

Closest Wannier functions to a given set of localized orbitals

- Motivations of the study
- Maximally localized Wannier function
- Closest Wannier functions
- Benchmark calculations
- Outlook

Refs:

[arXiv:2306.15296](https://arxiv.org/abs/2306.15296)

<https://www.openmx-square.org/cwf/>

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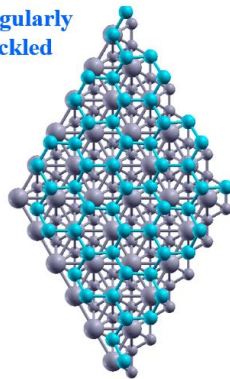
How to analyze DFT results?

- The DFT-KS method is a versatile framework to calculate electronic structures of real materials.

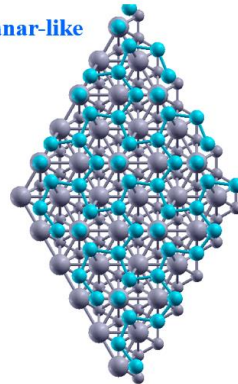
$$E[\rho] = \int dr^3 \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) + T[\rho] + J[\rho] + E_{\text{xc}}[\rho]$$

$$\hat{H}_{\text{KS}} \phi_i = \varepsilon_i \phi_i \quad \hat{H}_{\text{KS}} = -\frac{1}{2} \nabla^2 + v_{\text{eff}}$$

Regularly
buckled



Planar-like



The right structure is energetically stable, being consistent with the experiment.

- However, it is always difficult to explain why one structure is more stable than the others. Other cases: effective charge, XPS binding energy, effective spin-spin interaction.
- We need to develop an analysis method to give a physically and chemically convincing interpretation.

Purpose of the study

- Our goal in this study is to establish methods to analyze electronic structures in a physically and chemically convincing manner.
- To do that, I consider that it is important to develop an efficient and robust method to calculate Wannier functions (WFs), while keeping the shape of atomic orbitals as much as possible.
- Such WFs can be utilized for calculations including
 - Effective atomic charge
 - Local decomposition of total energy
 - Analysis of magnetic interaction by the Liechtenstein method
 - Coherent potential method
 - Speed-up of the SCF calculation

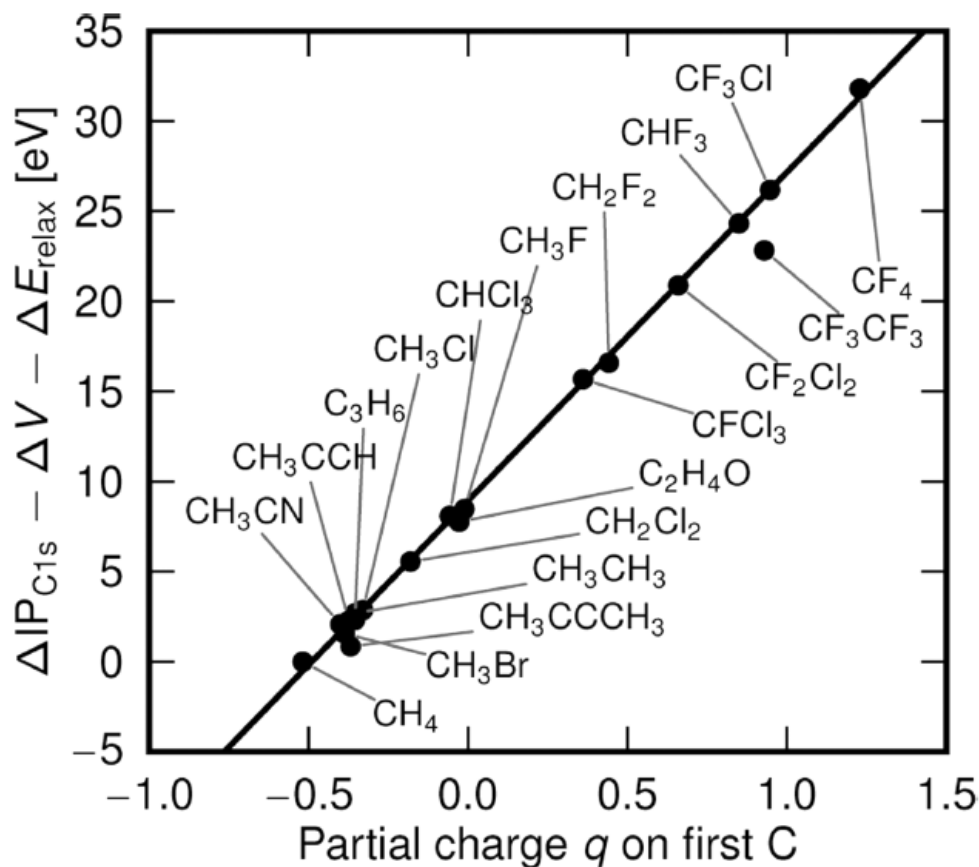
Intrinsic Atomic Orbital (IAO)

Intrinsic Atomic Orbitals: An Unbiased Bridge between Quantum Theory and Chemical Concepts

Gerald Knizia*

J. Chem. Theory Comput., 9, 4834 (2013).

Institut für Theoretische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany



$$\Delta IP_{C1s} = k \cdot q_A + \sum_{B \neq A} \frac{q_B}{\|\mathbf{R}_A - \mathbf{R}_B\|} + \Delta E_{relax}$$

The IAO charge seems to be a good descriptor to explain the XPS binding energies.

SOME METRIC INEQUALITIES IN THE SPACE OF MATRICES¹

Proc. Amer. Math. Soc. 6, 111 (1955).

KY FAN AND A. J. HOFFMAN

In the paper, they showed a theorem on a matrix inequality:

2. THEOREM 1. *Let $A \in M_n$ and $A = UH$, where U is unitary and H is Hermitian positive semi-definite. Then for any unitary matrix $W \in M_n$,*

$$(4) \quad \|A - U\| \leq \|A - W\| \leq \|A + U\|$$

$\| \cdot \|$ is the Frobenius norm.

It is found that the inequality is very important for our formulation.

Maximally Localized Wannier Functions 6/25

Maximally localized generalized Wannier functions for composite energy bands

Nicola Marzari and David Vanderbilt

Phys. Rev. B 56, 12847 (1997).

Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

(Received 10 July 1997)

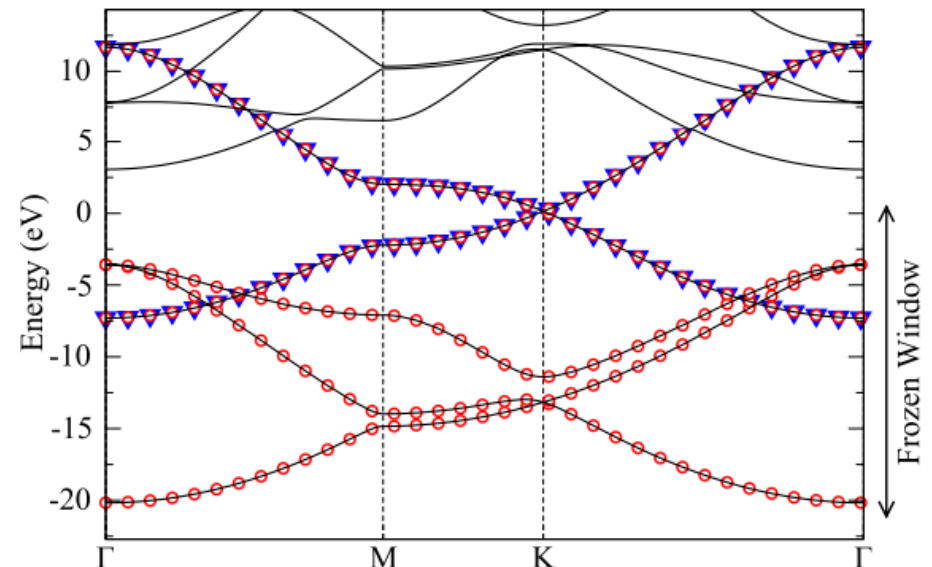
The MLWFs are obtained by minimizing the **spread function**, while keeping the unitary transformation.

$$\Omega = \sum_n \left[\langle r^2 \rangle_n - \overline{\mathbf{r}}_n^2 \right] \quad |u_{n\mathbf{k}}\rangle \rightarrow \sum_m U_{mn}^{(\mathbf{k})} |u_{m\mathbf{k}}\rangle,$$

Wannier interpolated bands

Graphene case

MLWFs



Closest Wannier Functions (CWFs)

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Closest Wannier functions to a given set of localized orbitals

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arXiv:2306.15296

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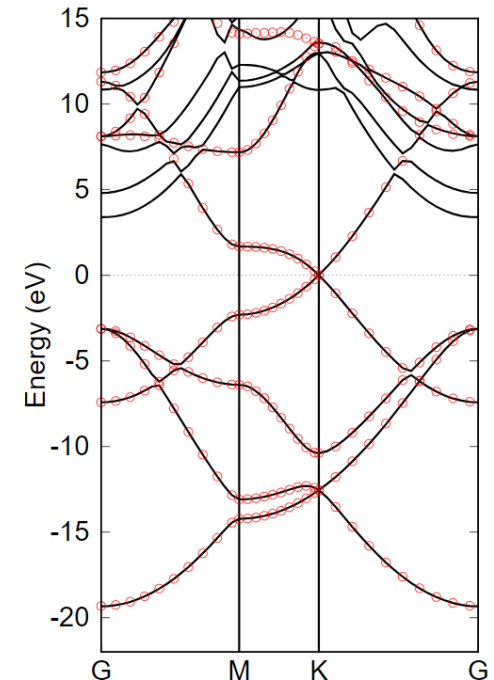
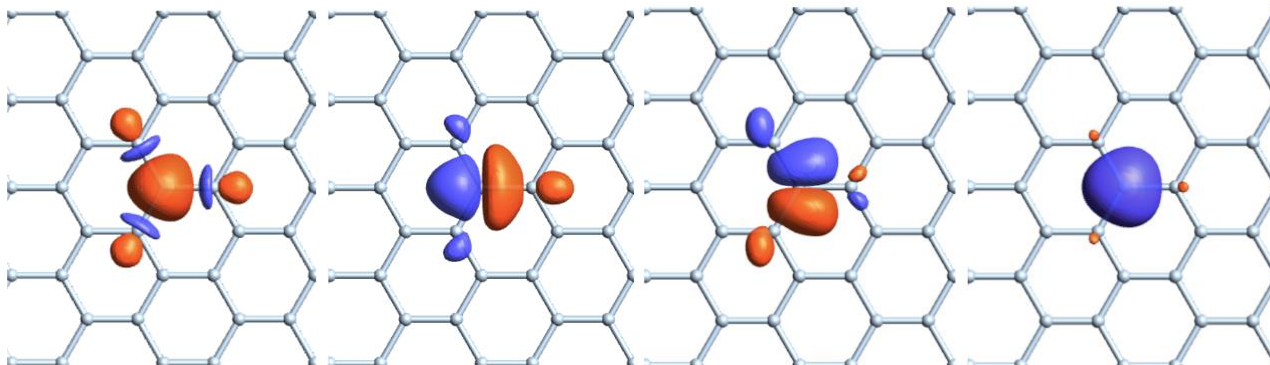
(Dated: June 30, 2023)

The CWFs are obtained by minimizing the **distance measure (DM) function**, while keeping the unitary transformation.

$$F[B] = \sum_p \langle R_{0p} | R_{0p} \rangle, \quad X[B, \mathbf{k}] = \text{tr} [(A^\dagger(\mathbf{k}) - B^\dagger(\mathbf{k})) (A(\mathbf{k}) - B(\mathbf{k}))]$$
$$= \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}} X[B, \mathbf{k}]$$

Graphene case

CWFs



Projection and window function

For a localized function of Q , the projection is considered with a window function:

$$|L_{\mathbf{R}p}\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{k}\mu}\rangle a_{\mathbf{k}\mu,p}$$

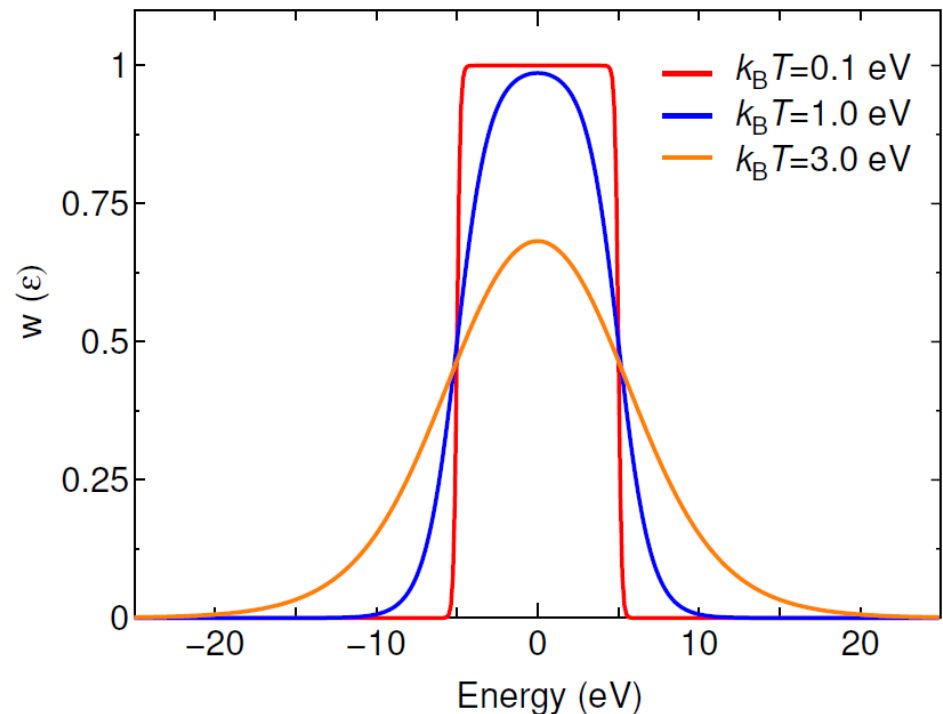
$$a_{\mathbf{k}\mu,p} = w(\varepsilon_{\mathbf{k}\mu}) \langle \phi_{\mathbf{k}\mu} | Q_{\mathbf{0}p} \rangle,$$

Window function:

$$w(\varepsilon) = \frac{1 - e^{x_0 + x_1}}{(1 + e^{x_0})(1 + e^{x_1})} + \delta$$

$$x_0 = \frac{\varepsilon_0 - \varepsilon}{k_B T_0} \quad x_1 = \frac{\varepsilon - \varepsilon_1}{k_B T_1}$$

The window function allows us to focus on the targeted states in the window region.



