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

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Electronic structure of solids and surfaces

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


J.C. Slater

O.K. Andersen

Wien2k is used worldwide by about 2600 groups

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 application in literature
- See [www.wien2k.at](http://www.wien2k.at)
Review articles

K.Schwarz, *Computation of Materials Properties at the Atomic Scale*

K.Schwarz, P.Blaha, *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

K.Schwarz, P.Blaha, S.B.Trickey, *Electronic structure of solids with WIEN2k*
Molecular physics, **108**, 3147 (2010)

K.Schwarz, *DFT calculations of solids with LAPW and WIEN2k*

K.Schwarz, P.Blaha, G.K.H.Madsen,
*Electronic structure calculations of solids using the WIEN2k package for material Sciences*
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
  - *Structure, surfaces, core-level spectra, NMR, hyperfine, Wannier,...*
- 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)
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 \( \mathbf{a}, \mathbf{b}, \mathbf{c} \), three basis vectors with
the best \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) 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>Description</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 (≠ 90°) + 3 fold</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>Two right and one 120° 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.
Finite particle with a length in nm

n=3  3x3x3 particle

Fraction of atoms on surface (black) or edge (red) as function of particle size n
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 Jabob’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:

\[ V(x) \text{ has lattice periodicity ("translational invariance")}: \]

\[ V(x) = V(x+a) \]

The electron density \( \rho(x) \) has also lattice periodicity, however, the \textbf{wave function} does \textbf{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 ($G \ a$: periodicity volume):

  $$\tau^G \Psi(x) = \Psi(x + Ga) = \mu^G \Psi(x) = \Psi(x)$$

  $$\Rightarrow \mu^G = 1$$

  $$\mu = e^{2\pi \frac{g}{G}}$$

  $g = 0, \pm 1 \pm 2, \ldots$

  Def.: $$k = \frac{2\pi}{a} \frac{g}{G} \Rightarrow \mu = e^{ika}$$

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

\[ e^{i\frac{2\pi}{a}K} = 1 \quad \text{where} \quad -\frac{\pi}{a} < k < \frac{\pi}{a} \]
Concepts when solving Schrödinger’s equation in solids

**Form of potential**
- (non-)selfconsistent
- “Muffin-tin” MT
- atomic sphere approximation (ASA)

**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)**

\[
\left[ -\frac{1}{2} \nabla^2 + V(r) \right] \phi_i^k = \epsilon_i^k \phi_i^k
\]

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

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

**Treatment of spin**
- Non-spinpolarized
- Spin polarized (with certain magnetic order)
## 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><strong>+</strong></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><strong>−</strong></td>
<td>• effective one-particle approach</td>
<td>• model Hamiltonian</td>
</tr>
</tbody>
</table>

**Diagram:**
- Time averaged electron density
- Model Hamiltonian
- Lattice potential
- Coulomb interactions

**Notes:**
- DFT vs. MBT (many body theory)
Ab-initio Hamiltonian

(non-relativistic/Born-Oppenheimer approximation)

\[ H = \sum_i \left[ -\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi \varepsilon_0} \frac{Z_l}{|r_i - \mathbf{R}_l|} \right] + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{4\pi \varepsilon_0} \frac{1}{|r_i - r_j|} \]

**LDA bandstructure** corresponds to

\[ H_{\text{LDA}} = \sum_i \left[ -\frac{\hbar^2 \Delta_i}{2m_e} + \sum_l \frac{-e^2}{4\pi \varepsilon_0} \frac{1}{|r_i - \mathbf{R}_l|} \right] + \int d^3r \frac{e^2}{4\pi \varepsilon_0} \frac{1}{|r_i - \mathbf{r}|} \rho(\mathbf{r}) + V_{xc}^{\text{LDA}}(\rho(r_i)) \]

---

**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!)

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

- $E_{\text{kinetic}}$ non interacting
- $E_{\text{ne}}$
- $E_{\text{coulomb}}$
- $E_{\text{ee}}$
- $E_{xc}$ exchange-correlation

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

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

1-electron equations (Kohn Sham)

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

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

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

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

LDA treats both, exchange and correlation effects, but approximately

GGA

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).
Walter Kohn

With 80 years

• 1923 born in Vienna
• 1938 had to leave Vienna
• 1946 Univ. Toronto (master, Math)
• 1948 Harvard (PhD, Schwinger)
• Carnegie Mellon, Pittsburgh (Luttinger), Bell Labs, Copenhagen, Washington (Seattle), Paris, Imperial College (London), ETH Zürich, Unv. California, San Diego
• 1979 Founding director Santa Barbara, California
• 1964 Hohenberg Kohn
• 1965 Kohn Sham
• 1998 Nobel prize: Chemistry
• 2016, he died on April 19
“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

