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Local-orbital occupancy formulation of density functional theory: Application to Si, C, and graphene

Y. J. Dappe,[1] R. Oszwaldowski,[2] P. Pou,[1] J. Ortega,[1] R. Pérez,[1] and F. Flores[1]
[1]*Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Spain*
[2]*Institute of Physics, Nicolaus Copernicus University, Department of Physics, ulica Grudziadzka 5, 87-100 Torun, Poland*

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A detailed discussion of the local linear combination of atomic orbitals (LCAO) orbital occupancy (OO) density functional approach, for calculating the total energy and electronic properties of solids, is presented. An approximation to the exchange-correlation energy within the OO approach is discussed to improve the computational efficiency. This exchange-correlation energy is incorporated into an efficient first-principles tight-binding code (FIREBALL) in which the Hartree contribution is also calculated as a function of the orbitals occupancies, combining the advantages of the FIREBALL and LCAO-OO approaches. The calculations performed for Si, diamond, and graphene (lattice parameter, cohesive energy, bulk modulus, and electronic band structure) show the good accuracy of the approximations discussed in the paper and indicate the suitability of the FIREBALL-OO approach for calculating the electronic properties of solids.

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I. INTRODUCTION

Density functional theory[1–3] (DFT) has become the method of choice in condensed matter physics for the prediction of the electronic and geometric structure of molecules, surfaces, and bulk solids. DFT shows that the total energy of this complicated many-body problem can be calculated solely in terms of the electron charge density. This charge density can be determined from an auxiliary one-body problem, where a single particle moves in an effective potential due to all the other electrons.[4] Thus, DFT provides, in principle, an exact mapping of the problem of a strongly interacting electron system (in the presence of the nuclei) onto that of a one-body problem. However, the effective potential, in particular the so called exchange-correlation (XC) potential, is not known exactly and approximations are needed. The simplicity and wide applicability of DFT rests on the continuous research effort in the development of approximate XC functionals with improved properties, with the goal of reaching chemical accuracy. Generalized gradient approximations[5] (GGAs) and meta-GGAs, where the charge density and some of its derivatives are included in the XC functional, are a significant step in this direction, correcting many of the deficiencies of the commonly used local density approximation[6] (LDA), in particular the overestimation of cohesive energies and energy barriers, that was limiting its massive application in the field of computational chemistry.

Although the solution of the effective one-body problem has been traditionally implemented in extended basis sets, like plane waves, local orbital basis sets have been used to improve significantly the computational performance of electronic structure calculations.[7–21] Among their many fundamental advantages, order-N algorithms can be easily implemented in a local-orbital framework (see, e.g., Refs. 22–24). Apart from the use of atomiclike orbitals, that is common to all these methods, in many of these approaches further approximations are made, with the purpose of increasing the computational efficiency, with as little loss of accuracy as possible. Following this idea, efficient first-principles tight-binding (TB) molecular dynamics methods,[25] like the FIREBALL code,[17–20] have been developed, whose main characteristics are (1) a real-space technique (i.e., no need for supercells or grids), (2) a reduced set of optimized atomiclike orbitals as basis set, and (3) efficient, two-dimensional, tabulation-interpolation schemes to obtain the effective TB Hamiltonian matrix elements as well as their derivatives to obtain the forces. One of the main difficulties to overcome in these methods is the efficient calculation of XC contributions to the Hamiltonian and total energy.[15,20]

Local-orbital schemes are also the natural playground for models, like the Anderson or Hubbard Hamiltonians, which have been used to describe systems where electron correlation effects are so important that the band picture, implicit in all the approaches described above, breaks down. The established methods in this field are based on Green's functions and self-energies which are naturally written in terms of local orbitals. This reflects the fact that the more important contributions to the correlation energy come from the local intrasite terms, an idea exploited in the dynamic mean-field method[26] (DMF), that is becoming one of the key tools for improving our understanding of these correlated systems. Orbital occupancies are the natural variables in these schemes, as exemplified by the DMF, where the essential idea is to replace a lattice model by a single-site impurity problem embedded in an effective medium determined self-consistently.

Traditionally these two fields, electronic structure calculations based on DFT for realistic materials and sophisticated many-body techniques applied to model Hamiltonians, appear as two completely different, even opposite, approaches to the electronic properties of the system. However, once the electronic structure calculations are formulated in terms of local orbitals several connections between the two approaches can be naturally established. The orbital occupancy (OO) method[27,28] discussed in this paper combines the natural advantages of these two approaches by expressing the energy and potentials in terms of the orbital occupancies $\{n_{\mu\sigma}\}$. These $\{n_{\mu\sigma}\}$ are the inherent variables of generalized

Hubbard Hamiltonians, from which our exchange-correlation energies are derived. This formalism allows us to include in a natural way the many-body corrections (with significant improvements on some basic deficiencies of standard XC implementations like the self-interaction correction[29]), while maintaining the calculational simplicity. This method is based on an alternative approach to DFT, in which instead of the electronic density $\rho(\vec{r})$ we use the orbital occupancies $\{n_{\mu\sigma}\}$ as the central quantity:

$$\rho(\vec{r}) \Rightarrow \{n_{\mu\sigma}\}. \tag{1}$$

The usual DFT is based on the Hohenberg-Kohn theorem.[1] This theorem can be rewritten in terms of $\{n_{\mu\sigma}\}$ (see Refs. 28 and 30), with the total energy as a function of the orbital occupancies, $E=E[\{n_{\mu\sigma}\}]$; then, the energy of the ground state is found at the minimum of the function. In a similar way to the Kohn-Sham equations[4] in the ρ-based DFT, we introduce an effective Hamiltonian $\hat{H}_{\text{eff}}$ using orbital-dependent potentials:

$$V^{\text{mb}}_{\mu\sigma} = \frac{\partial E^{\text{mb}}[\{n_{\nu\sigma}\}]}{\partial n_{\mu\sigma}}, \tag{2}$$

where E^{mb} is the many-body energy associated with the electron-electron interaction; the $\{n_{\mu\sigma}\}$ are determined self-consistently from $\hat{H}_{\text{eff}}$. In similarity with the standard DFT, it is not possible in general to find an analytical expression for the exact exchange-correlation energy $E^{\text{XC}}[\{n_{\nu\sigma}\}]$, but accurate approximations can be developed.

The purpose of this paper is to present recent advances in the OO method. First, we provide a full account of its theoretical basis, with a detailed explanation of how the different contributions to the total energy, and in particular the exchange-correlation terms, can be written in terms of the orbital occupancies. This complete analysis, presented in Sec. II, is based on different ideas covered individually in previous papers.[27–29,31,32] We should stress that this one-electron solution (with $V^{\text{XC}}[\{n_{\nu\sigma}\}]$) facilitates the description of electron correlated effects and it can be used as a starting point for the many-body calculations needed to properly describe strongly correlated systems.[31] Then, we show in Sec. III how this linear combination of atomic orbitals (LCAO) OO approach, applicable in principle to any scheme based on a local-orbital basis, can be implemented within the framework of the FIREBALL code.[17–20] Finally, we discuss a practical simplification of our expression for the exchange energy, that reduces significantly the computational burden, that is one of the possible limitations of this and other approaches (like exact-exchange methods) where an improved description of exchange is attempted. In this paper we have chosen to analyze the case of well-known crystals like Si, diamond, and graphene; although we believe that the main advantage of our LCAO-OO approach appears for analyzing the cases of strongly correlated systems, it is in order to check first that we recover the well-known solutions of those conventional crystals. In particular, our analysis shows that our treatment of exchange and correlation represents a substantial improvement upon DF-LD approximations. Moreover, our results of Sec. IV also show that the FIREBALL-OO approach provides an accurate and efficient alternative for the calculation of the electronic and structural properties of solids.

II. BASIC FORMULATION, LCAO-OO HAMILTONIAN, HARTREE, EXCHANGE, AND CORRELATION ENERGIES

We follow Ref. 27 and start from the general Hamiltonian

$$\hat{H}_0 = \sum_{i\mu\sigma} (\varepsilon_{i\mu} + V^{\text{PS}}_{i\mu,i\mu})\hat{n}_{i\mu\sigma} + \sum_{\substack{i\mu\sigma,j\nu\sigma\\ j\nu\neq i\mu}} (t_{i\mu,j\nu} + V^{\text{PS}}_{i\mu,j\nu})\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma} + \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma\\ k\lambda\sigma',l\omega\sigma'}} O^{i\mu j\nu}_{l\omega k\lambda}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{j\nu\sigma'}\hat{c}_{k\lambda\sigma'}\hat{c}_{l\omega\sigma} \tag{3}$$

where a Löwdin orthogonal basis $\phi_{i\mu}=\Sigma_{j\nu}(S^{-1/2})_{i\mu j\nu}\psi_{j\nu}$ has been used as the basis set to define the operators $\hat{c}^{\dagger},\hat{c}$ and $\hat{n}=\hat{c}^{\dagger}\hat{c}$; $S_{i\mu j\nu}=\langle\psi_{i\mu}|\psi_{j\nu}\rangle$ is the orbital overlap and $\psi_{i\mu}$ is the local basis set (atomiclike) which is going to be used in our LCAO-OO method, i indicating an atom and μ an orbital. In Eq. (3), $\varepsilon_{i\mu}+V^{\text{PS}}_{i\mu,i\mu}$ and $t_{i\mu,j\nu}+V^{\text{PS}}_{i\mu,j\nu}$ define the one-electron terms of our initial Hamiltonian [with the pseudopotential (PS) contributions included], and $O^{i\mu j\nu}_{l\omega k\lambda}$ is the many-body term:

$$O^{i\mu j\nu}_{l\omega k\lambda} = \int \phi_{i\mu}(\vec{r})\phi_{j\nu}(\vec{r}\,')\frac{1}{|\vec{r}-\vec{r}\,'|}\phi_{k\lambda}(\vec{r}\,')\phi_{l\omega}(\vec{r})d^3r\, d^3r'. \tag{4}$$

