Density functional theory (DFT) and the concepts of the augmented-plane-wave plus local orbital (L)APW+lo method

Karlheinz Schwarz
Institute for Material Chemistry
TU Wien
Vienna University of Technology
Electronic structure of solids and surfaces

hexagonal boron nitride on Rh(111)
2x2 supercell (1108 atoms per cell)


Wien2k is used worldwide by about 2500 groups

K.Schwarz, P.Blaha, S.B.Trickey,
The WIEN2k code: comments

- Walter Kohn: density functional theory (DFT), 1965
- J.C. Slater: augmented plane wave (APW) method, 1937
- O.K. Andersen: Linearized APW (LAPW), 1975
- **Wien2k code:** developed during the last 35 years
  - In the year 2000 (2k) the WIEN code (from Vienna) was called wien2k
  - One of the most accurate DFT codes for solids
  - All electron, relativistic, full-potential method
  - Widely used in academia and industry

- **Applications:**
  - **Solids:** insulators, covalently bonded systems, metals
  - **Surfaces:** catalysis
  - Electronic, magnetic, elastic, optical, … properties
  - Many applications in literature
  - See [www.wien2k.at](http://www.wien2k.at)
Review articles

K. Schwarz, P. Blaha, S. B. Trickey, *Electronic structure of solids with WIEN2k*  
open access book  
dx.doi.org/10.5772/59108

K. Schwarz, P. Blaha, G. K. H. Madsen, *Electronic structure calculations of solids using the WIEN2k package for material Sciences*  

K. Schwarz, Computation of Materials Properties at the Atomic Scale  
dx.doi.org/10.5772/59108

K. Schwarz, P. Blaha, G. K. H. Madsen, *Electronic structure of solids and surfaces with WIEN2k*  
in *Practical Aspects of Computational Chemistry I: An Overview of the Last Two Decades and Current Trends*,  
J. Leszczynski, M. K. Shukla (Eds),  
ISBN 978-94-007-0918-8

S. Cottenier, *Density Functional Theory and the family of (L)APW methods: A step by step introduction*  
Freely available at: [http://www.wien2k.at/reg-user/textbooks](http://www.wien2k.at/reg-user/textbooks)
Aspects at this workshop

- Atomic structure
  - Periodic boundary condition (approximation)
- Quantum mechanical treatment
  - DFT (functionals) and beyond (GW, DMFT, RPA, BSE, …)
- How to solve the QM (basis set)
  - LAPW method and local orbitals as implemented in WIEN2k
- Applications
  - Verwey transition, EFG, NMR, surfaces, spectra …
- Software development
  - Accuracy, efficiency, system size, user-friendliness, commercial
- Insight and understanding
  - Analysis to find trends, computer experiments (artificial cases)
- Combination of expertise
  - Chemistry, physics, mathematics, computer science, application
Four big challenges for theorists:

- **large scale applications to simulate “real” materials**
  - at the atomic scale

- **A proper quantum mechanical treatment (accurate)**
  - develop more accurate DFT functionals
  - beyond DFT (GW, DMFT, BSE, RPA…)

- **Efficiency (make calculations faster):**
  - improve numerics, parallelization, algorithms (iterative diagonalization)

- **calculate “new” properties**
  - for direct comparison with experiment
The atomic structure

- A crystal is represented by a unit cell
  - We assume periodic boundary condition (approximation)
  - The unit cell is repeated to infinity (makes calculations feasible)
  - A real crystal is finite (with surfaces, impurities, defects …)
  - Nano materials differ from bulk
  - Symmetry helps (space group, Bloch theorem, …)

- In theory
  - The atomic structure is an input and thus well defined.
  - Artificial structures can be studied too

- In experiment
  - The atomic structure is not perfectly known
  - Single crystals, micro crystals, powder samples, nano
  - e.g. by X-ray: averaged with uncertainties (defects, disorder)
A few solid state concepts

**Crystal structure**
- Unit cell (defined by 3 lattice vectors) leading to 7 crystal systems
- Bravais lattice (14)
- Atomic basis (Wyckoff position)
- Symmetries (rotations, inversion, mirror planes, glide plane, screw axis)
- Space group (230)
- Wigner-Seitz cell
- Reciprocal lattice (Brillouin zone)

**Electronic structure**
- Periodic boundary conditions
- Bloch theorem (k-vector), Bloch function
- Schrödinger equation (HF, DFT)
**Unit cell**

Assuming an ideal infinite crystal we define a unit cell by

**Unit cell**: a volume in space that fills space entirely when translated by all lattice vectors.

The obvious choice:

- a parallelepiped defined by \( a, b, c \), three basis vectors with
- the best \( a, b, c \) are as orthogonal as possible
- the cell is as symmetric as possible (14 types)

A unit cell containing one lattice point is called **primitive cell**.
Crystal system: e.g. cubic

Axis system

\[ a = b = c \]
\[ \alpha = \beta = \gamma = 90^\circ \]

primitive

body centered

face centered

P (cP)

I (bcc)

F (fcc)
## 3D lattice types:

### 7 Crystal systems and 14 Bravais lattices

<table>
<thead>
<tr>
<th>Lattice Type</th>
<th>Number</th>
<th>Symmetry Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>“no” symmetry</td>
</tr>
<tr>
<td>Monoclinic (P, C)</td>
<td>2</td>
<td>Two right angles</td>
</tr>
<tr>
<td>Orthorhombic (P, C, I, F)</td>
<td>4</td>
<td>Three right angles</td>
</tr>
<tr>
<td>Tetragonal (P, I)</td>
<td>2</td>
<td>Three right angles + 4 fold rotation</td>
</tr>
<tr>
<td>Cubic (P, I, F)</td>
<td>3</td>
<td>Three right angles + 4 fold + 3 fold</td>
</tr>
<tr>
<td>Trigonal (Rhombohedral)</td>
<td>1</td>
<td>Three equal angles ($\neq 90^\circ$) + 3 fold</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>Two right and one $120^\circ$ angle + 6 fold</td>
</tr>
</tbody>
</table>
Wigner-Seitz Cell