Distance measure (DM) function

Projection function:

$$|L_{\mathbf{R}p}\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{k}\mu}\rangle a_{\mathbf{k}\mu,p}$$

Wannier function:

$$|W_{\mathbf{R}p}\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{k}\mu}\rangle b_{\mathbf{k}\mu,p},$$

Residual function: $|R_{\mathbf{R}p}\rangle = |L_{\mathbf{R}p}\rangle - |W_{\mathbf{R}p}\rangle$

We define the distance measure function as

$$\begin{aligned} F[B] &= \sum_p \langle R_{0p} | R_{0p} \rangle, \\ &= \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}} X[B, \mathbf{k}] \end{aligned}$$

where X is given by a squared Frobenius norm:

$$X[B, \mathbf{k}] = \text{tr} \left[(A^\dagger(\mathbf{k}) - B^\dagger(\mathbf{k})) (A(\mathbf{k}) - B(\mathbf{k})) \right]$$

Minimization of the DM function #1

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It is proven that the minimum is obtained when $B=U$ which is calculated from the polar decomposition of A as.

$$A = W\Sigma V^\dagger = \underbrace{WV^\dagger}_U \underbrace{V\Sigma V^\dagger}_P = UP.$$

The difference of X at U and B is given by $X[B, \mathbf{k}] = \text{tr} [(A^\dagger(\mathbf{k}) - B^\dagger(\mathbf{k})) (A(\mathbf{k}) - B(\mathbf{k}))]$

$$\begin{aligned} X[U] - X[B] &= 2\text{tr} \left[\frac{1}{2} (A^\dagger B + B^\dagger A) - P \right] \\ &= 2\text{tr} [\Sigma D - \Sigma], \quad D = \frac{1}{2} (V^\dagger U^\dagger B V + V^\dagger B^\dagger U V) \\ &= 2 \sum_n \sigma_n (d_{nn} - 1) \end{aligned}$$

From the Cauchy-Schwarz inequality, the diagonal term of D is bounded by 1.

Thus, we obtain

$$X[U] \leq X[B]$$

Minimization of the DM function #2

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Thus, we find the minimum of $F[B]$ at U as

$$\begin{aligned} \min_B F[B] &= F[U] & A &= W\Sigma V^\dagger \\ &= \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}p} (\sigma_{\mathbf{k}p} - 1)^2 & U &= WV^\dagger \end{aligned}$$

This means that the mean squared distance between L and W is related to the deviation of the singular values σ from unity.

$$\left| L_{\mathbf{R}p} \right\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} \left| \phi_{\mathbf{R}p} \right\rangle a_{\mathbf{k}\mu,p}$$

$$\left| W_{\mathbf{R}p} \right\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} \left| \phi_{\mathbf{R}p} \right\rangle u_{\mathbf{k}\mu,p}$$

Algorithm

1. Determining the target region.
2. Choosing a set of localized orbitals $\{Q\}$.
3. Calculation of the projection matrix of $A(\mathbf{k})$.
4. Performing the SVD of $A(\mathbf{k}) \Rightarrow W\Sigma V^\dagger$.
5. Calculation of $U(\mathbf{k})$ as $W(\mathbf{k})V^\dagger(\mathbf{k})$.
6. Summation over \mathbf{k} and μ .

No iterative calculation is required.

Cancellation of nondeterministic phases ^{13/25}

Nondeterministic phases appear in three places:

$$|W_{\mathbf{R}p}\rangle = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} e^{-i\mathbf{k}\cdot\mathbf{R}} |\phi_{\mathbf{R}p}\rangle u_{\mathbf{k}\mu,p}$$

1. Calculation of Bloch functions at each k-point

2. SVD of A:

$$A = W\Sigma V^\dagger = WX\Sigma X^\dagger V^\dagger = W'\Sigma V'^\dagger$$
$$U = W'V'^\dagger = WV^\dagger \quad X \text{ is a diagonal phase matrix.}$$

3. Singular vectors for degenerate singular values

$$A = W\Sigma V^\dagger = WK\Sigma K^\dagger V^\dagger = W'\Sigma V'^\dagger$$
$$U = W'V'^\dagger = WV^\dagger \quad K \text{ is a unitary matrix.}$$

It is quite important to note that the three nondeterministic phases are all canceled out through the polar decomposition.

Thus, it turns out that the proposed method is free from complications arising from the choice of gauge.

Relation to the Löwdin orthogonalization ^{14/25}

The CWF method is closely related to the Löwdin orthogonalization. By Fourier-transforming overlap integrals of L , we have

$$\sum e^{i\mathbf{k}\cdot\mathbf{R}} \langle L_{\mathbf{0}p} | L_{\mathbf{R}q} \rangle = \sum_{\mu} a_{\mathbf{k}\mu,p} a_{\mathbf{k}\mu,q} \quad \Rightarrow \quad A^{\dagger}(\mathbf{k})A(\mathbf{k}) = S(\mathbf{k})$$

By using the polar decomposition of A , we have

$$S(\mathbf{k}) = A^{\dagger}(\mathbf{k})A(\mathbf{k}) = V^{\dagger}(\mathbf{k})\Sigma^2(\mathbf{k})V(\mathbf{k}) \quad \cdot \cdot \cdot \quad (\text{A})$$

Comparing (A) with $P(\mathbf{k}) = V^{\dagger}(\mathbf{k})\Sigma(\mathbf{k})V(\mathbf{k})$, one obtains

$$P(\mathbf{k}) = S^{1/2}(\mathbf{k})$$

Remembering $A(\mathbf{k}) = U(\mathbf{k})P(\mathbf{k})$, and if $P(\mathbf{k})$ is invertible, we have

$$U(\mathbf{k}) = A(\mathbf{k})S^{-1/2}(\mathbf{k})$$

Thus, we see that in some cases the CWF is equivalent to the Löwdin orthogonalization.

The closest property is also shown in B.C. Carlson and J.M. Keller, PR 105, 102 (1957).

Guiding functions

- Atomic orbitals (AOs)

PAOs are used as the guiding functions.

- Hybrid Orbitals (HOs)

By diagonalizing the on-site density matrix, one can obtain the hybrid orbitals, which will be used as the guiding functions.

