Electronic structure, atomic forces and structural relaxations by WIEN2k

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Outline:

- APW-based methods (history and state-of-the-art)
- WIEN2k
  - program structure + usage
  - forces, structure relaxation
- Applications
  - Phonons in matlockite PbFI
  - Phasetransitions in Aurivillius phases
  - Structure of Pyrochlore Y$_2$Nb$_2$O$_7$
The unit cell is partitioned into:
- atomic spheres
- Interstitial region

Bloch wave function:
- atomic partial waves
- Plane Waves (PWs)

**APW Augmented Plane Wave method**

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

**Atomic partial waves**
$$\sum_{\ell m} a_{\ell m}^K \psi_{\ell m}(\mathbf{r}', \varepsilon) Y_{\ell m}(\mathbf{\hat{r}}')$$

**Matching coefficient, radial function, spherical harmonics**
Atomic partial waves

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

Energy dependent
Radial basis functions lead to

H Hamiltonian
S Overlap matrix

Non-linear eigenvalue problem

Numerically search for the energy, for which $\det|H-ES|$ vanishes.

Computationally very demanding
“Exact” solution for a given (spherical) potential!
**Linearization of energy dependence**

**LAPW** suggested by

O.K. Andersen,


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

expand \( u_\ell \) at fixed energy \( E_\ell \) and add \( \partial_\ell u_\ell / \partial \varepsilon \)

\( A_{lm}^k, B_{lm}^k \): join PWs in value and slope

→ General eigenvalue problem (diagonalization)

→ additional constraint requires more PWs than APW

![Graph showing energy dependence and linearization](image)
The potential (and charge density) can be of general form (no shape approximation):

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

Inside each atomic sphere a local coordinate system is used (defining LM).
Problems of the LAPW method:

EFG Calculation for Rutile TiO$_2$ as a function of the Ti-$\rho$ linearization energy $E_p$

Problems of the LAPW method

Problems with semi-core states
Extending the basis: Local orbitals (LO)

\[ \Phi_{LO} = [ A_{\ell m} u_{l}^{E_{1}} + B_{\ell m} u_{l}^{E_{1}} + C_{\ell m} u_{l}^{E_{2}} ] Y_{\ell m}(\hat{r}) \]

- LO
  - 4p
  - 3p

- 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)

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

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

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

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

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 $\ell$
Improved convergence of APW+lo


- changes sign and converges slowly in LAPW
- better convergence in APW+lo

Force (Fy) on oxygen in SES (sodium electro sodalite) vs. # plane waves
APW based schemes

- APW (J.C. Slater 1937)
  - Non-linear eigenvalue problem
  - Computationally very demanding
- LAPW (O.K. Andersen 1975)
  - Generalized eigenvalue problem
  - Full-potential (A. Freeman et al.)
- Local orbitals (D.J. Singh 1991)
  - Treatment of semi-core states (avoids ghostbands)
- APW+lo (E. Sjöstedt, L. Nordstöm, D.J. Singh 2000)
  - Efficiency of APW + convenience of LAPW
  - Basis for

Quantum mechanics at work
WIEN2k software package

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

WIEN97: ~500 users
WIEN2k: ~1190 users
mailinglist: 1800 users
WIEN code as benchmark

- Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme (FPLO)
  - Secular equation
  - Core-valence transformation
  - Site representation of density and potential
  - Basis optimization

- Comparison of results from FPLO and WIEN97
  - Example of band structure: CaCuO$_2$
  - Total energies
  - Example of a semiconductor: diamond

- Summary
General remarks on WIEN2k

- WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts (needs Unix/Linux)
- real/complex version (inversion)
- 10 atom cells on 256Mb PC / 100 atom cells require 1-2 Gb
- k-point parallel on clusters with common NFS (slow network)
- MPI/Scalapack parallelization for bigger cases (>50 atoms) and fast network

h-BN/Rh(111) nanomesh: 1108 atoms+vacuum on 64 cpus

- You can run WIEN2k using any www-browser and the w2web interface, but also at the command line of an xterm.
**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*

**StructGen™**

You have to click "Save Structure" for changes to take effect!

