Appl Phys A (2009) 95: 257–263
DOI 10.1007/s00339-008-5022-0

Applied Physics A
Materials Science & Processing

Corrections to the density-functional theory electronic spectrum: copper phthalocyanine

H. Vázquez · P. Jelínek · M. Brandbyge · A.P. Jauho · F. Flores

Received: 24 August 2008 / Accepted: 24 November 2008 / Published online: 24 December 2008

Abstract A method for improving the electronic spectrum of standard Density-Functional Theory (DFT) calculations (i.e., LDA or GGA approximations) is presented, and its application is discussed for the case of the copper phthalocyanine (CuPc) molecule. The method is based on a treatment of exchange and correlation in a many-body Hamiltonian, and it leads to easy-to-evaluate corrections to the DFT eigenvalues. Self-interaction is largely corrected, so that the modified energy levels do not suffer from spurious crossings, as often encountered for CuPc in DFT, and they remedy the standard underestimation of the gap. As a specific example we study the sequence and position of the CuPc molecular orbitals, which are wrongly calculated by standard DFT, and show that they are correctly reproduced after our corrections are included. The suggested method is fast and simple and, while not as accurate as hybrid or semiempirical functionals for molecular levels, it can be easily applied to any local-orbital DFT approach, improving on several important limitations of standard DFT methods.

H. Vázquez (✉) · M. Brandbyge · A.P. Jauho
DTU Nanotech, Technical University of Denmark, 2800, Kgs. Lyngby, Denmark
e-mail: hector.vazquez@nanotech.dtu.dk

P. Jelínek
Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53, Prague, Czech Republic

A.P. Jauho
Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, 02015 Helsinki, Finland

F. Flores
Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain

PACS 31.15.E- · 31.10.+z · 73.30.+y

1 Introduction

In the last two decades, the field of organic semiconductors has experienced an enormous growth due to the potential use of these materials in technological applications such as organic light-emitting diodes (OLEDs) [1], organic field-effect transistors (OFETs) [2] or organic photovoltaic cells [3]. The performance of these devices often depends strongly on the electronic properties of the interfaces of these organic semiconductors with other materials, such as organic or inorganic semiconductor layers or metal electrodes. Consequently, the structural and electronic properties of such systems have been investigated using several experimental techniques [4, 5], while theoretical calculations provide important information on the basic mechanisms that determine the electronic structure of these systems, as well as aiding the interpretation of experimental results [6–9].

Amongst these organic materials, metal phthalocyanines have been studied because of their chemical stability and favorable film growth and electronic properties. Copper phthalocyanine (CuPc) is one such metal phthalocyanine which has been studied rather extensively [10–16]. The CuPc molecule is planar and has fourfold symmetry, and consists of a central copper atom surrounded by four ligands which have pyrrole and benzene rings (see Fig. 1(a)). Theoretical calculations on CuPc based on Density-Functional Theory (DFT) have been carried out to investigate band alignment and interface properties [14–17], but their interpretation (such as the magnitude of the gap or the position of molecular levels) has not been straightforward due to intricacies in the DFT approach; in some cases these are related to the different 'flavors' that can be used in the calculation, while others are intrinsic limitations of DFT. In particular, contradictory results have been obtained as to the sequence and position of occupied states near the gap (e.g., states of π or σ symmetry are interchanged). Moreover, while the description of the interface (with both metal and molecule) certainly does not make matters simpler, these problems are already present when studying the isolated CuPc molecule, and have been shown [18] to be related to self-interaction errors and the description of exchange and correlation in DFT. The local-density (LDA) or generalized-gradient (GGA) approximations (which we refer to hereafter as 'standard' DFT) do not properly correct for self-interaction and yield a distorted ordering of molecular orbitals, while functionals containing exact (Fock) exchange perform significantly better. The semiempirical functional B3LYP [19] (containing a fraction of exact exchange which is fitted to a set of molecular properties) is the usual choice for calculating isolated organic molecules, but it is probably not a good choice for metal/organic interfaces since it fails for metals [20]. While several hybrid functionals have been proposed (see the discussion in [21]), they generally have the disadvantage of a higher computational cost.

