Quantifying the relative molecular orbital alignment for molecular junctions with similar chemical linkage to electrodes

Ioan Bâldea

Theoretische Chemie, Universität Heidelberg, Im Neuenheimer Feld 229, D-69210 Heidelberg, Germany

E-mail: ioan@pci.uni-heidelberg.de.

Received 4 August 2014, revised 29 September 2014
Accepted for publication 30 September 2014
Published 20 October 2014

Abstract

Estimating the relative alignment between the frontier molecular orbitals (MOs) that dominates the charge transport through single-molecule junctions represents a challenge for theory. This requires approaches beyond the widely employed framework provided by the density functional theory, wherein the Kohn–Sham orbitals are treated as if they were real MOs, which is not the case. In this paper, we report results obtained by means of quantum chemical calculations, including the equation-of-motion coupled-cluster singles and doubles, which is the state-of-the-art of quantum chemistry for medium-size molecules like those considered here. These theoretical results are validated against data on the MO energy offset relative to the electrodes’ Fermi energy extracted from experiments for junctions based on 4,4′-bipyridine and 1,4-dicyanobenzene.

Keywords: molecular junctions, molecular orbital alignment, transition voltage spectroscopy, dicyanobenzene, bipyridine

(Some figures may appear in colour only in the online journal)

1. Introduction

The last decades marked significant advances in the fabrication and characterization of a variety of molecular electronic devices based on a single or a small number of molecules. For understanding an impressive amount of experimental material accumulated, results of numerical calculations are usually presented. They are performed within theoretical frameworks, which are often completely opaque and preclude a straightforward interpretation in terms of properties having a simple and clear physical meaning.

An important property of this kind is the relative alignment of the frontier orbitals relative to the electrodes’ Fermi energy $E_F$ of a molecule embedded in a molecular junction [1]. The energy offset $\epsilon_0 = \min (E_{\text{LUMO}} - E_F, E_F - E_{\text{HOMO}})$ of the highest occupied or lowest unoccupied molecular orbital (HOMO or LUMO, respectively), whichever is closest to the Fermi level $E_F$, is usually compared to a tunneling energy barrier [2]. It is a key quantity in molecular transport, because it controls the charge transfer efficiency. Current experimental methods to estimate the energy offset $\epsilon_0$ employ ultraviolet photoelectron spectroscopy [3], thermopower [4–7], and transition voltage spectroscopy (TVS) [8]. TVS is a method that became very popular in the molecular electronic community due to its simplicity [2, 9–17]. TVS-based results deduced from [2], a work that significantly contributed to the TVS popularity, represent an essential piece of experimental data to be used in the present study.

Postulating the existence of a single orbital that dominates the charge transport in a molecular junction might appear to be a too crude approximation. However, recent extensive analysis [18–24] of existing transport data measured for a variety of molecular junctions demonstrated that, in the entire voltage accessed experimentally, current–voltage $(I-V)$ curves can indeed be excellently be reproduced by assuming just the contribution of a single dominant molecular orbital (MO). Although this is an enormous simplification, the
quantitative description of the relative alignment $\epsilon_0$ of the dominant orbital of the embedded molecule remains an important challenge for \textit{ab initio} approaches to the charge transport. The vast majority of the theoretical approaches of the charge transport through molecular devices utilized to date are based on the combination of the nonequilibrium Green’s functions (NEGF) and density functional theory (DFT) [25]. The most important drawback of such approaches directly related to the main issue considered in this paper is the fact that they treat the eigenvalues of the Kohn–Sham (KS) equations as if they were energies with physical meaning. In reality, as is well known, KS orbitals are mathematical objects rather than true MO [26]. So, it is not at all surprising that their ‘energies’ cannot provide an adequate physical description [26, 27]. Unoccupied orbitals are especially difficult to describe theoretically [22, 24]. Therefore, molecular junctions exhibiting an n-type (LUMO-mediated) conduction, like the ones to be considered in this study, deserve a special consideration.

