Joint Psi-k/CECAM Workshop

Maximally Localized Wannier Functions: Concepts, Applications, and Beyond

Lyon, France, 27–29 June 2007

with PWSCF/Wannier90 Tutorial on June 26.

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Program of Tutorial

Tuesday 26 June 2007

9:30–12:30	**PWSCF Tutorial** *Plane wave selfconsistent calculations, non-selfconsistent diagonalizations, band structures*
12:30–15:00	Lunch break
15:00–18:00	**Wannier90 Tutorial** *Wannier functions of occupied manifolds, disentanglement, and metals*

Program of Workshop

Wednesday 27 June 2007

Introductory Session, Chairman **A. Pasquarello**

8:45–8:50	Opening remarks
8:50–9:30	**D. Vanderbilt**
	Wannier Functions: Past, Present, and Future
9:30–9:45	Discussion

General Theory and Algorithms, Chairman **N. Marzari**

9.45–10:15	**Ch. Brouder**
	Exponential Localization of Wannier Functions in Insulators
10:15–10:30	Discussion
10:30–11:00	Coffee break
11:00–11:30	**E. Prodan**
	The Complex Analytic Structure of the Bands in Linear Molecular Chains
11:30–11:45	Discussion
11:45–12:15	**F. Gygi**
	Large-Scale Computations of Maximally Localized Wannier Functions and Compact Representations of Kohn-Sham Invariant Subspaces
12:15–12:30	Discussion
12.30-14:30	Lunch break

Polarization, Chairman **R. Resta**

14:00–14:30	**A. Pasquarello**
	Wannier Functions for Locally Probing Dielectric and Spectral Properties
14:30–14:45	Discussion
14.45–15:15	**M. Stengel**
	First-Principles Modeling of Field Effects at Metal-Oxide Heterojunctions
15:15–15:30	Discussion
15:30-16:00	Coffee break
16.00–16:30	**O. Dieguez**
	Wannier-Based Definition of Layer Polarizations in Perovskite Superlattices
16:30–16:45	Discussion
16:45–17:15	**M. Posternak**
	Structural and Electronic Properties of TiO_2 Polymorphs: a Wannier Functions Approach
17:15–17:30	Discussion

Applications I, Chairman **A. Pasquarello**

17.30–18:00	**P. Umari**
	Faster GW Calculations in Larger Model Structures Using Ultralocalized Nonorthogonal Wannier Functions
18:00–18:15	Discussion

Thursday 28 June 2007

Applications II, Chairman **F. Gygi**

8:45–9:15	**R. Car**
	Dipolar Correlations and Dielectric Permittivity of Water
9:15–9:30	Discussion
9:30–10:00	**M. E. Tuckerman**
	Computational Spectroscopy and Theory of Molecular Pseudopotentials: Two Applications of Wannier Functions
10:00–10:15	Discussion
10:15–10:45	Coffee break

Interpolation, Chairman **D. Vanderbilt**

10:45–11:15	**N. Marzari**
	Making Mountains out of Molehills, and Other Tails of Disentanglement
11:15–11:30	Discussion
11:30–12:00	**J. R. Yates**
	Spectral and Fermi Surface Properties from Wannier Interpolation
12:00–12:15	Discussion
12:15–12:45	**F. Giustino**
	Electron-Phonon Interaction with Wannier Functions
12:45–13:00	Discussion
13:00–14:30	Lunch break

Transport, Chairman **R. Car**

14:30–15:00	**M. Buongiorno Nardelli**
	Wannier Functions and Quantum Transport in Nanostructures
15:00–15:15	Discussion
15:15–15:45	**Y.-S. Lee**
	Predicting the Electronic Transport Properties of Chemically Functionalized Carbon Nanotubes: A Maximally Localized Wannier Function Approach
15:45–16:00	Discussion
16.00–16:30	Coffee break
16:30–17:00	**K. S. Thygesen**
	Partially Occupied Wannier Functions and Quantum Transport in Nano-Scale Contacts
17:00–17:15	Discussion
17:15–17:45	**A. Ferretti**
	Maximally Localized Wannier Functions: Ultrasoft Pseudopotentials and Related Applications
17:45–18:00	Discussion

Friday 29 June 2007

Applications III, Chairman **A. Pasquarello**

8:45–9:15	**O. V. Yazyev**
	Wannier Function Analysis as a Tool for Interpreting Core-Level Photoelectron Spectra
9:15–9:30	Discussion

Magnetic Systems, Chairman **O. K. Andersen**

9:30–10:00	**R. Resta**
	Hermaphrodite Orbitals with and without Time-Reversal Symmetry
10:00–10:15	Discussion
10:15–10:45	Coffee break
10:45–11:15	**I. Souza**
	Dichroic f-Sum Rule and the Orbital Magnetization of Many-Electron Systems
11:15–11:30	Discussion
11:30–12:00	**T. Thonhauser**
	On the Impossibility of Constructing Maximally Localized Wannier Functions in Chern Insulators
12:00–12:15	Discussion

Strongly Correlated Electrons, Chairman **I. Souza**

12:15–12:45	**O. K. Andersen**
	Direct Generation of Wannier Functions by Downfolding, Polynomial Approximation, and Symmetrical Orthonormalization
12:45–13:00	Discussion
13:00–14:30	Lunch break
14:30–15:00	**W. Ku**
	Symmetry-Respecting Wannier Functions and Their Applications in Strongly Correlated Materials: New Development of First-Principles Many-Body Down-Folding Approach
15:00–15:15	Discussion
15:15–15:45	**F. Lechermann**
	Wannier Functions for Strongly Correlated Systems: the Intriguing Physics of $BaVS_3$ as a Test Case
15:45–16:00	Discussion

Closing Session

16.00–16:05	Concluding remarks
16.05	End of Workshop

Wannier Functions: Past, Present, and Future

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In this talk I will give an introduction to the theory of Wannier functions (WFs) and discuss some of the reasons why interest in WFs has expanded rapidly in recent years.

