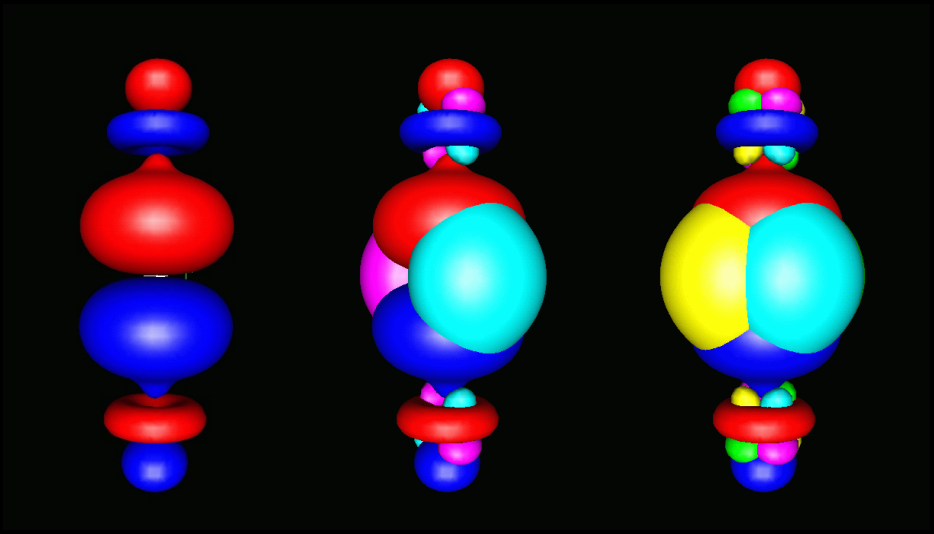
Maximally localized Wannier functions: Theory, and some applications

Nicola Marzari, EPFL and PSI



Origins: linear-scaling methods

PHYSICAL REVIEW B VOLUME 47, NUMBER 16 15 APRIL 1993-II

Density-matrix electronic-structure method with linear system-size scaling

X.-P. Li, R. W. Nunes, and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, P.O. Box 849, Piscataway, New Jersey 08855-0849
(Received 27 July 1992)

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 15 15 APRIL 1993-I

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Orbital formulation for electronic-structure calculations with linear system-size scaling

Francesco Mauri, Giulia Galli, and Roberto Car
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), PHB-Ecublens, 1015 Lausanne, Switzerland
(Received 19 January 1993)

PHYSICAL REVIEW B VOLUME 48, NUMBER 19 15 NOVEMBER 1993-I

Unconstrained minimization approach for electronic computations that scales linearly with system size

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Department of Physics, University of Illinois, Urbana, Illinois 61801

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Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701-2979

Matthew P. Grumbach and Richard M. Martin
Department of Physics, University of Illinois, Urbana, Illinois 61801
(Received 8 March 1993)

… and the definition of the polarization (position operator)

Original Articles

Theory of the electric polarization in crystals

R. Resta

Pages 51-55 | Received 03 Feb 1992, Published online: 10 Feb 2011

Download citation https://doi.org/10.1080/00150199208016065

RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 3 15 JANUARY 1993-I

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 **ΔP** which occurs upon making an adiabatic change in the Kohn-Sham Hamiltonian of the solid. A simple expression for **ΔP** is derived in terms of the valence-band wave functions of the initial and final Hamiltonians. We show that physically **ΔP** 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.

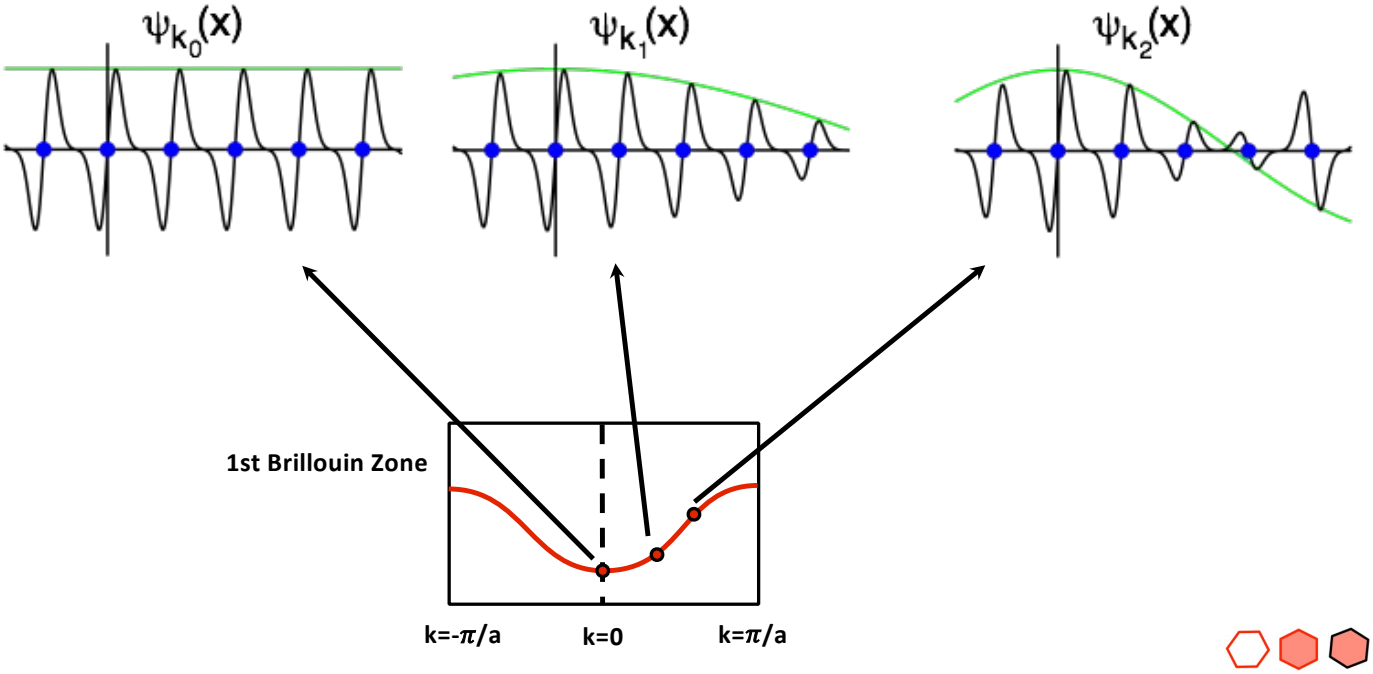
Bloch theorem

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

$$[\,\hat{H},\,\hat{T}_{\mathrm{R}}\,] = 0 \;\;\Rightarrow\;\; \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}$$

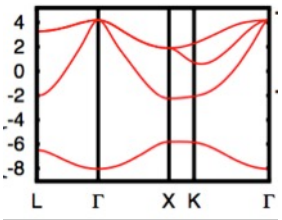
- *n, k* are the quantum numbers (band index and crystal momentum), *u* is periodic
- From two requirements: a translation can't change the charge density, and two translations must be equivalent to one that is the sum of the two

Bloch wavefunctions in 1d



From Bloch orbitals to Wannier functions

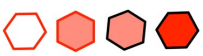
$$|\mathbf{R}n\rangle = \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Gauge freedoms

- Arbitrary phase factor for every $n\mathbf{k}$ (Schrödinger)

$$|\mathbf{R}n\rangle = \int_{BZ} \left[e^{i\phi_n(\mathbf{k})}\psi_{n\mathbf{k}}(\mathbf{r})\right] e^{-i\mathbf{k}.\mathbf{R}} d\mathbf{k}$$



Long-range decay (heuristic…)

Isolated band, Wannier function around the origin

$$w_0(\mathbf{r}) = \int_{BZ} \Psi_{\mathbf{k}}(\mathbf{r})\, d\mathbf{k} = \int_{BZ} u_{\mathbf{k}}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k}$$

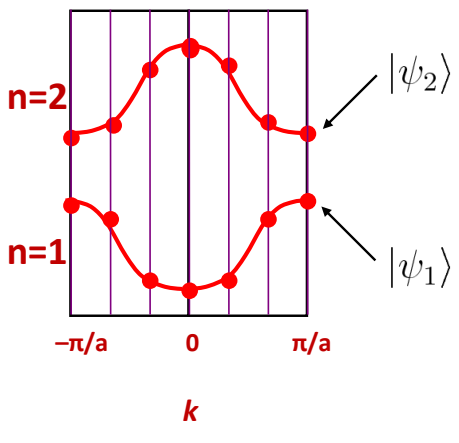
For $\mathbf{r} \to \infty, \mathbf{r} = \mathbf{R}_i$

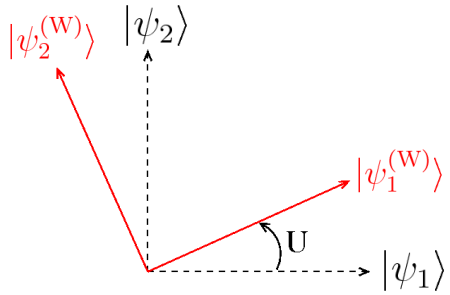
$$w_0(\mathbf{R}_i) = \int_{BZ} u_{\mathbf{k}}(0)\, e^{i\mathbf{k}\cdot\mathbf{R}_i}\, d\mathbf{k}$$

