Variational formulation for finding Wannier functions with entangled band structure

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Joint work with Anil Damle and Antoine Levitt
(arXiv:1801.08572)

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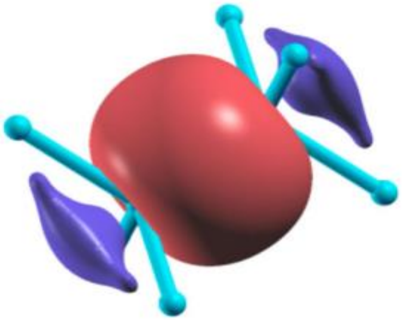
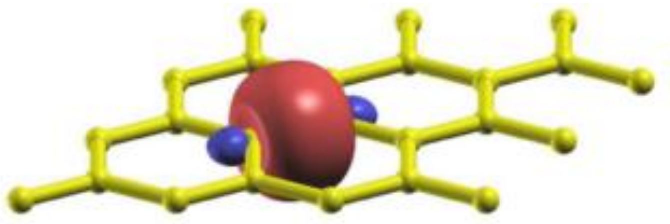
Wannier functions

- Maximally localized Wannier function (MLWF) [Marzari-Vanderbilt, Phys. Rev. B 1997]. Examples below from [Marzari et al. Rev. Mod. Phys. 2012]



Silicon



Graphene

- Reason for the existence of MLWF for insulating systems [Kohn, PR 1959] [Nenciu, CMP 1983] [Panati, AHP 2007], [Brouder et al, PRL 2007] [Benzi-Boito-Razouk, SIAM Rev. 2013] etc

Application of Wannier functions

- Analysis of chemical bonding
- Band-structure interpolation
- Basis functions for DFT calculations (representing occupied orbitals ψ_i)
- Basis functions for excited state calculations (representing Hadamard product of orbitals $\psi_i \odot \psi_j$)
- Strongly correlated systems (DFT+U)
- Phonon calculations
- etc

Maximally localized Wannier functions

- Geometric intuition: Minimization of “spread” or second moment.

$$\min_{\substack{\Phi=\Psi U,\\ U^*U=I}} \Omega[\Phi]$$

$$\Omega[\Phi] = \sum_{j=1}^{n} \int |\phi_j(x)|^2 x^2 \, dx - \left(\int |\phi_j(x)|^2 x \, dx \right)^2$$

- U: gauge degrees of freedom

Maximally localized Wannier functions

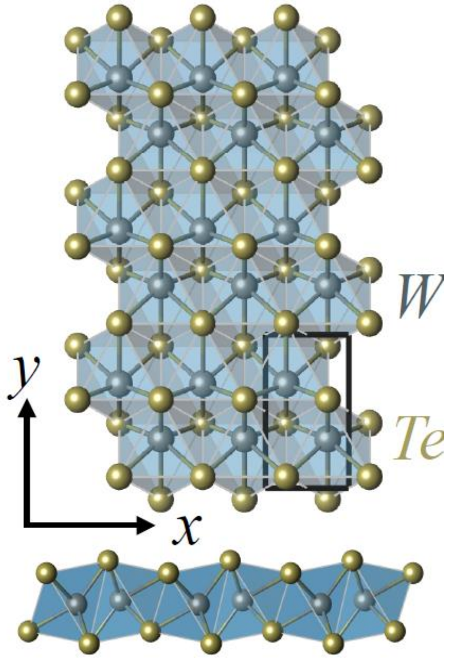
Robustness

- Initialization: Nonlinear optimization and possible to get stuck at local minima.
- Entangled band: Localization in the absence of band gap.
- Both need to be addressed for high throughput computation.

Example: WTe2

Old:

```
Begin Projections
W:s
c=0.10667692,1.1235077,0.869249688:s
c=0.10667692,1.1235077,2.607749065:s
End Projections
```



New:

```
scdm_proj: true
scdm_entanglement: 1
scdm_mu:  -0.43
scdm_sigma: 2.0
```

Selected columns of density matrix (SCDM)

[A. Damle, LL, L. Ying, JCTC, 2015]
[A. Damle, LL, L. Ying, JCP, 2017]
[A. Damle, LL, L. Ying, SISC, 2017]
[A. Damle, LL, arXiv:1703.06958]

Density matrix perspective

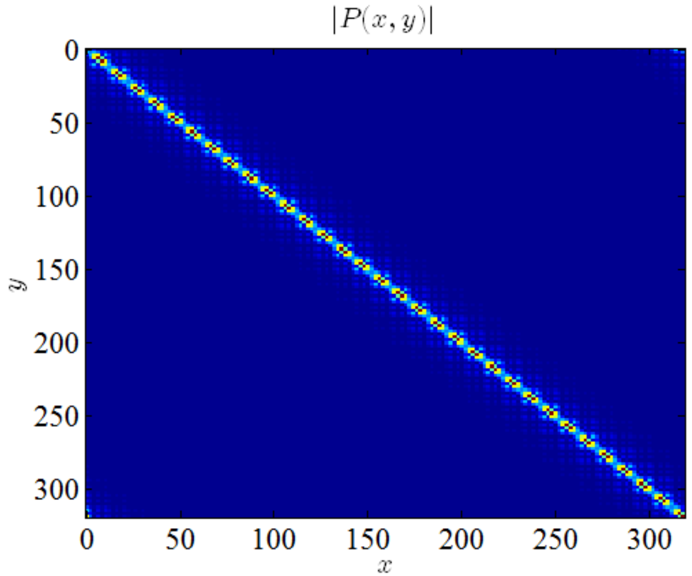
Ψ is unitary, then

$$P = \Psi\Psi^*$$

is a projection operator, and is gauge invariant.

$$P = \Psi\Psi^* = \Phi(U^*U)\Phi^* = \Phi\Phi^*$$

is close to a sparse matrix.



