

Localized crystalline orbitals and related quantities.

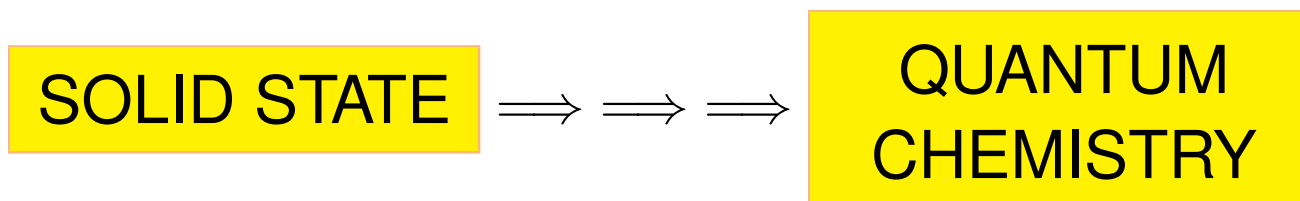
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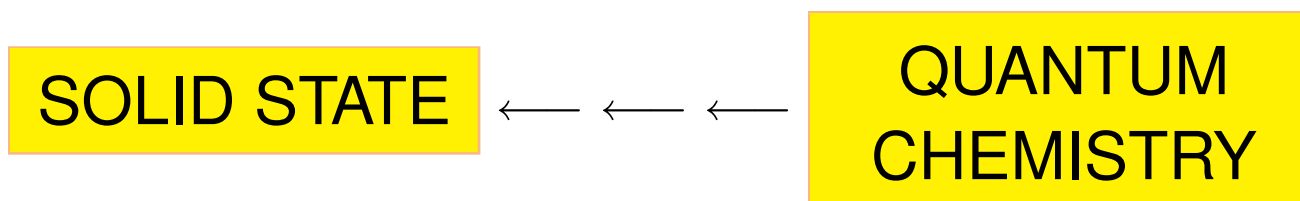
Ab initio Simulation of Crystalline Systems ASCS2006
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IMPORTANT MOVEMENT IN QUANTUM CHEMISTRY



OTHER TRENDS?



REAL crystals and the periodic model

REAL CRYSTAL

- ★ A finite (large) system whose inner part is constituted by pieces

*translational
equivalent*

to each other



PERIODIC MODEL

- ★ An infinite system that is

*translational
invariant*

Wigner Theorem can be used.



Symmetry equivalence \Leftrightarrow symmetry invariance

★ Symmetry equivalence

- ▶ Irreducible objects are kind of regions: can be used to partition the space
- ▶ Compatible with spatial **localization**
- ▲ Primitive cells (or asymmetric units) in crystals

★ Symmetry invariance

- ▶ Irreducible objects are subspaces: irreducible representations
- ▶ Essentially **delocalized**
- ▲ Eigenfunctions of a totally symmetric Hamiltonian

Variational approximations to the solutions of the periodic model

- I The **many-electron** solution is often estimated through a variational procedure (Hartree-Fock, DFT)
- II The variational manifold is expressed in terms of unitary transformations into a model space of one-electron wave functions:
 - ★ a point in the manifold has a correspondence with a set of wavefunctions.
- III The optimum along the manifold is usually computed under the Self-Consistent Field (SCF) scheme:
 - ★ the set of wavefunctions are the eigenvectors of an **auxiliary** one-electron Hamiltonian
- IV Although it is not strictly necessary, the resulting eigenvectors are basis of the irreducible representations of the translational group \longrightarrow Bloch Functions (**delocalized functions**)



General case: Canonical and localized orbitals

Canonical: Eigenfunctions of a one-electron Hamiltonian (HF,KS,...)

Localized: Span the same occupied space, but are chosen so as to optimize a given spatial spread functional.

Unitary Transformation:

$$\tilde{\psi}_m(\mathbf{r}) = \hat{U} \psi_m(\mathbf{r})$$

Localized Orbitals are usually obtained from canonical Orbitals after the SCF calculation



Molecules: Foster-Boys Functional

$$\begin{aligned}\Omega^B &= \sum_n \langle \psi_n | \mathbf{r}^2 | \psi_n \rangle - |\langle \psi_n | \mathbf{r} | \psi_n \rangle|^2 \\ &= \sum_n \langle \mathbf{r}^2 \rangle_n - |\langle \mathbf{r} \rangle_n|^2\end{aligned}$$

Sum of the traces of the second moment of electronic distributions

Usefulness of the localized description

- Characterization of the electronic structure (covalent bonds, lone pairs, etc).
- Computation of molecular orbitals transferable between similar systems.
- Estimation of correlation energies:
 1. Virtual orbital localization,
 2. Local Correlation methods (towards linear scaling behavior): [LMP2](#), [LCCSD](#), ...
 3. ...



