Wannier Functions: Localization Properties and Explicit Construction

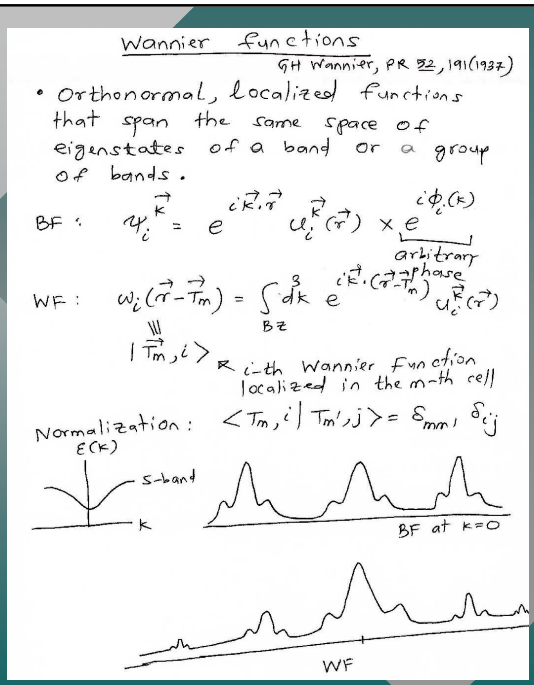
Look-alikes of Ole and Sashi in the spherical cow approximation

Resurrecting the paper from its grave

S. Satpathy and Z. Pawlowska, MPI, Stuttgart (1988)

*Currently: U. of Missouri (SS), Israel (ZP)

Ref: Construction of Bond-Centered Wannier Functions for Silicon Valence Bands, Phys. Stat. Sol. (b) 145, 555 (1988)



WF

Good points:

- Nice to think about electron states in terms of localized states Cu(d), O(p), etc.
- Localized orbitals natural way to build models for correlated systems, e.g., Hubbard models

$\langle W|H|W\rangle = \bar{E}_{band}$

Implemented by Kane and Kane (1978) - Too cumbersome!

Bad points:

- Not uniquely defined - can vary strongly in shape or range as opposed to Bloch functions that are unique (except for an overall phase factor)

How to build them

- Kohn's variational method
- Superposition of Bloch functions
- NMTO

SS+ZP (1988,LMTO),
Marzari+Vanderbilt (1997,plane waves)
Choice of phase.

Andersen et al, in progress

Localization Properties of WF

Q. How well can we localize the WF?

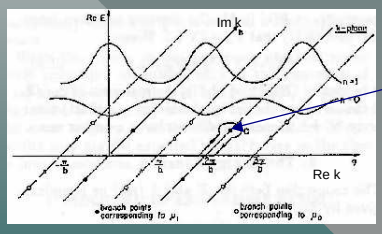
People involved: Kohn (1959), Des Cloizeaux (1964), Nenciu (1990)

1 D : For every band, there exists one and only one WF, which has all three of the properties:

1. It is real.
2. It is either symmetric or AS.
3. It falls off exponentially, W ~ exp (-Ad).

Related to the analyticity of the band structure in the complex k space

Energy



Decay constant A is related to how far away is the branch point in the complex k plane:

$A \sim (Gap)^{1/2}$

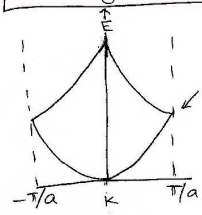
If Bloch functions $\Psi_k(x)$ are differentiable in k and analytic in a complex neighborhood of k, then the WF falls off exponentially. (Nenciu, RMP, 1991)

Q. Can one construct more localized function by relaxing reality and symmetry conditions?

Answer: NO!

For touching bands, there is no exponential localization !!

No exponential localization for touching bands : An example



Free-electron in a simple-cubic lattice, WF corresponding to the lowest band :

$$W(r) = \frac{a^{3/2}}{\pi^3} \frac{\sin(\frac{\pi x}{a})}{x} \cdot \frac{\sin(\frac{\pi y}{a})}{y} \cdot \frac{\sin(\frac{\pi z}{a})}{z}$$

- If variational calculation (à la Kohn) to obtain exponentially localized WF, energy bands near zone boundary will not be properly reproduced.
- Also, if cut off the WF at a finite distance $r \approx r_0$, bands within $\Delta k \sim \frac{\pi}{r_0}$ of ZB will be significantly affected !

