

ON THE THEORY OF CHARGE TRANSFER ENERGIES AT DONOR-ACCEPTOR INTERFACES IN SOLAR CELLS

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ABSTRACT

Charge transfer states at the donor–acceptor interface in organic solar cells determine the device performance. Therefore a basic description, understanding and estimation of the energetics of the charge transfer states at donor-acceptor interfaces are crucial for the improvement of the efficiency especially of organic solar cells. In the presentation, we report about the results of theoretical studies on donor–acceptor combinations used in molecular solar cells. As an example, we discuss especially zinc phthalocyanine – C60 blends. Several computational schemes based on constrained density functional theory (c-DFT), Hartree-Fock based configuration interaction of singles (CIS) and time-dependent density functional theory (TD-DFT) using the hybrid functional B3LYP were used to assess the energy of the lowest charge transfer (CT) state in such systems. The results of the calculations are discussed in comparison with available spectroscopic data, and in comparison with solid state calculations. For example, the results from c-DFT and CIS calculations reproduce the correct Coulomb asymptotics between cationic donor and anionic acceptor configurations, whereas TD-DFT gives qualitatively wrong excitation energies.

INTRODUCTION

During the last decades, organic photovoltaics have benefitted from several innovative concepts including donor-acceptor (DA) blends and tandem cells, reaching now a technologically relevant power conversion efficiency of 12%. In such systems the light is first absorbed at the donor (D) or the acceptor (A) site. The created exciton diffuses then to the interface between D and A. At this interface the optical excitation is transformed into a charge transfer (CT) complex with the electron localized on an acceptor site and the hole on a donor site. These CT complexes form a reservoir of localized charge pairs which may be ionized into free electrons and holes, diffusing eventually towards the electrodes of the solar cell.

The efficiency of organic photovoltaics relies heavily on the energetic alignment of molecular singlet excitations, triplet configurations, and CT states. In a previous paper [1] we have discussed in detail the present situation and the lack of proper theoretical studies about the energy alignment of these states. Hartree-Fock based linear response calculations like configuration of singles (CIS) overestimate molecular excitations and CT energies by a large amount [2], whereas more advanced methods like coupled cluster theory (CC2) prove to be more reliable but become computationally much more demanding [3]. Both schemes share the advantage that, due to the inclusion of exact non-local exchange, the

asymptotic $-1/r$ dependence of the Coulomb interaction between a pair of oppositely charged donor and acceptor molecules is correctly included. In contrast, most of the standard excited state calculations (time-dependent density functional theory - TD-DFT) do not correctly describe the asymptotics of the anion-cation interaction, due to the application of local exchange-correlation functionals [4]. Several procedures, including especially long-range corrections of the exchange-correlation functional, have been described in the literature to correct this systematic failure – see e.g. [4, 5, 6]. One elegant way to avoid the spurious errors introduced by the wrong asymptotics of the exchange-correlation functional and problems related to the incorrect description of the self-interaction in DFT is the application of constraints in the DFT [7]. For applications to description of charged donor-acceptor complexes, the net charges on each constituent are fixed – as a constraint.

In this way the DFT calculations are decomposed into ground state calculations of the ionized donor and acceptor molecules D^+ and A^- together with their mutual Coulomb interaction, which guarantees the correct Coulomb asymptotics $-1/r$ [8]. In constrained DFT (c-DFT), the excitation energy of a D^+A^- pair with respect to the neutral ground state D^0A^0 relies mainly on ground state calculations of molecules in different charge states [1]. The ionization potentials and electron affinities calculated in this way are rather robust against the use of different exchange- correlation functionals [9,10] and can give reliable results even with quite small variational basis sets [11, 12].

The c-DFTB scheme can also be easily extended with an embedding scheme accounting for the polarizable medium, which allows the estimation of the external quantum efficiency of photovoltaic cells. The proposed computational scheme reproduces the observed trends of the observed open circuit voltages in photovoltaic devices relying on several donor–acceptor blends.

In [1], we have applied a constrained DFT scheme together with an embedding scheme accounting for an isotropic dielectric constant of a donor-acceptor blend, allowing to compute the CT excitation energy of a donor-acceptor pair in direct contact and the energy required for separating the opposite charges to infinite distance. The calculated values for the CT excitation energy are in semi-quantitative agreement with corresponding experimental data. This result is a strong hint that the basic photophysics in photovoltaic devices containing either small molecules or polymer- fullerene blends rely on similar considerations concerning CT energies. The results are encouraging for the application of similar constrained DFT schemes to larger oligomers as a model for polymer-fullerene solar cells.

