Wannier functions

Macroscopic polarization (Berry phase) and related properties

Effective band structure of alloys

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Wannier functions
Bloch functions

\[ \psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) e^{i \mathbf{k} \cdot \mathbf{r}} \]

Indexed by the wave vector

\( \Gamma \)-point

\( \psi_{k_0}(x) \)

\( \psi_{k_1}(x) \)

\( \psi_{k_2}(x) \)

Both sets: complete and orthonormal

Wannier functions (localized orbitals)

\[ |\mathbf{R}n\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{-i \mathbf{R} \cdot \mathbf{r}} |\psi_{nk}\rangle. \]

Indexed by the lattice vector in real space

\( w_0(x) \)

\( w_1(x) \)

\( w_2(x) \)

Wannier:
PRB 52, 191 (1937)
Marzari et al.:
PRB 56, 12847 (1997)
Max. localized Wannier functions (MLWF)

Bloch functions (more precisely):

\[ \psi_{nk}(\mathbf{r}) = u_{nk}(\mathbf{r}) \, e^{i\mathbf{k} \cdot \mathbf{r}} \, e^{i\phi_{nk}} \]

gauge freedom \rightarrow ambiguity

\[ \Omega = \sum_n \left[ \langle 0n | r^2 | 0n \rangle - \langle 0n | \mathbf{r} | 0n \rangle^2 \right] = \sum_n \left[ \langle r^2 \rangle_n - \bar{r}_n^2 \right] \]
Two flavours of Wannier functions

- Atom centered sp$^3$-like
- Bond centered s-like

- includes bonding and antibonding states
- building effective hamiltonian

- includes valence states
- charge transfer and polarization

Workflow

- Regular SCF calculation
- Band structure plot

- Initialize wien2wannier (init_w2w):
  - select bands, init. projections, # of WF (case.inwf file)
  - projected band structure “bands_plot_project” (case.win file)
  - additional options related to entanglement (case.win file)

- Compute overlap matrix element $S_{mn}$ and projections $M_{mn}$ (x w2w)

- Perform Wannierization (x wannier90):
  - position of Wannier centers and spreads (case.wout file)
  - Wannier hamiltonian (case_hr.dat file)

- Initialize plotting, select plotting range, r-mesh (write_inwplot)
- Evaluate WF on the r-mesh selected (x wplot)
- Convert the output of wplot into xcrysden format for plotting (wplot2xsf)

- Plot WF
Wannier functions as a tight-binding basis (atom centered FW)

(Atom-centered WF)

\$ \text{less GaAs-WANN_hr.dat} \$

\[
\begin{array}{cccc}
0 & 0 & 0 & 1 \\
0 & 0 & 0 & 2 \\
0 & 0 & 0 & 3 \\
0 & 0 & 0 & 4 \\
0 & 0 & 0 & 5 \\
0 & 0 & 0 & 6 \\
0 & 0 & 0 & 7 \\
0 & 0 & 0 & 8 \\
\end{array}
\]

\[
\begin{array}{cccc}
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
1 & 1 & 1 & 1 \\
\end{array}
\]

\[
\begin{array}{c}
-4.335108 \\
-0.000001 \\
0.000000 \\
-0.000001 \\
-1.472358 \\
-1.157088 \\
-1.157088 \\
-1.157088 \\
-0.001219 \\
\end{array}
\]

\[
\begin{array}{c}
0.000000 \quad \text{Im part} = 0 \\
\end{array}
\]

Matrix element (eV)
\[
\langle s_1|H|s_1 \rangle = E_{s_1}
\]

\[
\begin{array}{c}
\langle s_2|H|s_1 \rangle = V_{ss\sigma} \\
\langle p_2|H|s_1 \rangle = V_{sp} \\
\end{array}
\]

Home unit cell
Neighbour unit cell

WF are well localized \( \Rightarrow \) nearest-neighbour suffice
Band structure

- original Wien2k band structure
- Band structure computed from Wannier hamiltonian
Relation to polarization (bond centered WF)

P = \frac{e}{V} \left( \sum Z_n r_n - \sum \sigma_n r_n \right)

(87)

(88)
Useful resources


• Wien2Wannier home and user guide: http://www.ifp.tuwien.ac.at/forschung/arbeitsgruppen/cms/software-download/wien2wannier/

• Wannier90 home and user guide: http://www.wannier.org/

Macroscopic polarization

+ 

+ BerryPI
Material properties related to polarization

Piezo- and Ferroelectricity

Dielectric screening

Effective charge

Pyroelectricity
What is polarization?