In this paper, therefore, we calculate the electronic structure of the CuPc molecule using standard DFT and present a method to correct the DFT level positions in a simple way. While this method has been previously described within the Orbital-Occupancy approach [22] and used to calculate the position of the Charge Neutrality Level of organic semiconductors (see, for example, [23–25]), here it is reformulated for standard DFT methods, with the aim of describing how the corrections could be implemented in any DFT code. Additionally, the origin of these corrections and their relation to self-interaction errors are discussed in detail and a careful analysis of the sequence of molecular orbitals in CuPc (which is not given correctly by standard DFT) is then performed.

The paper is organized as follows: Sect. 2 discusses the corrections to the molecular level positions, while their application to the CuPc spectrum is presented in Sect. 3; in the final section we give a summary and describe how our approach can be generalized to metal/organic interfaces.

2 Corrections to molecular levels

We recall the fact that DFT eigenvalues are not a proper representation of quasiparticle excitation energies: in conjugated organic molecules, the difference between the DFT HOMO and LUMO eigenvalues is significantly smaller that the transport gap measured experimentally [10, 11, 13]. This discrepancy largely arises from the fact that the DFT gap refers to the N-electron calculation, while the transport gap E^t is the difference between the ionization (I) and affinity (A) levels: $E^t = I - A$, where

$$\begin{aligned} I &= E[N] - E[N-1]; \\ A &= E[N+1] - E[N], \end{aligned} \tag{1}$$

and $E[N_i]$ is the energy of the system with N_i electrons.

In this paper, we propose a simple scheme to calculate the electronic spectrum of a molecular solid by approximating its total energy in a charged configuration; we do so by considering the corresponding many-body contributions to the total energy using the wavefunctions of the uncharged (N-electron) case [22]. The position of molecular levels is determined here by considering the effect on the total energy of adding an electron to, or removing it from, a certain molecular orbital and neglecting the electron rearrangement that takes place upon charging in analogy with Koopmans' theorem in Hartree–Fock theory. We have previously shown [22, 27] that these rearrangement effects are larger in small molecules such as benzene but that this approximation gives no appreciable differences in bigger molecules, such as the case considered here.

We analyze the addition or removal of an electron from a system using the following many-body generalized Hubbard-like Hamiltonian:

$$\hat{H} = \hat{H}^{\text{o.e.}} + \sum_i U_i \hat{n}_{i\uparrow}\hat{n}_{i\downarrow} + \sum_{i\sigma, j\sigma'} J_{ij}\hat{n}_{i\sigma}\hat{n}_{j\sigma'}, \tag{2}$$

where the first term represents the one-electron part, while the latter two are the electron–electron (Coulomb) interaction between the same or different sites; indices i and j label sites (typically atomic orbitals), while σ is the spin state.[1] In a mean-field approximation, the ground-state energy for this Hamiltonian is [22, 26, 27]:

$$\begin{aligned} E[N] = {} & \sum_i^N \epsilon_i^{\text{o.e.}} + \sum_i U_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2}\sum_{i\sigma \neq j\sigma'} J_{ij} n_{i\sigma} n_{j\sigma'} \\ & - \frac{1}{2}\sum_{i\sigma} J^x_{i\sigma} n_{i\sigma}(1 - n_{i\sigma}). \end{aligned} \tag{3}$$

Here, $n_{i\sigma} = \langle \hat{n}_{i\sigma} \rangle_{GS}$ are the atomic orbital occupations. The first term in (3) represents the one-body contributions to the energy, followed by the (intra- and inter-site) Hartree terms, while the last term is the exchange energy [26], which describes the interaction between the electron density $n_{i\sigma}$ and the corresponding hole density $1 - n_{i\sigma}$, through a weighted Coulomb integral [26] (see below); this description of exchange-correlation effects [22, 26] has several advantages over LDA, as we shall show below. Indices i and j

---

[1] Note that our method is not restricted to this particular form of Hamiltonian, and it is possible to include higher-order many-body terms, such as those discussed in [34].

run over the atomic orbitals and the Coulomb integrals

$$J_{ij} = \iint \frac{\psi_i^2(\vec{r})\psi_j^2(\vec{r}')}{|\vec{r}-\vec{r}'|}\, d\vec{r}\, d\vec{r}' \tag{4}$$

include intra- and interatomic integrals depending on whether orbitals i and j belong to the same atom or not. The exchange integrals J_i^x are the average of the J_{ij} weighed over the sites on which the exchange hole is delocalized (typically nearest-neighbors): $J^x_{i\sigma} = \sum_j J_{ij} n^2_{ij\sigma} / \sum_j n^2_{ij\sigma}$.