Graph showing the difference in energy ($\Delta E$ in mRy) for bcc and fcc Fe phases using LSDA and GGA methods. The graph also includes experimental data (exp.).
DFT thanks to Claudia Ambrosch (previously in Graz)

GGA follows LDA
Kopmanns' and Janak's theorem

**Single-electron picture**

**Koopmans' theorem:**

\[ IP = \Delta E \approx \varepsilon_i \]

\[ \text{Atom A} \quad \text{Ion A}^+ \]

\[ \text{Koopmans} \quad \Delta_{\text{SCF}} \quad \text{HF} (\psi_o) \quad \text{HF} (\psi_+) \]

\[ E_{\text{corr.}} \quad E_{\text{exact}} \quad \varepsilon_i = \frac{\partial E}{\partial n_i} \]

**Slater's transition state:**

Cl atom

**Janak's theorem:**

\[ \varepsilon_i = \frac{\partial E}{\partial n_i} \]

K. Schwarz
Chem. Physics Z, 100 (1975)
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
CoO why is GGA better than LSDA

\[ \Delta V_{xc}^{\uparrow} = V_{xc}^{GGA} - V_{xc}^{LSDA} \]

- Central Co atom distinguishes between \( Co^{\uparrow} \) and \( Co^{\downarrow} \)
- Angular correlation
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

<table>
<thead>
<tr>
<th>Element</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>
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<tr>
<td>Pd</td>
<td>3.88</td>
<td>3.85</td>
<td>3.95</td>
<td>3.89</td>
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<tr>
<td>Ag</td>
<td>4.07</td>
<td>4.01</td>
<td>4.15</td>
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<tr>
<td>Ir</td>
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<td>3.90</td>
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<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>Functional</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>
</tr>
<tr>
<td>SO-GGA</td>
<td>-0.014</td>
<td>0.029</td>
<td>0.37</td>
</tr>
<tr>
<td>PBEsol</td>
<td>-0.005</td>
<td>0.029</td>
<td>0.17</td>
</tr>
<tr>
<td>WC</td>
<td>0.000</td>
<td>0.031</td>
<td>0.03</td>
</tr>
<tr>
<td>AM05</td>
<td>0.005</td>
<td>0.035</td>
<td>0.01</td>
</tr>
<tr>
<td>PBE</td>
<td>0.051</td>
<td>0.055</td>
<td>1.05</td>
</tr>
</tbody>
</table>

**diagram:**
- LDA
- AM05
- PBEsol
- WC
- PBE
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:** $E_{xc}^{LDA} = \int f(\rho(r)) d^3 r$

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

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

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

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

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

where

$$E_{x}^{HF} = -\frac{1}{2} \sum_{\sigma} \sum_{n,k} w_k w_{k'} \int \int \frac{\psi^{\sigma*}_{nk}(r) \psi^{\sigma*}_{n'k'}(r') \psi^{\sigma}_{n'k'}(r) \psi^{\sigma}_{nk}(r')}{|r - r'|} d^3 r d^3 r'$$
Hybrid functional: only for (correlated) electrons

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

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

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

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

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**

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

**DFT Kohn-Sham**

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

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

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

Properties

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

Kohn Sham

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

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

Variational method

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

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:

$$
\Psi_k = \sum_{K_n} c_{kn} \Phi_{kn}
$$

$$
\left\langle E_k \right\rangle = \frac{\left\langle \Psi_k^* \right| H \left| \Psi_k \right\rangle}{\left\langle \Psi_k^* \right| \Psi_k \right\rangle} \quad \frac{\partial E_k}{\partial c_{kn}} = 0
$$

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

$$
H \mathbf{C} = \mathbf{E} \mathbf{S} \mathbf{C}
$$

$H, S :$ 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) \(\rightarrow\)

\[\psi_{\text{exact}}, \rho_{\text{exact}}, V_{\text{exact}}\] \(\rightarrow\) 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

---


K.Schwarz,
DFT calculations of solids with LAPW and WIEN2k

K.Schwarz, P.Blaha, S.B.Trickey,
Molecular physics, **108**, 3147 (2010)
APW Augmented Plane Wave method

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

### Basis set:

**PW:**
\[ e^{i(\mathbf{k} + \mathbf{K} \cdot \mathbf{r})} \]

**Atomic partial waves**
\[ \sum_{\ell m} A_{\ell m}^K u_{\ell}(r', \varepsilon) Y_{\ell m}(\hat{r}') \]

**u_{\ell}(r, \varepsilon) are the numerical solutions of the radial Schrödinger equation in a given spherical potential for a particular energy \( \varepsilon \).**

