On the Wannier functions of carbon materials: cumulene and graphene

Alexys Bruno Alfonso

@ Workshop on Research Collaboration FAPESP – Trinity

(23 June 2017)
Abstract

Single-band and multiband Wannier functions of cumulene and graphene are calculated. Results of tight-binding and DFT approaches are compared. Similarities of the calculated functions to either molecular or hybrid atomic orbitals are discussed.
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Collaboration

Allan Victor Ribeiro, Denis Rafael Nacbar, Alexys Bruno-Alfonso

Graduate Program in Materials Science and Technology (POSMAT, Unesp)
Bloch–Kohn and Wannier–Kohn functions in one dimension

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Abstract
Bloch and Wannier functions of the Kohn type for a quite general one-dimensional Hamiltonian with inversion symmetry are studied. Important clarifications on null minigaps and the symmetry of those functions are given, with emphasis on the Kronig–Penney model. The lack of a general selection rule on the miniband index for optical transitions between edge states in semiconductor superlattices is discussed. A direct method for the calculation of Wannier–Kohn functions is presented.
Wannier-function approach to electron states in superlattices under an electric field

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Abstract

Electron quasi-stationary states in a periodic semiconductor superlattice are calculated, as linear combinations of Wannier–Kohn functions, for different values of an electric field applied along the heterostructure. A comparison with an alternative approach, which is based on the localization of quasi-stationary states, is performed.
Our previous Works on 1D Wannier functions (2007)

PHYSICAL REVIEW B 75, 115428 (2007)

Wannier functions of isolated bands in one-dimensional crystals

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(Received 14 June 2006; revised manuscript received 10 January 2007; published 30 March 2007)

We present a simple procedure to obtain the maximally localized Wannier function of isolated bands in one-dimensional crystals with or without inversion symmetry. First, we discuss the generality of dealing with real Wannier functions. Next, we use a transfer-matrix technique to obtain nonoptimal Bloch functions which are analytic in the wave number. This produces two classes of real Wannier functions. Then, the minimization of the variance of the Wannier functions is performed, by using the antiderivative of the Berry connection. In the case of centrosymmetric crystals, this procedure leads to the Wannier-Kohn functions. The asymptotic behavior of the Wannier functions is also analyzed. The maximally localized Wannier functions show the expected exponential and power-law decays. Instead, nonoptimal Wannier functions may show reduced exponential and anisotropic power-law decays. The theory is illustrated with numerical calculations of Wannier functions for conduction electrons in semiconductor superlattices.
Our previous Works on 1D Wannier functions (2010)

Wannier functions of a one-dimensional photonic crystal with inversion symmetry

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The maximally localized magnetic and electric Wannier functions of a one-dimensional photonic crystal with inversion symmetry are investigated. The calculated Wannier functions are real and either symmetric or anti-symmetric about an inversion centre of the crystal. The magnetic and electric Wannier functions of each band are centred at the same point, but they have opposite inversion symmetries. Interestingly, for the first band, they show different kinds of asymptotic behaviour. In turn, for higher bands, both types of Wannier functions decay in the same way. When dealing with localized electromagnetic modes in a perturbed one-dimensional crystal, the knowledge of these properties should help to build an appropriate basis set of Wannier functions.
Analytical optimization of spread and change of exponential decay of generalized Wannier functions in one dimension

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Generalized Wannier functions of a couple of bands in a one-dimensional crystal are investigated. A lower bound for the global minimum of the total spread is obtained. Assumption of such a value being the minimum leads to a first-order differential equation for the transformation matrix. Simple analytical solutions leading to real generalized Wannier functions are presented for consecutive bands in a crystal with inversion symmetry. Results are displayed for a particle in a diatomic Kronig-Penney potential. For the lowest couple of bands, calculated single-band Wannier functions resemble orbitals of a diatomic molecule, whereas generalized Wannier functions seem like orthogonalized atomic orbitals. The latter functions are neither symmetric nor antisymmetric and display increased exponential decay. For the next two pairs of bands, Wannier functions retain their centers and symmetries, and exponential decay does not increase. Results are also shown to be in agreement with solutions of the eigenvalue problem of the band-projected position operator.
Electrons in crystals