- Embedded Molecular Orbitals (EMOs)

The EMOs can be obtained by the singular value decomposition for the local trace of occupation projector.

$$N_{\text{ele}}^{(0)} = 2 \sum_g \text{tr}_g \left[(\tilde{\chi}_{0g} | \hat{P} | \chi_{0g}) \right] = 2 \sum_g \text{tr}_g [\Lambda_g]$$

$$\Lambda_g = \sum_{\mathbf{R}_{g'}} \rho_{0g, \mathbf{R}_{g'}} S_{\mathbf{R}_{g'}, 0g} \quad \Lambda_g^\dagger \Lambda_g = Y_g \Omega_g^2 Y_g^\dagger$$

Embedded molecular orbitals (EMOs)

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Embedded molecular orbitals are calculated by considering a partial trace of a projection operator and performing SVD for Λ for a group of atomic basis orbitals.

Bloch function

$$|\phi_{\mathbf{k}\mu}\rangle = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{i\alpha} c_{k\mu,i\alpha} |\chi_{\mathbf{R}i\alpha}\rangle$$

Projection operator for the occupied states

$$\hat{P} = \frac{1}{N_{\text{BC}}} \sum_{\mathbf{k}\mu} |\phi_{\mathbf{k}\mu}\rangle f(\varepsilon_{\mathbf{k}\mu}) \langle \phi_{\mathbf{k}\mu}|$$

The total number of electrons is given by

$$\begin{aligned} N_{\text{ele}}^{(0)} &= 2\text{tr}[\hat{P}] \\ &= 2\sum_g \text{tr}_g \left[\left(\tilde{\chi}_{\mathbf{0}_g} | \hat{P} | \chi_{\mathbf{0}_g} \right) \right] = 2\sum_g \text{tr}_g \left[\Lambda_g \right] \end{aligned}$$

where

$$|\chi_{\mathbf{0}_g}\rangle = (\cdots, |\chi_{\mathbf{0}_g i_1}\rangle, |\chi_{\mathbf{0}_g i_2}\rangle, \cdots) \quad \Lambda_g = \sum_{\mathbf{R}_g'} \rho_{\mathbf{0}_g, \mathbf{R}_g'} s_{\mathbf{R}_g', \mathbf{0}_g}$$

Performing SVD for $\Lambda_g^\dagger \Lambda_g$, we obtain Y_g as EMOs.

$$\Lambda_g^\dagger \Lambda_g = Y_g \Omega_g^2 Y_g^\dagger$$

OpenMX **Open** source package for **M**aterial **eX**plorer

- Software package for density functional calculations of molecules and bulks
- Norm-conserving pseudopotentials (PPs)
- Variationally optimized numerical atomic basis functions

Basic functionalities

- SCF calc. by LDA, GGA, DFT+U
- Total energy and forces on atoms
- Band dispersion and density of states
- Geometry optimization by BFGS, RF, EF
- Charge analysis by Mulliken, Voronoi, ESP
- Molecular dynamics with NEV and NVT ensembles
- Charge doping
- Fermi surface
- Analysis of charge, spin, potentials by cube files
- Database of optimized PPs and basis functions

Extensions

- $O(N)$ and low-order scaling diagonalization
- Non-collinear DFT for non-collinear magnetism
- Spin-orbit coupling included self-consistently
- Electronic transport by non-equilibrium Green function
- Electronic polarization by the Berry phase formalism
- Maximally localized Wannier functions
- Effective screening medium method for biased system
- Reaction path search by the NEB method
- Band unfolding method
- STM image by the Tersoff-Hamann method
- etc.

Benchmark calculation: Si

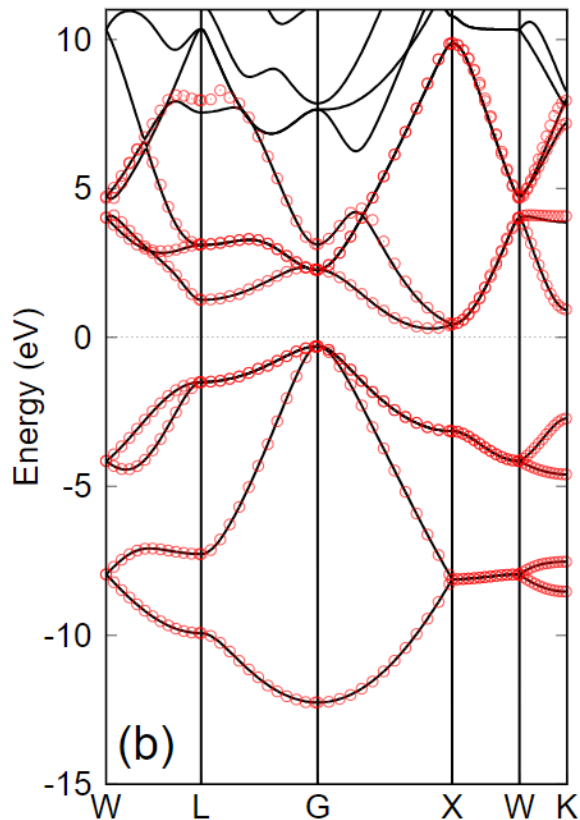
I have performed the benchmark calculations for 30 systems, and found that the method works well. <https://www.openmx-square.org/cwf/>