If an electron is now added to the system, the orbital occupations $\{n_i\}$ are increased with respect to the uncharged case; for a spin-up electron, for instance, we have:

$$\begin{aligned} n_{i\uparrow} &\longrightarrow n_{i\uparrow} + \delta n_{i\uparrow}, \\ n_{i\downarrow} &\longrightarrow n_{i\downarrow}, \end{aligned} \tag{5}$$

with an analogous expression for an added spin-down electron.

The total energy for this $N+1$ electron case is obtained by approximating the Hartree and exchange energies up to second order in δn and substituting (5) in (3). The affinity level (1) is then given by

$$\begin{aligned} A &= E[N+1] - E[N] \\ &= \epsilon^{\text{o.e.}}_{N+1} + \sum_i U_i \delta n_{i\uparrow} n_{i\downarrow} \\ &\quad + \frac{1}{2} \sum_{i\sigma \neq j\sigma'} J_{ij} \big(n_{i\sigma} \delta n_{j\uparrow} + n_{j\sigma'} \delta n_{i\uparrow} + \delta n_{i\uparrow} \delta n_{j\uparrow} \big) \\ &\quad - \frac{1}{2} \sum_{i\sigma} J^x_{i\sigma} \big[-n_{i\uparrow} \delta n_{i\uparrow} + (1-n_{i\uparrow}) \delta n_{i\uparrow} - \delta n^2_{i\uparrow} \big]. \end{aligned} \tag{6}$$

An equivalent equation can be written for the removal of an electron, which corresponds to the ionization energy, where the orbital populations vary upon charging by $\delta n'_{i\uparrow}$ (which are, in general, not equal to $\delta n_{i\uparrow}$; see (12) below):

$$\begin{aligned} n_{i\uparrow} &\longrightarrow n_{i\uparrow} - \delta n'_{i\uparrow}, \\ n_{i\downarrow} &\longrightarrow n_{i\downarrow}. \end{aligned} \tag{7}$$

In a similar way, we arrive at

$$\begin{aligned} I &= E[N] - E[N-1] \\ &= \epsilon^{\text{o.e.}}_{N} - \sum_i U_i \delta n'_{i\uparrow} n_{i\downarrow} \\ &\quad - \frac{1}{2} \sum_{i\sigma \neq j\sigma'} J_{ij} \big(-n_{i\sigma} \delta n'_{j\uparrow} - n_{j\sigma'} \delta n'_{i\uparrow} + \delta n'_{i\uparrow} \delta n'_{j\uparrow} \big) \\ &\quad + \frac{1}{2} \sum_{i\sigma} J^x_{i\sigma} \big[n_{i\uparrow} \delta n'_{i\uparrow} - (1-n_{i\uparrow}) \delta n'_{i\uparrow} - \delta n'^2_{i\uparrow} \big]. \end{aligned} \tag{8}$$

Notice that, within the same approximation of E^H and E^x up to second order in δn, we can rewrite (6) and (8) as

$$\begin{aligned} I &= E[N] - E[N-1] \\ &= \epsilon^{\text{o.e.}}_{N} - \frac{\partial(E^H + E^x)}{\partial n_{i\uparrow}} \delta n_{i\downarrow} \\ &\quad - \frac{1}{2} \left(\frac{\partial^2 E^H}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n_{i\uparrow} \delta n_{j\uparrow} - \frac{\partial^2 E^x}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n^2_{i\uparrow} \right), \\ A &= E[N+1] - E[N] \\ &= \epsilon^{\text{o.e.}}_{N+1} + \frac{\partial(E^H + E^x)}{\partial n_{i\uparrow}} \delta n_{i\downarrow} \\ &\quad + \frac{1}{2} \left(\frac{\partial^2 E^H}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n_{i\uparrow} \delta n_{j\uparrow} - \frac{\partial^2 E^x}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n^2_{i\uparrow} \right). \end{aligned} \tag{9}$$

