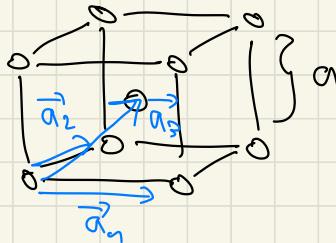
$$\vec{a}_1 = a(1,0,0)$$

$$\vec{a}_2 = a(0,1,0)$$

$$\vec{a}_3 = a(0,0,1)$$

1 atom per unit cell

→ each lattice point
has $\frac{1}{8}$ atoms



body-centered
cubic (bcc)

$$\vec{a}_1 = a(1,0,0)$$

$$\vec{a}_2 = a(0,1,0)$$

$$\vec{a}_3 = \frac{a}{2}(1,1,1)$$

2 atoms per unit cell

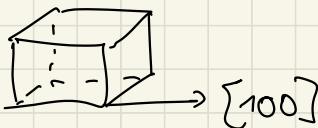
Common notation for lattice vectors $[u \ v \ w] =$

$$u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$$

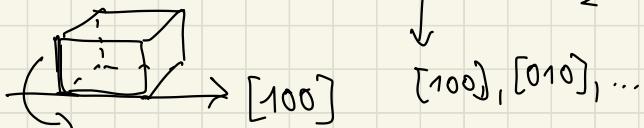
1.3 Symmetry operations

Simple cubic lattice : Which symmetry operations leave the system invariant?

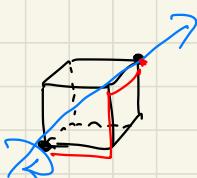
i) Translation



ii) Rotation around <100> or $\frac{\pi}{2}$



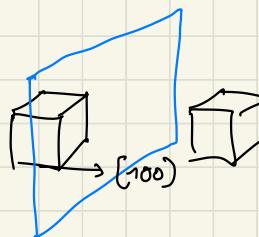
iii)



Rotation around <111>

by $\frac{2\pi}{3}$

iv)



Reflection at one of
the {100} plane

[100], [010], [001],
...

We can therefore describe all symmetries as a combination of rotation and/or reflection & translations:

$$\vec{r} \rightarrow \vec{r}' = A \vec{r} := \underline{D} \vec{r} + \vec{R}$$

"rigid"
rotation / reflection matrix translation vector
symmetry operations

Classifications: 1) Translation group: $\underline{\underline{D}} = \underline{\underline{1}}$, $\vec{R} \neq 0$
 \Rightarrow Bravais lattice 14 in 3D

2) Point group: $\underline{\underline{D}} \neq \underline{\underline{1}}$, $\vec{R} = 0$
32 in 3D

3) Space groups: $\underline{\underline{D}} \neq \underline{\underline{1}}$, $\vec{R} \neq 0$
230 in 3D

4) Crystal system: Bravais lattices with the same symmetries w/ respect to point group operations
7 in 3D

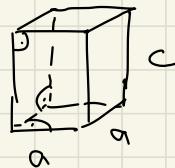
Crystal system

Cubic

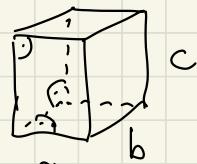
Representation



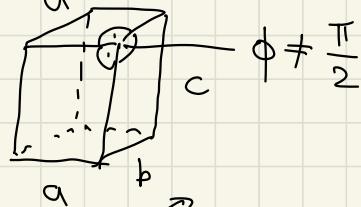
Tetragonal



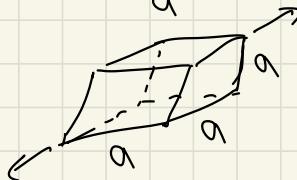
Orthorhombic



Monoclinic

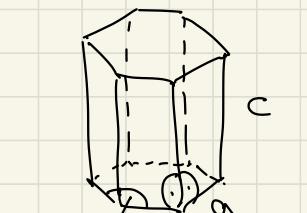


Trigonal

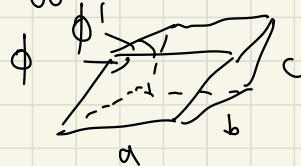


Pull a cube along [111]

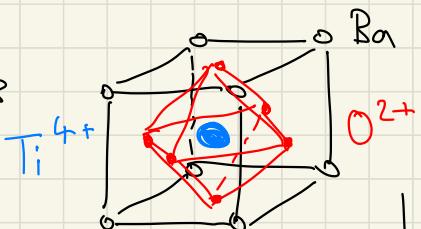
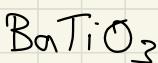
Hexagonal



Triclinic

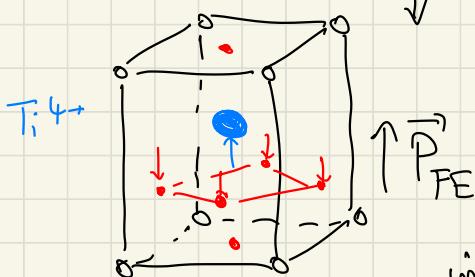


Example 1: Ferroelectric material breaks inversion symmetry



"Perovskite oxide"

Cubic at high T



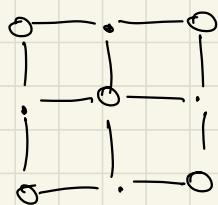
Cooling down below

$$T < T_c = 393 \text{ K}$$

Ferroelectric dipole moment emerges

$\vec{P} = 2 \cdot \vec{J}$ needs inversion symmetry breaking and a stretch of the unit cell along one direction

Example 2: Magnetic material breaks time reversal symmetry

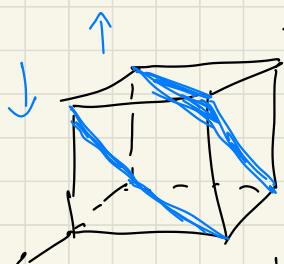


"simple cubic / fcc" like NaCl

at high T : paramagnetic

Cooling down below $T < T_N = 523 \text{ K}$

becomes antiferromagnetic

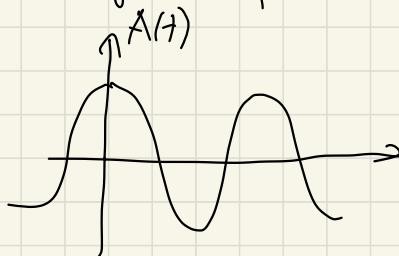


Planes \perp to [111]: spins align antiferromagnetically

\Rightarrow material goes into trigonal phase \Rightarrow spins need symmetry breaking to order

1.4 The reciprocal lattice

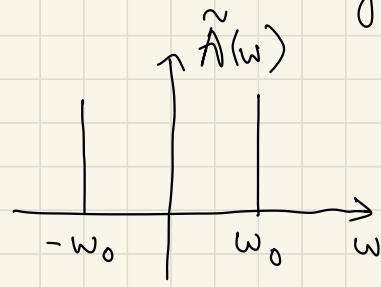
(Imagine an example from signal analysis's of em waves travelling through free space:



Sinusoidal wave

$$A(t) = \sin(\omega_0 t)$$

\Rightarrow
Fourier
transform



$$\hat{A}(\omega) = \mathcal{F}(A(t)) = \int dt \sin(\omega_0 t) e^{-i\omega t}$$

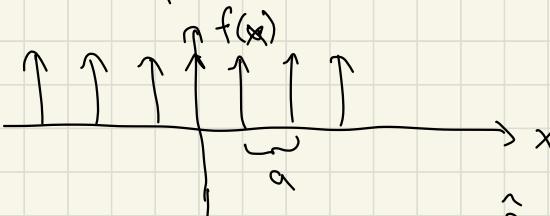
$$= \frac{1}{2i} (\delta(\omega - \omega_0) - \delta(\omega + \omega_0))$$

Consider the equivalent for a crystal lattice in 1D, which has a spatial frequency, not temporal.



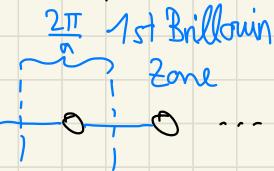
$$f(x) = \sum_{n=-\infty}^{\infty} \delta(x - n\alpha)$$

1D lattice can be represented as a "Dirac comb"



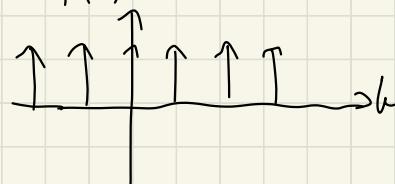
\Rightarrow
Fourier
Transform

$$\hat{f}(k) = \mathcal{F}(f(x)) = \frac{2\pi}{a} \sum_{n=-\infty}^{\infty} \delta(k - \frac{n}{a})$$



$\frac{2\pi}{a}$ Reciprocal lattice

of the 1D lattice



Now: generalize to 3D and find an equivalent definition of the reciprocal lattice.

What is a reciprocal lattice? An infinite set of points constructed by a set of linearly independent reciprocal lattice vectors with integer coefficients.

Need: Plane waves $e^{i\vec{K} \cdot \vec{r}}$ possess the periodicity of the Bravais lattice

$$e^{i\vec{K}(\vec{r} + \vec{R})} = e^{i\vec{K}\vec{r}} \\ \Leftrightarrow \boxed{e^{i\vec{K} \cdot \vec{R}} = 1} \Leftrightarrow \vec{K} \cdot \vec{R} = 2\pi n, \quad n \in \mathbb{Z}$$

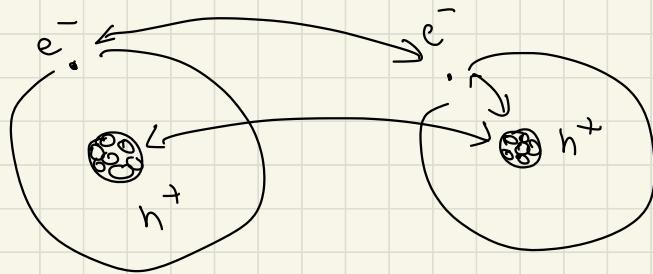
"von Laue criterion" for constructive interference in X-ray scattering

$$\vec{K} = m_1 \vec{b}_1 + m_2 \vec{b}_2 + m_3 \vec{b}_3, \quad m_i \in \mathbb{Z} \text{ and } \vec{b}_i \text{ are noncollinear}$$

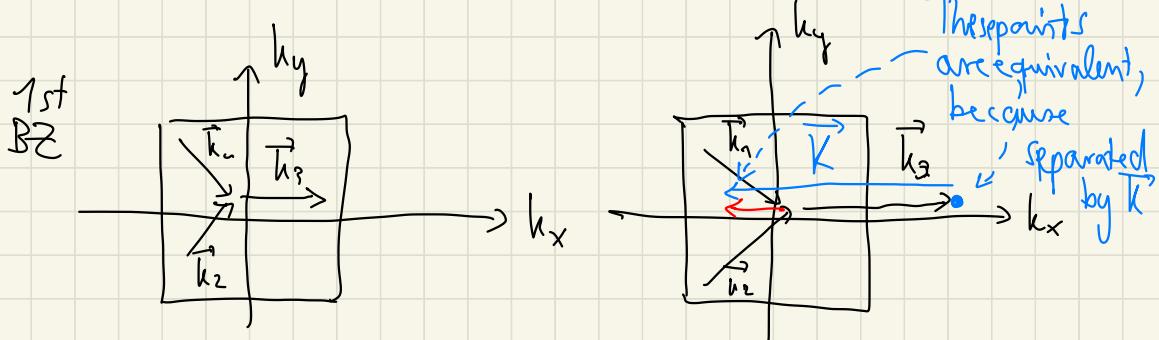
Reciprocal lattice vectors can be constructed from the direct lattice vectors:

$$\vec{b}_i = 2\pi \frac{\vec{a}_j \times \vec{a}_k}{(\vec{a}_j \times \vec{a}_k) \cdot \vec{a}_i} = \frac{2\pi}{V} \vec{a}_j \times \vec{a}_k$$

$\underbrace{\qquad\qquad\qquad}_{V_c \text{ unit-cell volume}}$



$$H = T_e + T_h + V_{ee} + V_{eh} + V_{nn}$$



Properties of the Brillouin zone are periodic with any reciprocal lattice vector \vec{K} .

\Rightarrow "Crystal momentum" is not a conserved quantity

Processes that seemingly violate momentum conservation, like the "Umklapp process" are allowed.