Silicon

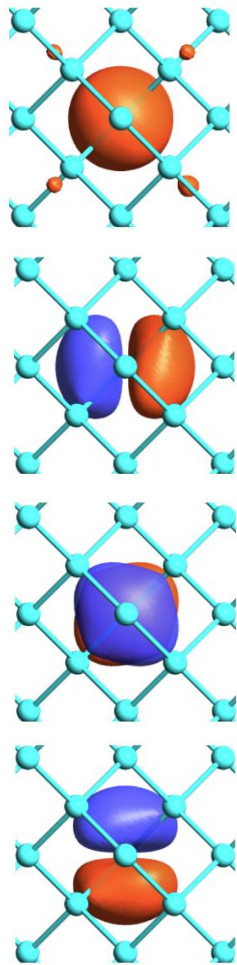
Wannier interpolated bands

Solid: conventional

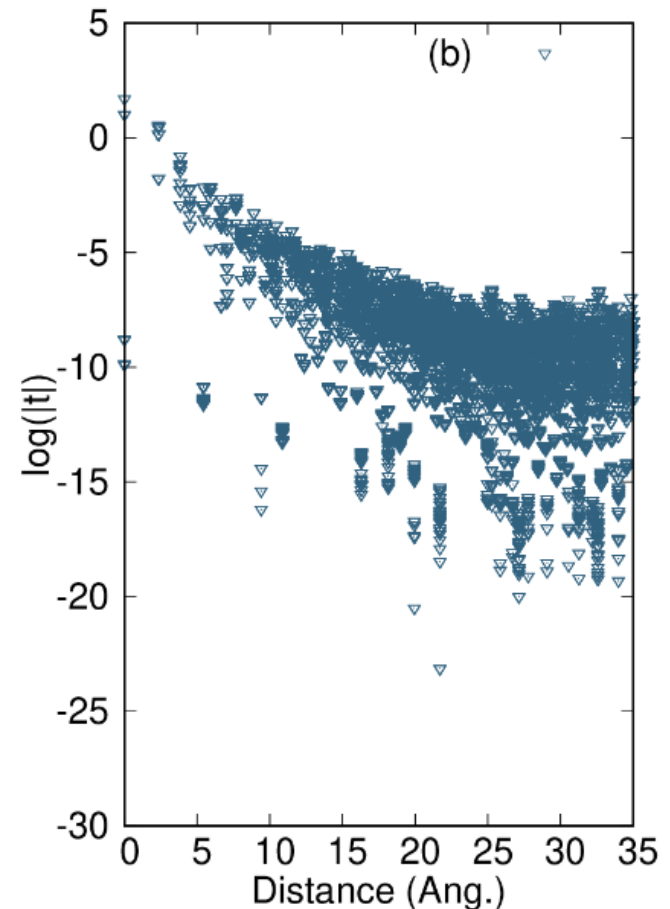
Red circle: Wannier interpolated



CWFs



Tight-binding hopping integrals as a function of distance



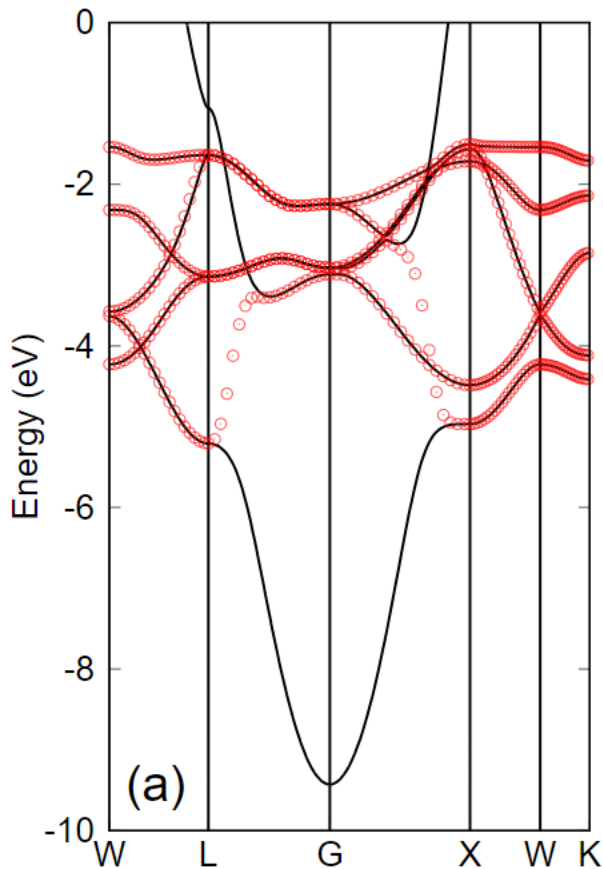
Benchmark calculation: Copper

FCC copper

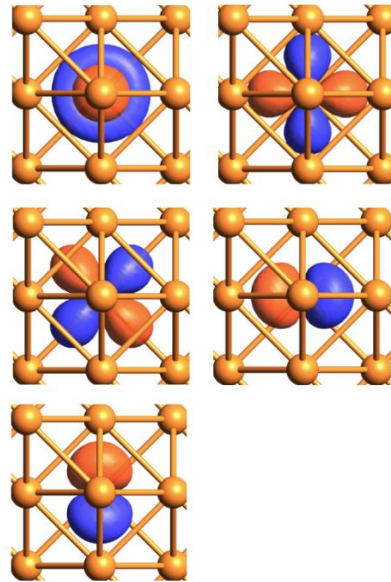
Wannier interpolated bands

Solid: conventional

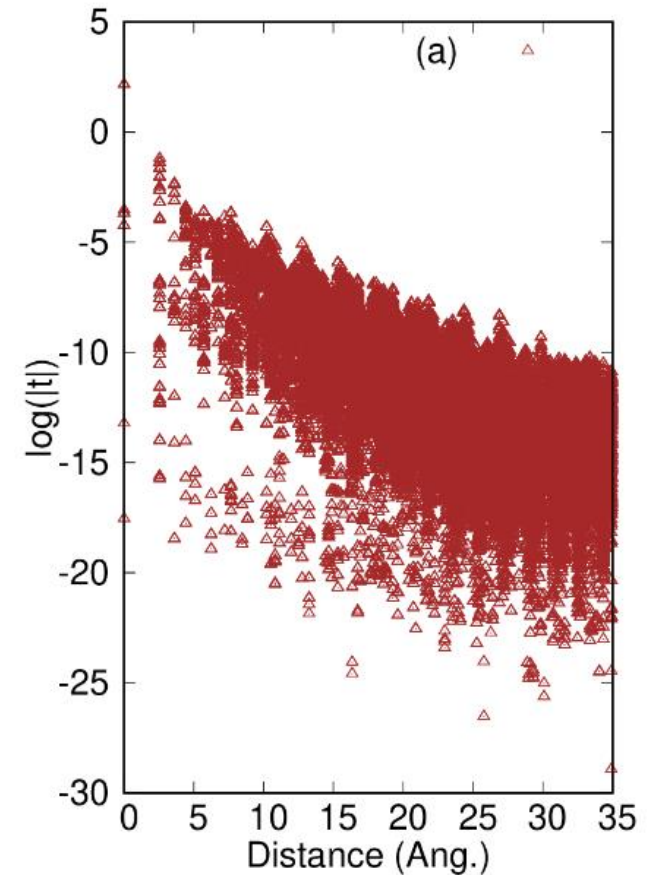
Red circle: Wannier interpolated



CWFs



Tight-binding hopping integrals as a function of distance



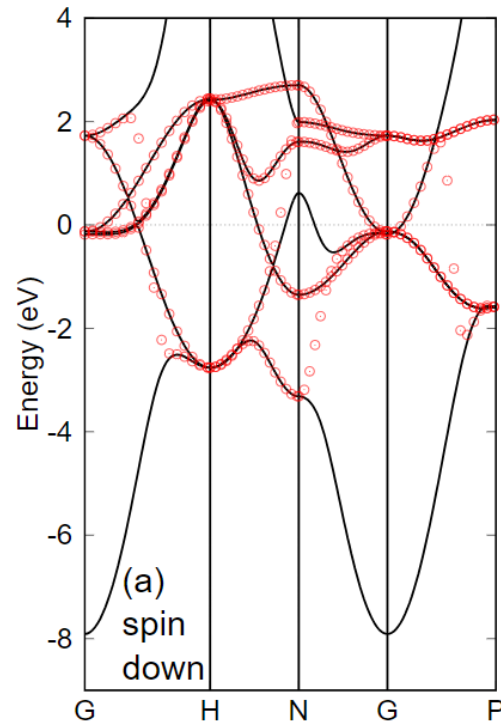
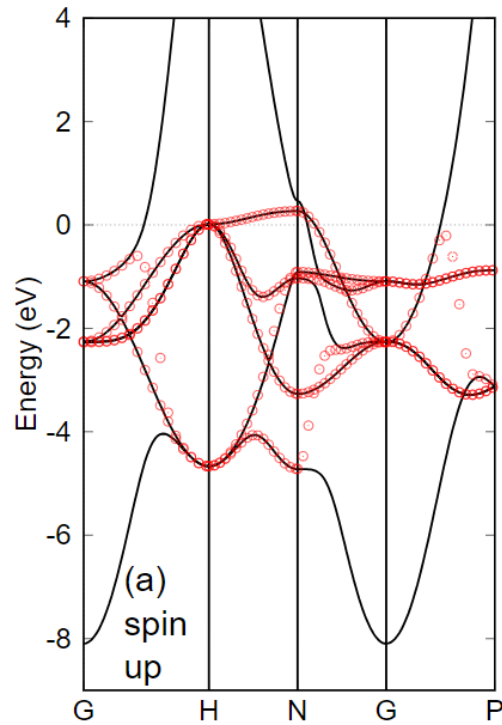
Benchmark calculation: Fe