Save Structure

- **Session: TiC**
  - /area51/plaha/lapw/2005-june/TiC

**StructGen™**

- **Title:** TiC
- **Lattice:**
  - Type: F
- **Spacegroups from Bilbao Cryst Server**
- **Lattice parameters in Å**
  - \( a = 4.3280000000 \)
  - \( b = 4.3280000000 \)
  - \( c = 4.3280000000 \)
  - \( \alpha = 90.0000000 \)
  - \( \beta = 90.0000000 \)
  - \( \gamma = 90.0000000 \)

- **Inequivalent Atoms:** 2
  - **Atom 1:**
    - Ti
    - \( Z = 22.0 \)
    - RMT = 2.0000
    - Pos 1: \( x = 0.0000000 \) \( y = 0.0000000 \) \( z = 0.0000000 \)
    - Pos 2: \( x = 0.5000000 \) \( y = 0.5000000 \) \( z = 0.5000000 \)

- **Atom 2:**
  - C
  - \( Z = 6.0 \)
  - RMT = 1.9000
  - Pos 1: \( x = 0.0000000 \) \( y = 0.0000000 \) \( z = 0.0000000 \)

Guided Tasks:

- **Energy band structure**
- **DOS**
- **Electron density**
- **X-ray spectra**
- **Optics**
Properties with WIEN2k - I

- **DFT**: LDA, various GGAs; meta-GGA, LDA+U; Hybrid-DFT for "correlated electrons"
- **Energy bands**
  - classification of irreducible representations
  - 'character-plot' (emphasize a certain band-character)
- **Density of states**
  - including partial DOS with l and m- character

\[
\text{h-BN/ Ni(111): } \sigma \text{ and } \pi \text{ bands}
\]

\[
\text{d-x^2-y^2}
\]
Properties with WIEN2k - II

- Electron densities, potential
  - total-, valence-, difference-, spin-densities, $\rho$ of selected states
  - 1-D, 2D- and 3D-plots (Xcrysden)
  - X-ray structure factors, STM pictures
  - Bader’s atom-in-molecule analysis, atomic basins and charges ($\nabla \rho \cdot \vec{n} = 0$)
  - spin+orbital magnetic moments (+ spin-orbit)

- Hyperfine parameters
  - Isomer shift
  - Electric field gradients
  - hyperfine fields (contact + dipolar + orbital contribution)
Properties with WIEN2k - III

- **Spectroscopy**
  - core levels (with core holes)
  - X-ray emission, absorption, electron-energy-loss
    - (core - valence/conduction-band transitions including matrix elements and angular dep.)
    - EELS inclusion of possible non-dipol transitions (momentum transfer)
  - optical properties (dielectric function in RPA, JDOS including momentum matrix elements and Kramers-Kronig)
  - fermi surface (2D, 3D)

**Mg-K XAS**
probes empty Mg-p

including a core-hole in supercell
(Final state rule)

from ground-state DOS
Properties with WIEN2k - IV

- Total energy and forces
  - optimization of internal coordinates, \((damped \text{ MD, BROYDEN})\)
  - cell parameter only via \(E_{\text{tot}}\) \((\text{no stress tensor})\)
  - elastic constants for cubic cells
  - Phonons via a direct method \((\text{based on forces from supercells})\)
    - interface to PHONON (K.Parlinski) – bands, DOS, thermodynamics, neutrons

Pyrochlore structure of \(Y_2Nb_2O_7\): strong phonon instabilities \(\rightarrow\) phase transition
Total energies and atomic forces
(Yu et al.; Kohler et al.)

