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Geometric phases, polarization, distribution of electron charge centers, Wannier functions and bonding in materials

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Geometric Phases, Polarization, Distribution of Electron Charge Centers, Wannier Functions and Bonding in Materials

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  (moving to L. Berkeley National Lab)
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BACKGROUND

Geometric phases: Modern theory of polarization

(King-smith and Vanderbilt, PRB 47, 1651 (93); R. Resta, Rev. Mod. Phys, 66, 899 (94)).

Polarization in multi-ferroic materials: *puzzles*

(Wang et al, Science 299, 1719 (03); Neaton et al, PRB 71, 014113 (05)).

Charge Density Partitioning:

Maximally Localized Wannier Functions (Marzari and Vanderbilt, PRB 56, 12847 (97)).

In 2 and 3 D: localization length of MLWFs > physical length-scale of the system.

In 1 D: they are equal

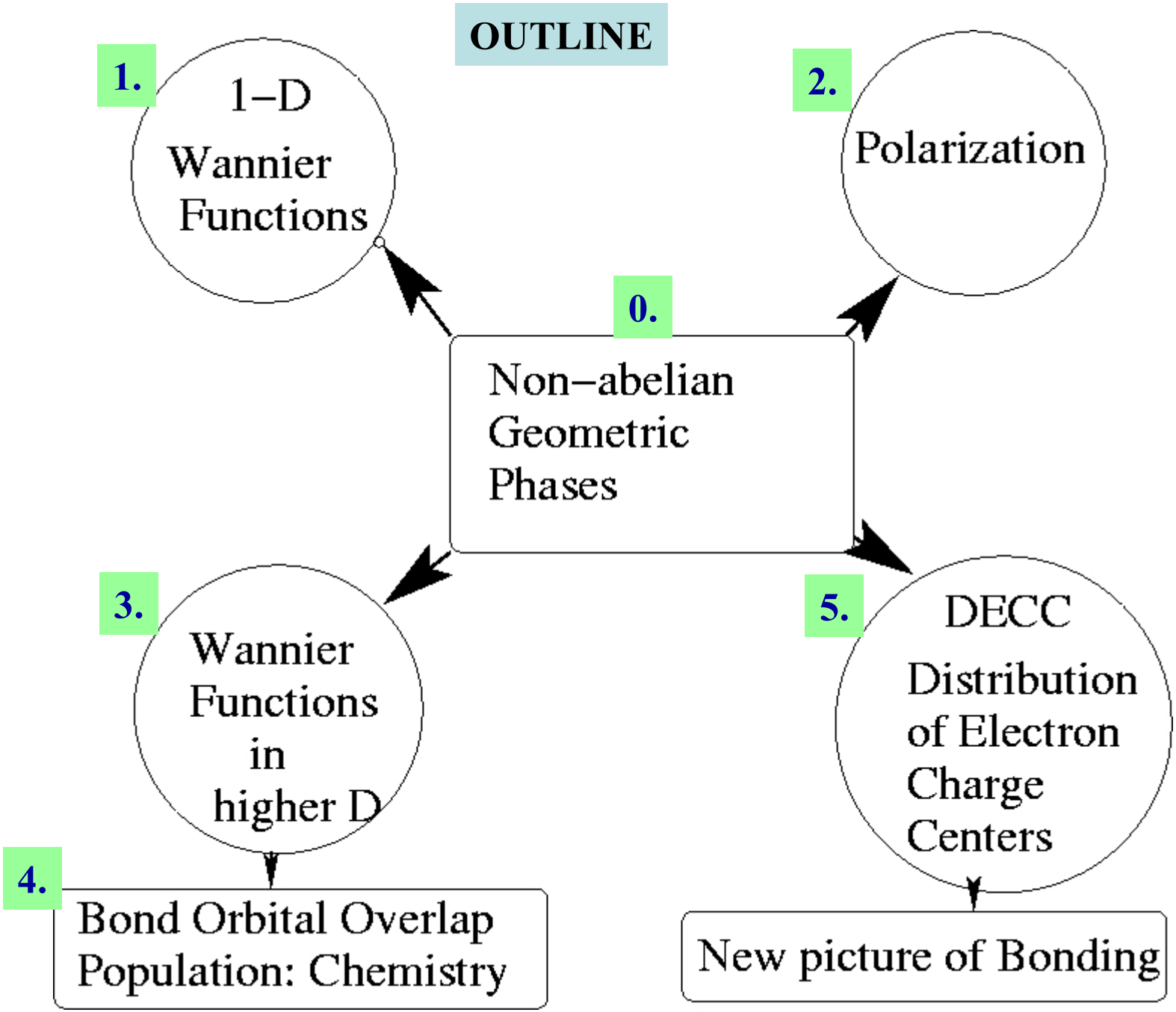
Chemistry of Materials:

Topological analysis of charge density, Electron Localization Functions

(Bader, Atoms in the Molecules (89); Silvi and Savin, Nature 371, 683 (94)).

is known *not* to yield estimation of polarization!

Non-abelian Geometric Phases: a frame-work to address all above points


OUTLINE
1.
1–D
Wannier
Functions
2.
Polarization
0.
Non–abelian
Geometric
Phases
3.
Wannier
Functions
in
higher D
5.
DECC
Distribution
of Electron
Charge
Centers
4.
Bond Orbital Overlap
Population: Chemistry
New picture of Bonding

Wannier Functions

- **Wannier function: A localized orbital description of Bloch electron (Wannier, 1937)**
- **W. Kohn: Analytic properties (1959); Construction (1973); Applications to $O(N)$ calculations (1993)**
- **Important Applications:**
  - **Semi-classical electron dynamics**
  - **Model hamiltonians for many body calculations**
  - **Linear scaling ($O(N)$) electronic structure calculations**
  - **Modern theory of polarization (geometric phase)**
  - **Analogus to Lewis molecular bond orbitals $\rightarrow$ chemistry**
- **Non-uniqeness of Wannier Functions: Phase factors**

$$W_n(\mathbf{r}) = \int_{\mathbf{BZ}} \mathbf{dk} (\mathbf{e}^{\mathbf{i}\theta_{\mathbf{kn}}}) \psi_{\mathbf{kn}}(\mathbf{r})$$

Wannier Functions

- **Fourier transforms of Bloch functions:**

$$W_n(x) = \sum_m \int dk\ \psi_{km}(x)\ e^{i\theta(k,m)}$$

Arbitrary phases θ(k,m) of Bloch fn: *non-uniqueness of W_n*

***Smoothness* of Bloch functions as a function of *k* determine the localization properties of W_n**

- **Marzari and Vanderbilt (1997):**

$$\Omega = \langle r^2 \rangle - \langle r \rangle^2$$

Θ(k,m) chosen to minimize Ω

- **Ω is finite for insulators (> physical length-scale^2) and ∞ for metals**

PROBLEM: Origin of phases

- Random phases from diagonalization

- Phases natural to the geometry of the QM problem

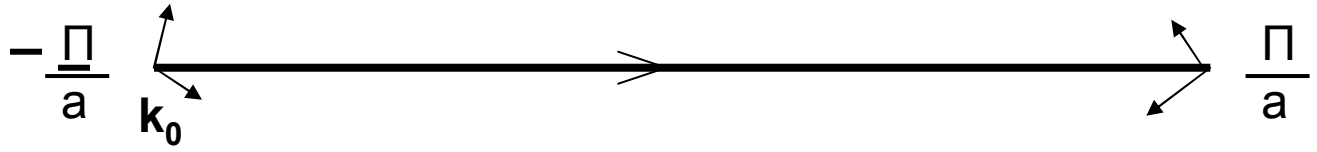
OUR SOLUTION:

- **We obtain Bloch functions that are smooth and periodic in *k*:**

1. **Starting with k_0, we obtain Bloch functions at all *k* using parallel transport.**
2. **Aperiodic factors associated with geometric phases are analytically filtered out.**

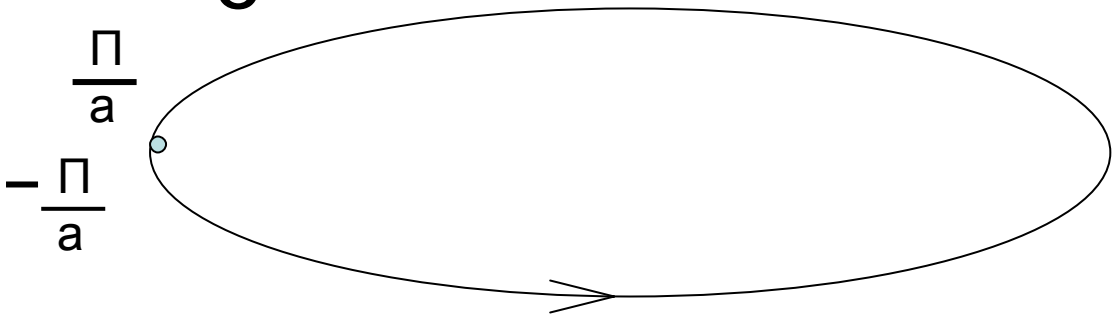
Geometric phases: Wannier functions in 1-dimension

- Generate Bloch functions at k, using parallel transport from k_0
- Filter out the geometric phase factors



Non-Abelian geometric phase matrix

$e^{i\Gamma}$



Wannier functions: eigenfunctions of Γ

Wannier centres: eigenvalues of Γ : <x>

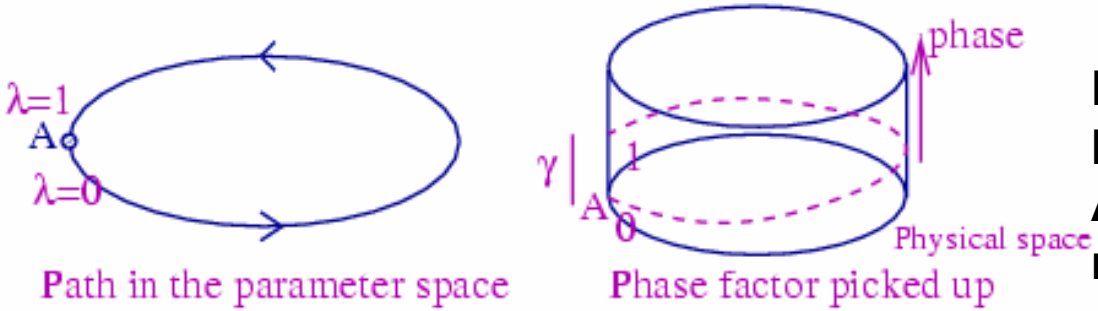
(Bhattacharjee and Waghmare, Phys Rev B 71, 045106 (05)).

Parallel Transported Wavefunctions and Geometric Phase

- **Parallel Transport:**

$$< n, \lambda | \frac{d}{d\lambda} | n, \lambda >= 0$$

- **Geometric phase:** $|n, \lambda + \Delta\lambda >_{||} = |n, \lambda >_{||} + \Delta\lambda \frac{d}{d\lambda} |n, \lambda >_{||}$



Many crossing bands lead to Non-Abelian phase matrix Γ

γ : recovered once the loop is closed!

$$\gamma = Im(Log(< n, \lambda = 0 | n, \lambda = 1 >))$$

Γ = Im(Log(<m, λ=0 | n, λ=1>))

- **No random phases if:**

  $\psi(\lambda_1)$ **and** $\psi(\lambda_2)$ **are related to each other by parallel transport**

Method (within density functional theory)

- Parallel Transport(PT) Bloch functions from $k = -\frac{\pi}{a}$ to $k = \frac{\pi}{a}$
  - Obtain $\frac{d}{dk}|u_{kn}>$ using DFT linear response s.t. $< u_{km}|\frac{d}{dk}|u_{kn}>= 0$
  - $|u_{k+\Delta kn}>= |u_{kn}> +\Delta k \frac{d}{dk}|u_{kn}>$: Runge-Kutta integrate from k to $k + \delta k$
  - Obtain $\Gamma = Im(Log(< u_{k+\frac{2\pi}{a}m}|P|u_{kn}>))$

$$[e^{i\Gamma}]_{mn} = \left\langle u^{\|}_{mk_0} \left| \exp\left(i\frac{2\pi x}{a} \right) \right| u^{\|}_{nk_0+2\pi/a} \right\rangle$$

- Rotate the PT Bloch functions with eigenvectors of $\Gamma(M)$: Different bands are decoupled
- Maximization of localization **results naturally**

$$W_n(x) = \sum_{m,k} e^{-ik.\gamma_n} M_{nm} \psi^{\|}_{km}(x)$$

- In 2 or 3-D: Γ_x may not commute with Γ_y: No perfectly localized Wannier function!

