

# Exchange–correlation energy in the orbital occupancy method: electronic structure of organic molecules

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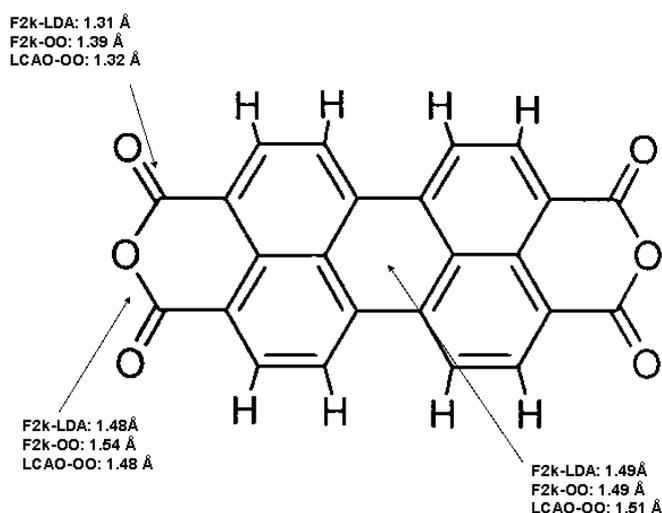
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## Abstract

A new DF-LCAO (density functional with local combination of atomic orbitals) method is used to calculate the electronic properties of 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA), C<sub>6</sub>H<sub>6</sub>, CH<sub>4</sub>, and CO. The method, called the OO (orbital occupancy) method, is a DF-based theory, which uses the OOs instead of  $\rho(\vec{r})$  to calculate the exchange and correlation energies. In our calculations, we compare the OO method with the conventional local density approximation approach. Our results show that, using a minimal basis set, we obtain equilibrium bond lengths and binding energies for PTCDA, C<sub>6</sub>H<sub>6</sub>, and CH<sub>4</sub> which are respectively within 6, and 10–15% of the experimental values. We have also calculated the affinity and ionization levels, as well as the optical gap, for benzene and PTCDA and have found that a variant of Koopmans' theorem works well for these molecules. Using this theorem we calculate the Koopmans relaxation energies of the  $\sigma$ - and  $\pi$ -orbitals for PTCDA and have obtained this molecule's density of states which compares well with experimental evidence.

## 1. Introduction

Organic molecule devices constitute a fast-developing field of microelectronics. Thin films of molecules such as phthalocyanines and products based on perylene have exciting optoelectronic properties [1]. A particular compound based on perylene: 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) (see figure 1) can be used in Schottky diodes [2]. In such a structure a thin, crystalline film of PTCDA would be added between the metal and semiconductor slabs. The electronic properties of this molecular crystal will influence the diode characteristics and its behaviour as a reliable device. From this point of view, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels, as well as the



**Figure 1.** The chemical structure of the PTCDA molecule. The distances shown in the figure are taken from our calculations (the C–C distance is averaged over the different bonds).

electron affinity and ionization potential, are important quantities characterizing the behaviour of the molecule. These levels are related to the Fermi level position in a metal/PTCDA heterojunction, a system that one needs to study as a part of the diode structure [3].

Density functional theory (DFT) computational methods offer a fashionable approach for the calculation of the electronic properties of molecules, surfaces, and solids. The majority of DFT methods use either plane waves [4] or localized orbitals [5] as their basis set to obtain the electronic structure of the material. The latter, which consists of a few orbitals localized on each atom, is the natural basis for the orbital occupancy (OO) [6, 7] method which we discuss below. This method is a novel approach to DFT, where occupancy numbers  $n_{i\alpha\sigma}$ , indexed by atom, orbital, and spin, are used as the independent variables, instead of the usual position-dependent charge density  $\rho(\vec{r})$ .

The main advantage of this new OO approach comes from its versatility for introducing many-body effects in the LD solution obtained in the local orbital basis. For example, in a recent paper [8], some of us have shown how this OO approach can be combined with a dynamical mean field approximation [9] to analyse electron correlation effects and ferromagnetism in Fe; this is reminiscent of the local density approximation LDA –  $U$  scheme [10], but formulated without any adjustable parameter. In this paper, we also show how this OO approach can be used advantageously to calculate, for an organic molecule such as PTCDA, its ionization and affinity levels, introducing appropriate electron relaxation effects, which are necessary for a correct description of the energy level alignment at metal/organic interfaces.

The first aim of this paper is to present results for the electronic properties of different molecules using the OO approach and to compare them with calculations performed using the LDA functional  $E_{\text{LDA}}^{\text{XC}}[\rho(\vec{r})]$  for the exchange–correlation energy. This comparison will allow us to assess the accuracy of our approach and its applicability to solid state systems such as metal/PTCDA/semiconductor interfaces. In our calculations, we first analyse three small molecules: CO, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>, which contain all atom pairs found in PTCDA and whose electronic properties are well known. Then we apply our method to PTCDA and calculate its electronic properties. In a second step, we also show how to calculate the ionization,  $I$ , and electron affinity,  $A$ , levels of large molecules using our OO approach. These are given by

$$I = E[N - 1] - E[N], \quad A = E[N] - E[N + 1], \quad (1)$$

where  $E[N_i]$  is the energy of the system with  $N_i = N - 1, N, N + 1$  electrons.

This paper shows how the OO approximation allows us to easily calculate  $I$  and  $A$  in a simple way, which, unlike the LDA approach, does not require the full calculation of either  $E[N + 1]$  or  $E[N - 1]$ . For our calculations of  $I$  and  $A$  we apply a version of Koopmans' theorem to the  $N$ -electron system and its OOs, which will be explained below.

The paper is organized as follows. In section 2 we introduce the OO method, emphasizing how the exchange and correlation energies are calculated and outlining its implementation in two computational codes. Section 3 explains how this approach can be easily applied to calculate the ionization and affinity levels of molecules and its relation to Koopmans' theorem. In section 4 we present results for bond lengths and energies for several molecules, and section 5 contains some concluding remarks.