Demonstrating that valuable information on the LUMO alignment in molecular junctions can be obtained within reliable quantum chemical approaches beyond DFT represents an important aim of the present paper. To validate the theoretical approach developed here, we will employ experimental data for molecular junctions based on 1,4-dicyanobenzene (BDCN) [2] and 4,4′-bipyridine (44BPY) [6].

2. Disentangling the contributions to the dominant MO energy offset

As a remedy of the main drawback of approaches to the charge transport through molecular devices that combine NEGF and DFT mentioned in Introduction, in more elaborate (so-called ‘DFT + $\Sigma$’) developments [6, 28] the occupied ($\epsilon_p < E_F$) and unoccupied ($\epsilon_p > E_F$) KS ‘orbitals’ are rigidly shifted in opposite directions by the same ($p$-independent) amount $\Delta$ obtained either by fitting experimental data [29] or in a two-step procedure as follows. First, a value $\Delta_0 = E_{LUMO} - E_{HOMO}$ of the HOMO–LUMO gap is deduced from the energies $\epsilon$ of the various (neutral, anionic and cationic) charge species in the gas phase $\Delta_0 = \epsilon_{\text{neutral}} - \epsilon_{\text{cation}} - 2\epsilon_{\text{neutral}}$, a method known as $\Delta$-SCF [26] (or, more appropriate, $\Delta$-DFT [22, 27, 30, 31]). Because the value $\Delta_0$ is usually much too large, it is then renormalized ($\Delta_0 \rightarrow \Delta$) by considering image charges of a LUMO (HOMO) modeled as a point-like electron (hole) formed in electrodes taken as infinite plates in the immediate vicinity of the active molecule [6, 28, 32]. Although the renormalization found in this way may render the corresponding $\Delta$-value compatible to experiments, recent work [27, 33–35] has drawn attention on the fact that these assumptions are inadequate for realistic molecular junctions [27, 33–35].

An aspect on which we want to draw attention in this study is the following. NEGF–DFT transport calculations done as described above utilize an extended molecule, which includes several atomic layers from electrodes in addition to the active molecule. On the other side, as it has been long recognized, the classical image potential originates from the interaction of the electron in the LUMO with electronic collective (long-wavelength polarization) modes in the metals, in particular, surface, interface and bulk plasmons [36–41]. So, the effect of the electrons of the atoms of the electrodes belonging to the extended molecule is also accounted for in the interaction energy $\Phi_{\text{im}}$ with the image charges. Therefore, the procedure of applying $\Sigma$-corrections (these corrections are due to image charges) on top of NEGF–DFT approaches is plagued by double counting.

To overcome this drawback, we propose here a disentangling procedure, which we then validate by comparing molecular junctions based on two molecules, namely BDCN and 44BPY. Previous studies demonstrated an n-type (LUMO-mediated) conduction for both types of junctions [2, 6, 22, 42]. So, it is the LUMO on which attention will be focused below.

The disentangling scheme for the LUMO energy is presented in figure 1. (For the numerical values given in figure 1 please refer to section 4.) In the absence of molecule–electrode couplings, the LUMO energy $E_1$ is given by the lowest electron attachment energy $\epsilon_A$ of the isolated molecule taken with reversed sign ($E_1 = -\epsilon_A$, Koopman’s theorem). The LUMO energy $E_{\text{LUMO}}$ of the molecule embedded in a nanojunction differs from that of the isolated molecule because an electron transferred to the LUMO interacts with the electrodes. The scheme proposed here holds in cases (and we will show below that such cases do exist) where it is possible to split this interaction into a short-range and a long-range part that can be analyzed separately. They yield two