I will briefly introduce WFs, starting with the simplest case of orthonormal WFs for a single isolated band in a periodic crystal and discussing the non-uniqueness associated with the choice of phases. I will then discuss some of the ways in which the definition of WFs can be generalized, including: (i) multiband WFs and their associated gauge freedom; (ii) non-orthonormal WFs; (iii) Wannier-like functions ("localized molecular orbitals") for the occupied states of finite systems (molecules and clusters) and of disordered infinite systems; (iv) "disentangled" or "downfolded" orbitals that can be used as a basis to describe the occupied states and/or the states near ε_F in a metal; and (v) hybrid or "hermaphrodite" WFs that are Bloch-like in one or more Cartesian directions while being Wannier-like in the orthogonal directions(s). Unfortunately the terminology in the field is not well established, and there is little consensus about whether or not such generalized objects still deserve to be called WFs. I will discuss my views on this question and make some modest suggestions about it.

I will then briefly discuss two approaches for resolving the phase or gauge freedom: the use of projection methods, and the generation of maximally localized WFs. I will make several comments about the projection methods, especially concerning how well-localized non-orthonormal WFs are best constructed using a projection method.

I will present only a very brief outline of the types of applications of WF methods that are currently of interest, as these will be well illustrated by other talks in the workshop.

I will devote the last part of the talk to discussing several problems connected with the theory of WFs that have only recently been solved or that remain unsolved. In the former category, a proof of the exponential localization of WFs in the three-dimensional multiband case has recently been given. Among the latter, I will focus mainly on issues relating to the definition of WFs for systems with broken time-reversal symmetry. Most of the work done in the last decade on the theory of electric polarization, finite electric fields, localization, and the nature of the insulating state have been limited, implicitly or explicitly, to the case in which time-reversal symmetry is preserved. However, much remains to be done to bring our understanding of systems with broken time-reversal symmetry up to the same level. For example, is there an appropriate generalization of the concept of WFs for a Chern insulator (that is, an insulator with a non-zero Chern invariant)? Can the recently given derivation for the orbital magnetization of an ordinary insulator be extended to the case of a metal or a Chern insulator using a derivation based on the Wannier representation? If time permits, some tentative and partial steps in these directions may be discussed.

Exponential Localization of Wannier Functions in Insulators

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The question of the exponential localization of generalized Wannier functions has long been one of the last open problems of one-body solid-state physics. The exponential localization of Wannier functions in two and three dimensions is important from a theoretical point of view, because it implies the existence of multipoles of all orders, and from a computational point of view, because it ensures the exponential convergence of some numerical algorithms.

We proved recently [1] that 2D and 3D generalized Wannier functions decay exponentially in insulators if and only if the single Chern number in 2D and the three Chern numbers in 3D are zero.

After a brief history of the problem, we sketch the steps of the proof, that boils down to a recent theorem on the topology of the Brillouin zone [2]. The role played by the Berry connection and the Chern numbers in the proof of the theorem is explained. Some of the practical consequences of exponential decay are presented.

[1] Ch. Brouder, G. Panati, M. Calandra, Ch. Mourougane, N. Marzari, Phys. Rev. Lett. **98**, 046402 (2007).

[2] G. Panati, Ann. Henri Poincaré **8**, (2007).

The Complex Analytic Structure of the Bands in Linear Molecular Chains

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In a classic paper [1], Walter Kohn found that the band energies of periodic Schroedinger operators in 1 dimension have a beautiful structure when one lets the k-wavevector be complex. He discovered that the energies of different bands are nothing but the same function evaluated on different sheets of a certain Riemann surface. This Riemann surface is generic in 1 dimension, in the sense that its shape does not depend on the particular form of the periodic potential. The asymptotic behavior of almost all correlation functions can be computed from the Riemann surface. In particular, properly defined Wannier functions decay exponentially with a decay rate dictated by the branch points of the Riemann surface.

In this talk I will review recent results [2] that generalize all the above to linear molecular chains in 3D. They are based on a new approach, which is quite different from the original one. The approach relies on topological arguments (plus elementary functional analysis) rather than the theory of second order differential equations. Based on this, I will discuss the generic structure of the Riemann surface for periodic molecular chains and present several explicitly computed examples.

I will conclude with a discussion of the exponential localization of the Wannier and Green's functions and of the density matrix. If time allows, I will also cover some recent applications to electronic nearsightedness [3] and transport [4].

[1] W. Kohn, Phys. Rev. **115**, 809 (1959).

[2] E. Prodan, Phys. Rev. B **73**, 035128 (2006).

[3] E. Prodan and W. Kohn, PNAS **102**, 11635 (2005).

[4] E. Prodan and R. Car, cond-mat/0702192 (2007).

Large-Scale Computations of Maximally Localized Wannier Functions and Compact Representations of Kohn-Sham Invariant Subspaces

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Maximally Localized Wannier Functions (MLWFs) can be computed using iterative algorithms to minimize the wavefunction spread, but also by approximate simultaneous diagonalization of non-commuting matrices [1]. In large-scale electronic structure calculations, the cost of a simultaneous diagonalization scales as $O(n^3)$ for n electrons. This unfavorable scaling makes it necessary to develop efficient scalable algorithms for massively parallel computers. We present a new parallel algorithm for simultaneous diagonalization and demonstrate its scalability on up to 1024 processors for applications to the calculations of MLWFs.

Simultaneous diagonalization can also be used to compute reduced numerical representations of the solutions of the Kohn-Sham equations. We present a data compression method that allows for *a priori* control of the error caused by the reduction process. When applied to Kohn-Sham wavefunctions expanded on a plane-wave basis, this approach leads to a substantial reduction of the size of the datasets used to restart first-principles simulations, with controlled loss of accuracy. Examples of applications to liquid water and carbon nanotubes will be presented.