Ref. Bhattacharjee and Waghmare, Phys. Rev. B 71, 045106 (2005).

Discretized Parallel Transport and Γ

Bloch functions of the form :

$$\psi_{kn}(r) = e^{ik.r} u_{kn}(r)$$

Connecting Bloch functions at k and k+Δk

Overlap matrix S : $S_{mn}(k, k+\Delta k) = \langle u_{mk} \mid u_{n,k+\Delta k} \rangle$

Overlap matrix, S, in terms of R and Γ_k as, $S = \mathrm{Re}^{i\Gamma_k}$

Determination of R and Γ matrices →

Singular Value Decomposition of overlap matrix, **S=U∑V†**

Rotate wave functions at k+Δk by $M = (UV^{\dagger})^*$ ⟶ S' = R'

⟶ Parallel transported wave functions satisfy "parallel transport" gauge:

$$\langle u^{\parallel}_{km} \mid \frac{\partial u^{\parallel}_{kn}}{\partial k} \rangle = 0$$

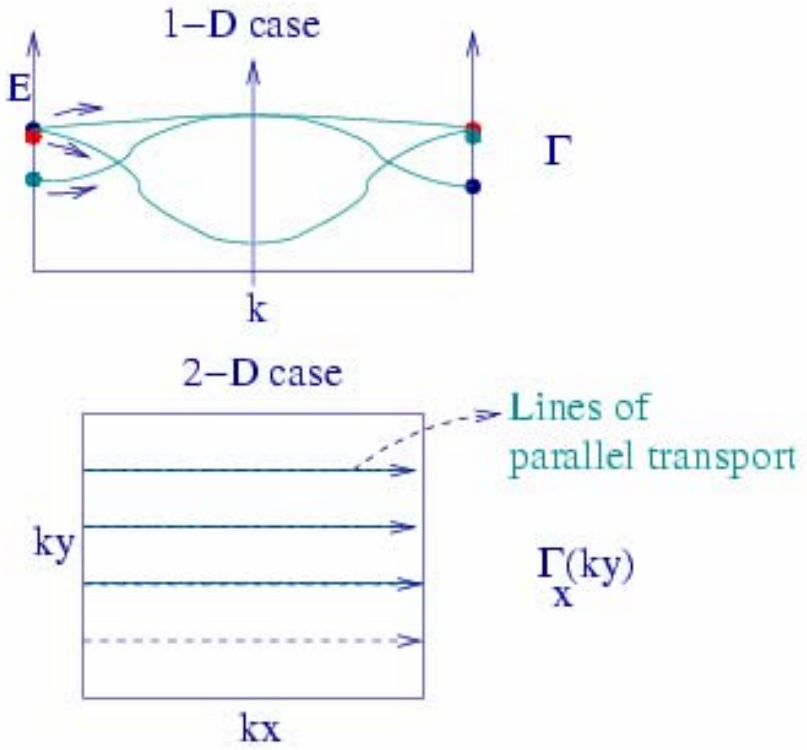
$$\left[e^{i\Gamma}\right]_{mn} = \langle u^{\parallel}_{mk_o} \mid e^{\frac{i2\pi x}{a}} \mid u^{\parallel}_{nk_o+\frac{2\pi}{a}} \rangle$$

$$\Gamma = \mathrm{Im}\log\langle u_{k+\frac{2\pi}{a}m} \mid e^{i\frac{2\pi x}{a}} \mid u_{kn} \rangle$$

Eigenvalues of Γ matrix, τ_i = eigenvalues of *PrP* * (2π/a)

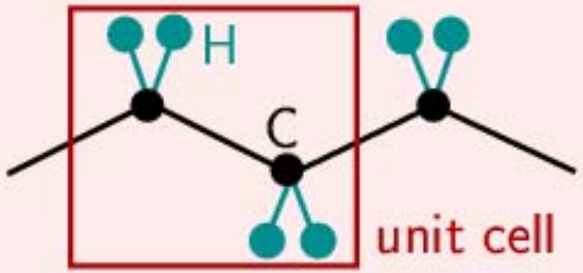
(Equivalent to Sgiarovello, Peressi, Resta, PRB64, 115202 (2001)).

Geometric Phases in 1-d and 2-d



- **Eigenvalues of Γ: Centre of Wannier function ("Bond")**
- **Eigenvectors of Γ: which bands make up the "Bond"**