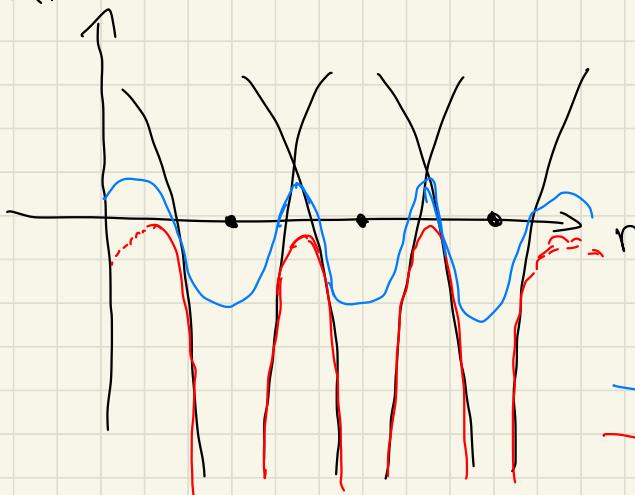
1.5 Bloch theorem

Now we want to see how the periodicity manifests in the wavefunctions of the electrons in the crystal.

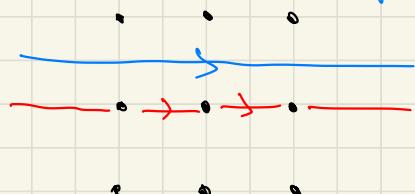
Schrödinger equation for a single e^- :

- (i) No interactions between e^- s : $V_{ee} = 0$
- (ii) Rigid lattice : $T_n = 0$, $V_{nn} = \text{const.}$
- (iii) V_{en} given by an effective single-particle potential

$$V_{en} \equiv \sum_i V(\vec{r}_i), \quad V(\vec{r}_i + \vec{R}) = V(\vec{r}_i)$$



Soft potential
along directions between
the ions, $\vec{r}_i - \vec{R}_j \neq 0$



Potential diverges along directions
crossing the nuclei.

$$H \Psi(\vec{r}) = (T_e + V_{en}) \Psi(\vec{r})$$

$$= \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \Psi(\vec{r})$$

$$= \sum \Psi(\vec{r})$$

Solutions of Ψ for this equation are called "Bloch electrons"

Formulation 1 The eigenfunction Ψ of H are of

the form

$$\boxed{\Psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{r}}}$$

Bloch wavevector

$$u_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r})$$

Properties/observables have to be periodic and are generally given by $\sigma \propto |\Psi|^2$

$$\Rightarrow |\Psi_{\vec{k}}(\vec{r} + \vec{R})|^2 = |\Psi_{\vec{k}}(\vec{r})|^2$$

$$\Psi_{\vec{k}}(\vec{r} + \vec{R}) = u_{\vec{k}}(\vec{r} + \vec{R}) e^{i\vec{k}(\vec{r} + \vec{R})} = \Psi_{\vec{k}}(\vec{r}) e^{i\vec{k}\vec{R}}$$

$u_{\vec{k}}(\vec{r})$ $e^{i\vec{k}\vec{r}} \cdot e^{i\vec{k}\vec{R}}$
 $\Psi_{\vec{k}}(\vec{r})$

Formulation 2: Then eigenfunction ψ of H can be

chosen so that for each ψ there is a \vec{k} :

$$\boxed{\psi(\vec{r} + \vec{R}) = e^{i\vec{k}\cdot\vec{R}} \psi(\vec{r})}$$

Possible \vec{k} values are given by

the periodic boundary conditions

"Born-von Karman boundary conditions".

2. Introduction to density functional theory (DFT)

Central problem of solid-state physics: Many e^- & n^+ connected by the Coulomb interaction.

$$H \psi(\vec{r}, \vec{R}) = \sum \psi(\vec{r}_i, \vec{R}) \quad \vec{r} \equiv \{\vec{r}_i\}$$

$$H = T_h + T_e + V_m + V_{ee} + V_{en} \quad i = 1 \dots N e^-$$

$$= - \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \vec{\nabla}_{\alpha}^2 - \sum_i \frac{\hbar^2}{2m_e} \vec{\nabla}_i^2 \quad \vec{R} \equiv \{\vec{R}_{\alpha}\} \quad \alpha = 1 \dots M n^+$$

$$+ \frac{e^2}{2} \sum_{\alpha\beta} \frac{Z_{\alpha} Z_{\beta}}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} + \frac{e^2}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e^2 \sum_{i\alpha} \frac{Z_{\alpha}}{|\vec{R}_{\alpha} - \vec{r}_i|}$$

avoid double
countings

} Many-body
problem w/
 $(M+N)$
variables

2.1 Born-Oppenheimer (adiabatic) approximation

Assumption: Nuclei move slower than the electrons

$$M_\alpha \gg m_e \rightarrow \frac{M_{\text{Hydrogen}}}{m_e} \approx 1836$$

⇒ Neglect kinetic energy of n^+ for the e^- dynamics

$$\Rightarrow H = T_h + \underbrace{T_e + V_{ee} + V_{en} + V_{nn}}_{H_{BO}}$$

Ansatz: Adiabatic basis w/ decoupled degrees of freedom

$$\Psi(\vec{r}, \vec{R}, t) = \sum_n X_n(\vec{R}, t) \psi_n^R(\vec{r})$$

e⁻ feel
 nuclear potential

$$H_{BO} \Psi(\vec{r}, \vec{R}, t) = \sum_n X_n(\vec{R}, t) \underbrace{H_{BO} \psi_n^R(\vec{r})}_{\epsilon_n^{BO} \psi_n^R(\vec{r})}$$

nuclear wavefunction electronic wavefunction
 nuclei are static w/ respect to e^-

⇒ $\vec{\nabla}_e$ only acts on Ψ , no $\vec{\nabla}_\alpha$

Influence of the nuclear dynamics on the electrons.

$$0 = (\mathrm{i}\hbar\partial_t - H) \Psi(\vec{r}, \vec{R}, t) = (\mathrm{i}\hbar\partial_t - T_n - H_{\text{BO}}) \Psi(\vec{r}, \vec{R}, t)$$

$$= \sum_{n'} \underbrace{(\mathrm{i}\hbar\partial_t - T_n)}_1 - \underbrace{\varepsilon_{n'}^{\text{BO}}}_2 X_{n'}(\vec{R}, t) \underbrace{\psi_{n'}^{\vec{R}}(\vec{r})}_3$$

2] Nuclear kinetic energy term acts on the e^- wavefunctions

$$\sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \vec{\nabla}_{\alpha}^2 \left(X_{n'}(\vec{R}, t) \psi_{n'}^{\vec{R}}(\vec{r}) \right)$$

Evaluate in e^- wavefunction

$$\int d\vec{r} \psi_m^{\vec{R}*}(\vec{r}) \times \Rightarrow \text{yields: } \int d\vec{r} \psi^* \psi = S_{mm}$$

$$\sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \left[\vec{\nabla}_{\alpha}^2 X_{n'}(\vec{R}) \underbrace{\langle \psi_m | \psi_{n'} \rangle}_{+ 2 \vec{\nabla}_{\alpha} X_{n'}(\vec{R}) \cdot \underbrace{\langle \psi_m | \vec{\nabla}_{\alpha} | \psi_{n'} \rangle}_{+ X_{n'}(\vec{R}) \underbrace{\langle \psi_m | \vec{\nabla}_{\alpha}^2 | \psi_{n'} \rangle}} \right]$$

$\rightarrow 0$ for BO approximation

\approx Transition matrix elements between e^- states

\rightarrow If zero, e^- and n^+ dynamics are adiabatically decoupled

$$1] \int d\vec{r} \gamma_m^{\vec{R}^*}(\vec{r}) \times \text{yields}$$

$$\sum_{n'} \underbrace{\langle \gamma_m | \gamma_{n'} \rangle}_{S_{mn'}} i\hbar \partial_{\vec{r}} \chi_{n'}(\vec{R}, t)$$

$$3] \int d\vec{r} \gamma_m^{\vec{R}^*}(\vec{r}) \times \text{yields}$$

$$\sum_{n'} \langle \gamma_m | \gamma_{n'} \rangle \Sigma_m^{\text{BO}} \chi_{n'}(\vec{R}, t)$$

$$1+2+3: 0 = (i\hbar \partial_{\vec{r}} + \sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \vec{\nabla}_{\alpha}^2 - \epsilon_m^{\text{BO}}) \chi_m(\vec{R}, t)$$

depends only on nuclear kinetic energy
and a constant term from the e^- system.

Approximation holds well for semiconductors & insulators,

where $E_{\text{gap}} \gg$ lattice vibration energy,
but also for a broad variety of metals.

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

↪ add to energy eigenvalue

We are therefore left to solve:

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

kinetic energy

e^-e^- Coulomb
interaction

static periodic
background, treat as
external single-particle
potential

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

↑
only relevant when comparing
energies between different
structural configurations

Still have a $3N$ variable many-body problem of interacting
 e^-
in a fixed potential of nuclei.

Two approach:

a) Wave-function methods to determine

ψ explicitly

(Hartree, Hartree-Fock approximation,
configuration interaction, ...)

↪ single-particle wfs

or Quantum Monte Carlo to sample the many-body wf directly

b) Density functional theory

2.2 Wave-function methods

Idea: Use (Ritz) variational principle to minimize the energy

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \geq E_0 \quad (\text{ground-state energy})$$

Assumption: Minimizing \uparrow will give a good approximation of the ground-state wavefunction.

Ansatz: "Hartree approximation"

Approximate many-body wavefunction w/ a product of "single-particle orbitals"

$$\Psi(\vec{r} = \{\vec{r}_i\}) = \prod_{i=1}^N \phi_i(\vec{r}_i) = \phi_1(\vec{r}_1) \dots \phi_N(\vec{r}_N)$$

w/ $\int d\vec{r}_i \phi_i^*(\vec{r}_i) \phi_i(\vec{r}_i) = 1$

Problem: doesn't account for

Normalized

Pauli exclusion principle or spin

"Hartree-Fock approximation": Approximate many-body wavefunction as a Slater determinant

$$\Psi(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \text{spatial} & \text{spin} \\ \downarrow & \downarrow \\ \phi_1(\vec{r}_1) \chi_1(\varepsilon_1) & \dots \phi_N(\vec{r}_1) \chi_N(\varepsilon_1) \\ \vdots & \ddots \quad \ddots \quad \vdots \\ \phi_1(\vec{r}_N) \chi_1(\varepsilon_N) & \dots \phi_N(\vec{r}_N) \chi_N(\varepsilon_N) \end{vmatrix}$$

If two states are the same: $(\vec{r}_i, \varepsilon_i) = (\vec{r}_j, \varepsilon_j)$

\Rightarrow two rows or columns are identical $\Rightarrow \det = 0$

Pauli principle ✓

Hartree approximation

$$H = -\frac{\hbar^2}{2m_e} \sum_i \vec{\nabla}_i^2 - e^2 \sum_{i\alpha} \frac{Z_\alpha}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{e^2}{2} \sum_{ij} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$\langle \Psi_H | H | \Psi_H \rangle = -\frac{\hbar^2}{2m_e} \left[\sum_i \underbrace{\int d\vec{r}_i \phi_i^*(\vec{r}_i) \phi_i(\vec{r}_i)}_{1} \right] \underbrace{- \sum_i \int d\vec{r}_i \phi_i^*(\vec{r}_i) \vec{\nabla}_i^2 \phi_i(\vec{r}_i)}_{1} - \underbrace{\dots - \sum_i \int d\vec{r}_N \phi_N^*(\vec{r}_N) \phi_N(\vec{r}_N)}_{1}$$

$\Psi_H = \phi_1(\vec{r}_1) \dots \phi_N(\vec{r}_N)$
 $\Psi_H^* = \int d\vec{r}_1 \dots \int d\vec{r}_N$

$$+ \int d\vec{r}_i \left[\sum_i \phi_i^*(\vec{r}_i) \phi_i(\vec{r}_i) \right] \sum_{\alpha} \frac{(-e^2) Z_{\alpha}}{|\vec{R}_{\alpha} - \vec{r}_i|}$$

↓
 \vec{r}
 ↓
 \vec{r}
 ↓
 \vec{r}
 ↓
 $n_i(\vec{r})$
 ↓
 $n(\vec{r})$

↓
 \vec{r}
 ↓
 \vec{r}^1
 ↓
 \vec{r}^1
 ↓
 $n_j(\vec{r})$
 $V_{ext}(\vec{r})$

$$+ \frac{1}{2} \sum_i \int d\vec{r}_i \phi_i^*(\vec{r}_i) \phi_i(\vec{r}_i) e^2 \sum_{i \neq j} \int d\vec{r}_j \frac{\phi_j^*(\vec{r}_j) \phi_j(\vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}$$