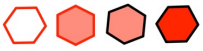
Unitary transformations

$$|\psi_{n\mathbf{k}}^{(\mathrm{W})}\rangle = \sum_m |\psi_{m\mathbf{k}}\rangle U_{mn}^{(\mathbf{k})}$$

Rotated Bloch function **Unitary matrix**

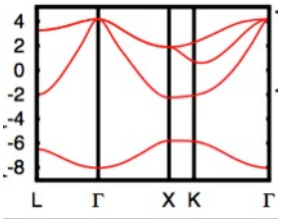






From Bloch orbitals to Wannier functions

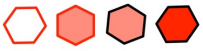
$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \Psi_{n\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Gauge freedoms

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

$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \sum_m U^{(\mathbf{k})}_{mn}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Generalized Wannier functions for composite bands

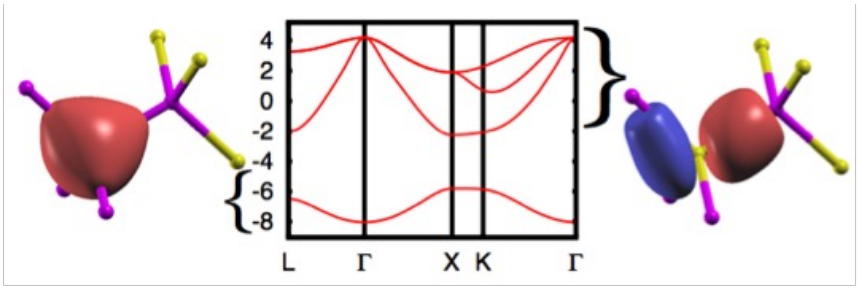
$$|\mathbf{R}n\rangle \;=\; \int_{BZ} \sum_m U^{(\mathbf{k})}_{mn}\, \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

- $\{|\mathbf{R}n\rangle\}$ span the same space as $\{|\Psi_{n\mathbf{k}}\rangle\}$
- $|\mathbf{R}n\rangle \;=\; w_n(\mathbf{r}-\mathbf{R})$ (translational images)
- $\langle \mathbf{R}n|\mathbf{R}'m\rangle \;=\; \delta_{n,m}\,\delta_{\mathbf{R},\mathbf{R}'}$

Generalized Wannier functions for composite bands

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

But how to choose U?



U and WFs by projection

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

$$|\phi_{n\mathbf{k}}\rangle = \sum_{m=1}^{J} |\psi_{m\mathbf{k}}\rangle\langle\psi_{m\mathbf{k}}|g_n\rangle$$

Can we choose U without reference to predetermined states?

U and WFs by localization

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

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

N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997)

Outline

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Outline

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Bloch states from favourite electronic-structure code

Outline

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

2 unitary transformations

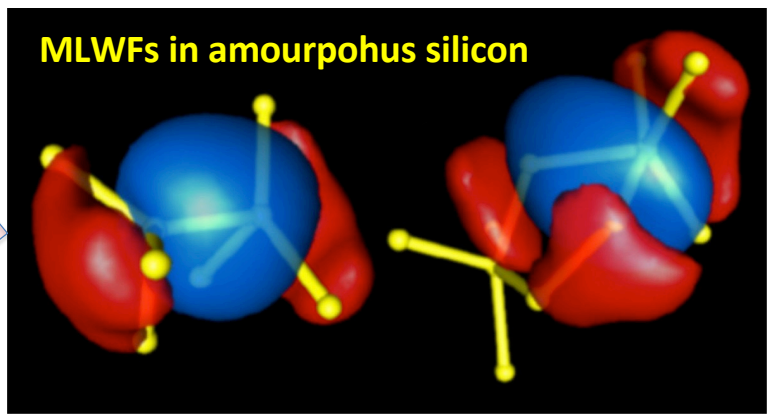
Outline

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$

Iteratively refine $U_{mn}^{(k)}$ to localize $|Rn\rangle$

Outline

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Decomposition of the localization functional

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

$$\Omega_{\rm I} = \sum_n \left[\langle r^2\rangle_n - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m|\mathbf{r}|0n\rangle \right|^2 \right] \quad ,$$

$$\widetilde{\Omega} = \sum_n \sum_{\mathbf{R}m\neq 0n} \left| \langle \mathbf{R}m|\mathbf{r}|0n\rangle \right|^2 \quad .$$

$\Omega_{\rm I}$ and $\widetilde{\Omega}$ are *positive-definite* and $\Omega_{\rm I}$ is *gauge-invariant !*

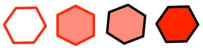
$\Omega_{\rm I}$ is gauge invariant, positive definite

projection operators $\mathbb{P} = \sum_{\mathbf{R}m} |\mathbf{R}m\rangle\langle\mathbf{R}m|$ and $\mathbb{Q} = \mathbb{I} - \mathbb{P}$

$$\Omega_{\rm I} = \sum_n \left[\langle r^2\rangle_n - \sum_{\mathbf{R}m} \left| \langle \mathbf{R}m|\mathbf{r}|0n\rangle \right|^2 \right] =$$

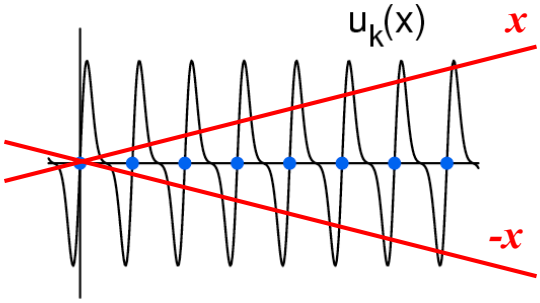
$$= \sum_{n,\alpha} \langle 0n|r_\alpha r_\alpha|0n\rangle_n - \sum_{n,\alpha} \left[\sum_{\mathbf{R}m} \langle 0n|r_\alpha|\mathbf{R}m\rangle\langle\mathbf{R}m|r_\alpha|0n\rangle \right] =$$

$$= \sum_{n,\alpha} \langle 0n|r_\alpha(\mathbb{I}-\mathbb{P})r_\alpha|0n\rangle = \sum_\alpha {\rm tr}_{\rm c}[r_\alpha \mathbb{Q}\, r_\alpha] = \sum_\alpha \|\mathbb{P}r_\alpha\mathbb{Q}\|_{\rm c}^2$$



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:

$$|\, w_0 \rangle = \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \, |\psi_{\mathbf{k}}\rangle$$

$$= \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \, e^{i\mathbf{k}\cdot\mathbf{r}} \, |u_{\mathbf{k}}\rangle$$

$$\mathbf{r} \,|\, w_0 \rangle = \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \, (\, -i\nabla_{\mathbf{k}} \, e^{i\mathbf{k}\cdot\mathbf{r}} \,) \, |u_{\mathbf{k}}\rangle$$

$$= i \, \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \, e^{i\mathbf{k}\cdot\mathbf{r}} \, (\, \nabla_{\mathbf{k}} \, |u_{\mathbf{k}}\rangle \,)$$

$$\boxed{\langle w_0 \,|\, \mathbf{r} \,|\, w_0 \rangle = i \, \frac{V}{(2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{k} \, \langle u_{\mathbf{k}}| \, \nabla_{\mathbf{k}} \, |u_{\mathbf{k}}\rangle}$$

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; i f cubic symmetry is assumed, with each of the N k-points having $Z = 6, 8$ or 12 first-neighbors $\mathbf{k} + \mathbf{b}$, then:

$$\nabla f(\mathbf{k}) \;=\; \frac{3}{Zb^2} \sum_{\mathbf{b}} \mathbf{b} \left[f(\mathbf{k}+\mathbf{b}) - f(\mathbf{k}) \right] \;\; .$$

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.

$$\mathbf{r}_n = \langle\, w_{n0} \,|\, \mathbf{r} \,|\, w_{n0} \,\rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k}} \langle\, u_{n\mathbf{k}} \,|\, i\frac{\partial}{\partial \mathbf{k}} \,|\, u_{n\mathbf{k}} \,\rangle$$

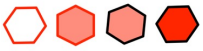
3

The reciprocal space representation

$$M_{mn}^{(\mathbf{k},\mathbf{b})} \;=\; \langle\, u_{m\mathbf{k}} \,|\, u_{n,\mathbf{k}+\mathbf{b}} \,\rangle$$

$$\bar{\mathbf{r}}_n = -\frac{1}{N} \sum_{\mathbf{k},\mathbf{b}} w_b \, \mathbf{b} \, \mathrm{Im} \ln M_{nn}^{(\mathbf{k},\mathbf{b})}$$

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

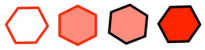


4

The localization procedure

We consider an infinitesimal rotation of the Bloch orbitals

$$|u_{n\mathbf{k}}\rangle \;\rightarrow\; |u_{n\mathbf{k}}\rangle + \sum_m dW^{(\mathbf{k})}_{mn}\,|u_{m\mathbf{k}}\rangle$$



The localization procedure

We consider an infinitesimal rotation of the Bloch orbitals

$$|u_{n\mathbf{k}}\rangle \;\rightarrow\; |u_{n\mathbf{k}}\rangle + \sum_m dW^{(\mathbf{k})}_{mn}\,|u_{m\mathbf{k}}\rangle$$