Crystalline systems

- Translational symmetry \longrightarrow

Canonic Orbitals
=
Bloch Functions

- Infinite Systems: Bloch Functions are integrable just within a finite spatial region (unit cell).
- In terms of Bloch Functions the idea of spatial localization is meaningless (i.e. integrals involved in the Boys functional do not converge; there is no algebraic method suitable to yield integrable functions)



Wannier Functions

Alternative representation of the electronic structure of a crystalline solid. Infinite set of quadratically integrable functions in the whole \mathbb{R}^3 space, that fulfill the following periodic conditions:

$$\begin{aligned}\omega_m^g(\mathbf{r}) &= \omega_m^0(\mathbf{r} - \mathbf{g}) \\ &\downarrow \\ \langle \omega_m^g | \omega_n^h \rangle &= \delta^{gh} \delta_{mn}\end{aligned}$$

$\mathbf{g} = g_1\mathbf{a}_1 + g_2\mathbf{a}_2 + g_3\mathbf{a}_3 \rightarrow$ **direct lattice vector**

The correspondence between Bloch and Wannier Functions

$$\omega_m^g(\mathbf{r}) = N \int_{\text{BZ}} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{g}} \psi_m(\mathbf{k}, \mathbf{r})$$

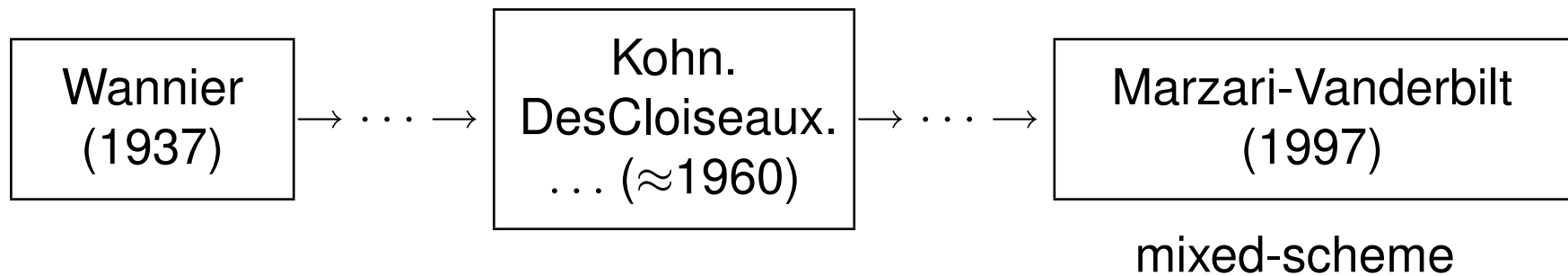
$\mathbf{k} \equiv$ reciprocal vector within de Brillouin Zone (BZ).



How well spatially localized are Wannier functions?

- Quadratically integrable \rightarrow vanish at infinite. (spatially localized)
- Bloch functions are given apart from a phase factor (infinite ways to transform BFs into WFs, with different degrees of localization)

A LARGE HISTORY \rightarrow A HUGE PROBLEM



Wannier Functions within the CRYSTAL program

- CRYSTAL use Atomic Orbital basis sets $\{\phi_{\mu}^{\mathbf{g}}(\mathbf{r})\}$ to span the canonic orbitals (Bloch Functions)
- Wannier Functions take a rather simple form:

$$\omega_m^{\mathbf{0}}(\mathbf{r}) = \sum_{\mathbf{g}\mu} c_{\mu m}^{\mathbf{g}} \phi_{\mu}^{\mathbf{g}}(\mathbf{r})$$

Sum can be truncated if $|c_{\mu m}^{\mathbf{g}}| \rightarrow 0$ when $|\mathbf{g}| \rightarrow \infty$. The number of terms depends on the balance between accuracy and degree of spatial localization.



A Boys-like functional suitable for crystalline solids

$$\begin{aligned}
 \Omega &= \sum_n \left[\langle \omega_n^0 | \mathbf{r}^2 | \omega_n^0 \rangle - \langle \omega_n^0 | \mathbf{r} | \omega_n^0 \rangle^2 \right] \leftarrow \approx \text{Boys} \\
 &= \underbrace{\sum_n \left[\langle \omega_n^0 | \mathbf{r}^2 | \omega_n^0 \rangle - \sum_{\mathbf{g}\mathbf{m}} \langle \omega_n^0 | \mathbf{r} | \omega_{\mathbf{m}}^{\mathbf{g}} \rangle^2 \right]}_{\text{gauge-invariant}} \\
 &\quad + \underbrace{\sum_n \sum_{(\mathbf{g},\mathbf{m}) \neq (0n)} \langle \omega_n^0 | \mathbf{r} | \omega_{\mathbf{m}}^{\mathbf{g}} \rangle^2}_{\tilde{\Omega}}
 \end{aligned}$$

Spatial spread functional:

$\Omega \left[\tilde{\Omega} \right] \downarrow \longrightarrow \text{degree of spatial localization} \uparrow$