In the previous study we have applied a quasi-molecular model, which accounts for the fundamental inter-molecular interactions. However, it does not account for effects appearing only when embedded in a solid. In the present study we therefore focus our attention on a corresponding solid state situation for the same system, C60-ZnPc, using a one-dimensional model solid and DFT methodology.

NOMENCLATURE

C60	[-]	Fullerene molecule
ZnPc	[-]	Zinc phthalocyanine molecule
E_F	[eV]	Fermi energy
m_0	[-]	Electron mass (reference value)
m_h^*	[m_0]	Effective mass of the hole in the valence band
m_e^*	[m_0]	Effective mass of the electron in the conduction band
μ	[m_0]	Reduced exciton mass
Special characters		
ϵ	[-]	Relative permittivity / dielectric constant
ω	[eV]	Photon energy

ONE-DIMENSIONAL MODEL SOLID

Geometry

The fullerene molecule (C60) has the form of a ball with about 0.65nm diameter. The zinc phthalocyanine (ZnPc) molecule on the other hand is a planar molecule with a width of about 1.3nm. This misfit in size makes it difficult to construct a suitable three-dimensional crystal unit cell.

Therefore, we constructed a model system with one periodic direction, as shown in Figure 1. The unit cell consists of one C60 and ZnPc molecule each, stacked in the periodic direction.

The geometries of C60 and ZnPc have been relaxed to their respective numerical equilibria separately. The relaxed geometries were then pasted together and the separation between the molecules was optimised. A separation of 0.24nm was found to be optimal. In addition a vacuum of 0.35nm was added in the two non-periodic directions on each side to allow proper descriptions of the wave functions and charge densities.

The omission of a relaxation of the complete system should have little influence on the properties presented here. In addition, one has to keep in mind that we treat merely a model system. While this system may present valuable insight into the interaction of C60 and ZnPc in a real solid, one cannot expect to obtain precise numerical data coinciding with measured values.

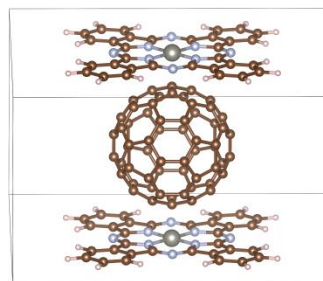


Figure 1 Geometry of stacked C60 and ZnPC with periodicity along the (vertical) stacking direction.

Computational details

The density-functional theory (DFT) based calculations were performed using the GPAW software package [13, 14]. The GLLB-sc [15] exchange-correlation functional was used because it tends to yield a better description of the unoccupied

bands than most common functionals. For the wave function the plane wave mode was used, together with a cut-off energy for the plane wave expansion of 500 eV. For the calculation of the band structure 5 k-points in the periodic direction are sufficient, for the dielectric function calculations 7 k-points were used.

RESULTS FOR MODEL SOLID

Band structure

The C60-ZnPc model system shows an indirect band gap of about 0.7eV in DFT, plus about 0.3eV discontinuity correction from GLLB-sc. The band structure without the discontinuity correction is shown in Figure 2. The highest occupied band shows only minimal dispersion with a maximum at the Γ -point. Its partial charge density is localised around the ZnPc carbon atoms. The lowest unoccupied band shows a larger dispersion with a minimum at the X-point ($X=(0, 0, 1/2)$). The partial charge analysis suggests that this state belongs to the C60 molecule.

The assignment of the valence band maximum and the conduction band minimum to the ZnPc and C60, respectively, is in agreement with the predictions of the molecular model [1]. The indirect band gap however, would drastically reduce the yield for the photo absorption. It is unclear though, whether the indirect band gap is a result of the model geometry or whether it would persist in realistic environments.