Equation (3) is still completely general; the LCAO-OO Hamiltonian analyzed here in more detail and introduced in Ref. 27 reads as follows:

$$\begin{aligned}\hat{H}_0 = {} & \sum_{i\mu\sigma} (\varepsilon_{i\mu} + V^{\text{PS}}_{i\mu,i\mu})\hat{n}_{i\mu\sigma} + \sum_{\substack{i\mu\sigma,j\nu\sigma\\ j\nu\neq i\mu}} (t_{i\mu,j\nu} + V^{\text{PS}}_{i\mu,j\nu})\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma}\\ & + \frac{1}{2}\sum_{\substack{i\mu\sigma,i\nu\sigma'\\ (i\nu\sigma'\neq i\mu\sigma)}} U_{i\mu,i\nu}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{i\nu\sigma'}\hat{c}_{i\nu\sigma'}\hat{c}_{i\mu\sigma}\\ & + \frac{1}{2}\sum_{\substack{i\mu\sigma,\nu\sigma'\\ \nu\sigma'\neq\mu\sigma}} U^{x}_{i\mu,i\nu}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{i\nu\sigma'}\hat{c}_{i\mu\sigma'}\hat{c}_{i\nu\sigma}\\ & + \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma'\\ (j\neq i)}} J_{i\mu,j\nu}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{j\nu\sigma'}\hat{c}_{j\nu\sigma'}\hat{c}_{i\mu\sigma}\\ & + \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma'\\ (j\neq i)}} J^{x}_{i\mu,j\nu}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{j\nu\sigma'}\hat{c}_{i\mu\sigma'}\hat{c}_{j\nu\sigma}\\ & + \sum_{\substack{i\mu\sigma,j\nu\sigma\\ k\lambda\sigma'\\ (j\nu\neq i\mu)\\ (k\lambda\sigma'\neq i\mu\sigma,j\nu\sigma)}} h_{k\lambda,i\mu j\nu}\hat{c}^{\dagger}_{k\lambda\sigma'}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma}\hat{c}_{k\lambda\sigma'}\end{aligned}$$

$$+ \sum_{\substack{i\mu\sigma,j\nu\sigma \\ k\lambda\sigma' \\ (j\nu\neq i\mu) \\ (k\lambda\sigma'\neq i\mu\sigma,j\nu\sigma)}} h^{x}_{k\lambda,i\mu j\nu}\hat{c}^{\dagger}_{k\lambda\sigma}\hat{c}^{\dagger}_{i\mu\sigma'}\hat{c}_{k\lambda\sigma'}\hat{c}_{j\nu\sigma}$$

$$+ \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma \\ k\lambda\sigma',l\omega\sigma' \\ \text{all different}}}^{}{}^{(\text{NN})} O^{i\mu j\nu}_{l\omega k\lambda}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{j\nu\sigma}\hat{c}_{k\lambda\sigma'}\hat{c}_{l\omega\sigma'}. \tag{5}$$

In this approximation, the many-body terms are written explicitly showing the contributions depending on one, two, three, or four orbitals. The different values U, J, U^{x}, J^{x}, h, h^{x}, and O can be explicitly found using Eq. (4) and the indices indicated for each case. In particular, $U_{i\mu,i\nu}$ and $U^{x}_{i\mu,i\nu}$ are associated with the interaction between electrons in the same atom i; $J_{i\mu,j\nu}$ and $J^{x}_{i\mu,j\nu}$ define part of the interaction between two orbitals in different atoms i and j; and $h_{k\lambda,i\mu j\nu}$ defines for $k\lambda = i\mu$ or $j\nu$ the rest of the interaction between two orbitals in atoms i and j while, for $k\lambda \neq i\mu$ or $j\nu$, it defines in combination with $h^{x}_{k\lambda,i\mu j\nu}$ the interaction between the three orbitals $k\lambda$, $i\mu$, and $j\nu$. We stress that terms varying like $\hat{c}^{\dagger}_{k\lambda\sigma}\hat{c}^{\dagger}_{k\lambda\sigma'}\hat{c}_{i\mu\sigma'}\hat{c}_{j\nu\sigma}$ or $\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{j\nu\sigma'}\hat{c}_{k\lambda\sigma'}\hat{c}_{k\lambda\sigma}$ have been neglected in Hamiltonian $\hat{H}_0$; this has been checked in our calculations to be a fair approximation to Hamiltonian (4), an expected result considering that their Hartree-Fock mean values are an order of magnitude smaller than the mean values of the terms included in Eq. (5), when the overlap between orbitals, S, is used as an expansion parameter (see Ref. 33 for a discussion of this point). Finally, in the term $O^{i\mu j\nu}_{l\omega k\lambda}$ we have included four different orbitals $i\mu$, $j\nu$, $l\omega$, and $k\lambda$, only if they all belong to either one atom or two nearest-neighbor (NN) atoms (this approximation is also validated by the calculations presented below; in practice, it means that the dipole-dipole interactions can be important for NN atoms). It is worth mentioning at this point that the Hamiltonian (5) can be easily generalized to include van der Waals forces keeping in Eq. (5) the appropriate $O^{i\mu j\nu}_{l\omega k\lambda}$ terms (see Ref. 34 for a discussion of this point).

Hartree, exchange, and correlation energies

$\hat{H}_0$ is our basic LCAO-OO Hamiltonian. The Hartree and exchange contributions to the energy of the system can be easily obtained by calculating the mean value of its different terms in a conventional way. The Hartree contribution is given by (we define $n_{i\mu\sigma} = \langle 0|\hat{n}_{i\mu\sigma}|0\rangle$ and $n_{i\mu j\nu,\sigma} = \langle 0|\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma}|0\rangle$, $|0\rangle$ as the ground state of the system)

$$E^{h} = \sum_{i\mu\sigma}(\varepsilon_{i\mu} + V^{\text{PS}}_{i\mu,i\mu})n_{i\mu\sigma} + \sum_{\substack{i\mu\sigma,j\nu\sigma \\ j\nu\neq i\mu}}(t_{i\mu,j\nu} + V^{\text{PS}}_{i\mu,j\nu})n_{i\mu j\nu,\sigma}$$

$$+ \frac{1}{2}\sum_{i\mu\sigma,i\nu\sigma'} U_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma'} + \frac{1}{2}\sum_{\substack{i\mu\sigma,i\nu\sigma' \\ \nu\neq\mu}} U^{x}_{i\mu,\nu}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma'}$$

$$+ \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma' \\ (j\neq i)}} J_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma'} + \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma' \\ (j\neq i)}} J^{x}_{i\mu,j\nu}n_{i\mu j\nu,\sigma}n_{j\nu i\mu,\sigma'}$$

$$+ \sum_{\substack{i\mu,j\nu\sigma \\ k\lambda\sigma' \\ (j\nu\neq i\mu) \\ (k\lambda\sigma'\neq i\mu,j\nu\sigma)}} h_{k\lambda,i\mu j\nu}n_{k\lambda\sigma'}n_{i\mu j\nu,\sigma}$$

$$+ \sum_{\substack{i\mu,j\nu\sigma \\ k\lambda\sigma' \\ (j\nu\neq i\mu) \\ (k\lambda\sigma'\neq i\mu,j\nu\sigma)}} h^{x}_{k\lambda,i\mu j\nu}n_{k\lambda j\nu,\sigma}n_{i\mu k\lambda,\sigma'}$$

$$+ \frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma \\ k\lambda\sigma',l\omega\sigma' \\ \text{all different}}} O^{i\mu j\nu}_{l\omega k\lambda}n_{i\mu l\omega\sigma}n_{j\nu k\lambda\sigma'}; \tag{6}$$

this energy is obtained by contracting the operators $\hat{c}^{\dagger}$ and $\hat{c}$ of Eq. (5) having the same spin, and eliminating any restriction on the spins; in this way, we introduce some self-interaction terms that we discuss below. Notice also that the restrictions on the indices introduced in Eq. (6) guarantee that there is no term repeated; for instance, in $J_{i,j}$, the condition $i\neq j$ avoids a U term already introduced before. The exchange contribution to the energy is obtained by contracting the operators $\hat{c}^{\dagger}_{\sigma}$ and $\hat{c}_{\sigma'}$ (taking $\sigma=\sigma'$) and, at the same time, subtracting those (self-interaction) terms that appear in Eq. (6) even if the commutation rules for $\hat{c}^{\dagger}$ and $\hat{c}$ forbid them to contribute to the Hartree energy [for instance, in $\frac{1}{2}\Sigma_{i\mu\sigma,\nu\sigma'}U_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma'}$, the term with $\sigma=\sigma'$ and $\mu=\nu$ does not contribute to the energy as can be seen by inspection of Eq. (5) since $\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}^{\dagger}_{i\mu\sigma}=\hat{c}_{i\nu\sigma}\hat{c}_{i\nu\sigma}=0$]. This yields the following exchange energy:

$$E^{x} = -\frac{1}{2}\sum_{i\mu\sigma} U_{i\mu,\mu}n_{i\mu\sigma}n_{i\mu\sigma} - \frac{1}{2}\sum_{\substack{i\mu,\nu\sigma \\ \nu\neq\mu}} U_{i\mu,\nu}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma}$$

