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Density functional theory orbital energies for predicting ionization energies

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Density Functional Theory Orbital Energies for Predicting Ionization Energies

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Abstract. The range-separated Baer-Neuhauser-Livshits functional with optimized range-separation parameter γ was employed to predict ionization energies of alkanes and oligothiophenes. For all systems negative orbital energies of neutral species are consistent with explicitly calculated states of cations. For σ-systems excellent agreement with experiment is obtained while for conjugated π-systems IPs are underestimated.

INTRODUCTION

Photoelectron spectroscopy and electron impact measurements (EI) are important experimental tools for studying electronic states of neutral and doped conducting organic polymers. Ultraviolet photoelectron spectroscopy (UPS) provides information about valence states and X-Ray photoelectron spectroscopy (XPS) reaches down to core levels. UPS and XPS data are usually identical to results from EI.

In solid state physics it is common to model electronic structures with band structure calculations. This means that energy levels of the neutral species are taken as the density of states of the corresponding cations. Using energy levels as approximation for states is possible if and only if electronic transitions are due to single electron excitations or single electron removal. This requirement is often but not always fulfilled.[1] Theoretical methods employed in band structure calculations should predict energy levels that are consistent with ionization energies. At the ab initio level this consistency is approximately achieved via Koopmans' theorem.[2]

Due to the size of the systems in research on polymers and solids, density functional theory (DFT) is the only method available that includes electronic interactions self-consistently and covers a large part of the correlation energy. However, there is no Koopmans' theorem for DFT. Within exact DFT only the negative energy of the highest occupied Kohn-Sham orbital is proven to be equal to the first IP.[3] The meaning of the energies of lower lying orbitals is subject to controversy.[3-6] DFT orbital energies with approximate functionals are far from ionization potentials because of the self-interaction or self-repulsion of electrons.[7,8] With approximate functionals, occupied energy levels are lying too high,[4] energies of charge transfer excitations and of Rydberg states are underestimated, radicals dissociate into fragments with fractional charges, delocalization in conjugated systems is overestimated, and energy gaps between occupied and unoccupied energy levels decrease too fast with increasing chain length.

As a remedy for the self-interaction problem, self-interaction corrected functionals are under development.[7,9] It was recently shown for small molecules that the range-separated Baer-Neuhauser-Livshits (BNL) functional,[10] with optimized range-separation parameter γ ameliorates the above mentioned problems for a range of species. It is therefore the aim of this investigation to extend the use of the BNL functional to longer oligomers and to test its performance on π-conjugated systems.

METHODS

Geometries of all species were optimized with the range-separated BNL[10] hybrid functional and the 6-311g* basis set. The range-split parameter γ was adjusted for each neutral system to reproduce $-\varepsilon_{HOMO} = IP_{\Delta SCF}$.[11]

Using optimized geometries of the neutral species, time-dependent DFT (TDDFT) single point calculations were carried out to obtain ground and excited states of the cations. First IPs are calculated with the ΔSCF method. Vertical IPs of lower energy electrons were obtained by adding the appropriate excitation energies of the cation to $IP1_{\Delta SCF}$. The method will be abbreviated in the following as $IP_{\Delta SCF}$/TD. The data are plotted as energy level diagrams. This means that negative ionization energies are used. BNL calculations were done with a modified version of the QChem (version 3.1) program,[12] all other calculations were done with Gaussian 03.[13]

RESULTS AND DISCUSSION

For small molecules γ-optimized BNL with Dunning's correlation consistent quadruple zeta basis (CC-PVQZ) produces an exact match between negative orbital energies and $IP_{\Delta SCF}$/TD states.[14] As an example an energy level diagram for formaldehyde at the BNL/CC-PVQZ level ($\gamma = 0.49$) is shown in Figure 1. Negative orbital energies $-\varepsilon_i$ and $IP_{\Delta SCF}$/TD match experiment closely and are as accurate as SAOP data.[6]
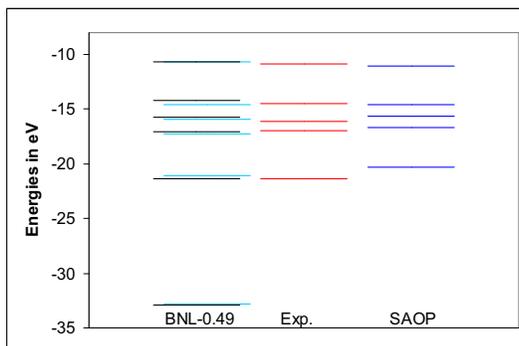
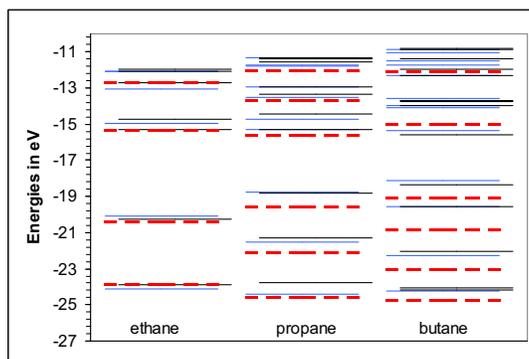
FIGURE 1. Energy levels of CH_2O, black lines: BNL states of cations, light blue lines BNL orbital energies. Experimental data ref.[15], SAOP results ref.[6]