Form **connection** to all neighbors and **span a plane normal** to the connecting line at half distance
The quantum mechanical treatment

- The electronic structure requires a QM treatment
- The main scheme is density functional theory (DFT)
  - It is a mean field approach and requires approximations
  - According to Hohenberg Kohn it is sufficient to know the electron density of a system to determine its total energy. The many electron wave function (which depends on many variables) is not needed. In principle this is an enormous simplification, but in practice approximations must be made.
  - The direction of improving the QM treatment is summarized pictorially in Jacob's ladder:
- There are schemes which go beyond DFT:
  - GW method (for excitations or band gaps)
  - The Bethe Salpeter equation (BSE) for excitons (core hole - electron)
  - Dynamical mean field theory (DMFT) based on DFT (wien2wannier)
Bloch-Theorem:

\[
\left[ -\frac{1}{2} \nabla^2 + V(r) \right] \Psi(r) = E \Psi(r)
\]

1-dimensional case:

\( V(x) \) has lattice periodicity ("translational invariance"): 
\( V(x) = V(x+a) \)

The electron density \( \rho(x) \) has also lattice periodicity, however, the wave function does **NOT**:

\[
\rho(x) = \rho(x + a) = \Psi^*(x) \Psi(x) \quad \text{but:} \\
\Psi(x + a) = \mu \Psi(x) \quad \Rightarrow \quad \mu^* \mu = 1
\]

Application of the translation \( \tau \) \( g \)-times:

\[
\tau^g \Psi(x) = \Psi(x + ga) = \mu^g \Psi(x)
\]
periodic boundary conditions:

- The wave function must be uniquely defined: after $G$ translations it must be identical ($G \cdot a$: periodicity volume):

\[
\tau^G \Psi(x) = \Psi(x + Ga) = \mu^G \Psi(x) = \Psi(x) \\
\Rightarrow \quad \mu^G = 1
\]

\[
\mu = e^{\frac{2\pi i g}{G}} \quad g = 0, \pm 1, \pm 2, \ldots
\]

**Def.:**

\[
k = \frac{2\pi g}{a G} \\
\mu = e^{ika}
\]

**Bloch condition:**

\[
\Psi(x + a) = e^{ika} \Psi(x) = \Psi_k
\]
Bloch functions:

- Wave functions with Bloch form:

\[
\Psi_k(x) = e^{ikx}u(x) \quad \text{where:} \quad u(x) = u(x + a)
\]

Replacing \( k \) by \( k + K \), where \( K \) is a reciprocal lattice vector, fulfills again the Bloch-condition.

\( k \) can be restricted to the first Brillouin zone.

\[
e^{\frac{i2\pi K}{a}} = 1 \quad \text{where} \quad -\frac{\pi}{a} < k < \frac{\pi}{a}
\]
Concepts when solving Schrödinger's equation in solids

- **Form of potential**
  - (non-)selfconsistent
  - “Muffin-tin” MT
  - atomic sphere approximation (ASA)
  - Full potential: FP
  - pseudopotential (PP)

- **Relativistic treatment of the electrons**
  - non relativistic
  - semi-relativistic
  - fully-relativistic

- **Exchange and correlation potential**
  - Hartree-Fock (+correlations)
  - Density functional theory (DFT)
    - Local density approximation (LDA)
    - Generalized gradient approximation (GGA)
    - Beyond LDA: e.g., LDA+U

- **Schrödinger – equation**
  - (Kohn-Sham equation)
  \[
  \left[-\frac{1}{2}\nabla^2 + V(r)\right] \phi_i^k = \epsilon_i^k \phi_i^k
  \]

- **Representation of solid**
  - non periodic (cluster)
  - periodic (unit cell)

- **Treatment of spin**
  - Non-spinpolarized
  - Spin polarized (with certain magnetic order)

- **Basis functions**
  - plane waves: PW
  - augmented plane waves: APW
  - atomic orbitals: e.g., Slater (STO), Gaussians (GTO), LMTO, numerical basis
DFT vs. MBT (many body theory)

Two communities in solid state theory

<table>
<thead>
<tr>
<th></th>
<th>LDA bandstructure</th>
<th>many body theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>• material-specific, “ab initio”</td>
<td>• electronic correlations</td>
</tr>
<tr>
<td></td>
<td>• often successful, quantitative</td>
<td>• qualitative understanding</td>
</tr>
<tr>
<td>–</td>
<td>• effective one-particle approach</td>
<td>• model Hamiltonian</td>
</tr>
</tbody>
</table>

- time averaged electron density
- W: Coulomb WW \(\Rightarrow\) correl. - lattice pot.
Ab-initio Hamiltonian

\[ H = \sum_i \left[ -\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{Z_l}{|r_i - R_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_i - r_j|} \]

LDA bandstructure corresponds to

\[ H_{LDA} = \sum_i \left[ -\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi\epsilon_0} \frac{1}{|r_i - R_l|} + \int d^3r \frac{e^2}{4\pi\epsilon_0} \frac{1}{|r_i - r|} \rho(r) + V_{xc}^{LDA}(\rho(r)) \right] \]