By realizing that the Hartree and exchange potentials are given by the derivative of the total energy with respect to the occupation numbers, $\frac{\partial E}{\partial n_i}$, these terms up to first order in δn are included in the DFT level positions. The difference between these DFT levels and the ionization and affinity energies is given by the remaining terms (second-order terms proportional to $\frac{\partial^2 E}{\partial n_i \partial n_j}$), which constitute the corrections we propose to the DFT levels:

$$\begin{aligned} I &= \epsilon^{\text{DFT}}_{N}(\text{HOMO}) \\ &\quad - \frac{1}{2} \left(\frac{\partial^2 E^H}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n_{i\uparrow} \delta n_{j\uparrow} - \frac{\partial^2 E^x}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n^2_{i\uparrow} \right) \\ &= \epsilon^{\text{DFT}}_{N}(\text{HOMO}) \\ &\quad - \frac{1}{2} \sum_{i \neq j} J_{ij} \delta n'_{i\uparrow} \delta n'_{j\uparrow} - \frac{1}{2} \sum_i J^x_i {\delta n'_{i\uparrow}}^2, \\ A &= \epsilon^{\text{DFT}}_{N}(\text{LUMO}) \\ &\quad + \frac{1}{2} \left(\frac{\partial^2 E^H}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n_{i\uparrow} \delta n_{j\uparrow} - \frac{\partial^2 E^x}{\partial n_{i\uparrow} \partial n_{j\uparrow}} \delta n^2_{i\uparrow} \right) \\ &= \epsilon^{\text{DFT}}_{N}(\text{LUMO}) \\ &\quad + \frac{1}{2} \sum_{i \neq j} J_{ij} \delta n_{i\uparrow} \delta n_{j\uparrow} + \frac{1}{2} \sum_i J^x_i {\delta n_{i\uparrow}}^2. \end{aligned} \tag{10}$$

In our calculations, we have used the N-electron Kohn–Sham orbitals to describe the wavefunctions of the excitations. This implies that the variations in the orbital populations are simply given by the projection of the corresponding wavefunction on the basis orbitals $\{\psi_i\}$; for the ionization and affinity energies, these are

$$\begin{aligned} \delta n'_{i\uparrow} &= -\big|\langle \psi_i | \text{HOMO} \rangle\big|^2, \\ \delta n_{i\uparrow} &= \big|\langle \psi_i | \text{LUMO} \rangle\big|^2. \end{aligned} \tag{11}$$

Normalization of the Kohn–Sham wavefunctions ensures that the charge variation is not a fraction but exactly one electron ($\sum_i \delta n_{i\uparrow} = 1$).

The above analysis can be extended not just for the ionization and affinity levels but for all molecular orbital positions E_α:

$$E_\alpha = \epsilon_N^{\mathrm{DFT}}(\alpha) \pm \frac{1}{2}\sum_{i\neq j} J_{ij}\delta n_{i\uparrow}\delta n_{j\uparrow} \pm \frac{1}{2}\sum_i J_i^x \delta n_{i\uparrow}^2, \tag{12}$$

$$\delta n_{i\uparrow} = \pm\big|\langle\psi_i|\Phi(\alpha)\rangle\big|^2,$$

where the plus (minus) sign should be used for empty (occupied) molecular orbitals.

Equation (12) is our main formal result: it expresses the energies of the molecular levels as a bare DFT result, plus a correction which is evaluated using the corresponding N-electron wavefunction. In DFT, the ith eigenvalue is the derivative of the total energy with respect to the (continuous) occupation of that orbital [28]. This is a formal result, valid for the exact exchange-correlation functional, and the approximations made in the description of exchange and correlation result in differences with the exact gap; in particular, it is well-known that LDA and GGA significantly underestimate the gap. From an analysis of the total energy for the charged configuration within a many-body Hamiltonian, we can identify certain terms, proportional to the second derivative of the energy with respect to the occupation number, which are not included in the DFT energy levels. These terms constitute the corrections we propose. Moreover, even though the description of exchange and correlation in LDA or GGA is very different to that of (3), we show that (12) captures the most important many-body contributions, making these corrections applicable for LDA or GGA functionals. This is analyzed below for the case of CuPc.