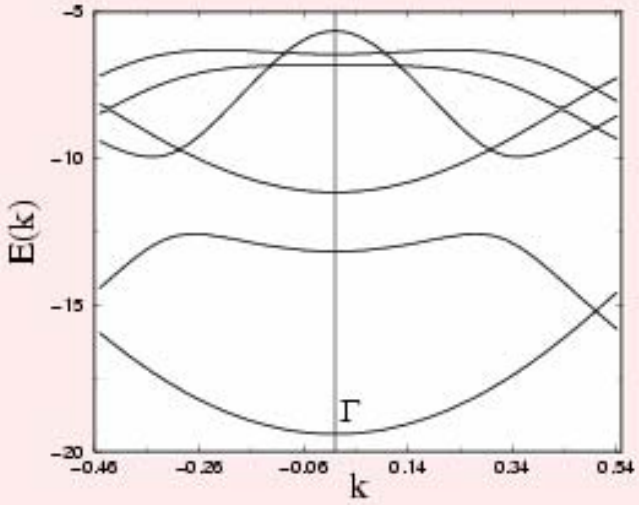
POLYETHYLENE

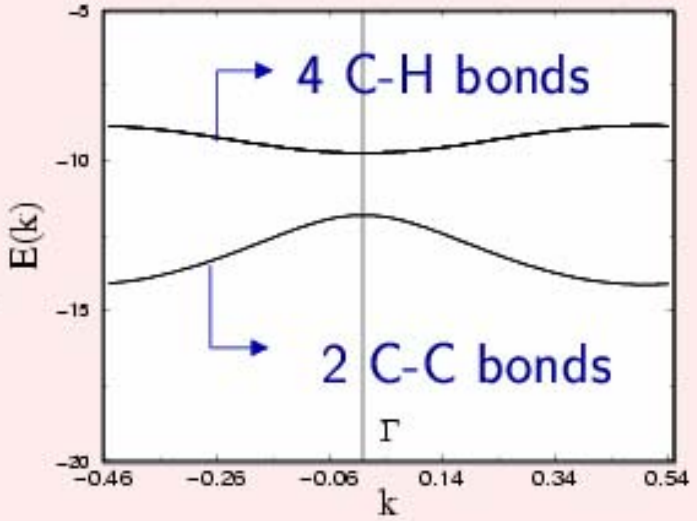


Two symmetry independent
Wannier functions

C-C bond
C-H bond

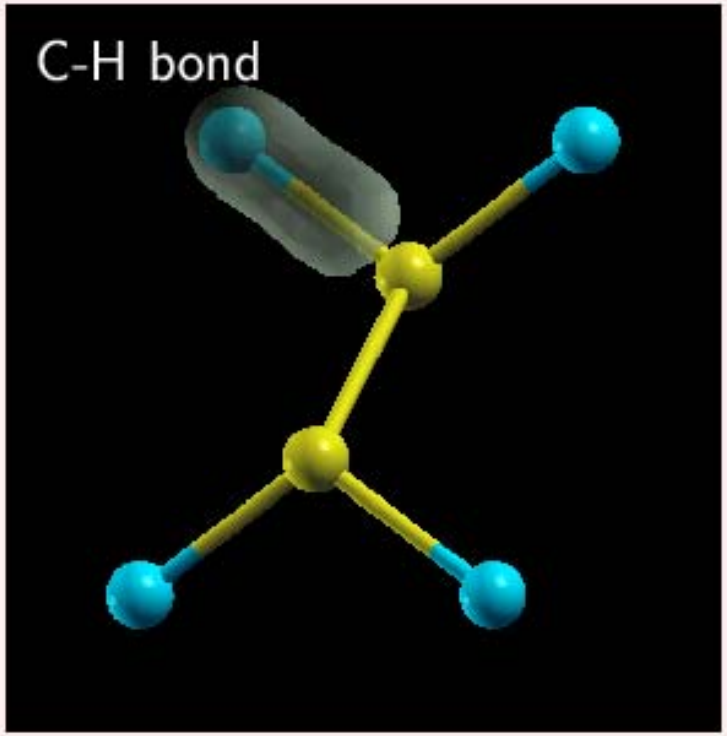
6 valence bands



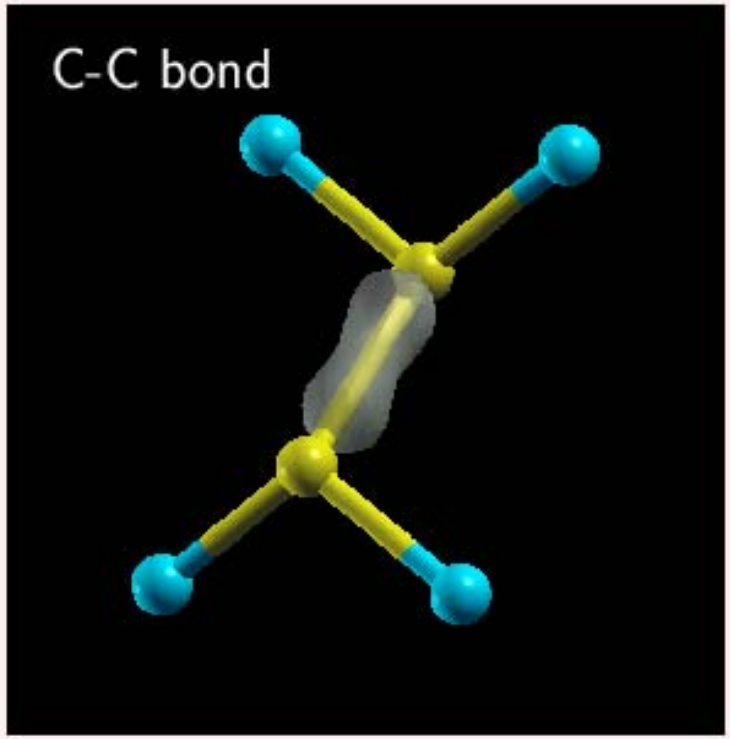


POLYETHYLENE

Wannier functions



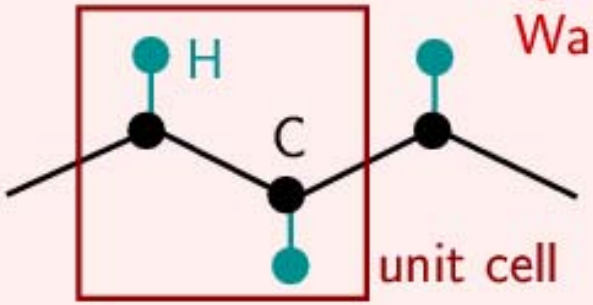
Ω =0.20Å^2



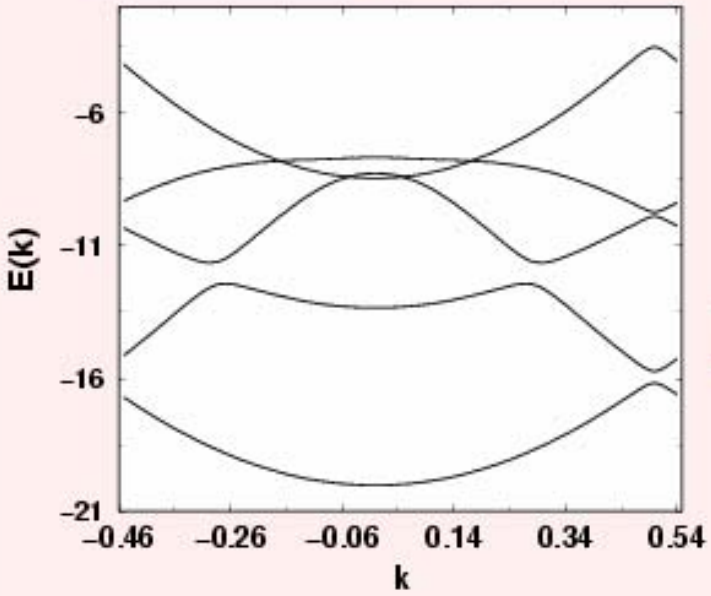
Ω =0.23Å^2

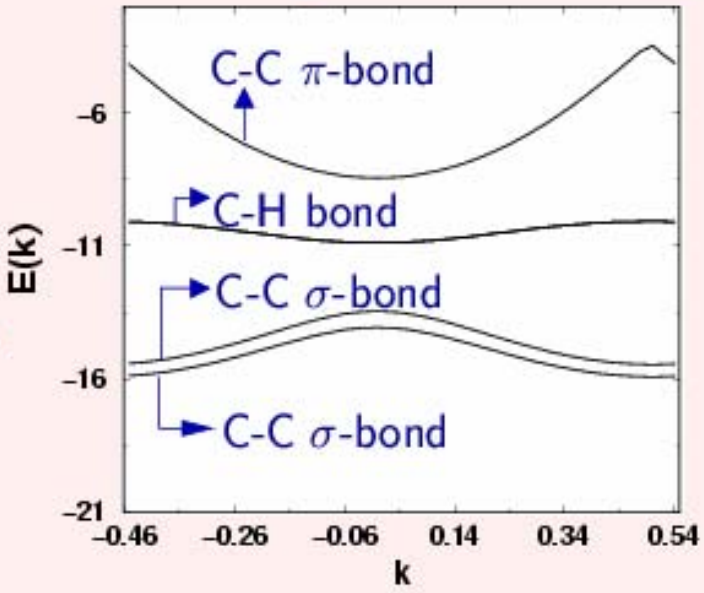
POLYACETYLENE

4 symmetry independent
Wannier functions



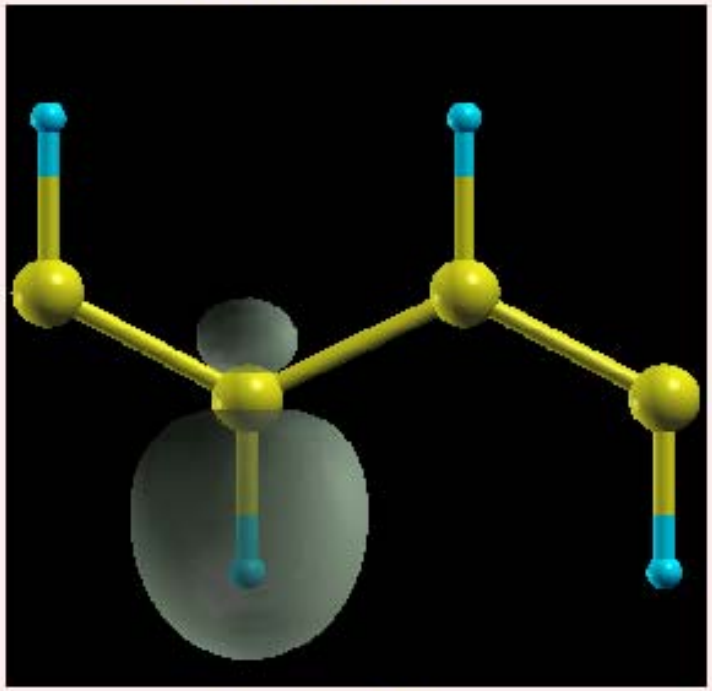
- 2 C-C σ-bond
- C-C π-bond
- C-H bond





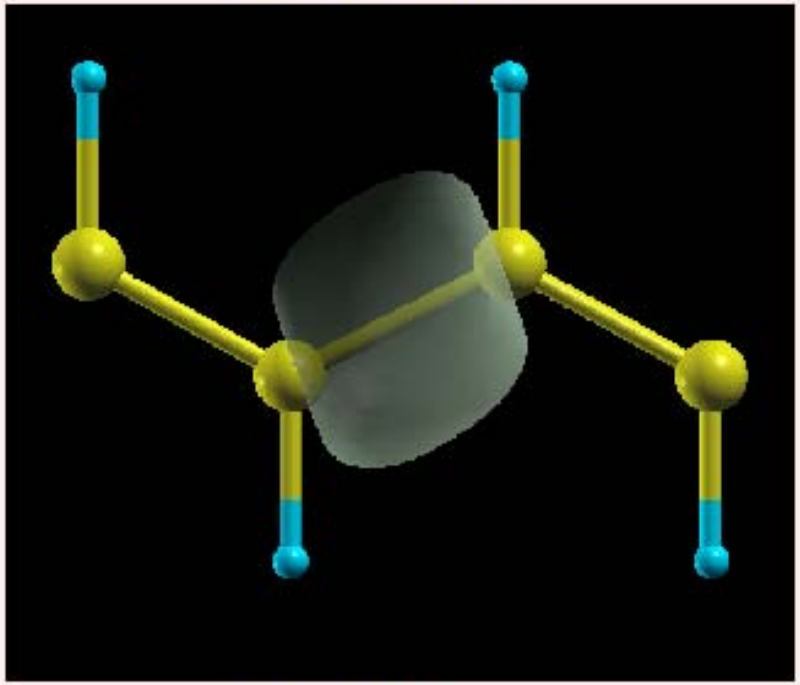
POLYACETYLENE

C-H bond



$\Omega = 20 Å^2$

C-C σ-bond

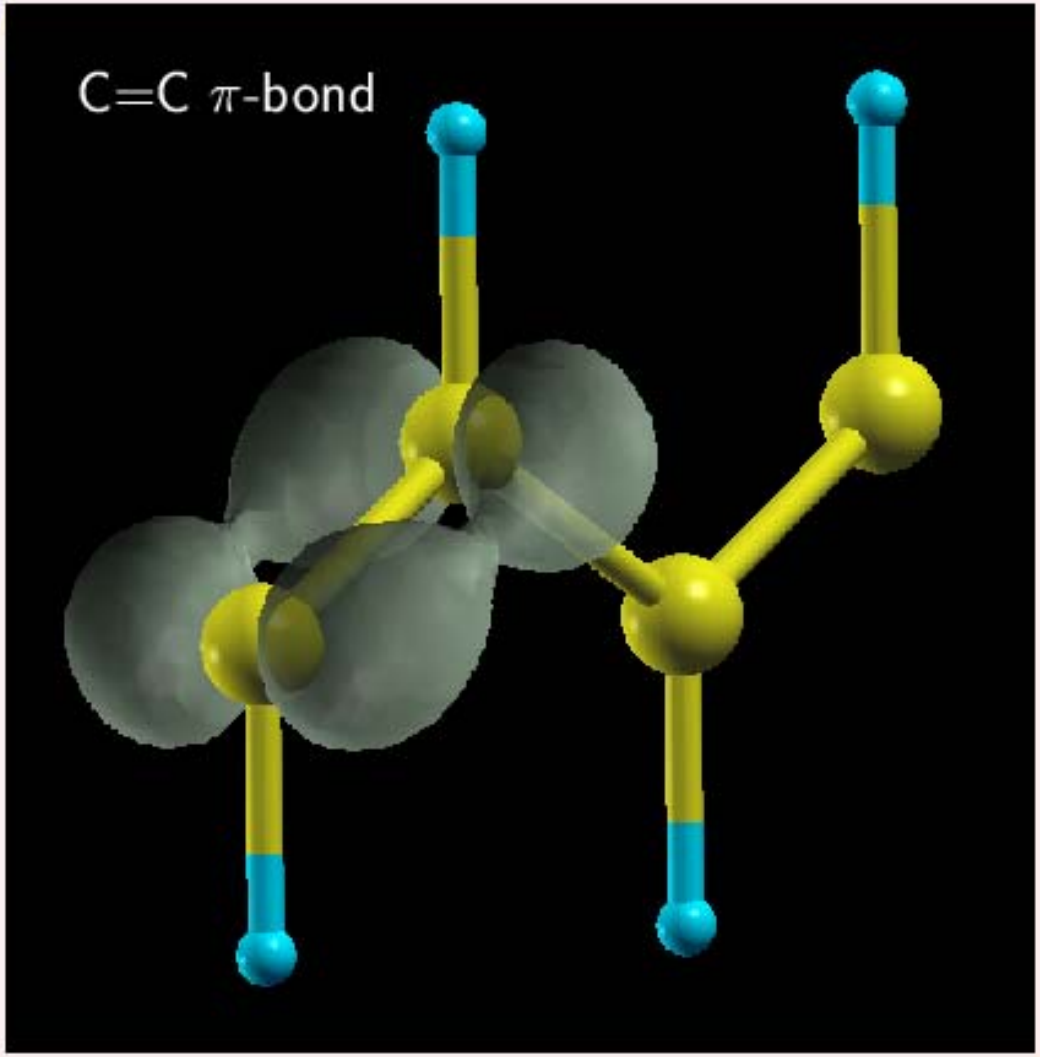


$\Omega = 22 Å^2$

POLYACETYLENE

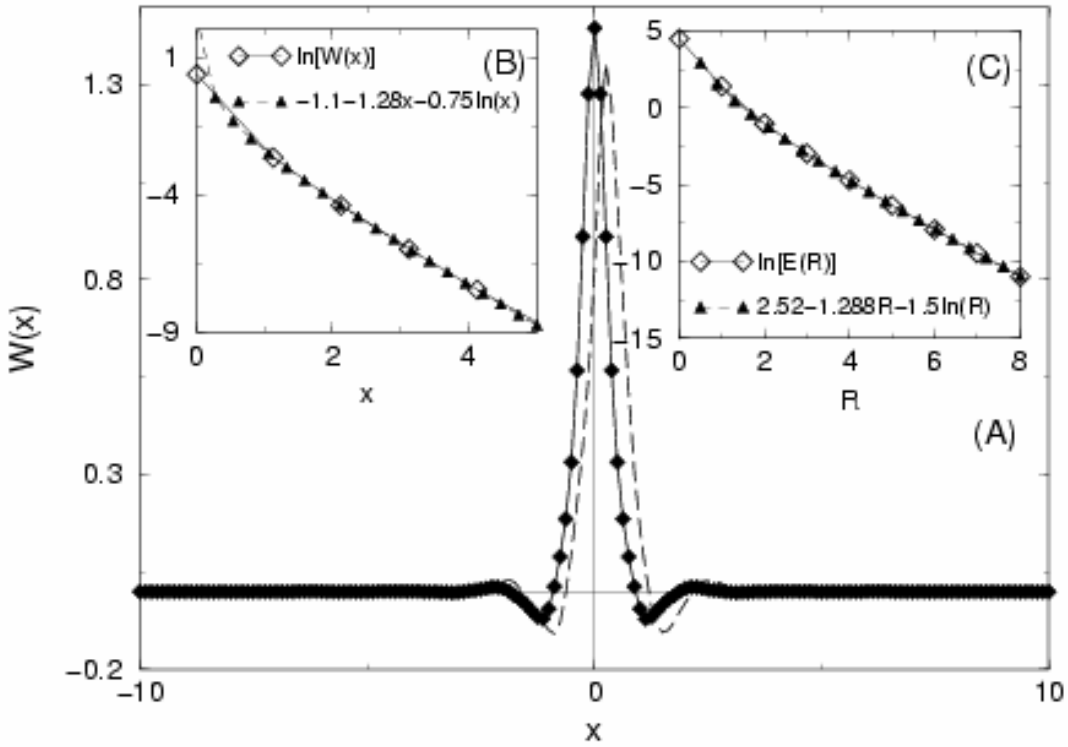
Wannier function
of the π electrons

Ω =2.95Å^2



Application to 1-d models

- **Insulator: centrosymmetric and a general asymmetric potential**

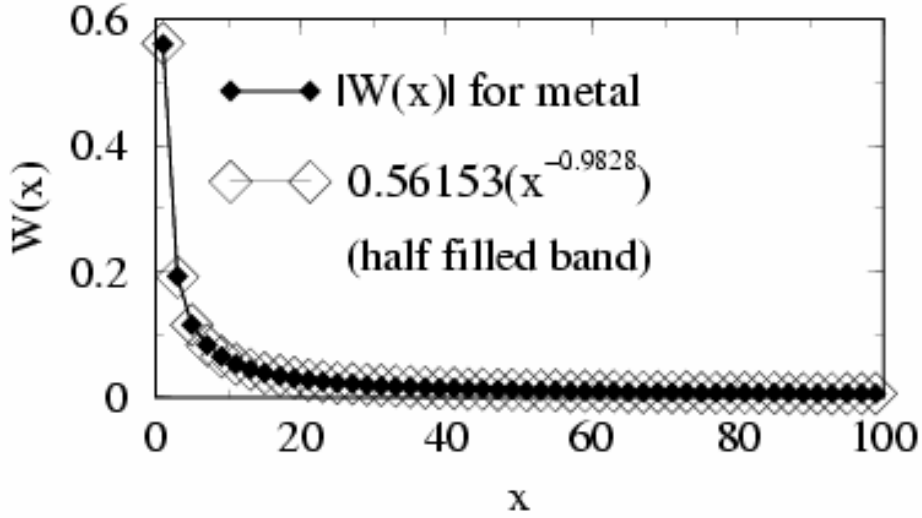


- **Reproduce results of He and Vanderbilt (2001)**
- **Universal exponents (0.75, 1.5) for both the potentials**

- **Metal (partially filled band): centrosymmetric potential**

$$|W_n^T(x,R)\rangle = \sum_{k,r} e^{ik(x-R)} C_{nr} \left[f(E_{rk},T)\right]^{\frac{1}{2}} |u_{rk}\rangle,$$

where $C_{nr} = \langle v_{nk}|u_{rk}\rangle$



Reproduce results of Beigi and Arias (1999)
$\rho^T(x,x') = \sum_{nR} W_n^{T\star}(x,R) W_n^T(x',R)$

- **localization length** $< x^2 > \to \infty$

Issues with computation of polarization

Polarization: Berry phase

(Ref. King-smith and Vanderbilt, Phys. Rev. B47, R1651 (1993); R. Resta, RMP 66, 899 (94)).

$P=1/V \int \rho(r)\, dr$: does *not* work for an infinite crystal

P has to be defined through a *change* ΔP, arising from an adiabatic flow of charge when a system is changed from one state to another:

$$\Delta P = \int_{\lambda_1}^{\lambda_2} J(\lambda)\, d\lambda = P(\lambda_2) - P(\lambda_1)$$

$$P(\lambda) = i\, e/(2\pi)^3 \sum_n \int \langle u_{kn}(\lambda) \mid d/dk \mid u_{kn}(\lambda) \rangle\, dk$$

$$= \gamma(\lambda) + e\, R/V \quad (R: \text{direct space lattice vector})$$

P forms a lattice

A Consequence:

1. P of a centrosymmetric phase can be nonzero!

P -> -P + eR/V *P = eR/V/2: half integer quantum P*

Implications for Real Materials: Biferroics

Eg. Biferroic $InMnO_3$
(isostructural to $YMnO_3$)

- P=19 μC/cm² (as obtained using Berry phase)

  But the reference paraelectric str:

  P = half integer quantum = 27 μC/cm²