Coulomb potential:
- nuclei
- all electrons
- including self-interaction

Quantum mechanics:
- exchange
- correlation
- (partly) cancel self-interaction
Jacob’s ladder: The grand challenge:

- Find a functional which leads to “DFT heaven”: predictive power with chemical accuracy
- J. Perdew’s “Jacob’s ladder” into DFT heaven:
  - DFT heaven
  - unoccupied orbitals (ACFDT-RPA)
  - occupied orbitals (hybrid-DFT)
  - meta-GGAs (kinetic energy density $\tau$)
  - GGA ($\nabla \rho$)
  - LDA ($\rho$)
  - Hartree
Hohenberg-Kohn theorem: (exact)

The total energy of an interacting inhomogeneous electron gas in the presence of an external potential $V_{\text{ext}}(\mathbf{r})$ is a functional of the density $\rho$.

$$ E = \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho] $$

Kohn-Sham: (still exact!)

$$ E = T_0[\rho] + \int V_{\text{ext}} \rho(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int \frac{\rho(\mathbf{r}) \rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho] $$

$E_{\text{kinetic}}$ non interacting

In KS the many body problem of interacting electrons and nuclei is mapped to a one-electron reference system that leads to the same density as the real system.
Exchange and correlation

- We divide the density of the N-1 electron system into the total density $n(r)$ and an exchange-correlation hole:

Properties of the exchange-correlation hole:
- Locality
- Pauli principle
- the hole contains ONE electron
- The hole must be negative

- The exchange hole affects electrons with the same spin and accounts for the Pauli principle
- In contrast, the correlation hole accounts for the Coulomb repulsion of electrons with the opposite spin. It is short range and leads to a small redistribution of charge. The correlation hole contains NO charge:
Kohn-Sham equations

\[ E = T_o[\rho] + \int V_{\text{ext}} \rho(\vec{r}) d\vec{r} + \frac{1}{2} \int \frac{\rho(\vec{r}) \rho(\vec{r}')}{|\vec{r}' - \vec{r}|} d\vec{r} d\vec{r}' + E_{xc}[\rho] \]

1-electron equations (Kohn Sham)

\[ \{ -\frac{1}{2} \nabla^2 + V_{\text{ext}} (\vec{r}) + V_C (\rho(\vec{r})) + V_{xc} (\rho(\vec{r})) \} \Phi_i (\vec{r}) = \varepsilon_i \Phi_i (\vec{r}) \]

- \( \rho(\vec{r}) = \sum_{\varepsilon_i \leq E_F} |\Phi_i|^2 \)

\( E^{\text{LDA}}_{xc} \propto \int \rho(r) \varepsilon_{xc}^{\text{hom.}} [\rho(r)] \ dr \)

\( E^{\text{GGA}}_{xc} \propto \int \rho(r) F[\rho(r), \nabla \rho(r)] \ dr \)

LDA treats both, exchange and correlation effects,

GGA but approximately

New (better ?) functionals are still an active field of research.
• Every observable quantity of a quantum system can be calculated from the density of the system ALONE (Hohenberg, Kohn, 1964).

• The density of particles interacting with each other can be calculated as the density of an auxiliary system of non-interacting particles (Kohn, Sham, 1965).
“Self-consistent Equations including Exchange and Correlation Effects”


Literal quote from Kohn and Sham’s paper: “… We do not expect an accurate description of chemical binding.”
DFT ground state of iron

- LSDA
- NM
- fcc
- in contrast to experiment

- GGA
- FM
- bcc
- Correct lattice constant

Experiment
- FM
- bcc
DFT thanks to Claudia Ambrosch (previously in Graz)

GGA follows LDA
CoO AFM-II total energy, DOS

- CoO
  - in NaCl structure
  - antiferromagnetic: AF II
  - insulator
  - $t_{2g}$ splits into $a_{1g}$ and $e_g'$
  - GGA almost splits the bands
Why is GGA better than LSDA?

- Central Co atom distinguishes between $Co^\uparrow$ and $Co^\downarrow$.
- Angular correlation.

$$\Delta V_{xc}^{\uparrow} = V_{xc}^{\uparrow\text{GGA}} - V_{xc}^{\uparrow\text{LSDA}}$$
FeF$_2$: GGA works surprisingly well

FeF$_2$: GGA splits $t_{2g}$ into $a_{1g}$ and $e_g'$

Fe-EFG in FeF$_2$:
- LSDA: 6.2
- GGA: 16.8
- exp: 16.5

LSDA and GGA agree.
# Accuracy of DFT for transition metals

## Lattice parameters (Å)

<table>
<thead>
<tr>
<th></th>
<th>Exp.</th>
<th>LDA</th>
<th>PBE</th>
<th>WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>2.51</td>
<td>2.42</td>
<td>2.49</td>
<td>2.45</td>
</tr>
<tr>
<td>Ni</td>
<td>3.52</td>
<td>3.42</td>
<td>3.52</td>
<td>3.47</td>
</tr>
<tr>
<td>Cu</td>
<td>3.61</td>
<td>3.52</td>
<td>3.63</td>
<td>3.57</td>
</tr>
<tr>
<td>Ru</td>
<td>2.71</td>
<td>2.69</td>
<td>2.71</td>
<td>2.73</td>
</tr>
<tr>
<td>Rh</td>
<td>3.80</td>
<td>3.76</td>
<td>3.83</td>
<td>3.80</td>
</tr>
<tr>
<td>Pd</td>
<td>3.88</td>
<td>3.85</td>
<td>3.95</td>
<td>3.89</td>
</tr>
<tr>
<td>Ag</td>
<td>4.07</td>
<td>4.01</td>
<td>4.15</td>
<td>4.07</td>
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<tr>
<td>Ir</td>
<td>3.84</td>
<td>3.84</td>
<td>3.90</td>
<td>3.86</td>
</tr>
<tr>
<td>Pt</td>
<td>3.92</td>
<td>3.92</td>
<td>4.00</td>
<td>3.96</td>
</tr>
<tr>
<td>Au</td>
<td>4.08</td>
<td>4.07</td>
<td>4.18</td>
<td>4.11</td>
</tr>
</tbody>
</table>