[1] F. Gygi, J.-L. Fattebert, and E. Schwegler, Comput. Phys. Comm. **155**, 1 (2003).

Wannier Functions for Locally Probing Dielectric and Spectral Properties

Alfredo Pasquarello[*]

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Two developments originating from the concept of maximally localized Wannier functions are discussed. In the first one, maximally localized Wannier functions are used within a theoretical scheme for determining local permittivities [1,2]. The local permittivity is obtained from the microscopic charge density induced by an applied electric field. By analyzing the permittivity in terms of maximally localized Wannier functions, we can relate variations of the microscopic dielectric response to specific features of the local bonding arrangement. The potential of our scheme is illustrated through an application to the permittivity of Si slabs of finite thickness [1]. Our approach indicates that the local permittivity in the slab interior approaches the corresponding value for bulk Si within a few atomic layers from the surface. Therefore, the decrease of the average slab permittivity with thickness originates from the lower permittivity of the outer planes and the increasing surface-to-volume ratio. In the second development, following up with a suggestion of Gygi *et al.* [3], we go beyond maximally localized Wannier functions to construct a partitioning of the electronic structure in terms of functions which simultaneously provide an approximate diagonalization of the Hamiltonian and the position operator [4]. These functions, that we call mixed Wannier-Bloch functions, carry both spatial localization and limited spectral broadening, and are therefore particularly convenient to associate specific spectral features to the underlying atomic-scale mechanisms. By introducing a lattice position operator analogous to the electronic Berry-phase position operator, Wannier-Bloch functions can trivially be extended to the analysis of vibrational modes [4]. Application to vitreous SiO_2 demonstrates that mixed Wannier-Bloch functions constitute a powerful tool for tracking fingerprints of short- and medium-range structural order in electronic and vibrational spectra [4].

* Work done in collaboration with Feliciano Giustino.

[1] F. Giustino and A. Pasquarello, Phys. Rev. B **71**, 144104 (2005).

[2] F. Giustino, P. Umari, and A. Pasquarello, Phys. Rev. Lett. **91**, 267601 (2003).

[3] F. Gygi, J.-L. Fattebert, and E. Schwegler, Comput. Phys. Comm. **155**, 1 (2003).

[4] F. Giustino and A. Pasquarello, Phys. Rev. Lett. **96**, 216403 (2006).

First-Principles Modeling of Field Effects at Metal-Oxide Heterojunctions

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When the thickness of an oxide film is reduced to few unit cells, its dielectric properties (which are relevant, e.g., for nonvolatile ferroelectric memories and as gate oxides in MOSFET transistors) start to deviate from those predicted by macroscopic models, and crucially depend on the atomic and electronic structure of the interfaces. One particularly important issue is the "dielectric dead layer", which plagues the performance of thin-film perovskite capacitors by substantially reducing the effective permittivity (κ) of the active high-κ material. The microscopic origins of this reduced permittivity, and in particular whether it stems from defects or from the fundamental properties of an ideal metal/insulator junction, are not well understood.

To address this problem from first principles, we will first show how the macroscopic polarization (and the coupling to an external field) can be rigorously defined for a periodic metal-insulator heterostructure [1], by using techniques and ideas borrowed from Wannier-function theory [2]. We will then demonstrate our new method by calculating the dielectric properties of realistic $SrRuO_3/SrTiO_3/SrRuO_3$ nanocapacitors [3]. Building on these ideas, we will finally present two recent applications of our finite-field method: i) critical thickness for monodomain ferroelectricity, and ii) carrier-mediated magnetoelectric effects at the interface between a dielectric and a metallic ferromagnet.

[1] M. Stengel and N. A. Spaldin, accepted in Phys. Rev. B, cond-mat/0511042.

[2] M. Stengel and N. A. Spaldin, Phys. Rev. B **73**, 075121 (2006).

[3] M. Stengel and N. A. Spaldin, Nature (London) **443**, 679 (2006).

Wannier-Based Definition of Layer Polarizations in Perovskite Superlattices

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In insulators, the method of Marzari and Vanderbilt [1] can be used to generate maximally localized Wannier functions whose centers are related to the electronic polarization. In the case of layered insulators, this approach can be adapted to provide a natural definition of the local polarization associated with each layer, based on the locations of the nuclear charges and one-dimensional Wannier centers comprising each layer. Here, we use this approach to compute and analyze layer polarizations of ferroelectric perovskite superlattices, including changes in layer polarizations induced by sublattice displacements (i.e., layer-decomposed Born effective charges) and local symmetry breaking at the interfaces. The method provides a powerful tool for analyzing the polarization-related properties of complex layered oxide systems.

[1] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12 847 (1997).

Structural and Electronic Properties of TiO$_2$ Polymorphs: a Wannier Functions Approach