- **Total Energy:**
  - **Electrostatic energy**
  - **Kinetic energy**
  - **XC-energy**

- **Force on atom** $\alpha$:
  - **Hellmann-Feynman-force**
  - **Pulay corrections**
    - Core
    - Valence

- expensive, contains a summation of matrix elements over all occupied states (done only in last scf-iteration)

\[
U[\rho] = \frac{1}{2} \int d^3 \vec{r} \rho(\vec{r}) V_{es}(\vec{r}) + \frac{1}{2} \sum_\alpha Z_\alpha V_{es}^\alpha(\vec{r})
\]

\[
T[\rho] = \sum_i n_i \varepsilon_i - \int d^3 \vec{r} \rho(\vec{r}) V_{eff}(\vec{r})
\]

\[
E_{xc}[\rho] = \int d^3 \vec{r} \rho(\vec{r}) \varepsilon_{xc}(\vec{r})
\]

\[
\vec{F}^\alpha = -\frac{dE_{tot}}{d\vec{R}_\alpha} = F_{HF}^\alpha + F_{core}^\alpha + F_{val}^\alpha
\]

\[
F_{HF}^\alpha = Z_\alpha \lim_{m \rightarrow 0} \sum_{r_\alpha} V_{1m}^{es}(r_\alpha) \nabla_\alpha \left[ r_\alpha Y_{1m}(\hat{r}) \right]
\]

\[
F_{core}^\alpha = -\int \rho_{core}(r) \nabla_\alpha V_{eff}(r) d\vec{r}
\]

\[
F_{val}^\alpha = \int \nabla_\alpha \rho_{val}(r) V_{eff} d\vec{r} + \sum_i n_i \sum_{K,K'} c_i^*(K') c_i(K) \times \\
\left[ (K^2 - \varepsilon_i) \int \phi_{K'}^*(r) \phi_K(r) dS_\alpha - i(K - K') \langle \phi_K | H - \varepsilon_i | \phi_K \rangle_\alpha \right]
\]
New developments (available)

- non-linear optics (B.Olejnik)
- non-collinear magnetism (spin-spirals to fully-relativistic) (R.Laskowski)
- transport properties (Fermi velocities, Seebeck, conductivity, thermoelectrics, ..) (G.Madsen)
- GW (M.Scheffler): excited states
- BSE (R.Laskowski) Bethe-Salpether equation for electron-hole interactions; excitons

Intra-atomic NCM, fcc $Pu$

Spin density maps of fcc Pu. Calculation in FULL mode with SO. Average momenta point to

(a) plane $x = 0$  
(b) plane $z = 1/10$
PHONON-I

PHONON
- by K.Parlinski (Crakow)
- runs under MS-windows
- uses a "direct" method to calculate Force-constants with the help of an ab initio program
- with these Force-constants phonons at arbitrary k-points can be obtained

- Define your spacegroup
- Define all atoms at previously optimized positions
- Define an interaction range (supercell)
  - create displacement file
  - transfer case.d45 to Unix

- Calculate forces for all required displacements
  - init_phonon_lapw
    - for each displacement a case_XX.struct file is generated in an extra directory
    - runs nn and lets you define RMT values like:
      - 1.85 1-16

- init_lapw: either without symmetry (and then copies this setup to all case_XX) or with symmetry (must run init_lapw for all case_XX) (Do NOT use SGROUP)
- run_phonon: run_lapw –fc 0.1 –i 40 for each case_XX
analyze_phonon_lapw
- reads the forces of the scf runs
- generates "Hellman-Feynman" file case.dat and a "symmetrized HF-file case.dsy (when you have displacements in both directions)
  - check quality of forces:
  - sum $F_x$ should be small (0)
  - abs($F_x$) should be similar for +/- displacements
- transfer case.dat (dsy) to Windows
- Import HF files to PHONON
- Calculate phonons
### Phonons in matlockite PbFI

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>c</th>
<th>c/a</th>
<th>z₁/c</th>
<th>zₚb/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc.</td>
<td>4.227</td>
<td>10.02</td>
<td>2.371</td>
<td>0.690 (0.659)</td>
<td>0.149 (0.167)</td>
</tr>
<tr>
<td>Expt</td>
<td>4.2374</td>
<td>8.800</td>
<td>2.077</td>
<td>0.663</td>
<td>0.164</td>
</tr>
</tbody>
</table>