$$P(1) - P(0) = \int_0^1 \frac{\partial P}{\partial \lambda} d\lambda$$

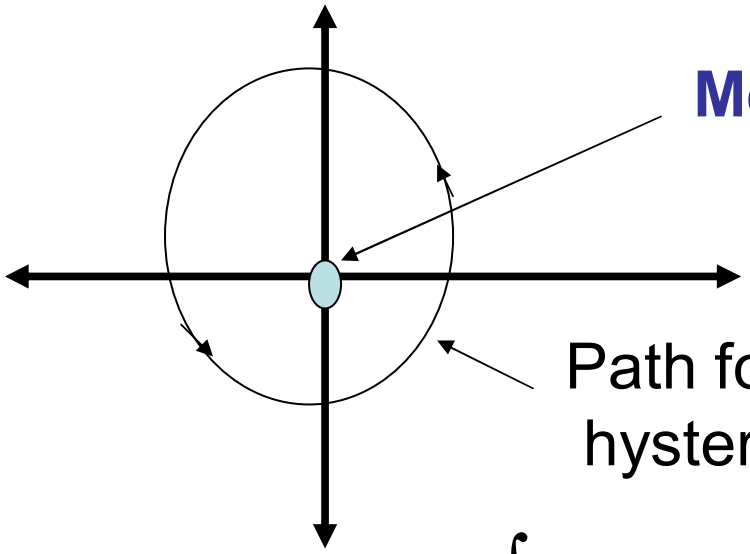
► Δ P = 8 μC/cm² should be a measured P

Serrao, Waghmare, Rao, et al, J. Appl. Phys 100, 076104 (2006).

A similar consideration holds true for $YMnO_3$!

Van Aken, Spaldin et al, Nat. Mat. 3, 164 (2004).

2. Measured polarization is dependent on the path followed by the system during a measurement, such as a switching transition path.



Metallic state

Path followed by the system during hysteresis measurement

$$\int \delta P = eR/V$$

(Ref. Waghmare, PhD thesis (1996)).

Has observable signatures in Raman spectra

(Ref. Sood and Waghmare in preparation).

Interpretation of absolute polarization estimated in MTP with observed P (order parameter of ferroelectrics) is tricky, and should be done with care.

Can the non-abelian geometric phases (Γ matrices) help?
Band-by-band decomposition of P.

Eg. Superlattices (Vanderbilt et al, PRL 06).

Here: How to use Γ matrices in obtaining P that is easier to connect with experimental P?

(Nirat Ray and U. V. Waghmare, a preprint).

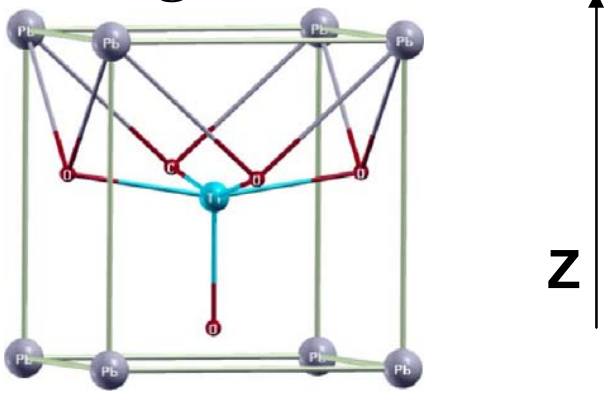
P determined with modern theory of polarization depends on the choice of unit cell!

Example: $PbTiO_3$ in tetragonal phase

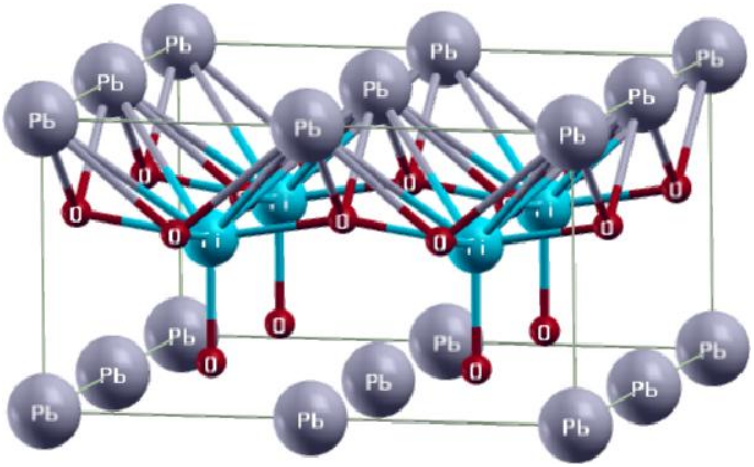
Atomic positions in reduced units

Pb	0.0
Ti	0.039
O_x, O_y	0.117
O_z	0.114

PTO Single Unit Cell



PTO Four Unit Cells



Unit cell is doubled in directions PERPENDICULAR to the direction along which we calculate polarization

P_z as calculated using different DFT codes (Modern Theory of P)

	Calculated using ABINIT (C/m^2)	Calculated using PWSCF (C/m^2)
$PbTiO_3$ Single unit cell	-0.90	1.19 (mod 2.10)
$PbTiO_3$ Four unit cells	0.15	0.15 (mod 0.52)

P determined within the Modern Theory of Polarization depends on the *choice of unit cell.*

Note that *changes in P* (if smaller than quantum P) are independent of the unit cell!

Our scheme to determine P

(With Nirat Ray)

- **Ionic polarization**

Ionic positions (d_i) are remapped between [-0.5,0.5)

$$P_{ion} = \frac{\sum_i Z_i d_i}{\Omega}$$

- **Electronic polarization**

Centre of ionic charge defined as: $d_{center} = \frac{\sum_i Z_i d_i}{\sum_i Z_i}$

Each eigenvalue of Γ matrix folded between [-0.5,0.5) is shifted **by -1 or +1 so that it is closer to the centre of an ionic charge**

Justification: *Implicitly, use paths expressed in the space of ionic displacements*

$$P_{el} = \frac{\sum_{k\perp}\sum_i e\tau_z^i(k_\perp)}{\Omega} \longrightarrow$$ **Electronic Polarization**