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The one–particle description of the electronic structure of periodic crystalline solids is usually based on extended Bloch functions (BF's). An alternative description can be derived in terms of localized Wannier functions (WF's), which are defined in real space via a unitary transformation performed on the BF's. By imposing the further condition of maximal localization, the problem of the nonuniqueness of WF's has been mostly resolved by Marzari and Vanderbilt [1], and their method has now become a standard tool for practical applications. In contrast to BF's, WF's are useful in visualizing chemical bonds, and provide furthermore complementary informations regarding dielectric properties. As an illustration of this aspect of the WF's description, we analyze here the microscopic origin of differences in structural and electronic properties of the four natural TiO$_2$ polymorphs, *i.e.*, rutile, anatase, brookite, and the monoclinic TiO$_2$ (B) form. Indeed, because of the similarity of the local crystal environment in these phases, the use of a delocalized–basis approach (BF's) precludes a conclusive explanation of the subtle differences observed in their physical properties. In the case of rutile and anatase, physical properties have been commonly analyzed in the literature assuming that the basic building units are TiO$_6$ octahedra, which are distorted and assembled differently [2]. In contrast, our WF's analysis for these two phases has shown that the OTi$_3$ triangular complex is in fact the relevant building unit for understanding their electronic properties [3]. WF's differences between the two phases are directly related to the opposite distortion from equilateral shape that the isosceles Ti$_3$ coordination triangle has in these structures. In particular, this explains quantitatively the opposite anisotropy of the calculated dynamical Born charge tensors. We have extended these results to the case of brookite [4], where the corresponding (non–planar) OTi$_3$ structural units break up into an equal number of rutilelike and anataselike units. The WF's of the two non–equivalent O sites display an anisotropy which is in line with the structural data, and this trend applies also to the case of the Born dynamical charge tensor. Physical properties of brookite are expected to be intermediate between those of rutile and anatase. A further phase, TiO$_2$ (B), which coexists with, and derives from natural anatase has been recently identified [5]. It is monoclinic with C_{2h}^3 space group, and its conventional cell contains 8 TiO$_2$ formula units. At variance with the three cases discussed above, the 16 O atoms in TiO$_2$ (B) are *not* all threefold coordinated: indeed, 12 O atoms belong to anataselike OTi$_3$ structural units, and the remaining 4 O atoms are twofold coordinated. The outcome of structural differences on electronic properties of these various TiO$_2$ phases is analyzed.

[1] N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

[2] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1975), p. 200.

[3] G. Cangiani, A. Baldereschi, M. Posternak, and H. Krakauer, Phys. Rev. B **69**, 121101(R) (2004).

[4] M. Posternak, A. Baldereschi, E.J. Walter, and H. Krakauer, Phys. Rev. B **74**, 125113 (2006).

[5] J.F.Banfield, D.R. Veblen, and D.J. Smith, Am. Mineral. **76**, 343 (1991).

Faster GW Calculations in Larger Model Structures Using Ultralocalized Nonorthogonal Wannier Functions

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We introduce a novel approach for performing first-principles GW calculations of large model structures. A description of the valence and conduction manifolds in terms of ultra-localized non-orthogonal generalized Wannier functions permits to minimize the dimension of the basis set required for describing the space of single electron transitions. This dimension scales linearly with the size of the system. Then a real-space imaginary-time approach is used to calculate the self-energy operator in the space of Kohn-Sham eigenstates. Ultrasoft pseudopotentials are straightforwardly implemented within this scheme. We validate our approach by calculating the vertical ionization energies of small molecules and find excellent agreement with the experiment. Then we shows its potentiality by addressing a model structure of vitreous silica. An overall speedup factor of up to two orders of magnitude is observed.

Dipolar Correlations and Dielectric Permittivity of Water

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The static dielectric properties of liquid and solid water are investigated within linear response theory in the context of ab-initio molecular dynamics. Using maximally localized Wannier functions to treat the macroscopic polarization we formulate a first-principle, parameter-free, generalization of the phenomenological theory due to Kirkwood and Onsager. Our calculated static permittivity is in good agreement with experiment [1]. The same approach based on Wannier functions is also useful to identify the effect of intramolecular and intermolecular dynamic dipolar correlations on the infrared spectrum of water [2].

[1] M. Sharma, R. Resta, and R. Car, Phys. Rev. Lett., in press (2007).

[2] M. Sharma, R. Resta, and R. Car, Phys. Rev. Lett. **95**, 187401 (2005).

Computational Spectroscopy and Theory of Molecular Pseudopotentials: Two Applications of Wannier Functions

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The methodology of *ab initio* molecular dynamics, wherein finite-temperature dynamical trajectories are generated using forces computed "on the fly" from electronic structure calculations, allows chemical bond breaking and forming events to be treated explicitly within a dynamical simulation. Direct access to the electronic structure also allows spectroscopic observables, such as the IR spectrum, to be determined in a relatively straightforward manner. *Ab initio* molecular dynamics has benefited substantially from its combination with maximally localized Wannier functions. The latter exploit the unitary invariance of the total energy to generate spatially localized electronic orbitals. Recently, we showed how ideas from quantum field theory can be used to reformulate the Car-Parrinello equations of motion such that these orbitals are preserved during an *ab initio* molecular dynamics calculation [1,2]. In this talk, these methods will be briefly reviewed. It will then be shown how Wannier functions can be used to compute both IR spectra and IR difference spectra with considerable efficiency. Next, the problem of QM/MM simulations will be considered, and it will be shown how Wannier functions can be used as the basis of a new theory of molecular pseudopotentials for use in such simulations. Finally, a new localized basis set approach [3,4,5,6] will be described, which, when combined with Wannier functions, could lead to a new linear-scaling approach.

[1] J. W. Thomas, R. Iftimie and M. E. Tuckerman, Phys. Rev. B **69**, 125105 (2004).

[2] R. Iftimie, J. W. Thomas and M. E. Tuckerman, J. Chem. Phys. **120**, 2169 (2004).

[3] Y. Liu, D. A. Yarne and M. E. Tuckerman, Phys. Rev. B **68**, 125110 (2003).

[4] H. S. Lee and M. E. Tuckerman, J. Phys. Chem. A **110**, 5549 (2006).

[5] H. S. Lee and M. E. Tuckerman, J. Chem. Phys. **125**, 154507 (2006).

[6] H. S. Lee and M. E. Tuckerman, J. Chem. Phys. **126**, 164501 (2007).

Making Mountains out of Molehills, and Other Tails of Disentanglement

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Maximally-localized Wannier functions (MLWFs) can be used as building blocks for the electronic-structure of complex and realistic nanostructures [1,2]. Two broad alternatives are envisioned: 1) MLWFs can act as a minimal basis set, alternative to LCAO, onto which the Hamiltonian is diagonalized with or without a self-consistent update of the charge density, or 2) the Hamiltonian in the MLWFs representation can be directly constructed from the short-ranged Hamiltonians of smaller constituent units, taken either as molecular or periodically-repeated fragments.