- Can one construct sparse representation directly from the density matrix?

Algorithm: Selected columns of the density matrix (SCDM)

Pseudocode (MATLAB. Psi: matrix of size m*n, m>>n)

```
[U,R,perm] = qr(Psi', 0);
```

Pivoted QR

```
Phi = Psi * U;
```

GEMM

- Very easy to code and to parallelize!
- Deterministic, no initial guess.
- perm encodes selected columns of the density matrix

[A. Damle, LL, L. Ying, JCTC, 2015]

k-point

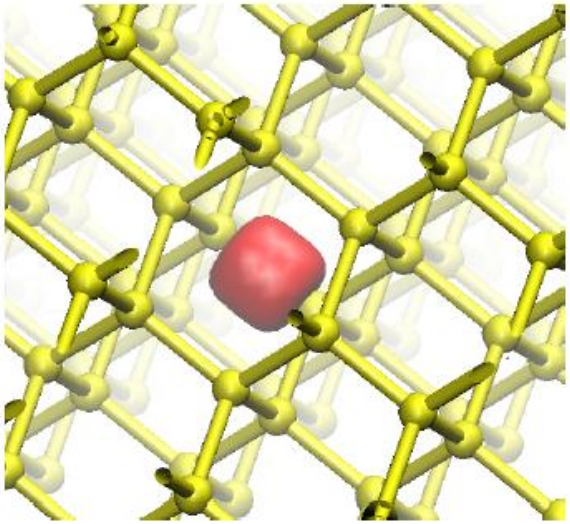
- Strategy: find columns using one “anchor” k-point (such as Γ), and then apply to all k-points

$$P(\mathbf{k}) = \sum_{\varepsilon_{b,\mathbf{k}} \in \mathcal{I}} |\psi_{b,\mathbf{k}}\rangle\langle\psi_{b,\mathbf{k}}| = \sum_{\varepsilon_{b,\mathbf{k}} \in \mathcal{I}} |\widetilde{\psi}_{b,\mathbf{k}}\rangle\langle\widetilde{\psi}_{b,\mathbf{k}}|$$

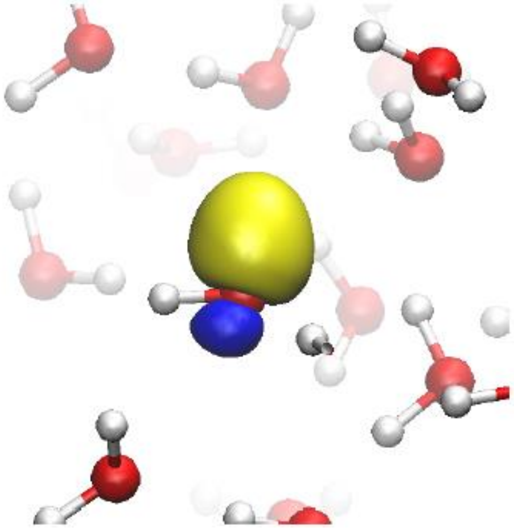
$$(\Xi^*(\mathbf{k})\Xi(\mathbf{k}))_{b,b'} = \sum_{b''=1}^{N_b} \psi_{b'',\mathbf{k}}(\mathbf{r}_b)\psi^*_{b'',\mathbf{k}}(\mathbf{r}_{b'}) = P(\mathbf{r}_b, \mathbf{r}_{b'}; \mathbf{k})$$

$$U(\mathbf{k}) = \Xi(\mathbf{k})\left[\Xi^*(\mathbf{k})\Xi(\mathbf{k})\right]^{-\frac{1}{2}}$$

Examples of SCDM orbitals (Γ-point)