### 3d elements:
- **PBE superior, LDA much too small**

### 4d elements:
- LDA too small, PBE too large
- **New functional Wu-Cohen (WC)**

### 5d elements:
- **LDA superior, PBE too large**
### Testing of DFT functionals:

**error of theoretical lattice parameters for a large variety of solids (Li-Th)**

<table>
<thead>
<tr>
<th>Method</th>
<th>me (Å)</th>
<th>mae (Å)</th>
<th>mre (%)</th>
<th>mare (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>-0.058</td>
<td>0.058</td>
<td>-1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>SO-GGA</td>
<td>-0.014</td>
<td>0.029</td>
<td>-0.37</td>
<td>0.68</td>
</tr>
<tr>
<td>PBEsol</td>
<td>-0.005</td>
<td>0.029</td>
<td>-0.17</td>
<td>0.67</td>
</tr>
<tr>
<td>WC</td>
<td>0.000</td>
<td>0.031</td>
<td>-0.03</td>
<td>0.68</td>
</tr>
<tr>
<td>AM05</td>
<td>0.005</td>
<td>0.035</td>
<td>0.01</td>
<td>0.77</td>
</tr>
<tr>
<td>PBE</td>
<td>0.051</td>
<td>0.055</td>
<td>1.05</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**Diagram:**

- LDA
- PBE
- SO-GGA
- PBEsol
- WC
- AM05
Can LDA be improved?

- Better GGAs and meta-GGAs ($\rho$, $\nabla \rho$, $\tau$): usually improvement, but often too small.
- LDA+U: for correlated 3d/4f electrons, treat strong Coulomb repulsion via Hubbard U parameter (cheap, “empirical U” ?)
- Exact exchange: imbalance between exact X and approximate C
  - hybrid-DFT (mixing of HF + GGA; “mixing factor” ?)
  - exact exchange + RPA correlation (extremely expensive)
- GW: gaps in semiconductors, expensive!
- Quantum Monte-Carlo: very expensive
- DMFT: for strongly correlated (metallic) d (f) -systems (expensive)
Treatment of exchange and correlation

Approximations for $E_{xc}$

- **LDA**: $E_{xc}^{\text{LDA}} = \int f(\rho(r))d^3r$

- **GGA**: $E_{xc}^{\text{GGA}} = \int f(\rho(r), |\nabla \rho(r)|)d^3r$

- **MGGA**: $E_{xc}^{\text{MGGA}} = \int f(\rho(r), |\nabla \rho(r)|, \nabla^2 \rho(r), t(r))d^3r$

- **LDA+U**: $E_{xc}^{\text{LDA+U}} = E_{xc}^{\text{LDA}} + E_{ee} - E_{dc}$

- **GGA+U**: $E_{xc}^{\text{GGA+U}} = E_{xc}^{\text{GGA}} + E_{ee} - E_{dc}$

- **hybrid**: $E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}} + \alpha \left( E_{x}^{\text{HF}} - E_{x}^{\text{DFT}} \right)$

where

$$E_{x}^{\text{HF}} = -\frac{1}{2} \sum_{\sigma} \sum_{n,k \to n',k'} W_k W_{k'} \int \int \frac{\psi_{nk}^{*}(r)\psi_{n'k'}^{*}(r')\psi_{n'k'}(r)\psi_{nk}(r')}{|r - r'|} d^3rd^3r'$$
Hybrid functional: only for *(correlated)* electrons

- Only for certain atoms and electrons of a given angular momentum $\ell$

\[
E_{xc}^{\text{hybrid}} = E_{xc}^{\text{DFT}}[\rho^\sigma] + \alpha \left( E_x^{\text{HF}}[n_{m_i,m_j}^\sigma] - E_{xc}^{\text{DFT}}[\rho_{\ell}^\sigma] \right)
\]

\[
E_x^{\text{HF}}[n_{m_i,m_j}^\sigma] = -\frac{1}{2} \sum_\sigma \sum_{m_1,m_2,m_3,m_4} n_{m_1,m_2}^\sigma n_{m_3,m_4}^\sigma \langle m_1 m_3 | v_{ee} | m_4 m_2 \rangle
\]

\[
\langle m_1 m_2 | v_{ee} | m_3 m_4 \rangle = \sum_{k=0}^{2\ell} a_k F_k
\]

The Slater integrals $F_k$ are calculated according to P. Novák et al., *phys.stat.sol* (b) **245**, 563 (2006)
Structure: \(a, b, c, \alpha, \beta, \gamma, R_\alpha, \ldots\)

Structure optimization

**DFT Kohn-Sham**

\[ V(\rho) = V_C + V_{xc} \]

Poisson, DFT

\[ E^{i+1} - E^i < \varepsilon \]

no

yes

\[ E^{\text{tot}}, \text{force} \]

Minimize \(E\), force \(\rightarrow 0\)

properties

\( k \in \text{IBZ} \) (irred. Brillouin zone)

Kohn Sham

\[ [-\nabla^2 + V(\rho)]\psi_k = E_k \psi_k \]

\[ \psi_k = \sum_{k_n} C_{k_n} \Phi_{k_n} \]