BCC iron

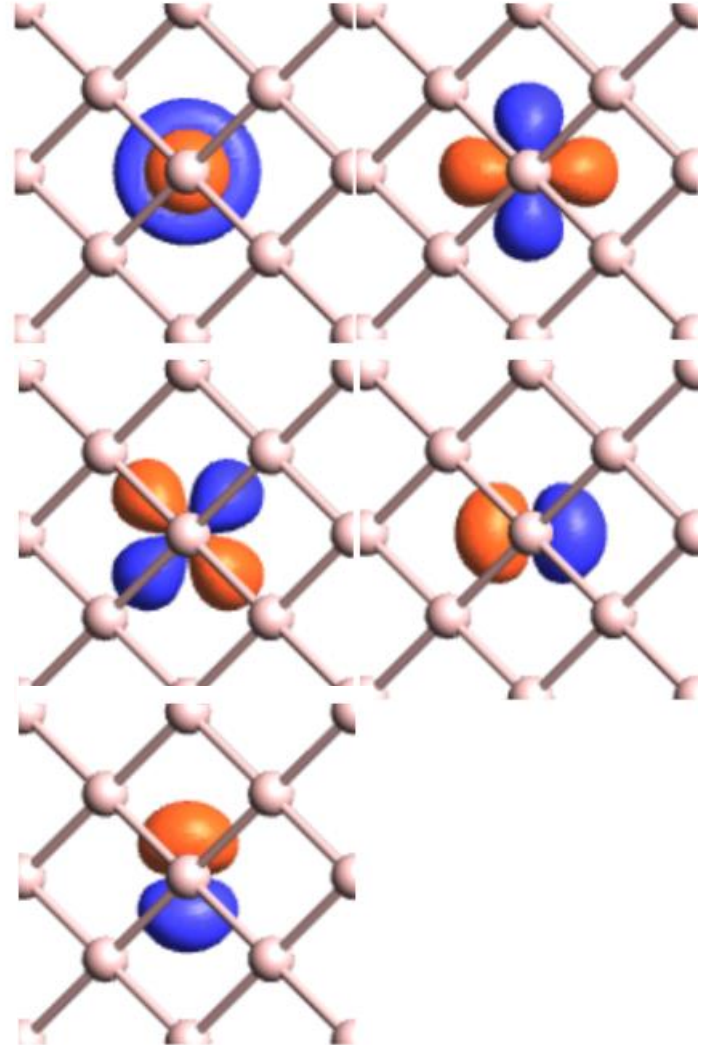
Wannier interpolated bands

Solid: conventional

Red circle: Wannier interpolated



CWFs for up-spin states

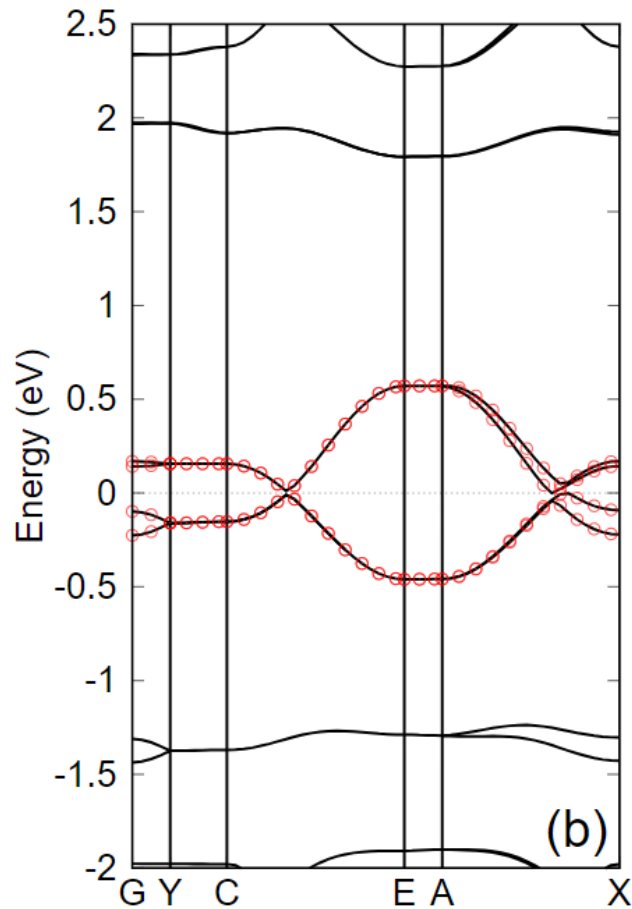


TTF-TCNQ

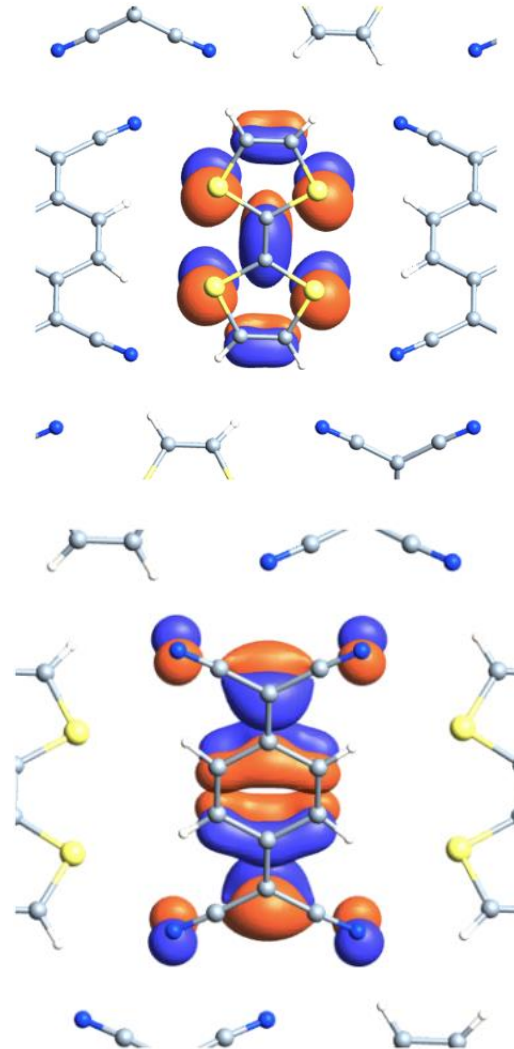
Wannier interpolated bands

Solid: conventional

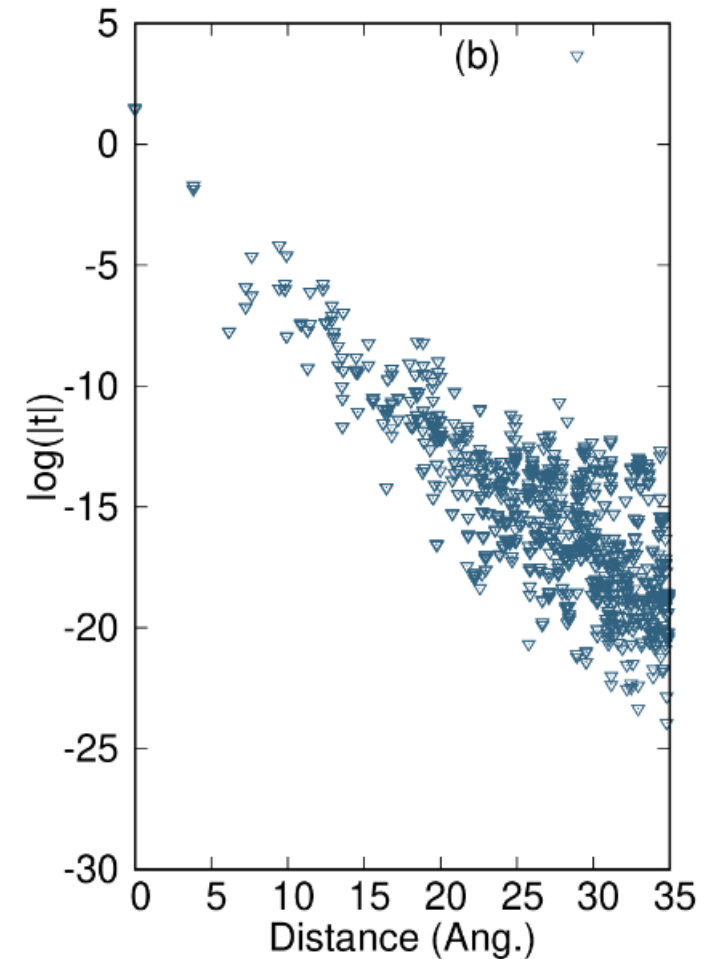
Red circle: Wannier interpolated



CWFs



Tight-binding hopping integrals as a function of distance



