Methods with parameters

- Tight binding (parameters $t_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle$, basis: atomic orbitals)

- Nearly free electrons (basis: plane waves)

Methods \textit{ab-initio}

potential depends on wave functions
iterative solution by SCF method (self-consistent field)

- Hartree-Fock (basis: atomic orbitals)

- LDA: Local Density Approximation (basis: atomic orbitals and plane waves)
program Wien2k
Born-Oppenheimer approximation

\[ \hat{H} = \hat{T} + \hat{V} \]
\[ \hat{H} = \hat{T}_Z + \hat{T}_e + \hat{V}_{Z\{e} + \hat{V}_{Ze} + \hat{V}_{ee} \]

\( \hat{T} \) : kinetic energy \quad \hat{V} \) : potential energy

\( Z \) : nucleus, \( e \) : electron

Born-Oppenheimer approximation:

\( m_Z >> m_e \rightarrow \) immobile atom nuclei, only electrons move.

\[ \hat{H} = \hat{T}_e + \hat{V}_{Ze} + \hat{V}_{ee} \quad \left( + \hat{T}_Z = 0 ; + \hat{V}_{Z\{e} = const \right) \]

\[ \hat{H} = \sum_{i=1}^{N} \hat{h}(i) + \sum_{i}^{N} \sum_{j>i}^{N} \hat{g}(i, j) \]

Sum of contributions:

- single electron (kinetic energy of electron + intercation between electron and nucleus)
- two electrons (interaction between electrons).

\[ \hat{h}(i) = -\frac{\hbar^2}{2m} \Delta_i - \sum_{l=1}^{N_Z} \frac{Z_l e^2}{4\pi\varepsilon_0 |r_i - R_l|} \]

\[ \hat{h}(i) = \hat{T}(i) + \hat{V}_{Ze}(i) \]

\[ \hat{g}(i, j) = \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|} \]
Hartree approximation

\[
\sum_{i}^{N} \sum_{j>i}^{N} \hat{g}(i, j) \approx \sum_{i} \hat{C}(i)
\]

\[
\hat{C}_i(r) = \sum_{i \neq j} \frac{e^2}{4\pi\varepsilon_0 |r_i - r_j|} \approx \int \frac{e\rho(r)}{4\pi\varepsilon_0 |r_i - r'|} dr'
\]

\[
\Psi(r_1, r_2, \cdots, r_n) = \Phi_1(r_i)\Phi_2(r_2) \cdots \Phi_n(r_n)
\]

\[
\hat{H}\Psi(r_1, r_2, \cdots, r_n) = E\Psi(r_1, r_2, \cdots, r_n)
\]

\[
\hat{h}_i\Phi_i(r_i) = \varepsilon_i\Phi_i(r_i)
\]

\[
E = \varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_n
\]

2-electrons interactions replaced by 1-electron interactions with a total electron density.

Many-electron function \( \Psi \) is expressed as a product of 1-electron functions \( \Phi \).

Many-electron Schrödinger equation is divided into \( n \) 1-electron equations.

\[
\hat{h}(i) = -\frac{\hbar^2}{2m} \Delta_i - \sum_{l=1}^{N_z} \frac{Z_l e^2}{4\pi\varepsilon_0 |r_i - R_l|} + \int \frac{e\rho(r)}{4\pi\varepsilon_0 |r_i - r'|} dr'
\]

\[
\hat{h}(i) = \hat{T}(i) + \hat{V}_{Ze}(i) + \hat{C}_{ee}(i)
\]

\[
\frac{N - 1}{N} \text{ factor to remove self-interaction}
\]
\[ \hat{H}\Psi(r_1, r_2, r_3) = E\Psi(r_1, r_2, r_3) \]
\[ \Psi(r_1, r_2, r_3) = \Phi_1(r_1)\Phi_2(r_2)\Phi_3(r_3) \]
\[ \hat{H} = \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \]
\[ E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \]
\[ \left( \hat{h}_1 + \hat{h}_2 + \hat{h}_3 \right)(\Phi_1\Phi_2\Phi_3) = (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)\Phi_1\Phi_2\Phi_3 \]
\[ \Phi_2\Phi_3\hat{h}_1\Phi_1 + \Phi_1\Phi_3\hat{h}_2\Phi_2 + \Phi_1\Phi_2\hat{h}_3\Phi_3 = \varepsilon_1\Phi_1\Phi_2\Phi_3 + \varepsilon_2\Phi_1\Phi_2\Phi_3 + \varepsilon_3\Phi_1\Phi_2\Phi_3 \]
\[ \Phi_2\Phi_3\left( \hat{h}_1\Phi_1 - \varepsilon_1\Phi_1 \right) + \Phi_1\Phi_3\left( \hat{h}_2\Phi_2 - \varepsilon_2\Phi_2 \right) + \Phi_1\Phi_2\left( \hat{h}_3\Phi_3 - \varepsilon_3\Phi_3 \right) = 0 \]
\[ \hat{h}_i\Phi_i - \varepsilon_i\Phi_i = 0 \]
Electrons are fermions, so function $\Psi$ must be made antisymmetric, i.e. it must change the sign if 2 electrons are swapped:

$$\Psi(r_1, \ldots, r_k, \ldots, r_j, \ldots, r_n) = -\Psi(r_1, \ldots, r_j, \ldots, r_k, \ldots, r_n)$$

This condition is fulfilled e.g. by wave function expressed like Slater’s determinant:

$$\Psi(r_1, r_2, \ldots, r_n) = \frac{1}{\sqrt{n!}} \det \begin{vmatrix} \Phi_1(r_1) & \Phi_1(r_2) & \cdots & \Phi_1(r_n) \\ \Phi_2(r_1) & \Phi_2(r_2) & \cdots & \Phi_2(r_n) \\ \vdots & \vdots & \ddots & \vdots \\ \Phi_n(r_1) & \Phi_n(r_2) & \cdots & \Phi_n(r_n) \end{vmatrix}$$
By placing the **Slatter determinant** into Hartree hamiltonian and minimizing energy (variation principle) we get:

\[
\hat{H}^{HF}_K \varphi_K(r_1) = \left[ -\frac{\hbar^2}{2m} \Delta - \frac{1}{4\pi\varepsilon_o} \frac{Ze^2}{|r_1|} \right] \varphi_K(r_1) \\
+ \sum \int \frac{1}{4\pi\varepsilon_o} \frac{e^2}{|r_1 - r_2|} \sum \varphi_j^*(r_2) \varphi_j(r_2) \, dr_2 \varphi_K(r_1) \\
- \sum \int \frac{1}{4\pi\varepsilon_o} \frac{e^2}{|r_1 - r_2|} \sum \varphi_j^*(r_2) \varphi_K(r_2) \, dr_2 \varphi_K(r_1) = \varepsilon_K \varphi_K(r_1)
\]

For \( j=k \) is \( C_j=K_{jj} \) and cancel each other (self-interaction)

\[
\hat{H}^{HF} = \hat{T} + \hat{V}_{Ze} + \hat{C}_{ee} + \hat{K}_{ee} = \hat{H}^{Hartree} + \hat{K}_{ee}
\]

\( \hat{T} \) - kinetic energy of electron.

\( \hat{V}_{Ze}(r_1) \) - Potential energy = potential in point \( r_1 \) created by atoms nuclei charge.

\( \hat{C}_J(r_1) \) - Coulombic term = potential in point \( r_j \) created by electrons from orbital \( J \).

\( \hat{K}_{JJ}(r_1) \) - Exchange term = energy connected with exchange of 2 electrons (fermions).
DFT, LSDA

\[ \hat{H}^{DFT} = \hat{H}^{Hartree} + \hat{V}_{xc} \]

\[ \frac{\partial E}{\partial \rho} = 0; \quad \hat{V}_{xc}(r) = \hat{V}_{xc}(\rho(r)) \]

DFT: Density Functional Theory
Energy of the ground state is uniquely derived from electron density.

L(S)DA: Local (Spin) Density Approximation
Correlation energy depends on the local electron density.
The dependence of the correlation energy on the electron density is calculated for homogeneous electron gas with a constant density.

\[ V_{xc} = \int \mu_{xc}(\rho_{\uparrow}, \rho_{\downarrow}) \ast [\rho_{\uparrow} + \rho_{\downarrow}] \, dr \]

GGA (Generalized Gradient Approximation):
adds gradient term to k LDA.

exchange correlation term \( V_{xc} \):
- exchange energy (exchange of 2 electrons)
- correlation energy
- change of kinetic energy
The theorems of Hohenberg and Kohn