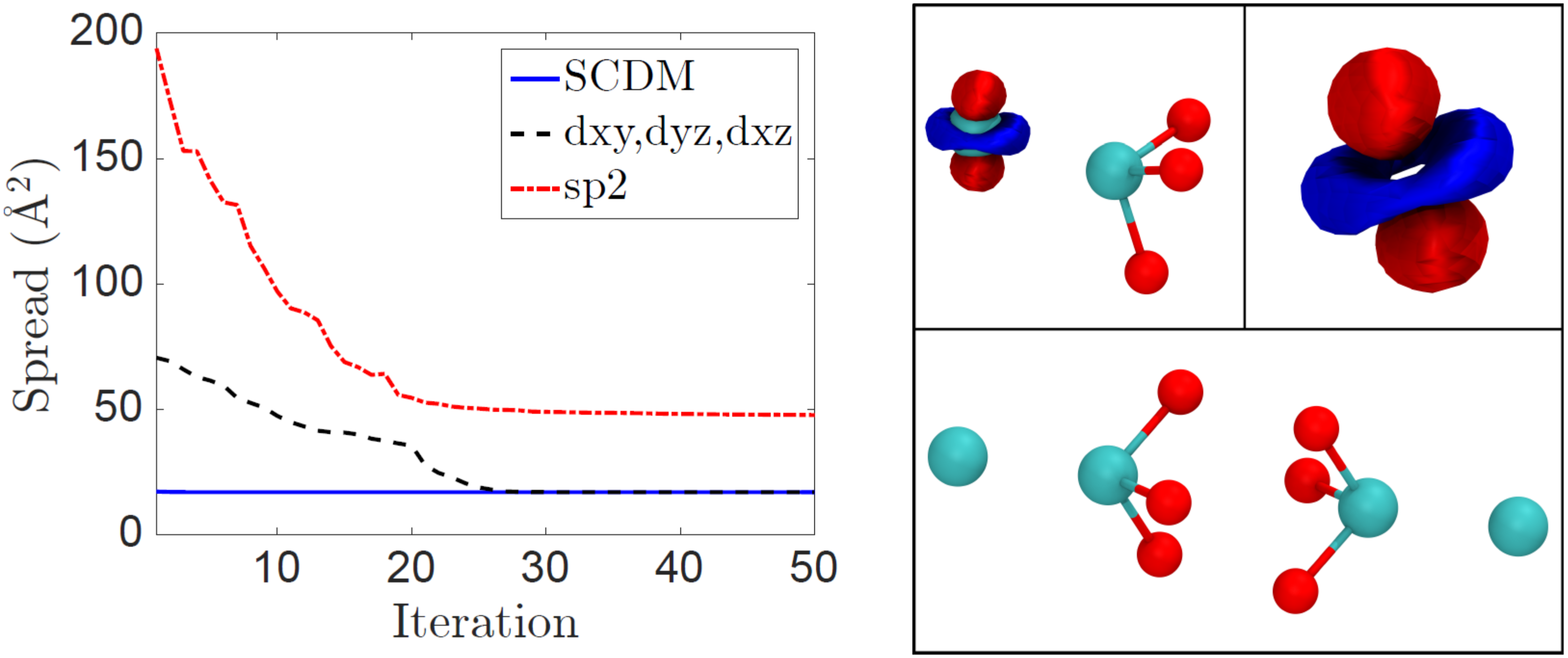


Silicon



Water

Examples of SCDM orbitals (k-point)



(a) (b)

Cr2O3. k-point grid $6 \times 6 \times 6$

Initial spread from SCDM: 17.22 Å^2

MLWF converged spread: 16.98 Å^2

Entangled bands

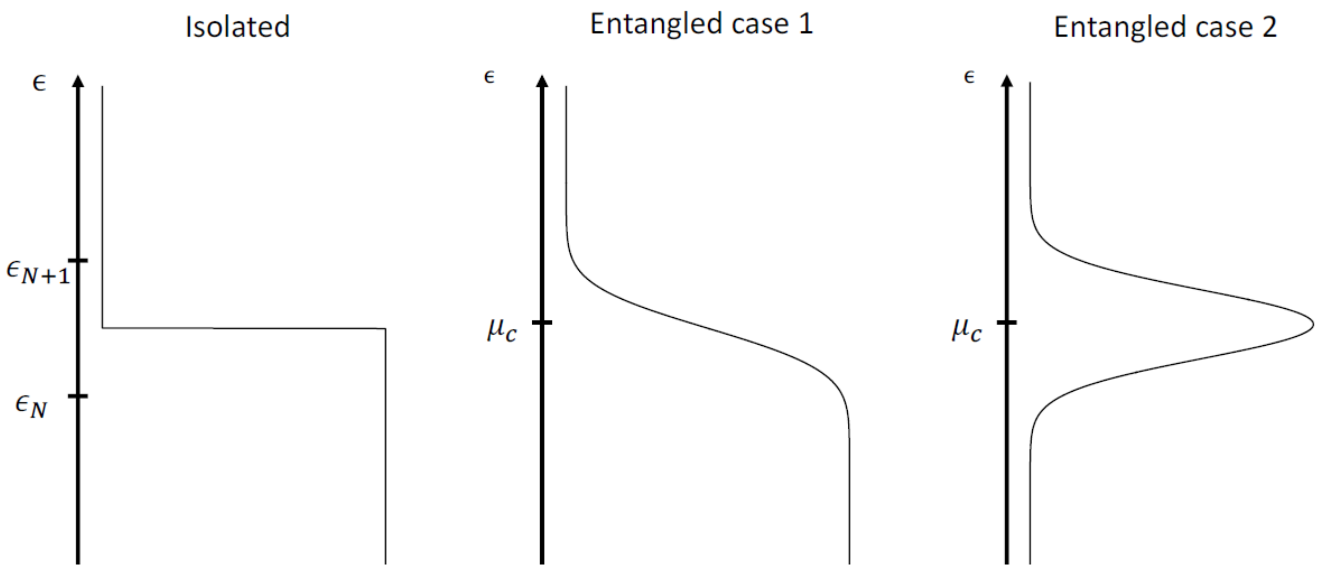
- Decay ⇔ Smoothness

- Quasi-density matrix

$$P(\mathbf{k}) = \sum_{\varepsilon_{b,\mathbf{k}}} |\psi_{b,\mathbf{k}}\rangle f(\varepsilon_{b,\mathbf{k}}) \langle\psi_{b,\mathbf{k}}|$$

- Choose f to be a smooth smearing function
- In localization, we can easily afford ~eV smearing.