We will now assume that in each atom there are charges $q$ separated by a distance $\delta$, so that $q\delta$ is the dipole moment per atom. (We use $\delta$ because we are already using $d$ for the plate separation.) If there are $N$ atoms per unit volume, there will be a dipole moment per unit volume equal to $Nq\delta$. This dipole moment per unit volume will be represented by a vector, $P$. Needless to say, it is in the direction of the individual dipole moments, i.e., in the direction of the charge.

Polarization for periodic solids is undefined.
Modern theory of polarization

Pioneered by King-Smith, David Vanderbilt and Raffaele Resta

All measurable physical quantities are related to the change in polarization!

$$\Delta P = P^{(0)} - P^{(1)}$$

\[ \frac{\Delta P}{\Delta \text{strain}} \]

\[ \frac{\Delta P}{\Delta E} \]

\[ \frac{\Delta P}{\Delta T} \]

"Fire" (-Air) Electricity
Components of polarization

\[ P = P_{\text{ion}} + P_{\text{el}} \]

\[ P_{\text{ion}} = \frac{e}{\Omega} \sum_s Z_s^{\text{ion}} r_s \]

In Wien2k, \( Z_s^{\text{ion}} \) is the core charge.

\[ -P_{\text{el}} = \Omega^{-1} \int d\mathbf{r} \mathbf{r} \rho(\mathbf{r}) = \Omega^{-1} \sum_n^{\text{occ. bands}} \langle \psi_n | \mathbf{r} | \psi_n \rangle \]

\[ \equiv \frac{2e\epsilon}{(2\pi)^3} \sum_n^{\text{occ. bands}} \int_{\text{BZ}} d\mathbf{k} \langle u_{nk} | \nabla_{\mathbf{k}} | u_{nk} \rangle \]
Need \texttt{wien2k}, \texttt{wien2wannier}, \texttt{python} 2.7.x and \texttt{numpy}

\begin{verbatim}
\end{verbatim}

![Diagram of BerryPi workflow]

Completed SCF cycle

- Generate k-mesh in the full BZ (\textsc{kgen})
- Prepare nearest-neighbour k-point list
- Calculate wavefunctions (\textsc{lapw1})
- Calculate overlap matrix $S_{mn}$ (\textsc{w2w})
- Determine electron. and ion. phases

Spin-polarized

- Orbital potential (e.g., LDA+U)
- Spin-orbit

Polarization vector

Choice of a reference structure

\[ \Delta P = P^{(0)} - P^{(1)} \]

- structure file must preserve the symmetry
- begin with the lowest symmetry (\( \lambda_1 \)) case
- copy case \( \lambda_1 \) to case \( \lambda_0 \)
- edit structure file for case \( \lambda_0 \)
- do not initialize calculation (\texttt{init\_lapw})
- update density (\texttt{x dstart})
- run SCF cycle (\texttt{run[sp]\_lapw [-so -orb]})
- run BerryPI
Demonstration: Effective charge of GaN

General definition

\[ Z_{s,ij}^{*} = \frac{\Omega}{e} \frac{\Delta P_i}{\Delta r_{s,j}} \]

\[ \varphi = \varphi_{\text{el}} + \varphi_{\text{ion}} \]

\[ \Delta \varphi = \varphi(\text{perturbed}) - \varphi(\text{unperturbed}) \]

\[ Z_{s,ii}^{*} = \frac{\Delta \varphi_i}{2\pi \Delta u_{s,i}} \]

“Shortcut” (i=j, no volume change)
**GaN: effective charge, dielectric constants**