![Figure 1. Disentangling the contributions to the LUMO energy offset for the two molecules—4,4′-bipyridine (44BPY) and 1,4-dicyanobenzene (BDCN)—embedded in the molecular junctions considered in the present paper. The electron attachment energy with reversed sign represents the LUMO energy of the isolated molecule ($E_l = -\epsilon_A$). $\Phi_{\text{im}}$ and $\Lambda$ represent LUMO energy shifts due to image charges and local (contact) effects resulting from long-range and short-range interactions between the embedded molecule and the electrodes, respectively. The nearly equal quantities $\Lambda_1 \approx \Lambda_2$ reflect the similar chemical linkage (nitrogen–gold affinity) to electrodes. See the main text for details.](image)
contributions (denoted $\Lambda$ and $\Phi_{im}$, respectively) to the corresponding LUMO energy shift

$$E_{\text{LUMO}} = E_I + \Lambda + \Phi_{im}. $$  \hspace{1cm} (1)

Equation (1) allows one to express the LUMO energy offset as

$$\varepsilon_0 = E_{\text{LUMO}} - E_F = -E_A + \Lambda + \Phi_{im} - E_F. $$  \hspace{1cm} (2)

To avoid the double counting issue mentioned above, in addition to the electrodes’ collective effect embodied in the image charge contribution $\Phi_{im}$, we will consider the local LUMO energy shift $\Lambda$ due to the interaction of the active molecule with the metal atoms at its ends. This accounts for the well known fact that a chemisorbed molecule strongly coupled to the substrate often has valence MO energies substantially different from that in the gas phase [43]. Experimental data on molecular junctions, indicating a substantial MO energy shift due to local (interface) dipoles [3], may also be taken as a confirmation of this hypothesis.

3. Method

To obtain the theoretical results presented in this paper we have utilized the EOM–CCSD (equation-of-motion coupled-cluster singles and doubles) [44–46]. This method represents the state-of-the-art of chemistry for medium-size molecules, like the ones to be considered here. The CCSD calculations were performed with the CFOUR package [47]. For comparison purposes, results based on hybrid coupled clusters (CC2) [48] and regular (strict) second-order algebraic-diagrammatic constructions (ADC(2)) [49, 50] will also be presented. ADC(2) calculations have been done with the fully parallelized PRICD-$\Sigma$(2) code [51], which is interfaced to MOLCAS [52].

The molecular geometries were optimized at the DFT level using the B3LYP hybrid functional as implemented in GAUSSIAN 09 [53], a package also employed to estimate the electroaffinities by means of $\Delta$-DFT calculations [26, 27, 30]. All results of the quantum chemical calculations reported here were obtained by employing aug-cc-pVDZ (Dunning augmented correlation consistent double zeta) basis sets. As shown in recent studies [22, 27, 31, 54], these basis sets include sufficient diffuse basis functions to properly describe anionic states, and the corresponding results for electron attachment energies can be trusted.

4. Results and discussion

Obtaining estimates for $\Lambda$ from quantum chemical calculations by comparing the LUMO energies of an isolated molecule and the same molecule with one or a few metal atoms attached at each of its ends will be the object of a further investigation. Here we will confine ourselves to quantify the difference in the LUMO energy offsets $\varepsilon_{0,2} = \varepsilon_{0,1}$ for two molecular junctions consisting of molecules (labeled 1 and 2) joined to electrodes of identical metals ($E_{F,1} = E_{F,2} = E_F$) by similar chemical linkage (nitrogen–gold affinity in the specific situations discussed below). In this case

$$\Lambda_1 \approx \Lambda_2, $$  \hspace{1cm} (3)

and equation (2) yields

$$\varepsilon_{0,2} - \varepsilon_{0,1} = \left[ \Phi_{im,2} - \Phi_{im,1} \right] + \left[ \Phi_{im,2} - \Phi_{im,1} \right]. $$  \hspace{1cm} (4)

Here, the under braces indicate the method to be used below for evaluating the corresponding quantities; the lhs can be estimated from available experimental data, the rhs can be obtained theoretically via quantum chemical calculations.

