Maximally localized Wannier functions: Theory, and some applications
Nicola Marzari, EPFL and PSI

Origins: linear-scaling methods
... and the definition of the polarization (position operator)

Original Articles
Theory of the electric polarization in crystals
R. Resta
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Theory of polarization of crystalline solids

R. D. King-Smith and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, P. O. Box 849, Piscataway, New Jersey 08855-0849
(Received 10 June 1992)

We consider the change in polarization $\Delta P$ which occurs upon making an adiabatic change in the Kohn-Sham Hamiltonian of the solid. A simple expression for $\Delta P$ is derived in terms of the valence-band wave functions of the initial and final Hamiltonians. We show that physically $\Delta P$ can be interpreted as a displacement of the center of charge of the Wannier functions. The formulation is successfully applied to compute the piezoelectric tensor of GaAs in a first-principles pseudopotential calculation.

Bloch theorem

The one-particle effective Hamiltonian $\hat{H}$ in a periodic lattice commutes with the lattice-translation operator $\hat{T}_R$, allowing us to choose the common eigenstates according to the prescriptions of Bloch theorem:

$$[\hat{H}, \hat{T}_R] = 0 \Rightarrow \Psi_{nk}(r) = u_{nk}(r) e^{i k \cdot r}$$

- $n, k$ are the quantum numbers (band index and crystal momentum), $u$ is periodic
- From two requirements: a translation can’t change the charge density, and two translations must be equivalent to one that is the sum of the two
Bloch wavefunctions in 1d

From Bloch orbitals to Wannier functions

\[ |R_n\rangle = \int_{BZ} \Psi_{nk}(r) e^{-i\mathbf{k} \cdot \mathbf{R}} \, dk \]

Gauge freedoms

- Arbitrary phase factor for every \( nk \) (Schrödinger)

\[ |R_n\rangle = \int_{BZ} [e^{i\phi_n(k)} \psi_{nk}(r)] e^{-i\mathbf{k} \cdot \mathbf{R}} \, dk \]
Long-range decay (heuristic...)

Isolated band, Wannier function around the origin

\[ w_0(r) = \int_{BZ} \Psi_k(r) \, dk = \int_{BZ} u_k(r) \, e^{ik \cdot r} \, dk \]

For \( r \to \infty, \, r = R_i \)

\[ w_0(R_i) = \int_{BZ} u_k(0) \, e^{ik \cdot R_i} \, dk \]

Unitary transformations

\[ |\psi_{nk}^{(W)}\rangle = \sum_{m} |\psi_{mk}\rangle U_{mn}^{(k)} \]

Rotated Bloch function

Unitary matrix

\[ |\psi_1^{(W)}\rangle \rightarrow |\psi'_1\rangle \]

\[ |\psi_2^{(W)}\rangle \rightarrow |\psi'_2\rangle \]
From Bloch orbitals to Wannier functions

\[ |R_n\rangle = \int_{BZ} \psi_{nk}(r) e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k} \]

Gauge freedoms

- Arbitrary phase factor for every \( nk \) (Schrödinger)
- Arbitrary unitary rotations \( U^{(k)}_{mn} \) for every \( k \) (DFT)

\[ |R_n\rangle = \int_{BZ} \sum_{m} U^{(k)}_{mn} \psi_{mk}(r) e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k} \]

Generalized Wannier functions for composite bands

\[ |R_n\rangle = \int_{BZ} \sum_{m} U^{(k)}_{mn} \psi_{mk}(r) e^{-i\mathbf{k}\cdot\mathbf{R}} d\mathbf{k} \]

- \( \{|R_n\rangle\} \) span the same space as \( \{ |\psi_{nk}\rangle\} \)
- \( |R_n\rangle = w_n(r - R) \) (translational images)
- \( \langle R_n|R'_m \rangle = \delta_{n,m} \delta_{R,R'} \)
Generalized Wannier functions for composite bands

\[ |R_n⟩ = \int_{BZ} \sum_m U^{(k)}_{mn} ψ_{mk}(r) e^{-i\mathbf{k} \cdot \mathbf{R}} \, d\mathbf{k} \]

But how to choose U?

U and WF's by projection

A simple route is to obtain U through a projection onto a pre-defined set of local orbitals \( g_n \)

\[ |φ_{nk}⟩ = \sum_{m=1}^{J} |ψ_{mk}⟩⟨ψ_{mk}|g_n⟩ \]

Can we choose u without reference to predetermined states?
U and WF's by localization

\[ \Omega = \sum_n \left[ \langle 0n | r^2 | 0n \rangle - \langle 0n | r | 0n \rangle^2 \right] \]

For a given set of Bloch orbitals, our goal is to minimize \( \Omega \) with respect all the sets of unitary transformations \( U_{mn}^{(k)} \).