Entangled bands



Entangled case 1 (metal, valence + conduction):

$$f(\varepsilon) = \frac{1}{2}\mathrm{erfc}\left(\frac{\varepsilon - \mu_c}{\sigma}\right) = \frac{1}{\sqrt{\pi\sigma^2}}\int_{\varepsilon}^{\infty} \exp\left(-\frac{(t-\mu_c)^2}{\sigma^2}\right)\,\mathrm{d}t.$$

Entangled case 2 (near Fermi energy):

$$f(\varepsilon) = \exp\left(-\frac{(\varepsilon - \mu_c)^2}{\sigma^2}\right)$$

Using SCDM

- MATLAB/Julia code

  https://github.com/asdamle/SCDM

  https://github.com/antoine-levitt/wannier

- Quantum ESPRESSO [I. Carnimeo, S. Baroni, P. Giannozzi, arXiv: 1801.09263]

- Wannier90 [V. Vitale et al]

  https://github.com/wannier-developers/wannier90

Interface to Wannier90

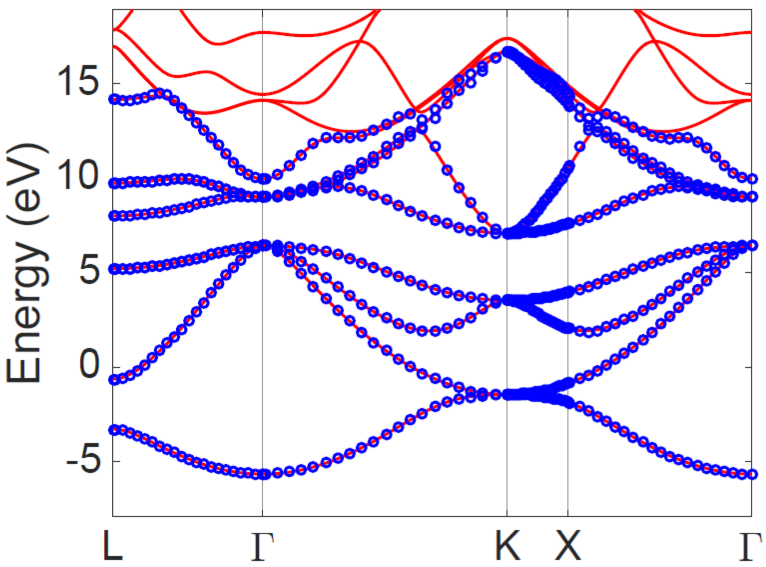
Example for isolated band:

scdm_proj: true
scdm_entanglement: 0

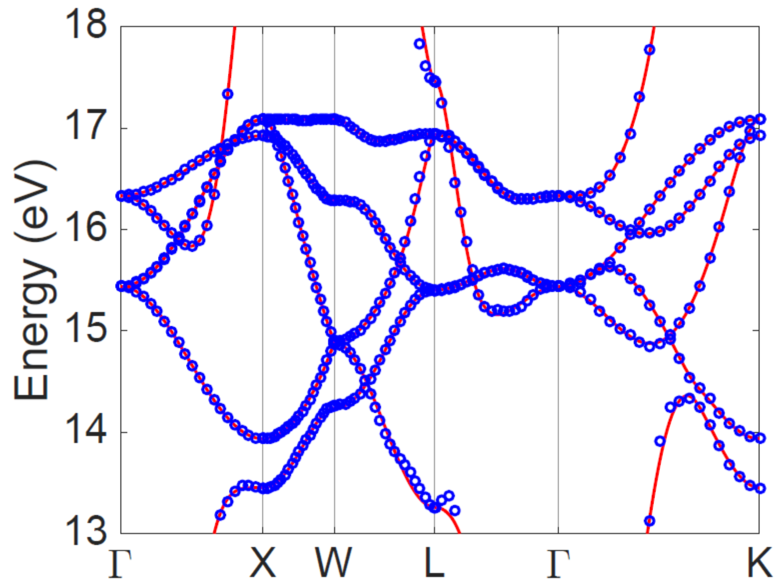
Example for entangled band:

scdm_proj: true
scdm_entanglement: 1
scdm_mu: -1.0
scdm_sigma: 1.0

Example: band interpolation



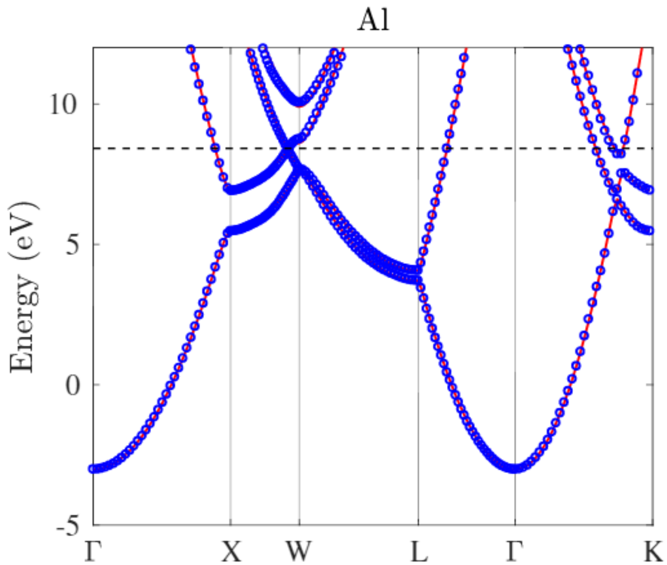
Si



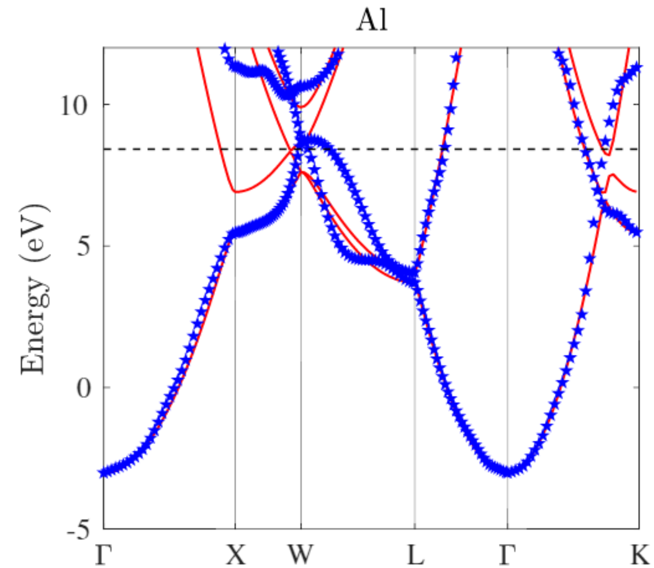
Cu

Band structure interpolation: Al

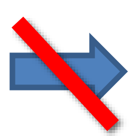
10x10x10 k-points, 6 bands ⇒ 4 bands (no disentanglement)



SCDM spread:
18.38 Å^2



Wannier: optimized spread:
12.42 Å^2

Smaller spread  Better interpolation

Variational formulation of Wannier functions for entangled systems

[A. Damle, LL, A. Levitt, arXiv:1801.08572]

Frozen band

- Disentanglement procedure [Souza-Marzari-Vanderbilt, PRB 2001]

$$P_f(\mathbf{k}) = \sum_{n \in \mathcal{N}_f(\mathbf{k})} |\psi_{n,\mathbf{k}}\rangle\langle\psi_{n,\mathbf{k}}|$$

$$P_w(\mathbf{k}) P_f(\mathbf{k}) = P_f(\mathbf{k}), \quad \forall \mathbf{k} \in \Gamma^*$$

- Subspace selection process with frozen band constraint

- $N_{outer} \geq N_w > N_f$: work with more bands!

How to enforce the constraint?

Proposition 3.1. *The following statements are equivalent:*

1. $P_w(\mathbf{k})P_f(\mathbf{k}) = P_f(\mathbf{k})$.
2. $U_f(\mathbf{k})U_f^*(\mathbf{k}) = I_{N_f(\mathbf{k})}$.
3. $U_f(\mathbf{k})U_r^*(\mathbf{k}) = 0$ *and* $U_f(\mathbf{k})$ *has full row rank.*
4. $U(\mathbf{k}) = \begin{bmatrix} I_{N_f(\mathbf{k})} & 0 \\ 0 & Y(\mathbf{k}) \end{bmatrix} X(\mathbf{k})$, *where* $X(\mathbf{k})$ *is a unitary matrix of size* $N_w \times N_w$, *and* $Y(\mathbf{k})$ *is a matrix with orthogonal columns of size* $(N_o - N_f(\mathbf{k})) \times (N_w - N_f(\mathbf{k}))$.

(X,Y) representation

Variational formulation

$$
\begin{aligned}
\inf_{\{X(\mathbf{k}),Y(\mathbf{k})\}} \quad & \Omega[\{U(\mathbf{k})\}], \\
\text{s.t.} \quad & U(\mathbf{k}) = \begin{bmatrix} I_{N_f(\mathbf{k})} & 0 \\ 0 & Y(\mathbf{k}) \end{bmatrix} X(\mathbf{k}), \\
& X^*(\mathbf{k})X(\mathbf{k}) = I_{N_w}, \\
& Y^*(\mathbf{k})Y(\mathbf{k}) = I_{N_w - N_f(\mathbf{k})}.
\end{aligned}
$$

Equivalent to “Partly occupied Wannier functions” [K. Thygesen, L. Hanse, K. Jacobsen, PRL 2005]

Julia code: https://github.com/antoine-levitt/wannier

Relation to disentanglement

- Split into gauge invariant part (Ω_I) and gauge-dependent part ($\widetilde{\Omega}$)

$$\Omega[\{U(\mathbf{k})\}] = \Omega_I[\{U(\mathbf{k})\}] + \widetilde{\Omega}[\{U(\mathbf{k})\}]$$