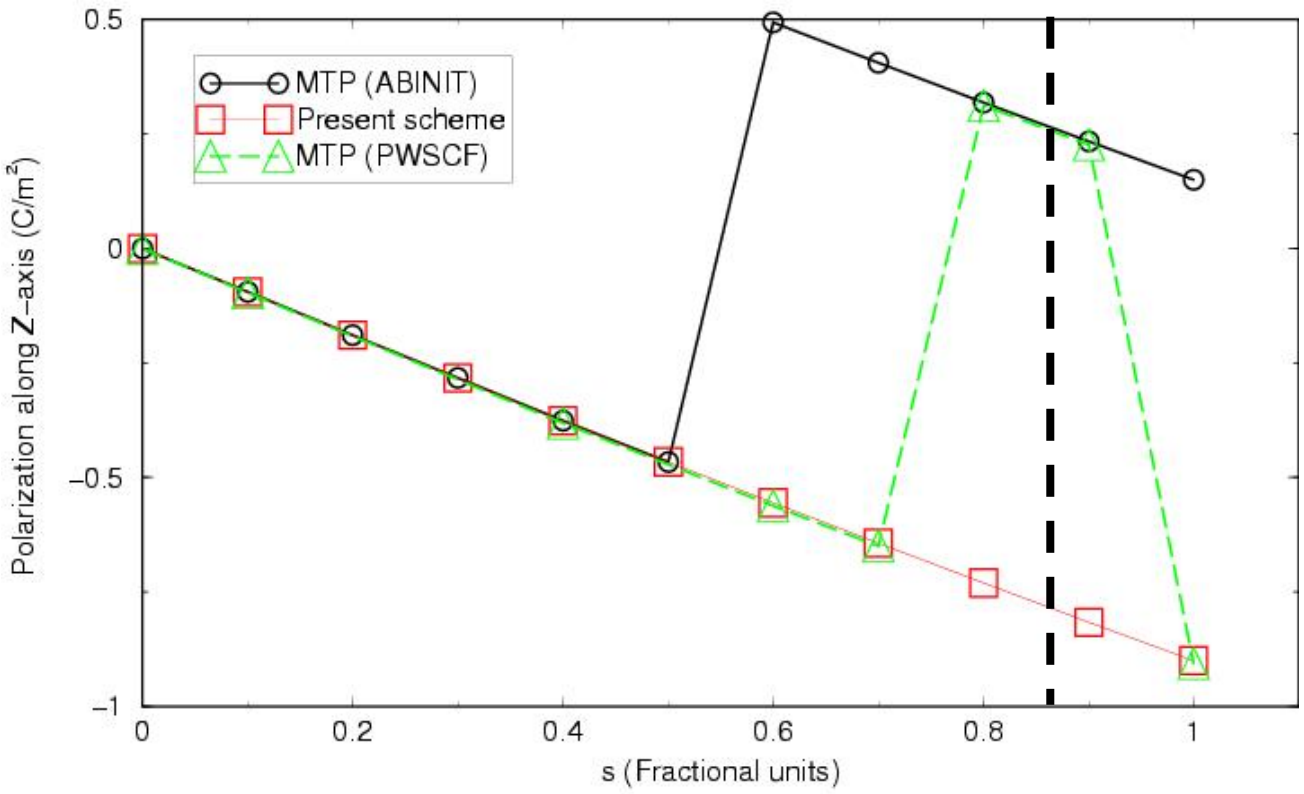
	Calculated using ABINIT (C/m^2)	Calculated using PWSCF (C/m^2)	Present scheme (C/m^2)
$PbTiO_3$ Single unit cell	-0.90	1.19 (mod 2.10)	-0.90
$PbTiO_3$ Four unit cells	0.15	0.15 (mod 0.52)	-0.90

Present scheme:

- Polarization which is independent of the choice of unit cell !!
- Easier to interpret

Polarization as a function of parameter "s"

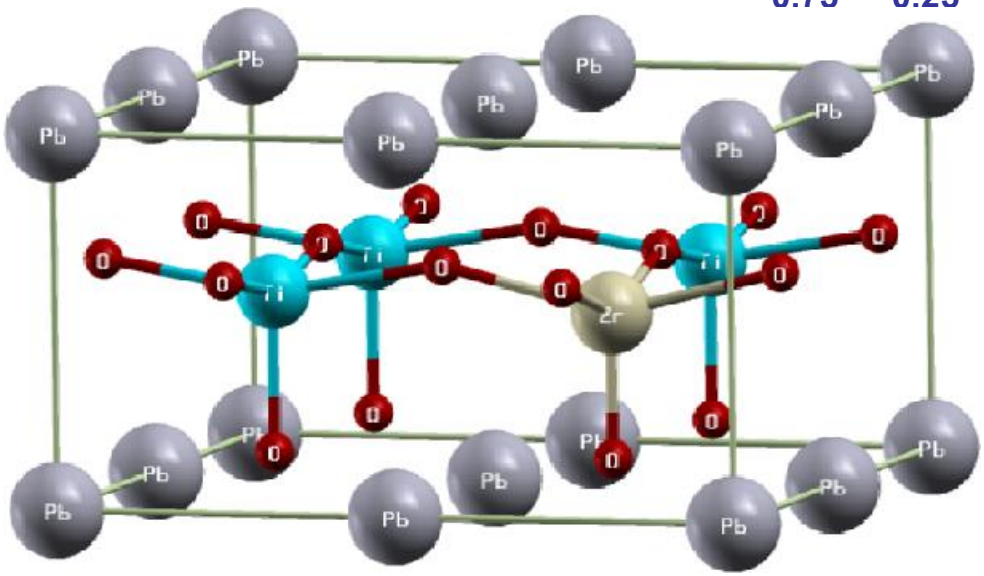
A *two unit supercell* of $PbTiO_3$ is evolved from the paraelectric (s=0) to the ferroelectric phase (s=1)



- **Discontinuity** in the Polarization as calculated in MTP, when the **|polarization|** becomes **greater than half the quantum of polarization**

Implications for Real Materials: Materials with chemical disorder, Solid solutions, Biferroics, etc

- Zr substituted $PbTiO_3$ forming a solid solution with $PbTi_{0.75}Zr_{0.25}0_3$

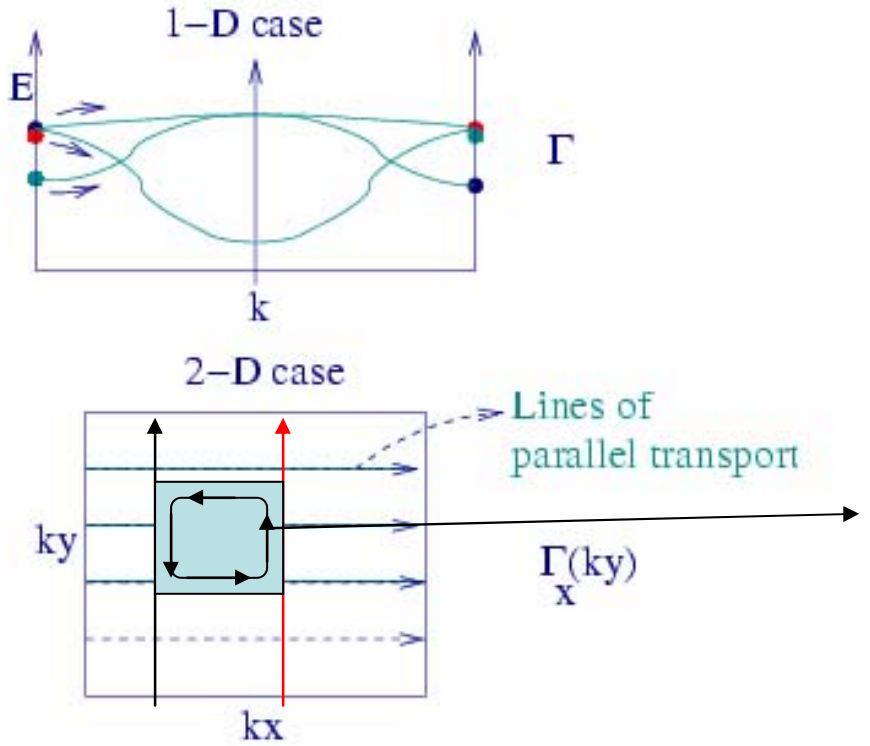


$PbTi_{0.75}Zr_{0.25}0_3$

Zr at centro-symmetric positions, and Ti off-centred by 0.04 Å

	ABINIT C/m^2	Present Scheme C/m^2
$PbTi_{0.75}Zr_{0.25}O_3$	0.099 (0.52)	-0.95

What about Wannier functions in 3-D ???

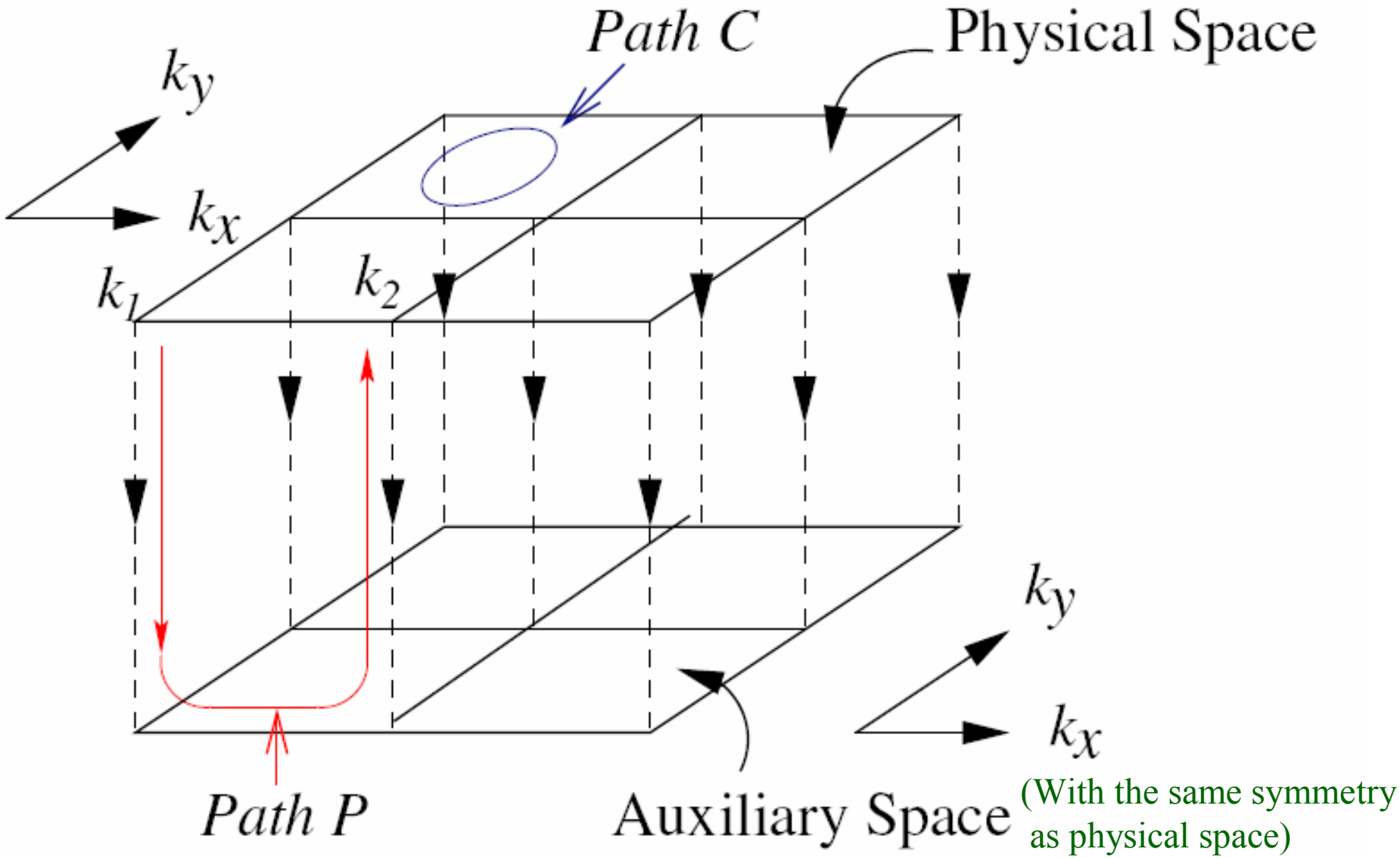


Problem in 2 or higher dimensions: *Nonzero Berry phases*

More than one path to go from one Bloch vector to another in D>1 !

Parallel transport of Bloch functions along different closed paths in the Brillouin zone generate different phase factors and it is no longer possible to generate Bloch functions that are smooth in k *using parallel transport as a function of k.*

WFs in higher dimensions: Basic Idea



(Bhattacharjee and Waghmare, Phys. Rev. 71, 121102(R), 2006.)