ONLY $\tilde{\Omega}$ HAS TO BE MINIMIZED



only matrix elements for
the r operator are
required

Two different strategies for Boys-like localization in crystalline solids

- ★ Taking advantage of the one-to-one correspondence between WFs and BFs, WFs are never explicitly constructed → Unitary transformations of BFs. Functional (implicit BF-WF integral transform) estimated in terms of BFs by numerical integration-derivation in **reciprocal space**. (**Accuracy** \equiv \uparrow **Cost**). Good within the plane wave approach. [Marzari-Vanderbilt 1997]
- ★ WFs are **EXPLICITLY** constructed and then unitary transformed so as to minimize the spatial spread. Matrix elements of r integrated in **real space** in terms of WFs (**Accuracy+Cost depend on the degree of localization of the WFs**). Good within the AO approach.[CRYSTAL03]



Stability conditions

Straightforward extension of the molecular Boys method:

$$\langle \omega_n^g | \mathbf{r} | \omega_m^0 \rangle \cdot [\langle \mathbf{r} \rangle_m - \langle \mathbf{r} \rangle_n - \mathbf{g}] = 0$$

where “.” means *dot product* in the coordinate space.

Orthogonal transformation of a set of WFs

$$\begin{aligned} |\omega'_n\rangle &= \sum_m O_{mn}^0 |\omega_m^0\rangle + \sum_{\mathbf{g} \in \mathcal{N}_1} \sum_m O_{mn}^{\mathbf{g}} |\omega_m^{-\mathbf{g}}\rangle \\ &+ \sum_{\mathbf{g} \in \mathcal{N}_2} \sum_m O_{mn}^{\mathbf{g}} |\omega_m^{-\mathbf{g}}\rangle + \dots \end{aligned}$$

- $\mathbf{g} \equiv$ cell label (lattice vector)
- $\mathcal{N}_i \equiv$ neighbors of the reference cell 0

The number of effective neighbors in the sum depends on the degree of localization of WFs ω_n^0

A general method to obtain well localized Wannier functions for composite energy bands in linear combination of atomic orbital periodic calculations

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Victor R. Saunders

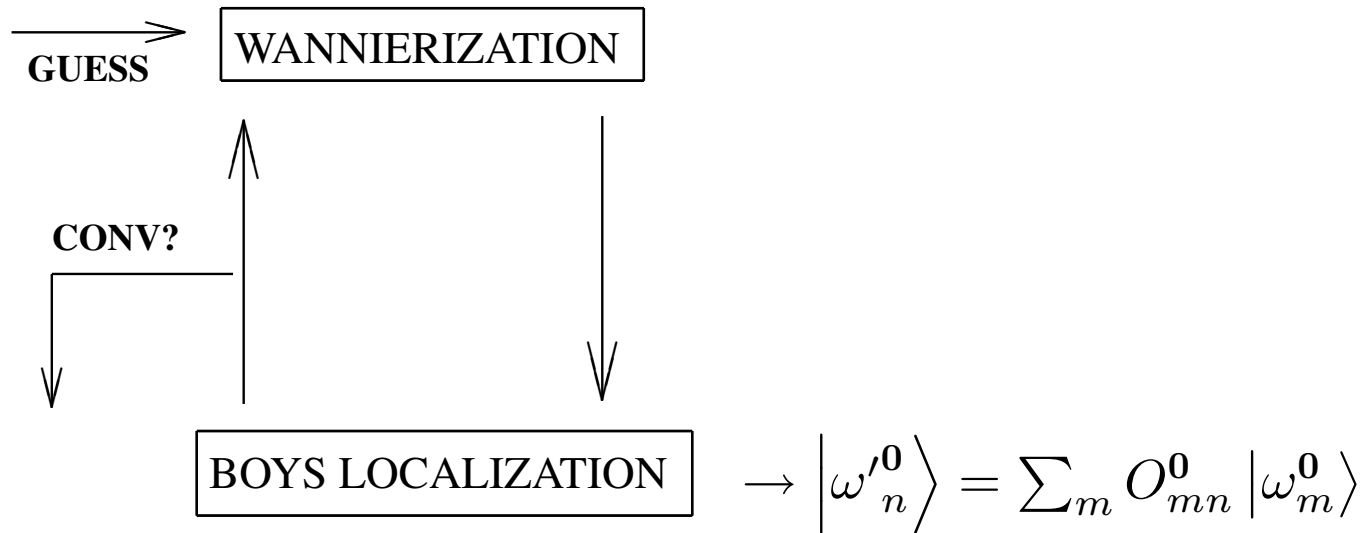
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(Received 6 June 2001; accepted 17 September 2001)

A method for obtaining spatially localized crystalline orbitals starting from delocalized Bloch functions is proposed. The method, that has been implemented in the LCAO CRYSTAL code, is intrinsic and general for nonconducting systems, and provides a set of well localized Wannier functions that can be used for applications that take advantage of their localized character. Examples are given that illustrate the performances and efficiency of the proposed scheme. © 2001 American Institute of Physics. [DOI: 10.1063/1.1415745]

Zero-th order localization

Considers just the WFs at the reference cell in the Boys localization.