Outline

\[ |R_n \rangle = \int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-i k \cdot R} \, dk \]
|$R_n$| = $\int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-ik \cdot R} dk$

Bloch states from favourite electronic-structure code

|$R_n$| = $\int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-ik \cdot R} dk$

2 unitary transformations
Iteratively refine $U_{mn}^{(k)}$ to localize $|R_n\rangle$
Decomposition of the localization functional

$$\Omega = \sum_n \left[ \langle 0n| r^2 |0n \rangle - \langle 0n| r |0n \rangle^2 \right]$$

$$\Omega_1 = \sum_n \left[ \langle r^2 \rangle_n - \sum_{R_m} \left| \langle R_m | r | 0n \rangle \right|^2 \right]$$,

$$\tilde{\Omega} = \sum_n \sum_{R_m \neq 0n} \left| \langle R_m | r | 0n \rangle \right|^2$$.

$\Omega_1$ and $\tilde{\Omega}$ are positive-definite and $\Omega_1$ is gauge-invariant!

$\Omega_1$ is gauge invariant, positive definite

projection operators $P = \sum_{R_m} |R_m \rangle \langle R_m |$ and $Q = I - P$

$$\Omega_1 = \sum_n \left[ \langle r^2 \rangle_n - \sum_{R_m} \left| \langle R_m | r | 0n \rangle \right|^2 \right] =$$

$$= \sum_{n, \alpha} \langle 0n | r_\alpha r_\alpha | 0n \rangle_n - \sum_{n, \alpha} \left[ \sum_{R_m} \langle 0n | r_\alpha | R_m \rangle \langle R_m | r_\alpha | 0n \rangle \right] =$$

$$= \sum_{n, \alpha} \langle 0n | r_\alpha (I - P) r_\alpha | 0n \rangle = \sum_\alpha \text{tr}_c [r_\alpha Q r_\alpha] = \sum_\alpha \|Pr_\alpha Q\|^2_c$$
Position operator is ill defined!

\[ \langle \psi_k | x | \psi_k \rangle = \int_{-\infty}^{\infty} x |u_k(x)|^2 \, dx \]

Blount identities

Centers of Wannier functions:

\[ |w_0\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} |\psi_k\rangle \]

\[ = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}} |u_k\rangle \]

\[ \mathbf{r} |w_0\rangle = \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} \left( -i \nabla_k e^{i\mathbf{k} \cdot \mathbf{r}} \right) |u_k\rangle \]

\[ = i \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}} \left( \nabla_k |u_k\rangle \right) \]

\[ \langle w_0 | \mathbf{r} | w_0 \rangle = i \frac{V}{(2\pi)^3} \int_{\text{BZ}} d\mathbf{k} \langle u_k | \nabla_k | u_k \rangle \]

E. I. Blount, Solid State Physics 13, 305 (1962)
The reciprocal space representation

a) we need to be able to calculate derivatives on regular meshes in k-space; if cubic symmetry is assumed, with each of the \( N \) \( k \)-points having \( Z = 6, 8 \) or \( 12 \) first-neighbors \( k + b \), then:

\[
\nabla f(k) = \frac{3}{Zb^2} \sum_b b [f(k+b) - f(k)] .
\]

b) we need to express the positions of the Wannier functions and their spread as a function of the phase relations between the Bloch orbitals.

\[
\mathbf{r}_n = \langle w_{n0} | \mathbf{r} | w_{n0} \rangle = \frac{1}{N_k} \sum_k \langle u_{nk} | i \frac{\partial}{\partial k} | u_{nk} \rangle
\]

\[3\]

The reciprocal space representation

\[
M_{mn}^{(k,b)} = \langle u_{mk} | u_{n,k+b} \rangle
\]

\[4\]

\[
\bar{r}_n = -\frac{1}{N} \sum_{k,b} w_b b \text{Im} \ln M_{mn}^{(k,b)}
\]

\[
\langle r^2 \rangle_n = \frac{1}{N} \sum_{k,b} w_b \left\{ \left[ 1 - |M_{nn}^{(k,b)}|^2 \right] + \left[ \text{Im} \ln M_{nn}^{(k,b)} \right]^2 \right\}
\]
The localization procedure

We consider an infinitesimal rotation of the Bloch orbitals

\[ |u_{nk}\rangle \rightarrow |u_{nk}\rangle + \sum_m dW_{mn}^{(k)} |u_{mk}\rangle \]

The Gradient

\[ G^{(k)} = \frac{d\Omega}{dW^{(k)}} = 4 \sum_b w_b \left( A[R^{(k,b)}] - S[T^{(k,b)}] \right) \]

provides an equation of motion (e.g. conjugate-gradient) for the evolution of the \( U_{mn}^{(k)} \) towards the minimum of \( \Omega \).