In all cases, a robust strategy for constructing MLWFs spanning both the occupied and unoccupied orbitals is required; we'll discuss here examples and applications drawn from the study of pristine and functionalized carbon nanotubes, silicon and silicon-germanium nanowires, and DNA helices [3].

[1] Y.-S. Lee, M. B. Nardelli, and N. Marzari, Phys. Rev. Lett. **95**, 076804 (2005).

[2] Y.-S. Lee and N. Marzari, Phys. Rev. Lett. **97**, 116801 (2006).

[3] A. Mostofi and N. Marzari, in preparation (2007).

Spectral and Fermi Surface Properties from Wannier Interpolation

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We describe a widely-applicable Wannier function (WF) based scheme for interpolating both the energy bands and any given one-electron operator. This provides an efficient first-principles approach for calculating Fermi surface averages and spectral properties of solids [1]. The first step is to perform a conventional first-principles calculation and store the low-lying Bloch functions evaluated on a uniform grid of k-points in the Brillouin zone. We then map those states onto a set of maximally-localized Wannier functions, and evaluate the matrix elements of the Hamiltonian and the other needed operators between the Wannier orbitals, thus setting up an "exact tight-binding model." In this compact representation the k-space quantities are evaluated inexpensively using a generalized Slater-Koster interpolation. Because of the strong localisation of the Wannier orbitals in real space, the smoothness and accuracy of the k-space interpolation increases rapidly with the number of grid points originally used to construct the Wannier functions. This allows k-space integrals to be performed with *ab-initio* accuracy at low cost. In the Wannier representation, band gradients, effective masses, and other k-derivatives needed for transport and optical coefficients can be evaluated analytically, producing numerically stable results even at band crossings and near weak avoided crossings. We present its application to the calculation of the spontaneous anomalous Hall conductivity [2] and magnetic circular dichroism [1] of ferromagnets. The possibility of similar field-induced effects in paramagnets, including an anomalous contribution to the low-field Hall effect, is discussed.
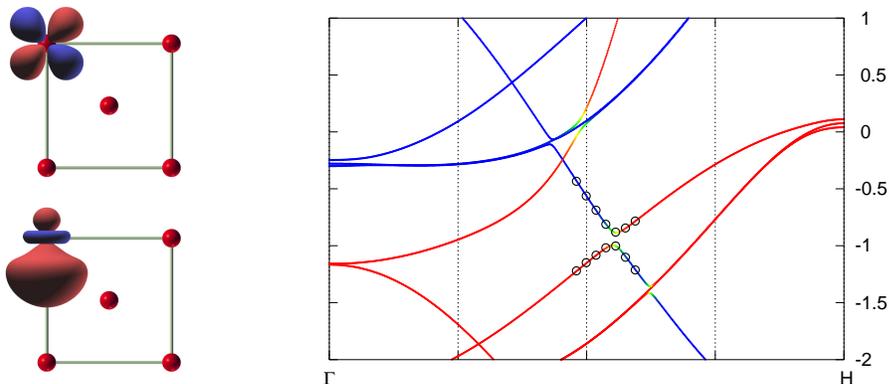
Figure 1: Left: WFs for bcc Fe. Right: Wannier-interpolated bands of bcc Fe along Γ–H. The bands are color-coded according to the value of $\langle S_z \rangle$: red for spin up and blue for spin down. The energies are given in eV and the Fermi level is at 0 eV. The vertical dashed lines indicate k-points on the *ab-initio* mesh used for constructing the WFs. For comparison, points from a full *ab-initio* calculation are shown as open circles.

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Electron-Phonon Interaction with Wannier Functions

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The electron-phonon interaction plays a central role in a variety of phenomena, including for example electrical resistivity, superconductivity, Peirls instability, and polaronic transport in conducting polymers. Despite the continued interest in the electron-phonon problem, modern first-principles calculations are still limited to simple bulk systems with a few atoms per unit cell, and only sporadic attempts have been made to address complex materials such as nanostructures or doped superconductors. The current situation is at least partly due to the significant computational burden in the study of phenomena involving electron-phonon coupling, where a detailed account of the electron and phonon scattering processes in proximity of the Fermi surface is required. In this talk I will present a methodology based on electronic and lattice Wannier functions which reduces by several orders of magnitude the computational cost of such studies [1]. The underlying idea is to exploit the spatial localization of electrons and phonons in the Wannier representation in order to compute from first-principles only a limited set of electronic and vibrational states and electron-phonon matrix elements. The results thus obtained are then used to calculate the corresponding quantities at arbitrary electron and phonon momenta in the Bloch representation through a Wannier-Fourier interpolation. In most practical cases the final results carry the same accuracy of a direct first-principles calculation, while the computational cost is comparable to that of a standard phonon dispersion calculation. In the first part of the talk I will describe how we calculate the electron-phonon vertex in the joint electron/phonon Wannier representation. The localization properties of the vertex will be analyzed by making connection with the electronic Hamiltonian in the Wannier basis and with the matrix of the Interatomic Force Constants [2]. By considering a simple virtual crystal model of boron-doped diamond, I will demonstrate the accuracy of the Wannier-Fourier interpolation in Bloch space, and discuss the convergence of the electron and phonon self-energies with the sampling of the Brillouin zone. In the second part of the talk I will review a few recent applications to systems of technological relevance. I will discuss the mechanism of superconductivity in boron-doped diamond [1], show how the electron-phonon interaction affects the carrier lifetimes and the velocity of Dirac fermions in graphene [2], and clarify the relation between the superconducting properties of super-hard transitions metal carbides and the Fermi surface topology in these materials [3].