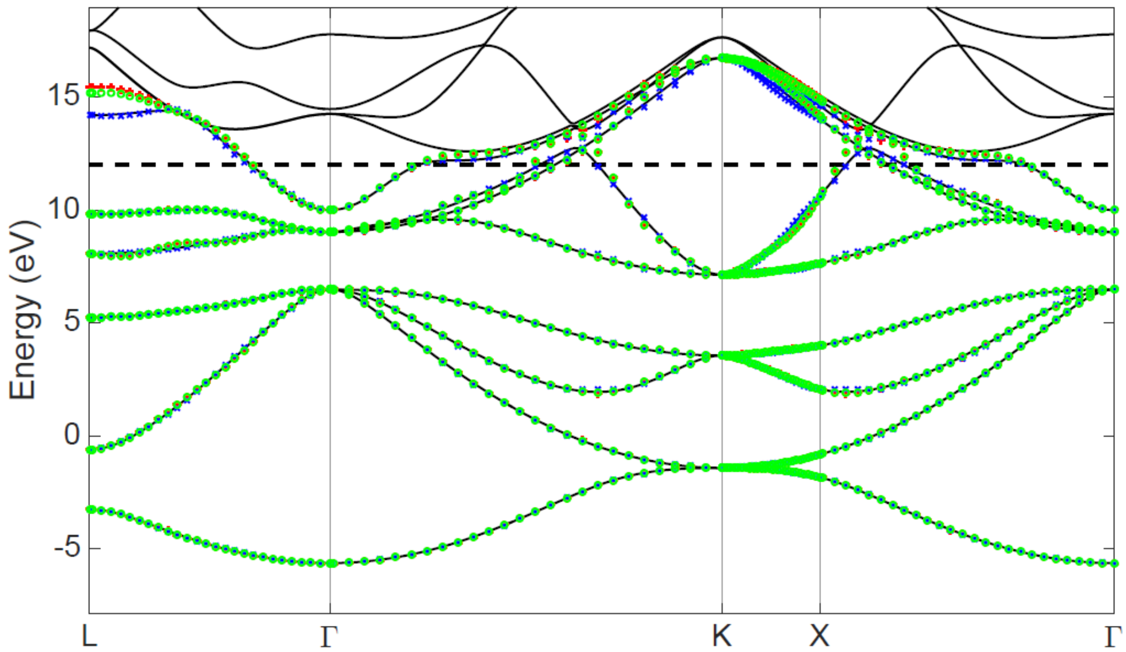
- Interpreted as one-step alternating minimization of the variational formulation

1. $$\inf_{\{Y(\mathbf{k})\}} \quad \Omega_I[\{U(\mathbf{k})\}]$$

2. $$\inf_{\{X(\mathbf{k})\}} \quad \widetilde{\Omega}[\{U(\mathbf{k})\}]$$

$\Rightarrow$ $$\Omega^{var} \leq \Omega^{dis}$$

Silicon: first 8 bands



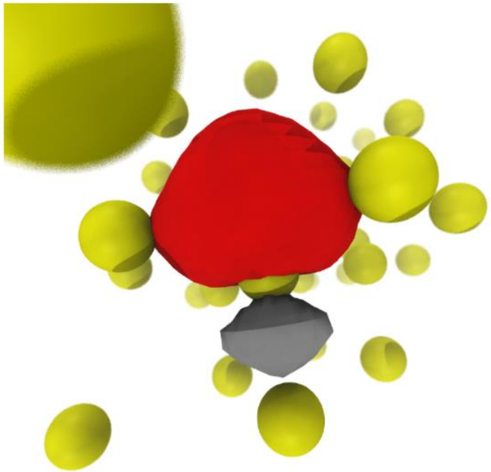
	Final spread $\left(\mathring{A}^2\right)$	max error (eV)	RMSE (eV)
Variational	25.177	0.069	0.021
`Wannier90`	27.00	0.083	0.023
SCDM	45.206	0.112	0.029

Silicon: first 8 bands

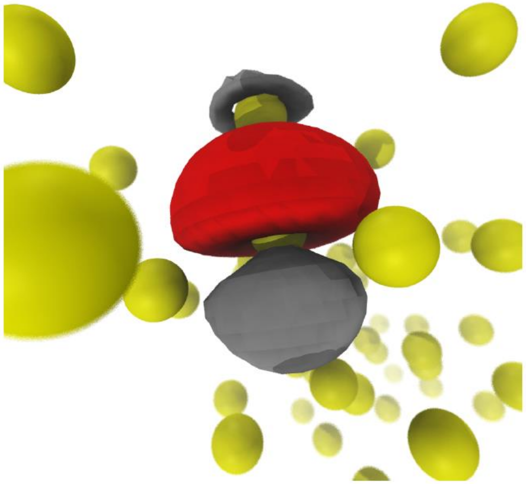
	Orbital spread $\left(\text{Å}^2\right)$							
Variational	3.15	3.15	3.15	3.15	3.15	3.15	3.15	3.15
Wannier90	3.16	3.16	3.16	3.16	3.59	3.59	3.59	3.59
SCDM	4.93	4.93	4.93	4.93	6.37	6.37	6.37	6.37

Symmetry restored!