To validate the disentangling scheme proposed here, on which the basic equation (4) relies, we will consider molecular junctions based on BDCN and 44BPY.

4.1. Quantities estimated from experimental data

The LUMO energy offset for the BDCN molecule can be deduced from the experimental value of the transition voltage $V_t \rightarrow V_{t,1} = 1.69 \pm 0.05 \text{V}$ extracted from the $I$–$V$ curve measured at zero gate potential ($V_G = 0$); see the supplementary information of [2]. Let us briefly remind that the transition voltage $V_t$ represents the bias at the minimum of the Fowler–Nordheim quantity $ln \left( \frac{I}{V_t^2} \right)$ [8]. Because the experimental $I$–$V$ curve [2] turned out to be practically symmetric ($I(V) \approx -I(-V)$), the LUMO energy offset can be estimated as [19]

$$\varepsilon_0 = \frac{\sqrt{3}}{2} V_t, $$  \hspace{1cm} (5)

which yields

$$\varepsilon_{0,1} = 1.46 \pm 0.04 \text{eV.} $$  \hspace{1cm} (6)

On the other side, the LUMO energy offset for 44BPY-based junctions deduced via thermopower data [6, 22] is

$$\varepsilon_{0,2} = 1.53 \pm 0.08 \text{eV.} $$  \hspace{1cm} (7)

4.2. Quantities estimated via quantum chemical calculations

4.2.1. Electron attachment energies. The results of the quantum chemical calculations for the lowest electron attachment energies $\Phi_{im,1,2}$ entering equation (4) are collected in table 1. In addition to the values obtained within the EOM–CCSD, EOM–CC2, and ADC(2) methods described in section 3, values obtained via energy difference ($\Delta$-) CCSD and DFT methods [27] are also presented there. In the latter, the lowest electron attachment energy is estimated as the difference between the ground state energies ($\varepsilon'$) of the neutral and anionic species at the equilibrium geometry of the

$^{2}$ The small difference between the present estimate and that of [2] is due to the different relation used in the latter ($\varepsilon_0 = \varepsilon;_V$ in [2] versus equation (5) here). That relation is based on the (‘barrier shape’ [61]) conjecture of [8], according to which the barrier changes from trapezoidal to triangular at $V = V_t$, which is by now known not to be the case [62, 63].
neutral molecule ($M = \text{CCSD, DFT}$)

$$E_A = E_{M, \text{neutral}} - E_{M, \text{anion}}.$$  

(8)

The inspection the values given in Table 1 is instructive. It reveals that although the absolute values of the electroaffinities $E_{A1} \equiv E_{\text{ADDCN}}$ and $E_{A2} \equiv E_{\text{A44BPY}}$ for the two molecules considered significantly depend on the quantum chemical method utilized, the differences $E_{A1} - E_{A2}$ deduced by using the aforementioned methods is within the experimental accuracy (see equations (6) and (7)).

4.2.2. Image charge effects. An extensive analysis of the effect of image charges in a two terminal setup was presented recently [22]. Therefore, only a few details will be given here. The interaction energy between two infinite planar electrodes and a point charge $e$ located at $z$ in vacuo can be expressed as

$$\phi_{im}(z) = \frac{e^2}{4d} \left\{ -2\psi(1) + \psi \left( \frac{z - z_d}{d} \right) \left[ 1 - e^{-\mu(z-z_d)} \right] + \psi \left( \frac{z - z_d}{d} \right) \left[ 1 - e^{-\mu(z-z_d)} \right] \right\},$$

(9)

where $\psi(z) \equiv \ln \Gamma(z)/d z$ is the digamma function. Equation (9) is obtained from the expression deduced within classical electrostatics [55] by inserting the expressions in the square parentheses, which ensure that the limits $\lim_{z \rightarrow z_d} \phi_{im}(z)$ remain finite and provide good fits of the microscopically calculated potential for the single-plane problem ($z \geq z_d$, $z \leq z_i$) [56, 57]. The positions $z_{i,j}$ ($z_i < z_j$) of the image planes are outwardly shifted by $z_d$ from the electrode surfaces $z_i, j = z_i, j \neq z_d$ [58, 59], where $z_i$ represents a quantum correction to the classical result. Numerical values appropriate for gold electrodes (Au(111) faces) are $\mu \approx 1.25 \text{ bohr}^{-1}$ and $z_d \approx 1.58 \text{ Å}$ [22].