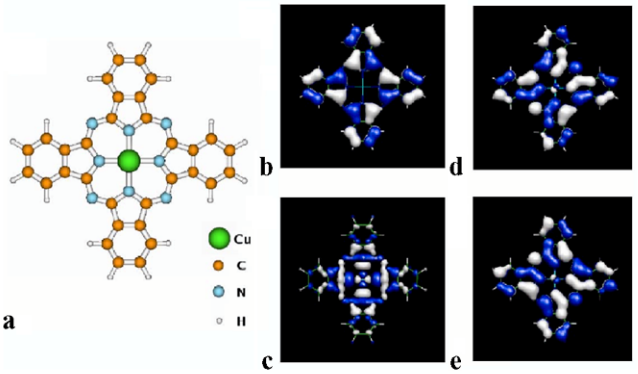

Fig. 1 (**a**) Chemical structure of the CuPc molecule. Molecular orbitals near the gap: (**b**) π orbital delocalized over the pyrrole and benzene rings, (**c**) orbital localized around the Cu atom, whose position in standard DFT is spuriously pushed close to the vacuum level due to self-interaction errors, (**d**, **e**) degenerate LUMO

Table 1 Some parameters used in the calculations

	Cu	C	N	H
J_{ij}^{intra} (eV)	24.5	17.0	19.0	20.5
J_i^x (eV)	4.5	6.0	6.0	11.5

3 Copper phthalocyanine

The CuPc molecule contains an odd number of electrons and the occupied spectrum has two orbitals whose relative position depends rather sensitively on the computational details, as discussed in the literature [14–17]. One of them is of π symmetry, delocalized over the pyrrole and benzene rings (see Fig. 1(b)), while the other one is a singly-occupied state of in-plane symmetry, with a large amplitude on the Cu and neighboring N atoms (Fig. 1(c)). Discerning which of these two is the HOMO is of obvious importance, yet contradictory results have been published [14–17]. The current understanding [18] is that the correct ordering of these states has the (doubly-occupied) π orbital as the HOMO, with the (singly-occupied) Cu-related orbital lower in energy. Moreover, it has been shown [18] that errors arising from self-interaction, which are present in standard DFT functionals, artificially shift the position of all molecular orbitals (especially the strongly Cu-localized orbital close to the vacuum level) in some cases giving rise to a spurious crossing with the HOMO level, complicating the interpretation of DFT level positions. Here we start with a DFT calculation of the molecule using a 'standard' exchange-correlation functional (i.e., LDA or GGA) and then correct the level positions according to the scheme described in Sect. 2.

The DFT calculations were carried out using the *SIESTA* [30] and *Fireball* [31] codes, using both the LDA and GGA, and spin-polarized and unpolarized approximations. We find that using either the LDA approximation or a spin-degenerate approach results in the wrong position of the Cu-localized orbital as the HOMO; these results are in agreement with other DFT results reported in the literature [18]. The HOMO-LUMO gap is ∼1.0 eV (zero for the spin-degenerate case, as the Cu-localized HOMO is singly-occupied), significantly smaller than the experimental value for the transport gap [10, 11, 13]. From our DFT calculations, the Kohn–Sham eigenvalues $\epsilon_N^{\mathrm{DFT}}(\alpha)$ and eigenvectors $\Phi(\alpha)$ are obtained. Values for J_{ij}^{intra} and J_i^x for CuPc are shown in Table 1, while the δn_i are square of the amplitude of molecular orbital α on the basis orbital i. (For nearest-neighbors we evaluate the integral in (4) directly, while for larger separations we can approximate $J_{ij}^{\mathrm{inter}} \simeq 1/R_{ij}$.) Thus, all parameters involved in (12) are determined by the N-electron (DFT) calculation of the first step.

The application of (12) to the CuPc molecule is shown in Fig. 2, which shows the value of the corrections (12) for

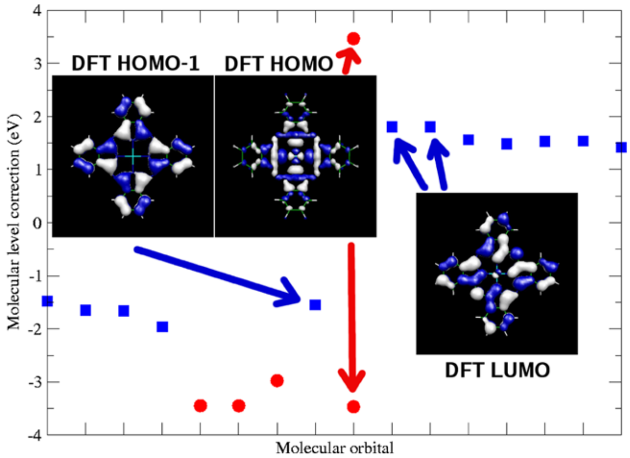

Fig. 2 Value of the corrections to the DFT spin-degenerate molecular levels (of π (*blue*) or σ (*red*) symmetry), as obtained using (12). Positive (negative) values correspond to empty (occupied) states. The spin-degenerate HOMO, localized in the Cu and N atoms, gives rise to two levels, each accommodating one electron, whose energy difference is the Hubbard U for this state, as discussed in the text