## 2. Orbital occupancy approach

In typical DFT approaches the total energy  $E$  of an atomic system is a functional of the charge density  $\rho$ ,  $E[\rho(\vec{r})]$ . The basic idea of the OO approach (exposed in detail in [6]) is to replace the functional dependence  $E[\rho(\vec{r})]$  by a function  $E[\{n_{i\alpha\sigma}\}]$  of the OOs  $n_{i\alpha\sigma}$ . Thus the first step in formulating the OO method is to write down all significant contributions to the total energy  $E[\{n_{i\sigma}\}]$  as an explicit function of the OOs. For this purpose, the following many-body Hamiltonian is introduced:

$$\begin{aligned} \hat{H} = & \sum_{i\alpha\sigma} E_{i\alpha\sigma} \hat{n}_{i\alpha\sigma} + \sum_{i\alpha \neq j\beta, \sigma} \hat{T}_{i\alpha, j\beta, \sigma} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma} + \frac{1}{2} \sum_{i\alpha\sigma \neq i\beta\sigma'} U_{i, \alpha\beta} \hat{n}_{i\alpha\sigma} \hat{n}_{i\beta\sigma'} \\ & + \frac{1}{2} \sum_{\substack{i\alpha, j\beta, \sigma, \sigma' \\ (i \neq j)}} J_{i\alpha, j\beta} \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma'} + \delta \hat{H}_0. \end{aligned} \quad (2)$$

In this formula,  $E_{i\alpha\sigma}$  are the diagonal pseudopotential and kinetic energy matrix elements,  $\hat{T}_{i\alpha, j\beta, \sigma}$  are 'hoppings' defined as

$$\hat{T}_{i\alpha, j\beta, \sigma} = t_{i\alpha, j\beta} + \sum_{k\gamma, \sigma'} h_{k\gamma; i\alpha, j\beta} \hat{n}_{k\gamma\sigma'} - \sum_{k\gamma} h_{k\gamma; i\alpha, j\beta}^X \hat{n}_{k\gamma\sigma}, \quad (3)$$

where  $t_{i\alpha, j\beta}$  are the one-electron contributions to the hoppings, while  $h_{k\gamma; i\alpha, j\beta}$  and  $h_{k\gamma; i\alpha, j\beta}^X$  are electron–electron interaction integrals containing three distinct orbitals (see equations (81), (82) in [6]). The  $U_{i, \alpha\beta}$  ( $J_{i\alpha, j\beta}$ ) are intra-atomic (interatomic) electron–electron integrals which represent the most important contributions to the two-body interactions. The terms contained in  $\delta \hat{H}_0$  are discussed below.

The exchange–correlation contributions,  $E_{\text{OO}}^{\text{XC}}$ , are the most intricate part of the formalism. Here we will just write them down; we refer the reader to [7] or [6] for details. The exchange hole contribution is obtained as

$$E^{\text{X}} = -\frac{1}{2} \sum_{\substack{i\alpha \neq j\beta \\ \sigma}} J_{i\alpha, j\beta} n_{i\alpha\sigma}^2 = -\frac{1}{2} \sum_{i\alpha\sigma} J_{i\alpha}^{\text{eff}} n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}), \quad (4)$$

where  $J_{i\alpha}^{\text{eff}}$  is the mean interaction between the charge  $n_{i\alpha\sigma}$  and its hole  $1 - n_{i\alpha\sigma}$ , obtained as in formula (11) of [6].  $E^{\text{X}}$  includes contributions from both the interatomic and intra-atomic exchange hole. If we denote by  $f_{i\alpha\sigma}$  the fraction of the exchange hole which is converted into an intra-atomic correlation hole, we obtain for the intra-atomic correlation energy

$$E^{\text{C}} = -\frac{1}{2} \sum_{i\alpha\sigma} f_{i\alpha\sigma} (\tilde{U}_i - J_{i\alpha}^{\text{eff}}) n_{i\alpha\sigma} (1 - n_{i\alpha\sigma}), \quad (5)$$

where  $\bar{U}_i$  is the average of the intra-atomic Coulomb integrals  $U_{i\alpha,\beta}$  over the orbitals  $\alpha, \beta$  of the atom  $i$ . The differences between these  $U_{i\alpha,\beta}$  are usually small.

The exchange–correlation energies derived above show explicit dependence on  $n_{i\alpha\sigma}$ . They are used to construct the following potential:

$$V_{i\alpha\sigma}^{\text{XC}} = \frac{\partial E_{\text{OO}}^{\text{XC}}[\{n_{j\beta\sigma'}\}]}{\partial n_{i\alpha\sigma}}, \quad (6)$$

with  $E^{\text{XC}} = E^{\text{X}} + E^{\text{C}}$ . This exchange–correlation potential is added (as  $\sum_{i\alpha\sigma} V_{i\alpha\sigma}^{\text{XC}} \hat{n}_{i\alpha\sigma}$ ) to the effective one-electron Hamiltonian of the system.

It is known [11] that self-interaction causes problems when using LDA, where it is not properly subtracted in the exchange–correlation functional. In our formulation the self-interaction term  $\frac{1}{2}U_{i\alpha,\alpha}n_{i\alpha\sigma}^2$  is not included in the Hamiltonian (2). The absence of this term corresponds to an exchange hole of charge  $n_{i\alpha\sigma}$ , which, together with the fraction  $1 - n_{i\alpha\sigma}$  of charge located outside the orbital, makes a total exchange hole of 1.