First theorem: There is a **one-to-one** correspondence between the ground-state density $\rho(\vec{r})$ of a many-electron system (atom, molecule, solid) and the external potential $V_{\text{ext}}$. An immediate consequence is that the ground-state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground-state electron density:

$$<\Psi | \hat{O} | \Psi> = O[\rho] \quad (1.3)$$

Second theorem: For $\hat{O}$ being the hamiltonian $\hat{H}$, the ground-state total energy functional $H[\rho] \equiv E_{\text{V_{ext}}}[\rho]$ is of the form

$$E_{\text{V_{ext}}}[\rho] = \frac{<\Psi | \hat{T} + \hat{V} | \Psi> + <\Psi | \hat{V}_{\text{ext}} | \Psi>}{F_{\text{HK}}[\rho]}$$

$$= F_{\text{HK}}[\rho] + \int \rho(\vec{r}) V_{\text{ext}}(\vec{r}) \, d\vec{r} \quad (1.5)$$

where the Hohenberg-Kohn density functional $F_{\text{HK}}[\rho]$ is **universal** for any many-electron system. $E_{\text{V_{ext}}}[\rho]$ reaches its **minimal** value (equal to the ground-state total energy) for the ground-state density corresponding to $V_{\text{ext}}$. 
An efficient and accurate scheme for solving the many-electron problem of a crystal (with nuclei at fixed positions) is the local spin density approximation (LSDA) within density functional theory (Hohenberg and Kohn 64, Kohn and Sham 65). Therein the key quantities are the spin densities $\rho_{\sigma}(r)$ in terms of which the total energy is

$$E_{\text{tot}}(\rho_{\uparrow}, \rho_{\downarrow}) = T_s(\rho_{\uparrow}, \rho_{\downarrow}) + E_{\text{ee}}(\rho_{\uparrow}, \rho_{\downarrow}) + E_{\text{Ne}}(\rho_{\uparrow}, \rho_{\downarrow}) + E_{\text{xc}}(\rho_{\uparrow}, \rho_{\downarrow}) + E_{\text{NN}}$$

with $E_{\text{NN}}$ the repulsive Coulomb energy of the fixed nuclei and the electronic contributions, labelled conventionally as, respectively, the kinetic energy (of the non-interacting particles), the electron-electron repulsion, nuclear-electron attraction, and exchange-correlation energies. Two approximations comprise the LSDA, i), the assumption that $E_{\text{xc}}$ can be written in terms of a local exchange-correlation energy density $\mu_{\text{xc}}$ times the total (spin-up plus spin-down) electron density as

$$E_{\text{xc}} = \int \mu_{\text{xc}}(\rho_{\uparrow}, \rho_{\downarrow}) \ast [\rho_{\uparrow} + \rho_{\downarrow}] \, dr$$

(2.1)

and ii), the particular form chosen for that $\mu_{\text{xc}}$. 
LDA+U or GGA+U: combination of DFT and Hartree-Fock

LDA, GGA: underestimate correlation energy, in particular for $d$ and $f$ electrons:
- They give smaller gap, metal instead of insulator
- $f$ orbitals on the Fermi level

Hartree-Fock: overestimate correlation energy.

LDA+U, GGA+U: combination of DFT and screened Hartree-Fock
Methods APW/LAPW

- Program: WIEN2K (TU Vienna, www.wien2k.at)
- LAPW: Linearized Augmented Plane Wave

**Interstitial**: Plane wave $e^{i(k+\vec{K}).\vec{r}}$

**Atomic spheres**: APW/LAPW
Atomic orbitals with smooth transition to PW

![](image-url)
Methods APW/LAPW

\[ \phi_{R}^k(\vec{r}, E) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K}).\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} A_{\ell m}^\alpha,\vec{k}+\vec{K} u^\alpha_{\ell}(r', E) Y_\ell^m(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \]

APW: calculated for a certain energy, that must be searched iteratively.

\[ \phi_{\overset{ightharpoonup}{K}}^k(\vec{r}) = \begin{cases} \frac{1}{\sqrt{V}} e^{i(\vec{k}+\vec{K}).\vec{r}} & \vec{r} \in I \\ \sum_{\ell,m} \left( A_{\ell m}^\alpha,\vec{k}+\vec{K} u^\alpha_{\ell}(r', E_0) + B_{\ell m}^\alpha,\vec{k}+\vec{K} \tilde{u}^\alpha_{\ell}(r', E_0) \right) Y_\ell^m(\hat{r}') & \vec{r} \in S_\alpha \end{cases} \]

LAPW: Taylor expansion from the initial \( E_0 \).

LAPW: \( E_0 \) is different for each \( l \). \( E_0 \) is recalculated during the calculation only if \( E \) is significantly deviated from \( E_0 \).

\( u_l(r', \varepsilon) \) are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy \( \varepsilon \).

\( Y_{l,m}(r', \varepsilon) \): Angular part

\( A_{l,m}, B_{l,m} \): are coefficients for matching the plane waves.