**A_{\ell m}^K 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

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


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

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

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

\[ \rightarrow \text{General eigenvalue problem (diagonalization)} \]

\[ \rightarrow \text{additional constraint requires more PWs than APW} \]
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=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)

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

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

SrTiO$_3$

Full potential

Muffin tin approximation

TiO$_2$ rutile
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)

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

- **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)

D.J. Singh,
An alternative combination of schemes

E. Sjöstedt, L. Nordström, D. J. Singh,
*An alternative way of linearizing the augmented plane wave method*,

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

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

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

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

- Plane Waves (PWs)
  \[ e^{i(\tilde{k} + \tilde{K}_n) \cdot \hat{r}} \]

- 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)
Method implemented in WIEN2k


- Use \textit{APW}, but at fixed $E_f$ (superior PW convergence)
- Linearize with additional lo (add a few basis functions)

\textbf{optimal solution: mixed basis}

- use \textit{APW+lo} for states which are difficult to converge: (\textit{f}- or \textit{d}- states, atoms with small spheres)
- use \textit{LAPW+LO} for all other atoms and angular momenta

A summary is given in

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 2600 licenses worldwide


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mailinglist: 10,000 emails/6 years
FULL-POTENTIAL, LINEARIZED AUGMENTED PLANE WAVE PROGRAMS FOR CRYSTALLINE SYSTEMS

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PROGRAM SUMMARY

Title of program: WIEN

Computer Physics Communications 59 (1990) 399–415
In the Heart of EUROPE

Austria

Vienna
WIEN2k入門

WIEN-codeは1980年ごろから、グループの指導者であるKarlheinzSchwarzによって書き始められ、1990年に最初のcopyrightedversionのWIENが発表された。その後UNIXversion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。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、極めて複雑な結果を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 (Free Univ. Berlin) 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 (McMaster Univ. Hamilton, ON) 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
- 3rd Vienna April 1997 Wien97
- 4th Trieste, Italy June 1998
- 5th Vienna April 1999
- 6th Vienna April 2000
- 7th Vienna Sept. 2001 Wien2k
- 8th Esfahan, Iran April 2002
- 9th Penn State, USA July 2002
- 10th Vienna April 2003
- 11th Kyoto, Japan July 2004
- 12th IPAM, Los Angeles, USA May 2005
- 13th Penn State, USA Nov. 2005
- 14th Vienna April 2006
- 15th Penn State, USA June 2007
- 16th Singapore July 2007
- 17th Vienna March 2008
- 18th Penn State, USA June 2009
- 19th Nantes, France July 2010
- 20th Penn State, USA June 2011
- 21th Tokyo, Japan Sept 2012
- 22nd Nantes, France Aug. 2013
- 23rd Warsaw, Poland July 2014
- 24th Warsaw, Poland Oct. 2014
- 25th Singapore Aug. 2015
- 26th McMaster, Canada June 2016

WIEN2k licenses

![Graph showing WIEN2k licenses over time, with 2650 users by 2016]
(L)APW methods

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

Total wave function \[ \Psi_k = \sum_{K_n} C_{k_n} \phi_{k_n} \] \( n...50-100 \) PWs /atom

Variational method:
\[ \langle E \rangle = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \]
\[ \frac{\delta \langle E \rangle}{\delta C_{k_n}} = 0 \]

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: \(a, b, c, \alpha, \beta, \gamma, R_\alpha, \ldots\)

unit cell  atomic positions

Structure optimization

iteration \(i\)

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

\( \rho = \sum_{E_k \leq E_F} \psi_k^* \psi_k \)

\( HC = ESC \)

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

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

Kohn Sham

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

\( \psi_k = \sum_{k_n} C_{kn} \Phi_{kn} \)

Variational method

Generalized eigenvalue problem

\( HC = ESC \)
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/
  - 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 ??