each molecular orbital. The magnitude of these corrections is large, and the sign is positive (negative) for empty (occupied) states. Not surprisingly, strongly-localized molecular orbitals give rise to important level corrections due to the large values of J_{ij} and δn_i (see Table 1 and (12)). We believe this to be important, since the form of (12) is clearly reminiscent of self-interaction correction terms [29], and the magnitude of the corrections, which increase with localization, follow the product of the densities, just as one would expect for self-interaction corrections.

Figure 3 compares the molecular spectrum for the LDA spin-degenerate approximation before and after the application of (12) (we choose the spin-degenerate case to focus on the many-body effects that determine the level positions, as described below). The corrections to the levels are introduced as a scissors operator, shifting the position of each DFT level by the amount given by (12) for that level. The right panels show both spectra broadened by a 0.4 eV Gaussian [15]. For clarity, the HOMO is aligned at the experimental ionization energy (−6.4 eV, [15]). The calculated spectra do not reproduce quantitatively the experimental results of [15], nor do they agree with all the details of the most sophisticated hybrid-functional calculations, as reported in [18], which agree quite well with experiment. The reason for this is the rather simple LDA calculation, Fig. 3, top panel, which underlies the subsequent corrected spectra. What is significant is that the application of (12) does provide substantial improvement over that of standard DFT in two main areas. The first one is the spurious sequence of molecular orbitals around the HOMO, associated to self-interaction errors, which is corrected by (12). The second one is the significant opening of the gap, which goes from ∼1.0 eV (DFT) to 4.7 eV (after the application of (12)). For the LDA case (top right), this underestimation of the gap is so important that the contribution from the empty states overlaps with the occupied one. The energy gap obtained through combined photoemission/inverse photoemission spectroscopy is 2.1–2.3 eV on thin films [10, 11, 13]. If we now consider that the difference in the ionization or affinity levels between the gas-phase and condensed-phase is ∼0.85 eV [10, 32], the previous values translate to 3.8–4.0 eV for the gas-phase gap, smaller than our value of 4.7 eV, which seems to indicate that our method leads to too large corrections. We note in passing that we compare with the transport gap obtained from combined direct/inverse photoemission gap, rather than the optical gap (∼1.5–1.7 eV [10, 11, 13]), as the latter includes a significant (∼0.6 eV) excitonic component.

Finally, while the LDA or GGA spectra show minor differences and suffer from the same shortcomings with respect to the gap and self-interaction errors (see also [18]), we chose to show the spin-degenerate spectrum to illustrate how the description of exchange-correlation beyond mean field can split a singly-occupied (spin-degenerate) level into two levels, each accommodating one electron, and whose energy difference gives the value of the Hubbard U (one can think of the electronic levels of the hydrogen atom). Our approach allows for the determination of this many-body parameter associated with the molecular orbital localized around the Cu and N atoms (Fig. 1(c)); this is twice the correction for that orbital (Fig. 2), or 7.0 eV, slightly larger than those obtained using LDA+U calculations [16].

4 Conclusions

In this paper, a method for improving the electronic spectrum of standard DFT calculations (i.e., LDA or GGA approximations) was presented, and discussed for the case of the CuPc molecule. The method is based on an analysis of the change in total energy when an electron or hole is added to a specific molecular orbital, neglecting orbital relaxation due to charging (i.e., using the N-electron Kohn–Sham orbitals). The corrections are introduced as shifts modifying each DFT eigenvalue by a quantity which depends on that particular molecular level, and whose magnitude reflects (through the corresponding wavefunction) the energy associated with creating a charge excitation at that molecular orbital. The approach is formally very similar to other methods of obtaining level positions beyond LDA [33] and is fast and simple, since all necessary quantities can be obtained from the N-electron DFT calculation. Moreover, the use of these corrections for CuPc with the LDA approximation shows that, even if the description of exchange and correlation used in the derivation of the corrections is different from LDA, the most important many-body contributions are captured.