↓
 \vec{r}
 ↓
 \vec{r}
 ↓
 \vec{r}
 ↓
 $n_i(\vec{r})$

↓
 \vec{r}_1
 ↓
 \vec{r}
 ↓
 \vec{r}^1
 ↓
 $V_H^i(\vec{r})$

Total energy:

$$\epsilon_H = \langle \Psi_H | H | \Psi_H \rangle = -\frac{\hbar^2}{2m_e} \sum_i \int d\vec{r} \phi_i^*(\vec{r}) \vec{\nabla}^2 \phi_i(\vec{r})$$

kinetic term

$$+ \int d\vec{r} n(\vec{r}) V_{ext}(\vec{r})$$

external potential

$$+ \frac{1}{2} \sum_i \int d\vec{r} n_i(\vec{r}) V_H^i(\vec{r})$$

classical
electrostatic Coulomb
energy "Hartree energy"

Now, we minimize the energy

$$\frac{\delta E_H[\phi_i]}{\delta \phi_i(\vec{r})} = 0 \quad \text{for all } i$$

This is a functional derivative

$$\frac{\delta F[f(x)]}{\delta f(y)} = \lim_{\epsilon \rightarrow 0} \frac{F[f(x) + \epsilon \delta(x-y)] - F[f(x)]}{\epsilon}$$

For example: $F[f(x)] = \int dx f(x) K(x)$

$$\Rightarrow \frac{\delta F[f(x)]}{\delta f(y)} = \int dx \lim_{\epsilon \rightarrow 0} \frac{f(x) + \epsilon \delta(x-y) - f(x)}{\epsilon} K(x)$$

$$= \int dx \delta(x-y) K(x) = K(y)$$

Variation (Exercise in CMT1) yields "Hartree equation"

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

Hartree-Fock approximation

Same procedure as for Hartree approx (inserting Slater determinant):

Total energy of HF:

$$E_{HF} = \langle \Psi_{HF} | H | \Psi_{HF} \rangle =$$

$$\Psi_{HF} = \frac{1}{\sqrt{N!}} | \dots \rangle$$

orbital & positions
are switched

$$= E_H - \frac{e^2}{2} \sum_{ij} S_{x_i x_j} \int d\vec{r} \int d\vec{r}' \frac{\phi_i^*(\vec{r}) \phi_j^*(\vec{r}') \phi_i(\vec{r}') \phi_j(\vec{r})}{|\vec{r} - \vec{r}'|}$$

exchange energy

quantum-mechanical result from
Pauli principle

Reduces the total energy w/ respect to
the classical result

Variation of the single-particle orbitals

$$\frac{\delta \epsilon_{HF}[\phi_i]}{\delta \phi_i(\vec{r})} = 0$$

yields the Hartree-Fock equations

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

↓ $\underbrace{\qquad\qquad\qquad}_{H_{BO}}$ ↓ ↓ $\equiv V_{ext}$
 $= 0$ constant

- a) Hartree approximation $\Psi(\vec{r}) = \prod_{i=1}^N \phi_i(\vec{r}_i)$
- b) Hartree-Fock approx: $\Psi(\vec{r}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1 & \dots & \dots \\ \vdots & \ddots & \end{vmatrix}$

$$\langle \Psi_H | H | \Psi_H \rangle$$

$$\epsilon_{HF} = \epsilon_A + \text{exchange term}$$

Variation of the single-particle orbitals $\frac{\delta \epsilon_{HF} [\phi_i]}{\delta \phi_i} = 0$
 yields the Hartree-Fock equations

$$\begin{aligned}
 & \left[\frac{-\hbar^2}{2m} \nabla^2 + V_{ext}(\vec{r}) + V_H(\vec{r}) \right] \phi_i(\vec{r}) \\
 & - \frac{e^2}{2} \sum_j S_{x_i x_j} \int d\vec{r}' \frac{\phi_j^*(\vec{r}') \phi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \phi_i(\vec{r}) \\
 & = \epsilon_i \phi_i(\vec{r})
 \end{aligned}$$

N coupled & nonlinear integro-differential equations

because the exchange energy contains a nonlocal potential
 (acts on ϕ_i at all \vec{r}')

Solve using an iterative process : self-consistent field (scf) method

(i) Given initial conditions for ϕ ; (e.g. atomic orbitals)

(ii) Compute potential energies

↷ (iii) Compute ϕ ; from the HF equation

(iv) Recompute potential energies from new single-particle orbitals

(v) Iterate until convergence

Problems of wave-function methods

► Complexity of equations grows exponentially w/N

► Many-body wf is a complicated object

$\Psi(\vec{r})$ if we sample this variable w/ q points

$\frac{1}{N}$

$\Rightarrow q^{3N}$ values have to be stored

$$q = 3 \Rightarrow N = 10 \Rightarrow 3^{3 \cdot 10} \approx 10^{15}$$

$$N = 100 \Rightarrow 3^{3 \cdot 100} \approx 10^{150}$$

$$\sim 1000 \Rightarrow 3^{3 \cdot 1000} \approx 10^{1500}$$

Nowadays $N \approx 10 - 100$

Baryons $\sim 10^{80}$

Approach: Many quantities of interest (energy, density, correlation fcts.) depend only on a small number of variables

explicitly:

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

↑ explicitly depends only on $\vec{r}_1 \rightarrow$ lot of redundancy in the many-body WFs.

\Rightarrow Avoid Ψ directly and compute

$n(\vec{r})$ or ϵ directly. \Rightarrow DFT

2.3 Hohenberg-Kohn theorems Walter Kohn Nobel Prize 1998

For any system of interacting particles in an external potential:

Theorem 1: The external potential V_{ext} is uniquely determined by the ground-state particle density $n_0(\vec{r})$ up to an additive constant.

Corollary 1: Since the Hamiltonian is thus fully determined, all properties of the system are uniquely determined by the ground-state density.

Theorem 2: An energy functional $E[n]$ exists for any external potential V_{ext} , where the exact ground-state energy of the system is given by the global minimum of $E[n]$, and the density that minimizes it is the ground-state density.

Corollary 2: The functional $E[n]$ alone is sufficient to determine the exact ground-state energy and density.

Hohenberg & Kohn "Inhomogeneous electron gas" 1964

Proofs (following Levy PNAS 1979 "constrained search")

Start w/ variational principle

$$E_{\text{gs}} = \min_{\Psi} \left[\langle \Psi | T_e + V_{ee} + V_{\text{ext}} | \Psi \rangle \right]$$

independent of Ψ

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

1. Minimize over Ψ
that give the same n

2. Minimize over n
to find the global minimum

$F[n]$ Levy-Lieb functional

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

$\hookrightarrow E[n]$

This is the first part of theorem 2: $\exists E[n]$, whose minimum is the ground-state energy

But is the $n(\vec{r})$ that minimizes it really the gs- n : $n_g(\vec{r})$?

$$F[n] = \min_{\Psi \rightarrow n} [\langle \Psi | T_e + V_{ee} | \Psi \rangle] \equiv \underbrace{\langle \Psi_n | T_e + V_{ee} | \Psi_n \rangle}_{\text{if that minimizes } F[n]}$$

Variational principle:

$$\epsilon_{gs} = \langle \Psi_{gs} | T_e + V_{ee} + V_{ext} | \Psi_{gs} \rangle$$

$$\leq \underbrace{\langle \Psi_{n_0} | T_e + V_{ee} + V_{ext} | \Psi_{n_0} \rangle}_{\text{↑}}$$

we don't know yet whether Ψ that give us n_0 are Ψ_{gs}

Subtract ext. potential on both sides $\Rightarrow \langle \Psi_{gs} | \Psi_{gs} \rangle = 1$

$$\Rightarrow \langle \Psi_{gs} | T_e + V_{ee} | \Psi_{gs} \rangle \leq \underbrace{\langle \Psi_{n_0} | T_e + V_{ee} | \Psi_{n_0} \rangle}_{\left\{ \begin{array}{l} \Psi_{gs} = \Psi_{n_0} \\ \Psi_{n_0} \text{ minimizes } F[n] \end{array} \right.} = \langle \Psi_{n_0} | \Psi_{n_0} \rangle$$

$$\Rightarrow \langle \Psi_{gs} | T_e + V_{ee} | \Psi_{gs} \rangle \geq \langle \Psi_{n_0} | T_e + V_{ee} | \Psi_{n_0} \rangle$$

$$\begin{aligned}
 \text{Therefore: } \mathcal{E}_{gs} &= \langle \Psi_{n_0} | T_e + V_{ee} + V_{ext} | \Psi_{n_0} \rangle \\
 &= \langle \Psi_{n_0} | T_e + V_{ee} | \Psi_{n_0} \rangle + \int d\vec{r} n_0(\vec{r}) V_{ext} \\
 &= F[n_0] + \int d\vec{r} n_0(\vec{r}) V_{ext}(\vec{r}) \\
 &\equiv \min_n [F[n] + \int d\vec{r} n(\vec{r}) V_{ext}(\vec{r})]
 \end{aligned}$$

$\Rightarrow \mathcal{E}[n]$ is indeed minimized by gs-density

□ Theorem 2

Now: Variational equation for $n(\vec{r})$

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

Lagrange multiplier for
particle number conservation

$$\Rightarrow \left. \frac{\delta F[n]}{\delta n(\vec{r})} \right|_{n=n_0} + V_{ext}(\vec{r}) - \mu = 0$$

$$\Leftrightarrow V_{ext}(\vec{r}) = \mu - \left. \frac{\delta F[n]}{\delta n(\vec{r})} \right|_{n=n_0} \quad \square \text{Theorem 1}$$

Ground-state density n_0

\Rightarrow determines the external potential V_{ext} up to an additive constant.

2.4 Kohn-Sham theory

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

$$= \min_{\Psi \rightarrow n} \left\langle \Psi \left| -\frac{\hbar^2}{2m} \sum_i \vec{\nabla}^2 \right| \Psi \right\rangle \text{ Kinetic energy}$$

$$+ \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{| \vec{r} - \vec{r}' |} E_H[n] \text{ Hartree energy}$$

$$+ \tilde{E}_{xc}[n] \text{ exchange-correlation energy}$$

Need a better approximation of the kinetic energy

We know: Kinetic energy of non-i.a. system looks like

Approach: Approximate T with a hypothetical non-i.a. system that has the same $n(\vec{r})$ as the i.a. system. \Rightarrow Kohn-Sham auxiliary system

Full i.a. system :

$$E[n] = T_0[n] + \int d\vec{r} n(\vec{r}) \left[V_{ext}(\vec{r}) + \frac{1}{2} V_H[n(\vec{r})] \right] +$$

ext. potential Hartree potential

kinetic energy

of non-i.a. system
w/ same density

$\underbrace{\tilde{E}_{xc}[n] + (T[n] - T_0[n])}_{\text{exchange correlation energy}} + E_{xc}[n]$

Auxiliary non-i.a. system

$$E_n[n] = T_0[n] + \int d\vec{r} n(\vec{r}) V_{\text{eff}}(\vec{r})$$

↑
choose V_{eff} so that $n(\vec{r})$
for non-i.a. & i.a. systems
are the same

Vary the energy w/rsped to $n(\vec{r})$)

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

Full i.a. System :

$$\frac{\delta T_0[n]}{\delta n(\vec{r})} + V_{\text{ext}}(\vec{r}) + V_H[n(\vec{r})] + \frac{\delta E_{\text{xc}}[n]}{\delta n(\vec{r})} = \mu$$

Non-i.a. system :

$$\frac{\delta T_0[n]}{\delta n(\vec{r})} + V_{\text{eff}}(\vec{r}) = \mu$$

Eliminate T_0 term and determine the effective potential as

$$V_{\text{eff}}(\vec{r}) = V_{\text{ext}}(\vec{r}) + V_H[n(\vec{r})] + \underbrace{\frac{\delta E[n]}{\delta n(\vec{r})}}_{V_{\text{xc}}[n]} + \text{const.}$$

Now: Compute the gs density $n_g(\vec{r})$ of the non-i.a. system w/ single-particle Schrödinger equation

\Rightarrow Kohn-Sham equations

$$\left[-\frac{\hbar^2}{2m} \vec{\nabla}^2 + V_{\text{eff}}[n(\vec{r})] \right] \phi_n(\vec{r}) = \epsilon_n \phi_n(\vec{r})$$

Kohn-Sham orbital
Kohn-Sham energies

$$n(\vec{r}) = \sum_{n, \text{ occupied}} \phi_n^*(\vec{r}) \phi_n(\vec{r}) \Rightarrow V_{\text{eff}}[n(\vec{r})]$$

Sum over N occupied
Kohn-Sham states

Equations have to be solved self consistently (iteratively).

Overall, similar to HF equations, but w/ effective local single-particle potential.