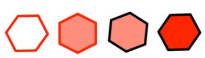
The Gradient

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

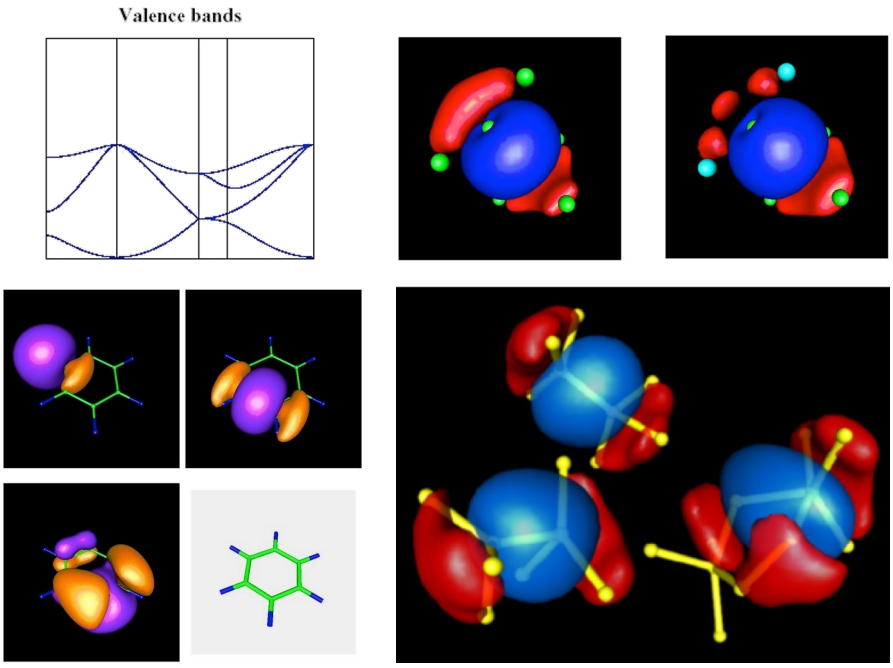
provides an equation of motion (e.g. conjugate-gradient) for the evolution of the $U^{(\mathbf{k})}_{mn}$ towards the minimum of Ω.

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

and defining $q^{(\mathbf{k},\mathbf{b})}_n = \mathrm{Im}\,\phi^{(\mathbf{k},\mathbf{b})}_n + \mathbf{b}\cdot\mathbf{r}_n$, $T^{(\mathbf{k},\mathbf{b})}_{mn} = \widetilde{R}^{(\mathbf{k},\mathbf{b})}_{mn}\, q^{(\mathbf{k},\mathbf{b})}_n$,



Silicon, GaAs, amorphous silicon, benzene



M. Fornari, N. Marzari, M. Peressi, and A. Baldereschi, Comp. Mater. Science 20, 337 (2001)

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?

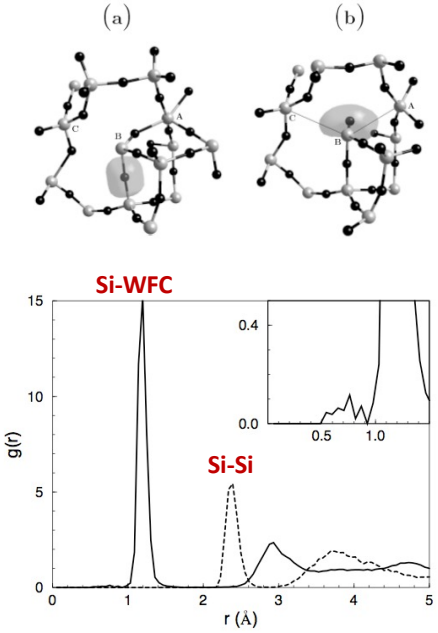
IV. Analysis of Chemical Bonding
- A. Crystalline solids
- B. Complex and amorphous phases
- C. Defects
- D. Chemical interpretation
- E. MLWFs in first-principles molecular dynamics

V. Electric Polarization and Orbital Magnetization
- A. Wannier functions, electric polarization, and localization
  1. Relation to Berry-phase theory of polarization
  2. Insulators in finite electric field
  3. Wannier spread and localization in insulators
  4. Many-body generalizations
- B. Local polar properties and dielectric response
  1. Polar properties and dynamical charges of crystals
  2. Local dielectric response in layered systems
  3. Condensed molecular phases and solvation
- C. Magnetism and orbital currents
  1. Magnetic insulators
  2. Orbital magnetization and NMR
  3. Berry connection and curvature
  4. Topological insulators and orbital magnetoelectric response

VI. Wannier Interpolation
- A. Band-structure interpolation
  1. Spin-orbit-coupled bands of bcc Fe
  2. Band structure of a metallic carbon nanotube
  3. *GW* quasiparticle bands
  4. Surface bands of topological insulators
- B. Band derivatives
- C. Berry curvature and anomalous Hall conductivity
- D. Electron-phonon coupling

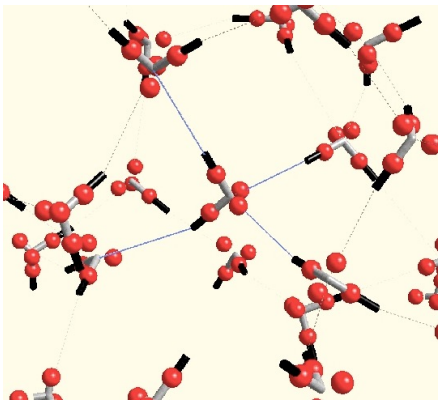
VII. Wannier Functions as Basis Functions
- A. WFs as a basis for large-scale calculations
  1. WFs as electronic-structure building blocks
  2. Quantum transport
  3. Semiempirical potentials
  4. Improving system-size scaling
- B. WFs as a basis for strongly correlated systems
  1. First-principles model Hamiltonians
  2. Self-interaction and DFT + Hubbard *U*

Wannier functions in *a-Si*



P. L. Silvestrelli, N. Marzari, D. Vanderbilt, and M. Parrinello, Solid State Comm. (1998)

Wannier functions in *l-H_2O*

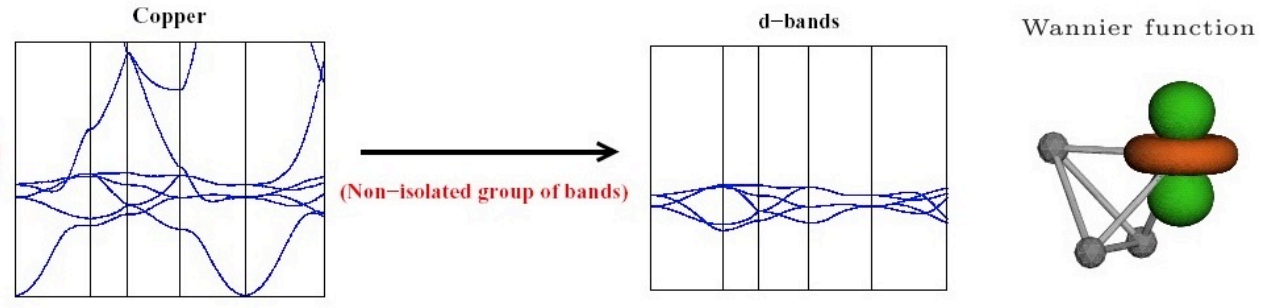


P. L. Silvestrelli and M. Parrinello, JCP (1999)

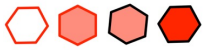
Disentanglement of attached bands

– Maximally-localized Wannier-like functions for conduction subspace

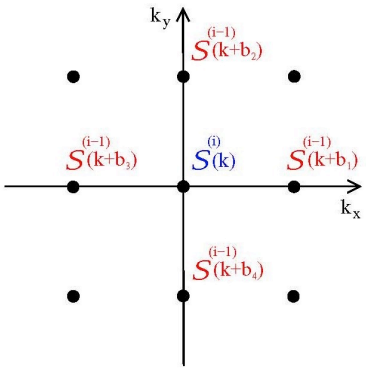
– Extract differentiable manifold with **optimal smoothness**



I. Souza, N. Marzari and D. Vanderbilt, Phys. Rev. B 65, 035109 (2002)



Iterative minimization of Ω_I



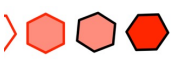
Minimize degree of mismatch between $\mathcal{S}^{(i)}(\mathbf{k})$ and $\mathcal{S}^{(i-1)}(\mathbf{k}+\mathbf{b})$, i.e., maximize overlap $\sum_{\mathbf{b}} \sum_{m=1}^{N} \left| \left\langle u_{n\mathbf{k}}^{(i)} \middle| u_{m,\mathbf{k}+\mathbf{b}}^{(i-1)} \right\rangle \right|^2$

- 1^{st} iteration: Choose trial subspace at each $\mathbf{k}$ (e.g. projected orbitals)
- i^{th} iteration: At each $\mathbf{k}$ pick the N highest eigenvectors of