Wannier functions

Bloch functions
Papers mentioning “Wannier functions” (Web of Science)
Unlike Bessel functions: do not appear in Tables

\[ J_\alpha(x) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m! \Gamma(m + \alpha + 1)} \left( \frac{x}{2} \right)^{2m+\alpha} \]

Friedrich Wilhelm Bessel
(1784 –1846)
Bloch and Wannier functions depend on both the crystal and a choice of Fourier series.
Linear Algebra: basis sets of a vector space

Bloch functions:
- $\psi_{k_0}(x)$
- $\psi_{k_1}(x)$
- $\psi_{k_2}(x)$

Wannier functions:
- $w_0(x)$
- $w_1(x)$
- $w_2(x)$

Extended

Localized

Linear Transform
Linear Algebra: basis sets of a vector space

Extended

\[ \vec{\psi}_1 = (1,1) \]
\[ \vec{\psi}_2 = (1,-1) \]

Localized

\[ \vec{w}_1 = (1,0) \]
\[ \vec{w}_2 = (0,1) \]

Linear Transform
1D crystalline lattice

\[ L = \left\{ \mathbf{R} = \sum_{l=1}^{p} \nu_l \mathbf{a}_l, \ \nu \in \mathbb{Z}^p \right\} \]

with \( a_l : l = 1, \ldots, p \leq n \) being LI vectors of \( \mathbb{R}^n \)

\[(n, p) = (3, 1)\]

\[ \mathbf{r}_\parallel = (x, 0, 0) \]

\[ \mathbf{r}_\perp = (0, y, z) \]
2D crystalline lattice

\[ L = \left\{ \vec{R} = \sum_{l=1}^{p} \nu_l \vec{a}_l, \; \vec{\nu} \in \mathbb{Z}^p \right\} \]

with \( a_l : l = 1, \ldots, p \leq n \) being LI vectors of \( \mathbb{R}^n \)

\[(n, p) = (3, 2)\]

\[\vec{r}_\parallel = (x, y, 0)\]

\[\vec{r}_\perp = (0, 0, z)\]
3D crystalline lattice

\[ L = \left\{ \vec{R} = \sum_{l=1}^{p} \nu_l \vec{a}_l, \ \vec{\nu} \in \mathbb{Z}^p \right\} \]

with \( a_l : l = 1, \ldots, p \leq n \) being LI vectors of \( \mathbb{R}^n \)

\[ (n, p) = (3, 3) \]

\[ \vec{r} = \vec{r}_{||} = (x, y, z) \]
Reciprocal lattice

\[ L' = \left\{ \vec{G} = \sum_{l=1}^{p} \nu_l \vec{b}_l, \; \vec{\nu} \in \mathbb{Z}^p \right\} \]

\[ f_{\vec{k}}(\vec{r}) = \exp(i \vec{k} \cdot \vec{r}), \quad \vec{k} \in \mathbb{R}^p \]

\[ f_{\vec{k}}(\vec{r} + \vec{R}) = f_{\vec{k}}(\vec{r}) \]

\[ \exp(i \vec{k} \cdot \vec{R}) = 1 \]

\[ \vec{a}_l \cdot \vec{b}_\nu = \delta_{l, \nu} \quad \mathbb{B} = 2\pi \tilde{\mathbb{A}}^{-1} \]

\[ C = \left\{ \vec{r} = \sum_{l=1}^{p} \sigma_l \vec{a}_l, \; \vec{\sigma} \in [0, 1]^p \right\} \]