We use mean field approximation to reduce the  $h$ - and  $h^{\text{X}}$ -dependent terms given in (3) to a one-electron form. That is, we treat them as off-diagonal elements of the effective OO Hamiltonian, which are simply proportional to  $n_{k\gamma\sigma'}$ ; for example, the hopping term  $\sum_{k\gamma,\sigma'} h_{k\gamma;i\alpha,j\beta} n_{k\gamma\sigma'}$  will enter the effective OO Hamiltonian as a non-diagonal Hartree potential matrix element:

$$\sum_{k\gamma,\sigma'} h_{k\gamma;i\alpha,j\beta} n_{k\gamma\sigma'} \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma}. \quad (7)$$

Also, this term gives rise to an important ‘exchange’ contribution to the total energy:

$$- \sum_{k\gamma} h_{k\gamma;i\alpha,j\beta} n_{k\gamma,j\beta\sigma} n_{i\alpha,k\gamma\sigma}. \quad (8)$$

Using the formula  $\sum_{k\gamma,(k\gamma \neq i\alpha,j\beta)} n_{k\gamma,i\alpha,\sigma} n_{k\gamma,j\beta,\sigma} = n_{i\alpha,j\beta,\sigma}(1 - n_{i\alpha\sigma} - n_{j\beta\sigma})$ , we can write (8) as  $-\sum_{i\alpha \neq j\beta,\sigma} h_{i\alpha,j\beta}^{\text{eff}} (1 - n_{i\alpha\sigma} - n_{j\beta\sigma}) n_{i\alpha,j\beta\sigma}$ . This energy can be understood as a modification of the electron hopping between the states  $i\alpha\sigma$  and  $j\beta\sigma$  due to the exchange hole  $(1 - n_{i\alpha\sigma} - n_{j\beta\sigma})$ . We introduce this contribution as a non-diagonal part of the OO Hamiltonian in a way analogous to that of (7):

$$- \sum_{i\alpha \neq j\beta,\sigma} h_{i\alpha,j\beta}^{\text{eff}} (1 - n_{i\alpha\sigma} - n_{j\beta\sigma}) \hat{c}_{i\alpha\sigma}^\dagger \hat{c}_{j\beta\sigma}. \quad (9)$$

In our approximation the last term in (2),  $\delta \hat{H}_0$ , contains all the *nearest-neighbour* electron–electron interactions not included in the previous terms. The most important contributions come from the dipole–dipole interaction and from the term

$$- \frac{1}{2} \sum_{i\alpha,j\beta,\sigma} J_{i\alpha,j\beta}^{\text{X}} \hat{n}_{i\alpha\sigma} \hat{n}_{j\beta\sigma}, \quad (10)$$

In principle the total Hamiltonian should also contain four-centre integrals and those three-centre terms which were not used above, but they were found to be small for all the molecules discussed in this paper and we will neglect their influence. The energy arising from the  $\delta \hat{H}_0$  two-centre interactions is included at a Hartree–Fock level.

The OO method has been implemented in two computational codes: Fireball OO and LCAO-OO. Both codes are based on conventional DFT, replacing the LDA exchange–correlation [12, 13] by the OO one. This means that in the one-electron Hamiltonian we have replaced the  $V_{\text{LDA}}^{\text{XC}}(\vec{r})$  matrix elements by the ones generated from equation (6). An equivalent substitution was done for the double-counting corrections.

For the calculations we have chosen minimal basis sets,  $\psi_{i\alpha}$ , different for those of the two codes. Although we are aware that a minimal basis is mainly useful in cases such as those

of large molecules or bulk crystals, we have found a reasonable description of the electronic properties of the small molecules studied in this paper. We are currently working on introducing a more complete basis set, and the results presented here should be regarded as a first step in this direction. Nevertheless, the effect of the basis will be discussed in detail below.

Then, interactions such as  $U_{i\alpha,\beta}$  and  $J_{i\alpha,j\beta}$  have to be calculated using the Löwdin orthonormal orbitals:

$$\phi_{i\alpha} = \sum_{j\beta} (S^{-1/2})_{i\alpha,j\beta} \psi_{j\beta} \quad (11)$$

where  $S_{i\alpha j\beta}$  is the overlap matrix  $\langle \psi_{i\alpha} | \psi_{j\beta} \rangle$ . This is the orthogonal basis associated with the operators  $c_{i\alpha}^\dagger$  and  $c_{i\alpha}$  of Hamiltonian (2).

In Fireball and LCAO-OO we have computed the Hartree interactions using the Harris approximation [14], allowing for charge transfer and imposing self-consistency on the OOs [5]. Exchange and correlation are calculated within the OO method. For every atom, we construct a nearest-neighbour cluster which resembles its chemical environment in the molecule. In this cluster we calculate the exchange integrals. Although this implies localizing the extra-atomic exchange hole in the nearest neighbours, we have found it to be a good approximation, checking this against bigger clusters.

### 2.1. The Fireball code using the OO method

Fireball 2000 [15] (abbreviated in this paper as F2k) is a DFT-based code which uses the standard DFT for the exchange–correlation energy. In the LDA it uses the functional derivative

$$V_{\text{LDA}}^{\text{XC}}(\vec{r}) = \frac{\delta E_{\text{LDA}}^{\text{XC}}}{\delta \rho(\vec{r})}. \quad (12)$$

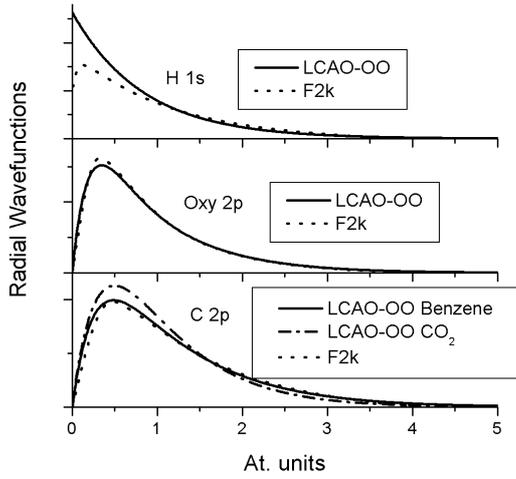
For the calculations presented here we have used Hamann-type pseudopotentials [16]. The valence electrons were described using a minimal basis set of localized atomic-like *Fireball* orbitals. These are numerical wavefunctions  $\psi_j$ , obtained by solving the atomic problem with the boundary condition of vanishing beyond a specified cut-off radius  $R_C$  [18]. The cut-off radii  $R_C$  used in this paper both for F2k LDA and F2k OO are 4.1, 4.0, and 4.0 (atomic units) for carbon, oxygen, and hydrogen respectively (see figure 2). For the OO implementation (F2k-OO) the LDA exchange–correlation part is replaced by the OO one.