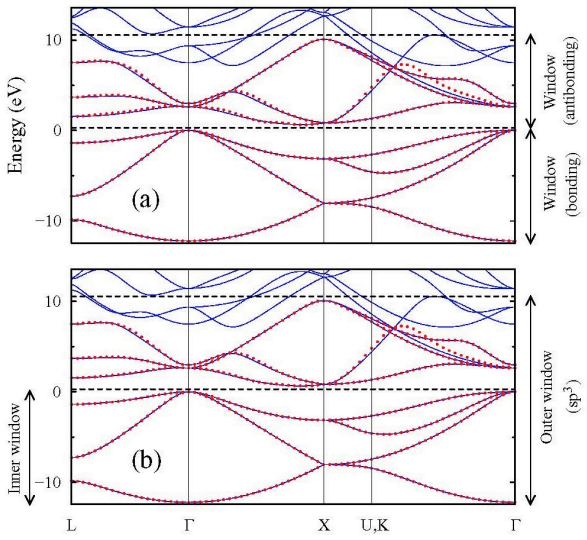
$$\left[\sum_{\mathbf{b}} \hat{P}_{\mathbf{k}+\mathbf{b}}^{(i-1)}\right] \left| u_{n\mathbf{k}}^{(i)} \right\rangle = \lambda_{n\mathbf{k}}^{(i)} \left| u_{n\mathbf{k}}^{(i)} \right\rangle$$

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

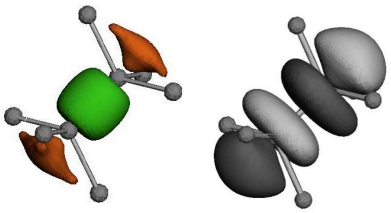
- Repeat until self-consistency (when spaces $\mathcal{S}(\mathbf{k})$ stabilize)



Silicon: bonding and antibonding orbitals

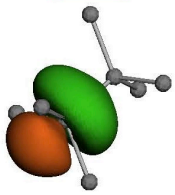


Bonding | Antibonding



7.53 bohr^2 24.37 bohr^2

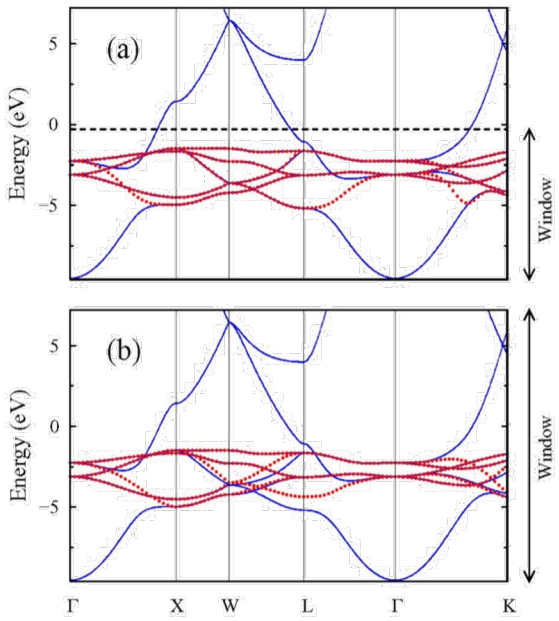
sp^3



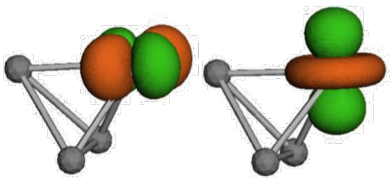
spread=10.68 bohr^2

d bands of copper

Two possible choices of energy window

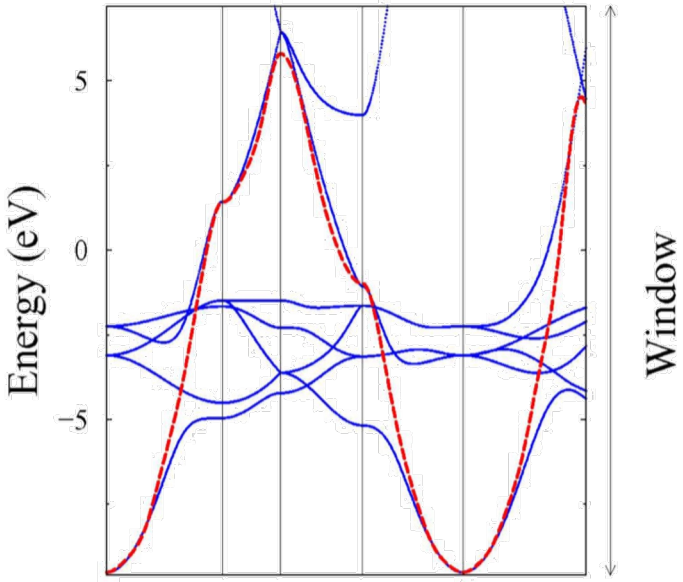


The e_g d WFs of panel (b)



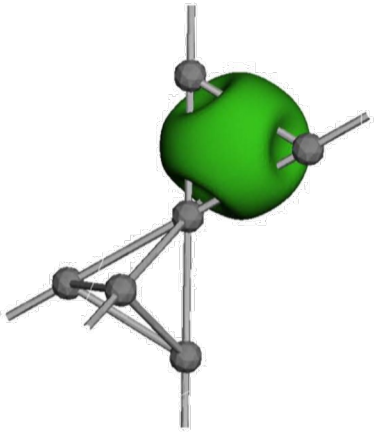
spread(e_g)=1.700 bohr^2
spread(e_g)=1.718 bohr^2

s bands of copper



s-like Wannier function

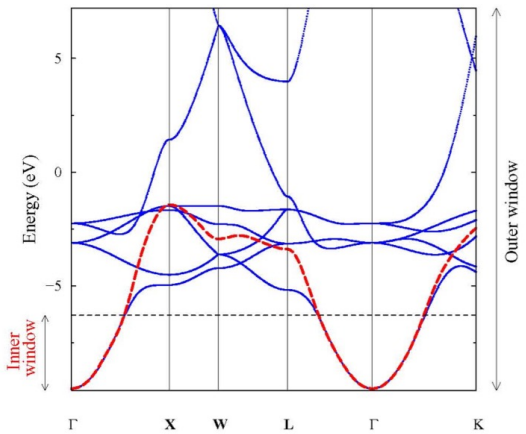
spread=13.03 bohr^2



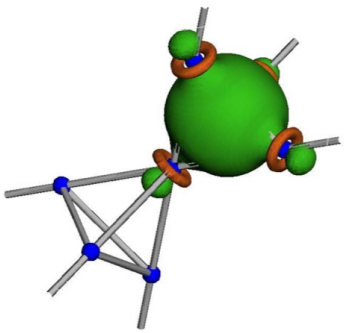
Exact constraint – frozen inner window

Suppose we want WFs to describe the original bands exactly in a prescribed energy range ("inner window").

⇒ Minimize Ω_I w/ constraint that states inside inner window are included in the optimal subspaces $\mathcal{S}(\mathbf{k})$



Hybrid *s*-*d* character:



Towards an ecosystem

PHYSICAL REVIEW B, VOLUME 65, 184422

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

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

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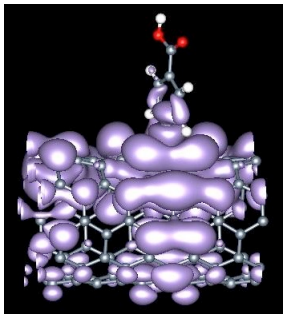
(Received 3 October 2001; published 30 April 2002)

1) Bloch-by-Bloch: The LEGO bricks of electronic structure

@LEGO

Electronic structure of nanostructures

Electronic Ground State From Static or Dynamical Large-Scale Simulations → **Optimal Unitary Transformation of the Bloch Orbitals** → **Real Space Maximally-Localized Wannier Functions**

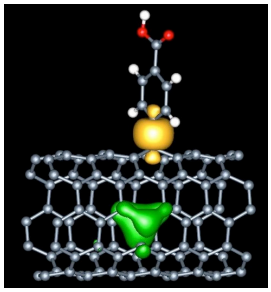


Minimization of the spread functional

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

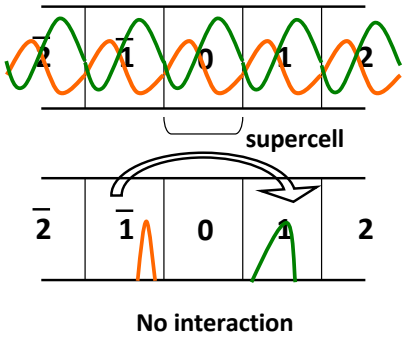
exploiting the arbitrariness of the unitary transformations between the Bloch orbitals

$$|\mathbf{R}n\rangle = \int_{BZ} \sum_m U_{mn}^{(\mathbf{k})} \Psi_{m\mathbf{k}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{R}}\, d\mathbf{k}$$



Electronic structure of nanostructures

Sparse Hamiltonian Matrix → **Green's Function Transmission Function** → **Ballistic Conductance Density of States**



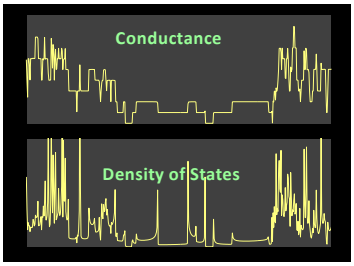
$$H_{00}\,,\, H_{01} \Rightarrow G_C^r(E)$$

$$T(E) = \mathrm{Tr}(\Gamma_L G_C^r \Gamma_R G_C^a)$$

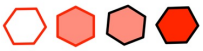
$$\mathbf{H} = \begin{pmatrix} H_{00} & H_{01} & 0 \\ H_{01}^{+} & H_{00} & H_{01} \\ 0 & H_{01}^{+} & H_{00} \end{pmatrix}$$