\[ K = \left\{ \vec{k} = \sum_{l=1}^{p} \sigma_l \vec{b}_l, \; \vec{\sigma} \in [0, 1]^p \right\} \]
Fourier series

\[ f(\vec{r} + \vec{R}) = f(\vec{r}) \]

\[ f(\vec{r}) = \sum_{\vec{G} \in \Lambda'} F_{\vec{G}}(\vec{r}_\perp) \exp(i \vec{G} \cdot \vec{r}_\parallel) \]

\[ F_{\vec{G}}(\vec{r}_\perp) = \frac{1}{V_\Lambda} \int_{\Lambda} \exp(-i \vec{G} \cdot \vec{r}_\parallel) f(\vec{r}) \, d^p r_\parallel \]
Bloch functions

\[ \hat{T}_{\vec{R}} f(\vec{r}) = f(\vec{r} + \vec{R}) \]

\[ \hat{H} \hat{T}_{\vec{R}} = \hat{T}_{\vec{R}} \hat{H} \]

\[ \hat{H} \psi_{j,\vec{k}}(\vec{r}) = E_{j,\vec{k}} \psi_{j,\vec{k}}(\vec{r}) \]

\[ \hat{T}_{\vec{R}} \psi_{j,\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{R}} \psi_{j,\vec{k}}(\vec{r}) \]

\[ \hat{H} \psi(\vec{r}) = E \psi(\vec{r}) \]

\[ \hat{T}_{\vec{R}} \psi(\vec{r}) = \tau_{\vec{R}} \psi(\vec{r}) \]

\[ \exists M > 0 \mid \psi(\vec{r}) \mid \leq M \]

\[ |\tau_{\vec{R}}| = 1, \quad \tau_{\vec{R}} = e^{i\vec{k} \cdot \vec{R}} \]

\[ E_{j,\vec{k} + \vec{G}} = E_{j,\vec{k}} \]

\[ \psi_{j,\vec{k} + \vec{G}} = \psi_{j,\vec{k}} \]
The Structure of Electronic Excitation Levels in Insulating Crystals

GREGORY H. WANNIER
Princeton University, Princeton, New Jersey*
(Received May 13, 1937)

In this article, a method is devised to study the energy spectrum for an excited electron configuration in an ideal crystal. The configuration studied consists of a single excited electron taken out of a full band of $N$ electrons. The multiplicity of the state is $N^2$. It is shown that because of the Coulomb attraction between the electron and its hole $N^{8/16}$ states are split off from the bottom of the excited Bloch band; for these states the electron cannot escape its hole completely. The analogy of these levels to the spectrum of an atom or molecule is worked out quantitatively. The bottom of the Bloch band appears as "ionization potential" and the Bloch band itself as the continuum above this threshold energy.

It would no doubt be more satisfactory for insulating crystals, to discuss the Hamiltonian using atomic functions rather than Bloch functions. But this line of attack has been hampered by the fact that atomic functions are not orthogonal. We can, however, build up orthogonal functions having all the advantages of atomic ones by starting out from a Bloch approximation. Let us assume then that ...
Effective mass theory

Electrons in Perturbed Periodic Lattices*

J. C. Slater

Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received June 17, 1949)

It is shown that the motion of an electron in a periodic potential, such as is found in a solid, plus a slowly varying perturbative potential, can be derived from the energy in the periodic lattice alone, as a function of momentum or wave number. A Schrödinger equation is set up, in which the Hamiltonian is the sum of this energy in the periodic lattice—the momentum being replaced by a differential operator—and of the perturbative potential energy. The resulting wave function modulates atomic functions to provide a solution of the perturbed problem. This method is applied to give proofs of simple theorems in conduction theory, to discuss the energy levels of impurity atoms in a semiconductor, and to consider excitons; all are problems which have been considered before, but which are treated more straightforwardly by the present method. Applying the method statistically, the combined Poisson's equation and Fermi-Dirac statistics is set up for impurities in metals and semiconductors, and for the theory of rectifying barriers.