Full Boys localization

- ▶ A Boys localization is carried out starting from the previous “well” localized WFs.
- ▶ The number of neighbors considered in the transformations and the computation of the r matrix elements, depends on the degree of localization of the starting WFs (Usually 3—5)

Publication in progress



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How “good” is the zero-th order approach

	MgO (Rock Salt)	BN (Zinc Blend)	Si (Diamond)	Al ₂ O ₃ (Corundum)
Ω	7.852	9.708	26.282	48.363
$\Omega^{(0)} - \Omega$	0.004	0.036	0.007	0.552

All numbers in atomic units.

Calculation of polarization properties

- Spontaneous polarization
- Piezoelectricity

Involved formalisms (**Berry Phase** based approaches) are to be used in the Bloch Function representation. Instead, **Wannier Functions** provide a very natural way to calculate polarization in crystals as all what one needs are the centroid positions.

Well localized crystalline orbitals obtained from Bloch functions: The case of KNbO_3

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The crystalline orbitals of KNbO_3 are localized according to an iterative mixed Wannier-Boys scheme. The transformed orbitals turn out to be extremely localized; their features and degree of localization are described in terms of various indices. The spontaneous polarization and the effective Born charges of the various atoms are evaluated starting from the localized Wannier function (LWF) centroids and from delocalized Bloch functions through the Berry phase (BP) scheme. It turns out that the results provided by both approaches agree very well (for example, the spontaneous polarization is 0.3361 and 0.3347 C/m² from the LWF and BP methods, respectively).



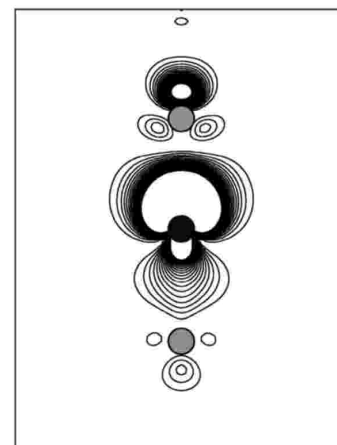
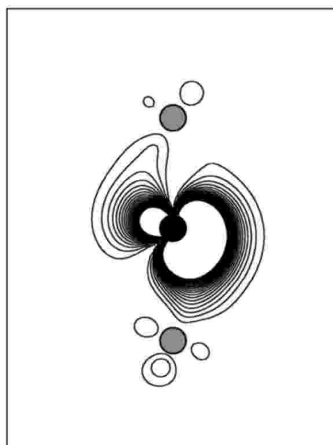
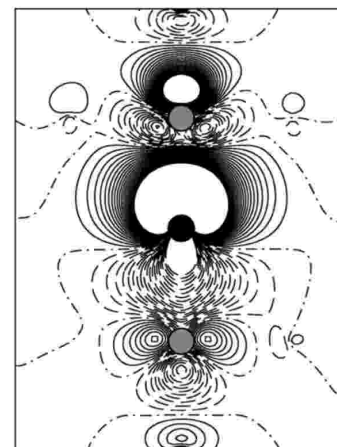
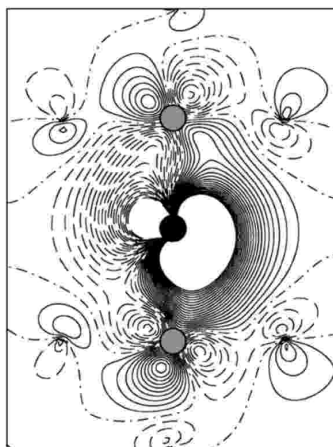
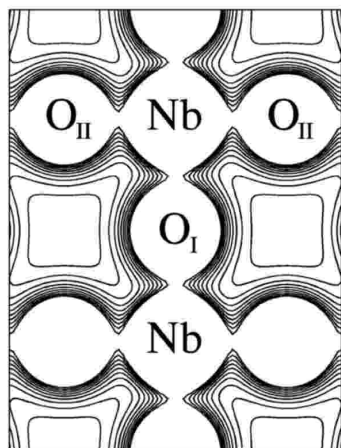
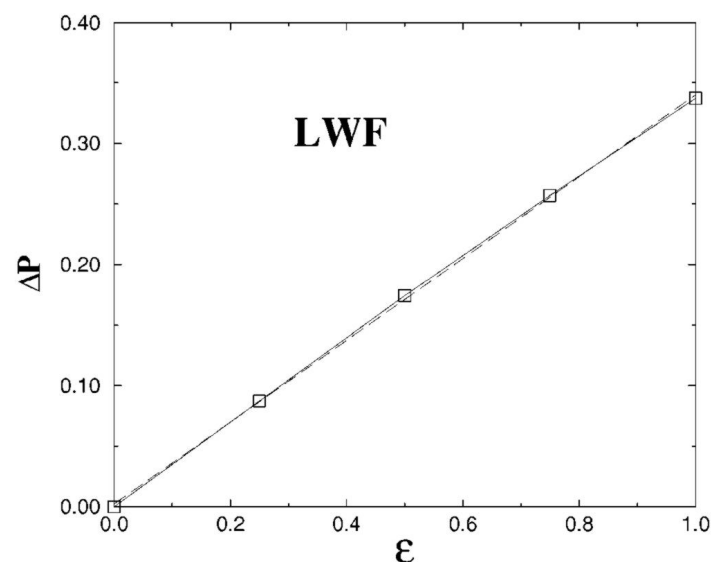
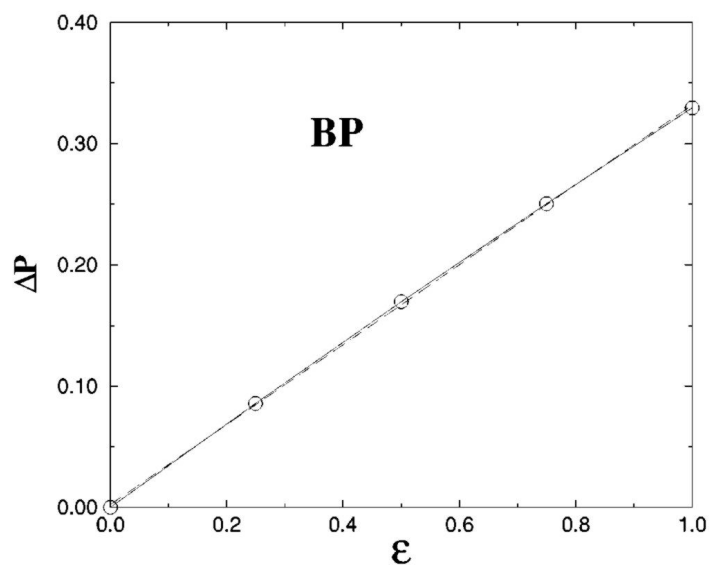