**substance:** gallium nitride (GaN)  
**property:** effective charge, dielectric constants (lattice properties)  

**Born effective charge** (wurtzite structure)

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Numerical Values</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z^*$</td>
<td>2.73(3)</td>
<td>from LO-TO splitting, Raman scattering from bulk GaN</td>
<td>01G</td>
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<tr>
<td></td>
<td>2.51</td>
<td>ab initio DFT(LDA) calculation</td>
<td>01Z</td>
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<td>$Z_{xx}^*$</td>
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<td>$Z_{zz}^*$</td>
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<td></td>
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<tr>
<td>$Z_{B,xx}^*$</td>
<td>1.14</td>
<td>$Z_{B,ij}^* = Z_{ii}^* / \sqrt{e_{ii}}$</td>
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<tr>
<td>$Z_{B,zz}^*$</td>
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<tr>
<td>$Z_{zz}^*$</td>
<td>2.75</td>
<td></td>
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</tbody>
</table>
Useful resources


• BerryPl home and tutorials: https://github.com/spichardo/BerryPl/wiki


Effective band structure of alloys

+ fold2Bloch
Semiconductor alloys

(\text{InGaAl})P \quad (\text{InGa})N

IR detector: (HgCd)Te

Solar radiation spectrum

Eg = 1 \text{ eV junction: (InGa)(NAs)}

Energy gap (eV) vs. Lattice constant (Å)

1.55 \mu m lasers:
(\text{InGa})\text{As}
(\text{InGa})(\text{NAsSb})
\text{Ga(AsBi)}
Band structure

Silicon
2-atom basis

Silicon
250-atom supercell

Effective mass

Forbidden optical transition

Energy gap

Si

Bloch wave vector

Wave vector

Energy (eV)

Silicon

Energy (eV)

Energy (eV)

Spectral weight

VBE

CBE
Unfolding the first-principle band structure

Plane wave expansion

$$\Psi_{n,K}(r) = \sum_{G} C_{n,K}(G) e^{i(K+G)\cdot r}$$

Bloch spectral weight

$$w_n(k) = \sum_{g} |C_{n,K}(k + g)|^2$$

Popescu & Zunger:

Rubel et al.
Workflow

- Construct primitive unit cell
- Make supercell (supercell)
- Run SCF calculation

**XCRYSDEN**

- Create k-path (case.klist_band file)

**fold2Bloch**

- Unfold band structure (fold2Bloch)

**MATLAB**

- Plot effective band structure (ubs_dots*.m)
Demonstration: Band structure of Si$_{1-x}$Ge$_x$ alloy ($x \sim 0.2$)
Thermoelectric material: $\text{Si}_{0.7}\text{Ge}_{0.3}$
(Hg,Cd)Te band structure evolution

Thus, have different “topology.” As the composition Hg are labeled with arrows. The disorder affects only the electronic states located 1

FIG. 6. (Color online) Evolution of the band structure in ternary (HgCd)Te alloy near the Hg8Te point (b). Regions of the band structure perturbed by disorder are labeled with arrows. The disorder affects only the electronic states located 1

The crossover is accompanied by emergence of massless Kane fermions at the Fermi energy irrespective of the Hg

Further increase of the cadmium content beyond 6

Limits their symmetry are shown at Fig.

The evolution of the Hg

limits their solubility.

The prominent feature of HCT is the presence of massless Kane fermions [46(b)] until 4

which experimental observation was recently reported by Or-

namous order of bands [27], which

Far, the successful incorporation of Bi in GaAs under 12%

γ

−

−

Hg8Te ↔ Hg8Bi and, thus, have different “topology.” As the composition Hg
Impact of alloying disorder on charge transport

CdTe → (HgCd)Te

GaAs → Ga(AsBi)

μ_ latino{h} = 200 \rightarrow 10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}

μ_ latino{e} = 4,000 \rightarrow 2,500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}

μ_ latino{e} = 1,100 \rightarrow 1,000,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}
Useful resources


• fold2Bloch home and tutorials: https://github.com/rubel75/fold2Bloch
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