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Wannier Functions and Quantum Transport in Nanostructures

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Determining the quantum ballistic conductance of a nanosystem has become of primary interest in recent years for the promise of novel technological applications for nanoscale quantum electronic devices. In particular, on the theoretical side, a fully first principle theory of electronic transport is highly desirable. In this talk, I will discuss how the use of Maximally-Localized Wannier functions has led to important advances in the development of efficient techniques to compute quantum conductance from first principles [1] and show examples of prototypical applications, ranging from molecular devices and carbon nanotubes systems to ferroelectric tunnel junctions.

[1] WanT project, http://www.wannier-transport.org

Predicting the Electronic Transport Properties of Chemically Functionalized Carbon Nanotubes: A Maximally Localized Wannier Function Approach

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Chemical functionalizations are one of the most promising routes to engineer the electronic properties of carbon nanotubes. While understanding the effect of various chemical groups is of fundamental interest, a full first-principles description on these complex nanostructures having thousands of atoms and randomly-distributed functional groups is still prohibitively expensive.

We calculate the quantum conductance of functionalized carbon nanotubes mapping first-principles calculations to tight-binding Hamiltonians built upon maximally localized Wannier function (MLWF) basis [1]. We apply this method to study two prototypical cases: monovalent and divalent functional groups, categorized according to the number of the covalent bonds that bind them to the nanotube backbone. One additional bond introduced by a monovalent group converts an sp^2 carbon to an sp^3 carbon on the sidewall. These sp^3 carbons strongly perturb the conduction π-manifold; a rapid decrease in the conductance is predicted as the number of the functional groups increases [1]. Divalent groups exhibit more interesting characteristic. The sidewall bond between the two neighboring carbon atoms associated with a functional group can either be broken or remain closed, which is determined by the curvature of the nanotubes and the chemical nature of the functional groups. Bond breaking transforms the two carbon atoms back to the sp^2 hybridized state; the conductance then approaches that of pristine nanotubes in contrast with the sp^3 hybridized case [2]. This theoretical prediction presents a novel concept of controlling the electronic transport of carbon nanotubes through an orbital rehybridization.

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Partially Occupied Wannier Functions and Quantum Transport in Nano-Scale Contacts

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I will present a method for constructing maximally localized Wannier functions (WFs) for general systems including non-periodic metallic systems such as molecules adsorbed on a metal surface or a molecule attached between metallic electrodes. The resulting partially occupied WFs [1] have improved symmetry and localization properties as compared to the WFs constructed from the occupied subspace. In the second part I discuss how the partially occupied WFs can be used to calculate the Landauer-Büttiker conductance of nano-scale contacts with plane-wave accuracy within a DFT framework [2]. As an application of the WF-transport scheme it is demonstrated how the presence of impurity gas atoms can affect the electrical properties of Ag and Au monatomic chains. Finally, it is shown how the minimal WF basis can be combined with the GW approximation to address correlation effects in quantum transport through realistic nano-scale contacts [3].

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Maximally Localized Wannier Functions: Ultrasoft Pseudopotentials and Related Applications

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The use of maximally localized Wannier functions (MLWFs) recently became very popular in the electronic structure community, as a supplementary analysis tool. On one hand, MLWFs are attractive because they constitute a localized basis set which is complete and orthonormal, while on the other hand, they also carry physical information. Is it therefore a direct interest of the community to improve and generalize the current methods and algorithms to compute MLWFs.

In the framework of the WanT [1] project, we developed and implemented [2] a theoretical scheme that enables the calculation of maximally localized Wannier functions in the formalism of projector-augmented-waves [3] and ultrasoft-pseudopotentials [4]. I will describe this formalism as well as some technical issues related to the computation of MLWFs. I will also discuss some application of the above method to the calculation of spontaneous polarization and surface dipole for SiC polytypes, and to the evalutation of transport properties in organic-silicon interfaces.

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Wannier Function Analysis as a Tool for Interpreting Core-Level Photoelectron Spectra

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X-ray photoemission spectroscopy (XPS) involving excitations of core electrons is a versatile experimental technique for the characterization of surfaces and interfaces. However, even in the cases of the Si(100)2×1 surface and technologically relevant Si(100)-SiO$_2$ interface, which have been the objects of numerous highly resolved XPS investigations, the origin of subsurface XPS signals is not fully understood. While the shifts pertaining to the first-layer dimer atoms of the Si(100)2×1 surface have been identified, the other lines appearing in highly resolved Si 2p spectra still lack a consensual assignment [1]. For the Si(100)-SiO$_2$ interface, highly resolved spectra show fine structure in the nonoxidized Si line, with extra components at lower (Si$^\alpha$) and higher binding energy (Si$^\beta$) with respect to the Si bulk line [2]. First principles calculations are able to predict accurately the Si 2p core-level binding energies at silicon surfaces and interfaces [3]. Binding energy shifts of the subsurface Si atoms with identically composed first-neighbor shells are caused by electron density displacements due to either the local strain fields or electronegativity effects. In order to distinguish between these two effects, we propose a simple analysis in terms of maximally localized Wannier functions (MLWFs) [4]. Our approach is based on the correlation between the core electron binding energies and the positions of MLWF centers and covalent bond centers [5]. For the Si(100)-c(4×2) surface, we find that, apart from the shifts associated with the dimer atoms, the other shifts mainly result from the local strain induced by the surface reconstruction. For the interface, the Si atoms with second-neighbor O atoms contribute to the Si$^\alpha$ line, while the Si$^\beta$ line originates from bond elongations of Si atoms without second-neighbor O atoms. From the experimental shift of about 0.3 eV, we infer the occurrence of Si atoms with an average bond length elongation of ∼0.05 Å. A key result of our work is that XPS spectra in combination with electronic structure calculations and Wannier function analysis provide an atomic-scale probe of the strain in the structure. This confers to photoelectron spectroscopy a new functionality.

* Work done in collaboration with A. Pasquarello.