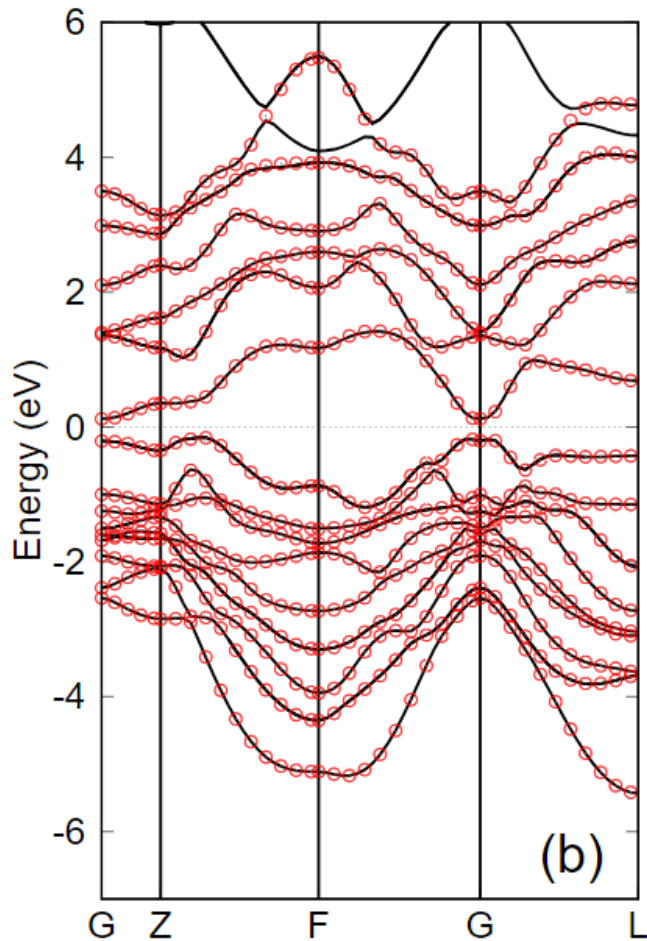
Benchmark calculation: Bi_2Se_3

Bi_2Se_3

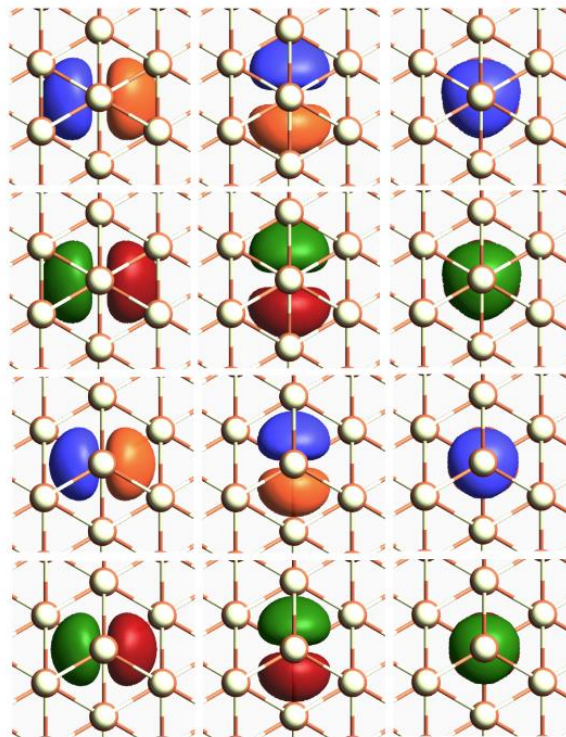
Wannier interpolated bands

Solid: conventional

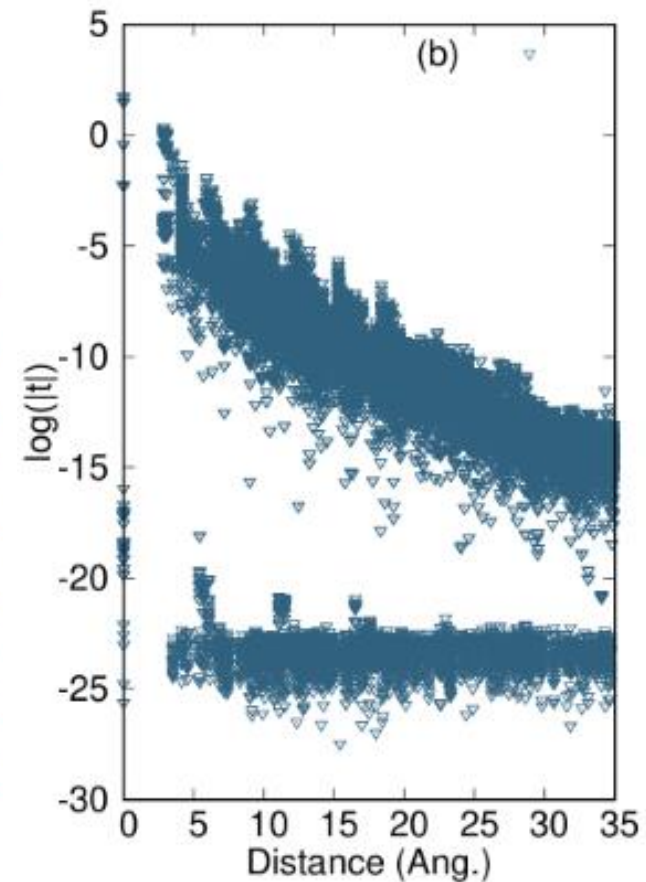
Red circle: Wannier interpolated



CWFs



Tight-binding hopping integrals as a function of distance



Effective charge

$$K_i = N_i^{(\text{val})} - \sum_{p \in \text{atom } i} \langle W_{0p} | \hat{P} | W_{0p} \rangle$$