Total energy expressions

$$\text{Kohn-Sham system: } \mathcal{E}_{KS} = T_0 + \int d\vec{r} n(\vec{r}) V_{\text{eff}}(\vec{r}) \\ = T_0 + \int d\vec{r} n(\vec{r}) \left[V_{\text{ext}}(\vec{r}) + e^2 \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \right] \\ + V_{xc}[n]$$

$$= \sum_{\substack{n \\ \text{occupied}}} \mathcal{E}_n \quad \text{Kohn-Sham energies}$$

Full i.a. system:

$$\mathcal{E} = T_0 + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r}) + \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')} {|\vec{r} - \vec{r}'|} \\ + E_{xc} \\ = \sum_{n, \text{occupied}} \mathcal{E}_n[n] - \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')} {|\vec{r} - \vec{r}'|} \\ + E_{xc}[n] - \int d\vec{r} n(\vec{r}) \frac{\delta E_{xc}[n]}{\delta n(\vec{r})}$$

If we find a good approximation for $E_{xc}[n]$, we can compute $n_0(\vec{r})$, \mathcal{E}_0 and any observable we know as a functional of n .

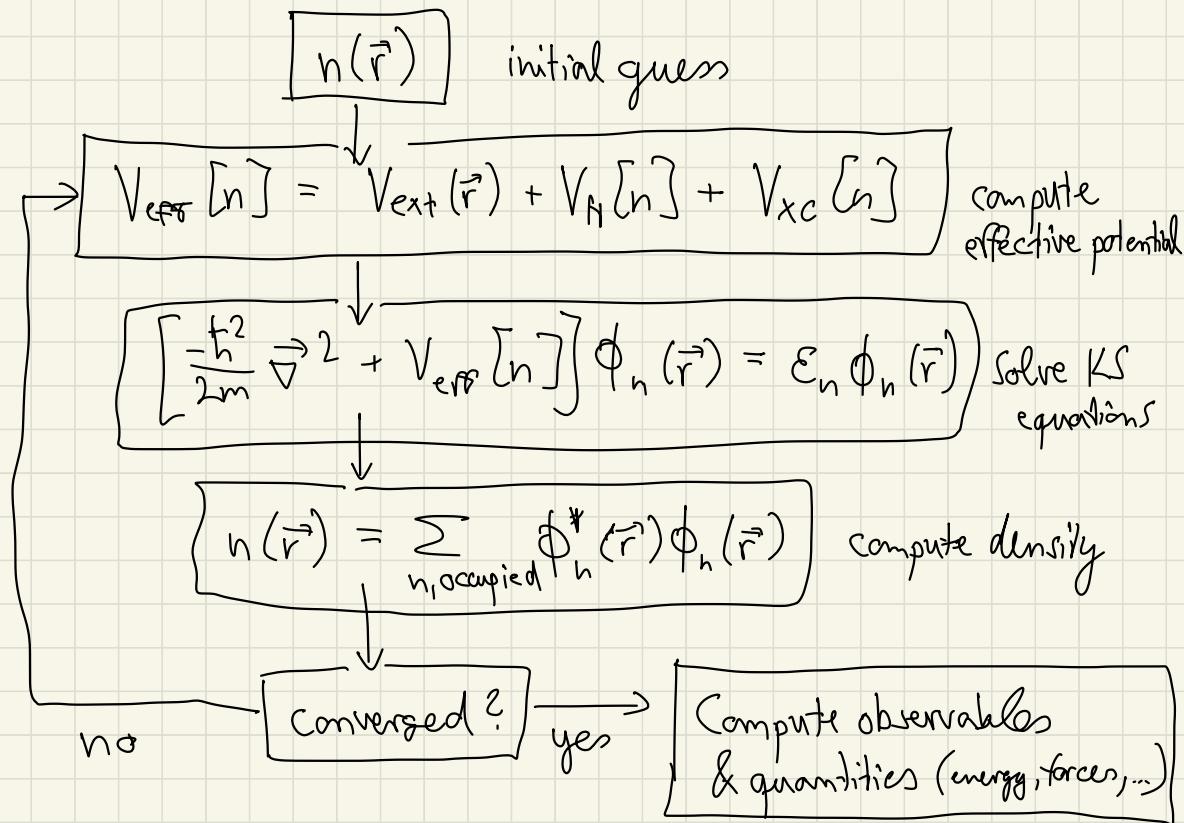
Summary : KS-theory

i.a. system $\Sigma[n] \rightarrow E_\sigma[n]$ non-i.a. system
w/ same density,
where we can compute
kinetic energy exactly.

Assumption: $T - T_\sigma$ small

$\Rightarrow n_\sigma(\vec{r})$ gs-density can be computed w/ single-particle KS-equations.

Self-consistent scheme



2.5 Local density approximation (LDA)

$$\begin{aligned} E_{xc} &= \tilde{\Sigma}_{xc} + T[n] - T_0[n] \\ &= \langle \psi_{gs} | V_{ee} | \psi_{gs} \rangle - E_{\text{Hartree}} \\ &\quad + \langle \psi_{gs} | T | \psi_{gs} \rangle - \langle \psi_{KS} | T | \psi_{KS} \rangle \end{aligned}$$

Full ground-state
many-body wf.

Kohn-Sham orbitals
(single-particle wf)
Slater determinant

Same procedure as for Thomas-Fermi-Dirac theory,
but only for the xc -part of the energy.

$$E_{xc}[n] = \int d\vec{r} n(\vec{r}) \underset{\uparrow}{\varepsilon_{xc}[n(\vec{r})]}$$

exchange-correlation energy
density of the homogeneous
electron gas w/ density $n(\vec{r})$

Remember: $E_{xc}[n]$ is universal, depends only on the type
of particle \Rightarrow same $E_{xc}[n]$ as for the
homogeneous electron gas

$$\mathcal{E}_{xc}[n] = \mathcal{E}_x[n] + \mathcal{E}_c[n]$$

As for the Thomas-Fermi-Dirac theory, known exactly from HF approximation for Jellium model

$$\mathcal{E}_x[n] = C_{ex} n^{1/3}$$

Can be computed w/ great accuracy w/ Quantum Monte Carlo methods parametrization in terms of n are available

LDA works (surprisingly) well for a great variety of systems, but also has many deficiencies. (bond lengths & bond gaps underestimated)

→ More sophisticated methods include gradient & higher-order derivatives of the density

"generalized gradient approximation (GGA)"

2.6 Extension of DFT to magnetic systems

For open-shell atoms & spin-polarized system, we need to extend the formalism to accommodate spin-dependent densities.

Need: Expression for the spin density

Hohenberg-Kohn Energy functional :

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

$$\text{Spin-DFT: } E[n, \vec{m}_s] = F[n, \vec{m}_s] + \int d\vec{r} n(\vec{r}) V_{ext}(\vec{r})$$

$$+ \int d\vec{r} \vec{m}_s(\vec{r}) \cdot \vec{B}_{ext}(\vec{r})$$

↑
spin density

In the collinear case ($\vec{m}_s \parallel \vec{B} \parallel \hat{z}$) :

$$m_{s,z}(\vec{r}) = n_\uparrow(\vec{r}) - n_\downarrow(\vec{r})$$

$$n(\vec{r}) = n_\uparrow(\vec{r}) + n_\downarrow(\vec{r})$$

⇒ Standard in most DFT codes

Further extensions to spin-DFT: relativistic current DFT

$$E[\gamma^{\mu}] = F[\gamma^{\mu}] + \frac{e}{c} \int d\vec{r} \gamma^{\mu}(\vec{r}) A_{ext}^{\mu}$$

Need to include spin density into the exchange-correlation functional: LSDA

$$E_{xc}[n_p, n_j] = \int d\vec{r} n(\vec{r}) \times E_{xc}[n_{\uparrow}(\vec{r}), n_{\downarrow}(\vec{r})]$$

\times E_{xc} - energy of the homogeneous spin-polarized electron gas

\Rightarrow spin-dependent xc -potential
in the Kohn-Sham equations

$$V_{xc\uparrow,\downarrow} = \frac{\delta E_{xc}[n]}{\delta n_{\uparrow,\downarrow}(\vec{r})}$$

Summary of chapter 2

- Goal: Compute physical properties of materials
 - Problem: many e^- and n^+ interacting through the Coulomb interaction
- \Rightarrow Born-Oppenheimer approximation separates e^- and n^+ degrees of freedom & dynamics, but the e^- many-body wavefunction is still practically impossible to compute

IS HK theorems: Ground-state electron density, $n_0(\vec{r})$
central quantity of interest,
"in principle" enough to determine all
properties of the solid

□ KS-equations: Practical method to compute gs-density
 $n_0(\vec{r})$ by solving a non-i.a. Hartree
problem with the same gs-density as the
i.a. system.

Reason: Easy to compute the kinetic energy
of an i.a. system & good
approximation of i.a. kinetic energy.

\Rightarrow LDA/LSDA approximate "beyond Hartree" effects
of the e^-e^- interaction by a local expression
derived from the homogeneous e^- gas.

Now:

- How to solve the Kohn-Sham equations?
(basis sets, pseudopotential)
- Approximations of E_{xc} beyond L(S)DA.
GGA, exact exchange, DFT+U, hybrid functionals,
Selfinteraction correction

3 Computational aspects of DFT

3.1 Basis sets

$$\left[\frac{-\hbar^2}{2m} \vec{\nabla}^2 + V_{\text{eff}}[\rho(\vec{r})] \right] \phi_n(\vec{r}) = \varepsilon_n \phi_n(\vec{r})$$

| effective potential | KS energies | KS orbitals

Ansatz: Expand Kohn-Sham orbitals in some basis set

$$H|\phi_n\rangle = \varepsilon_n |\phi_n\rangle \quad \text{with} \quad |\phi_n\rangle = \sum_{\alpha} c_{\alpha}^n |X_{\alpha}\rangle$$

$$\Rightarrow \sum_{\alpha} \langle X_{\beta} | H | X_{\alpha} \rangle c_{\alpha}^n = \varepsilon_n \sum_{\alpha} \langle X_{\beta} | X_{\alpha} \rangle c_{\alpha}^n$$

evaluate by
multiplying
 $\langle X_{\beta} |$ from left
side

$$\Rightarrow \sum_{\alpha} \underbrace{| H_{\beta\alpha} |}_{\text{Hamilton matrix}} c_{\alpha}^n = \varepsilon_n \sum_{\alpha} \underbrace{| S_{\beta\alpha} |}_{\text{overlap matrix}} c_{\alpha}^n$$

Generalized linear eigenvalue problem: $\underbrace{A}_{B \neq 0} \vec{x} = \lambda \vec{x}$

Using an orthogonal basis $S_{\beta\alpha} = S_{\alpha\beta}$

\Rightarrow reduces to linear eigenvalue problem

$$\sum_{\alpha} H_{\beta\alpha} c_{\alpha}^n = \varepsilon_n c_{\beta}^n \Rightarrow \text{General: } (\underbrace{H}_{=} - \varepsilon_n \underbrace{S}_{=}) \vec{c}_n = 0$$

- Full solution scales with D^3 (D dimension of matrix
= basis-set dimension)
- Full matrix diagonalization
 $D \sim N$ (# electrons) (LAPACK, BLAS)
- For $D \gg N \rightarrow$ look at $N+x$ lowest eigenvalues/
energies
⇒ Iterative matrix diagonalization

How to choose the basis?

Criteria:

- 1) Bias
- 2) Completeness
- 3) Simplicity
- 4) Efficiency

Classes of basis sets:

- (i) Plane waves (unbiased, simple, complete, not very efficient)
- (ii) Augmented function: Augmented plane waves (APW)
Muffin-tin orbitals (MTO)
(biased, incomplete, complicated, highly efficient)
- (iii) Local orbitals : Linear combination of atomic orbitals (LCAO),
Gaussian orbitals due to dealing w/
(chemically intuitive, mixture of both, allow $O(N)$ scaling)

70s - 80s first plane-wave methods developed

> ^{Late} 90s DFT booms due to computer power & efficient methods

Sparse matrix: $n \times n$
 $n \begin{pmatrix} \cdot & \cdot & \cdot \end{pmatrix}$

but only n elements are nonzero

3.1 Basis sets

Kohn-Sham equations

$$\left(\frac{-\hbar^2}{2m} \vec{\nabla}^2 + V_{\text{eff}}[n(\vec{r})] \right) \phi_n(\vec{r}) = \varepsilon_n \phi_n(\vec{r})$$

↓
 effective
 single-particle
 potential

↓
 Kohn-Sham orbitals
 ↘ KS energies

$$H |\phi_n\rangle = \varepsilon_n |\phi_n\rangle, |\phi_n\rangle = \sum_{\alpha} c_{\alpha}^n |x_{\alpha}\rangle$$

$$\Rightarrow \sum_{\alpha} H_{\beta\alpha} c_{\alpha}^n = \varepsilon_n \sum_{\alpha} S_{\beta\alpha} c_{\alpha}^n$$

↓
 Hamilton matrix ↓
 Overlap matrix
 $\equiv S_{\alpha\beta}$

$$\Rightarrow (\underline{H} - \varepsilon_n \underline{S}) \vec{c}_n = 0$$

Types of basis sets:

- Plane waves
- Augmented functions
- Local orbitals

Challenge: Which basis set for which materials?