Auxiliary Subspace: Definite Geometric Properties

$$\Psi_\mu(\mathbf{R},\mathbf{r}) = (\alpha/2\pi)^{3/2} e^{-\alpha|\mathbf{r}-\tau_\kappa-\mathbf{R}|^2} Y_{lm}(\widehat{r-\tau_\kappa-R})$$

$$\langle \mathbf{r}|v_{\mu\mathbf{k}}\rangle = \sum_R e^{i\mathbf{k}.(\mathbf{R}-\mathbf{r})} \Psi_\mu(\mathbf{R},r)$$

A || Transport between Auxiliary and Physical Subspaces

$$S^{\mathbf{k}}_{\mu n} = \langle v_{\mu\mathbf{k}}|u_{n\mathbf{k}}\rangle \qquad R_{\mathbf{k}} = U_{\mathbf{k}}\Sigma_{\mathbf{k}}U^\dagger_{\mathbf{k}}, e^{i\Gamma_{\mathbf{k}}} = U_{\mathbf{k}}V^\dagger_{\mathbf{k}}$$

$$S^{\mathbf{k}} = R_{\mathbf{k}} e^{i\Gamma_{\mathbf{k}}}, \qquad M_{\mathbf{k}} = (U_{\mathbf{k}}V^\dagger_{\mathbf{k}})^*$$

$$S^{\mathbf{k}} = U_{\mathbf{k}}\Sigma_{\mathbf{k}}V^\dagger_{\mathbf{k}} \qquad \tilde{S}^{\mathbf{k}} = S^{\mathbf{k}}(V_{\mathbf{k}}U^\dagger_{\mathbf{k}}) = U_{\mathbf{k}}\Sigma_{\mathbf{k}}U^\dagger_{\mathbf{k}},$$

↓ ↓

Nonzero Zero

Geometric Phases

Wannier functions

$$|\tilde{u}_{\mu\mathbf{k}}\rangle = \sum_j M_{\mu j} |u_{j\mathbf{k}}\rangle f_{nk}^{1/2},$$

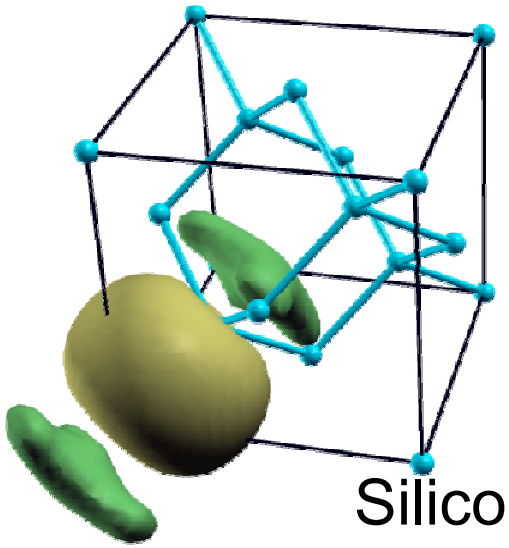
$$< \mathbf{r}|\Phi_\mu(\mathbf{R})\rangle = \frac{\Omega}{(2\pi)^3} \sum_{\mathbf{k}} e^{i(\mathbf{k}-\mathbf{R}).\mathbf{r}} < \mathbf{r}|\tilde{u}_{\mu\mathbf{k}}\rangle$$

"bonding orbitals"

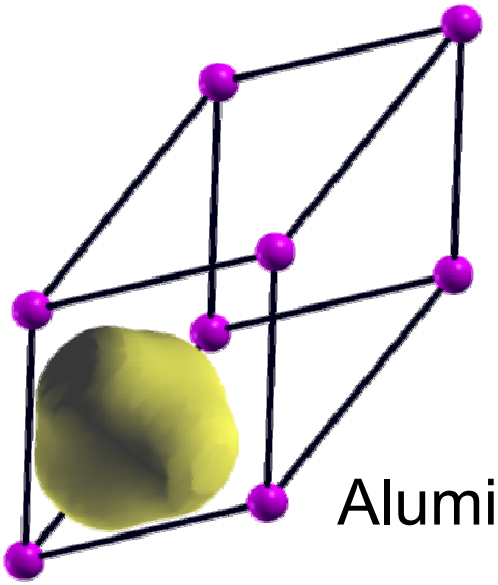
$$\rho(r,r') = \sum_{R,\mu} \langle r|\Phi_\mu(R)\rangle\langle\Phi_\mu(R)|r'\rangle$$

- **Applicable to insulators, metals, molecules, cluster, any dimensionality, unoccupied states**
- **Localization comparable with the MLWFs.**
- **Further localization can be achieved through Joint Diagonalization of x, y, z (Cardoso, J. Math. Anal. App. (96)).**

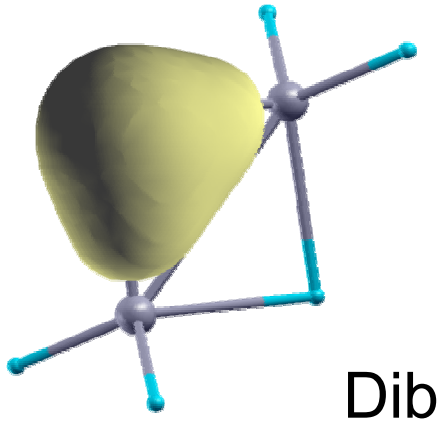
Examples of Wannier Functions



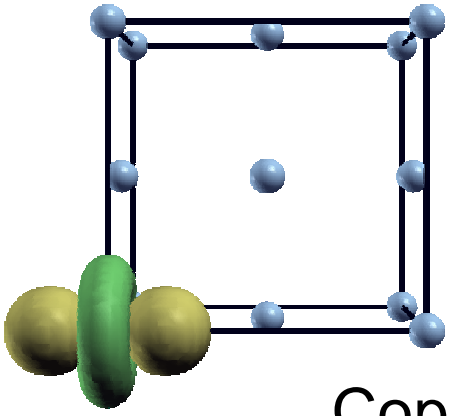
Silicon



Aluminium



Diborane (B_2H_6)



Copper

(Bhattacharjee and Waghmare, Phys. Rev. B 71, 121102(R), 2006.)

From Wannier functions to Atomic Orbitals: *Bonding*

Pure atomic orbitals: $|\phi_n\rangle$, $(n = \{i_a, l, m\}\ )$; $S_{lm} = \langle\phi_l|\phi_m\rangle$

Wannier function: $|W_I\rangle$

Bond Orbital Overlap Population (BOOP):

$$B^I_{lm} = \langle W_I|\phi_l\rangle(S^{-1\dagger})_{lm}\langle\phi_m|W_I\rangle$$

(Similar to COOP of Roald Hoffman)

Break up of effective charge:

$$Z^I_{lm} = \frac{q_e}{u_x}\Delta[\langle W_I|\phi_l\rangle(S^{-1\dagger}XS^{-1})_{lm}\langle\phi_m|W_I\rangle]$$

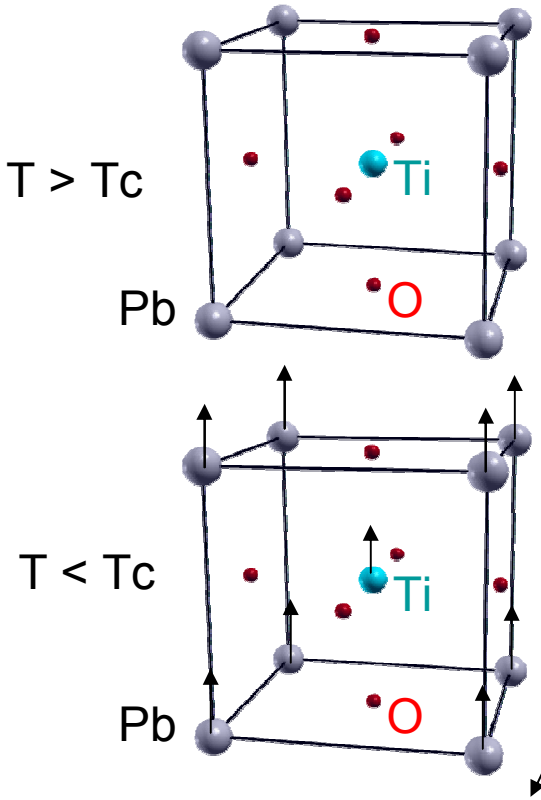
Bond Orbital Position Population (BOPP)

where, $X_{ij} = \langle\phi_i|x|\phi_j\rangle$

Born effective charge: $Z^\star_x = \sum_I \sum_{lm} Z^I_{lm}$:

BOPP: covalency, charge transfer and local polarizability

Anomalously Large Effective Charges



$PbTiO_3$: A Ferroelectric material

~ Ionic materials, with ionic charges of +2 (Pb), +4 (Ti) and -2 (O).

But the dynamical charge of Ti (Z^*):

dipole: $\mu = Z^* d_{Ti}$ **Force: $F = Z^* E$**

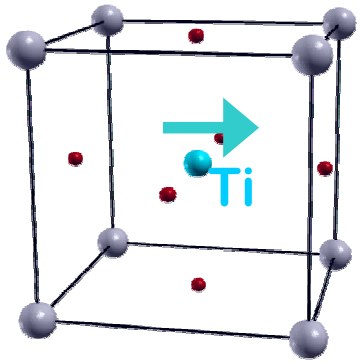
is anomalously large: Z^* (Ti) = 7.1

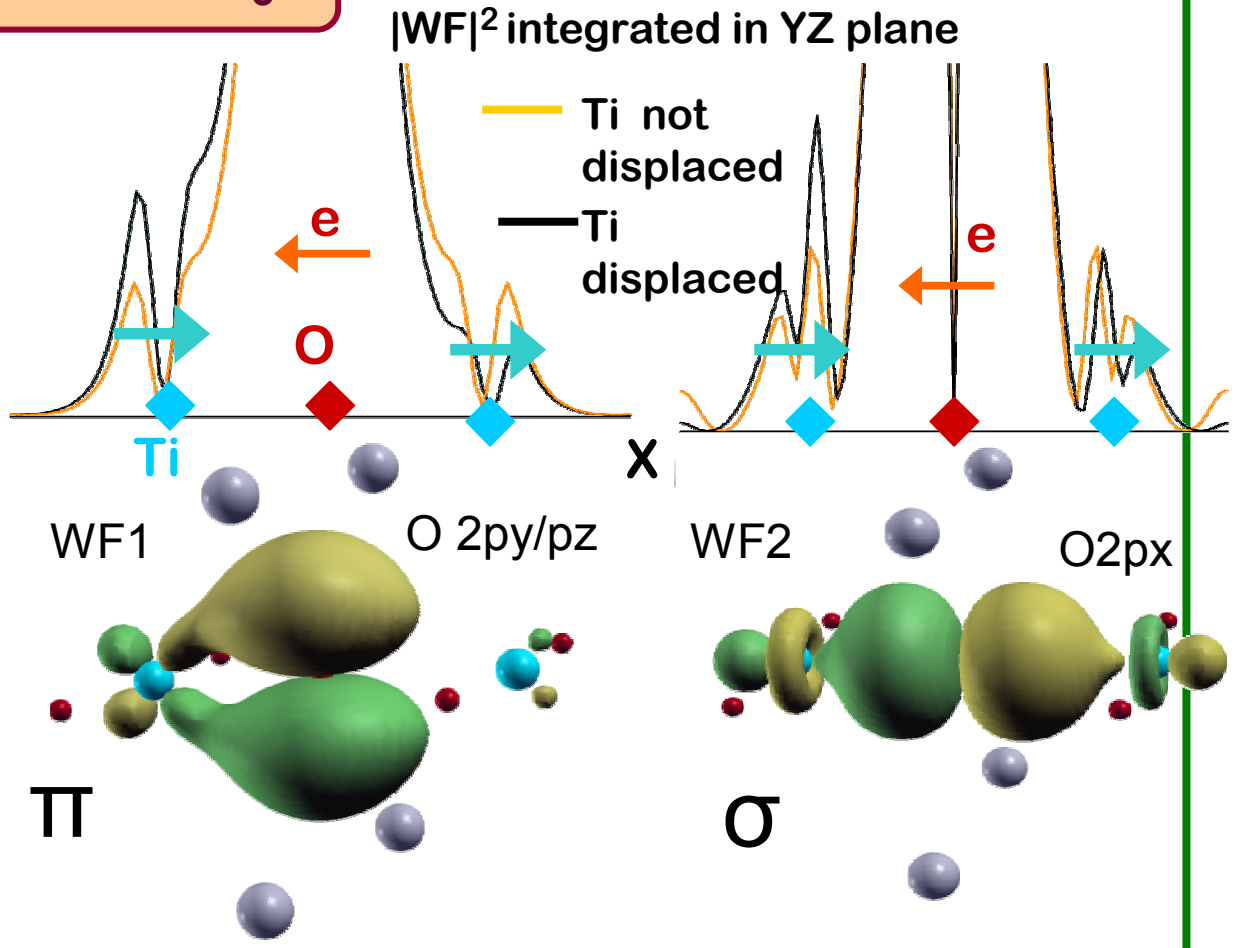
This is a generic feature of most ferroelectric perovskite oxides, eg. $BaTiO_3$, $KNbO_3$.