Equation (9) cannot directly applied to a real molecular junction. Contrary to the usual claim [6, 28, 32], for cases relevant for molecular electronics [22, 27], realistic LUMO’s are not point-like but rather extended over the entire molecule. LUMO spatial distributions $\rho_{\text{LUMO}}$ of the two molecules considered in this study are shown in figures 2 and 3. Because spatial densities of KS LUMO’s are completely unphysical and Hartree–Fock LUMO’s may represent a too crude approximation, like in [27, 54], we have calculated the natural orbital expansion of the LUMO’s may significantly depend on the method utilized, their difference (last column) is quite insensitive to it.

Table 1. Results for the electron attachment energies $E_A$ of the isolated molecules (BDCN and 44BPY) considered in this study computed by means of various quantum chemical calculations indicated in the left column and described in the main text. The geometries of the neutral molecules have been optimized at DFT/B3LYP/6-311+G(d,p) level. Notice that although the absolute values $E_{\text{ADDCN}}$ and $E_{\text{A44BPY}}$ may significantly depend on the method utilized, their difference (last column) is quite insensitive to it.

| Method     | $E_{\text{ADDCN}}$ (eV) | $E_{\text{A44BPY}}$ (eV) | $E_{\text{ADDCN}} - E_{\text{A44BPY}}$ (eV) |
|------------|--------------------------|--------------------------|-----------------------------------------|
| EOM–       | 0.717                    | 0.032                    | 0.685                                   |
| CCSD       | 1.047                    | 0.360                    | 0.687                                   |
| EOM–CCSD   | 1.107                    | 0.370                    | 0.737                                   |
| ADC(2)     | 0.678                    | 0.0043                   | 0.678                                   |
| $\Delta$-CCSD     | 1.127                    | 0.444                    | 0.683                                   |

For properly estimate the image-driven shifts $\Phi_{im1} \equiv \Phi_{im,\text{BDCN}}$ and $\Phi_{im2} \equiv \Phi_{im,\text{A44BPY}}$ via equation (10), attention should be paid to the difference between the experimental setups employed in [2] and [6], respectively. This difference is illustrated by the two cartoons in the left and right panels of figure 4.

In an asymmetric STM-setup like that used in the measurements for 44BPY-based junctions considered here [6], the usual assumption [6, 28, 32] of an infinite plate in the immediate vicinity of the (nitrogen) atom at one molecular end is justified only for one electrode (STM substrate). As shown recently [22], to model an atomically sharp (e.g., pyramidal) STM-tip with a height $h_{\text{Au}}$, one can consider an infinite planar electrode displaced from the tip apex by an effective number of Au(111) surfaces. That is (for atom notation see figure 4, $z_i = z_{N_i} - d_{\text{Au-Au}} + z_0$ and $z_i = z_{N_i} + d_{\text{Au-Au}} - z_0 + nd_{\text{Au}}$ ($d_{\text{Au}} \approx 2.354 \text{ Å}, d_{\text{Au-Au}} \approx 2.336 \text{ Å}$) [22]. An estimate

$$\Phi_{im,2} \mid_{n=3} \approx -1.39 \text{ eV}$$

(11)

is obtained by using $n \approx 3$, a value that turned out to be in excellent agreement with the experimental data on 44BPY-based junctions analyzed in [22].