\[ A[B] = \frac{B - B^\dagger}{2}, \quad S[B] = \frac{B + B^\dagger}{2i}, \]

and defining \( q_n^{(k,b)} = \text{Im} \phi_n^{(k,b)} + b \cdot r_n \), \( T_{mn}^{(k,b)} = R_{mn}^{(k,b)} q_n^{(k,b)} \).
First conclusions

- **general algorithm** to characterize the Wannier functions (or localized orbitals) of any given system

- applicable to periodic crystals, disordered systems, isolated molecules, in the spirit of supercell calculations

- **post-processing** of a conventional electronic-structure calculation

- maximal localization in the orbitals obtained in the Bloch-to-Wannier transformation
What to do next?

IV. Analysis of Chemical Bonding
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      2. Local dielectric response in layered systems
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      4. Improving system-size scaling
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      1. First-principles model Hamiltonians
      2. Self-interaction and DFT + Hubbard $U$

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Wannier functions in $\alpha$-Si

Wannier functions in $l$-$H_2O$

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P. L. Silvestrelli and M. Parrinello, JCP (1999)

Disentanglement of attached bands

– Maximally-localized Wannier-like functions for conduction subspace
– Extract differentiable manifold with optimal smoothness


Iterative minimization of $\Omega_i$

Minimize degree of mismatch between $\mathcal{S}^{(i)}(k)$ and $\mathcal{S}^{(i-1)}(k + b)$, i.e.,

$$\text{maximize overlap } \sum_{b} \sum_{m=1}^{N} \left| \left\langle u_{n,k}^{(i)} | u_{m,k+b}^{(i-1)} \right\rangle \right|^2$$

1st iteration: Choose trial subspace at each $k$ (e.g. projected orbitals)

$i$th iteration: At each $k$ pick the $N$ highest eigenvectors of

$$\begin{bmatrix} \sum_b \hat{P}_{k+b}^{(i-1)} | u_{n,k}^{(i)} \rangle \langle u_{n,k}^{(i)} | & \hat{P}_{k+b}^{(i-1)} \end{bmatrix}$$

$\hat{P}_{k+b}^{(i-1)}$ : Projector onto $\mathcal{S}^{(i-1)}(k + b)$

Repeat until self-consistency (when spaces $\mathcal{S}(k)$ stabilize)
Silicon: bonding and antibonding orbitals

- **Bonding**
  - $7.53 \text{ bohr}^2$
  - $24.37 \text{ bohr}^2$
  - $sp^3$
  - Spread $= 10.68 \text{ bohr}^2$

$d$ bands of copper

- **Panel (a)**
  - Two possible choices of energy window

- **Panel (b)**
  - The $e_g$ WFs of panel (b)
  - Spread $e_g = 1.700 \text{ bohr}^2$
  - Spread $e_g = 1.718 \text{ bohr}^2$
s bands of copper

Exact constraint – frozen inner window

Suppose we want WF’s to describe the original bands exactly in a prescribed energy range (“inner window”).

⇒ Minimize $\Omega_1$ w/ constraint that states inside inner window are included in the optimal subspaces $S(k)$.

Hybrid s-d character:
Maximally localized Wannier functions in antiferromagnetic MnO within the FLAPW formalism

Michel Posternak* and Alfonso Baldereschi
Institute of Theoretical Physics, Swiss Federal Institute of Technology Lausanne, EPFL, PHB-Ecublens,
CH-1015 Lausanne, Switzerland

Sandro Massidda
Istituto Nazionale di Fisica della Materia–Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria,
I-09042 Monserrato (CA), Italy

Nicola Marzari
Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307
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1) Bloch-by-Bloch: The LEGO bricks of electronic structure
Electronic structure of nanostructures

Minimization of the spread functional

\[ \Omega = \sum_n [(\langle \mathbf{r}^2 \rangle_n - \langle \mathbf{r} \rangle_n^2)] \]

exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

\[ |R_n\rangle = \int_{BZ} \sum_m U_{mn}^{(k)} \Psi_{mk}(r) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k} \]

Electronic Ground State
From Static or Dynamical Large-Scale Simulations

Optimal Unitary Transformation of the Bloch Orbitals

Real Space Maximally-Localized Wannier Functions

Electronic structure of nanostructures

Sparse Hamiltonian Matrix

Green’s Function
Transmission Function

Ballistic Conductance
Density of States

\[ G(E) = \frac{2e^2}{h} T(E) \]

\[ N(E) = -(1/n) \text{Im}[\text{Tr}G_C^\dagger(E)] \]