$$- \frac{1}{2}\sum_{\substack{i\mu,\nu\sigma \\ \nu\neq\mu}} U^{x}_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma} - \frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma \\ (j\neq i)}} J_{i\mu,j\nu}n_{i\mu j\nu,\sigma}n_{j\nu i\mu,\sigma}$$

$$- \frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma \\ (j\neq i)}} J^{x}_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma} - \sum_{\substack{i\mu,j\nu\sigma \\ j\nu\neq i\mu}}(h_{i\mu,i\mu j\nu}n_{i\mu\sigma}n_{i\mu j\nu,\sigma}$$

$$+ h_{j\nu,i\mu j\nu}n_{j\nu\sigma}n_{i\mu j\nu,\sigma}) - \sum_{\substack{i\mu,j\nu\sigma \\ k\lambda \\ (j\nu\neq i\mu) \\ (k\lambda\neq i\mu,j\nu)}} h_{k\lambda,i\mu j\nu}n_{i\mu k\lambda,\sigma}n_{k\lambda j\nu,\sigma}$$

$$- \sum_{\substack{i\mu,j\nu\sigma \\ k\lambda \\ (j\nu\neq i\mu) \\ (k\lambda\neq i\mu,j\nu)}} h^{x}_{k\lambda,i\mu j\nu}n_{k\lambda\sigma}n_{i\mu j\nu,\sigma}$$

$$- \frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma \\ k\lambda,l\omega \\ \text{all different}}} O^{i\mu j\nu}_{l\omega k\lambda}n_{i\mu l\omega,\sigma}n_{j\nu k\lambda,\sigma}. \tag{7}$$

In this equation, $-\frac{1}{2}\Sigma_{i\mu\sigma}U_{i\mu,\mu}n_{i\mu\sigma}n_{i\mu\sigma}$ is the self-interaction correction for the electron $i\mu$, while $-\Sigma_{\substack{i\mu,j\nu\sigma \\ j\nu\neq i\mu}}(h_{i\mu,i\mu j\nu}n_{i\mu\sigma}n_{i\mu j\nu,\sigma}+h_{j\nu,i\mu j\nu}n_{j\nu\sigma}n_{i\mu j\nu,\sigma})$ is also a self-interaction correction associated with the hopping

$h_{k\lambda,i\mu j\nu}n_{k\lambda\sigma}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma}$; the other terms $-\frac{1}{2}U_{i\mu,\nu}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma}$, $-\frac{1}{2}U^{x}_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma}$, $-\frac{1}{2}J_{i\mu,j\nu}n_{i\mu j\nu,\sigma}n_{j\nu i\mu,\sigma}$, $-\frac{1}{2}J^{x}_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma}$, $-h_{k\lambda,i\mu j\nu}n_{i\mu k\lambda,\sigma}n_{k\lambda j\nu,\sigma}$, $-h^{x}_{k\lambda,i\mu j\nu}n_{k\lambda\sigma}n_{i\mu j\nu,\sigma}$, and $-\frac{1}{2}O^{i\mu j\nu}_{l\omega k\lambda}n_{i\mu l\omega,\sigma}n_{j\nu k\lambda,\sigma}$ come from contracting $\hat{c}^{\dagger}_{\sigma}$ and $\hat{c}_{\sigma'}$, taking $\sigma=\sigma'$.

E^{x} can be written in a more convenient way with the following arguments.

(a) Terms associated with $U_{i\mu,\nu}$ and $J_{i\mu,j\nu}$ in E^{x}. The contribution $-\frac{1}{2}\sum_{\substack{i\mu,\nu\sigma\\ \nu\neq\mu}}U_{i\mu,\nu}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma}-\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}}J_{i\mu,j\nu}n_{i\mu j\nu,\sigma}\times n_{j\nu i\mu,\sigma}$ can be written as follows:[33]

$$-\frac{1}{2}\sum_{\substack{i\mu,\nu\sigma\\ \nu\neq\mu}}U_{i\mu,\nu}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma}-\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}}J_{i\mu,j\nu}n_{i\mu j\nu,\sigma}n_{j\nu i\mu,\sigma}$$
$$=-\frac{1}{2}\sum_{i\mu,\sigma}J^{\mathrm{eff}}_{i\mu\sigma}n_{i\mu\sigma}(1-n_{i\mu\sigma}) \tag{8}$$

using the identity $\sum_{j\nu(\neq i\mu)}n_{i\mu j\nu,\sigma}n_{j\nu i\mu,\sigma}=n_{i\mu\sigma}(1-n_{i\mu\sigma})$. This means that the charge $n_{i\mu\sigma}$ interacts with the hole $1-n_{i\mu\sigma}$ via the effective interaction $J^{\mathrm{eff}}_{i\mu\sigma}$. Part of this hole, say $x_i(1-n_{i\mu\sigma})$, is localized in the atom i (and is associated with the contribution $\sum_{\nu(\neq\mu)}n_{i\mu i\nu,\sigma}n_{i\nu i\mu,\sigma}$), while the fraction $(1-x_i)(1-n_{i\mu\sigma})$ is localized outside the atom. This means that Eq. (8) can also be rewritten as

$$-\frac{1}{2}\sum_{i\mu,\sigma}J^{\mathrm{eff}}_{i\mu\sigma}n_{i\mu\sigma}(1-n_{i\mu\sigma})=-\frac{1}{2}\sum_{i\mu\sigma}x_i\tilde{U}_{i\sigma}n_{i\mu\sigma}(1-n_{i\mu\sigma})$$
$$-\frac{1}{2}\sum_{i\mu\sigma}(1-x_i)J_{i\sigma}n_{i\mu\sigma}(1-n_{i\mu\sigma}) \tag{9}$$

where $\tilde{U}_i$ is the mean value of U for the atom i, and $J_{i\sigma}$ the mean interaction between $n_{i\mu\sigma}$ and the hole $(1-x_i)n_{i\mu\sigma}$ localized outside the atom in such a way that $J^{\mathrm{eff}}_{i\mu\sigma}=x_i\tilde{U}_{i\sigma}+(1-x_i)J_{i\sigma}$. In this paper we will consider systems for which $x_i=0$ due to their symmetry; then $J^{\mathrm{eff}}_{i\mu\sigma}$ is practically the spin-independent interaction (we only consider here nonmagnetic systems) between NN orbitals.[32] The rest of the hole, $n_{i\mu\sigma}$, is associated with the self-interaction correction $-\frac{1}{2}\sum_{i\mu\sigma}U_{i\mu,\mu}n_{i\mu\sigma}n_{i\mu\sigma}$.

Then, terms in $U_{i\mu,\mu}$ and $J_{i\mu,j\nu}$ can be written as follows:

$$-\frac{1}{2}\sum_{i\mu,\sigma}\{U_{i\mu,\mu}n_{i\mu,\sigma}+J^{\mathrm{eff}}_{i\mu}(1-n_{i\mu\sigma})\}n_{i\mu\sigma}. \tag{10}$$

(b) Terms associated with $h_{k\lambda,i\mu j\nu}$. The terms associated with $h_{k\lambda,i\mu j\nu}$, $h_{i\mu,i\mu j\nu}$, and $h_{j\nu,i\mu j\nu}$ can be written as

$$-\sum_{\substack{i\mu,j\nu\\ k\lambda\sigma\\ (j\nu\neq i\mu)}}h_{k\lambda,i\mu j\nu}n_{i\mu k\lambda,\sigma}n_{k\lambda j\nu,\sigma}. \tag{11}$$

Noticing that $\sum_{k\lambda}n_{i\mu k\lambda,\sigma}n_{k\lambda j\nu,\sigma}=n_{i\mu j\nu,\sigma}$ allows us to define an effective spin-independent $h^{\mathrm{eff}}_{i\mu,j\nu}$ such that[32]

$$-\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda\\ (j\nu\neq i\mu)}}h_{k\lambda,i\mu j\nu}n_{i\mu k\lambda,\sigma}n_{k\lambda j\nu,\sigma}=-\sum_{\substack{i\mu,j\nu\sigma\\ (j\nu\neq i\mu)}}h^{\mathrm{eff}}_{i\mu,j\nu}n_{i\mu j\nu,\sigma}. \tag{12}$$

In this equation, $h^{\mathrm{eff}}_{i\mu,j\nu}$ is the effective hopping integral created by the hole of one electron upon the $i\mu j\nu$ bond, $h^{\mathrm{eff}}_{i\mu,j\nu}\hat{c}^{\dagger}_{i\mu\sigma}\hat{c}_{j\nu\sigma}$; $h^{\mathrm{eff}}_{i\mu,j\nu}$ is obtained from Eq. (12), calculating $n_{i\mu j\nu,\sigma}$ from the self-consistent Hamiltonian. In practice, $h^{\mathrm{eff}}_{i\mu,j\nu}$ is an average of $h_{i\mu,i\mu j\nu}$ and $h_{j\nu,i\mu j\nu}$.