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

$$N(E) = -(1/\pi)\,\mathrm{Im}[\mathrm{Tr} G_C^r(E)]$$



A. Calzolari, N. Marzari, I. Souza, M. B. Nardelli, Phys. Reb. B 69, 035108 (2004)

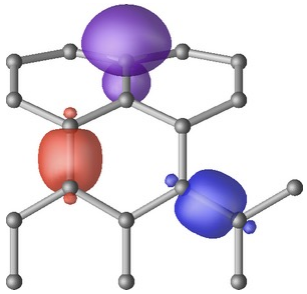


Max-loc WFs ↔ "Exact" Tight-Binding

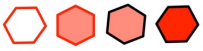
Compact mapping of Bloch states into local orbitals

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

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_R}}\sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\ \omega_n(\mathbf{r}-\mathbf{R})$$



$$\left\langle \psi_{i\mathbf{k}} \middle| \hat{\mathrm{H}} \middle| \psi_{j\mathbf{k}} \right\rangle = H_{ij}^{00} + e^{i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{01} + e^{-i\mathbf{k}\cdot\mathbf{R}}H_{ij}^{0\bar{1}}$$ ⇨ Diagonalize H Matrix

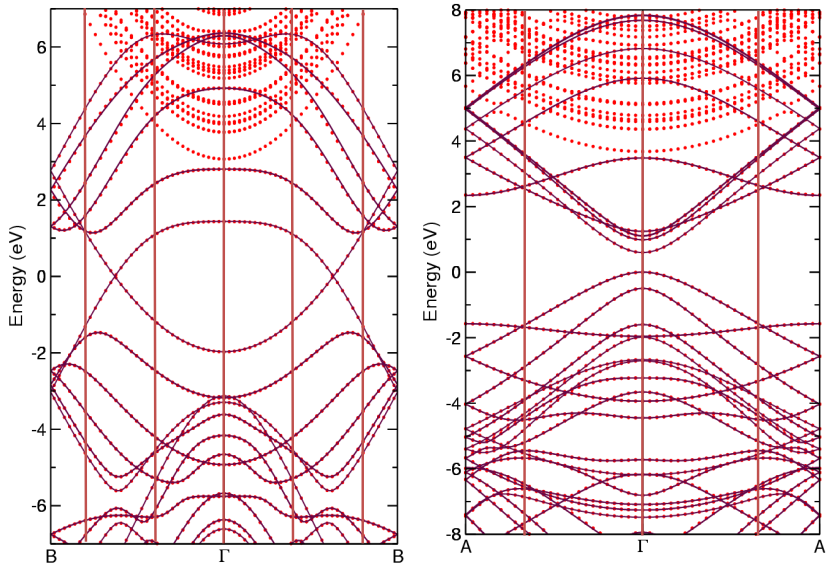


Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

1

Max-loc WFs ↔ "Exact" Tight-Binding

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



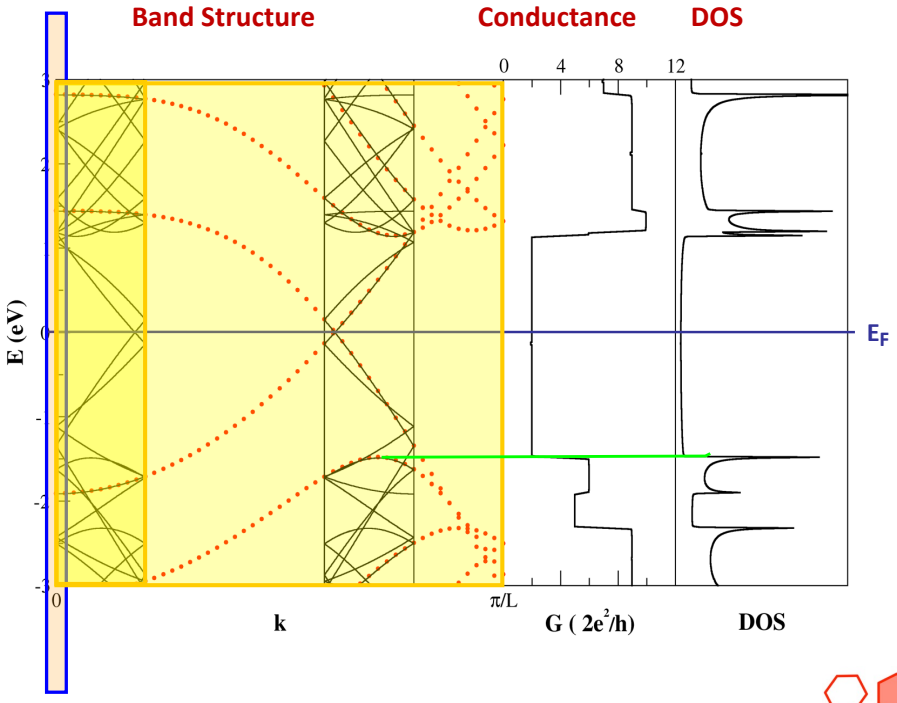
Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

2

Band structure and conductance of a SWCNT

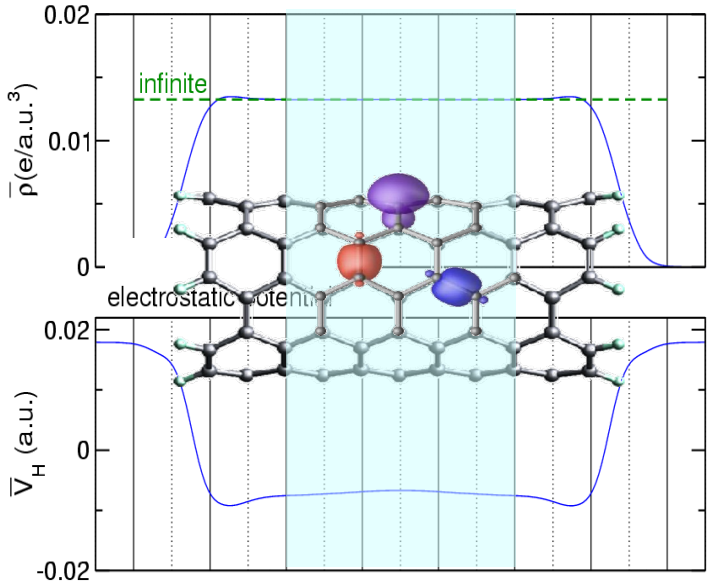
Γ-point:
2eV pseudo gap

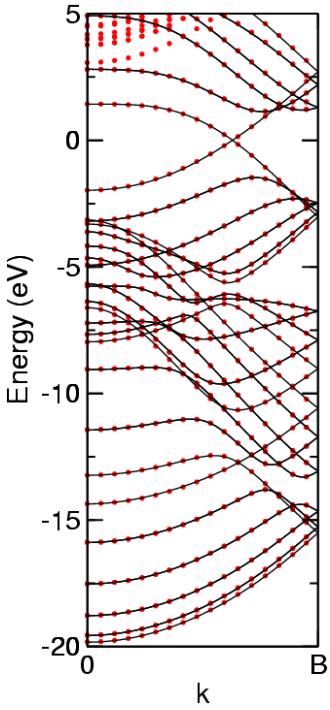
Two eigenchannels at E_F
⇨ perfect recovery of metallic character !



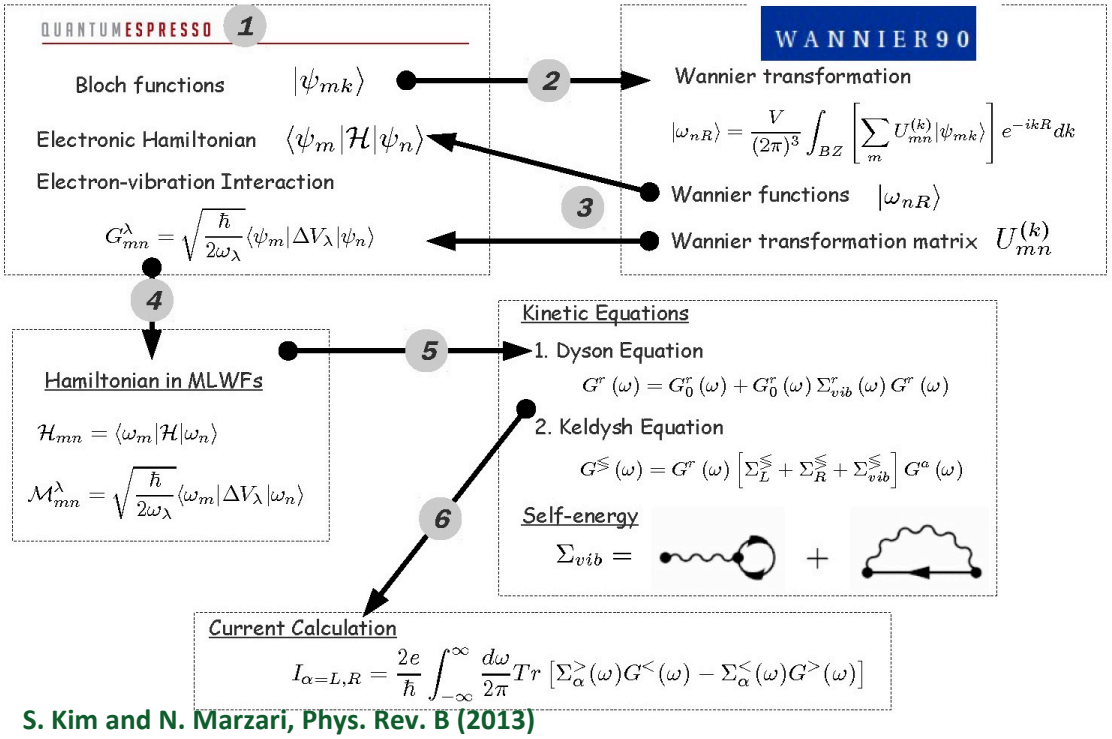
Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. 95, 076804 (2005)