HCN	CWF			MLWF			MP			Bader		
Basis	H	C	N	H	C	N	H	C	N	H	C	N
A6.0-s1p1	0.077	-0.052	-0.025	0.665	0.303	-0.969	0.384	-0.164	-0.221	1.000	1.746	-2.746
A6.0-s2p2	0.069	0.003	-0.073	0.793	0.067	-0.860	-0.070	0.321	-0.252	0.201	2.439	-2.639
A6.0-s2p2d1	0.066	0.009	-0.076	0.793	0.102	-0.907	-0.008	0.393	-0.385	0.183	2.523	-2.706
A6.0-s3p3d2	0.066	0.008	-0.074	0.699	0.343	-1.042	0.110	0.298	-0.408	0.182	2.539	-2.721
A6.0-s3p3d2f2	0.066	0.008	-0.074	0.721	0.344	-1.065	0.167	0.297	-0.464	0.182	2.532	-2.715
NaCl	CWF		MLWF		MP		Bader					
Basis	Na	Cl	Na	Cl	Na	Cl	Na	Cl				
A9.0-s2p1	0.391	-0.391	0.760	-0.760	0.716	-0.716	0.858	-0.858				
A9.0-s3p2	0.422	-0.422	0.628	-0.628	0.595	-0.595	0.865	-0.865				
A9.0-s3p3d2	0.421	-0.421	0.876	-0.876	0.158	-0.158	0.853	-0.853				
A9.0-s3p3d2f2	0.421	-0.421	0.877	-0.877	-0.062	0.062	0.850	-0.850				

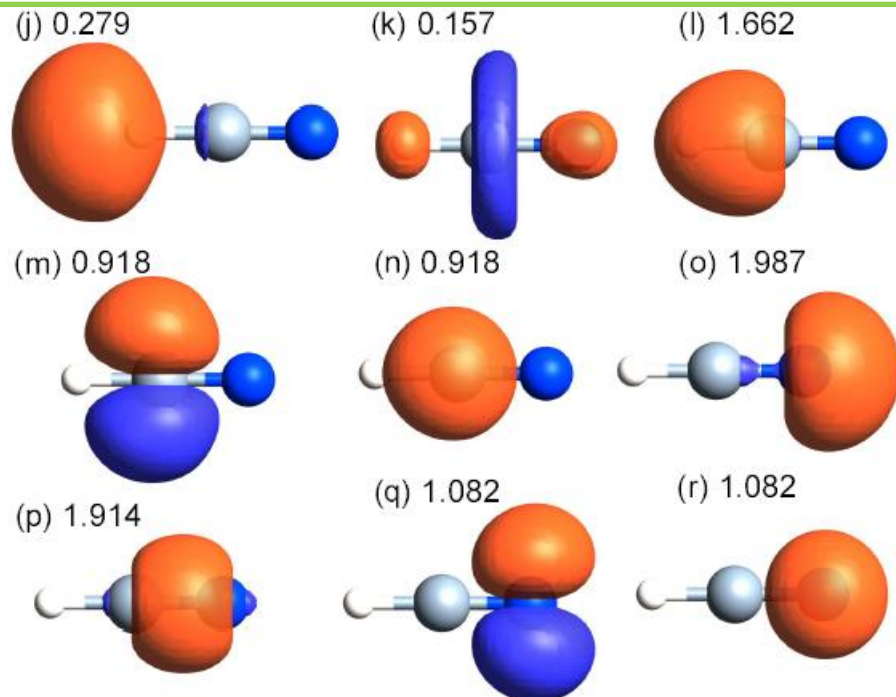
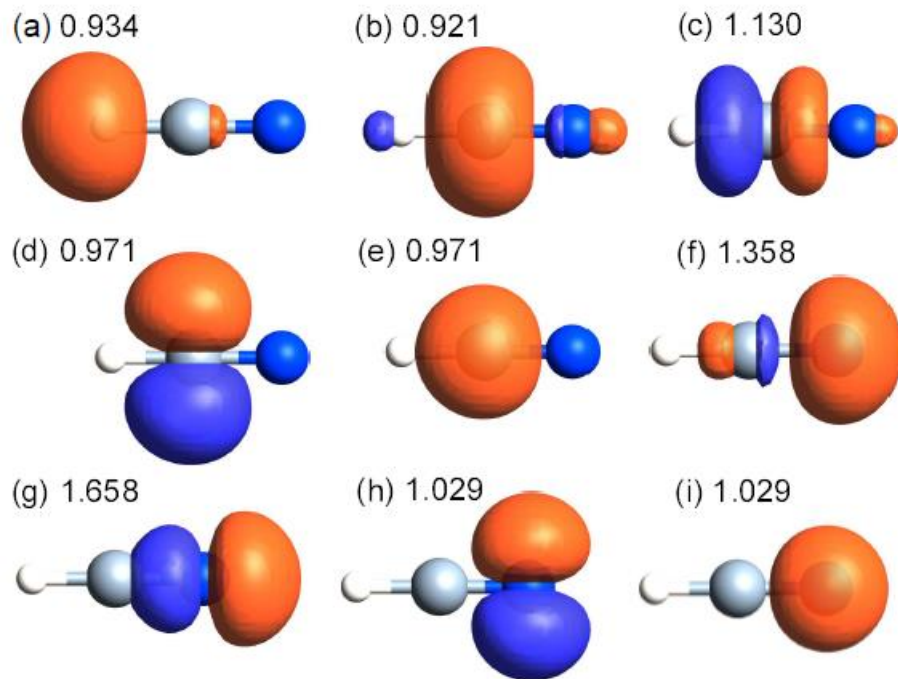
- The calculated charges by CWF quickly converge as a function of basis functions.
- MLWF and Bader overestimate the charge transfer in a HCN molecule.

CWF vs. MLWF for HCN

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CWFs

MLWFs



The number that follows is the population number considering the spin degeneracy.

The CWFs preserve the shape of atomic orbitals, while the MLWFs (j), (k), (l), (o), and (p) largely deform as a result of the maximally localization. In particular, (l) and (p) are bond-centered, leading to no justification for attributing the population to a single atom.

Summary

- We introduced a distance measure function of $F[B]$, and defined CWFs as WFs which minimize $F[B]$.
- The minimization of $F[B]$ can be performed by a polar decomposition of the projection matrix with a window function.
- The disentanglement of bands is inherently addressed by introducing a smoothly varying window function and a greater number of Bloch functions, even for isolated bands.
- Wannier interpolated bands well reproduce the conventional bands of a wide variety of systems.
- We further showed the usefulness of the proposed method in calculating effective atomic charges.

Refs: arXiv:2306.15296

<https://www.openmx-square.org/cwf/>