In the same spirit, to model the (basically symmetric) experimental setup of the electromigrated BDCN-based junctions of [2], we will use $z_i = z_{N_i} - d_{\text{Au-Au}} + z_0 - md_{\text{Au}}$ and $z_i = z_{N_i} + d_{\text{Au-Au}} - z_0 + md_{\text{Au}}$, which amounts to consider image planes displaced by an effective number of Au (111) layers. Taking a value of $m$ smaller than $n$ is in accord to the fact that the two gold electrodes in an electromigrated setup [2] are not so sharp as an STM tip [6]. Therefore, to get a simple estimate we will assume $m \approx n/2$, which yields via
Figure 2. The almost singly occupied natural orbital corresponding to the anion’s extra electron of the $\text{BDCN}^{\cdot -}$ anion (‘LUMO’) obtained via EA–EOM–CCSD/aug-cc-pVDZ calculations is delocalized over the whole molecule. The LUMO density presented here and in figure 3 was generated by using Gabedit [60].

Figure 3. The almost singly occupied natural orbital corresponding to the anion’s extra electron of the $44\text{BPY}^{\cdot -}$ anion (‘LUMO’) obtained via EA–EOM–CCSD/aug-cc-pVDZ calculations is delocalized over the whole molecule.

Figure 4. Cartoons illustrating the basic features of an asymmetric STM setup with a sharp STM-tip [6] (left panel) and the less sharp electrodes of a rather symmetric electromigrated junction [2] (right panel).
The energetic alignment $\epsilon_0$ relative to electrodes’ Fermi energy of the dominant orbital represents a key quantity that controls the charge transport by tunneling in molecular junctions. Disentangling $\epsilon_0$ in contributions with clear physical origin may be important not only for fundamental nanoscience but also for designing electronic nanodevices.

Methodologically, to validate such disentangling schemes, it is preferable to compare two molecular junctions that basically differ in a single respect. The disentangling scheme analyzed recently [22], where we have considered junctions based on the same molecule 44BPY but placed in different environments (solvent [42] versus ambient conditions [6]), was a first step in this direction. As a further step in the same vein, in this paper we have considered a disentangling scheme for nanojunctions, wherein the two molecules considered BDCN and 44BPY are different but their chemical linkage to electrodes is similar (nitrogen–gold affinity).

We believe that the validation of the presently proposed disentangling scheme against available experimental data [2, 6] is noteworthy. Still, considering more transport data for molecular junctions exhibiting n-type conduction to generalize the proposed method beyond the two aforementioned cases is highly desirable. $I$–$V$ curves for extended bias ranges well beyond the Ohmic regime ($|V| \geq V_T$), allowing to determine the transition voltage $V_T$ and thence the MO energy offset $\epsilon_0$, supplemented by thermopower data [6] or employing electrodes with different work functions [3] as evidence for a (LUMO-mediated, n-type) conduction, would be best suited for this purpose. Oligophenylene chains with isocyanide linkages NC–(C$_6$H$_4$)$_n$–CN, i.e. series with several ($n$) phenylene rings instead of the single ($n=1$) ring of the BDCN $\equiv$ NC–C$_6$H$_4$–CN considered above and in [2], may represent good candidates for such investigations. Reliable quantum chemical methods like those used here or elsewhere [27] can still be applied for molecular species with up to $n = 3 \leq 4$ rings. Unfortunately, we were unable to find such experimental transport data in existing publications, which are very often restricted to the Ohmic conductance. Still, we hope that the present theoretical study will encourage accompanying experimental (and further theoretical) efforts to validate similar disentangling schemes that could certainly contribute to a better microscopical understanding of the nanotransport.