Variational method

\[ \frac{\delta \langle E \rangle}{\delta C_{k_n}} = 0 \]

Generalized eigenvalue problem

\[ HC = ESC \]

\[ \rho = \sum_{E_k \leq E_F} \psi_k^* \psi_k \]
Solving Schrödinger's equation:

- \( \Psi \) cannot be found analytically
- complete “numerical” solution is possible but inefficient
- Ansatz:
  - linear combination of some “basis functions”
  - different methods use different basis sets!
- finding the “best” wave function using the variational principle:

\[
\Psi_k = \sum_{K_n} c_k \Phi_{kn}
\]

\[
\langle E_k \rangle = \frac{\langle \Psi_k^* | H | \Psi_k \rangle}{\langle \Psi_k^* | \Psi_k \rangle}
\]

\[
\frac{\partial E_k}{\partial c_{kn}} = 0
\]

- this leads to the famous “Secular equations”, i.e. a set of linear equations which in matrix representation is called “generalized eigenvalue problem”

\[
H C = E S C
\]

\( H, S : \) hamilton and overlap matrix; \( C: \) eigenvectors, \( E: \) eigenvalues
Basis Sets for Solids

- **plane waves**
  - *pseudo potentials*
  - *PAW (projector augmented wave) by P.E. Blöchl*

- **space partitioning (augmentation) methods**
  - *LMTO (linear muffin tin orbitals)*
    - ASA approx., linearized numerical radial function
      + Hankel- and Bessel function expansions
    - full-potential LMTO
  - *ASW (augmented spherical wave)*
    - similar to LMTO
  - *KKR (Korringa, Kohn, Rostocker method)*
    - solution of multiple scattering problem, Greens function formalism
    - equivalent to APW
  - *(L)APW (linearized augmented plane waves)*

- **LCAO methods**
  - *Gaussians, Slater, or numerical orbitals, often with PP option*
pseudopotential plane wave methods

- Plane waves form a “complete” basis set, however, they “never” converge due to the rapid oscillations of the atomic wave functions $\chi$ close to the nuclei.

- Let’s get rid of all core electrons and these oscillations by replacing the strong ion–electron potential by a much weaker (and physically dubious) pseudopotential.

- Hellmann’s 1935 combined approximation method.
“real” potentials vs. pseudopotentials

- “real” potentials contain the Coulomb singularity \(-Z/r\)
- the wave function has a cusp and many wiggles,
- chemical bonding depends mainly on the overlap of the wave functions between neighboring atoms (in the region between the nuclei)

→ exact form of V only needed beyond \(r_{\text{core}}\)
APW based schemes

- **APW (J.C. Slater 1937)**
  - Non-linear eigenvalue problem
  - Computationally very demanding

- **LAPW (O.K. Anderssen 1975)**
  - Generalized eigenvalue problem
  - Full-potential

- **Local orbitals (D.J. Singh 1991)**
  - treatment of semi-core states (avoids ghostbands)

  - Efficiency of APW + convenience of LAPW
  - Basis for

---


APW Augmented Plane Wave method

The unit cell is partitioned into:
- atomic spheres
- Interstitial region

Basis set:

**PW:** $e^{i(\mathbf{k} + \mathbf{K}).\mathbf{r}}$

Atomic partial waves

$$\sum_{\ell m} A^K_{\ell m} u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

$u_{\ell}(r, \varepsilon)$ are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy $\varepsilon$. $A^K_{\ell m}$ coefficients for matching the PW.
Slater’s APW (1937)

Atomic partial waves 

$$\sum_{\ell m} a^K_{\ell m} u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}')$$

Energy dependent basis functions lead to a Non-linear eigenvalue problem

H Hamiltonian
S overlap matrix

Numerical search for those energies, for which the $\det|H-ES|$ vanishes. Computationally very demanding. “Exact” solution for given MT potential!
Linearization of energy dependence

**LAPW** suggested by O.K. Andersen,

\[
\Phi_{k_n} = \sum_{\ell m} \left[ A_{\ell m}(k_n)U_{\ell}(E_\ell, r) + B_{\ell m}(k_n)\dot{U}_{\ell}(E_\ell, r) \right]Y_{\ell m}(\vec{r})
\]

expand \( u_i \) at fixed energy \( E_i \) and add \( \dot{u}_i = \frac{\partial u_i}{\partial \varepsilon} \)

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

\( \rightarrow \) General eigenvalue problem (diagonalization)

\( \rightarrow \) additional constraint requires more PWs than APW
shape approximations to “real” potentials

- Atomic sphere approximation (ASA)
  - overlapping spheres “fill” all volume
  - potential spherically symmetric

- “muffin-tin” approximation (MTA)
  - non-overlapping spheres with spherically symmetric potential +
  - interstitial region with $V=\text{const.}$

- “full”-potential
  - no shape approximations to $V$
Full-potential in LAPW (A. Freeman et al)

- The potential (and charge density) can be of general form (no shape approximation)

\[
V(r) = \begin{cases} 
\sum_{ LM } V_{ LM }(r) Y_{ LM } (\hat{r}) & r < R_a \\
\sum_{ K } V_{ K } e^{ i \mathbf{K} \cdot \mathbf{r} } & r \in I 
\end{cases}
\]

- Inside each atomic sphere a local coordinate system is used (defining LM)
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 (charge leakage)