Combining Eqs. (7), (10), and (12), we can rewrite E^{x} as follows:

$$E^{x}=-\frac{1}{2}\sum_{i\mu,\sigma}\{U_{i\mu,\mu}n_{i\mu,\sigma}+J^{\mathrm{eff}}_{i\mu}(1-n_{i\mu\sigma})\}n_{i\mu\sigma}$$
$$-\frac{1}{2}\sum_{\substack{i\mu,\nu\sigma\\ \nu\neq\mu}}U^{x}_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma}-\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}}J^{x}_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma}$$
$$-\sum_{\substack{i\mu,j\nu\sigma\\ (j\nu\neq i\mu)}}h^{\mathrm{eff}}_{i\mu,j\nu}n_{i\mu j\nu,\sigma}-\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda\\ (j\nu\neq i\mu)\\ (k\lambda\neq i\mu,j\nu)}}h^{x}_{k\lambda,i\mu j\nu}n_{k\lambda\sigma}n_{i\mu j\nu,\sigma}$$
$$-\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda,l\omega\\ \text{all different}}}O^{i\mu j\nu}_{l\omega k\lambda}n_{i\mu l\omega,\sigma}n_{j\nu k\lambda,\sigma}. \tag{13}$$

We should stress that, in the extended systems we are going to consider $J^{\mathrm{eff}}_{i\mu}$ can be approximated by $J_{i\mu}$, the interaction between electrons in nearest-neighbor atoms, if $0.1\leq n_{i\mu\sigma}\leq 0.9$;[28] for $n_{i\mu\sigma}\rightarrow 0$ (or $n_{i\mu\sigma}\rightarrow 1$), $J^{\mathrm{eff}}_{i\mu}$ behaves like $n^{1/3}_{i\mu\sigma}$ [or $(1-n_{i\mu\sigma})^{1/3}$] (see Ref. 28), yielding the conventional LDA limit. In reduced systems, like diatomic molecules, $J^{\mathrm{eff}}_{i\mu}$ is exactly $J_{i\mu}$; for instance, in H_2 taking one s orbital per atom E^{x} can be written as follows:

$$E^{x}[H_2]=-\frac{1}{2}\sum_{i\mu,\sigma}\{U_{i\mu,\mu}n_{i\mu,\sigma}+J_{i\mu}(1-n_{i\mu\sigma})\}n_{i\mu\sigma}$$
$$-\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}}J^{x}_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma}-\sum_{i\mu,j\nu\sigma}h^{0}_{i\mu,j\nu}n_{i\mu j\nu,\sigma} \tag{14}$$

where $h^{0}_{i\mu,j\nu}$ is the hopping integral one electron in orbital $i\mu=1s$ creates between the two $1s$ orbitals of the molecule.

Finally we discuss our approximation to the correlation energy. Following Ref. 27, we obtain the correlation energy of $\hat{H}_0$, by analyzing the generalized Hubbard terms

$$\frac{1}{2}\sum_{\substack{i\mu\sigma,\nu\sigma'\\ (\mu\sigma\neq\nu\sigma')}}U_{i\mu,\nu}\hat{n}_{i\mu\uparrow}\hat{n}_{i\mu\downarrow}+\frac{1}{2}\sum_{\substack{i\mu\sigma,j\nu\sigma'\\ (j\neq i)}}J_{i\mu,j\nu}i\hat{n}_{i\mu\sigma}\hat{n}_{j\nu\sigma'}. \tag{15}$$

As discussed in Ref. 27, the correlation energy associated with these terms is the following:

$$E^c = -\frac{1}{2}\sum_{i\mu\sigma} f_{i\mu}(\tilde{U}_{i\mu} - J^{\text{eff}}_{i\mu}) n_{i\mu\sigma}(1 - n_{i\mu\sigma}) \qquad (16)$$

where $\tilde{U}_{i\mu}$ and $J^{\text{eff}}_{i\mu}$ have been defined above [Eq. (9)]; we interpret Eq. (16) as the energy associated with a modification of the exchange hole (now exchange-correlation hole) whereby a fraction $f_{i\mu}(1-n_{i\mu\sigma})$ of the exchange hole, $(1-n_{i\mu\sigma})$, is transferred to the atom i [which depends[27] also on $n_{i\mu\sigma}(1-n_{i\mu\sigma})$]. In Eq. (16), $\tilde{U}_{i\mu}$ is an average of the intra-atomic interactions,[27] while $f_{i\mu}$ $(f_{i\mu} \leq 1)$ is a function of $\tilde{U}_{i\mu} - J^{\text{eff}}_{i\mu}$ and the self-consistent charges $n_{i\mu\sigma}$ (see Ref. 27 for an equation defining $f_{i\mu}$). Equations (6), (13), and (16) define our Hartree, exchange, and correlation energies within our LCAO-OO approach.

III. FIREBALL-OO APPROACH

Our LCAO-OO method, through Eqs. (6), (13), and (16), defines the many-body interactions we have to introduce in our problem. Although this is a straightforward picture, we should say that the main problem it presents for its friendly implementation (e.g., molecular dynamics) is the calculation of the different parameters appearing in these equations, ϵ, t, U, U^x, J, J^x, h, h^x, and O, as functions of the particular structure one considers. In this paper, we discuss two simplifications we introduce to that problem: (i) In a first step we analyze the Hartree energy of our system using the approximations introduced in the FIREBALL code[17–20] (an efficient DFT tight-binding molecular dynamics technique); (ii) in a second step, we will show how the exchange energy given by Eq. (13) can be approximated by a simpler equation.

Regarding the first step, we should say that in this paper we are going to use the FIREBALL picture. This means taking local orbitals with a given cutoff in distance,[17] and a self-consistent version, in terms of the orbital occupancies $\{n_{i\mu\sigma}\}$,[18] of the Harris-functional approach[7,8] for calculating the Hartree energy. All these FIREBALL ingredients amount to taking the following approximations.

(a) Calculate the one-electron terms, say $T\{n\}$ and the Hartree energy $E^h\{n\}$, using a FIREBALL code (subtracting the exchange-correlation terms).

(b) Then, calculate the exchange-correlation energies with Eqs. (13) and (16), which is equivalent to introducing in the one-electron Schrödinger equations the following local exchange-correlation potential $V^{\text{XC}}_{i\mu\sigma}\{n\}$:

$$V^{\text{XC}}_{i\mu\sigma}\{n\} = \frac{\partial E^x\{n\}}{\partial n_{i\mu\sigma}} + \frac{\partial E^c\{n\}}{\partial n_{i\mu\sigma}}. \qquad (17)$$

Then, the effective one-electron Hamiltonian, whose self-consistent solution yields $n_{i\mu\sigma}$, is defined by

$$\hat{H}^{\text{eff}} = \hat{H}^h + \sum_{i\mu\sigma} V^{\text{XC}}_{i\mu\sigma}\hat{n}_{i\mu\sigma} \qquad (18)$$

where $\hat{H}^h$ represents the Hartree part of the Hamiltonian,

$$\hat{H}^h = \hat{T} + \hat{V}^{\text{PS}} + \hat{V}^h \qquad (19)$$

($\hat{T}$ represents the kinetic energy, $\hat{V}^{\text{PS}}$ the ionic pseudopotential, and $\hat{V}^h$ the electron-electron Hartree potential), which, in the rest of the paper, is going to be calculated using the FIREBALL approach. In this approach an *input* electron density $\rho_{\text{in}}(\vec{r})$, a sum of atomiclike densities, is introduced,

$$\rho_{\text{in}}(\vec{r}) = \sum_{i\mu\sigma} n_{i\mu\sigma}|\psi_{i\mu}(\vec{r})|^2, \qquad (20)$$

where $\{\psi_{i\mu}\}$ are the atomiclike fireball orbitals[17] that define our basis set, and $\{n_{i\mu\sigma}\}$ are the orbital occupation numbers for the Löwdin-orthogonalized orbitals $\{\phi_{i\mu}\}$ associated with the $\{\psi_{i\mu}\}$ basis set, which are determined in a self-consistent fashion.[18] This procedure is introduced for reasons of computational efficiency, and is justified by the fact that $\{\phi_{i\mu}\}$ is the set of orthonormal orbitals that are closest to the original nonorthogonal orbitals $\{\psi_{i\mu}\}$ in a least-square sense.[35] The electron-electron potential $\hat{V}^h$ is

$$\hat{V}^h(\vec{r}) = \int \frac{\rho_{\text{in}}(\vec{r}\,')d^3r'}{|\vec{r} - \vec{r}\,'|}. \qquad (21)$$

The double-counting correction to the total energy is also written in terms of ρ_{in}:

$$E_{dc} = -\frac{1}{2}\int\int \frac{\rho_{\text{in}}(\vec{r})\rho_{\text{in}}(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\, d\vec{r}\,'. \qquad (22)$$

A. Treatment of the FIREBALL-OO Hamiltonian

In Eq. (17), the main problem appears for calculating $\partial/\partial n_{i\mu\sigma}$ in all the terms of Eq. (13); in Ref. 27, the exchange potential $V^x_{i\mu\sigma}$, was calculated in the following way. First, we write

$$E^x = E^x_0 + \tilde{E}^x \qquad (23)$$

where

$$E^x_0 = -\frac{1}{2}\sum_{i\mu\sigma}\{U_{i\mu,\mu}n_{i\mu\sigma} + J^{\text{eff}}_{i\mu}(1 - n_{i\mu\sigma})\}n_{i\mu\sigma} - \frac{1}{2}\sum_{\substack{i\mu,\nu\sigma\\ \nu\neq\mu}} U^x_{i\mu,\nu}n_{i\mu\sigma}n_{i\nu\sigma} \qquad (24)$$

and

$$\tilde{E}^x = -\sum_{\substack{i\mu,j\nu\sigma\\ (j\nu\neq i\mu)}} h^{\text{eff}}_{i\mu,j\nu}n_{i\mu j\nu,\sigma} - \sum_{\substack{i\mu,j\nu\sigma\\ k\lambda\\ (j\nu\neq i\mu)\\ (k\lambda\neq i\mu,j\nu)}} h^x_{k\lambda,i\mu j\nu}n_{k\lambda\sigma}n_{i\mu j\nu,\sigma} - \frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}} J^x_{i\mu,j\nu}n_{i\mu\sigma}n_{j\nu\sigma} - \frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda,l\omega\\ \text{all different}}} O^{i\mu j\nu}_{l\omega k\lambda}n_{i\mu l\omega,\sigma}n_{j\nu k\lambda,\sigma}. \qquad (25)$$