\[ H_0 \phi_0(p, q) = E_0(p) \phi_0(p, q) \]
\[ H \phi_n(q) = E_n \phi_n(q) \]
\[ H = H_0 + H_1 \]

\[ \psi_n(q) = \sum_k \psi_n(Q_k) a(q-Q_k) \]

By means of it, we effectively reduce the problem of electrons in periodic lattices and additional perturbing potentials to a problem much like that of free electrons in the perturbing potential.
Wannier functions: definition

\[ \psi_{j, \bar{k} + \bar{G}} = \psi_{j, \bar{k}} \]

\[ \psi_{j, \bar{k}}(\vec{r}) = \sum_{\bar{R} \in L} w_{j, \bar{R}}(\vec{r}) \exp(i \bar{R} \cdot \bar{k}) \]

\[ w_{j, \bar{R}}(\vec{r}) = \frac{1}{V_K} \int_{K} \exp(-i \bar{R} \cdot \bar{k}) \psi_{j, \bar{k}}(\vec{r}) \, d^{p} k \]

\[ w_{j, \bar{R}}(\vec{r}) = w_{j}(\vec{r} - \bar{R}) \]

\[ w_{j}(\vec{r}) = \frac{1}{V_K} \int_{K} \psi_{j, \bar{k}}(\vec{r}) \, d^{p} k = \overline{\psi_{j, \bar{k}}(\vec{r})} \]
Wannier functions: localization

$$\psi_{j,k}(\vec{r}) = \sum_{\vec{R} \in L} w_{j,\vec{R}}(\vec{r}) \exp(i \vec{R} \cdot \vec{k})$$

$$\left[ \psi_{j,k}(\vec{r}) \text{ continuous in } \vec{k} \right] \Rightarrow \lim_{\vec{r} \to \infty} |\vec{r}| w_{j}(\vec{r}) = 0$$

$$\left[ \psi_{j,k}(\vec{r}) \text{ } m \text{ times diff. in } \vec{k} \right] \Rightarrow \lim_{\vec{r} \to \infty} |\vec{r}|^m w_{j}(\vec{r}) = 0$$

A Wannier function decays exponentially when:

$$\exists \ h > 0 \ \lim_{\vec{r} \to \infty} e^{h|\vec{r}|} w_{j}(\vec{r}) = 0$$
Wannier functions: lack of uniqueness

Considering \( \phi : \mathbb{R}^p \rightarrow \mathbb{R} \) with the periodicity of \( L' \),

\[
\tilde{\psi}_{j,k}(\vec{r}) = \exp(i \phi_{\vec{k}}) \psi_{j,k}(\vec{r})
\]

\[
\tilde{w}_j(\vec{r}) = \frac{1}{V_K} \int_K \exp[i \phi_{\vec{k}}] \psi_{j,k}(\vec{r}) \, dpk
\]

\[
\tilde{r}_{\parallel,j} = \langle \tilde{w}_j(\vec{r}) \mid \vec{r}_{\parallel} \mid \tilde{w}_j(\vec{r}) \rangle = \int_{\mathbb{R}^n} \tilde{w}^*_{j,\vec{R}}(\vec{r}) \, \vec{r}_{\parallel} \, \tilde{w}_{j',\vec{R}'}(\vec{r}) \, d^n\vec{r}
\]

\[
\tilde{\sigma}_{\parallel,j}^2 = \langle \tilde{w}_j(\vec{r}) \mid (\vec{r}_{\parallel} - \vec{r}_{\parallel,j})^2 \mid \tilde{w}_j(\vec{r}) \rangle = \text{functional of } \phi_{\vec{k}}.
\]

This functional must be minimized!
In 1D with inversion symmetry, the single-band MLWFs are:

- Real,
- Symmetric or anti-symmetric
- Exponentially localized.