- **Core states**
  - *Low* in energy
  - *Reside inside sphere*

1 Ry = 13.605 eV
Local orbitals (LO)

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

- LOs
  - are confined to an atomic sphere
  - have zero value and slope at \( R \)
  - Can treat two principal QN \( n \) for each azimuthal QN \( \ell \) (e.g. 3p and 4p)
  - Corresponding states are strictly orthogonal (e.g. semi-core and valence)
  - Tail of semi-core states can be represented by plane waves
  - Only slightly increases the basis set (matrix size)

An alternative combination of schemes

E. Sjöstedt, L. Nordström, D.J. Singh,

- Use **APW**, but at fixed $E_i$ (superior PW convergence)
- Linearize with additional local orbitals (lo)
  (add a few extra basis functions)

\[
\Phi_{kn} = \sum_{\ell m} A_{\ell m}(k_n) u_{\ell}(E_{\ell}, r) Y_{\ell m}(\hat{r})
\]

\[
\Phi_{lo} = [A_{\ell m}(E_i) + B_{\ell m}(E_i)] Y_{\ell m}(\hat{r})
\]

**optimal solution**: mixed basis
- use APW+lo for states, which are difficult to converge:
  (f or d- states, atoms with small spheres)
- use LAPW+LO for all other atoms and angular momenta
Improved convergence of APW+lo

Representative Convergence:

- e.g. force ($F_y$) on oxygen in SES vs. # plane waves:
  - in LAPW changes sign and converges slowly
  - in APW+lo better convergence
  - to same value as in LAPW

SES (sodium electro solodalite)

Summary: Linearization LAPW vs. APW

- **Atomic partial waves**
  - *LAPW*
    \[
    \Phi_{k_n} = \sum_{\ell m} [A_{\ell m}(k_n)u_\ell(E_\ell, r) + B_{\ell m}(k_n)\hat{u}_\ell(E_\ell, r)]Y_{\ell m}(\hat{r})
    \]
  - *APW+lo*
    \[
    \Phi_{k_n} = \sum_{\ell m} A_{\ell m}(k_n)u_\ell(E_\ell, r)Y_{\ell m}(\hat{r})
    \]

- **Plane Waves (PWs)**

- **match at sphere boundary**
  - *LAPW*
    - value and slope
      \[A_{\ell m}(k_n), B_{\ell m}(k_n)\]
  - *APW*
    - value
      \[A_{\ell m}(k_n)\]

**plus another type of local orbital (lo)**

**Atomic sphere**

**Fe**

**PW**

**LAPW**

**APW**

**r [au]**
Method implemented in WIEN2k


• Use APW, but at fixed $E_f$ (superior PW convergence)
• Linearize with additional lo (add a few basis functions)

optimal solution: mixed basis
• use APW+lo for states which are difficult to converge: ($f$- or $d$- states, atoms with small spheres)
• use LAPW+LO for all other atoms and angular momenta

A summary is given in

The WIEN2k authors

An Augmented Plane Wave
Plus Local Orbital Program for
Calculating Crystal Properties

Peter Blaha
Karlheinz Schwarz
Georg Madsen
Dieter Kvasnicka
Joachim Luitz

November 2001
Vienna, AUSTRIA
Vienna University of Technology

http://www.wien2k.at
International users

about 2500 licenses worldwide


America: ARG, BZ, CDN, MX, USA (MIT, NIST, Berkeley, Princeton, Harvard, Argonne NL, Los Alamos NL, Oak Ridge NL, Penn State, Purdue, Georgia Tech, Lehigh, John Hopkins, Chicago, Stony Brook, SUNY, UC St.Barbara, UCLA)

far east: AUS, China, India, JPN, Korea, Pakistan, Singapore, Taiwan (Beijing, Tokyo, Osaka, Kyoto, Sendai, Tsukuba, Hong Kong)

75 industries (Canon, Eastman, Exxon, Fuji, Hitachi, IBM, Idemitsu Petrochem., Kansai, Komatsu, Konica-Minolta, A.D.Little, Mitsubishi, Mitsui Mining, Motorola, NEC, Nippon Steel, Norsk Hydro, Osram, Panasonic, Samsung, Seiko Epson, Siemens, Sony, Sumitomo, TDK, Toyota).

mailinglist: 10,000 emails/6 years
The first publication of the WIEN code

FULL-POTENTIAL, LINEARIZED AUGMENTED PLANE WAVE PROGRAMS FOR CRYSTALLINE SYSTEMS

P. BLAHA, K. SCHWARZ, and P. SORANTIN
Institut für Technische Elektrochemie, Technische Universität Wien, A-1060 WIEN, Austria

and

S.B. TRICKEY
Quantum Theory Project, Depts. of Physics and of Chemistry, University of Florida, Gainesville, FL 32611, USA

PROGRAM SUMMARY

Title of program: WIEN

Computer Physics Communications 59 (1990) 399–415
In the Heart of EUROPE
『WIEN2k 入門』追加版

固体の中の電子

バンド計算の基礎と応用

和光システム研究所 著

WIEN2k 入門

WIEN-code は 1980 年ごろから、グループの指導者である Karlheinz Schwarz によって書き始められ、1990 年に最初の copyrighted version の WIEN が発表された。その後 UNIX version となり、WIEN93、WIEN95、WIEN97 を経て、Fortran90 対応の WIEN2k へと改良・拡張されてきた*1。基礎となるシュレーディンガー方程式はコーン・シャム方程式であり、バンド計算法は主として FLAPW 法、ポテンシャルは LSDA、GGA などである。最新の WIEN2k では、APW+lo も取り入れられており、ポテンシャルとしては電子相関が強いときに必要であると云われている補正 +U も扱えるようになっている。また、並列計算機を使えば、極めて複雑な結晶も計算の対象とすることができる。
Development of WIEN2k