Start with $\rho_{in}(\mathbf{r})$

Do the mixing of $\rho(\mathbf{r})$

Calculate $V_{eff}(\mathbf{r}) = f[\rho(\mathbf{r})]$

SCF cycles

Compute $\rho(\mathbf{r}) = \sum_{\varepsilon_i \leq E_F} |\Phi_i(\mathbf{r})|^2$

Solve $\left\{-\frac{1}{2} \nabla^2 + V_{eff}(\mathbf{r})\right\}\Phi_i(\mathbf{r}) = \varepsilon_i \Phi_i(\mathbf{r})$
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

lcore

mixer

converged? yes done!

no

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
- LAPW1
- LAPW2
- LCORE
- MIXER

self consistent?

yes

no

END

Iteration

LAPW0
LAPW1
LAPW2
SUMPARA
LCORE
MIXER

self consistent?

yes

no

END

Iteration

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 basis set, 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 → 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
Structure given by:
- spacegroup
- lattice parameter
- positions of atoms
  (basis)

**Rutile TiO$_2$:**
P4$_2$/mnm (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

$\Delta_1$: 4.23mRyd
$\Delta_2$: 6.20mRyd
$\Delta_5$: 6.36mRyd

$C_p$-Ti$_d$ $\sigma$

$Ti_d$-$Ti_d$ $\sigma$

$C_p$-$Ti_d$ $\pi$

P.Blaha, K.Schwarz,
Int.J. Quantum Chem. 23, 1535 (1983)
TiC, energy bands

spaghetti

irred. rep.

character bands

\[ 1 = q_{out} + \sum_{t} \sum_{\ell} q_{t\ell} \]

unit cell interstitial atom \( t \) \( \ell = s, p, d, \ldots \)

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

P. Blaha, K. Schwarz,
Int. J. Quantum Chem. 23, 1535 (1983)
Bonding and antibonding state at $\Delta 1$

**Antibonding**

$C_p$-$Ti_d\,\sigma$

**Bonding**

$C_p$-$Ti_d\,\sigma$
Rigid band model: limitations

Electron density $\rho$: decomposition

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

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

P.Blaha, K.Schwarz,
Int.J.Quantum Chem. 23, 1535 (1983)
TiC, TiN, TiO

Atomic form factors for Ti and C

Experimental difference electron density

Paired reflections

\[ s = |\vec{s}| \approx \frac{\sin \theta}{\lambda} \]

\[ \begin{array}{ccc}
  h & k & l \\
  10 & 2 & 2 \\
  6 & 6 & 6 \\
\end{array} \]

\[ h^2 + k^2 + l^2 = 108 \]

\[ F(\vec{s}) = F(\vec{s}) \]

spheric. symm. density

\[ F(\vec{s}_1) \neq F(\vec{s}_2) \]

non spherical

with \( |\vec{s}_1| = |\vec{s}_2| \)
Reproducibility in density functional theory calculations of solids
Kurt Lejaeghere et al.
Science 351, (2016);
DOI: 10.1126/science.aad3000

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Guo-Xu Zhang,44 Stefaan Cottenier1,44

New methods Mutual agreement
Old methods Different values

Scorecard

SCIENCE sciencemag.org
Reproducibility in density functional theory calculations of solids
Kurt Lejaeghere et al.
Science 351, (2016); DOI: 10.1126/science.aad3000

from 45 institutions
The most accurate code

AE: all electron

Fig. 4. $\Delta$ values for comparisons between the most important DFT methods considered (in millielectron volts per atom). Shown are comparisons of all-electron (AE), PAW, ultrasoft (USPP), and norm-conserving pseudopotential (NCPP) results with all-electron results (methods are listed in alphabetical order in each category). The labels for each method stand for code, code/specification (AE), or potential set/code (PAW, USPP, and NCPP) and are explained in full in tables S3 to S42. The color coding illustrates the range from small (green) to large (red) $\Delta$ values. The mixed potential set SSSP was added to the ultrasoft category, in agreement with its prevalent potential type. Both the code settings and the DFT-predicted EOS parameters behind these numbers are included in tables S3 to S42, and fig. S1 provides a full $\Delta$ matrix for all methods mentioned in this article.
Precision of DFT calculations illustrated for Si

Fig. 1. Historical evolution of the predicted equilibrium lattice parameter for silicon. All data points represent calculations within the DFT-PBE framework. Values from literature (data points before 2016) (15, 16, 18, 56–62, 63–65) are compared with (i) predictions from the different codes used in this study (2016 data points, magnified in the inset; open circles indicate data produced by older methods or calculations with lower numerical settings) and (ii) the experimental value, extrapolated to 0 K and corrected for zero-point effects (red line) (26). The concepts of precision and accuracy are illustrated graphically.
“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 $r_{core}$
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

- stoichiometry
- disorder
- impurities, defects
- electron core-hole
- satellites
- all electron
- relativistic effects
- vacuum
- supercell
- $\ell$ quantum n.
- average
- vibrations

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

- 1997 DFT Conference in Vienna
  - Walter Kohn Main speaker

- 1998 Nobel Prize for Chemistry

- 2001 invited lecturer
  - My 60th birthday
Wien2k

- World of
- Interacting
- Electrons and
- Nuclei

due to

Walter Kohn