Localization of WF in 3D

- Isolated single band

exponential localization is proved. (Nenciu, Commun. Math. Phys., 91, 81 (1983)

- Multiple bands (Des Cloizeaux, PR 135, A698 (1964)

In "many" cases, it can be proved that:

If Bloch functions are analytic in the domain of K = K' + iK'' for |K''| < A, then the corresponding WF falls off exponentially.

Working conjecture: For all cases of isolated groups of bands, exponentially localized WF exists, altho proof for existence has not been found yet!

Calculation Details

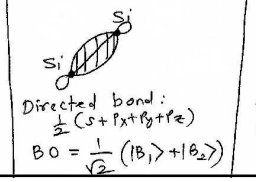
- With that conjecture, we proceed to compute WF for a 3D composite bands. (valence bands of Si)
- Stick to the established ideas in 1D
  - a) Reality of ψ_k
  - b) symmetry (maximum symmetry compatible with 3D bands) (Γ_1 irrep of D_{3d} group)

← Compute ψ_k using LMTO in the 1/48th BZ and construct ψ_k in full zone from symmetry

- Choice of phase factor:

$$|W_{nR}\rangle = \sum_k \sum_{m=1}^{4} U_{nm}(k)\,|\psi_{mk}\rangle\, e^{-ik\cdot R}/\sqrt{N} * e^{i\phi_k^m}$$

sp^3 Bond orbital (BO)

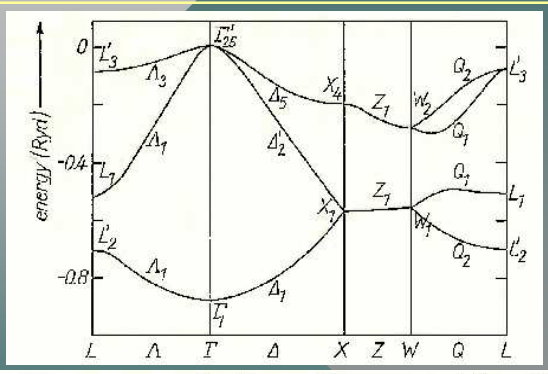


choose such that $\langle BO|\psi_{mk}\rangle e^{i\phi_k^m}$ is real and positive.

⇓

Only way to get the maximum sp^3 BO at central bond

The four sp^3 Bond orbitals span the same symmetry as the four valence bands at every k point in the Brillouin zone



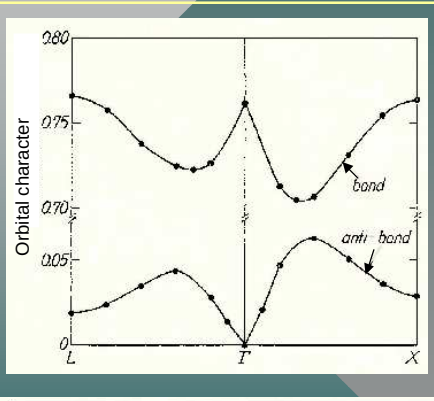
WF will have to have the same symmetry as that of the sp^3 bond orbital, viz., the Γ_1 irep of the D_{3d} (tetrahedral) group.

Else, stuff such as degeneracies etc. will not be correct for bands obtained with the WF of wrong symmetry.

orbital	Γ	Δ	X	Λ	L
Si-s	$\Gamma_1 + \Gamma'_2$	$\Delta_1 + \Delta'_2$	X_1	$2\Lambda_1$	$L_1 + L'_2$
Si-p	$\Gamma'_{25} + \Gamma_{15}$	$\Delta_1 + \Delta'_2 + 2\Delta_3$	$X_1 + X_3 + X_4$	$2\Lambda_1 + 2\Lambda_3$	$L_1 + L'_2 + L_3 + L'_3$
Si–Si B	$\Gamma_1 + \Gamma'_{25}$	$\Delta_1 + \Delta'_2 + \Delta_5$	$X_1 + X_4$	$2\Lambda_1 + \Lambda_3$	$L_1 + L'_2 + L'_3$
Si–Si AB	$\Gamma'_2 + \Gamma_{15}$	$\Delta_1 + \Delta'_2 + \Delta_5$	$X_1 + X_3$	$2\Lambda_1 + \Lambda_3$	$L_1 + L'_2 + L_3$

"continuity chord" ideas: see J. Zak, PRL 54, 1075 (1985)

sp^3 bond orbital character dominates in the valence charge density of Group-IV semiconductors