The LEGO bricks of electronic structure



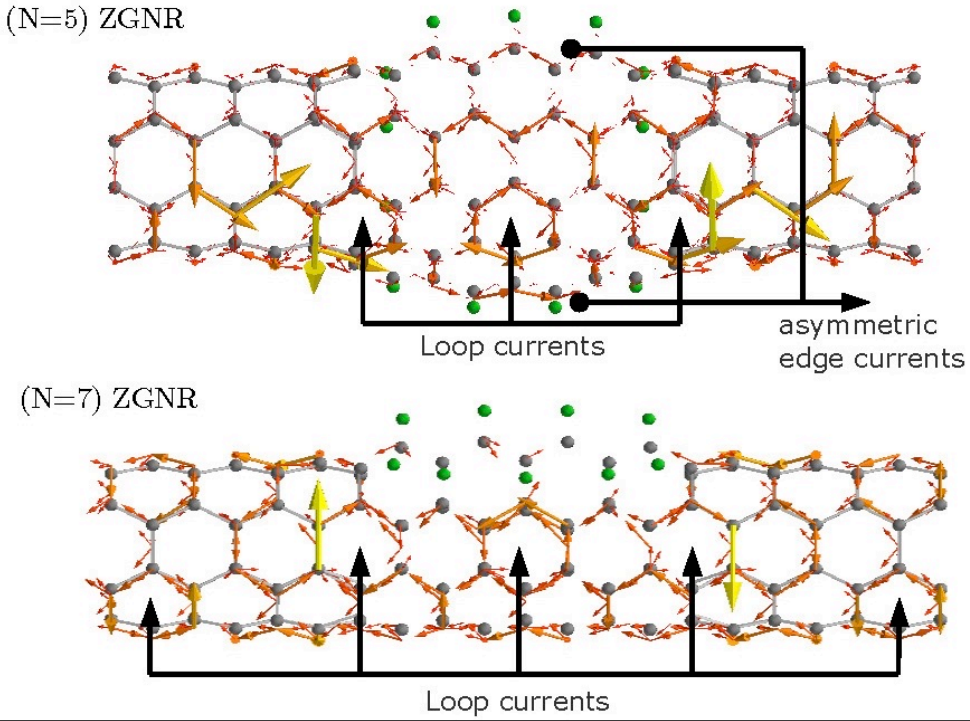


Inelastic quantum transport

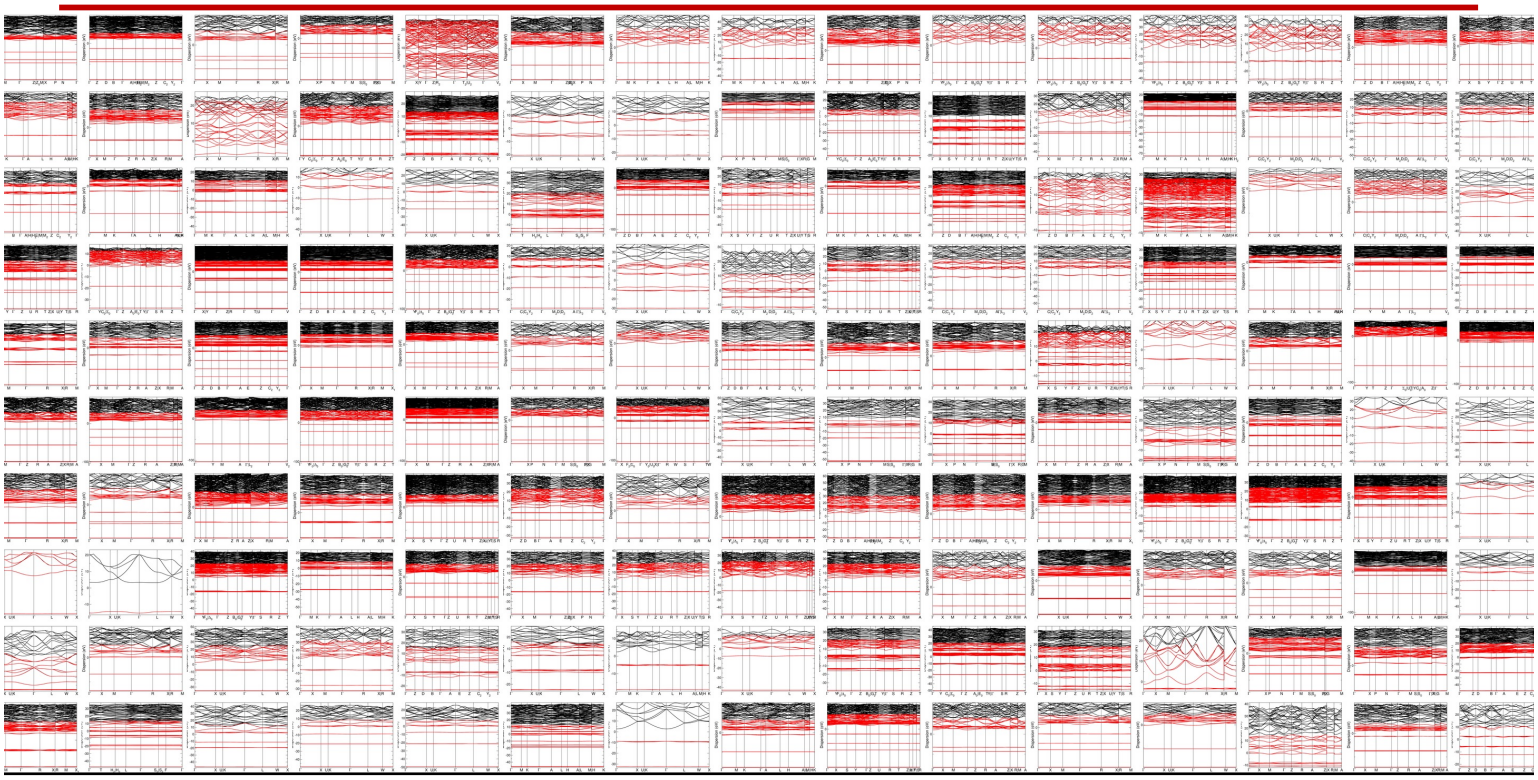


S. Kim and N. Marzari, Phys. Rev. B (2013)

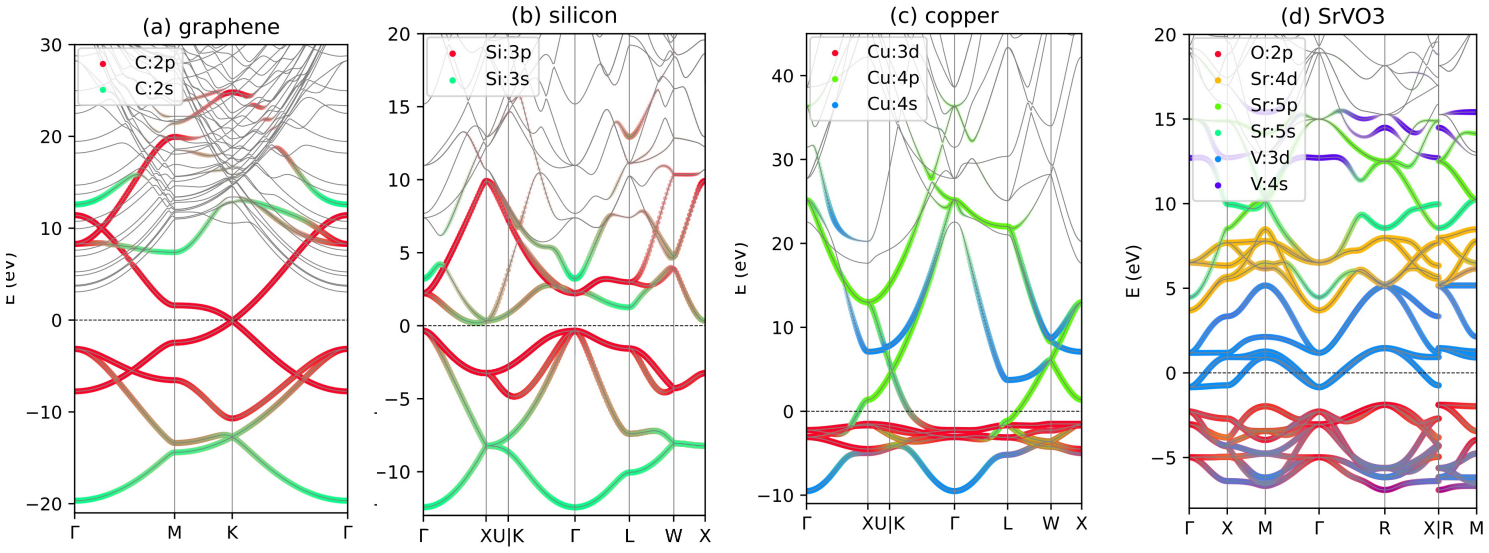
Inelastic quantum transport



2) AUTOMATED WANNIERIZATION

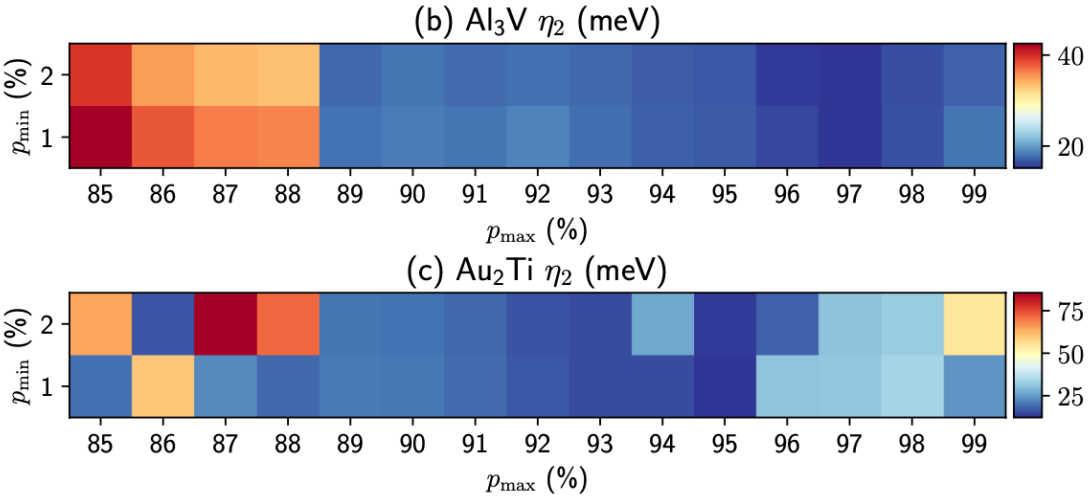


PROJECTABILITY DISENTANGLEMENT

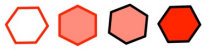


J. Qiao, G. Pizzi, and N. Marzari, in preparation (2022)

PROJECTABILITY DISENTANGLEMENT

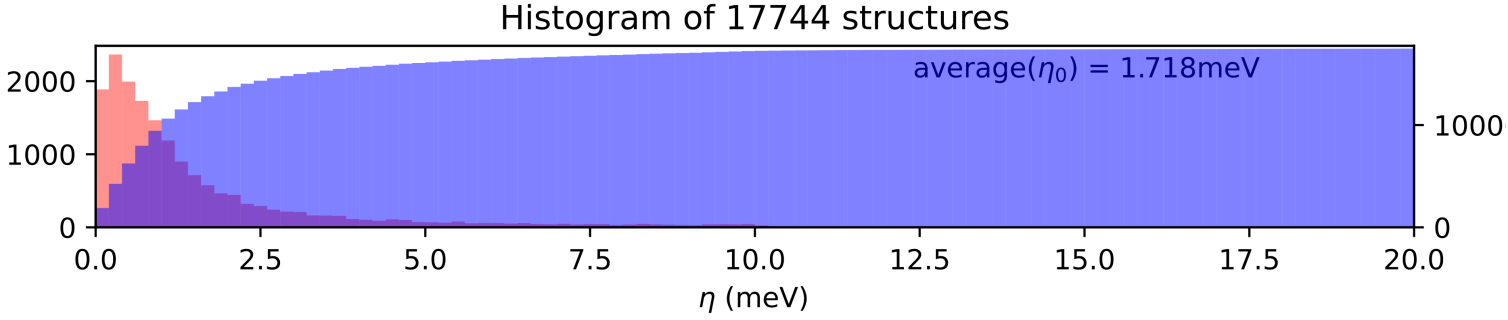


J. Qiao, G. Pizzi, and N. Marzari, in preparation (2022)

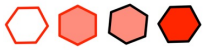


PROJECTABILITY DISENTANGLEMENT

- Automated Wannierization of 17,744 materials, **1,155,049 MLWFs**
- **Average error of 1.7 meV in the band distance η between original and Wannier-interpolated bands**

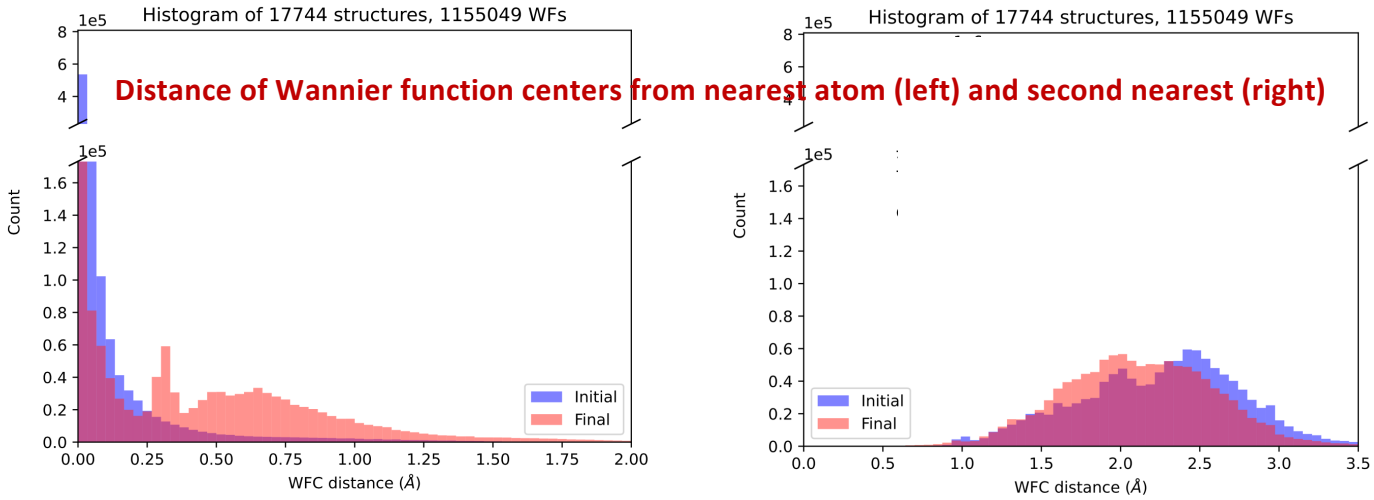


J. Qiao, G. Pizzi, and N. Marzari, in preparation (2022)



PROJECTABILITY DISENTANGLEMENT

- **Atom-centered Wannier functions**



Distance of Wannier function centers from nearest atom (left) and second nearest (right)