**Symmetry Atoms**

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Atoms</th>
<th>Calc.</th>
<th>Calc.</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eg (R)</td>
<td>Pb₁(x, y), Pb₂(−x, −y), I₁(−x, −y), I₂(x, y)</td>
<td>36</td>
<td>41</td>
<td>36</td>
</tr>
<tr>
<td>Eu (I)</td>
<td>Pb₁(−x, −y), Pb₂(−x, −y), F₁(x, y), F₂(x, y), I₁(x, y), I₂(x, y)</td>
<td>35</td>
<td>47</td>
<td>50, 62 [16]</td>
</tr>
<tr>
<td>Eg (R)</td>
<td>Pb₁(−x, −y), Pb₂(x, y), F₁(x, −y), F₂(−x, y), I₁(−x, −y), I₂(x, y)</td>
<td>40</td>
<td>64</td>
<td>61</td>
</tr>
<tr>
<td>A₂u (I)</td>
<td>Pb₁(−z), Pb₂(−z), I₁(z), I₂(z)</td>
<td>79</td>
<td>71</td>
<td>67</td>
</tr>
<tr>
<td>A₁g (R)</td>
<td>Pb₁(z), Pb₂(−z), I₁(−z), I₂(z)</td>
<td>61</td>
<td>73</td>
<td>105</td>
</tr>
<tr>
<td>A₁g (R)</td>
<td>Pb₁(z), Pb₂(−z), I₁(z), I₂(−z)</td>
<td>108</td>
<td>109</td>
<td>142, 154 [16]</td>
</tr>
<tr>
<td>E_u (I)</td>
<td>F₁(x, y), F₂(x, y)</td>
<td>141</td>
<td>150</td>
<td>206</td>
</tr>
<tr>
<td>B₁g (R)</td>
<td>F₁(−z), F₂(z)</td>
<td>212</td>
<td>217</td>
<td></td>
</tr>
<tr>
<td>Eg (R)</td>
<td>F₁(−x, −y), F₂(x, y)</td>
<td>274</td>
<td>259</td>
<td>318, 332 [16]</td>
</tr>
</tbody>
</table>

**Calc.** Calculated at the experimental lattice parameters.

**Calc.** Calculated at the theoretical lattice parameters.

Ferroelectricity in Aurivillius phases

- **Bilbao**: J. Manuel Perez-Mato, M. Aroyo
  Universidad del País Vasco
- **Vienna**: P. Blaha, K. Schwarz,
  J. Schweifer
- **Cracow**: K. Parlinski
- J.M. Perez-Mato et al. PRB, **70**, 214111
Ferroelectric Perovskites: PbTiO$_3$

PbTiO$_3$

- Ferroelectric PT due to symmetry break at $T_c$:
  - cubic $\longrightarrow$ tetragonal
  - $Pm-3m$ $\longrightarrow$ $P4mm$

- A single (degenerate) *normal mode* is responsible for the PT

- Structure in Ferroelectric Phase:
  
  high-symmetry structure + frozen polar mode
Ab-initio “prediction” of the ferroelectric instability

PbTiO$_3$

Waghmare & Rabe 1997

King-Smith & Vanderbilt 1994
Ab-initio Phonon Branches

Ghosez et al. 1999

Polar unstable mode
The Aurivillius Compounds

\[ [Bi_2O_2]-[A_{n-1}B_nO_{3n+1}] \]

\[ \text{Bi}_2\text{O}_2 \]

\[ \text{n-sized perovskite slab} \]

cation deficient perovskites:

\[ [\text{Bi},A]_B_{1-x}O_3 \]

Dipl. Thesis - S. Borg 2001
Bi$_2$SrTa$_2$O$_9$ - SBT

Spontaneous polarization

polar $E_u$ mode (deg. 2)
Previous ab-initio calculations in SBT

Stachiotti et al. 2000

- Unstable $E_u$ polar mode
- Strong contribution of Bi displacement:
  Bi-O(2) hybridization
From symmetry analysis (group/subgroup relations) the $E_u$ mode alone cannot explain the complete phase transition.

Ferroelectric Phase = $E_u + X_3^- + X_2^+$ mode
Phonons in SBT

CALCULATED “PHONON” BRANCHES
Ferroelectric Phase = $E_u + X_3^- + X_2^+$ mode

Theoretical $E_u$ and $X_3^-$ modes agree well with experimental modes

BUT! .... The experimental frozen mode $X_2^+$ does not
Comparing exp. and calculated $X_2^+$ Modes

Two independent normal-modes

Part 1

coincides approx. with calculated soft-mode $X_2^+$

Part 2

coincides approx. with a second (hard) mode $X_2^+$
Predicted Ground State:

Only mode $X_3^-$ frozen!