TABLE III. Characterization of $\omega_{\text{type 1}}$ and $\omega_{\text{type 2}}$ (first and second entries in Table II). q_{A,\mathbf{R}_l}^s (in $|e|$) is the fraction of the total density of the ω_s attributed to atom A in cell l according to a Mulliken partition [see Eq. (6)]. Q^s is the incremental sum of the q_{A,\mathbf{R}_l}^s contributions to the ω_s total charge (only contributions larger than $|0.0001||e|$ are reported). Charge density is normalized to 1.

Type	A	\mathbf{R}_l	q_{A,\mathbf{R}_l}^s	A	\mathbf{R}_l	q_{A,\mathbf{R}_l}^s	A	\mathbf{R}_l	q_{A,\mathbf{R}_l}^s	Q^s
1	O _I	(0,0,0)	0.9380							0.9380
	Nb	(0,0,0)	0.0380	Nb	(0,0,-1)	0.0205				0.9973
	O _{II}	(0,1,0)	0.0009	O _{II}	(1,0,0)	0.0006	O _{II}	(0,0,-1)	0.0004	
	O _{II}	(0,0,0)	0.0002	Nb	(0,1,0)	0.0002	Nb	(0,1,-1)	0.0001	
	Nb	(0,-1,-1)	0.0001	O _I	(0,0,1)	0.0001	Nb	(1,1,0)	-0.0001	
	K	(1,1,0)	-0.0003							0.9995
2	O _I	(0,0,0)	0.8880							0.8880
	Nb	(0,0,-1)	0.0861	Nb	(0,0,0)	0.0179				0.9920
	O _{II} (2)	(0,0,-1)	0.0019	O _{II} (2)	(1,0,-1)	0.0018	O _I	(0,0,-1)	-0.0022	0.9972
	O _{II} (2)	(0,1,0)	0.0006	O _{II} (2)	(0,0,0)	0.0004	O _I	(0,0,1)	0.0002	
	Nb	(0,0,-2)	0.0002	Nb	(0,0,1)	0.0001				0.9997

Spontaneous polarization ΔP as a function of the ferroelectric distortion ϵ



Polarization properties of ZnO and BeO: An *ab initio* study through the Berry phase and Wannier functions approaches

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The spontaneous polarization and the piezoelectric constants of ZnO and BeO are calculated at an *ab initio* quantum-mechanical level by using two alternative strategies, namely, through the Berry phase scheme applied to delocalized crystalline orbitals, and through the definition of well-localized Wannier functions. The two sets of results, obtained in the same computational conditions (both schemes are implemented in the CRYSTAL code) compare extremely well, and are in good agreement with available experimental data.



The computation of IR absorption intensities

$$I_i^{\text{IR}} \propto \sum_{\alpha} \left(\sum_{A\beta} Z_{A,\alpha\beta}^* e_{i,A\beta} \right)^2$$

where

- $Z_{A,\alpha\beta}^* = \partial\mu_{\alpha}/\partial x_{\beta}^A$: Born charge tensor
- $e_{i,A\beta}$: contribution from atom A , cart. component β to mode i .