Variety of elements & shell structures (s, p, d, f) makes it hard to find a "one-size-fits-all" basis set.

Chemical bonding is done by the outermost shells

⇒ Divide \mathbb{E} in two groups

(i) Core states: localized, atomic like

(ii) Valence states: delocalized, Bloch waves,

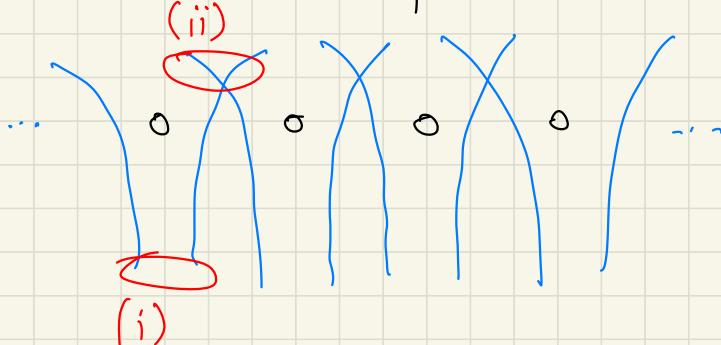
determine physical properties & bonding

→ How to describe these different states w/ same basis set?

Look at $V_{eff}(\vec{r})$ for different regions:

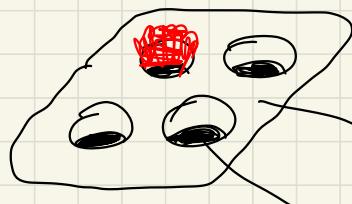
(i) Deep Coulomb potential close to nuclei

(ii) Smooth & flat potential in interstitial region



Two approaches:

1) muffin-tin approximation

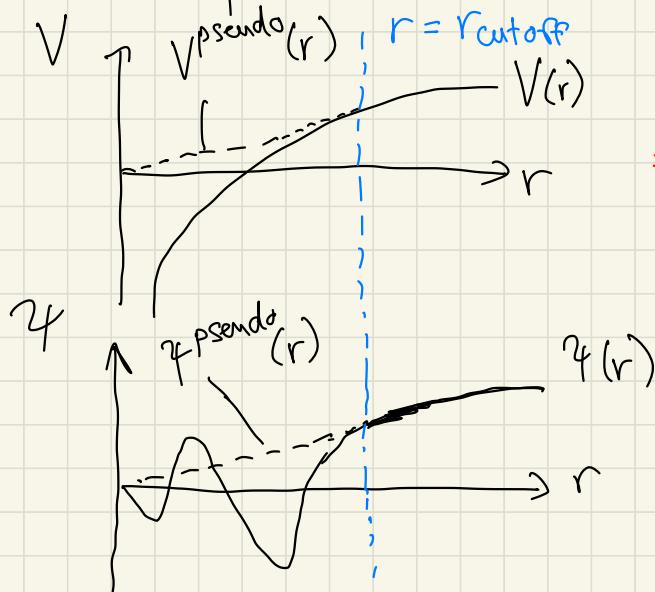


interstitial region: constant potential
around nucleus: spherically symmetric potential

\Rightarrow Create augmented basis functions as approximate solutions to the muffin-tin potential

2) Pseudopotential approximation

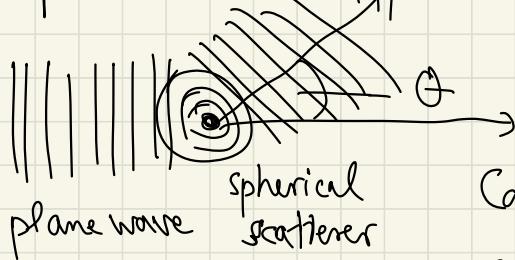
Deep potential well around nuclei replaced w/
smooth potential that has the same scattering properties



In exercise: POTCAR
 $\#\text{valence } \epsilon: \text{ZVAL}$

\Rightarrow "Pseudo" wavefunctions shall match the real atomic wavefunctions beyond a certain cutoff radius.

Scattering properties should be reproduced by V^{pseudo} & V^{pseudo}



Construct $V^{\text{pseudo}}(\vec{r})$

so that scattering cross-section & phase shift of "real" $V(\vec{r})$ are reproduced

3.2 Augmented basis sets

Start from the muffin-tin approximation : Construct wavefunctions in core and interstitial regions

In core region! Spherical potential as in hydrogen atom

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \right] \phi(\vec{r}) = \epsilon \phi(\vec{r})$$

with $\phi(\vec{r}) \xrightarrow[\text{polar coordinates}]{\quad} \phi_{nlm}(r) \propto R_{nl}(r) Y_{lm}(\theta, \varphi)$

Inside muffin-tin

$$\Rightarrow \left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) \right] r R_{nl}(r)$$

$$= E_{nl} r R_{nl}(r)$$

m : projection of
 $l, -l, \dots, 0, \dots, l$

main quantum number } total angular momentum } in $R_{nl}(r)$
nodes } $n-l-1$

Create basis function in core region as

$$\chi_{\alpha}^{\text{core}}(\vec{r}, \varepsilon) = \sum_{nlm} C_{\alpha l m}(\varepsilon) R_{nl}(r) Y_{lm}(\theta, \varphi),$$

where $C_{\alpha l m}$ are determined by matching conditions at the tin boundary. (w/ scattering properties: cross section, phase shift)

Interstitial region: Constant potential

Expand our basis functions $\chi_{\alpha}^{\text{inter}}(\vec{r}, \varepsilon)$

Plane waves

→ Augmented plane waves (APWs)

Atom-centered

Hankel functions

→ Muffin-tin orbitals
(MTOs)

$$(h_{lm} \sim r^{-(l+1)} \chi_{lm})$$

Together: $|\psi_n\rangle = \sum_{\alpha} C_{\alpha}^n |\chi_{\alpha}\rangle,$

$$|\chi_{\alpha}\rangle = \begin{cases} \chi_{\alpha}^{\text{inter}}(\vec{r}, \varepsilon), & \vec{r} \in \text{interstitial} \\ \chi_{\alpha}^{\text{core}}(\vec{r}, \varepsilon), & \vec{r} \in \text{muffin-tin} \end{cases}$$

Remarks: \square R_{nl} needs to be computed for energy of the Kohn-Sham wavefunction

$$\Rightarrow (\hat{H} - \varepsilon_n) \vec{C}_n = 0 \text{ becomes}$$

$$\stackrel{M(\varepsilon_n)}{=} \vec{C}_n = 0$$

\swarrow depends nonlinearly
on ε_n

Two approaches: (i) Linearize energy dependence of R_{nl} around some average energy

\Rightarrow recover linear eigenvalue problem
(\rightarrow LAPW, LMTO)

(ii) Construct LAPW basis functions from muffin-tin potential, but use full potential in eigenvalue equation

\square R_{nl} depends on spherical potential $V(r)$

\rightarrow recalculated at every SCF step within the KS potential

3.3 Plane waves and pseudopotentials

Bloch theorem: $\exists v(\vec{r}) = v(\vec{r} + n\vec{a}_i)$

$$\Rightarrow \phi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(\vec{r})$$

direct lattice vector

Bloch wave $u_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r} + n\vec{a}_i)$

Expand in plane waves: $u_{\vec{k}}(\vec{r}) = \sum_{\vec{K}} c_{\vec{k}}(\vec{K}) e^{i\vec{K}\cdot\vec{r}}$

with $\vec{K} \cdot \vec{a}_i = 2\pi h, h \in \mathbb{Z}$

reciprocal lattice vector

Lattice periodic & we can write

$$\phi_{\vec{k}}(\vec{r}) = \frac{1}{V} \sum_{\vec{K}} e^{i(\vec{k} + \vec{K})\vec{r}} c_{\vec{k}}(\vec{K}),$$

where we limit the sum at

$$|\vec{k} + \vec{K}| \leq k_{\max}$$

→ ENCUT parameter
in INCAR

Advantage: Easy & formal way to compute the kinetic energy

$$\chi_{\vec{k}} = \frac{1}{V} e^{i\vec{k}\vec{r}} \Rightarrow \langle \chi_{\vec{k}_1} | T | \chi_{\vec{k}_2} \rangle = \frac{\hbar^2 k^2}{2m} \delta(\vec{k}_1 - \vec{k}_2)$$

Disadvantage: Works well in interstitial region, but we have oscillating, localized wavefunctions close to nucleus
 \Rightarrow high energy cutoff required
 \Rightarrow bad scaling

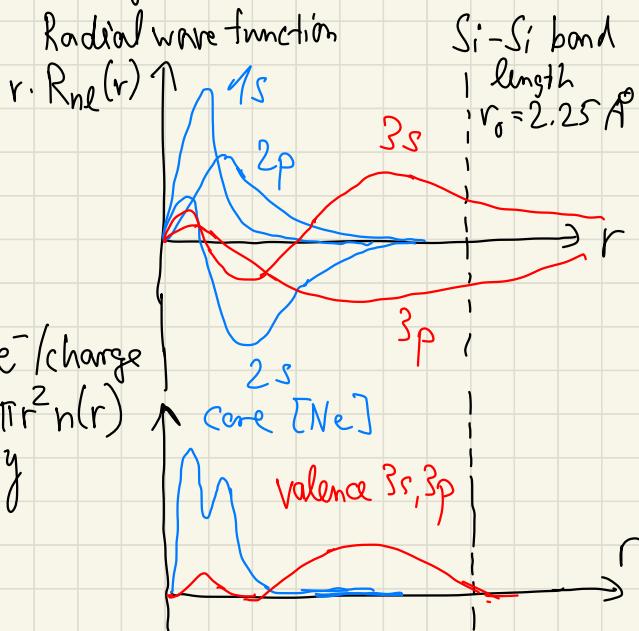
Approach: Many physical properties (chemical bonding, transport) are determined by the interstitial region

\Rightarrow Fix core e^- to resemble those of the free atom
" frozen core approximation" & match them w/ valence e^- beyond cut-off radius



$$\gamma_{\text{hem}} = \frac{R_{\text{ne}}(r)}{r} Y_{lm}(\theta, \varphi)$$

Radial e^-/charge
 $4\pi r^2 n(r)$
density



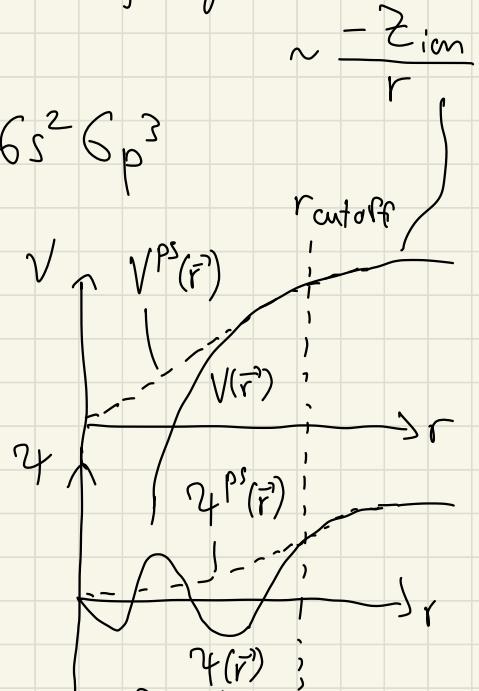
\Rightarrow Pseudopotentials try to remove / smoothen out
the oscillatory part near the core area
that require a lot of plane-wave sampling.

Becomes the more important the further you go down the
periodic table

Bi (83 e⁻) [Xe] 5d¹⁰ 6s² 6p³

\downarrow Pseudopotentials
15 e⁻ problem

Construct $\psi^{ps}(\vec{r}) = V^{ps}(\vec{r})$ so that
 $V^{ps}(\vec{r}) = \psi(\vec{r})$ for $|r| > r_{\text{cutoff}}$

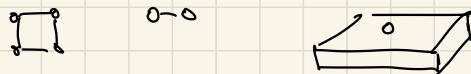


\Rightarrow Smooth & nodeless pseudo wavefunction
can be represented by a small number of plane waves.