Then, we approximate E^x by E^x_0, neglecting $\tilde{E}^x$. This is rea-

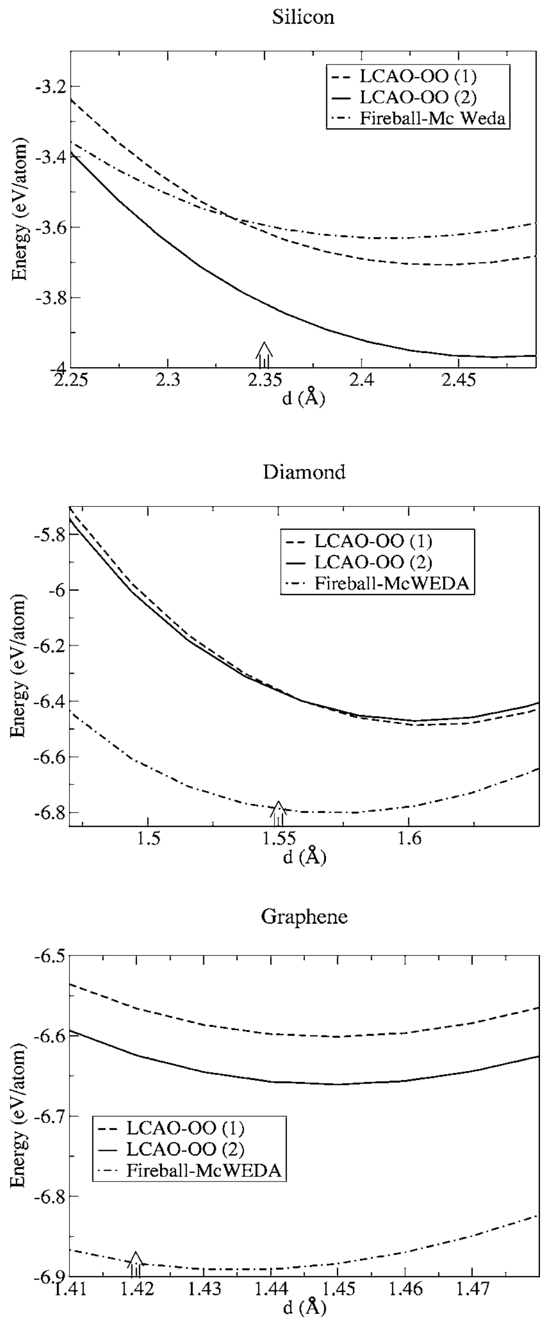

FIG. 1. Cohesive energies for Si, diamond, and graphene as a function of the NN distance. Different results correspond to LCAO-OO (1 and 2) and FIREBALL-MCWeda calculations (see text). The arrows indicate the experimental position minimum.

sonable because the terms neglected in $\tilde{E}^x$ are small compared with the ones included (see below); in the cases discussed below, it is also a good approximation to take $J^{\mathrm{eff}}_{i\mu} \approx J_{i\mu}$ (nearest-neighbor interaction). $E^x = \tilde{E}^x_0$ is used together with Eq. (21), to calculate $n_{i\mu\sigma}$ self-consistently. In the final step, the total energy $E\{n_{i\mu\sigma}\}$ is obtained; however, by using the full equation $E^x = E^x_0 + \tilde{E}^x$, adding $\tilde{E}^x$ in a zero-order approximation.

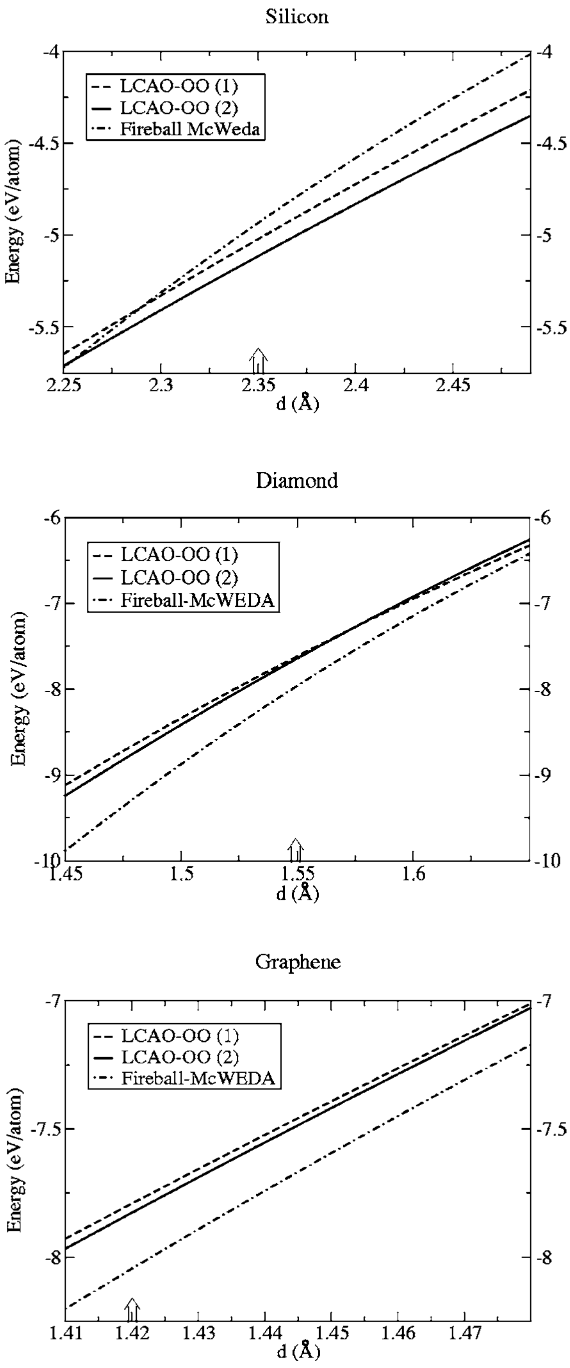

FIG. 2. Exchange-correlation energy per atom for Si, diamond, and graphene. The arrows indicate the experimental position minimum.

In this paper we have explored a second approximation to E^x, including the terms neglected above, $\tilde{E}^x$, using the following approximation:

$$\tilde{E}^x \approx -\frac{1}{2}\sum_{i\mu\sigma} h_{i\mu} n^{\beta}_{i\mu\sigma}(1 - n_{i\mu\sigma})^{\beta}. \tag{26}$$

This approximation is suggested by the fact that $-\sum_{\substack{i\mu,j\nu\sigma\\(j\nu\neq i\mu)}} h^{\mathrm{eff}}_{i\mu,j\nu} n_{i\mu j\nu,\sigma}$ is the dominant term in $\tilde{E}^x$, and by the

TABLE I. Cohesive and exchange-correlation energies for silicon, as calculated with different methods at the equilibrium distance. The experimental values are also shown, taken from Ref. 39.

	FIREBALL-OO-1	FIREBALL-OO-2	FIREBALL-MCWEDA	PW-LDA	Expt.
E_{coh} (eV)	3.6	3.8	3.6	5.1	4.6
E_{XC} (eV)	5.0	5.1	4.9	5.6	5.1

behavior of this term in the case of a homopolar diatomic molecule (one orbital per site). In this limit, $h^{\mathrm{eff}}_{i\mu,j\nu}$ is a constant (does not depend on $\{n_{i\mu\sigma}\}$), h^0, and $-\sum_{(j\nu\neq i\mu)}^{i\mu,j\nu\sigma} h^0_{i\mu,j\nu} n_{i\mu j\nu,\sigma} = -h^0 \sum_{(j\nu\neq i\mu)}^{i\mu,j\nu\sigma} n_{i\mu j\nu,\sigma} = -h^0 \sum_{(j\nu\neq i\mu)}^{i\mu,j\nu\sigma} n^{1/2}_{i\mu\sigma}(1-n_{i\mu\sigma})^{1/2}$ $[n_{i\mu j\nu,\sigma} = n^{1/2}_{i\mu\sigma}(1-n_{i\mu\sigma})^{1/2} = n^{1/2}_{j\nu\sigma}(1-n_{j\nu\sigma})^{1/2}]$. In extended systems, $h_{i\mu,j\nu}$ is expected to depend on $n_{i\mu\sigma}$ as a function of $n_{i\mu\sigma}(1-n_{i\mu\sigma})$, as $J^{\mathrm{eff}}_{i\mu}$ and $f_{i\mu}$ do. This suggests approximating $-\sum_{(j\nu\neq i\mu)}^{i\mu,j\nu\sigma} h^{\mathrm{eff}}_{i\mu,j\nu} n_{i\mu j\nu,\sigma}$, and $\widetilde{E}^x$ by $-\frac{1}{2}\sum_{i\mu\sigma} h_{i\mu} n^{\beta}_{i\mu\sigma}(1-n_{i\mu\sigma})^{\beta}$, $h_{i\mu}$ being a constant, as shown in Eq. (26).

The calculations shown below for Si, C, and graphene suggest that $h_{i\mu}$ is well approximated by the equation

$$h_{i\mu} \approx \alpha (J^{\mathrm{eff}}_{i\mu} d_0)^{\beta} \tag{27}$$

where α, β, and d_0 are parameters obtained by fitting Eq. (26) to $\widetilde{E}^x$ (see below and Table IV).