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

3) KOOPMANS SPECTRAL FUNCTIONALS

For every orbital the expectation value

$$\epsilon_i = \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle$$

does not depend on the occupation of the orbital

I. Dabo, M. Cococcioni, and N. Marzari, arXiv:0910.2637 (2009)
I. Dabo *et al.*, Physical Review B 82, 115121 (2010)

LINEARIZATION

add linear Koopmans

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

remove ~quadratic Slater

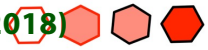
I. Dabo et al., Physical Review B 82, 115121 (2010)
G. Borghi et al., Physical Review B 90, 075135 (2014)

SCREENING

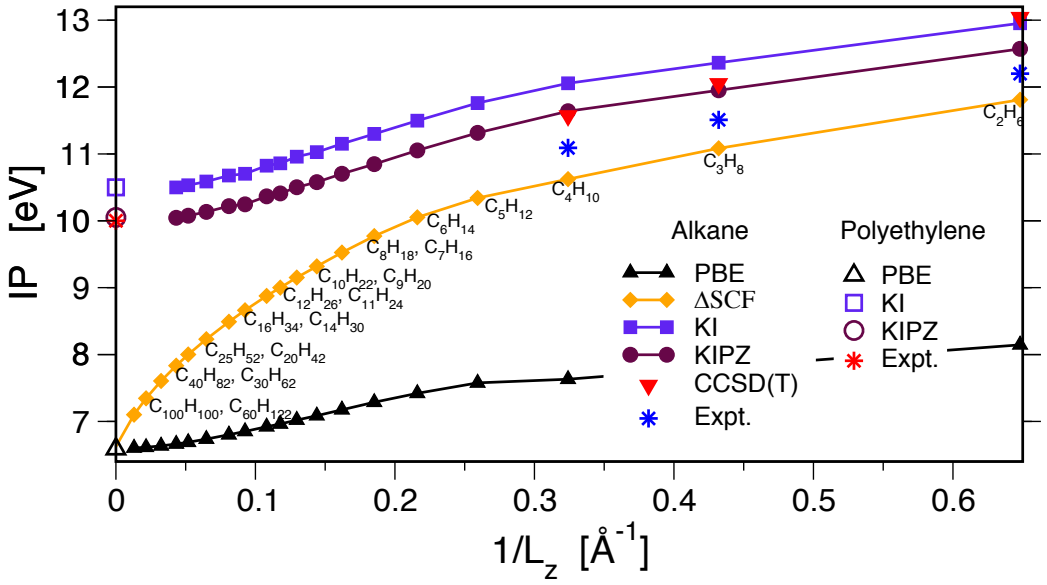
$$E^{\mathrm{KI}} = E^{\mathrm{DFT}} + \sum_i \alpha_i \left[- \int_0^{f_i} \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle + f_i \int_0^1 \langle \varphi_i | \hat{H}^{\mathrm{DFT}} | \varphi_i \rangle \right]$$

orbital-dependent
screening coefficient

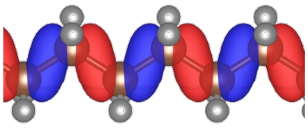
I. Dabo *et al.*, Physical Review B 82, 115121 (2010)
N. Colonna *et al.*, Journal of Chemical Theory and Computation 14, 2549 (2018)