F2k OO has been successfully used to calculate properties of bulk semiconductors, and its accurate treatment of the self-interaction correction yields the correct band structure for GaN [7].

### 2.2. LCAO-OO approach

To make the comparison of the OO and LDA functionals more complete we have performed calculations with yet another OO-based approach. In this formulation both the treatment of core electrons and the orbital basis are different from the ones used in F2k OO.

Our description of the core electrons is not strictly related to the pseudopotential concept. The oscillations of valence orbitals in the core region are not eliminated. We use, however, a ‘frozen core’ approach. The influence of the core electrons upon the valence ones is contained in a shift of valence levels and hoppings. These shifts are calculated approximating interactions between the core and valence orbitals by up to second order in their mutual overlap. The shifts have contributions coming from electrostatic interaction and repulsion due to the valence–core overlap and hybridization [20] (for clarity the formulae provided here are slightly simplified



**Figure 2.** Radial parts of the wavefunctions used in the calculation. Solid and dash-dot curves show orbitals used in the LCAO-OO method, while dashed curves show the F2k ones. From top to bottom panel: hydrogen 1s, oxygen 2s and 2p, carbon 2s and 2p orbitals. The carbon orbitals for the LCAO-OO were optimized for benzene rings and CO<sub>2</sub> separately.

with respect to the ones used in the actual calculation):

$$\Delta V_{v\sigma} = \sum_c [S_{vc}^2 (E_{v\sigma}^{\text{at}} - E_{c\sigma}^{\text{at}}) + J_{vc}^{(0)} (n_{c\sigma} + n_{c\bar{\sigma}}) + J_{vc}^{(0)} S_{vc}^2 n_{c\sigma} - J_{vc}^{X(0)} n_{c\sigma}], \quad (13)$$

$$\begin{aligned} \Delta V_{v\sigma} = & \sum_c \left[ S_{vc} S_{v'c} \left( \frac{E_{v\sigma}^{\text{at}} + E_{v'\sigma}^{\text{at}}}{2} - E_{c\sigma}^{\text{at}} \right) + h_{c,vv'}^{(0)} (n_{c\sigma} + n_{c\bar{\sigma}}) \right] \\ & + \sum_c \left( \frac{J_{vc}^{(0)} + J_{v'c}^{(0)}}{2} S_{vc} S_{v'c} - h_{c,vv'}^{X(0)} \right) n_{c\sigma}. \end{aligned} \quad (14)$$

Here  $S_{cv}$  are overlap matrix elements ( $c = \text{core}$ ,  $v = \text{valence}$ ),  $E_{v\sigma}^{\text{at}}$  ( $E_{c\sigma}^{\text{at}}$ ) are atomic valence (core) levels, and  $J_{vc}^{(0)}$ ,  $h_{c,vv'}^{(0)}$ ,  $h_{c,vv'}^{X(0)}$  are interactions as used at the beginning of this section, but calculated for atomic (non-orthogonal) orbitals.

The first term, both in (13) and in (14), represents the repulsion due to the overlap and hybridization. The other terms stem from the electrostatic repulsion and exchange interaction of the valence and core electrons.

In the LCAO-OO approach we use a minimal basis set of atomic-like orbitals  $\Psi_i$  (see figure 2). Each  $\Psi_i$  is a ‘double-zeta’ linear combination of Slater-type orbitals [21], except the single-zeta hydrogen one,  $\Psi_{1s}$ .

The basis sets used in this paper have been variationally optimized for each molecule by maximizing the binding energy while changing the exponents ( $\zeta$ ) of the Slater-type orbitals. For PTCDA however the optimization was made in smaller molecules, which resemble each atom’s chemical environment. In particular, H and the perylene C were optimized in benzene, and O and the carboxyl C in CO<sub>2</sub>.

The LCAO-OO method presented above allows us to perform fast and precise calculations of the electronic properties of molecules. Its validity has been verified, obtaining high-quality results for a number of systems: small molecules and bulk semiconductors [7, 20].

### 3. Transport and optical gaps

In DFT calculations the one-electron eigenvalues do not represent real electron or hole excitations. In particular the DFT gap is not directly related to either the transport or the optical gap.

### 3.1. Ionization and affinity levels

Both  $I$  and  $A$  have exact expressions (equation (1)) in terms of the total energies of the system with  $N \pm 1$  electrons. However, a good approximation can be made using the following modification of Koopmans' theorem. The idea is to calculate  $E[N + 1]$ ,  $E[N - 1]$  neglecting orbital relaxation, i.e. using only the molecular orbitals from the  $N$ -electron solution. That is, we approximate the wavefunction of the  $[N + 1]$ th (or  $[N - 1]$ th) electron by the LUMO (or HOMO) level of the  $N$ -electron system and calculate the new occupation numbers for the systems with  $N \pm 1$  electrons:

$$n_{i\alpha\sigma}^{N+1} = n_{i\alpha\sigma}^N + \delta n'_{i\alpha\sigma}; \quad n_{i\alpha\sigma}^{N-1} = n_{i\alpha\sigma}^N - \delta n_{i\alpha\sigma}, \quad (14a)$$

with

$$\delta n'_{i\alpha\uparrow} = |\langle \phi_{i\alpha} | \text{LUMO}^N \rangle|^2; \quad \delta n_{i\alpha\uparrow} = |\langle \phi_{i\alpha} | \text{HOMO}^N \rangle|^2,$$

whereas for the cases that we consider in this subsection,  $\delta n'_{i\alpha\downarrow}$  and  $\delta n_{i\alpha\downarrow}$  are zero. Now we can apply the  $n_{i\alpha\sigma}$ -dependent OO approach to approximate  $I$  and  $A$  using the new occupancies. The approximate ionization potential  $\tilde{I}$  and affinity  $\tilde{A}$  are given by

$$\tilde{I} = -\epsilon_{\text{HOMO}}^N + \delta I; \quad \tilde{A} = -\epsilon_{\text{LUMO}}^N + \delta A,$$