With this approximation we write

$$E^x = -\frac{1}{2}\sum_{i\mu\sigma} \{U_{i\mu,\mu} n_{i\mu\sigma} + J^{\mathrm{eff}}_{i\mu}(1-n_{i\mu\sigma})\} n_{i\mu\sigma} - \frac{1}{2}\sum_{\substack{i\mu,\nu\sigma\\ \nu\neq\mu}} U^x_{i\mu,\nu} n_{i\mu\sigma} n_{i\nu\sigma} - \frac{1}{2}\sum_{i\mu\sigma} h_{i\mu} n^{\beta}_{i\mu\sigma}(1-n_{i\mu\sigma})^{\beta} \tag{28}$$

which defines our second approximation for E^x. Then, the exchange-correlation energy is given by Eqs. (28) and (16).

IV. RESULTS: Si, DIAMOND, AND GRAPHENE

We have applied our previous formulation to the cases of Si, diamond, and graphene (graphene is chosen for the sp^2 character of its bonds, which allows us to make an interesting comparison with the sp^3 bonds of Si and diamond). In our discussion we are going to present results for the total energies and electron bands of these crystals using different approximations. (i) First, we consider the FIREBALL-OO approach with the exchange energy given only by Eq. (24), and calculate the total energy by adding $\widetilde{E}^X$ in zeroth-order approximation (approximation 1). (ii) In a second set of calculations, we use Eq. (28) for the exchange energy (approximation 2). Both calculations will be compared with standard FIREBALL-LDA [FIREBALL-multicenter weighted exchange density approximation[26] (MCWEDA)] results[20].

In these calculations, we have used optimized sp^3 basis sets for carbon and silicon, which have been obtained by mixing atomiclike fireball orbitals[17] corresponding to two different atomic calculations. In particular, the optimized orbitals ψ are

$$\psi(\vec{r}) = A[c\psi_0(\vec{r}) + (1-c)\psi_1(\vec{r})] \tag{29}$$

(A is a normalizing constant) where $\psi_0(\vec{r})$ is the standard fireball orbital for a neutral atom, and $\psi_1(\vec{r})$ corresponds to a double-excited (+2) atom. In both atomic calculations we have used a cutoff radius of R_c=4.5 a.u. (5.5 a.u.) for the s and p orbitals of carbon (silicon). The parameter c is obtained by minimizing the total energy for the system under study;[36] at the same time, the optimized orbitals yield significantly improved structural parameters (details will be published elsewhere[37]). This basis optimization yields similar results to those obtained with the optimization proposed in Ref. 21. For example, for carbon, our optimization yields a lowering of the total energy, as compared with the standard fireball basis set ψ_0, for diamond of the order of 0.9 eV per C atom in similarity with the findings of Ozaki and Kino.[21] A further comparison with the results presented by these authors for converged basis sets suggests that our results are ~0.4 eV/C atom above converged basis set results. A similar analysis shows that for the case of Si our results are ~0.9 eV per Si atom above converged basis set results.

We should also mention that the different parameters of Hamiltonian $\hat{H}_0$—U, U_x, J, J_x, etc.—that correspond to the orthogonal orbitals, $\phi_{i\mu} = \sum_{j\nu}(S^{-1/2})_{i\mu j\nu}\psi_{j\nu}$, are calculated using small clusters of up to eight atoms including the atoms associated with the interaction; for example, an intra-atomic $U_{i\mu,\nu}$ interaction is calculated with a five-atom cluster (four for graphene), i being the central atom and the other four atoms its nearest neighbors. This approach has been tested with clusters of different sizes.

Figure 1 shows the cohesive energy for Si, C, and graphene as a function of their NN distance. For each case, this figure represents the results of our FIREBALL-OO method using the two approximations mentioned above (referred to as approximations 1 and 2); in the same figure we also represent for the sake of comparison the cohesive energies calculated using the MCWEDA approximation to the LDA exchange-correlation energy in the FIREBALL code (MCWEDA is an approximation introduced for the efficient calculation of exchange-correlation terms in first-principles tight-binding molecular-dynamics methods[20]). A comparison of the total energy for the different OO methods shows that approximations 1 and 2 yield very similar results for diamond, while for graphene (Si) they differ by 0.1 (0.3) eV. We should say that in Figs. 1 and 2, the total energy per atom (cohesive energy) and the exchange-correlation energy are shown as functions of the nearest-neighbor distance to facilitate the comparison between different structures. The atomic reference (which is subtracted from all the values discussed below) for the total energy or the exchange-correlation en-

TABLE II. As Table I for diamond.

	FIREBALL-OO-1	FIREBALL-OO-2	FIREBALL-MCWEDA	PW-LDA	Expt.
E_{coh} (eV)	6.4	6.4	6.8	8.7	7.4
E_{XC} (eV)	7.5	7.5	7.8	9.4	8.1

ergy is calculated as follows: (a) in the case of FIREBALL-OO, from a FIREBALL-OO calculation of the isolated atom,[38] taking into account spin-polarization effects; (b) for FIREBALL-MCWEDA, from a LDA calculation of the corresponding atom, adding also spin-polarization corrections (0.66 and 1.09 eV for Si and C, respectively). A fair estimation of the relative merit of the different methods used in this paper for the description of the total and exchange-correlation energies of solids is provided by the results obtained for a converged plane-wave (PW) LDA calculation (see Tables I and II). For Si and diamond, the PW LDA yields (Si) $E_{\mathrm{cohesive}}=-5.1$ eV and $E_{\mathrm{XC}}=-5.6$ eV; (C) $E_{\mathrm{cohesive}}=-8.7$ eV and $E_{\mathrm{XC}}=-9.4$ eV, at the experimental lattice constant. Comparing the cohesive energies of the PW-LDA calculations and the experimental data, and assuming that the Hartree and kinetic energies are well converged in the PW-LDA, we deduce that the XC energies are overestimated in the PW-LDA by (Si) -0.5 eV; (C) -1.3 eV. Accordingly, we subtract these energies from the PW-LDA XC energies and define the "experimental" values (Si) $E_{\mathrm{XC}}^{\mathrm{expt}}=-5.1$ eV; (C) $E_{\mathrm{XC}}^{\mathrm{expt}}=-8.1$ eV (these are the values an exact DFT should yield for the XC energy at the equilibrium distance). The experimental XC energies should be compared with the values of Fig. 2 at the equilibrium distances: (Si) $E_{\mathrm{XC}}(\mathrm{OO\text{-}1})=-5.0$ eV; $E_{\mathrm{XC}}(\mathrm{OO\text{-}2})=-5.1$ eV; $E_{\mathrm{XC}}(\mathrm{MCWEDA})=-4.9$ eV; (C) $E_{\mathrm{XC}}(\mathrm{OO\text{-}1})=-7.5$ eV; $E_{\mathrm{XC}}(\mathrm{OO\text{-}2})=-7.5$ eV; $E_{\mathrm{XC}}(\mathrm{MCWEDA})=-7.8$ eV (see also Tables I and II). These values show that our OO approach yields a fair approximation to the XC energy of the system, underestimating it by 0.6 eV/atom in the case of C, while yielding an accurate value for the case of Si. The MCWEDA, on the other hand, yields values of the XC energies within 0.2–0.3 eV/atom for C and Si in the diamond structure. This is due to a cancellation of errors: the MCWEDA underestimates the LDA values which, in turn, overestimate XC energies.

The consistency of the previous analysis can be checked using the cohesive energies calculated at the experimental equilibrium distances (see Tables I and II). We obtain (Si) $E_{\mathrm{coh}}(\mathrm{OO\text{-}1})=-3.6$ eV; $E_{\mathrm{coh}}(\mathrm{OO\text{-}2})=-3.8$ eV; $E_{\mathrm{coh}}(\mathrm{MCWEDA})=-3.6$ eV; (C) $E_{\mathrm{coh}}(\mathrm{OO\text{-}1})=-6.4$ eV; $E_{\mathrm{coh}}(\mathrm{OO\text{-}2})=-6.4$ eV; $E_{\mathrm{coh}}(\mathrm{MCWEDA})=-6.8$ eV. Using the above estimated values for the deviation of the XC energies, and comparing with the experimental cohesive energies, we deduce that our results are above converged basis set results by ~0.8–0.9 eV and ~0.3–0.4 eV for Si and C, respectively, in excellent agreement with our previous analysis on the convergency of the basis sets employed in these calculations.

Table III shows the Si, diamond, and graphene experimental cohesive energies, lattice parameters and bulk modulus, compared with the theoretical values calculated with FIREBALL-OO-1 and 2, as well as FIREBALL-MCWEDA. Typically, d (the nearest-neighbor distance) is around 2–4 % larger in all the calculations than in experiments, while E_{coh} is a little smaller (0.6–0.9 eV for Si, 0.6–0.9 eV for diamond, and 0.7–0.9 eV for graphene (see also the discussion above); the bulk modulus is within 10% of the experimental data.[39] All these results are very satisfactory, showing the good accuracy of our FIREBALL-OO approach as well as the FIREBALL-MCWEDA for the ground state of the system. Figure 3 shows the different terms of $\widetilde{E}^X$ except the self-interaction correction $-\frac{1}{2}\Sigma_{i\mu\sigma}U_{i\mu,\mu}n_{i\mu\sigma}n_{i\mu\sigma}$. As shown in this figure, $E_x^I=-\frac{1}{2}\Sigma_{i\mu,\sigma}J_{i\mu}^{\mathrm{eff}}n_{i\mu\sigma}(1-n_{i\mu\sigma})$ is the dominant (apart from the self-interaction contribution) term of the exchange-correlation energy. From the different contributions to $\widetilde{E}^x$, Eq. (25),

$$E_h^x=-\sum_{\substack{i\mu,j\nu\sigma\\(j\nu\neq i\mu)}} h_{i\mu,j\nu}^{\mathrm{eff}}n_{i\mu j\nu,\sigma} \tag{30}$$

is the most important one; the other terms

TABLE III. Si, diamond, and graphene cohesive energies, nearest-neighbor distance, and bulk modulus from experiment (Ref. 39) and our various calculations.