---

Fe

Atomic sphere

LAPW

PW

---

radial part of \( \rho_{F}^{1s} \)
Linearization of energy dependence

**LAPW** suggested by

O.K. Andersen,

\[
\Phi_{\kappa n} = \sum_{\ell m} \left[ A_{\ell m}(k_n) u_{\ell}(E_{\ell}, r) + B_{\ell m}(k_n) \dot{u}_{\ell}(E_{\ell}, r) \right] Y_{\ell m}(\hat{r})
\]

expand \( u_\ell \) at fixed energy \( E_\ell \) and add \( \dot{u}_\ell = \partial u_\ell / \partial \varepsilon \)

\( A_{\ell m}, B_{\ell m} \): join PWs in value and slope

→additional constraint requires more PWs than APW

→basis flexible enough for single diagonalization
Core, semi-core and valence states

For example: Ti

- Valences states
  - High in energy
  - Delocalized wavefunctions

- Semi-core states
  - Medium energy
  - Principal QN one less than valence (e.g. in Ti 3p and 4p)
  - Not completely confined inside sphere

- Core states
  - Low in energy
  - Reside inside sphere
Extending the basis: Local orbitals (LO)

\[ \Phi_{LO} = [A_{\ell m} u_{\ell}^{E_1} + B_{\ell m} \hat{u}^{E_1}_{\ell} + C_{\ell m} u_{\ell}^{E_2}] Y_{\ell m}(\hat{r}) \]

- **LO**
  - is confined to an atomic sphere
  - has zero value and slope at \( R \)
  - can treat two principal QN \( n \) for each azimuthal QN \( \ell \) (3p and 4p)
  - corresponding states are strictly orthogonal (no "ghostbands")
  - tail of semi-core states can be represented by plane waves
  - only slight increase of basis set (matrix size)

Semi-core states are described with the help of local orbitals (LO)

\[
\phi_{\alpha, LO}^m(\vec{r}) = \begin{cases} 
0 & \vec{r} \notin S_\alpha \\
(A_{\ell m}^{LO} u_\ell^\alpha(\vec{r}, E_{1, \ell}^\alpha) + B_{\ell m}^{LO} \hat{u}_\ell^\alpha(\vec{r}, E_{1, \ell}^\alpha) + C_{\ell m}^{LO} u_\ell^\alpha(\vec{r}, E_{2, \ell}^\alpha)) Y_m^\ell(\vec{r'}) & \vec{r} \in S_\alpha
\end{cases}
\]

**LO** - Zero value and derivation on the border of atomic sphere
- \( E_1 \) is equal to \( E_0 \) of orbital with higher \( n \).
- Hybridize with valence state inside atomic sphere.

![Graph showing radial functions](image)

*Example:*
- 4p: \( E_1 \)  valence
- 3p: \( E_1, E_2 \)  semi-core
Initialization:

**NN**: check atomic sphere

**SGROUP**: check space groups.

**SYMMETRY**: analysis of symmetry.

**LSTART**: Electron density of ree atoms, partition of orbitals into core and valence.

**KGEN**: create k-points network.

**DSTART**: create initial electron density by superposition of atomic densities from LSTART.

Parameters:

- \( R_{MT} \): number of \( k \)-points, number of PW, partition on core and valence orbitals

**SCF:**

**LAPW0**: calculates potential from el. density.

**LAPW1**: calculates valence bands (eigen values and eigen vectors) in individual \( k \)-points.

**LAPW2**: calculates el. density of valence electron密度 from eigen vectors.

**LCORE**: calculates core states

**MIXER**: mix input and output el. densities, creates resulting el. density.

[www.wien2k.at](http://www.wien2k.at)
Calculated properties

- electron density
- band struktura
  - orbital’s character
- density of states (DOS)
  - total, for atoms and orbitals

\texttt{tic atom 1D-t2g size 0.20}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram1}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram2}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram3}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram4}
\end{figure}
Fermi level

DFT
FIG. 2: (Color online) Charge density contour (0.01-0.1 e/Å³ in a step of 0.01 e/Å³) of BiCoO₃ in the (100) plane of (a) the hypothetical ideal cubic structure and of (b) the LS-relaxed structure with the experimental c/a ratio. The directional Bi-O covalency is apparent in (b).
Calculated properties

- Magnetic moments – spin, orbitál
- Optimization of the structure, comparison of the stability of various structures
- Preference of the substitution into various sublattices
- Elektrons between energy levels:
  - core electrons – X-ray absorption and emission spectra (XAS, XES, EELS)
  - valence electrons – optical spectra
- hyperfine field, isomer shift, gradient of electrical field:
  - NMR, Mössbauer
- Elastic properties
- With the help of PHONON program: phonon spectrum – infrared spectra, specific heat.
- Cohesion energy (for T = 0 K + specific heat)
- electrical resistivity, Seebeck coefficient (thermopower)
Preference of the site

Example: substitution of Al into Y-hexaferrite $\text{Ba}_2\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$.