We end with the following technical remark. To validate the disentangling scheme proposed in [22] we have resorted to $\Delta$-DFT calculations. As compared to more elaborate quantum chemical methods, the $\Delta$-DFT method is computationally considerably less demanding. As revealed by the comparison between the first and the last line in table 1 and also discussed elsewhere [27], $\Delta$-DFT-based estimates for $\epsilon_0$ of a given molecular junction may not be satisfactory. Still, differences $\epsilon_{0,1} - \epsilon_{0,2}$ between relevant MO offsets $\epsilon_{0,1}$ and $\epsilon_{0,2}$ characterizing different (but not too different) molecular junctions estimated within $\Delta$-DFT can be of an accuracy comparable to those based on the computationally very costly EOM–CCSD, which represents the state-of-the-art of quantum chemistry of medium size molecules. This is also an important aspect, as it allows to understand differences between properties of various nanojunctions by resorting to lower cost computational approaches.
Acknowledgments

Financial support for this work provided by the Deutsche Forschungsgemeinschaft (grant BA 1799/2-1) is gratefully acknowledged.

References

[1] Zahid F, Paulsson M and Datta S 2003 Electrical conduction through molecules. Advanced Semiconductors and Organic Nano-Techniques vol 3 ed H Morkoç (New York: Academic)

[2] Song H, Kim Y, Jang Y H, Jeong H, Reed M A and Lee T 2009 Nature 462 1039

[3] Kim B, Choi S H, Zhu X-Y and Frisbie C D 2011 J. Am. Chem. Soc. 133 19864

[4] Paulsson M and Datta S 2003 Phys. Rev. B 67 241403

[5] Baheti K, Malen J A, Doak P, Reddy P, Jang S-Y, Tilley T D, Majumdar A and Segalman R A 2008 Nano Lett. 8 715 PMID: 18269258.

[6] Widawsky J R, Darancet P, Neaton J B and Venkataraman L 2012 Nano Lett. 12 354

[7] Guo S, Zhou G and Tao N 2013 Nano Lett. 13 4326

[8] Beeje J M, Kim B, Gadzuk J W, Frisbie C D and Kushmerick J G 2006 Phys. Rev. Lett. 97 026801

[9] Beeje J M, Kim B, Frisbie C D and Kushmerick J G 2008 ACS Nano 2 827

[10] Coll M, Miller L H, Richter L J, Hines D R, Jurchescu O D, Jones R O and Gunnarsson O 2009 J. Chem. Phys. 1221 689

[11] Song H, Reed M A and Lee T 2011 Adv. Mater. 23 1583

[12] Guo S, Hihath J, Diez-Pérez I and Tao N 2011 J. Am. Chem. Soc. 133 19189

[13] Wang G, Kim Y, Na S-I, Kahng Y H, Ku J, Park S, Jang Y H, Kim D-Y and Lee T 2011 J. Phys. Chem. C 115 17979

[14] Lee W and Reddy P 2011 Nanotechnology 22 485703

[15] Lennartz M C, Atodiresei N, Caciuc V and Karthaueser S 2011 J. Phys. Chem. C 115 15025

[16] Tran T K, Smaali K, Hardouin M, Bricaud Q, Oafraïn M, Blanchard P, Lenfant S, Godey S, Roncali J and Vuillemue D 2013 Adv. Mater. 25 427

[17] Fracasso D, Muglali M I, Rohwerder M, Terfort A and Chiechi R C 2013 J. Phys. Chem. C 117 13167

[18] Băldea I 2010 J. Chem. Phys. 377 15

[19] Băldea I 2012 Phys. Rev. B 85 035442

[20] Băldea I 2012 J. Chem. Phys. 400 65

[21] Băldea I 2012 J. Am. Chem. Soc. 134 7958

[22] Băldea I 2013 Nano scale 5 9222

[23] Băldea I 2013 J. Phys. Chem. C 117 25798

[24] Băldea I 2014 J. Phys. Chem. C 118 8676

[25] Xue Y, Datta S and Ratner M A 2002 J. Chem. Phys. 281 151

[26] Jones R O and Gunnarsson O 1989 Rev. Mod. Phys. 61 689

[27] Băldea I 2014 Faraday Discuss. at press (doi:10.1039/C4FD00101J)