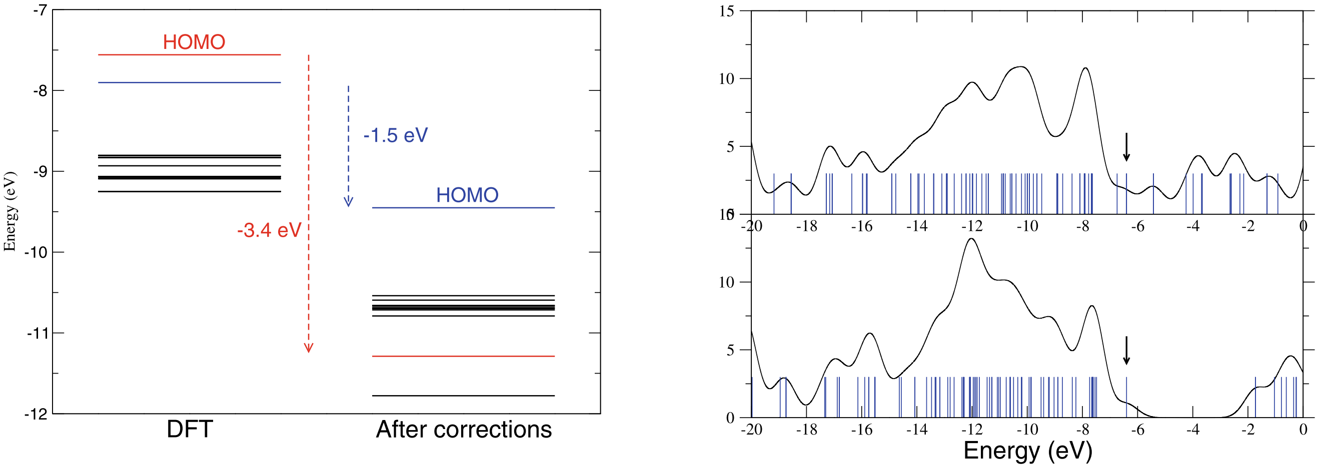

Fig. 3 (**a**) Position of molecular levels near the gap. The *dashed arrows* show the corrections for the Cu-localized σ (*red*) and pyrrole-delocalized π (*blue*) orbitals; (**b**) Electronic spectrum of the CuPc molecule, broadened by a 0.4 eV Gaussian, with the HOMO aligned at the experimental value of -6.4 eV (*arrows*): (*top*) spin-degenerate LDA calculation; (*bottom*) after the corrections to the molecular levels have been introduced, as discussed in the text. Molecular levels are shown as vertical bars. Notice that the LDA spectrum shows contributions from empty states, as the gap is so small

For the case of the CuPc molecule, the corrections do not perform as well as hybrid or semiempirical functionals, but they remedy important deficiencies of standard DFT, such as the spurious crossing of levels and symmetry of the HOMO, associated with self-interaction errors, or the underestimation of the gap. The large value of the gap and of the Hubbard U for the Cu-localized orbital suggest that we are overestimating the level corrections, but the inclusion of other many-body terms to (2) (as discussed in [34]) would reduce the magnitude of the level corrections.

Finally, the corrections described here can be introduced for the general case of a metal/organic interface by computing the level shifts projected on the molecular basis; that is, by computing (12) when indices i and j are basis orbitals belonging to molecular atoms. This way, the localized nature of molecular states would result (through the quantity $|\langle\psi_i|\Phi(\alpha)\rangle|^2$) in significant level corrections, while these would be negligible for Bloch states, delocalized over the metal, scaling the magnitude of the level corrections with the 'molecular character' of the orbital. In this case, though, this would have to be done within the self-consistency cycle to obtain a proper charge transfer. We are currently working in this direction.

Acknowledgements We gratefully acknowledge financial support from the Danish Research Council (Forskningsrådet for Teknologi og Produktion), the Spanish CICYT under projects NAN-2004-09183-C10-07 and MAT2007-60966, and the Comunidad de Madrid CAM under contract 0505/MAT/0303. P.J. acknowledges funding from GAAV under grants no. KAN400100701, IAA100100616 and IAA1010413. A.P.J. is grateful to the FiDiPro program of the Finnish Academy for financial support.