**Max-loc WFs ↔ “Exact” Tight-Binding**

Compact mapping of Bloch states into local orbitals

\[
\omega_n(r - R) = \frac{V}{8\pi^3} \int_{BZ} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{nk}(r) d\mathbf{k}
\]

\[
\psi_{nk}(r) = \frac{1}{\sqrt{N_R}} \sum_{R} e^{i\mathbf{k}\cdot\mathbf{R}} \omega_n(r - R)
\]

\[
\langle \psi_{ik} | \hat{H} | \psi_{jk} \rangle = H_{ij}^{00} + e^{i\mathbf{k}\cdot\mathbf{R}} H_{ij}^{01} + e^{-i\mathbf{k}\cdot\mathbf{R}} H_{ij}^{0\dagger}
\]

\(\Rightarrow\) Diagonalize H Matrix


---

**Max-loc WFs ↔ “Exact” Tight-Binding**

(5,5) SWCNT  (8,0) SWCNT

Band structure and conductance of a SWCNT

Γ-point:
2eV pseudo gap

Two eigenchannels at $E_F$ ⇒ perfect recovery of metallic character!


The LEGO bricks of electronic structure
Inelastic quantum transport

2) AUTOMATED WANNIERIZATION

PROJECTABILITY DISENTANGLEMENT

J. Qiao, G. Pizzi, and N. Marzari, in preparation (2022)
Automated Wannierization of 17,744 materials, \textbf{1,155,049 MLWFs}

Average error of 1.7 meV in the band distance $\eta$ between original and Wannier-interpolated bands
**PROJECTABILITY DISENTANGLEMENT**

- Atom-centered Wannier functions

![Distance of Wannier function centers from nearest atom (left) and second nearest (right)](image)

J. Qiao, G. Pizzi, and N. Marzari, in preparation (2022)

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### 3) KOOPMANS SPECTRAL FUNCTIONALS

For every orbital the expectation value

\[
\epsilon_i = \langle \varphi_i | \hat{H}^{DFT} | \varphi_i \rangle
\]

does not depend on the occupation of the orbital

LINEARIZATION

\[ E^{KI} = E^{DFT} + \sum_i \left[ - \int_0^{f_i} \langle \varphi_i | \hat{H}^{DFT} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{DFT} | \varphi_i \rangle \right] \]

remove \sim quadratic Slater

G. Borghi et al., Physical Review B 90, 075135 (2014)

SCREENING

\[ E^{KI} = E^{DFT} + \sum_i \alpha_i \left[ - \int_0^{f_i} \langle \varphi_i | \hat{H}^{DFT} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{DFT} | \varphi_i \rangle \right] \]

orbital-dependent screening coefficient

N. Colonna et al., Journal of Chemical Theory and Computation 14, 2549 (2018)
LOCALIZATION

![Graph showing IP vs. 1/L_z for alkanes and polyethylene, with various theoretical methods indicated.]


OUT OF WHICH KOOPMANS BAND

![Graphs showing band structures for GaAs using LDA, HSE, and KI methods.]

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>HSE</th>
<th>GW_0</th>
<th>scGW</th>
<th>KI</th>
<th>Exp.</th>
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<tbody>
<tr>
<td>E_{gap}(eV)</td>
<td>0.19</td>
<td>1.28</td>
<td>1.55</td>
<td>1.62</td>
<td>1.57</td>
<td>1.52</td>
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<tr>
<td>⟨ε_d⟩(eV)</td>
<td>-14.9</td>
<td>-15.6</td>
<td>-17.3</td>
<td>-17.6</td>
<td>-17.7</td>
<td>-18.9</td>
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<tr>
<td>W(eV)</td>
<td>12.8</td>
<td>13.9</td>
<td>–</td>
<td>–</td>
<td>12.8</td>
<td>13.1</td>
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</table>

OUT OF WHICH KOOPMANS BAND

ZnO

<table>
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<tr>
<th></th>
<th>LDA</th>
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<tr>
<td>Eₙₐₜₙ (eV)</td>
<td>0.79</td>
<td>2.79</td>
<td>3.0</td>
<td>3.2</td>
<td>3.62</td>
<td>3.60</td>
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<tr>
<td>⟨εₜₜₜ⟩ (eV)</td>
<td>-5.1</td>
<td>-6.1</td>
<td>-6.4</td>
<td>-6.7</td>
<td>-6.9</td>
<td>-7.5/-8.0</td>
</tr>
</tbody>
</table>


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http://www.wannier.org/

Welcome! This is the home of maximally-localised Wannier functions (MLWFs) and Wannier90, the computer program that calculates them.

Maximally localized Wannier functions: Theory and applications
Nicola Marzari, Arash A. Mostofi, Jonathan R. Yates, Ivo Souza, David Vanderbilt
Rev. Mod. Phys. 84, 1419-1475 (2012)

Wannier90 as a community code: new features and applications

THANKS!