- Authors of WIEN2k
  
  **P. Blaha, K. Schwarz, D. Kvasnicka, G. Madsen and J. Luitz**

- Other contributions to WIEN2k
  
  - C. Ambrosch-Draxl (Univ. Graz, Austria), optics
  - E. Assmann (Vienna) Wannier functions
  - F. Karsai (Vienna) parallelization
  - **R. Laskowski (Singapore)**, non-collinear magnetism, NMR chemical shifts, BSE
  - **L. Marks (Northwestern, US)**, various optimizations, new mixer
  - P. Novák and J. Kunes (Prague), LDA+U, SO
  - B. Olejnik (Vienna), non-linear optics,
  - C. Persson (Uppsala), irreducible representations
  - V. Petricek (Prague) 230 space groups
  - O. Rubel (Lakehead) Berry phases
  - M. Scheffler (Fritz Haber Inst., Berlin), forces
  - **D.J. Singh (NRL, Washington D.C., Oak Ridge)**, local orbitals (LO), APW+lo
  - E. Sjöstedt and **L Nordström (Uppsala, Sweden)**, APW+lo
  - J. Sofo (Penn State, USA) and J. Fuhr (Barriloche), Bader analysis
  - F. Tran (Vienna) Hartree Fock, DFT functionals
  - B. Yanchitsky and A. Timoshevskii (Kiev), space group

- and many others ....
A series of **WIEN workshops** were held

- **1st** Vienna April 1995 Wien95
- **2nd** Vienna April 1996 Wien97
- **3rd** Vienna April 1997 Wien97
- **4th** Trieste, Italy June 1998
- **5th** Vienna April 1999 Wien99
- **6th** Vienna April 2000 Wien2k
- **7th** Vienna Sept. 2001 Wien2k
- **8th** Esfahan, Iran April 2002
- **9th** Vienna July 2002
- **10th** Penn State, USA April 2003
- **11th** Penn State, USA July 2004
- **12th** Kyoto, Japan May 2005
- **13th** Metals and Alloys, USA Nov. 2005
- **14th** Vienna April 2006
- **15th** Penn State, USA June 2007
- **16th** Singapore July 2007
- **17th** Vienna March 2008
- **18th** Nantes, France June 2009
- **19th** Penn State, USA July 2010
- **20th** Tokyo, Japan June 2011
- **21st** Nantes, France July 2012
- **22nd** Warsaw, Poland Oct. 2014
- **23rd** Singapore Aug. 2015

**WIEN2k licenses**

- **2500 users**
(L)APW methods

APW + local orbital method
(linearized) augmented plane wave method

Total wave function

\[ \Psi_k = \sum_{K_n} C_{k_n} \phi_{k_n} \]

Variational method:

\[ < E > = \frac{< \Psi | H | \Psi >}{< \Psi | \Psi >} \]

\[ \delta < E > = 0 \]

upper bound

minimum

Generalized eigenvalue problem:

\[ H \ C = E \ S \ C \]

Diagonalization of (real or complex) matrices of size 10,000 to 50,000 (up to 50 Gb memory)
Structure: \( a, b, c, \alpha, \beta, \gamma, R_\alpha, \ldots \)

Structure optimization

iteration \( i \)

DFT Kohn-Sham

\( V(\rho) = V_C + V_{xc} \) Poisson, DFT

\( E^{i+1} - E^i < \varepsilon \)

yes

\( E^{tot}, \text{force} \)

Minimize \( E, \text{force} \rightarrow 0 \)

no

properties

\( k \in \text{IBZ} \) (irred. Brillouin zone)

Kohn Sham

\[ [-\nabla^2 + V(\rho)]\psi_k = E_k \psi_k \]

\[ \psi_k = \sum_{kn} C_{kn} \Phi_{kn} \]

Variational method

Generalized eigenvalue problem

\[ \frac{\delta <E>}{\delta C_{kn}} = 0 \]

\[ HC = ESC \]

\[ \rho = \sum_{E_k \leq E_F} \psi_k^* \psi_k \]
The Brillouin zone (BZ)

- Irreducible BZ (IBZ)
  - The irreducible wedge
  - Region, from which the whole BZ can be obtained by applying all symmetry operations

- Bilbao Crystallographic Server:
  - [www.cryst.ehu.es/cryst/](http://www.cryst.ehu.es/cryst/)
  - The IBZ of all space groups can be obtained from this server
  - using the option KVEC and specifying the space group (e.g. No.225 for the fcc structure leading to bcc in reciprocal space, No.229)
Self-consistent field (SCF) calculations

- In order to solve $H\Psi = E\Psi$ we need to know the potential $V(r)$.
- For $V(r)$ we need the electron density $\rho(r)$.
- The density $\rho(r)$ can be obtained from $\Psi(r)^*\Psi(r)$.
- $\Psi(r)$ is unknown before $H\Psi = E\Psi$ is solved.