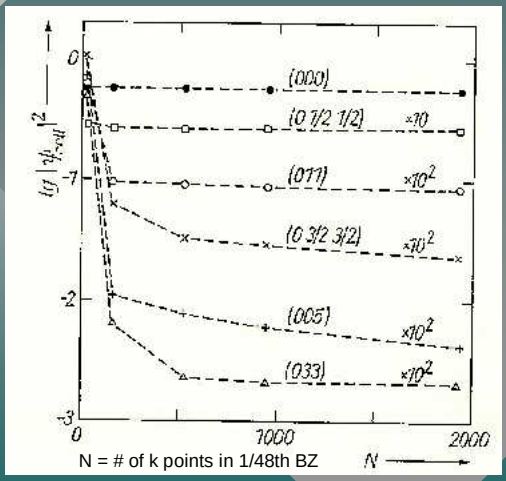


crystal	lattice constant*) (nm)	character (%) Si–Si B	Si–Si AB	Si-d	E-s, p, d
C	0.356	77	1	3	19
Si	0.542	72	4	5	20
Ge	0.566	72	5	3	20
α-Sn	0.649	71	5	4	20

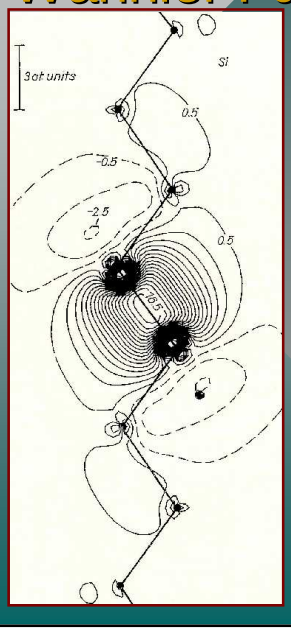
- Bond orbital 72% for Si, while AB is just 4%.
- "Bond-order" (B-AB) progressively weakens in going from C to a-Sn.
- Quantitative justification for focusing on the sp3 BO part in constructing the WF.

- Construct WF such that the projection of it to the central BO is maximized.

Test of convergence of log $|\Psi_{cell}|^2$ as a function of the number of k points



Wannier Function for Silicon



WF constructed with LMTO

(SS+ZP, 1988)

Charge-density character of the WF

Charge-density character of the Wannier function (in %)

cell location	silicon				empty sphere	total
	central sp^3 bond	central sp^3 anti-bond	rest s, p	d	s, p, d	
central cell	54	0	2	2	1	59
nearest-neighbor cells	—	—	2	1	13	16
rest	—	—	18	2	5	25
total	54	0	22	5	19	100

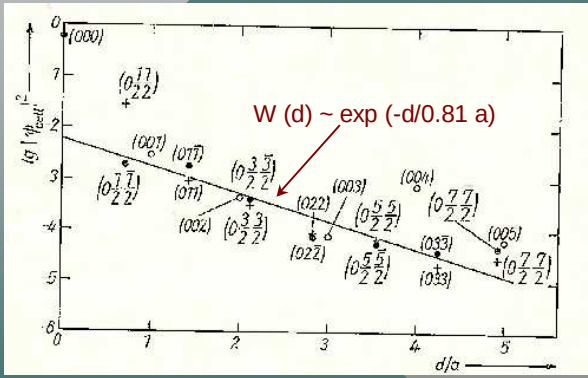
Character of the valence charge-density for C, Si, Ge, and α-Sn

crystal	lattice constant*) (nm)	character (%) Si–Si B	Si–Si AB	Si-d	E-s, p, d
C	0.356	77	1	3	19
Si	0.542	72	4	5	20
Ge	0.566	72	5	3	20
α-Sn	0.649	71	5	4	20

Exponential localization of the calculated WF

Complex band structure of Chang using empirical TB (PRB, 25, 605 (1982):

Branch-points of E(k) at k $\pm i0.7$ π/a k_{111} and k $\pm i0.5$ π/a k_{100}



If we assume no other branch point in the range |Im (K)| < 0.5 π/a, then that indicates a decay of

W ~ exp (-d/0.64 a).