Per orbital spread (isosurface=$\pm$0.5 for normalized orbitals)



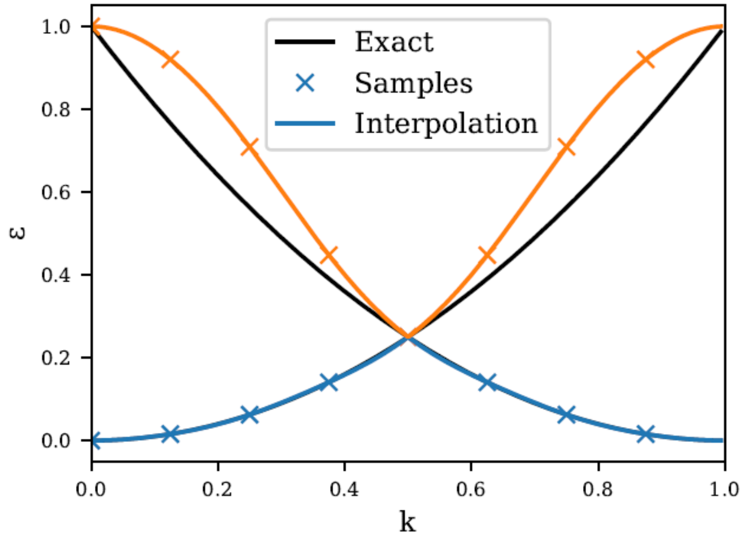
Variational (spread=3.15)

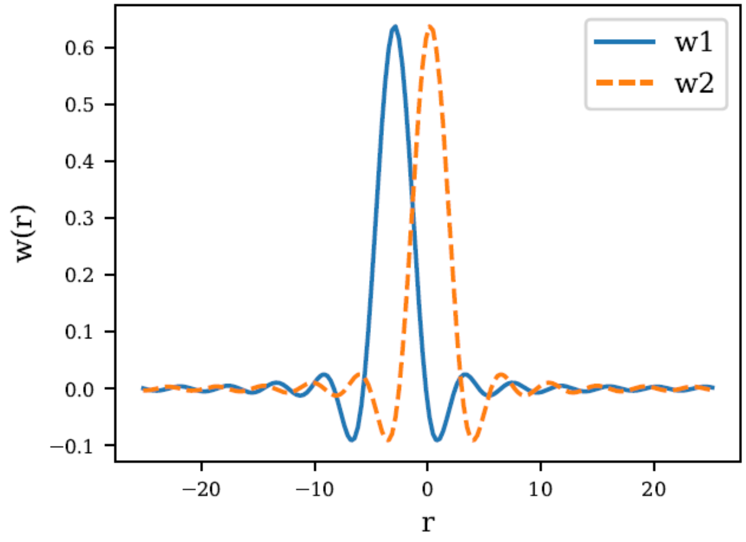


Wannier (spread=3.59)

Uniform electron gas

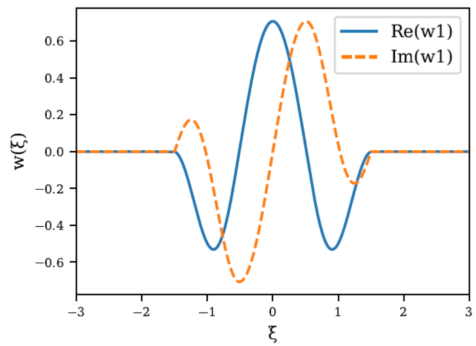
- Wannier function with frozen band constraints?
- One dimension

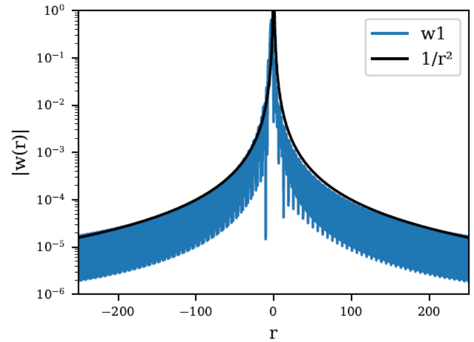




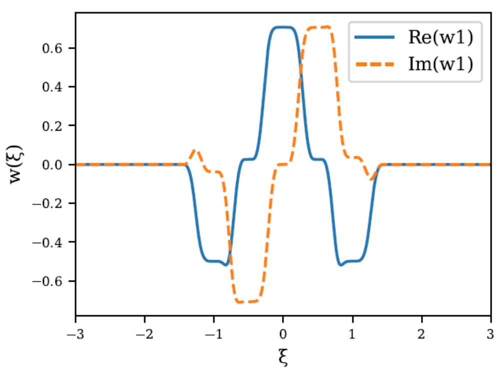
Decay properties

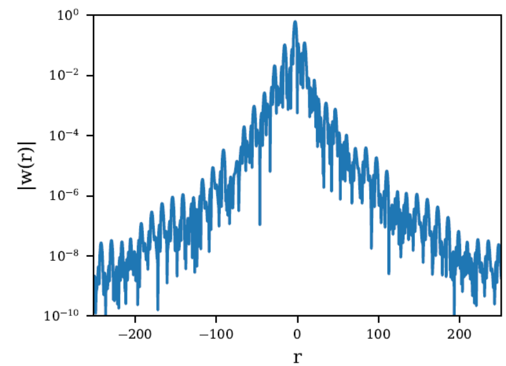
- Algebraic decay: only minimize second moment





- Can be enhanced to super-algebraic decay!