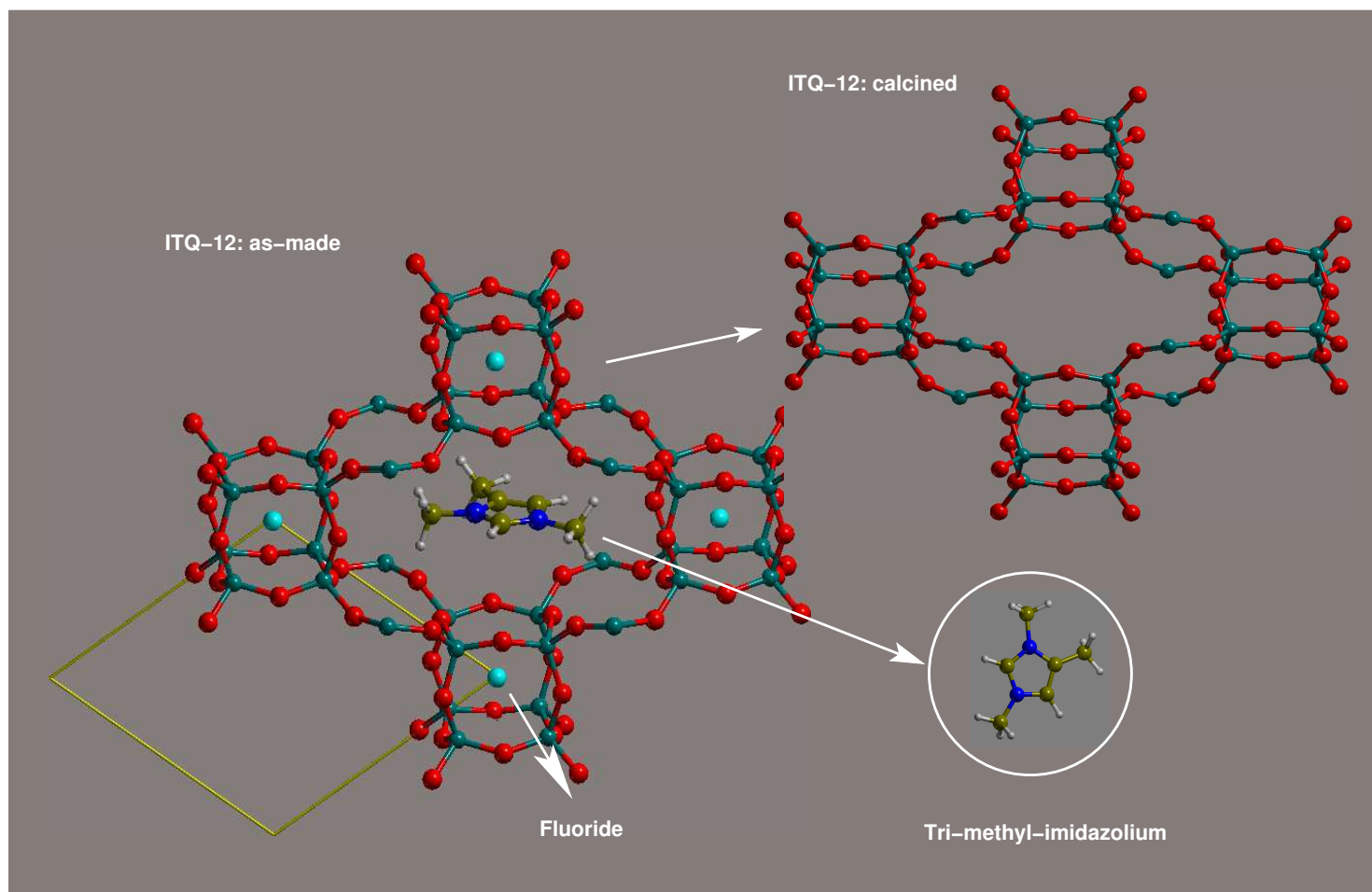


Computation of the Born Charge Tensor

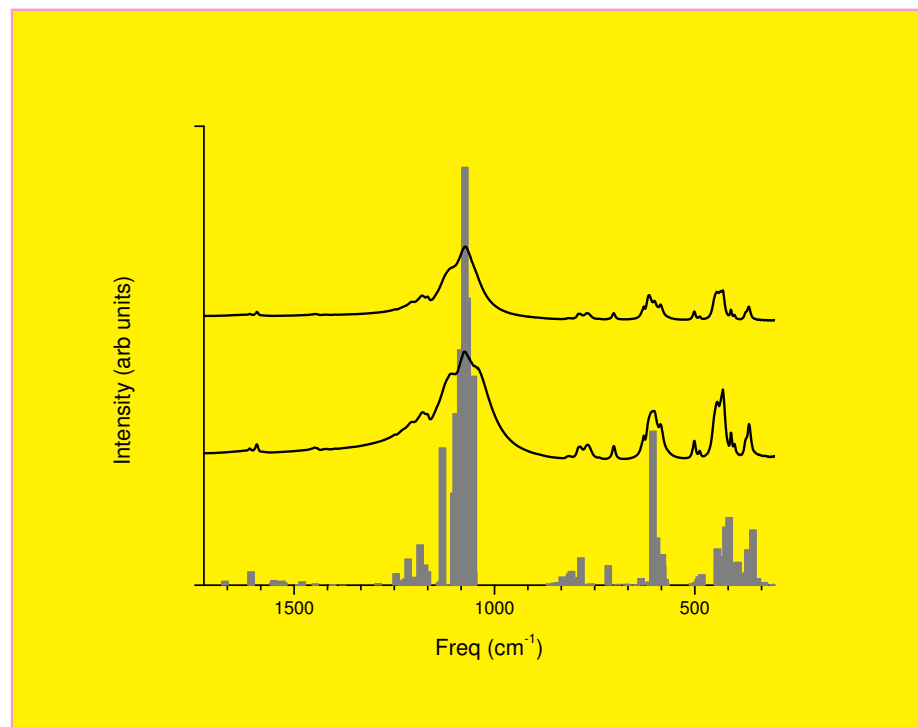
- ▶ Exploiting the steps adopted for the numerical calculation of the Hessian, the derivatives of the dipole moment (sum of centroid positions) are also performed during the Hessian construction.
- ▶ Actually, localization is just performed at the central point: the Wannier functions of the displaced points are computed by projection of those obtained at the central point onto the occupied space of the actual point. This provides a substantial decrease in CPU time.