Gives *large* dielectric (αZ^{*2}) and electromechanical (αZ^*) couplings

What is the origin?

Tetragonal $PbTiO_3$ & $BaTiO_3$





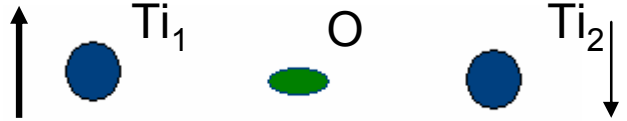
	Z*x(Ti)		
PbTiO3 :	7.02 a.u.	+1.43	+0.53
BaTiO3 :	7.13 a.u.	+1.49	+0.52

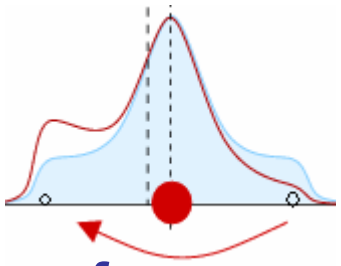
Inter atomic charge transfer through π like orbitals

BOPP Analysis: $PbTiO_3$

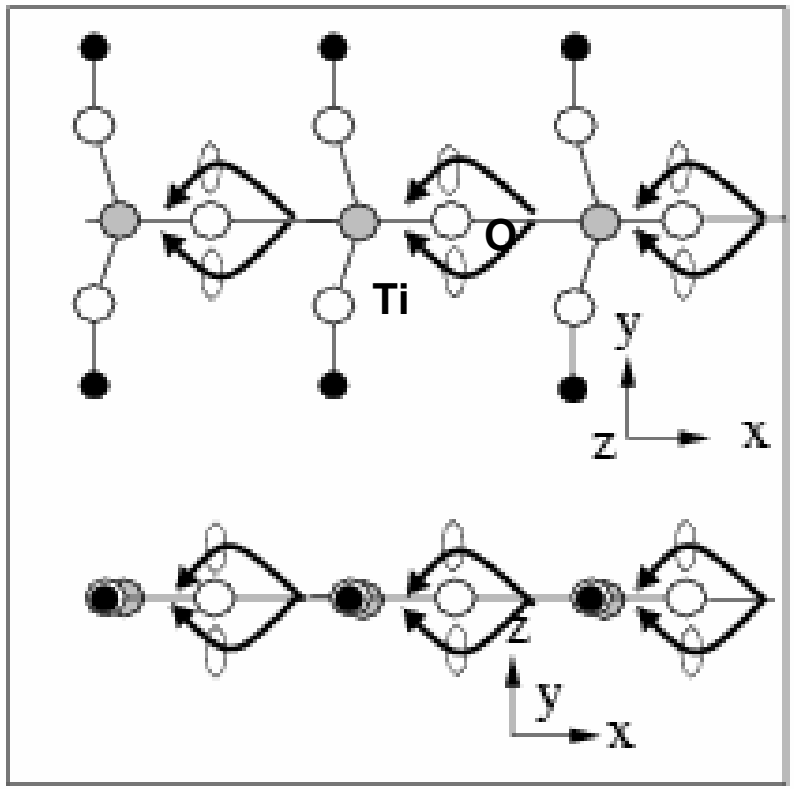
	WF1 π	WF2 σ	WF3 σ
Charge Transfer	1.10	0.33	0.21
Local (O) Polarizability	0.00	-0.06	-0.10
Covalency	0.27	0.30	0.41
Nonlocal Changes	0.06	0.01	0.01

BOOP Analysis





In the O-centered WF1, population of $3d_{xz}$ state of Ti_1 atom increases by 0.038 e, whereas that at Ti_2 decreases by 0.034 e: large part of anomalous charge ~ 2 e!



Local charges remain the same

Mechanism of anomalous effective charge:

Transfer of a small fraction of electrons from one Ti to the neighboring one is facilitated by the oxygen *p* orbitals perpendicular to the -Ti-O-Ti- chain.

Bhattacharjee, Waghmare, submitted to JACS.

Like "*charge double-exchange*"

► Why perovskites are so great: O(2)-TM-O(2) chains in all three directions!

Distribution of Electron Charge Centres (DECC): A gauge invariant scheme for charge partitioning; A new way of looking at bonding

(With Joydeep Bhattacharjee and Shobhana Narasimhan,
cond-mat/0612468).

Thanks to a referee from Nature whose comments forced us to generalize the DECC formulation.

Distribution of Electron Charge Centres (DECC)

Conventional thinking of Crystal Structure:
Where are the atoms?

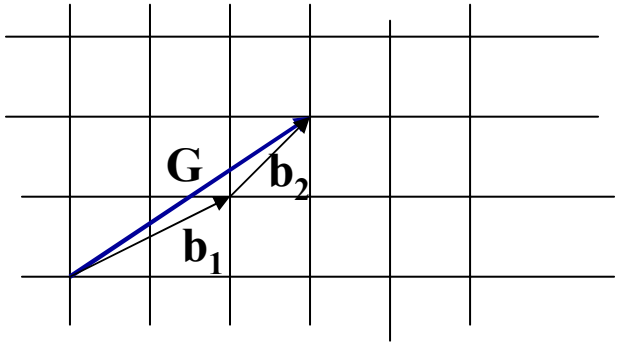
We ask:
Where are the electrons?

- **As Γ_x and Γ_y do not commute,** it is not possible to determine both x and y coordinate of electron charge centre simultaneously.
  This is partly why Ω(MLWF) > Ω(physical);
  Ω(physical) accessible by linear response (Waghmare et al, PRB 67, 125111 (03)).

- **Only a joint probability may be formulated:** eg. x and y coordinates are (x_i, y_j)

- **Coordinate axis are not unique!** Eg. x and $x+y$ are also good choices.
  Sum over all possible choices limited by the lattice.
  ie. sum over all possible primitive unit cells.
  A primitive real space lattice unit cell ↔ G-vector (rec. lattice) shortest along its dir.
  → sum over all "G"s (like in a path integral)

Distribution of Electron Charge Centres (DECC)



G: a rec. lattice vector shortest along its dir.
$\mathbf{b}_1$, $\mathbf{b}_2$: two linearly independent vectors forming the shortest path to **G**
define a rec. space primitive cell
$\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the corresponding vectors in real space.

For each $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ (**G**), obtain non-abelian geometric phase matrices Γ_i's, whose eigenvalues give a point in real space as an electron charge centre:

$$\mathbf{T}_{lmn}(\mathbf{k}) = \tau_l^1(\mathbf{k})\mathbf{a}_1 + \tau_m^2(\mathbf{k})\mathbf{a}_2 + \tau_n^3(\mathbf{k})\mathbf{a}_3$$

- **Use eigenvalues and vectors of P r_i P given by geometric phase matrix**
- **Use quantum joint probability distribution function (Barut, Foundations of Physics, 18, 999 (1988)).**

$$D(\mathbf{r}) = \frac{1}{N_G}\sum_G \int_{K_G} dk \sum_{lmn} \delta(\mathbf{r} - \mathbf{T}_{lmn}(\mathbf{k}))\left\langle v_{\mathbf{k}l}^1 \middle| v_{\mathbf{k}m}^2 \right\rangle\left\langle v_{\mathbf{k}m}^2 \middle| v_{\mathbf{k}n}^3 \right\rangle\left\langle v_{\mathbf{k}n}^3 \middle| v_{\mathbf{k}l}^1 \right\rangle$$

Eigenvalues and eigenfunctions of r_i (Γ_i's).

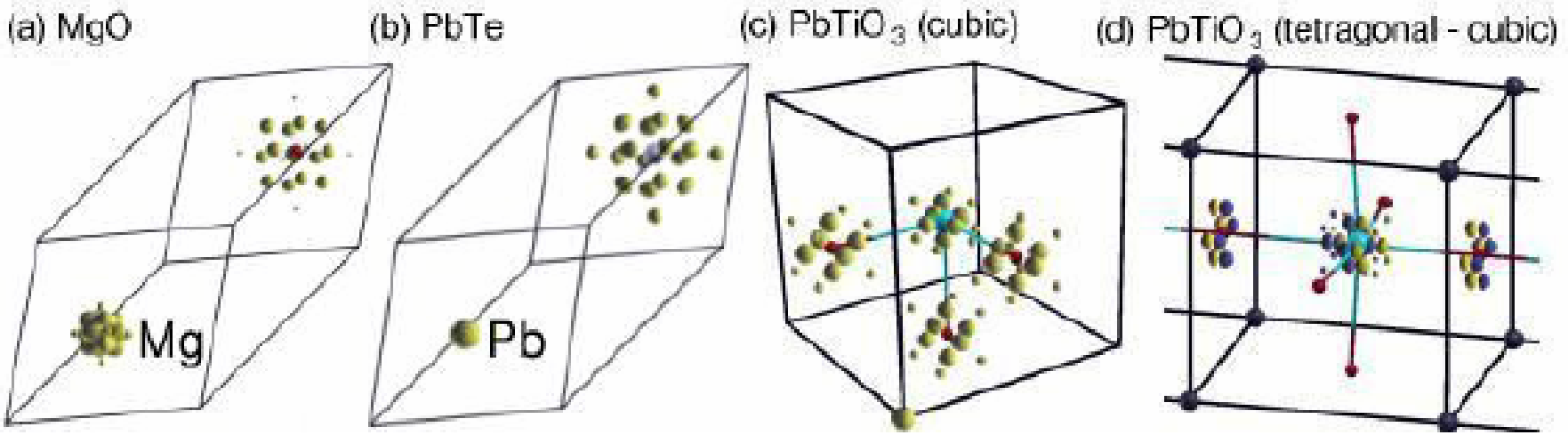
<><><> : Bargmann invariants (Ref. Simon and Mukunda, PRL 70, 880 (93)).
$\sum_G$ can be suitably terminated: eg. G < Gcut

Properties of DECC

- DECC has the symmetry of the system; symmetrization can save much of computation.
- It is a real function (but can be negative).
- For an insulator, peaks of DECC function are well-isolated and a given set of peaks contains integer quantum (e) charge.
- Generalization to metals involves including occupation numbers (with appropriate powers) in parallel transport.
- ***N*-electron *M*-center bond** defined by the peaks of DECC associated with *M* nuclei and containing *N* electrons.
- $\int dr\, D(r)\, r$ gives polarization.
- $\int dr\, D(r) = N_e$.