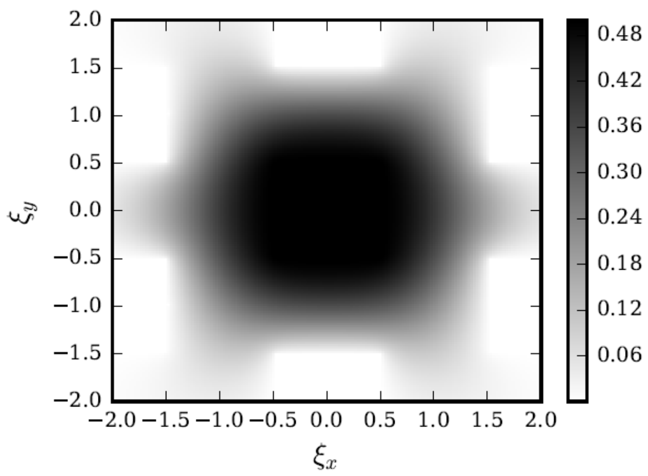




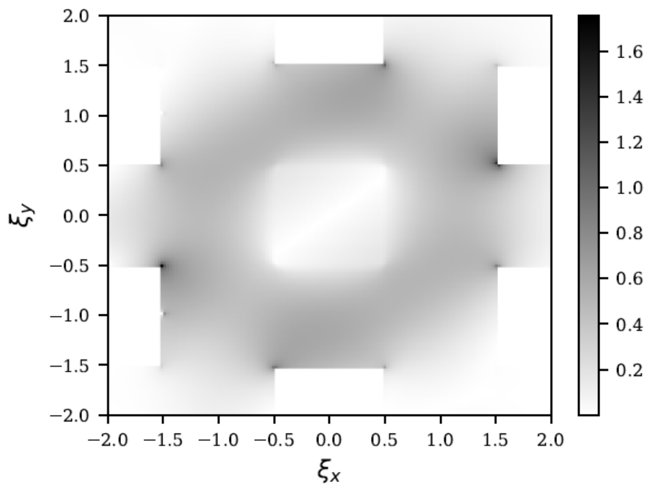
- [H. Cornean, D. Gontier, A. Levitt, D. Monaco, arxiv:1712.07954]

Two dimension

- Fourier space



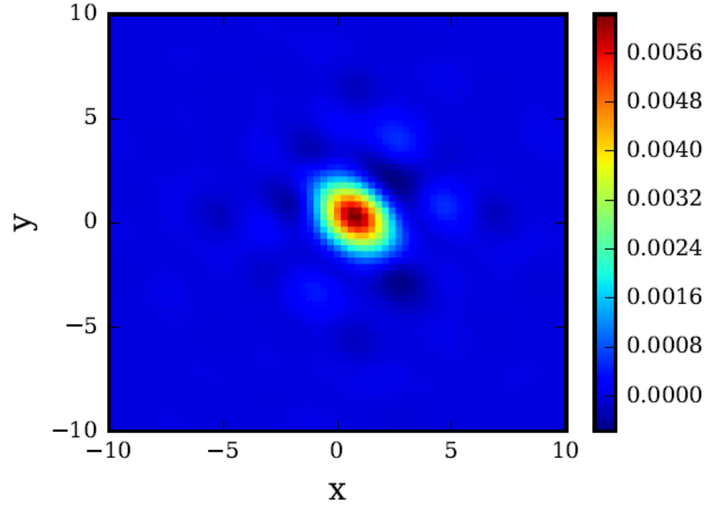
(a) $|\widehat{w}_2(\xi)|$. The function has components on arbitrarily large wave vectors.



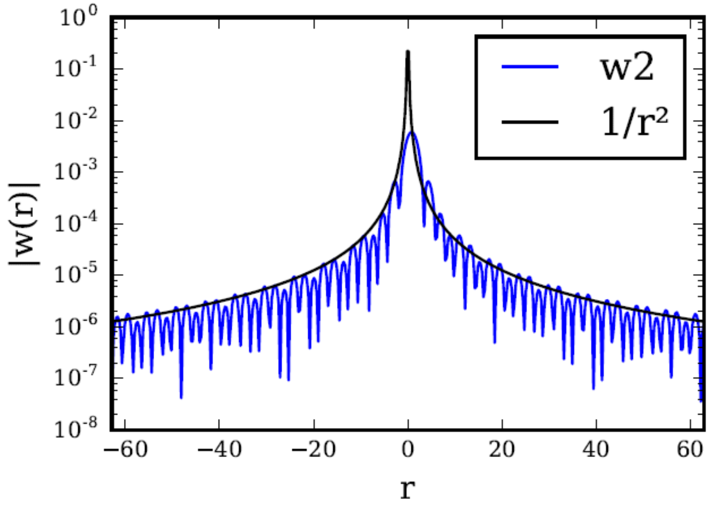
(b) $|\nabla_\xi \widehat{w}_2(\xi)|$, clearly showing the divergence on corners and discontinuity on edges.

Two dimension

- Real space



(c) $w_2(\mathbf{r})$.



(d) Slice of w_2 at $y = 0$, showing the $1/r^2$ decay.

Conclusion

- Wannier localization can be robustly initialized with SCDM (already in Wannier90). High-throughput materials simulation
- Variational optimization can lead to smaller spread with comparable computational cost, esp. entangled band
- Spread is not everything!
- Future: Symmetry. Topological materials.

DOE Base Math, CAMERA, SciDAC, Early Career
NSF CAREER.

Thank you for your attention!