where

$$\begin{aligned} \delta I &= \frac{1}{2} \sum_{i\alpha \neq j\beta} J_{i\alpha j\beta} \delta n_{i\alpha\uparrow} \delta n_{j\beta\uparrow} + \frac{1}{2} \sum_{i\alpha} J_{i\alpha}^{\text{eff}} \delta n_{i\alpha\uparrow}^2 + \frac{1}{2} \sum_{i\alpha} f_{i\alpha} (\tilde{U}_i - J_{i\alpha}^{\text{eff}}) \delta n_{i\alpha\uparrow}^2, \\ \delta A &= -\frac{1}{2} \sum_{i\alpha \neq j\beta} J_{i\alpha j\beta} \delta n'_{i\alpha\uparrow} \delta n'_{j\beta\uparrow} - \frac{1}{2} \sum_{i\alpha} J_{i\alpha}^{\text{eff}} \delta n_{i\alpha\uparrow}^2 - \frac{1}{2} \sum_{i\alpha} f_{i\alpha} (\tilde{U}_i - J_{i\alpha}^{\text{eff}}) \delta n_{i\alpha\uparrow}^2, \end{aligned} \quad (14b)$$

which give the changes in Hartree and exchange–correlation energies due to the variations in the OOs. The quantities  $\delta I$ ,  $\delta A$  and similar corrections for the optical gap will be called here Koopmans relaxation energies. In this approximation, apart from the Hartree term, we have only included exchange–correlation contributions associated with equations (4) and (5), which are the dominant ones. The one-electron levels  $\epsilon_{\text{HOMO}}^N$  and  $\epsilon_{\text{LUMO}}^N$  are calculated within the OO approach for a system of  $N$  particles.

The transport gap of a molecular crystal, defined as the energy necessary to create a well-separated electron–hole pair, is not exactly equal to  $I - A$  due to intermolecular interactions. However, these interactions are weak because distances between molecules are large. Thus the  $(I - A)$  contribution to the transport gap is dominant over the polarization effects. The main component of the polarization is the electronic one; in the case of PTCDA it has been calculated to be 1.8 eV in the crystal [22]. This value should be reduced if the charge is created near the organic crystal surface, which is the case for (inverse) photoemission measurements [23].

### 3.2. Optical excitations

Following an argument similar to the one used for equations (14b) we can calculate the optical energy gap if the HOMO and LUMO levels are not degenerate. In this case, we create an electron–hole pair and define, using the same Koopmans approximation, the changes  $\delta n'_{i\alpha\sigma'}$ ,  $\delta n_{i\alpha\sigma}$  associated with the excited pair. Depending on whether  $\sigma = \sigma'$  or  $-\sigma'$  we obtain singlet and triplet transitions respectively. Thus the equivalent of (14a) reads

$$\begin{aligned} \text{SINGLET: } n_{i\alpha\uparrow}^* &= n_{i\alpha\uparrow} + \delta n'_{i\alpha} - \delta n_{i\alpha}; & n_{i\alpha\downarrow}^* &= n_{i\alpha\downarrow}, \\ \text{TRIPLET: } n_{i\alpha\uparrow}^* &= n_{i\alpha\uparrow} + \delta n'_{i\alpha}; & n_{i\alpha\downarrow}^* &= n_{i\alpha\downarrow} - \delta n_{i\alpha}. \end{aligned}$$

This allows us to define the change in the optical gap with respect to the OO HOMO–LUMO gap:

$$\delta E_{\text{opt}}^{\text{S}} = \frac{1}{2} \sum_{i\alpha \neq j\beta} J_{i\alpha, j\beta} (\delta n'_{i\alpha} - \delta n_{i\alpha}) (\delta n'_{j\beta} - \delta n_{j\beta}) + \frac{1}{2} \sum_{i\alpha} (J_{i\alpha}^{\text{eff}} + U_{i\alpha}^{\text{eff}}) (\delta n'_{i\alpha} - \delta n_{i\alpha})^2; \quad (15a)$$

the triplet case can be obtained from a similar equation:

$$\delta E_{\text{opt}}^{\text{T}} = \delta E_{\text{opt}}^{\text{S}} + \sum_{i\alpha} (J_{i\alpha}^{\text{eff}} + U_{i\alpha}^{\text{eff}} - U_{i\alpha\alpha}) \delta n'_{i\alpha} \delta n_{i\alpha}. \quad (15b)$$

In both formulae,  $U_{i\alpha}^{\text{eff}} = f_{i\alpha} (\tilde{U}_i - J_{i\alpha}^{\text{eff}})$ . One can see from equation (15b) that singlet–triplet transitions lie below the singlet–singlet ones ( $U_{i\alpha\alpha} > J_{i\alpha}^{\text{eff}} + U_{i\alpha}^{\text{eff}}$ ). However, the optical singlet–triplet transition is spin-forbidden and will not be discussed further.

If the HOMO and/or LUMO levels are degenerate, calculating the optical gap is more complicated. Different transitions, associated with distinct symmetries, can be coupled to each other. In this case our Koopmans approximation amounts to using an effective Hubbard Hamiltonian (in the language of chemistry this is the Pariser–Pople–Parr one [24]), which is given by the first part of Hamiltonian (2) neglecting  $\delta \hat{H}_0$ . The optical gap can be calculated, within this approximation, by analysing the excited states of this many-body Hamiltonian. For benzene, this analysis has been carried out by Pariser [25] who obtained for the  $\pi$ -orbitals of this molecule the following optical spectrum. For singlet excitations:

$$\delta E_{\text{opt}}^{\text{S}} = \begin{cases} \frac{2U - 5J_1 + 7J_2 - 4J_3}{6} & {}^1\text{B}_{1u} \\ \frac{U + 4J_1 - 4J_2 - J_3}{6} & {}^1\text{E}_{1u} \\ \frac{J_1 - 3J_2 + 2J_3}{6} & {}^1\text{B}_{2u}; \end{cases} \quad (16)$$

while for triplet excitations:

$$\delta E_{\text{opt}}^{\text{T}} = \begin{cases} \frac{-2U + 3J_1 - J_2}{6} & {}^3\text{B}_{1u} \\ \frac{U + 2J_1 - 2J_2 + J_3}{6} & {}^3\text{E}_{1u} \\ \frac{J_1 - 3J_2 + 2J_3}{6} & {}^3\text{B}_{2u}, \end{cases} \quad (17)$$

where  ${}^1\text{B}_{1u}, \dots, {}^3\text{B}_{2u}$  define the symmetry of each excited many-electron state;  $J_1, J_2$ , and  $J_3$  are the Coulomb interactions between the  $\pi$ -orbitals located at first, second, and third neighbours respectively. Thus we find that each excitation corresponds to a different correction to the energy gap calculated in DF theory. As we will discuss below, these corrections in general are not very large and we conclude that, with a reasonable accuracy, the optical gaps can be approximated by the LD energy gap.