Infrared spectrum of a zeolite: ITQ-12+F⁻+TMI⁺



Infrared spectrum of a zeolite



ITQ-12 as-made

Analysis of the Electronic Structure

- ♣ Localized WFs \longrightarrow electron pairs.
- ♣ Chemical meaning according to qualitative (Lewis) theories.

Characterization of the electronic structure of crystalline compounds through their localized Wannier functions

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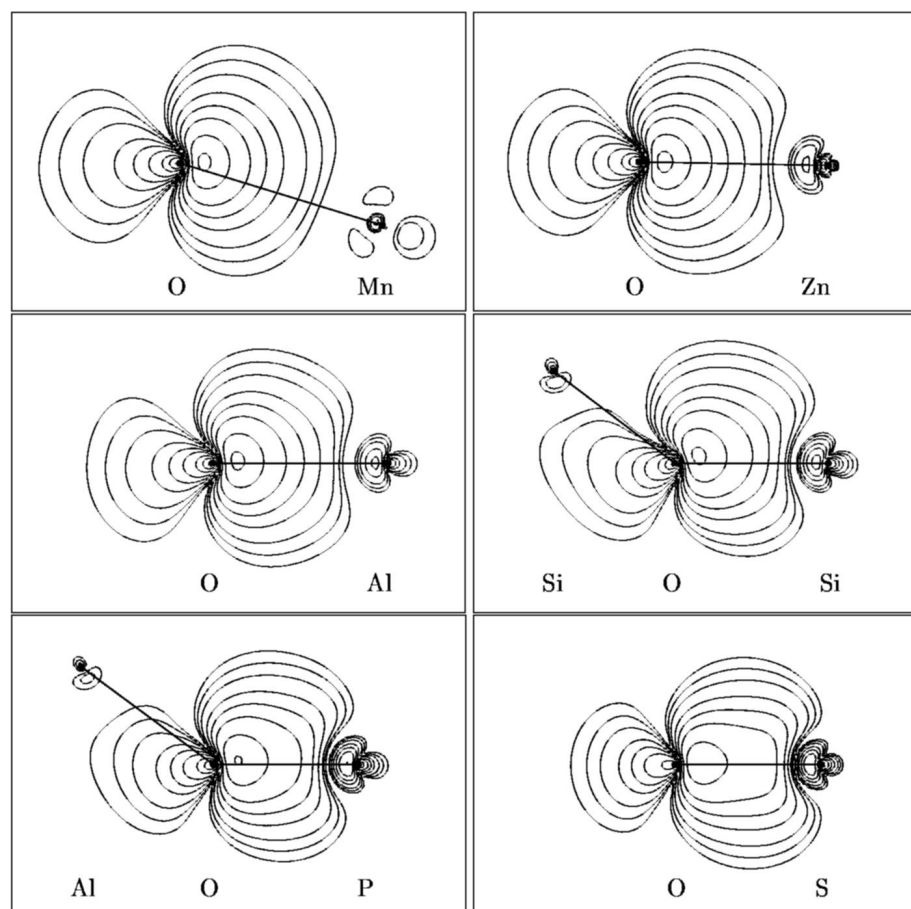
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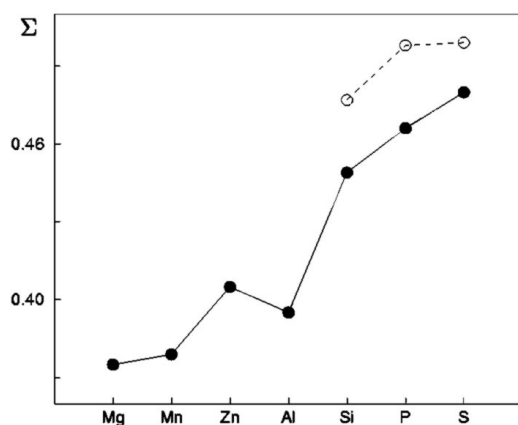
(Received 13 August 2001; accepted 16 October 2001)