3.4 Generation of norm-conserving pseudopotentials

Criteria for pseudopotentials:

- Softness: Allow expansion in terms of small number of plane waves
- ▷ Transferability: Allow accurate description of different electronic configurations (solids, molecules, free ions/atoms)



→ Compromise of two seemingly opposing criteria

Manual for creating pseudopotentials

1. Compute "all-electron" wavefunctions for atomic reference configuration, e.g. Si: $[Ne]3s^23p^2$ in a Kohn-Sham approach
⇒ "ab-initio norm-conserving pseudopotentials"
2. Choose a cutoff radius & construct pseudo-Wf that matches the all-electron Wf beyond $r_{\text{cutoff}} \equiv r_c$
3. Invert the Schrödinger equation to extract the pseudo potential
4. "Unscreen" the potential: get rid of Hartree & xc contributions

Step 1: Assume to be done w/ high accuracy

Step 2: Match pseudo wavefunction

- Eigenvalue of nodalless ψ^{ps} is identical to ψ^{ae}

$$H |\phi^{ae}\rangle = \epsilon^{ae} |\phi^{ae}\rangle$$



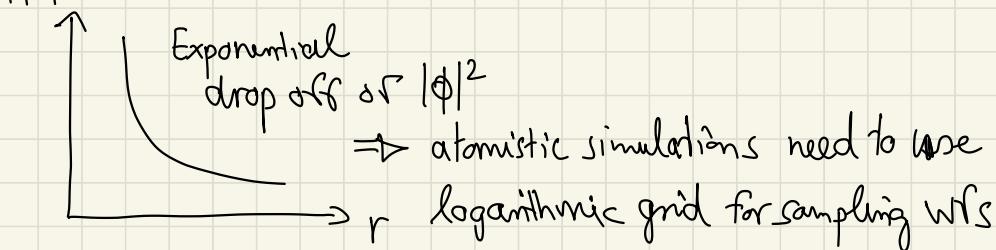
$$H^{ps} |\phi^{ps}\rangle = \epsilon^{ae} |\phi^{ps}\rangle$$

- Match radial parts of wfs:

$$R_e^{ps}(r) \stackrel{!}{=} R_e^{ae}(r), r > r_c$$



- Match logarithmic derivative of wfs:



$$\begin{aligned} \left. \frac{d}{dr} \ln [R_e^{ps}(r)] \right|_{r=r_c} &= \left. \frac{1}{R_e^{ps}(r_c)} \frac{dR_e^{ps}(r)}{dr} \right|_{r=r_c} \\ &\stackrel{!}{=} \left. \frac{1}{R_e^{ae}(r_c)} \frac{dR_e^{ae}(r)}{dr} \right|_{r=r_c} \end{aligned}$$

□ Match integrated charge densities (Norm conservation!):

$$\int_0^{r_c} dr r^2 [R_{\ell}^{ps}(r)]^2 \stackrel{!}{=} \int_0^{r_c} dr r^2 [R_{\ell}^{ae}(r)]^2$$



Why is norm conservation important?

Shaw & Harrison Phys. Rev. 163 (1967):

$$\rightarrow \frac{d}{d\epsilon} \frac{d}{dr} \ln [R_{\ell}(\epsilon, r)] \Big|_{r=r_c} = \frac{2}{[r_c R_{\ell}(\epsilon, r_c)]^2} \int_0^{r_c} dr r^2 [R_{\ell}(\epsilon, r)]^2$$

Because and \Rightarrow Also the first energy derivative for pseudo and all-electron WFs are the same.

\Rightarrow Any difference between ψ^{ps} and ψ^{ae} is of the order of $\Delta\epsilon^2$

\Rightarrow Better transferability

Softness — Transferability

$r_c = \begin{cases} \text{large} \Rightarrow V^{ps} \text{ soft} \Rightarrow \text{less transferable} \\ \text{small} \Rightarrow V^{ps} \text{ hard} \Rightarrow \text{more transferable} \end{cases}$

Step 3: Invert the radial Schrödinger equation and extract V_{ℓ}^{PS}

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2r^2} + \tilde{V}_{\ell}^{PS}(r) \right] r R_{\ell}^{PS}(r) = \underbrace{\epsilon_{\ell}}_{\text{identical to}} r R_{\ell}^{PS}(r)$$

$$\Rightarrow \tilde{V}_{\ell}^{PS}(r) = \epsilon_{\ell} - \frac{\ell(\ell+1)}{2r^2} + \frac{1}{2rR_{\ell}^{PS}(r)} \frac{d^2}{dr^2} r R_{\ell}^{PS}(r)$$

all-electron energy

Step 4: "Unscreening"

Remember: $V_{eff}[n(\vec{r})] = V_{ext}(\vec{r}) + V_H[n(\vec{r})] + V_{xc}[n(\vec{r})]$

$$n(\vec{r}) = n_C(\vec{r}) + n_V(\vec{r})$$

In Step 1, we have included all e^- , core & valence.

To be able to transfer V^{PS} to different environments, we need to subtract the effect of the valence electrons:

$$V_{\ell}^{PS}(\vec{r}) = \tilde{V}_{\ell}^{PS}(\vec{r}) - e^2 \underbrace{\int d\vec{r}' \frac{n_V(\vec{r}')}{|\vec{r}-\vec{r}'|}}_{\text{Hartree contribution of valence } e^- \text{ density}} - \underbrace{V_{xc}[n_V(\vec{r})]}_{x<- \text{potential of valence } e^- \text{ density}}$$

linear in $n(\vec{r}')$
 \Rightarrow works well

nonlinear in $n(\vec{r}')$
 \Rightarrow difficult to separate

$$\underset{xc}{V} [n_V(\vec{r}) + n_c(\vec{r})] \neq V_{xc}[n_V(\vec{r})] + V_{xc}[n_c(\vec{r})]$$

\Rightarrow Nonlinear core corrections

$$V_{\ell}^{ps}(\vec{r}) = \tilde{V}_{\ell}^{ps}(\vec{r}) - V_H[n_V(\vec{r})] - V_{xc}[n_V(\vec{r})] \\ + \delta n_c(\vec{r})$$



$$V_{xc}[n_V(\vec{r}) + \delta n_c(\vec{r})] = V_{xc}[n_V(\vec{r})]$$

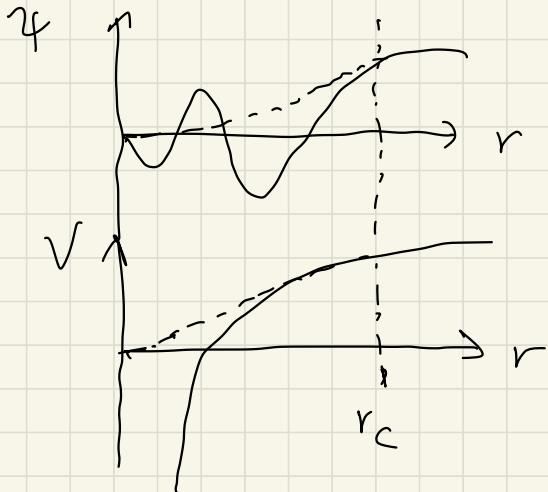
$$+ \left\{ V_{xc}[n_V(\vec{r}) + n_c(\vec{r})] - V_{xc}[n_c(\vec{r})] \right\}$$

Recap previous lecture

$$H |\phi_n\rangle = \epsilon_n |\phi_n\rangle, |\phi_n\rangle = \sum_{\alpha} c_{\alpha}^n |x_{\alpha}\rangle$$

- i) core e^-
- ii) valence e^-

- 1) Muffin-tin approximation
2) Pseudopotential - II -



$$X_{\vec{k}} = \frac{1}{V} e^{i \vec{k} \cdot \vec{r}} \Rightarrow \langle x_{\vec{k}} | T | X_{\vec{k}'} \rangle = \frac{\hbar^2 k^2}{2m} \delta(\vec{k} - \vec{k}')$$

4. Advanced methods for the exchange - correlation energy

$$E_{xc}[n] = \underbrace{E_{xc}}_T + T[n] - T_0[n]$$

contains xc-effects
"beyond Hartree"

$$= \langle \phi_{gs} | V_{ee} | \phi_{gs} \rangle - E_{\text{Hartree}}$$

$$+ \langle \phi_{qs} | T | \phi_{qs} \rangle - \langle \phi_{ks} | T | \phi_{ks} \rangle$$

full many-body
Wfs

Slater determinants
of KS orbitals

Levy - Lieb functional

$$F(h) = \min_{\phi \rightarrow h} \langle \phi | T^+ V_{ee} | \phi \rangle$$

$$\min_{\phi \rightarrow n} \langle \phi | T | \phi \rangle = \langle \phi_{ks} | T | \phi_{ks} \rangle = T_0[n]$$

$$\Rightarrow T_o[n] \leq T[n]$$

Kinetic energy of i.a. system is higher than that of the non-i.a. system.

\Rightarrow Kinetic correlations increase energy of the system

4.1. Exchange - correlation hole

Idea: Similar to an adiabatic change in thermodynamics, turn on the interaction strength adiabatically

"Adiabatic connection"

$$V_{ee} \rightarrow \lambda V_{ee}, \lambda \in [0, 1]$$

↗ non-ia. ↘ full ia.

$$H_\lambda = T + V_{\text{eff}}^\lambda + \lambda V_{ee}$$

|
 adjust V_{eff}^λ so that $n(\vec{r})$ is the gs density
 for all λ

Hohenberg-Kohn theorems: $n(\vec{r}) \longleftrightarrow V_{\text{ext}}$

uniquely determine each other

$$\lambda = 0 \quad (\rightarrow V_{\text{eff}} \text{ needs to contain full interaction}) \quad V_{\text{eff}}^0 \equiv V_{KS} = V_{\text{ext}} + V_{\text{Hartree}} + V_{XC}$$

$$\lambda = 1 \quad (\rightarrow \text{all interaction is contained in } V_{ee}) \quad V_{\text{eff}}^1 = V_{\text{ext}}$$

$$\text{We have: } \langle \phi_\lambda | H_\lambda | \phi_\lambda \rangle = E_\lambda$$

↓
 gs wavefunction
 for a given λ

$$E[h] = E_1 = E_0 + \int_0^1 d\lambda \frac{\partial}{\partial \lambda} E_\lambda$$

(*)

$$= E_0 + \int_0^1 d\lambda \langle \phi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \phi_\lambda \rangle$$

$$f(1) = f(0) + \int_0^1 dx f'(x)$$

$\underbrace{f(1) - f(0)}$

$$\frac{\partial}{\partial \lambda} \langle \phi_\lambda | H_\lambda | \phi_\lambda \rangle$$

(*)

(*) - F = $\frac{\partial E_\lambda}{\partial \lambda} = \underbrace{\langle \frac{\partial \phi_\lambda}{\partial \lambda} | H_\lambda | \phi_\lambda \rangle}_{E_\lambda \phi_\lambda} + \underbrace{\langle \phi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \phi_\lambda \rangle}_{\langle \phi_\lambda | H_\lambda | \frac{\partial \phi_\lambda}{\partial \lambda} \rangle}$

$\downarrow \quad \downarrow$

$$E_\lambda \frac{\partial}{\partial \lambda} \underbrace{\langle \phi_\lambda | \phi_\lambda \rangle}_1 = 0$$

$$= \langle \phi_\lambda | \frac{\partial H_\lambda}{\partial \lambda} | \phi_\lambda \rangle$$

single-particle potential

(*) Now: $\frac{\partial}{\partial \lambda} H_\lambda = \frac{\partial}{\partial \lambda} (T + V_{\text{eff}}^\lambda + \lambda V_{ee}) = V_{ee} + \frac{\partial V_{\text{eff}}}{\partial \lambda}$

~~$$E[h] = \underbrace{E_0 + \int d\vec{r} n(\vec{r}) V_{\text{eff}}^0(\vec{r})}_{E_0} + \int_0^1 d\lambda \langle \phi_\lambda | V_{ee} | \phi_\lambda \rangle + \int_0^1 d\lambda \langle \phi_\lambda | \frac{\partial V_{\text{eff}}}{\partial \lambda} | \phi_\lambda \rangle$$~~

(*)

 Evaluate: $\int_0^1 d\lambda \langle \phi_\lambda | \frac{\partial V_{\text{eff}}}{\partial \lambda} | \phi_\lambda \rangle$

$$\langle \phi_\lambda | \frac{\partial V_{\text{eff}}}{\partial \lambda} | \phi_\lambda \rangle = \int d\vec{r} n(\vec{r}) \frac{\partial V_{\text{eff}}^\lambda(\vec{r})}{\partial \lambda}$$

$$= \frac{\partial}{\partial \lambda} \int d\vec{r} n(\vec{r}) V_{\text{eff}}^\lambda(\vec{r})$$

$$\int_0^1 d\lambda \frac{\partial}{\partial \lambda} \int d\vec{r} n(\vec{r}) V_{\text{eff}}^\lambda(\vec{r}) = \int d\vec{r} n(\vec{r}) [V_{\text{eff}}^1(\vec{r}) - V_{\text{eff}}^0(\vec{r})]$$