DECC for ionic insulators

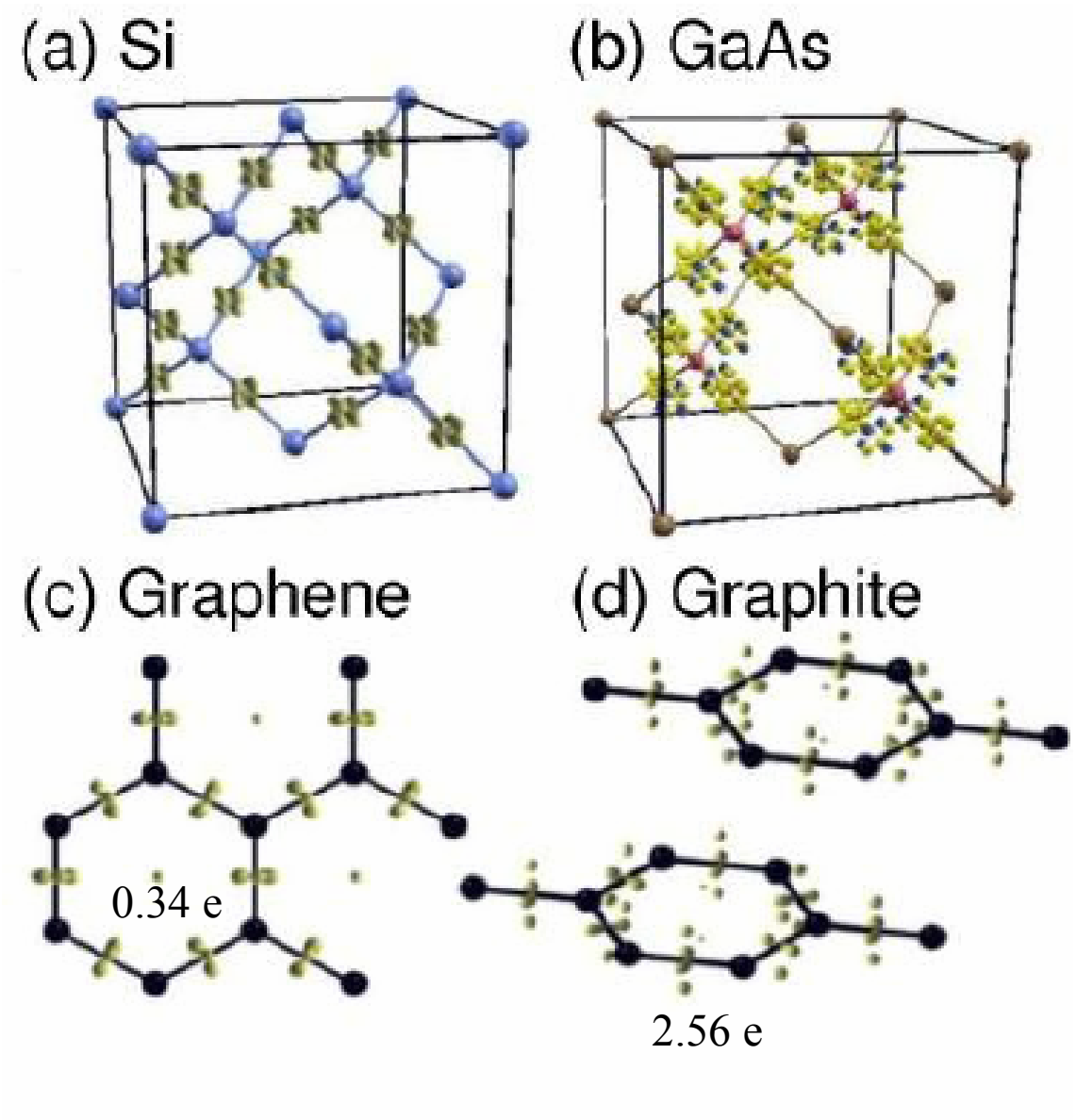
Z_{static}-electron Uni-centerd bond



Charge contained in a set of peaks localized on an atom: static charge

Difference in DECC with atomic displacements: change in P → Z*

DECC for covalent systems



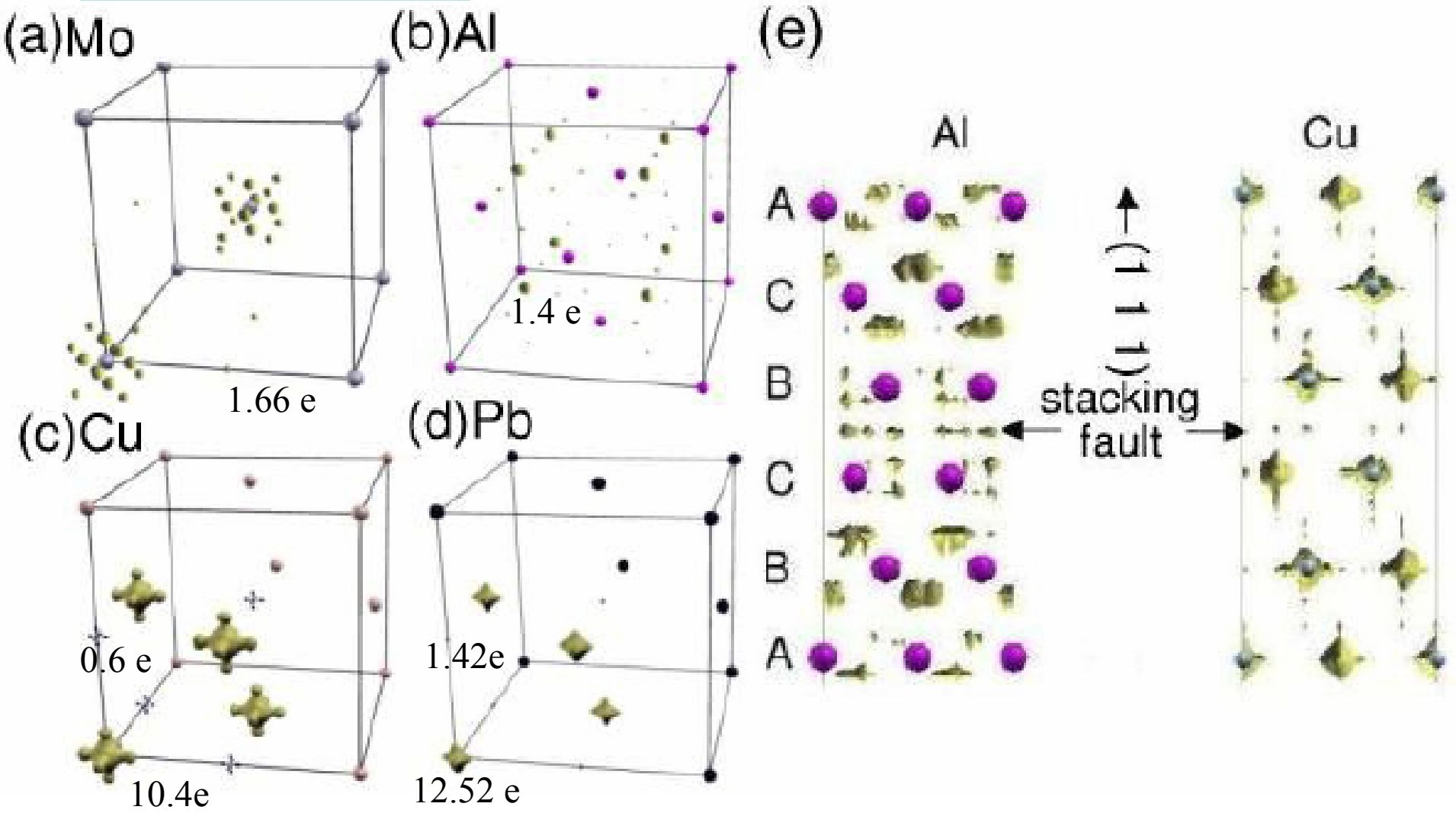
A covalent bond:
2-electron 2-centered bond

Negative values at the anti-bonding sites:
Violation of L'Espegnat inequality in QM

We interpret covalent bonds are truly quantum mechanical in nature!

Note the complete shell containing 8 electrons for each atom!

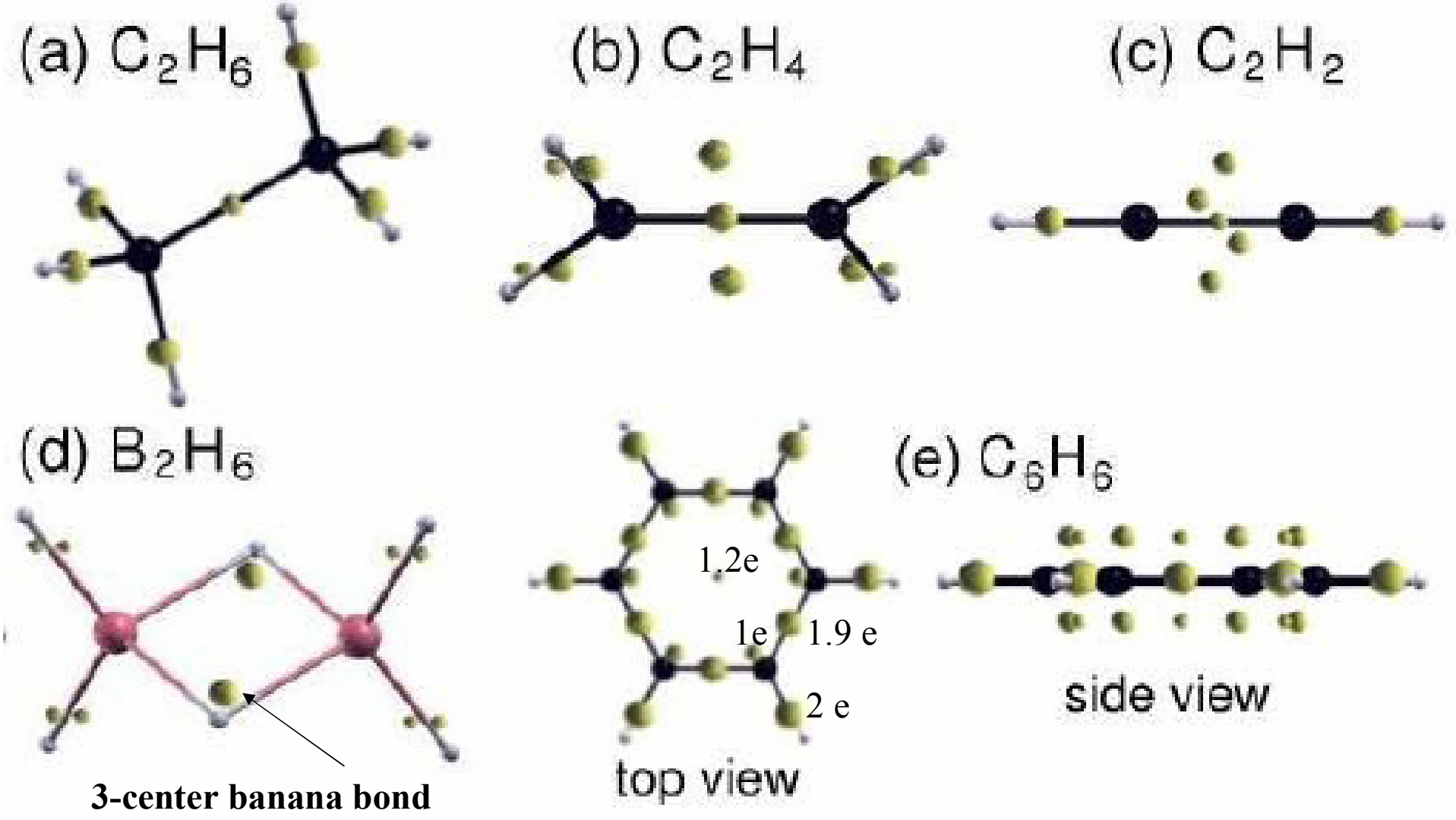
DECC for metals



Covalency scale (Number of shared e /atom): Al > Mo > Pb > Cu

►Explanation for Al has greater mechanical shear strength than Cu (Yip et al, Science (2002)).

DECC for molecular systems



3-center banana bond

$\sum$ electrons associated with each to C = 8.

Summary

Non-abelian geometric phases

1. Help with estimation of polarization
2. Used in formulating Wannier functions
3. Have been used in formulating a new scheme for charge partitioning: DECC
4. Link with bonding and chemistry of materials