In addition to the charge transfer process for the photo-absorption, there exists also the possibility of excitonic photo absorption. Simulations of excitons demand enormous computational numerical resources. In the case of Wannier excitons, however, one can employ a simple hydrogen model, as described in many textbooks, like Mahan [16]. The electron-hole pair of the exciton forms a bound state. Similarly to the positronium textbook case, the exciton energy and radius can be estimated by replacing the mass in the hydrogen problem by the effective mass of the exciton. This effective mass is given by the masses of the involved bands at their maximum/minimum, which translate into the second derivative of the energy with respect to the k-vector. While excitons can exist in indirect band gap materials, the hydrogen model in this form is only valid for direct band gaps. Nevertheless, for the sake of discussion we shall ignore this for the moment. For our model system we predict a hole mass for the valence band maximum at Γ of $m_h^* \approx 3.3 m_0$, where m_0 is the rest mass an electron. The excited electron in the conduction band minimum at X has a mass of $m_e^* \approx 1.1 m_0$. This yields an effective mass of the exciton of $\mu \approx 0.85 m_0$. This extremely large effective mass would result in unrealistically large exciton energy in the order of eV, even if the C60-ZnPc system is embedded in a material with large dielectric constant. Therefore, despite all approximations, we can conclude that there exists no Wannier exciton in this model system. The large effective mass in the hydrogen model stems from the large mass of the hole at the ZnPc valence band maximum. It is plausible that this wouldn't change in a more realistic environment because the system consists of separated large molecular building blocks. Their

electronic structure should only be slightly perturbed by the details of the embedding environment. It is therefore likely, that Wannier excitons do not exist in our model system with ZnPc valence band maxima.

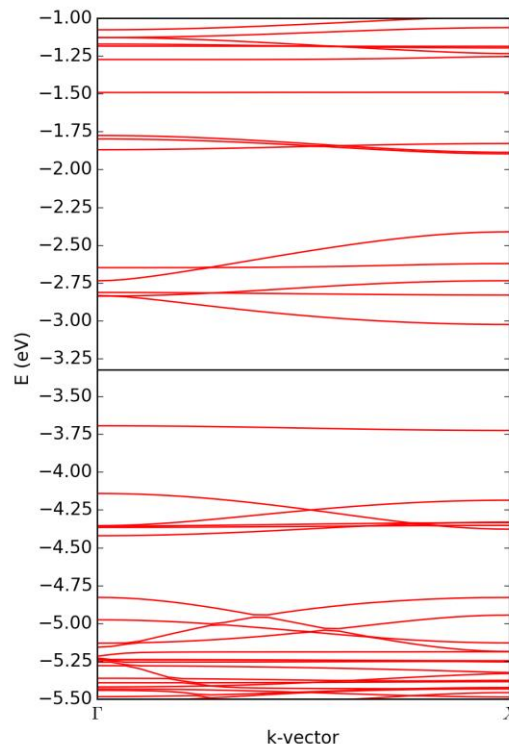


Figure 2 Band structure of the 1D C60-ZnPc model system along the periodic direction. The Fermi level at the centre of the band gap is $E_F = -3.32\text{eV}$.

Dielectric function

Additional information about the photo-absorption properties of mixed C60 and ZnPc materials can be derived from the dielectric function. The calculated dielectric function of the model system in the periodic direction is shown in Figure 3. The first absorption peak can be found at about 2.1eV. This is surprising as the calculated band gap is much smaller. A comparison with the band structure in Figure 2 reveals that this peak can indeed only come from the third set of bands below the Fermi level around -4.5eV to -5.1eV and the first set of conduction bands above the Fermi level. The absence of an absorption peak from the lowest energy transition can indicate incompatible band symmetries, as expected for the forbidden highest occupied to lowest unoccupied molecular orbital (HOMO-LUMO) transition of C60 and/or a missing overlap of the wave functions (small oscillator strength), typical for weak CT transitions.

Further investigations are required to confirm that the present calculations give a proper description of the charge transfer processes. If true, the results imply that the suggested charge transfer process may be suppressed, although the energy levels of C60 and ZnPc do align as predicted by the molecular model.

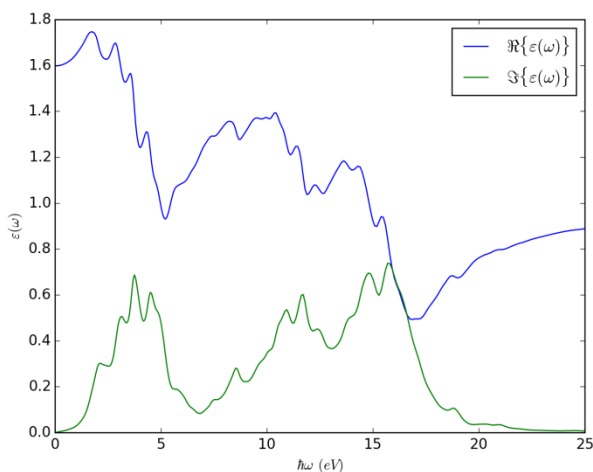


Figure 3 Dielectric function of the 1D C60-ZnPc model system along the periodic direction.