\[
\lim_{x \to \infty} a(x)e^{qx} = \begin{cases} 
0, & q < h_n \\
\infty, & q > h_n.
\end{cases}
\]
Exponential Decay Properties of Wannier Functions and Related Quantities

Lixin He and David Vanderbilt
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849
(Received 19 January 2001)

The spatial decay properties of Wannier functions and related quantities have been investigated using analytical and numerical methods. We find that the form of the decay is a power law times an exponential, with a particular power-law exponent that is universal for each kind of quantity. In one dimension we find an exponent of $-3/4$ for Wannier functions, $-1/2$ for the density matrix and for energy matrix elements, and $-1/2$ or $-3/2$ for different constructions of nonorthonormal Wannier-like functions.

$$w(x) \approx x^{-3/4} e^{-hx}$$
Maximally localized generalized Wannier functions for composite energy bands

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(Received 10 July 1997)

We discuss a method for determining the optimally localized set of generalized Wannier functions associated with a set of Bloch bands in a crystalline solid. By “generalized Wannier functions” we mean a set of localized orthonormal orbitals spanning the same space as the specified set of Bloch bands. Although we minimize a functional that represents the total spread $\sum_n (r^2)_n - (r^2)$ of the Wannier functions in real space, our method proceeds directly from the Bloch functions as represented on a mesh of $k$ points, and carries out the minimization in a space of unitary matrices $U_{mn}$ describing the rotation among the Bloch bands at each $k$ point. The method is thus suitable for use in connection with conventional electronic-structure codes. The procedure also returns the total electric polarization as well as the location of each Wannier center. Sample results for Si, GaAs, molecular C$_2$H$_4$, and LiCl will be presented. [S0163-1829(97)02944-5]

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Computer Physics Communications

N. Marzari

D. Vanderbilt

wannier90: A tool for obtaining maximally-localised Wannier functions

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Maximally localized Wannier functions: Theory and applications

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Exponential Localization of Wannier Functions in Insulators

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(Received 28 June 2006; published 25 January 2007)

The exponential localization of Wannier functions in two or three dimensions is proven for all insulators that display time-reversal symmetry, settling a long-standing conjecture. Our proof relies on the equivalence between the existence of analytic quasi-Bloch functions and the nullity of the Chern numbers (or of the Hall current) for the system under consideration. The same equivalence implies that Chern insulators cannot display exponentially localized Wannier functions. An explicit condition for the reality of the Wannier functions is identified.
Optimization of Wannier functions: Variational Calculus

\[ \tilde{\sigma}_{\parallel,j}^2 = \sigma_{\parallel,j}^2 + \left( \tilde{\nabla}_{\vec{k}} \phi_{\vec{k}} \right)^2 - 2 \tilde{X}_{j,\vec{k}} \cdot \tilde{\nabla}_{\vec{k}} \phi_{\vec{k}} \]

\[ X_{l,j,\vec{k}} = i \int_C w_{j,\vec{k}}(\vec{r}) \frac{\partial u_{j,\vec{k}}(\vec{r})}{\partial k_l} d^n r \]

\[ \tilde{\nabla}_{\vec{k}} \cdot (\tilde{\nabla}_{\vec{k}} \phi_{\vec{k}} - \tilde{X}_{j,\vec{k}}) = 0 \]

\[ \nabla_{\vec{k}}^2 \phi_{\vec{k}} = \tilde{\nabla}_{\vec{k}} \cdot \tilde{X}_{j,\vec{k}} \]

Condensed Matter Physics

\[ \nabla_{\vec{k}}^2 \phi_n(\vec{k}) = \tilde{\nabla}_{\vec{k}} \cdot \tilde{R}_{nk}. \quad (8.61) \]