[log $|\Psi_{cell}|^2$ vs. distance of cell from origin d (units of lattice constant), showing exponential decay. SS and ZP (1988)]

Marzari + Vanderbilt's ansatz using plane waves PRB 56, 12847 (1997)

- $|W_{n\vec{R}}\rangle = \sum_{m=1}^{4} U_{nm}^{(k)} \sum_{k} \psi_{nk} e^{-i\vec{k}\cdot\vec{R}} / \sqrt{N}$

  ↑ 4×4 unitary matrix

- By steepest descent, find $U_{nm}^{(k)}$ such that the spread function

$$\Omega = \sum_{n} \left[\langle r^2 \rangle_n - \bar{r}_n^2 \right]$$

is minimized.

$$\langle r^2 \rangle_n \equiv \langle W_n | r^2 | W_n \rangle$$

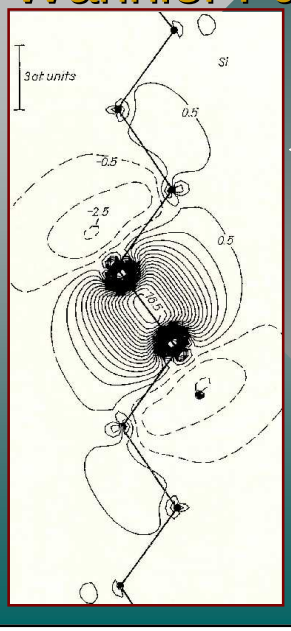
↑ n-th WF in the unit cell

- Define this WF to be "maximally localized."
- Minimization of a function in $6N_K$ space

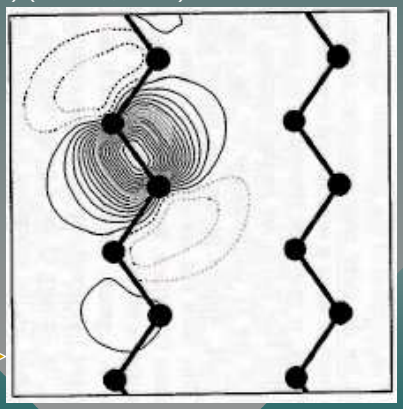
  N_K = # of k points used in construction of WF

Grid used = $N_K = 8 \times 8 \times 8 \approx 500$

Wannier Function for Silicon

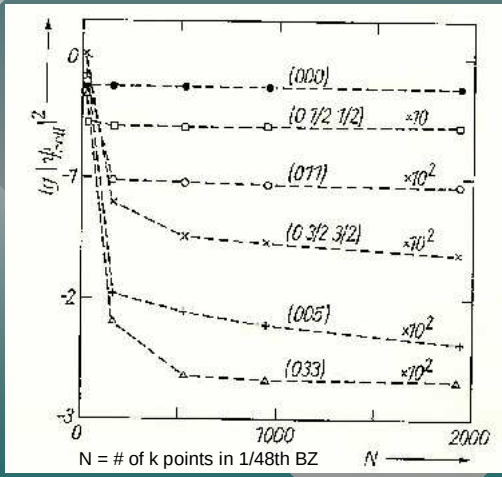


So-called "Maximally projected" WF constructed with LMTO (to maximize BO contribution) (SS+ZP, 1988)

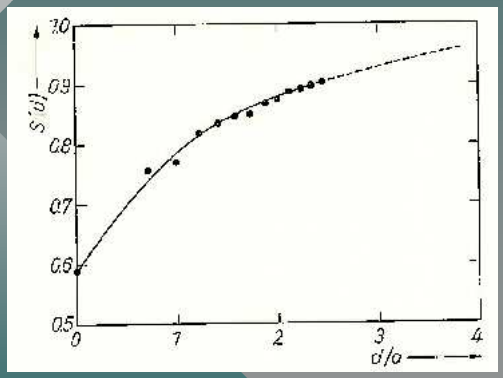


So-called "Maximally localized" WF constructed with plane-wave pseudopotential (Marzari & Vanderbilt, 1997)

Test of convergence of log $|\Psi_{cell}|^2$ as a function of the number of k points (SS+ZP)



Integrated charge-density character of the WF, S(d), within a sphere of radius 'd'



Conclusion

- Bond-centered WF constructed for the Si valence bands, by direct superposition of Bloch functions and a choice of phase to maximize the sp^3 BO contribution.
- Exponential fall off of the WF demonstrated: W ~ exp (-d/0.8 a)
- This is the most localized in the sense that the central sp^3 character is maximum; this character will necessarily reduce if we maximize some local operator, such as $\langle W|1/r^2|W\rangle$, instead.

Issues and Questions

- Uniqueness
- How universal is the method for calculating WF?
- NMTO as a method to compute WF
- How to compute parameters (U etc) for model Hamiltonians in some unique manner?
- WF for non-isolated bands - How crucial is the lack of exponential localization?