Insertion of the substituting atom (Al) into various crystal sublattices (Fe) and calculation of the total energy.

The dependence of the dislocation of Al into sublattices on the temperature

\[
\begin{array}{|l|l|l|l|}
\hline
\text{site} & \text{multiplicity} & \text{E}_{\text{tot}}(\text{Ry}) & \Delta\text{E}(\text{eV}) \\
\hline
\text{Al}(1) & 1 & -71537.677587 & 2.397 \\
\text{Al}(2) & 1 & -71537.818165 & 0.484 \\
\text{Al}(3) & 2 & -71537.805122 & 0.661 \\
\text{Al}(4) & 1 & -71537.853740 & 0.000 \\
\text{Al}(5) & 6 & -71537.843736 & 0.136 \\
\text{Al}(6) & 1 & -71537.816569 & 0.506 \\
\hline
\end{array}
\]
Calculation of the total energy of all the possible spin orientations in individual sublattices.
Atoms In Molecules – the “real” valence

Electrons in the interstitial pace can not be uniquely assigned to atoms. AIM: Based on the calculated electron density, regardless of the atomic sphere, it searches for electron density minimum - the boundary between the atoms. Calculated valency differs from ideal due to the hybridization between the cation and the anion, depending on the difference in their electronegativity.

<table>
<thead>
<tr>
<th>Formula</th>
<th>ideal.</th>
<th>AIM</th>
<th>ratio</th>
<th>$E_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$<em>{0.5}$Ca$</em>{0.5}$CoO$_3$:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>+2</td>
<td>+1.57</td>
<td>0.79</td>
<td>1.0</td>
</tr>
<tr>
<td>Pr</td>
<td>+3</td>
<td>+2.10</td>
<td>0.70</td>
<td>1.1</td>
</tr>
<tr>
<td>Co</td>
<td>+3.5</td>
<td>+1.52</td>
<td>0.44</td>
<td>1.9</td>
</tr>
<tr>
<td>O</td>
<td>−2</td>
<td>−1.12</td>
<td></td>
<td>3.5</td>
</tr>
</tbody>
</table>

| CsF:   | | | | |
| Cs     | +1     | +0.89|       | 0.7   |
| F      | −1     | −0.89|       | 4.0   |

<table>
<thead>
<tr>
<th>Sr$^{2+}$Mn$^{4+}$O$_3$:</th>
<th>+1.58</th>
<th>+1.98</th>
<th>−1.19</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$^{3+}$Mn$^{3+}$O$_3$:</td>
<td>+2.09</td>
<td>+1.77</td>
<td>−1.29</td>
</tr>
</tbody>
</table>
In DFT methods it is not possible to calculate mixed occupation of one crystal site (solid solution).

1. Lower the symmetry and create supercell – only for rational values of occupation
2. Virtual atom method – for atoms with ionic bonds, whose DOS is not on Fermi level.

<table>
<thead>
<tr>
<th>Solid solution</th>
<th>La$<em>{0.75}$Sr$</em>{0.25}$MnO$_3$</th>
<th>LaMn$<em>{0.75}$Co$</em>{0.25}$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supeccell:</td>
<td>La$_3$Sr Mn$<em>4$O$</em>{12}$</td>
<td>La$_4$Mn$<em>3$CoO$</em>{12}$</td>
</tr>
<tr>
<td>Virtual atom:</td>
<td>La(Z=56.75)MnO$<em>3$ (La$</em>{0.75}$Ba$_{0.25}$)</td>
<td>?</td>
</tr>
</tbody>
</table>
Structural transitions MgH$_2$ induced by pressure

\[ p = \frac{\partial E}{\partial V} \quad (E = pV) \]

\[ E \sim aV^2 + bV + c \Rightarrow p \sim 2aV + b = 2a(V - V_0) \]

\[ B = V_0 \frac{\partial p}{\partial V} = V_0 \frac{\partial^2 E}{\partial V^2} \]
Comparison of a wavefunction in the Coulomb potential:
- of the nucleus (blue)
- of the pseudopotential (red).
The real and the pseudo wavefunction and potentials match above a certain cutoff radius $r_c$. 