In general, this is as far as one can go without proceeding to numerical solutions of the Poisson equation, of which examples can be found in Marzari and Vanderbilt (1997). However, in one dimension, one can write immediately

\[ \phi(k) - \phi(0) = \int_0^k dk' \ R_{k'}. \quad (8.62) \]
Solving the Poisson equation through Fourier series

\[ \nabla_k^2 \phi_{\vec{k}} = \vec{\nabla}_{\vec{k}} \cdot \vec{X}_{j,\vec{k}} \]

\[ \phi_{\vec{k}} = \sum_{\vec{R} \in L} \Phi_{\vec{R}} \exp(i \vec{R} \cdot \vec{k}) \]

\[ \vec{X}_{j,\vec{k}} = \sum_{\vec{R} \in L} \vec{X}_{j,\vec{R}} \exp(i \vec{R} \cdot \vec{k}) \]

\[ \vec{X}_{j,\vec{R}} = \frac{1}{V_K} \int_K \vec{X}_{j,\vec{k}} \exp(-i \vec{R} \cdot \vec{k}) d^p k \]

\[ \Phi_{\vec{R}} = -i \frac{\vec{R} \cdot \vec{X}_{j,\vec{R}}}{R^2} \]

\[ \Phi_0 = 0 \]
Maximal localization in the presence of inversion symmetry

\[ \hat{S}_{\vec{v},\vec{v}_0} f(\vec{v}) = f(2\vec{v}_0 - \vec{v}) \]

\[ \psi_{j,-\vec{k}}(2\vec{r}_j - \vec{r}) = s_j \psi_{j,\vec{k}}(\vec{r}) \quad s = \pm 1 \]

\[ w_j(2\vec{r}_j - \vec{r}) = s_j w_j(\vec{r}) \]

\[ \omega_j(\vec{r}) \in \mathbb{R} \]

\[ \sigma_j^2 < \infty \]

\[ \vec{X}_{j,\vec{k}} = 0 \implies \phi_{\vec{k}} = 0 \]

Kohn, 1959 is a particular case!
Generalized Wannier functions (MLWFs)

$$\tilde{\psi}_{j', \vec{k}}(\vec{r}) = \sum_{j \in S} U_{j', j}(\vec{k}) \psi_{j, \vec{k}}(\vec{r})$$

$$U(\vec{k} + \vec{G}) = U(\vec{k})$$

Further energy uncertainty!

$$U(\vec{k})U^\dagger(\vec{k}) = U^\dagger(\vec{k})U(\vec{k}) = I$$

$$\tilde{\Omega}_l = \sum_{l=1}^{p} \tilde{\Omega}_l = \sum_{l=1}^{p} I_l + \sum_{l=1}^{p} P_l$$

$$P_l = \sum_{j' \in S'} \sum_{(j, \vec{R}) \in M' - (j', \vec{0})} |\langle \tilde{w}_{j'} | x_l | \tilde{w}_{j, \vec{R}} \rangle|^2$$

MLWFs in 1D

$$\sum_{(j'', \vec{R}'') \in S} (x_l)_{(j, \vec{R}), (j'', \vec{R}'')} c_{(j'', \vec{R}'')} = \lambda_l c_{j, \vec{R}}$$

$$(x_l)_{(j, \vec{R}), (j'', \vec{R}'')} = \langle w_{j, \vec{R}} | x_l | w_{j'', \vec{R}''} \rangle$$
On the Wannier functions of cumulene

Wannier functions of cumulene: A tight-binding approach

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Keywords carbon chains, cumulene, hybrid orbitals, tight-binding calculations, Wannier functions

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Exponentially localized Wannier functions of cumulene are calculated from the Bloch functions obtained through a tight-binding approach. Numerical results and discussions are given for the \( \pi \) and \( \sigma \) bands. In the latter case, the single-band Wannier functions are similar to the orbitals of a diatomic molecule, while the two-band Wannier functions resemble hybrid atomic orbitals.