The crystalline orbitals of seven oxygen containing compounds with increasing degree of covalent character (MgO, MnO, ZnO, Al₂O₃, SiO₂, AlPO₄, and CaSO₄) are localized according to a Wannier–Boys mixed scheme recently implemented. The resulting Wannier functions are analyzed in terms of various indices (centroids positions, second-order central moment tensor, its eigenvalues and principal axes, Mulliken population analysis, and atomic localization indices). Systematic trends are observed along the series. © 2002 American Institute of Physics. [DOI: 10.1063/1.1425406]

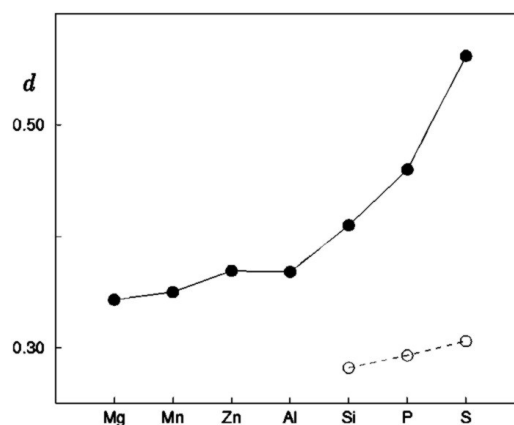
Density maps of the XO bonding WFs



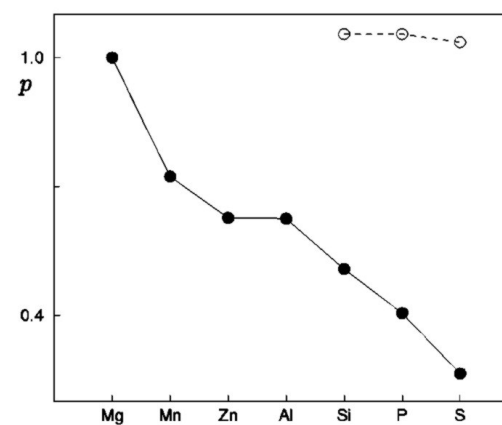
Dependence of localization indices on the cation nature



standard spread of the electronic distribution



distance between centroid and O atom



polarization fraction (1-ionic,0-covalent)

Symmetry Adapted Localized Wannier Functions

Translational equivalence \longrightarrow just one representative can be taken to account for the properties of a set.
Spatial Localization \longrightarrow minimize coupling between different LWFs for some local operators

- ♣ Interesting for some applications: Bielectronic integrals in LMP2 (see CRYSCOR presentation by Silvia Casassa)
- ♣ The same strategy can be extended for general symmetry equivalence (not only translational but every space operator)

Target: **maximize** localization and **minimize** the number of representatives that generate the whole set by symmetry equivalence

Symmetry Adapted Localized Wannier Functions

- ▲ Full symmetry equivalence is not in general possible for every group representation. **only the regular representation may have full equivalence into its basis sets**
- ▲ The group can be always partitioned in cosets under a given subgroup so as to obtain representations whose basis sets are partially equivalent and partially invariant.
- ▲ The partition can be chosen to fulfill the conditions of: maximal localization and minimal number of representatives.



Symmetry Adapted Localized Wannier Functions

- ★ Most simple way is the *a posteriori* strategy.
- ★ **AFTER** localization, the rough symmetry properties of the LWFs (not fully reached for numerical reasons during the localization process) are determined and projectors are used to make the LWFs perfectly symmetric.
- ★ The LWFs are classified as *petals* \in *flowers* \in *bunchs* according to their symmetry properties.
- ★ Whenever there is no significant loss in the localization properties the set is unitary transformed to minimize the number of representatives.



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REGULAR ARTICLE

Silvia Casassa · Claudio M. Zicovich-Wilson
Cesare Pisani

Symmetry-adapted localized Wannier functions suitable for periodic local correlation methods

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Summary

- ▲ Efficient electronic localization method for crystalline systems. (The scheme could be extended to other less expensive methods: Pipek-Mezey)
- ▲ Easy to control the balance between Localization degree and computational effort.
- ▲ Computation of properties of interest for crystalline materials:
 1. Polarization (spontaneous, piezoelectricity, IR Intensities)
 2. Chemical characterization
- ▲ First step for the computation of the correlation energy in solids. Work in progress together with the Dresden group (Birkenheuer *et al.*) and the Turin group (Pisani *et al.*).



In progress...

- ▶ *A priori* symmetry adapted LWFs:
 - ♣ symmetry constraints imposed **during** the localization process.
- ▶ variational methods based on manifolds of LWFs:
 - ♣ Crystals under electric fields
 - ♣ Wavefunction calculation for large systems
 - ♣ Multiconfiguration methods for non-conducting crystals (static electron correlation)