$\int_0^1 dx f'(x) = f(1) - f(0)$

 $V_{\text{ext}}(\vec{r})$

$$\Rightarrow E[n] = T_0 + \int_0^1 d\lambda \langle \phi_\lambda | V_{\text{ee}} | \phi_\lambda \rangle + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r})$$

At the same time, the starting point was:

$$E[n] = T_0 + E_{\text{Hartree}} + E_{\text{xc}} + \int d\vec{r} n(\vec{r}) V_{\text{ext}}(\vec{r})$$

$$E_{\text{xc}} = \int_0^1 d\lambda \langle \phi_\lambda | V_{\text{ee}} | \phi_\lambda \rangle - \underbrace{E_{\text{Hartree}}}_{\text{Hartree}}$$

Now: Express $\langle \phi_\lambda | V_{\text{ee}} | \phi_\lambda \rangle$

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

in a similar way as E_{Hartree} in order to summarize them.

$$\text{Regular } \bar{\epsilon}\text{-density} : n_1(\vec{r}) = N \int d\vec{r}_2 \dots d\vec{r}_N \phi^*(\vec{r}, \vec{r}_2 \dots \vec{r}_N)$$

describes probability to find
a particle at a position \vec{r}

$$\phi(\vec{r}, \vec{r}_2 \dots \vec{r}_N)$$

"1-particle density"

$$\text{Introduce "2-particle density": } n_2(\vec{r}, \vec{r}') = \frac{N(N-1)}{2} \int d\vec{r}_3 \dots d\vec{r}_N$$

describing the probability of finding
two particles at two positions
 \vec{r} and \vec{r}'

$$\times \phi^*(\vec{r}, \vec{r}', \vec{r}_3 \dots \vec{r}_N) \\ \phi(\vec{r}, \vec{r}', \vec{r}_3 \dots \vec{r}_N)$$

$$n_2^\lambda(\vec{r}, \vec{r}') \equiv \frac{1}{2} n(\vec{r}) n(\vec{r}') \underbrace{g^\lambda(\vec{r}, \vec{r}')}_{\text{pair correlation function}}$$

pair correlation function :

describes to which extent the joint probability
 $n_2(\vec{r}, \vec{r}')$ is different from the product of the
individual probabilities $n(\vec{r}) \cdot n(\vec{r}')$

→ depends on the interaction strength λ

$$\Rightarrow \langle \phi_\lambda | V_{ee} | \phi_\lambda \rangle = e^2 \int d\vec{r} \int d\vec{r}' \frac{n_2^\lambda(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$\Rightarrow E_{xc} = \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} \left[\underbrace{\int_0^1 d\lambda g^\lambda(\vec{r}, \vec{r}')}_{\text{coupling-averaged pair correlation function}} - 1 \right]$$

$= g(\vec{r}, \vec{r}')$

$$\Rightarrow E_{xc} = \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n_{xc}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|}$$

Where $n_{xc}(\vec{r}, \vec{r}') = n(\vec{r}') [g(\vec{r}, \vec{r}') - 1]$

This means that E_{xc} can be described as a Coulomb interaction of the charge density $n(\vec{r})$ with a "fictitious" charge density $n_{xc}(\vec{r}, \vec{r}')$.

$n_{xc}(\vec{r}, \vec{r}')$ describes effective charge depletion at \vec{r}' around an electron at \vec{r}

How many e^- does n_{xc} contain?



$$\int d\vec{r}' n_{xc}(\vec{r}, \vec{r}') = \underbrace{\int d\vec{r}' n(\vec{r}') g(\vec{r}, \vec{r}')}_{\text{N}} - \underbrace{\int d\vec{r}' n(\vec{r}')}_{-1} = -1$$

n_{xc} contains one missing electron



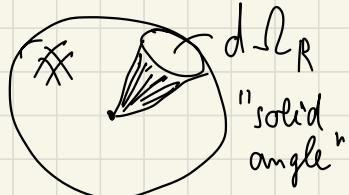
exchange-correlation hole

$$\frac{2}{n(\vec{r})} \int d\vec{r}' n_2(\vec{r}, \vec{r}') = \frac{N-1}{2} n(\vec{r})$$

$n(\vec{r}) = N \int d\vec{r}_2 \dots d\vec{r}_N \phi \phi^*$
 $n_2(\vec{r}, \vec{r}') = \frac{N(N-1)}{2} \int d\vec{r}_3 \dots d\vec{r}_N \phi \phi^*$
 $\Rightarrow \int d\vec{r}' n_2(\vec{r}, \vec{r}') = \frac{N(N-1)}{2} \int d\vec{r}' \dots d\vec{r}_N \phi \phi^* = \frac{N-1}{2} n(\vec{r}) n(\vec{r}) / N$

Remarks :

- Correlations are localized : $n_{xc}(\vec{r}, \vec{r}') \xrightarrow[|\vec{r}-\vec{r}'| \rightarrow \infty]{} 0$
- Generally, not spherical : $n_{xc}(\vec{r}, \vec{r}') \neq n_{xc}(|\vec{r}-\vec{r}'|)$
except for the homogeneous e^- gas
- Since the Coulomb interaction depends only on $|\vec{r}-\vec{r}'|$
 $\Rightarrow E_{xc} = \frac{e^2}{2} \int d\vec{r} n(\vec{r}) \int_0^\infty dR R^2 \frac{1}{R} \int d\Omega_R n_{xc}(\vec{r}, \vec{r} + \vec{R})$
 $(\vec{R} \text{ is just distance})$
 $|\vec{r}-\vec{r}'| \sim R$



depends only on the spherical average
of the xc -hole density n_{xc} .

- Exact formulation of E_{xc} in terms of n_{xc}

$$E_{xc} = \frac{e^2}{2} \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r}) n_{xc}(\vec{r}, \vec{r}')} {|\vec{r}-\vec{r}'|},$$

with

$$n_{xc}(\vec{r}, \vec{r}') = n(\vec{r}) [g(\vec{r}, \vec{r}') - 1]$$

All xc -terms beyond Hartree are contained

in the pair-correlation function

4.2. The LDA exchange-correlation hole

We connect n_{xc} with the LDA that we have discussed before:

$$\mathcal{E}_{xc}^{\text{LDA}}[n] = \int d\vec{r} n(\vec{r}) \mathcal{E}_{xc}[n(\vec{r})]$$

\downarrow
xc - energy density of
the homogeneous e⁻ gas

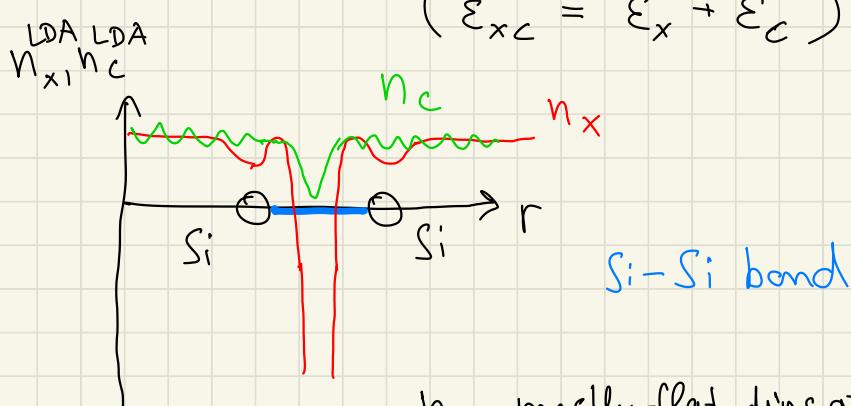
Now: $n_{xc}(\vec{r}, \vec{r}') = n(\vec{r}') \left[g(\vec{r}, \vec{r}') - 1 \right]$ $\xrightarrow{\text{can be computed to high accuracy}}$

$$\rightarrow n_{xc}^{\text{LDA}}(\vec{r}, \vec{r}') = n(\vec{r}') \left[g^{\text{hom.}} \left[|\vec{r} - \vec{r}'|, n(\vec{r}) \right] - 1 \right]$$

$$\Leftrightarrow \mathcal{E}_{xc}^{\text{LDA}}[n(\vec{r})] = \frac{e^2}{2} \int d\vec{r}' \frac{n_{xc}^{\text{LDA}}[|\vec{r} - \vec{r}'|, n(\vec{r}')] }{|\vec{r} - \vec{r}'|}$$

n_{xc}^{LDA} fulfills the sum rule $\int d\vec{r}' n_{xc}^{\text{LDA}}(\vec{r}, \vec{r}') = -1$
as the xc-hole of the homogeneous electron gas.

Example 1: Silicon $n_{xc}(\vec{r}, \vec{r}') = n_x(\vec{r}, \vec{r}') + n_c(\vec{r}, \vec{r}')$

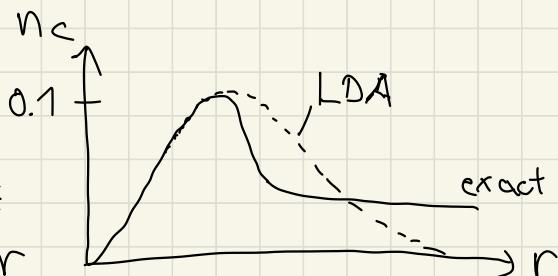
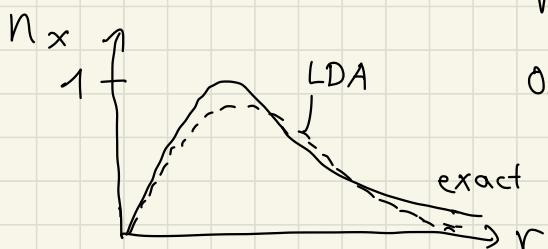


$$|n_c| \sim \frac{1}{3} |n_x|$$

n_x mostly flat, dips at the respective Si cores, and deep & wide hole at center of the Si-Si bond

n_c complex shape everywhere, narrow and shallow hole at the Si-Si bond center

Example 2: xc -hole around a Ne atom



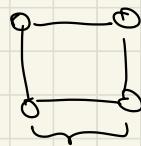
(spherical averages of n_x & n_c)

n_{xc}^{LDA} matches reasonably well with n_{xc}^{exact}

⇒ big success for such simple approximation, explains wide usage

Problems & limitations of LDA

- Overestimates bonding \Rightarrow underestimates lattice constants



$$a_{\text{LDA}} < a_{\text{exp}}$$

- Underestimates band gap, $E_g = E_g^{\text{KS}} + \Delta$
↑
needs an extra contribution

- Predicts non-magnetic fcc structure of Fe to be more stable than FM bcc structure
- Mott-Hubbard insulators (NiO , V_2O_3) are predicted to be metals
- No inhomogeneities of $n(\vec{r})$ taken into account (no nonlocal effects)
- $V_{xc} \xrightarrow[r \rightarrow \infty]{} e^{-r}$ instead of $\frac{1}{r^n}$ \Rightarrow problem for van der Waals interactions, H bonds, adsorption energies, etc.

\Rightarrow Expand E_{xc} in gradients of $n(\vec{r})$

4.3 Generalized gradient approximation (GGA)

LDA is exact for the homogeneous e^- gas

($n(\vec{r})$ is constant \Rightarrow no variation, local description is sufficient)

Next step: Take local variation into account through

the weakly inhomogeneous electron gas

$$E_{xc}^{\text{GEN}}[n] = \int d\vec{r} \ n(\vec{r}) \Sigma_x^{\text{hom.}}[n(\vec{r})] F_{xc}[n(\vec{r}), |\vec{\nabla} n(\vec{r})|, \vec{\nabla}^2 n(\vec{r}), \dots]$$

↑
exchange energy
density of homogeneous
 e^- gas known exactly
for Fock exchange

enhancement
factor $\bar{F}_{xc} = \bar{F}_x + \bar{F}_c$
(dimensionless)

4.3 Generalized gradient approximation (GGA)

LDA is exact for the homogeneous e^- gas

Next step: weakly inhomogeneous e^- gas takes into account local variations

$$E_{xc}^{\text{GGA}}[n] = \int d\vec{r} n(\vec{r}) \sum_x^{\text{hom.}} [n(\vec{r})] F_{xc}[n(\vec{r}), |\vec{\nabla} n(\vec{r})|, \vec{\nabla}^2 n(\vec{r}), \dots]$$

↑
exchange energy,
density of homog.
 e^- gas
(exact \rightarrow Fock)

$$F_{xc} = F_x + F_c$$

$$\begin{aligned} \text{Analytical expansion : } F_x &= \sum_m S_m C_m \\ &= \sum_m \frac{|\vec{\nabla}^m n|}{(2k_F)^m n} C_m \end{aligned}$$

dimensionless reduced density,
normalized by the average radius
of the e^- , $k_F \propto \frac{1}{r_s}$

$$\text{Perdew & Burke 1996 } F_x = 1 + \frac{10}{81} S_1^2 + \frac{146}{2025} S_2^2 + \dots$$