		Expt.	FIREBALL-OO-1	FIREBALL-OO-2	FIREBALL-MCWEDA
Si	E_{coh} (eV)	4.6	3.71	3.97	3.63
Si	d (Å)	2.35	2.45	2.47	2.42
Si	B (Mbar)	0.99	1.01	0.87	0.79
C	E_{coh} (eV)	7.4	6.49	6.47	6.8
C	d (Å)	1.55	1.60	1.60	1.58
C	B (Mbar)	4.4	4.77	4.49	4.56
Graphene	E_{coh} (eV)	7.6	6.59	6.66	6.89
Graphene	d (Å)	1.42	1.45	1.45	1.43

$$E^x_{h_x} = -\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda\\ (j\nu\neq i\mu)\\ (k\lambda\neq i\mu,j\nu)}} h^x_{k\lambda,i\mu j\nu} n_{k\lambda\sigma} n_{i\mu j\nu,\sigma}, \tag{31}$$

$$E^x_{J_x} = -\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ (j\neq i)}} J^x_{i\mu,j\nu} n_{i\mu\sigma} n_{j\nu\sigma}, \tag{32}$$

and

$$E^x_4 = -\frac{1}{2}\sum_{\substack{i\mu,j\nu\sigma\\ k\lambda,l\omega\\ \text{all different}}} O^{i\mu j\nu}_{l\omega k\lambda} n_{i\mu l\omega,\sigma} n_{j\nu k\lambda,\sigma} \tag{33}$$

are also represented in Fig. 3, as well as $\widetilde{E}^x = E^x_h + E^x_{h_x} + E^x_{J_x} + E^x_4$.

Figure 4 shows $\widetilde{E}^x$ and the curve

$$-\frac{1}{2}\sum_{i\mu\sigma} h_{i\mu} n^{\beta}_{i\mu\sigma}(1-n_{i\mu\sigma})^{\beta} = -\frac{\alpha}{2}\sum_{i\mu\sigma} (J^{\text{eff}}_{i\mu} d_0)^{\beta} n^{\beta}_{i\mu\sigma}(1-n_{i\mu\sigma})^{\beta} \tag{34}$$

whose parameters α, β, and d_0 have been chosen to give a good fitting to $\widetilde{E}^x$. In Eq. (34) d_0 is the experimental distance between nearest neighbors, while α and β are given in Table IV [taking for d_0 the theoretical values 2.42, 1.60, and 1.45 Å (see Table III), yields α=5.92, 5.96, and 5.75 hartrees].

Notice that in Eq. (34) we have used atomic units in such a way that α is given in hartrees. The good fitting of Eq. (34) to the calculated $\widetilde{E}^X$ explains the good agreement found between our results for FIREBALL-OO-1 and -2: the small difference between both cases comes from the change in the self-consistent charges $n_{i\mu\sigma}$ introduced by the exchange potential $\partial\widetilde{E}^X/\partial n_{i\mu\sigma}$. It should be mentioned, however, that our FIREBALL-OO-2 approach represents a substantial improvement of the calculation efficiency over FIREBALL-OO-1, since in FIREBALL-OO-2 for calculating E^{XC} we only used the parameters U, U^X, and J, while in FIREBALL-OO-1 we also have to calculate h^{eff}, h^x, J^x, and O. We should also stress the universal behavior found for h, with α and β almost independent of the material considered.

Finally, Figs. 5–7 show the band structure for Si, C, and graphene, respectively, as calculated with FIREBALL-MCWEDA and FIREBALL-OO-1 and -2. Although the three cases yield similar bands, we can appreciate some differences. (a) The valence bands are narrower for FIREBALL-MCWEDA (the bands found in this case are closer to conventional LDA calculations[20]), while in FIREBALL-OO-2 the valence bandwidths are ≈10% larger. (b) The energy gaps are the largest for FIREBALL-MCWEDA and the smallest for FIREBALL-OO-2, this case being closer to the experimental evidence. Typically, the valence bandwidth yielded by FIREBALL-OO is within 10% of the values provided by other approaches. In spite of these small differences, we find that the conduction bands are not very accurate due to the use of a minimal local orbital basis in our calculations.[40]

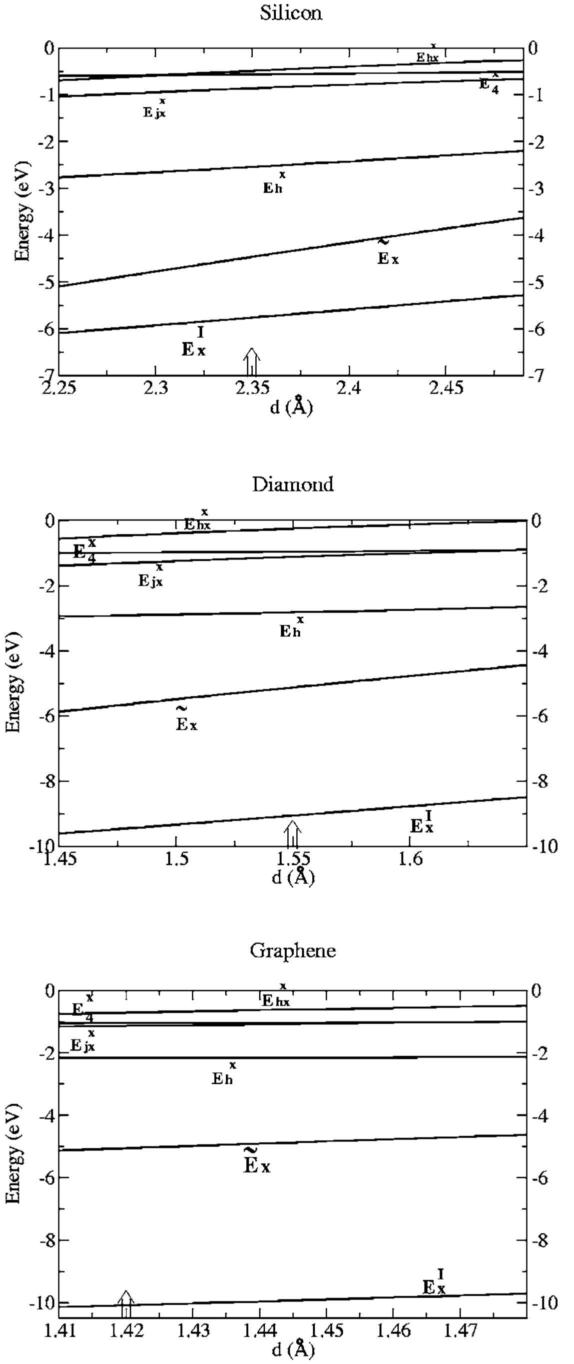

FIG. 3. Different contributions E^X_h, $E^X_{h_x}$, $E^X_{J_x}$, and E^X_4 to the exchange energy $\widetilde{E}_X$ (see text) for Si, diamond and graphene. E^I_X is also shown for each crystal. The arrows indicate the experimental position minimum.

V. CONCLUSIONS

In conclusion, we have presented a detailed discussion of the LCAO-OO Hamiltonian introduced for calculating the electronic properties of solids using a local-orbital basis and an orbital occupancy formulation. This Hamiltonian defines the starting point used for calculating the exchange-correlation energy of our system, Eqs. (13) and (16). In this paper we also present two important implementations of this

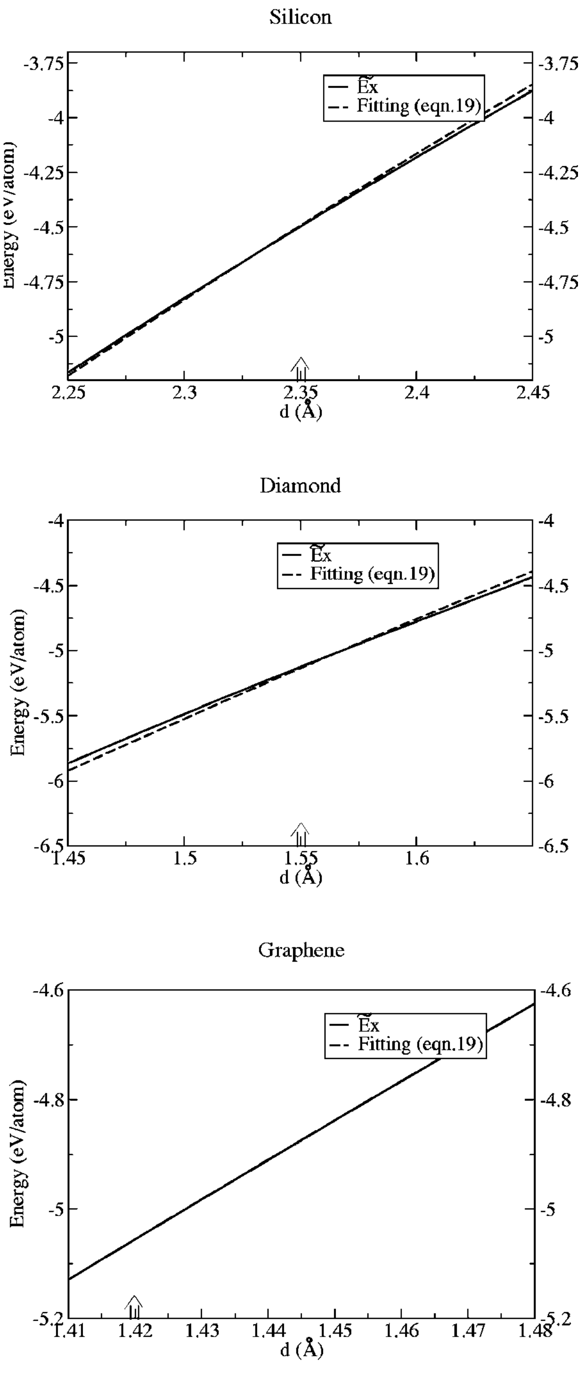

FIG. 4. $\widetilde{E}_X$ and the fitting function (34) for Si, diamond, and graphene. The arrows indicate the experimental position minimum.