SCF cycles

1. Start with $\rho_{in}(r)$
2. Compute $\rho(r) = \sum_{\varepsilon_i \leq E_F} |\Phi_i(r)|^2$
3. Solve $\{-\frac{1}{2}\nabla^2 + V_{eff}(r)\}\Phi_i(r) = \varepsilon_i\Phi_i(r)$
4. Calculate $V_{eff}(r) = f[\rho(r)]$
5. Do the mixing of $\rho(r)$

Diagram:
- Start with $\rho_{in}(r)$
- Compute $\rho(r) = \sum_{\varepsilon_i \leq E_F} |\Phi_i(r)|^2$
- Solve $\{-\frac{1}{2}\nabla^2 + V_{eff}(r)\}\Phi_i(r) = \varepsilon_i\Phi_i(r)$
- Calculate $V_{eff}(r) = f[\rho(r)]$
- Do the mixing of $\rho(r)$
- SCF cycles
Effects of SCF

Band structure of fcc Cu
Program structure of WIEN2k

- **init_lapw**
  - initialization
  - symmetry detection (F, I, C-centering, inversion)
  - input generation with recommended defaults
  - quality (and computing time) depends on k-mesh and R.Kmax (determines #PW)

- **run_lapw**
  - scf-cycle
  - optional with SO and/or LDA+U
  - different convergence criteria (energy, charge, forces)

- **save_lapw tic_gga_100k_rk7_vol0**
  - cp case.struct and clmsum files,
  - mv case.scf file
  - rm case.broyd* files
Flow Chart of WIEN2k (SCF)

Input $\rho_{n-1}(r)$

lapw0: calculates $V(r)$

lapw1: sets up $H$ and $S$ and solves the generalized eigenvalue problem

lapw2: computes the valence charge density

Icore

mixer

converged?

no

yes

done!

WIEN2k: P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz
Workflow of a WIEN2k calculation

- individual FORTRAN programs linked by shell-scripts
- the output of one program is input for the next
- lapw1/2 can run in parallel on many processors

SCF cycle

Iteration

- LAPW0: 3 %
- LAPW1: 75 %
- LAPW2: 20 %
- LCORE: 1 %
- MIXER: 1 %

Self consistent?

END

single mode

parallel mode

k-point parallelization

* fraction of total computation time
Advantage/disadvantage of WIEN2k

+ robust all-electron full-potential method (new effective mixer)
+ unbiased basisset, one convergence parameter (LDA-limit)
+ all elements of periodic table (comparable in CPU time), metals
+ LDA, GGA, meta-GGA, LDA+U, spin-orbit
+ many properties and tools (supercells, symmetry)
+ w2web (for novice users)

? speed + memory requirements

+ very efficient basis for large spheres (2 bohr) (Fe: 12Ry, O: 9Ry)
- less efficient for small spheres (1 bohr) (O: 25 Ry)
- large cells, many atoms ($n^3$, but new iterative diagonalization)
- full H, S matrix stored $\rightarrow$ large memory required
+ effective dual parallelization (k-points, mpi-fine-grain)
+ many k-points do not require more memory

- no stress tensor
- no linear response
w2web GUI (graphical user interface)

- Structure generator
  - spacegroup selection
  - import cif file
- step by step initialization
  - symmetry detection
  - automatic input generation
- SCF calculations
  - Magnetism (spin-polarization)
  - Spin-orbit coupling
  - Forces (automatic geometry optimization)
- Guided Tasks
  - Energy band structure
  - DOS
  - Electron density
  - X-ray spectra
  - Optics
Spacegroup P4\(_2\)/mmn

**Structure given by:**
- spacegroup
- lattice parameter
- positions of atoms (basis)

**Rutile TiO\(_2\):**
P4\(_2\)/mmn (136)
a=8.68, c=5.59 bohr

Ti: (0,0,0)

O: (0.304,0.304,0)
Wyckoff position: x, x, 0
Quantum mechanics at work

thanks to Erich Wimmer
TiC electron density

- NaCl structure (100) plane
- Valence electrons only
- plot in 2 dimensions
- Shows
  - charge distribution
  - covalent bonding
    - between the Ti-3d and C-2p electrons
  - $e_g/t_{2g}$ symmetry
TiC, three valence states at $\Delta$

Energy bands

- Ti-4s
- Ti-3d
- C-2p
- C-2s

$\Delta_1$ 423mRyd  $\Delta_2$ 620mRyd  $\Delta_5$ 636mRyd

C$\text{p}$-Ti$_d \sigma$  Ti$_d$-Ti$_d \sigma$  C$\text{p}$-Ti$_d \pi$

TiC, energy bands

P. Blaha, K. Schwarz, 
Int. J. Quantum Chem. 23, 1535 (1983)
TiC, bonding and antibonding states

Bonding and antibonding state at $\Delta 1$

antibonding

$C_p$-$Ti_d \sigma$

bonding

$C_p$-$Ti_d \sigma$
TiC, TiN, TiO

Rigid band model: limitations

Electron density $\rho$: decomposition

$$1 = q_{out} + \sum_{t} \sum_{\ell} q_{t\ell}$$

unit cell interstitial atom $t$ $\ell$=s, p, d, ...

TiC, TiN, TiO

Experimental difference electron density

Atomic form factors for Ti and C

Paired reflections

\[ s = | \mathbf{\Sigma} | \sim \frac{\sin \theta}{\lambda} \]

\[ F(\mathbf{\Sigma}) = F(\mathbf{\Sigma}) \]

spherical symm. density

\[ F(\mathbf{\Sigma}_1) + F(\mathbf{\Sigma}_2) \]

non spherical

\[ \text{with } |\mathbf{\Sigma}_1| = |\mathbf{\Sigma}_2| \]
Crucial aspects for a simulation

Theory vs. experiment: Agreement or disagreement: What can cause it?

Structure model:
- unit cell
- supercell
- surface

Quantum mechanics:
- mean field (DFT)
- many body theory
- ground vs. excited states

Convergence:
- basis sets
- k-points

Other effects:
- temperature T > 0 K
- pressure

stoichiometry
disorder
impurities, defects
electron core-hole
satellites
all electron
vacuum
supercell
ℓ quantum n.
average
vibrations

These aspects need to be considered when comparing theory with experiment.
Vienna, city of music and the Wien2k code