#### 4. Results

We have applied the three different methods, F2k-LDA, F2k-OO, and LCAO-OO, to the molecules CO, CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and PTCDA (see figure 1). As described in section 3, the only difference between F2k-OO and F2k-LDA is in how the exchange and correlation are introduced. On the other hand, F2k-OO and LCAO-OO differ in:

- (i) the description of the effect of the core electrons (F2k-OO uses standard pseudopotentials, while in LCAO-OO these effects are introduced as described in section 2.2);
- (ii) the basis set, for which the two methods use different atomic-like orbitals (see section 2).

**Table 1.** Calculated and experimental equilibrium bond lengths (Å).

		F2k-LDA	F2k-OO	LCAO-OO	Experiment [26, 27]
CO		1.255	1.29	1.30	1.13
CH <sub>4</sub>		1.17	1.21	1.15	1.09
C <sub>6</sub> H <sub>6</sub>	C–H	1.17	1.20	1.15	1.10
C <sub>6</sub> H <sub>6</sub>	C–C	1.41	1.48	1.50	1.40
PTCDA	C=O	1.31	1.39	1.32	1.23
PTCDA	C–O	1.48	1.54	1.48	1.38
PTCDA	C–C	1.49	1.49	1.51	1.47

A comparison of the radial parts of the two types of orbital is given in figure 2. The carbon 2s and 2p orbitals were optimized for CO<sub>2</sub> and benzene environments separately. Differences between F2k-OO and LCAO-OO orbitals are found mostly in the core region; this is due to the different treatments of the core. In the bonding region the orbitals are similar, although their differences introduce non-negligible effects in our calculations.

Table 1 displays the equilibrium bond lengths (in ångströms) obtained for the molecules CO, CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and PTCDA with the three methods (we are not aware of any detailed experimental information about the bond lengths of PTCDA, so AM1 [28] calculation results are given). The different values obtained with F2k-LDA and F2k-OO are due to the description of exchange–correlation effects: it is well known that LDA overestimates the exchange–correlation energy [11], F2k-LDA therefore yielding shorter bond lengths than F2k-OO. On the other hand, the differences between LCAO-OO and F2k-OO are basically due to the basis sets used (see, for example, the C 2p orbitals in figure 2). Notice that the bond lengths obtained in the three cases are all significantly longer than the experimental values. This is mainly due to the minimal basis sets used in this paper. At this point it is worth mentioning that the different basis sets have not been optimized to provide good values for the bond lengths and curvatures (around the minimum of the total energy as a function of those bond lengths): this is an advisable procedure if one is interested in using minimal basis sets to analyse with good accuracy the behaviour of large systems (e.g. a system of PTCDA molecules interacting with a metal surface). Since the purpose of this paper is to discuss the applicability of the OO approach to the study of organic compounds, we have left for future work the question of determining the optimum minimal basis sets for specific molecules.

Table 2 compares the results for the binding and correlation energies in the different methods at their equilibrium geometries calculated within each approach. In order to provide a direct comparison of the LDA and OO exchange–correlation approaches, the F2k-OO results for the F2k-LDA equilibrium geometries are also given (in parentheses). To calculate the binding energies  $E_B$  we use Hartree–Fock atomic reference energies obtained within the corresponding core pseudopotential (or potential) and basis set. For the F2k-LDA and F2k-OO reference energies we numerically calculate the atomic wavefunctions solving the pseudoatomic problem in the LDA using a large  $R_C$ . With these orbitals we obtain the corresponding Hartree–Fock energy. In the case of LCAO-OO the reference atomic energies are the double-zeta Clementi–Roetti results [21]. The experimental correlation energies  $E_C$  are defined as the difference between the experimental binding energy and a basis-converged Hartree–Fock result, as appears in [27]. The OO correlation energy represents the contribution to the binding energy  $E_B$  arising from the correlation functional given by equation (5). In table 3 the binding and correlation energies for CO, CH<sub>4</sub>, and benzene at the experimental geometries are shown, and compared to the experimental results.

**Table 2.** Binding ( $E_B$ ) and correlation ( $E_C$ ) energies at equilibrium geometries (eV).

	CO	CH <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	PTCDA
$E_B$ (F2k-LDA)	-10.2	-13.3	-51.7	-222.2
$E_B$ (F2k-OO)	-4.6(-4.5)	-11.0(-10.9)	-40.8(-40.0)	-140.5(-133.2)
$E_B$ (LCAO-OO)	-6.3	-15.8	-52.9	-202.3
Experiment	-11.2	-18.4	-59.7	-235.1 <sup>a</sup>
$E_C$ (F2k-OO)	-4.3(-4.0)	-3.1(-2.9)	-16.6(-15.25)	-74.8(-65.7)
$E_C$ (LCAO-OO)	-3.6	-2.7	-16.9	-73.2
Experiment	-3.4	-4.0	-14.5	—

<sup>a</sup> Estimated as the sum of bond energies; see [29].