CONCLUSION

The simulation of organic solids is a challenging task. Molecular models provide highly accurate descriptions of the molecular properties, but fail to represent properties of extended systems. Solid state models on the other hand are often less accurate and/or fail to represent the complex structure of organic solids.

Molecular models predict promising charge transfer properties of fullerene (C60) - zinc phthalocyanine (ZnPc) compounds for solar cell applications. Our 1D solid model system confirms the positions of donor and acceptor levels on the ZnPc and C60. The model suggests however a low photo-absorption yield. Further studies with more realistic environments are needed to shed more light on the details of the C60-ZnPc charge transfer process.

REFERENCES

- [1] Scholz R., Luschtinetz R., Jägeler-Hoheisel T., Seifert G., Leo K., Riede M., and Rapacioli M., Quantifying charge transfer energies at donor-acceptor interfaces in small-molecule solar cells with constrained DFTB and spectroscopic methods, *Journal of Physics: Condensed Matter*, Vol. 25(47), 2013, 473201
- [2] Subotnik J.E., Configuration interaction singles has a large systematic bias against charge-transfer states, *The Journal of Chemical Physics*, Vol. 135(7), 2011, 071104
- [3] Settels V., Liu W., Pflaum J., Fink R.F., and Engels, B., Comparison of the electronic structure of different perylene-based dye-aggregates, *Journal of Computational Chemistry*, Vol. 33(18) 2012, pp.1544–1553
- [4] Dreuw A., Weisman J.L., and Head-Gordon M., Long-range charge-transfer excited states in time-dependent density functional theory require non-local exchange, *The Journal of Chemical Physics*, Vol. 119(6), 2003, pp. 2943–2946
- [5] Tawada Y., Tsuneda T., Yanagisawa S., Yanai T., and Hirao K., A long-range-corrected time-dependent density functional theory. *The Journal of Chemical Physics*, Vol. 120(18), 2004, pp.8425–8433
- [6] Gritsenko O., and Baerends E.J., Asymptotic correction of the exchange-correlation kernel of time-dependent density functional

theory for long-range charge-transfer excitations. *The Journal of Chemical Physics*, Vol. 121(2), 2004, pp.655–660

- [7] Wu Q., and van Voorhis T., Direct optimization method to study constrained systems within density-functional theory. *Phys. Rev. A*, Vol. 72, 2005, 024502
- [8] Wu Q., and vanVoorhis T., Constrained density functional theory and its application in long-range electron transfer. *Journal of Chemical Theory and Computation*, Vol. 2(3), 2006, pp. 765–774
- [9] Curtiss L.A., Redfern P.C., Raghavachari K., and Pople J.A., Assessment of gaussian-2 and density functional theories for the computation of ionization potentials and electron affinities. *The Journal of Chemical Physics*, Vol. 109(1), 1998, pp.42–55
- [10] Ernzerhof M., and Scuseria G.E., Assessment of the perdew-burke-ernzerhof exchange-correlation functional. *The Journal of Chemical Physics*, Vol. 110(11), 1999, pp. 5029–5036
- [11] Boltalina O.V., Ioffe I.N., Sidorov L.N., Seifert G., and Vietze K., Ionization energy of fullerene, *Journal of the American Chemical Society*, Vol. 122(40), 2000, pp. 9745–9749
- [12] Kumar A., Knapp-Mohammady M., Mishra P. C., and Suhai S., A theoretical study of structures and electron affinities of radical anions of guanine-cytosine, adenine-thymine, and hypoxanthine-cytosine base pairs. *Journal of Computational Chemistry*, Vol. 25(8), 2004, pp.1047–1059
- [13] Mortensen J. J., Hansen L. B., and Jacobsen K. W., Real-space grid implementation of the projector augmented wave method, *Physical Review B*, Vol. 71, 2005, 035109
- [14] Enkovaara J., Rostgaard C., Mortensen J. J. et al., Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, *Journal of Physics: Condensed Matter* Vol. 22, 2010, 253202
- [15] Kuisma M., Ojanen J., Enkovaara J., and Rantala T. T., Kohn-Sham potential with discontinuity for band gap materials, *Physical Review B*, Vol. 82, 2010, 115106
- [16] Mahan G.D., *Condensed Matter in a Nutshell*, Princeton University Press, 4. October 2010, ISBN-13: 978-0691140162