[28] Quack S Y, Venkataraman L, Choi H J, Louie S G, Hybertsen M S and Neaton J B 2007 Nano Lett. 7 3477

[29] Rangel T, Ferretti A, Trevisanutto P E, Olevano V and Rignanese G-M 2011 Phys. Rev. B 84 045426

[30] Băldea I 2012 Europhys. Lett. 99 47002

[31] Băldea I, Köppel H and Wenzel W 2013 Phys. Chem. Chem. Phys. 15 1918

[32] Neaton J B, Hybertsen M S and Louie S G 2006 Phys. Rev. Lett. 97 216405

[33] Băldea I 2012 Europhys. Lett. 98 17101

[34] Băldea I and Köppel H 2012 Phys. Status Solidi b 249 1791

[35] Băldea I 2013 Electrochem. Commun. 36 19

[36] Ritchie R H 1972 Phys. Lett. A 38 189

[37] Inkson J C 1973 J. Phys.: Solid St. Phys. 6 1350

[38] Lenac Z and Sunjic M 1976 Nuovo Cimento B 33 681

[39] Jonson M 1980 Solid State Commun. 33 743

[40] Sunjić M and Marusić I 1991 Phys. Rev. B 44 9092

[41] Xi H and Fisher A J 1998 J. Phys.: Condens. Matter 10 3697

[42] Xu B and Tao N J 2003 Science 301 1221

[43] Gustafsson T and Plummer E W 1978 Photoemission and the Electronic Properties of Surfaces ed B Feuerbacher, B Fitton and R F Willis (New York: Wiley) pp 353–79 chapter 12

[44] Stanton J F and Gauss J 1995 J. Chem. Phys. 103 1064

[45] Nooijen M and Bartlett R J 1995 J. Chem. Phys. 102 3629

[46] Nooijen M and Snijders J G 1995 J. Chem. Phys. 102 1681

[47] Stanton J F et al CFOUR, Coupled-cluster techniques for computational chemistry, a quantum-chemical program package Almlof J and Taylor P R Integral packages MOLECULE Taylor P R PROPS Helgaker T, Jenson H J Aa, Jørgensen P and Olsen J ABACUS Mitan A V and van Wullen C ECP routines For the current version, see www.cfour.de.

[48] Christiansen O, Koch H and Jørgensen P 1995 Chem. Phys. Lett. 243 409

[49] Schrimer J 1982 Phys. Rev. A 26 2395

[50] Schrimer J 1991 Phys. Rev. A 43 4647

[51] Vysotskii V P and Cederbaum L S 2010 J. Phys.: Condens. Matter 22 1918

[52] Aquilante F et al 2010 J. Comput. Chem. 31 224

[53] Frisch M J et al 2010 Gaussian 09, Revision B.01 (Wallingford CT: Gaussian)

[54] Klaiman S, Gromov E V and Cederbaum L S 1996 J. Chem. Phys. 105 79

[55] Sommerfeld A and Bethe H 1933 Elektronentheorie der metalle Handbuch der Physik vol 24 ed H Geiger and K Scheel (Berlin: Springer) p 446

[56] Jones R O, Jennings P J and Jepsen O 1984 Phys. Rev. B 29 6474

[57] Smith N V, Chen C T and Jepsen O 1989 Phys. Rev. B 40 7565

[58] Lang N D and Kohn W 1973 Phys. Rev. B 7 3541

[59] Desjonqueres M-C and Spanjaard D 1996 Concepts in Surface Physics 2nd edn (Berlin: Springer)

[60] Allouche A-R 2011 J. Phys.: Condens. Matter 23 427

[61] Băldea I and Köppel H 2012 Phys. Lett. A 376 1472

[62] Araud M and Tsukada M 2010 Phys. Rev. B 81 235114

[63] Băldea I 2012 J. Phys. Chem. Solids 73 1151