Problem: S_m not necessarily small $S_1^2 S_2^2 \dots$

→ expansion in lowest orders does not necessarily converge to the correct results & violate sum rules

⇒ Find modified form $F_x[n, s]$ that fulfills boundary conditions & limits

Two strategies: 1) Fit parameters by minimizing the error
compared to molecular database

"training set"

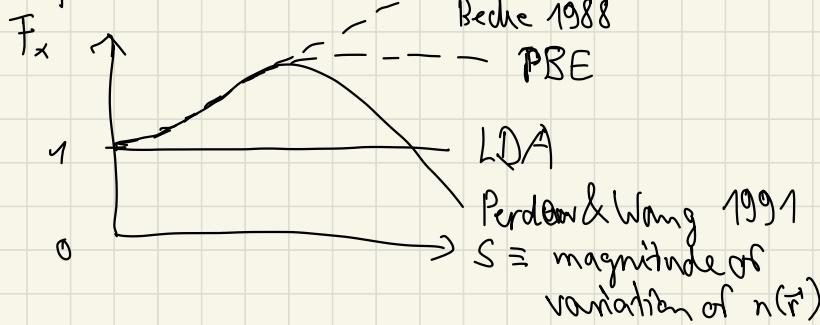
→ Empirical GGAs, e.g. BLYP
(Becke-Lee-Yang-Parr)

2) Choose parameters such that they enforce
exact properties & limits (sum rules)

→ Non-empirical GGAs, e.g. PBE, PBEsol

(Perdew-Burke-Ernzerhof)
PRL 77, 3865 (1997)

Comparison of different "GGA flavors"

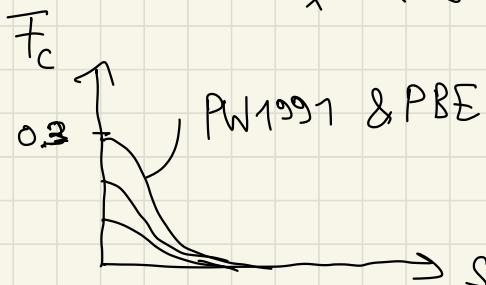


All GGA variants yield the same F_x for small r .

Analytic expression of the correlation part in a similar way

$$F_C = \frac{\epsilon_c^{\text{LDA}}[n]}{\epsilon_x^{\text{LDA}}[n]} (1 - a s_1^2 + b s_2^2 + \dots)$$

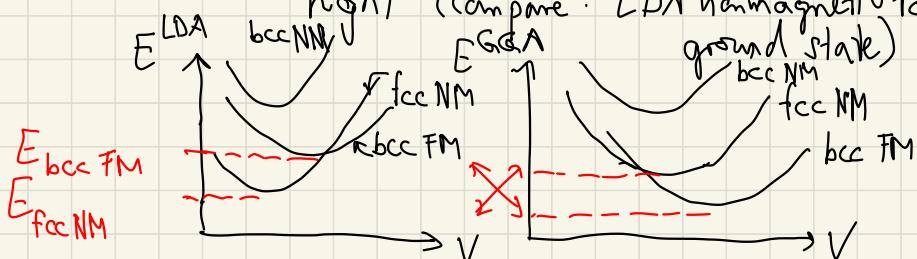
(Perdew, Burke, Ernzerhof 1996)



Quickly decaying compared to F_x and $F_C^{\text{GGA}} \approx 0.1 F_x^{\text{GGA}}$

Advantages:

- Improves binding energies & bond lengths, fixed LDA overbinding & lattice constants
- Better description of H bonds
- Gets FM bcc ground state of F_C right (compare: LDA nonmagnetic fcc ground state)



Possible improvements over GGA : include Laplacian ($\vec{\nabla}^2$) or the e^- density, include kinetic energy density

$$\frac{1}{2} \sum_i |\vec{\nabla} \phi_i(\vec{r})|^2 \text{ to account for kinetic correlations}$$

→ Meta-GGA (improve bond chemistry, atomization energies & bond breaking)

General problem of LDA & GGA : Strongly correlated materials,

in particular antiferromagnetic 3d compounds (MnO, NiO, CoO), cuprates ($YBCO$), and also 4f materials (rare earth compounds).

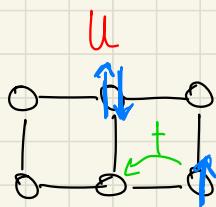
Strong $e^- - e^-$ interactions due to localized orbitals, for which local & semilocal approximations fail.

4.4 DFT + U for strongly correlated materials

Physics of these systems are well described by model theory

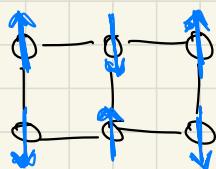
Hubbard model

$$H = \underbrace{+ \sum_{\substack{i,j \\ \sigma}} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma})}_{\text{hopping term}} + \underbrace{U \sum_i \underbrace{n_{i\uparrow} n_{i\downarrow}}_{a_{i\uparrow}^\dagger a_{i\uparrow}}}_{\text{Hubbard term}}$$



e^- can hop (move) between lattice sites and interact locally

Case of half filling: $\begin{cases} \text{high } T: \text{metallic behaviour} \\ \text{low } T: \text{strong } U \text{ can prevent hopping between sites} \end{cases}$



Low T / high U : insulating state despite bond theory predicting metallic behaviour, leading to a magnetic interaction

$J = \frac{t^2}{U}$ between sites \Rightarrow AFM ordering
AFM "Mott-Hubbard" insulator

DFT+U, because LDA & GGA underestimate the
 $(LDA+U, GGA+U)$ tendency for formation of local magnetic moments.

Approach: Treat e^- in two subsystems

- Delocalized s & p e^- : L(S)DA (regular KS approach)
 - Localized d & f c^- : Hubbard-style treatment

$$E = E_{\text{LDA}} + \sum_i (E_u[n_i] - E_{dc}[n_i])$$

Hubbard correction for electron density corresponds to localized orbitals on an atom; double-counting correction cancels out interactions already included at LDA level

Hubbard correction:

$$E_U[n_m^5] = \frac{1}{2} \sum_{m=1}^5 U_{mm} n_m^5 n_{m'}^{-5} + \frac{1}{2} \sum_{m \neq m'} (U_{mm'} -) n_m^5 n_{m'}^{-5}$$

(similar to Hartree term)

and

(similar to Fock term)

A diagram showing two coupled oscillators. Each oscillator is represented by a circle with a vertical double-headed arrow through its center, indicating a back-and-forth motion. A horizontal line connects the two circles, representing the coupling between them.

Today: Rotationally invariant formulation,

independent on the basis set & transformations thereof.

In practice: $[U \& J] \longrightarrow$ Computed w/ constrained DFT calculations
 ↓
 Empirical parameters,

used to fit magnetic properties of a material to experimentally known ones

Ab-initio determinations of $[U \& J]$: Do DFT calculations with fixed occupations of the localized (d or f) orbitals, and compare them to the unconstrained results.

Given the energy of a 3d orbital: $\epsilon_{3d\uparrow}(n_\uparrow, n_\downarrow)$
 ↓ \|
 eigenvalue of spin-up state for a given spin occupation Occupations of ↑ and ↓ spin manifolds

In the unpolarized case: $n_\uparrow = n_\downarrow = \frac{n}{2}$

$$\Rightarrow \epsilon_{3d\uparrow}(\frac{n}{2}, \frac{n}{2}) = \epsilon_{3d\downarrow}(\frac{n}{2}, \frac{n}{2})$$

Anisimov & Gunnarsson (1991):

$$U = \epsilon_{3d\uparrow}(\frac{n}{2} + \frac{1}{2}, \frac{n}{2}) - \epsilon_{3d\uparrow}(\frac{n}{2} + \frac{1}{2}, \frac{n}{2} - 1)$$

$$J = \epsilon_{3d\uparrow}(\frac{n}{2} + \frac{1}{2}, \frac{n}{2} - \frac{1}{2}) - \epsilon_{3d\downarrow}(\frac{n}{2} + \frac{1}{2}, \frac{n}{2} - \frac{1}{2})$$

energy ↑ of ↑-polarized w/ extra ϵ - energy of ↓-polarized w/ less ϵ

energy ↑ of ↑-polarized - energy ↓ of ↑-polarized

Keep the e^- densities fixed at these values of the $3d$ orbital, while doing the full KS scf cycle for the remaining e^- .

For example: Fe $3d^7 \rightarrow \Sigma_{3d\uparrow} \left(\frac{n}{2} + \frac{1}{2}, \frac{n}{2} \right)$

Create supercell w/ many atoms where all, but one atom has $n_\uparrow = n_\downarrow = 3.5$ and one atom has $n_\uparrow = 4$
 $n_\downarrow = 3.5$

→ Compensate charges w/ homogeneous background charge

Double-counting correction

Subtract interaction between localized orbitals from LDA part: Problem!

↳ LDA is formulated in terms of $n(\vec{r})$
(total e^- density)

vs. Hubbard correction, which is formulated in terms of the occupation no. of the localized orbital

⇒ Explicit form of double-counting correction is unknown

Two common approximations:

1) "Around mean-field": Retrieve LDA for $U=J=0$

$$E_U - E_{dc} = \frac{1}{2} \sum_m U_{mm'} (n_m^5 - \bar{n}^5) (n_{m'}^5 - \bar{n}^5)$$

$$+ \frac{1}{2} \sum_{m \neq m'} \left(U_{mm'} - J_{mm'} \right) \left(n_m^5 - \bar{n}^5 \right) \times \left(n_{m'}^5 - \bar{n}^5 \right)$$

$n_m^5 - \bar{n}^5$ = expansion around mean value from LDA

2) "Fully localized limit":

$$E_{dc}[n_i] = \frac{U}{2} N(N-1) - \frac{J}{2} \sum_b N_b (N_b - 1)$$

$N = N_\uparrow + N_\downarrow$ $N_b = \sum_m n_m^b$

basically E_U with one less e^-

Disadvantages of DFT+U: somewhat unsatisfying fix w/
many adjustable parameters
(choice of "strongly correlated orbitals")

Advantages of DFT+U: • No additional computational cost

- Works well & implemented in many DFT codes

4.5 The band-gap problem

All treatments of the xc - energy so-far suffer from the same problem : They underestimate the band gap systematically

We can define the band gap in three different ways:

$$1) \text{ Fundamental gap: } E_g = I - A$$

ionization energy electron affinity

energy for adding/removing an e^- to/from system

Measurements: Photoemission /absorption spectroscopy

2) Optical gap: $E_g = E_{gs} - E_{1st\ excited\ state}$

Measurement: Optical excitation

$$3) \text{ Kohn-Sham gap: } \Sigma_g = E_{N+1} - E_N = E_{\substack{\text{lowest} \\ \text{unoccupied}}} - E_{\substack{\text{highest} \\ \text{occupied}}}$$

Computation: KS equations

Non-interacting system : All three gaps are identical

Interacting system : $I - A = \epsilon_{N+1} - \epsilon_N + \Delta_{xc}$
 generally unknown \downarrow

In practice: KS eigenvalues serve as first guess for the band gap

⇒ Additional methods for accurate calculations

- 1) TDDFT: time-dependent formulation of HK theorems & KS equations
- 2) GW : Green's function method to estimate quasiparticle self energy
- 3) Bethe-Salpeter equation : bound-state description of two particles
 $e^- - h^+$ pair → exciton

5 Overview of DFT

Hohenberg-Kohn theorems

Energy functional: $E[n] = T_0 + \int d\vec{r} n(\vec{r}) V_{xc}(\vec{r}) + e^2 \int d\vec{r} \int d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|} + E_H[n]$

Kohn-Sham equations

$$\left(-\frac{\hbar^2}{2m} \nabla + V_{\text{eff}}[n(\vec{r})] \right) \phi_n(\vec{r}) = \varepsilon_n \phi_n(\vec{r})$$

How to solve the KS equations?

Approximations for $E_{xc}[n]$

- Pseudopotential plane-wave method

↓
separating core & valence electrons
to approximate the core part

$$H_{\vec{k},\vec{k}'}^{\text{K}} = \frac{\hbar^2 |\vec{k}-\vec{k}'|^2}{2m} S(\vec{k}-\vec{k}') + V_{\text{PS}}(\vec{k}-\vec{k}')$$

- Other methods (augmented wavefunctions, muffin-tin orbitals)

- Local & semilocal functionals (LDA, GGA, meta-GGA)
- DFT + U for localized electrons (strongly correlated systems)

Computed properties

- gs crystal structure (lattice constants, bond-lengths, etc.)
- atomic forces, elastic constants
- phonon spectra / dispersion
- dielectric properties
- band structures
- gs magnetism (AFM vs FM)
- magnon spectra & dispersion
- ...