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Hermaphrodite Orbitals
with and without Time-Reversal Symmetry

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The localization tensor, alias second cumulant moment $\langle r_\alpha r_\beta \rangle_c$ of the electron distribution, is an intensive quantity characterizing the ground-state wavefunction, and is finite in any insulator [1]. In absence of time-reversal (TR) symmetry, this same tensor acquires an off-diagonal imaginary part [2], proportional to the Chern number C_1 (in 2d). I specialize here to the case of noninteracting electrons (either HF or KS). Within either periodic or "open" (cluster-like) boundary conditions we have

$$\mathrm{Re}\,\langle r_\alpha r_\beta \rangle_c = \frac{1}{2N}\int d\mathbf{r}\,d\mathbf{r}'(\mathbf{r}-\mathbf{r}')_\alpha(\mathbf{r}-\mathbf{r}')_\beta|\rho(\mathbf{r},\mathbf{r}')|^2, \tag{1}$$

where ρ is the one-body density matrix, and single orbital occupancy is assumed. When performing a localization transformation upon the occupied orbitals, the real part of $\langle r_\alpha r_\beta \rangle_c$ sets a minimum for the quadratic spread in any given direction, averaged over all the orbitals; this statement holds, again, within both kinds of boundary conditions [3]. From now on, I further specialize to the crystalline case. Then the trace of $\langle r_\alpha r_\beta \rangle_c$ equals the Marzari-Vanderbilt Ω_I (divided by the number of occupied bands) while the orbitals which actually minimize the quadratic spread in a given direction have been called "hermaphrodite orbitals" (Wannier-like in one direction, Bloch-like in the orthogonal ones); they decay faster than any polynomial [4]. As for the cases where TR symmetry is broken, we have some experience only in 2d, for either the quantum-Hall (noninteracting) fluid, or the Haldane model Hamiltonian [5]. In a quantum-Hall fluid the dc longitudinal conductance vanishes, hence the system is effectively an insulator. Then $\mathrm{Re}\,\langle r_\alpha r_\beta \rangle_c$ is finite, while $\mathrm{Im}\,\langle r_\alpha r_\beta \rangle_c$ is proportional to C_1 (hence to the Hall conductivity). Despite the finiteness of $\mathrm{Re}\,\langle r_\alpha r_\beta \rangle_c$, two-dimensional localization of the orbitals *cannot* be achieved. Instead, the hermaphrodite orbitals do exist. All can be worked out analytically in the case of a flat substrate potential, where the density matrix appearing in Eq. (1) has a Gaussian decay and the trace of $\langle r_\alpha r_\beta \rangle_c$ equals precisely the squared magnetic length (at filling one). The hermaphrodite orbitals happen to coincide with the Landau-gauge orbitals [2]; notice that ρ is *not* gauge-invariant by a change of the magnetic gauge (although its modulus is such). Depending on its parameters, the Haldane model may represent either a normal insulator ($C_1 = 0$) or a Chern insulator ($C_1 = \pm 1$). While the normal case is such by all counts, the Chern case is like the quantum-Hall case: $\mathrm{Re}\,\langle r_\alpha r_\beta \rangle_c$ is finite, $\mathrm{Im}\,\langle r_\alpha r_\beta \rangle_c$ is proportional to C_1, and two-dimensional localization of the orbitals *cannot* be achieved [6]. I conjecture that hermaphrodite orbitals still exist. Other issues, related to macroscopic orbital magnetization, will be possibly discussed.

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Dichroic f-Sum Rule and the Orbital Magnetization of Many-Electron Systems

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Magnetic circular dichroism (MCD), the difference in absorption of left- and right-circularly-polarized light by magnetic systems, is described by $\sigma''_{A,\alpha\beta}(\omega)$, the imaginary, antisymmetric part of the optical conductivity. We obtain a sum rule for the MCD spectrum of many-electron systems which is the dichroic counterpart of the f-sum rule for linearly polarized light:

$$\int_0^\infty \boldsymbol{\sigma}''_A(\omega)d\omega = \frac{\pi ec}{\hbar}\mathbf{M}_{CD},$$

where $\sigma''_{A,\gamma} = (1/2)\epsilon_{\alpha\beta\gamma}\sigma''_{A,\alpha\beta}$. The conventional wisdom is that the total ground state orbital magnetization $\mathbf{M}_{orb}$ should appear on the right-hand-side [1]. Instead, we find that the sum rule yields a subtly different quantity $\mathbf{M}_{CD}$, which turns out to be one of the two contributions to $\mathbf{M}_{orb}$ recently identified in the theory of bulk magnetism [2–4]:

$$\mathbf{M}_{orb} = \mathbf{M}_{CD} + \boldsymbol{\Delta M}.$$

$\boldsymbol{\Delta M}$ is generally nonzero for systems with more than one electron, and $\mathbf{M}_{CD}$ is basically the wavepacket self-rotation term of Ref. [2]. By independently measuring their sum via gyromagnetic experiments, $\mathbf{M}_{CD}$ and $\boldsymbol{\Delta M}$ can in principle be separated out in macroscopic samples with a net magnetization. The dichroic f-sum rule is discussed alongside three other sum rules for optical absorption, including one which relates the dichroic spectrum to the interband (Karplus-Luttinger) Hall conductivity in solids. The sum rules for bounded and extended systems are first considered separately. We then show that for conventional insulators the bulk sum rules can be recovered from the bounded-system ones by taking the thermodynamic limit using a Wannier-function representation.