References

1. R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. Lögdlund, W.R. Salaneck, Nature **397**, 121 (1999)
2. G. Horowitz, J. Mater. Res. **19**, 1946 (2004)
3. P. Peumans, S. Uchida, S.R. Forrest, Nature **425**, 158 (2003)
4. W.R. Salaneck, K. Seki, A. Kahn, J.J. Pireaux (eds.), *Conjugated Polymer and Molecular Interfaces* (Dekker, New York, 2001)
5. N. Koch, J. Phys.: Condens. Matter **20**, 184008 (2008)
6. P.S. Bagus, V. Staemmler, C. Wöll, Phys. Rev. Lett. **89**, 096104 (2002)
7. R. Scholz, A.Y. Kobitski, D.R.T. Zahn, M. Schreiber, Phys. Rev. B **72**, 245208 (2005)
8. G. Heimel, L. Romaner, J.-L. Brédas, E. Zojer, Phys. Rev. Lett. **96**, 196806 (2006)
9. M.G. Betti, A. Kanjilal, C. Mariani, H. Vázquez, Y.J. Dappe, J. Ortega, F. Flores, Phys. Rev. Lett. **100**, 027601 (2008)
10. I.G. Hill, A. Kahn, Z.G. Soos, R.A. Pascal Jr., Chem. Phys. Lett. **327**, 181 (2000)
11. T. Schwieger, H. Peisert, M.S. Golden, M. Knupfer, J. Fink, Phys. Rev. B **66**, 155207 (2002)
12. S. Kera, Y. Yabuuchi, H. Yamane, H. Setoyama, K.K. Okudaira, A. Kahn, N. Ueno, Phys. Rev. B **70**, 085304 (2004)
13. D.R.T. Zahn, G.N. Gavrila, M. Gorgoi, Chem. Phys. **325**, 99 (2006)
14. V.Yu. Aristov, O.V. Molodtsova, V. Maslyuk, D.V. Vyalikh, V.M. Zhilin, Yu.A. Ossipyan, T. Bredow, I. Mertig, M. Knupfer, Appl. Surf. Sci. **254**, 20 (2007)
15. F. Evangelista, V. Carravetta, B. Jansik, S. Stranges, A. Ruocco, J. Chem. Phys. **126**, 124709 (2007)
16. A. Calzolari, A. Ferretti, M. Buongiorno Nardelli, Nanotechnology **18**, 424013 (2007)
17. A. Rosa, E.J. Baerends, Inorg. Chem. **33**, 584 (1994)
18. N. Marom, O. Hod, G.E. Scuseria, L. Kronik, J. Chem. Phys. **128**, 164107 (2008)
19. A.D. Becke, J. Chem. Phys. **98**, 5648 (1993)
20. J. Paier, M. Marsman, G. Kresse, J. Chem. Phys. **127**, 024103 (2007)
21. S. Kümmel, L. Kronik, Rev. Mod. Phys. **80**, 3 (2008)

22. R. Oszwaldowski, H. Vázquez, P. Pou, J. Ortega, R. Pérez, F. Flores, J. Phys.: Condens. Matter **15**, S2665 (2003)
23. H. Vázquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, A. Kahn, Europhys. Lett. **65**, 802 (2004)
24. H. Vázquez, W. Gao, F. Flores, A. Kahn, Phys. Rev. B **71**, 041306(R) (2005).
25. H. Vázquez, Y.J. Dappe, J. Ortega, F. Flores, J. Chem. Phys., J. Chem. Phys. **126**, 144703 (2007)
26. P. Pou, R. Pérez, F. Flores, A. Levy Yeyati, A. Martín-Rodero, J.M. Blanco, F.J. García-Vidal, J. Ortega, Phys. Rev. B **62**, 4309 (2000)
27. H. Vázquez, Ph.D. dissertation, Universidad Autónoma de Madrid (2006)
28. J.F. Janak, Phys. Rev. B **18**, 7165 (1978)
29. J.P. Perdew, A. Zunger, Phys. Rev. B **23**, 5048 (1981)
30. J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002)
31. P. Jelínek, H. Wang, J.P. Lewis, O.F. Sankey, J. Ortega, Phys. Rev. B **71**, 235101 (2005)
32. W.R. Salaneck, Phys. Rev. Lett. **40**, 60 (1978)
33. J.D. Sau, J.B. Neaton, H.J. Choi, S.G. Louie, M.L. Cohen, Phys. Rev. Lett. **101**, 026804 (2008)
34. Y.J. Dappe, R. Oszwaldowski, P. Pou, J. Ortega, R. Pérez, F. Flores, Phys. Rev. B **73**, 235124 (2006)