Contour plot of an \( sp \)-like Wannier function of cumulene.
On the Wannier functions of cumulene

Confined linear carbon chains as a route to bulk carbyne

Lei Shi¹, Philip Rohringer¹, Kazu Suenaga², Yoshiko Niimi², Jani Kotakoski¹, Jannik C. Meyer¹, Herwig Peterlik¹, Marius Wanko³, Seymur Cahangirov³⁴, Angel Rubio³⁵, Zachary J. Lapin⁶, Lukas Novotny⁶, Paola Ayala¹⁷ and Thomas Pichler¹*
On the Wannier functions of cumulene: tight binding

- Schrödinger equation
- Atomic orbitals
- Tight Binding
- Energy bands and Bloch functions
- Quasi-Bloch functions
- Single-band Wannier functions
- Generalized Wannier functions

\[ X e = \lambda S e \]
On the Wannier functions of cumulene: tight binding

$$\psi_{2s} = \psi_{2,0,0} = \frac{e^{-rZ_{2s}/(2a_B)}}{4\sqrt{2\pi}(a_B/Z_{2s})^3} \left(2 - \frac{Z_{2s}r}{a_B}\right)$$

$$\psi_{2p_0} = \psi_{2,1,0} = \frac{e^{-rZ_{2p}/(2a_B)} r \cos(\theta)}{4\sqrt{2\pi}(a_B/Z_{2p})^5}$$

$Z_{2s} = 3.2166$

$Z_{2p} = 3.1358$
On the Wannier functions of cumulene
On the Wannier functions of cumulene

occupied $p_y$

(a)

(b)

C C C C C C

1.3 Å

x (Å)

Energy (eV)

$\Gamma_2$

$j=2$

$s = p_x$

$X_1$

$\rho_y, \rho_z$

$\Gamma_1$

$j=3, 4$

$j=1$

$s = p_x$

$X_2$

$\Gamma_1$

k ($\pi/a$)

0.0 0.2 0.4 0.6 0.8 1.0
On the Wannier functions of cumulene

\[ s - p_x \]
On the Wannier functions of cumulene

\[ s - p_x \]

![Diagram showing the Wannier functions and energy dispersion](image)
On the Wannier functions of cumulene (TB × DFT)

Kim & Marzari, 2013

Calzolari, 2004
On the Wannier functions of cumulene

generalized $s - p_x$

(a) C C C C C C

1.3 Å

x (Å)

Energy (eV)

0 -10 -20 0.0 0.2 0.4 0.6 0.8 1.0 k (π/a)

$\Gamma_1$

j=1

$s = p_x$

$\rho_{y,z}$

j=3, 4

$\Gamma_2$

j=2

$\Gamma_1$

$X_1$

$X_2$

(b) sp
On the Wannier functions of cumulene

\[ X_{(\beta, \mu, n), (\beta', \mu', n')} = \langle \varphi_\mu(r - (x_\beta + na)e_x) | x | \varphi_{\mu'}(r - (x_{\beta'} + n'a)e_x) \rangle \]

\[ S_{(\beta, \mu, n), (\beta', \mu', n')} = \langle \varphi_\mu(r - (x_\beta + nae_x)) | \varphi_{\mu'}(r - (x_{\beta'} + n'a)e_x) \rangle \]
On the Wannier functions of graphene
On the Wannier functions of graphene (tight binding)
On the Wannier functions of graphene (tight binding)
On the Wannier functions of graphene (PWscf + Wannier functions)

(MARZARI et al., RMP 2012)
Conclusions

The tight binding approximation has been used to successfully generate the maximally localized Wannier functions of **cumulene**:

- $p_y$ band has a Wannier function similar to the **atomic orbital**.

- Lower (upper) $s$- $p_x$ band has a Wannier function resembling bonding (anti-bonding **molecular orbitals**).

- The generalized Wannier function of the pair of $s$- $p_x$ bands are similar to **hybrid atomic orbital**.

- A direct method has been able to produce the generalized Wannier functions.

Partial results have been given for **graphene**.
Thanks!

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