**Table 3.** Binding ( $E_B$ ) and correlation ( $E_C$ ) energies at experimental geometries (eV).

	CO	CH <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>
$E_B$ (F2k-LDA)	-9.4	-12.9	-51.1
$E_B$ (F2k-OO)	-3.3	-10.1	-38.8
$E_B$ (LCAO-OO)	-3.9	-15.8	-51.2
Experiment	-11.2	-18.4	-59.7
$E_C$ (F2k-OO)	-3.1	-2.6	-14.6
$E_C$ (LCAO-OO)	-2.7	-2.4	-15.1
Experiment	-3.4	-4.0	-14.5

From the results of table 3 we see that the OO approach yields a fair approximation to the correlation energy. Moreover, since in the F2k-OO and LCAO-OO calculations the contributions from the neglected three- and four-centre electron–electron integrals have been checked to be small, the exchange energy can be considered reasonably accurate, within the given basis set. Thus, comparing the F2k-LDA and F2k-OO results to the ‘experimental’ correlation energies we can conclude that, for the basis set used in these calculations (see figure 2), F2k-LDA overestimates the exchange–correlation energy by  $\sim 6$  eV for CO,  $\sim 1.5$  eV for CH<sub>4</sub>, and  $\sim 12$  eV for C<sub>6</sub>H<sub>6</sub>.

On the other hand, the comparison of F2k-OO and LCAO-OO (tables 1–3) suggests that LCAO-OO yields slightly better results for all the molecules. This is associated with the different orbital basis, and in particular with the different C p orbitals used for carbon (figure 2).

The contributions to the electron density from PTCDA HOMO and LUMO eigenfunctions were found to agree with results of other (GGA, tight-binding) calculations [30]. This is the case for all three approaches. The bonding pattern can be used to explain STM pictures [31] of PTCDA deposited on highly oriented pyrolytic graphite.

HOMO and LUMO levels for benzene and PTCDA are given in table 4, while the ionization and affinity levels calculated from equation (1) are given in table 5. We give vertical values, since the adiabatic energies, calculated allowing for molecular structure relaxation, were found to be only slightly different.

The experimental ionization potential  $I$  for gas phase benzene is 9.24 eV [26], which compares favourably with the F2k-LDA and F2k-OO results, while the experimental electron affinity is  $-1.14$  eV [32]. Our results for  $A$  have a higher error—its negative value reflects the fact that the  $(N + 1)$ -electron bound state lies in the continuum of states with  $N$  electrons bound and one free—a situation which our basis cannot describe accurately.

For PTCDA the gas phase experimental ionization potential  $I$  is 8.15 eV [33]. A DFT calculation performed with the B3LYP hybrid potential and 6-31G\* basis set was reported [34],

**Table 4.** Calculated HOMO and LUMO levels (eV).

	HOMO			LUMO		
	F2k-LDA	F2k-OO	LCAO-OO	F2k-LDA	F2k-OO	LCAO-OO
C <sub>6</sub> H <sub>6</sub>	−6.1	−4.4	−3.6	−0.7	0.8	2.0
PTCDA	−5.8	−4.2	−4.0	−4.3	−3.0	−2.4

**Table 5.**  $I$  and  $A$  (in eV) as calculated from equation (1).

	$I$			$A$		
	F2k-LDA	F2k-OO	LCAO-OO	F2k-LDA	F2k-OO	LCAO-OO
C <sub>6</sub> H <sub>6</sub>	9.35	8.6	6.6	−2.5	−4.0	−5.3
PTCDA	7.6	5.9	5.9	2.6	1.1	0.4

**Table 6.** The transport gap (in eV) as calculated from equation (1).

	Transport gap		
	F2k-LDA	F2k-OO	LCAO-OO
C <sub>6</sub> H <sub>6</sub>	11.8	12.6	11.9
PTCDA	5.0	4.8	5.5

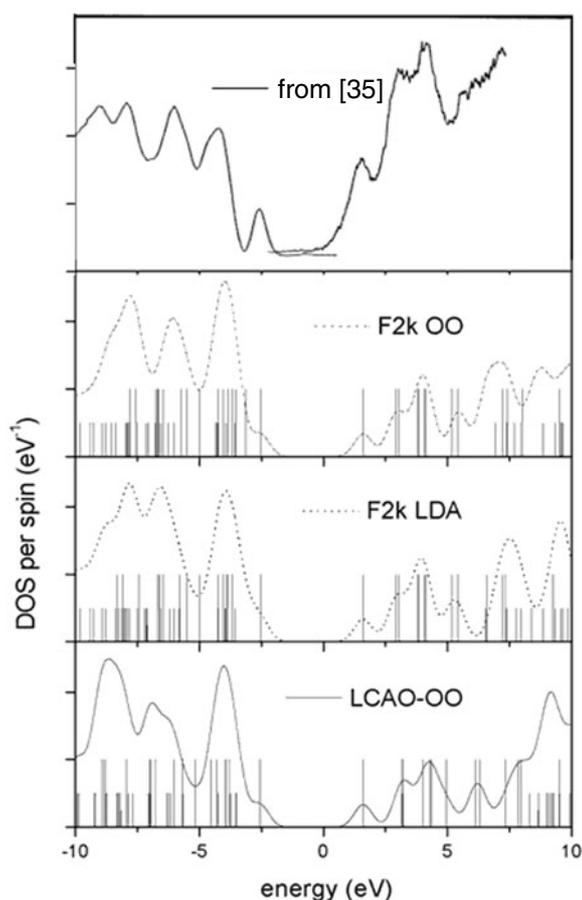
**Table 7.**  $I$ - and  $A$ -levels as calculated from Koopmans' theorem (eV). Differences from table 5 are given in parentheses.

	F2k-OO		LCAO-OO
	C <sub>6</sub> H <sub>6</sub>	$-\epsilon_{\text{HOMO}} + \delta I$	8.2(0.4)
	$-\epsilon_{\text{LUMO}} + \delta A$	−4.6(0.6)	−5.7(0.4)
PTCDA	$-\epsilon_{\text{HOMO}} + \delta I$	6.1(−0.2)	6.2(−0.3)
	$-\epsilon_{\text{LUMO}} + \delta A$	1.2(−0.05)	0.3(0.1)

yielding  $I = 7.79$  eV and  $A = 2.59$  eV. These values are very similar to the F2k-LDA ones; in F2k-OO and LCAO-OO the ionization and affinity levels are shifted to higher energies by about 1.5 eV. For PTCDA, the three methods yield, however, a similar transport gap  $I-A$ , which is shown in table 6.