TABLE IV. α, β, and d_0 for Si, diamond, and graphene.

	Si	C	Graphene
α (h)	6.35	6.43	6.05
β	2.4	2.4	2.4
d_0 (Å)	2.35	1.55	1.42

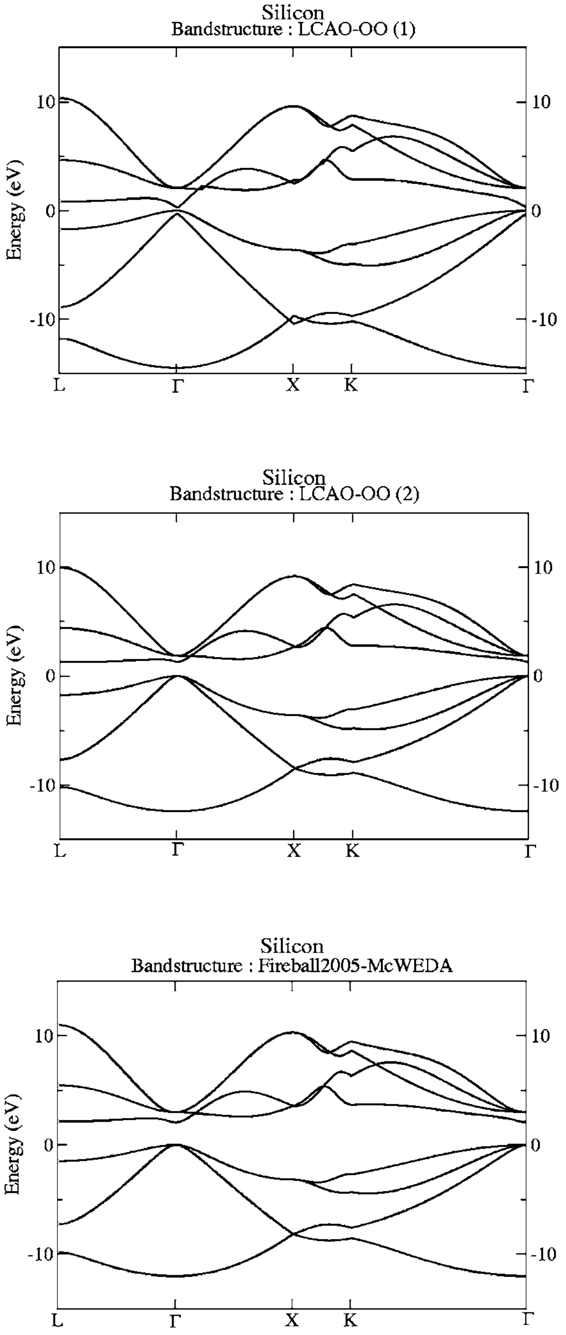

FIG. 5. Electron band structure for Si as calculated with LCAO-OO (1 and 2) and FIREBALL-MCWeda approaches.

LCAO-OO approach: (i) first, we combine the DF FIREBALL code with our LCAO-OO method to define the FIREBALL-OO density functional approximation. This approach combines the Hartree approximation of FIREBALL with the exchange-correlation energy of the LCAO-OO method. (ii) In a second step, we have introduced a simplified LCAO-OO exchange energy, Eq. (28), that represents, in terms of computational efficiency, a substantial improvement as compared to a direct calculation of this exchange energy.

The results presented in this paper for Si, diamond, and graphene show the good accuracy of the approximation presented here and indicate the suitability of our FIREBALL-OO

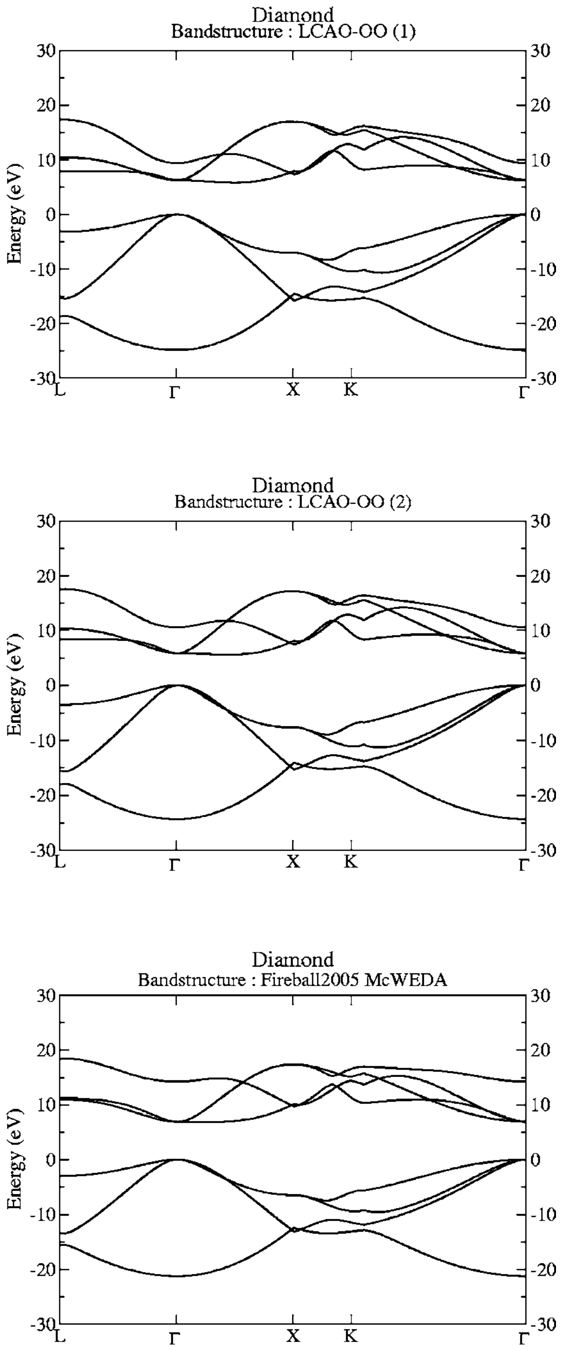

FIG. 6. As Fig. 5 for diamond.

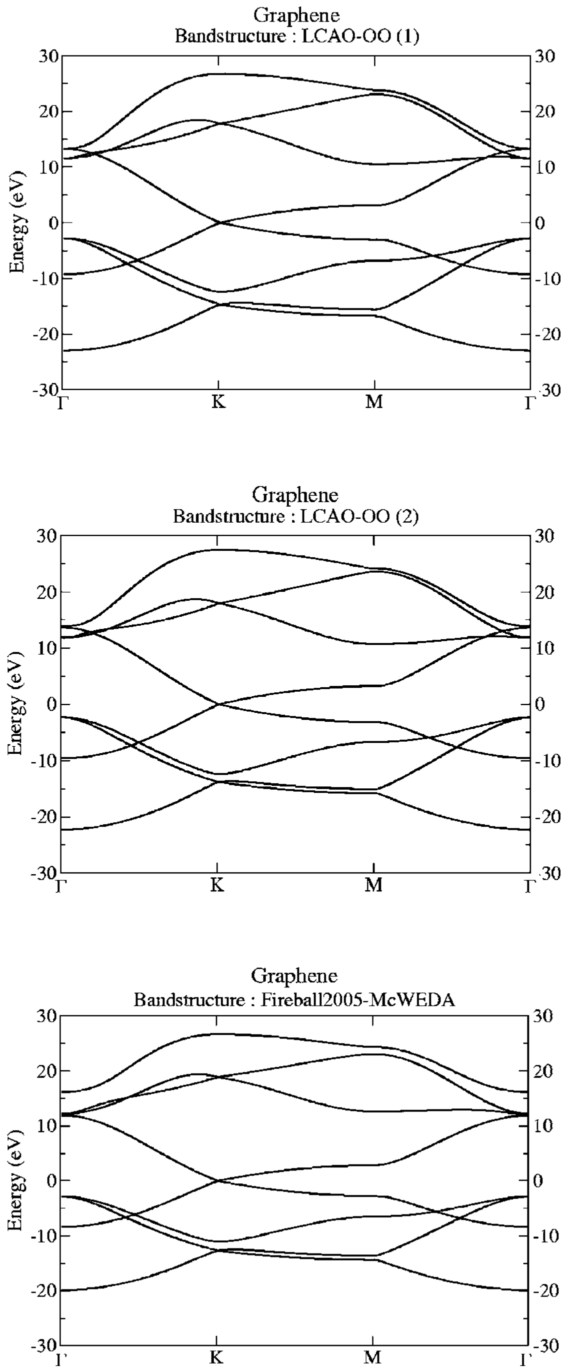

FIG. 7. As Fig. 5 for graphene.

approach for calculating the electronic properties of solids.

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