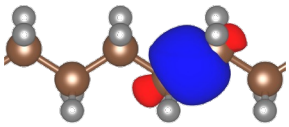
LOCALIZATION



Canonical orbital



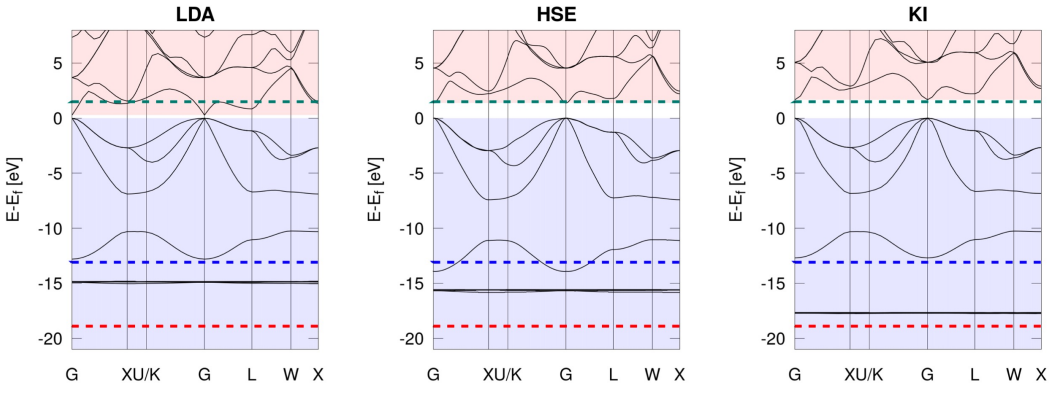
Variational (minimizing) orbital



G. Borghi *et al.*, Physical Review B 91, 155112 (2015)
N.L. Nguyen *et al.*, Physical Review X 8, 02105 (2018)

OUT OF WHICH KOOPMANS BAND

GaAs

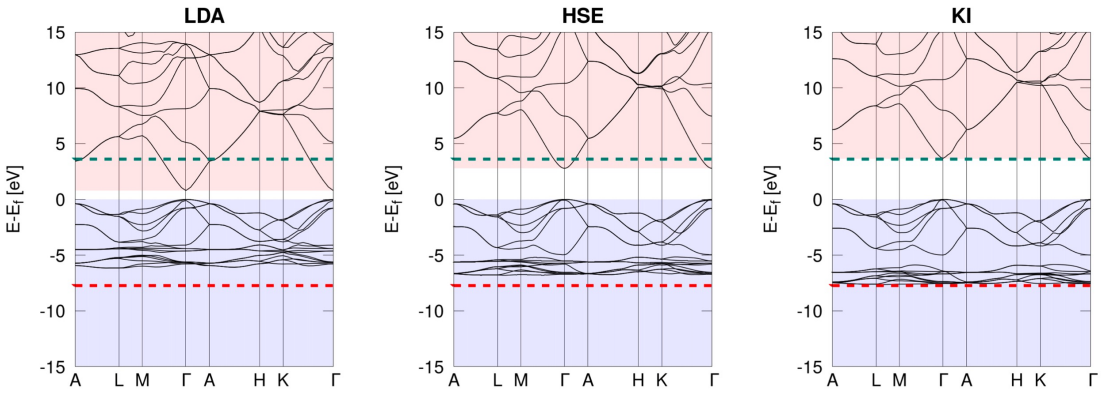


	LDA	HSE	GW_0	$scG\tilde{W}$	KI	Exp.
E_{gap}(eV)	0.19	1.28	1.55	1.62	1.57	1.52
$\langle\varepsilon_d\rangle$(eV)	-14.9	-15.6	-17.3	-17.6	-17.7	-18.9
W(eV)	12.8	13.9	–	–	12.8	13.1

R. De Gennaro, N. Colonna, E. Linscott, and N. Marzari, arXiv preprint arXiv:2111.09550 (2021)
N. Colonna, R. De Gennaro, E. Linscott, and N. Marzari, arXiv preprint arXiv:2202.08155 (2022)

OUT OF WHICH KOOPMANS BAND

ZnO

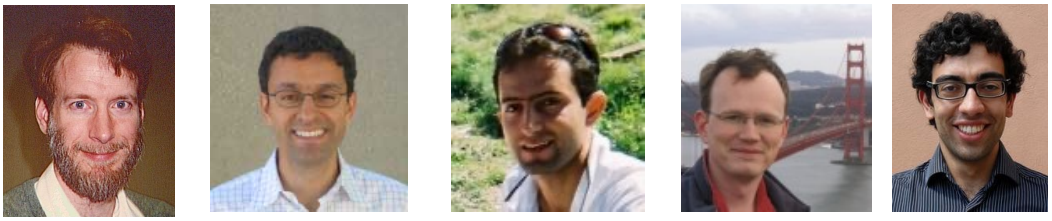


	LDA	HSE	GW_0	$scG\tilde{W}$	KI	Exp.
E_{gap}(eV)	0.79	2.79	3.0	3.2	3.62	3.60
$\langle\varepsilon_d\rangle$(eV)	-5.1	-6.1	-6.4	-6.7	-6.9	-7.5/-8.0

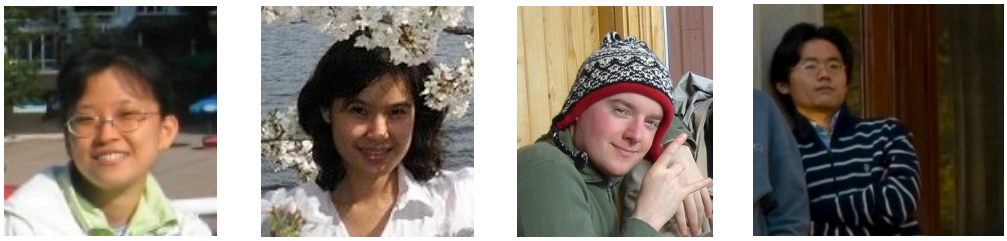
R. De Gennaro, N. Colonna, E. Linscott, and N. Marzari, arXiv preprint arXiv:2111.09550 (2021)
N. Colonna, R. De Gennaro, E. Linscott, and N. Marzari, arXiv preprint arXiv:2202.08155 (2022)

Acknowledgments

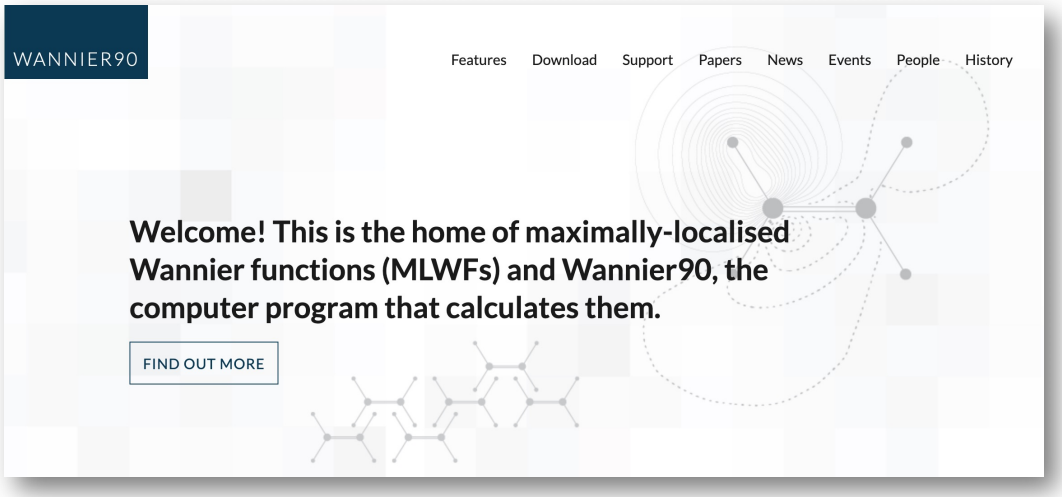
- David Vanderbilt (Rutgers University), Ivo Souza (San Sebastian)



- Wannier 90: Arash Mostofi (Imperial College, London), Jonathan Yates (University of Oxford), Giovanni Pizzi (EPFL), Junfeng Qiao (EPFL)
- Transport: Young-Su Lee (MIT->KIST), Elise Li (MIT->NTNU), Matt Shelley (Imperial), Nicolas Poilvert (MIT->Penn S.), Giovanni Cantele (University of Naples), S. Kim (MIT->KIAS)
- Koopmans: Nicola Colonna (PSI), Andrea Ferretti (CNR), and Edward Linscott, Riccardo de Gennaro, Linh Nguyen, et al… at EPFL



http://www.wannier.org/



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