We have applied our version of Koopmans' theorem to calculate  $I$  and  $A$  for benzene and PTCDA; the results are given in table 7. The differences between the results in table 5 and these approximate results are given in parentheses. We see that although Koopmans' theorem is not very precise for benzene, it yields fairly accurate ionization and affinity levels for PTCDA.

Figure 3 shows the density of states for PTCDA as calculated with the different methods used in this paper. To compare with experimental UPS/IPS spectra measured from a PTCDA thin film [36], we have renormalized the one-electron states in energy (equations (14b)) and broadened each level with a Gaussian function having a FWHM of 1 eV. Equations (14b) allow us to define the shifts separately for  $\pi$ - and  $\sigma$ -symmetry spectra. The transport gap in bulk or thin films has significant contributions not present in the gas phase, such as the polarization effects mentioned above, which are beyond the single-molecule calculation presented here. We have taken this into account in figure 3 by fitting the affinity and ionization levels to the experimental spectrum.



**Figure 3.** The density of states for PTCDA as calculated with the different methods ( $\text{eV}^{-1}$ ). The direct and inverse photoemission spectra are also shown for comparison (in arbitrary units). Long bars:  $\pi$ -states. Short bars:  $\sigma$ -states.

The general shape of the calculated spectra around the gap agrees well with the experiment. The  $\pi$ -type LUMO is well separated and lies about 1.6 eV below a wider band, also of  $\pi$ -character, close to the experimental value of 1.4 eV. The HOMO is of  $\pi$ -type symmetry and is separated by 1.5 eV from a band (1 eV wide) of  $\sigma$ -states related to oxygen lone pairs. In the theoretical spectra of figure 3 the HOMO is not well resolved due to the large number of close-lying states. In the experiment this group of states lies 1.7 eV from the HOMO-related peak.

We have also analysed the optical gap of benzene and PTCDA using the discussion provided above. For PTCDA we have found that  $\delta E_{\text{opt}}^{\text{S}}$  is very small,  $\sim 0.05$  eV, this result showing that the singlet PTCDA optical gap should be very close to the difference between the HOMO and LUMO LDA energies (which we have called the LDA gap). For benzene, as discussed above, we have many more optical excitations: their values can be calculated using equations (16) and (17). At this point we should mention that, as has been discussed by several authors (see for instance [37] and [38]), equations (16) and (17) can be improved by using ‘relaxed’ Coulomb interactions,  $U$ ,  $J_1$ ,  $J_2$ , and  $J_3$ : this takes into account, in an effective way, the electronic relaxation of the system. In our approach one can use similar arguments to modify  $U$ . This means basically that the electron–electron interaction inside a carbon atom is changed by intra-atomic electron relaxation effects which reduce  $U$  from  $\sim 18$  eV to around 16 eV. Taking this value and using our values for  $J_1 = 8.4$  eV,  $J_2 = 5.7$  eV,  $J_3 = 5.0$  eV,

yields the following excitation energies (in eV):

SINGLET	TRIPLET
$^1B_{1u}$ : 6.8(6.18)	$^3B_{1u}$ : 3.1(3.95)
$^1E_{1u}$ : 8.7(6.95)	$^3E_{1u}$ : 4.3(4.75)
$^1B_{2u}$ : 5.4(4.89)	$^3B_{2u}$ : 5.4(5.60)

where in parentheses we give the experimental values [39]. The comparison with the experimental data is satisfactory, taking into account the approximations made in the calculations. Notice that the discrepancy between theory and experiment is about  $\sim 0.7$  eV, similar to the one found in table 7 when comparing Koopmans'  $I$ - and  $A$ -levels with the ones calculated using full relaxed wavefunctions for the  $(N \pm 1)$ -electron ground state.

On the other hand, we find that for PTCDA, our calculated optical gaps are 1.5, 1.2, and 1.6 eV (F2k LDA, F2k OO, and LCAO-OO respectively), to be compared to the experimental value of 2.4 eV [40].

## 5. Conclusions

The main aim of this work is the implementation of a new LCAO-OO method to calculate the electronic properties of PTCDA. For the sake of comparison we have also performed calculations for small molecules, CO, CH<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>, which contain all the bonds found in PTCDA and whose electronic properties are well known.

The LCAO-OO method is a DFT-like approach based on using the OOs  $n_{i\sigma}$  as the independent variables instead of  $\rho(\vec{r})$ . In particular, the correlation energy is calculated with the help of a parametrized Hubbard (or Pariser–Pople–Parr) Hamiltonian. In the implementation presented in this paper we use a minimal local basis. Although this basis seems to give reasonable results for CH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>, and PTCDA, for CO it yields too large bond lengths and too small binding energies. This suggests that this basis set, after a better optimization for bond lengths and energy curvatures, can be appropriately used to calculate the PTCDA electronic properties.

In our analysis of the OO method, we have also used other approximations, namely F2k-LDA and F2k-OO. Our analysis confirms that a conventional LDA approach (e.g. F2k-LDA) yields too large exchange–correlation energies. This, however, results in the bond lengths and binding energies comparing well with experiment, which is only a consequence of an overestimation of the many-body energy. On the other hand, the results that we find for the F2k-OO approach are similar to the LCAO-OO ones, although some differences appear due to the different basis set.

As regards our LCAO-OO approach, we can say that for the molecules analysed in this paper (excluding CO), the calculated bond lengths and the total binding energies are within 6 and within 10–15%, respectively, of the experimental values. This is very satisfactory and shows that our LCAO approach can be used with confidence for large molecules such as C<sub>6</sub>H<sub>6</sub> and PTCDA, even with a minimal basis set. Obviously, if more precision is required, one expects the biggest improvement to come from applying a larger basis set. We are currently working along these lines in our group.

We have also successfully calculated the ionization and affinity levels of benzene and PTCDA, as well as their optical gaps. To obtain these quantities we have introduced and applied a version of Koopmans' theorem. In particular we have obtained the different Koopmans relaxation energies for the  $\sigma$ - and  $\pi$ -orbitals in PTCDA and have calculated the appropriate density of states for the molecule: this is a quantity deeply related to the Fermi level position in a metal/PTCDA junction [41].

In conclusion: LCAO-OO offers an accurate approach for calculating the electronic properties of organic molecules.

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