The performance of smaller basis sets was tested on butadiene. A series of calculations with CC-PVTZ, CC-PVDZ, 6-311+G*, 6-311G*, 6-31+G*, and 6-31G* showed that the smallest basis set that produces results close to those with CC-PVTZ is 6-311G*. This gives us reason to believe that the 6-311G* basis set is appropriate for larger systems.
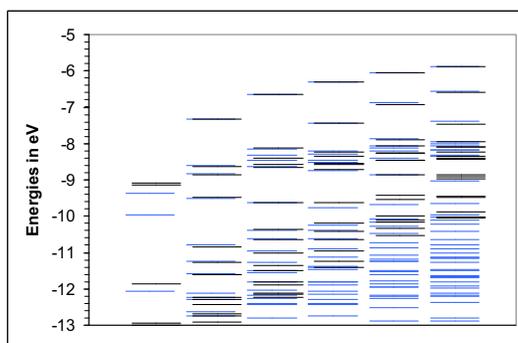
In Figure 2 orbital energies and states are presented for ethane, propane, and butane. Optimization of γ leads to decreasing values with increasing chain length: 0.445 for ethane, 0.400 for propane, and 0.380 for butane. The dependence of γ on 1/number or repeat units is linear and the value for infinite chain length is 0.314.

In all three cases orbital energies and states are consistent down to the inner valence part at about -25 eV. Slight differences between orbital energies and states are visible for the upper levels where analysis of the states reveals configuration interaction due to close lying energy levels. The red lines in Figure 2 show experimental IPs.[16] The agreement between theory and experiment is very good for the low lying states. There are differences between theory and experiment for the upper valence states. It was shown experimentally[16] that the upper valence electrons give rise to broad bands that cannot be resolved. Therefore the peaks are computationally deconvoluted and not all theoretically predicted levels could be assigned. All states predicted with BNL lie within the experimentally detected bands. Thus BNL appears to be as accurate for larger σ-systems as for small molecules.

FIGURE 2. Energy levels of ethane, propane, butane (black lines: BNL states of cations, light blue lines BNL orbital energies, red dashed lines experimental IPs).

In Figure 3 BNL energy levels and states are shown for oligothiophenes (OTs) with one to six rings. Optimization of γ leads to decreasing values with increasing chain length. As for alkanes plotting γ vs. inverse chain lengths gives a straight line. γ values start with 0.41 for thiophene and extrapolation leads to a value of 0.135 for infinitely long chains. For OTs, the first couple IPs are well resolved and a band forms for lower lying states, where the narrow band arising from the HOMO-1 and the wide band arising from the HOMO of thiophene cross. For the thiophene monomer, there is no exact internal consistency between states energy levels. For the longer oligomers the agreement is very good, although there is considerable configuration interaction for lower lying states.

FIGURE 3. Energy levels of thiophene-sexithiophene, (black lines: BNL states of cations, light blue lines BNL orbital energies of neutral systems).

Although there is internal consistency between orbital energies and states, the agreement between theory and experiment is poor for OTs. In Figure 4 theoretical and experimental first IPs are compared. It turns out that BNL
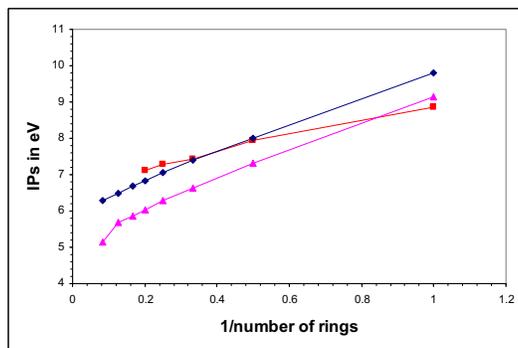
FIGURE 4. ΔSCF IPs of thiophene oligomers vs. inverse chain length at BNL/6-311G* (pink triangles) and B3P86-30%/CEP-31G* (blue diamonds) compared to experiment (red squares).[17]

with optimized γ underestimates the first IP of thiophene oligomers by more than 0.6 eV. For comparison, Figure 4 shows also IP$_{\Delta SCF}$ obtained at the B3P86-30%/CEP-31G* level.[18] The decrease of IPs with increasing chain lengths is very similar with both DFT methods and larger than the experimental decrease. Part of this difference may be attributed to increasing non-planarity of the longer oligomers. With exception of thiophene, B3P86-30% results are close to experiment. The agreement between BNL predictions and experiment could be improved by increasing γ with increasing chain length, however, to match IP$_{\Delta SCF}$ and orbital energies, γ needs to decreases with increasing chain length so that the results deteriorate.

CONCLUSIONS

The BNL functional with optimized range-split parameter γ is the only density functional that produces consistency between orbital energies of neutral systems and states of the corresponding cations. This success gives further support to the claim[6] that DFT orbital energies have physical meaning. For all σ-systems BNL predicted IPs are in close agreement with experiment. Oligothiophenes are the first examples encountered so far where internal consistency between energy levels and states was found but where the predicted IPs do not agree with experiment. Since the band gap problem and too high lying occupied orbitals were assumed to be caused by self-repulsion, it is surprising that BNL that corrects self-repulsion cannot improve the results on conjugated oligomers. Conjugated π-systems need further investigation.

ACKNOWLEDGMENTS

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