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On the Impossibility of Constructing Maximally Localized Wannier Functions in Chern Insulators

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The Haldane model [1] is a simple tight-binding model that exhibits a regular insulating phase ($C = 0$) as well as a Chern-insulator phase ($C = \pm 1$), depending on the model parameters φ and Δ/t_2 (see Fig. a). This provides us with a simple means to study the behavior of several physical properties as the system turns into a Chern insulator. In particular, we can use this approach to clarify how the usual algorithms for constructing Wannier functions break down as one crosses into the Chern-insulator region of the phase diagram. Using numerical calculations on finite and periodic samples, we find that the total spread Ω of the maximally-localized Wannier functions [2] diverges for Chern insulators. However, its gauge-invariant part Ω_I, related to the localization length of Resta and Sorella [3], is finite in both insulating phases and diverges as the phase boundary is approached, as depicted in Fig. b. Furthermore, we find that the usual Wannier-function construction is bound to fail in Chern insulators because of singularities that appear in overlap matrices in both the real-space finite-sample and **k**-space extended-sample approaches. In addition, we find that the density matrix has exponential decay in both insulating phases, while having a power-law decay, more characteristic of a metallic system, precisely at the phase boundary [4].
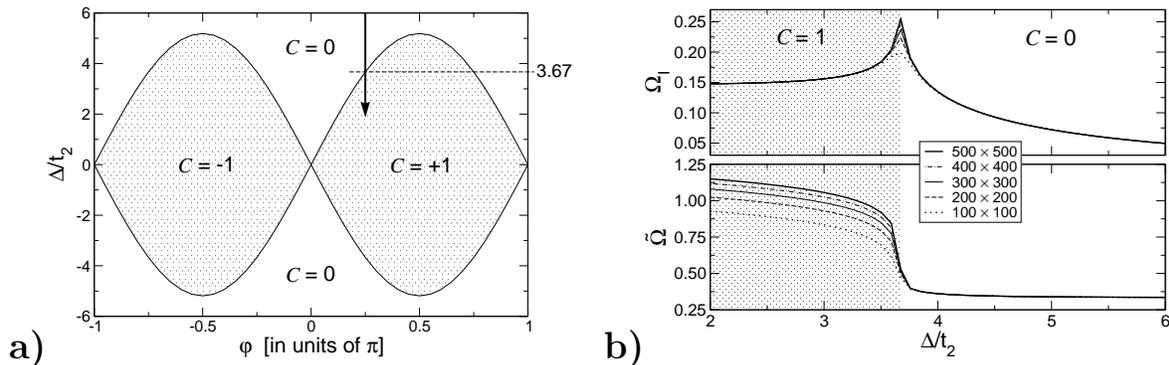
a) Phase diagram of the Haldane model as a function of the model parameters φ and Δ/t_2. For our study we have chosen to cross into the Chern insulator phase along the vertical line at $\varphi = 1/4$. **b)** Gauge-independent part Ω_I and gauge-dependent part $\tilde{\Omega}$ of the spread $\Omega = \Omega_I + \tilde{\Omega}$ for different dense **k**-point meshes. The divergence is clearly visible at $\Delta/t_2 \approx 3.67$.

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Direct Generation of Wannier Functions by Downfolding, Polynomial Approximation, and Symmetrical Orthonormalization

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Localized, minimal basis sets are useful for numerous purposes in electronic-structure calculations. Such a basis may pick a single band or a complex of bands, say the occupied bands, and may uncover the bonding, enable real-space order-N calculations, provide understanding, or be used to construct low-energy Hubbard Hamiltonians for correlated systems. We shall explain how to generate such basis sets directly by Löwdin downfolding (partitioning) from a large, complete, basis set of energy-independent, highly localized orbitals such as AOs or LMTOs, and subsequent removal of the energy dependence of the downfolded orbitals by the N-ization technique [1,2]. When applied to energy-dependent partial waves, rather than AOs or LMTOs, this gives rise to the NMTO method [3-6]. An orbital of the minimal basis set is simply the original orbital, dressed by a cloud of those orbitals which have been removed from the original set by downfolding. If the minimal basis set is chosen to span particular bands, symmetrical orthogonormalization yields a set of localized Wannier functions. Wannier functions which are maximally localized in some other sense may be obtained by a subsequent unitary transformation for a local cluster [1,2]. For most correlated d- and f-electron systems, no further localization is achieved by the last step [1,2,7]. Examples from NMTO calculations will be presented [8-12].

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Symmetry-Respecting Wannier Functions and Their Applications in Strongly Correlated Materials: New Development of First-Principles Many-Body Down-Folding Approach

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Based on a flexible first-principles construction of symmetry-respecting Wannier functions, a novel many-body down-folding approach is recently developed to derive the low-energy effective Hamiltonian that governs the physics of strongly correlated materials. In this talk, representative applications of these Wannier functions will be surveyed, including studies of ferromagnetism in half-filled cuprates [1], gapless charge density wave in dichalcogenides [2], charge/orbital order in manganites [3,4], and charge excitations in the oxides [5,6]. As an illustration of the new many-body down-folding method, detail discussions will focus on the recent discovery of the super-repulsion effect in the high-Tc cuprates and its significant implications [7].

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Wannier Functions for Strongly Correlated Systems: the Intriguing Physics of BaVS$_3$ as a Test Case

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An understanding of the physics of strongly correlated multi-orbital electron systems is one of the key ingredients in order to describe a wide range of novel solid state compounds. The complex interplay of the crystal structure with the competition between the localized and the itinerant character of electrons in a manifestly multi-orbital case is giving rise to highly interesting physical phenomena.

By combining the Dynamical Mean Field Theory (DMFT) with the Local Density Approximation (LDA) to Density Functional Theory, a powerful many-body approach is provided to tackle the given problem on a realistic level. This unified approach is naturally formulated by introducing Wannier(-like) functions as the basis representation for the electronic structure problem [1,2,3]. The choice of Wannier functions is not unique in various senses and has to be tailored to the physical problem of interest as well as to the utilized theoretical framework.

We will discuss recent developments in this important area of interfacing realistic band-structure methods with DMFT by presenting results for the complex BaVS$_3$ compound. In the latter system, electronic correlations are relevant in driving orbital charge transfers and Fermi-surface deformations in the metallic regime [3,4,5]. The paramagnetic insulating charge-density wave state shows moreover a complex orbital structure with important differences between the V ions [5].

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