Space group Amam

Essential reason:
Strong biquadratic coupling penalizes "mixed" states

Something missing?
• coupling with $X_2^+$
Coupling with $X_2^+$

- Coupling with **soft** $X_2^+$ mode relatively weak!
- **Strong renormalization** of hard (second) $X_2^+$ mode

![Graph showing energy change vs. Q (bohr)]
including only soft $X_2^+$ mode with additional hard $X_2^+$ mode

only with the additional hard $X_2^+$ mode the experimentally observed combination of 3 different modes can be established
Phase diagram for Bi$_2$SrTa$_2$O$_9$ - SBT

- Finite temperature renormalization of the T=0 energy map
- Landau theory suggests linear T-variation of the quadratic stiffness coefficients $\kappa_{Eu}$ and $\kappa_{X3}$

The topology of this phase diagram predicts two second order phase transitions and implies the existence of an intermediate phase of Amam symmetry. A single first order PT is impossible.
Pyrochlore $Y_2Nb_2O_7$

Insulating and non-magnetic 4d TM-oxide

Metal Sublattice: Corner-shared tetrahedral network

First theoretical results:

- Ionic model: $Y_2^3+\text{Nb}_2^{4+}\text{O}_7^{2-}$  \text{Nb}^{4+}: 4d$^1$

- → metallic or localized system with spin $1/2$
  (neither one observed in exp.)

- LDA gives nonmagnetic metallic ground-state with conventional $t_{2g}$-$e_g$ splitting due to the octahedral crystal field of the oxygen atoms.

“degenerate” $t_{2g}$ states are only partly filled.
- Antiferromagnetic s=1/2 solution
  - (on geometrically frustrated lattice !?)
- Localization, strong e⁻-e⁻ correlation:
  - 4d (not 3d !) electrons,
  - thus correlation should be small (Hubbard-U ~ 2-3 eV)
  - LDA+U with U=6 eV gives insulator (FM ground state, no AFM)
  - bandwidth of t₂g bands: 2.5 eV (similar to U)
- structural distortion, which breaks the dominant octahedral crystal field

→ Search for phonon-instabilities
  - 88 atom supercell, 46 symmetry adapted selected distortions from PHONON; resulting forces → back into PHONON
- strong Phonon-instabilities, lowest at X, K, L
- select a certain (unstable) phonon, freeze it into the structure with a certain amplitude and perform full structural optimization
Γ, X and K-point phonons:

- energy lower than in ideal pyrochlore structure, but still not insulating
L-point (111) phonon:

- Relaxed structure is an **Insulator**
- Energy gain of 0.5 eV/FU

![Graph showing electronic structure with relaxed and unrelaxed states, indicating a gap and a metal phase.](image)
Relaxed structure:

- Primitive supercell with 88 atoms
- all atoms inequivalent
due to numerical optimization of the positions in P1
  - Tests possible symmetries with increasing tolerance
- Space group → P-43m, 88 atoms/cell,
  - Inequivalent atoms:
    - 2 Y
    - 2 Nb
    - 3 O1
    - 5 O2
Main change in structural relaxation

Original pyrochlore

Relaxed structure

$3.65 \text{ Å} \quad \text{equal}$

$2.91 \text{ Å}$

$3.90 \text{ Å}$

$3.89 \text{ Å}$

$\text{Nb1–triangle: } 3.40 \text{ Å}$
Peak A ($\text{Nb}_2$) 4-center bond ($d-z^2$)

O-2p
(Nb-4d)
(Y-4d)

Nb-4d (O-2p), Y-4d
Conclusions

- WIEN2k is a powerful tool to understand solids
  - *electronic and geometric structure*
  - *interpretation of experiments (spectra)*
- Together with PHONON you can calculate phonons also in rather complicated structures
- Use “phonons” not only to match with experiment but to investigate interesting physics
  - *phase transitions*
  - *search for unknown structures*

Thank you for your attention!