

Direct Delocalization for Calculating Electron Transfer in Fullerenes

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A method is introduced for simple calculation of charge transfer between very large solvated organic dimers (fullerenes here) from isolated dimer calculations. The individual monomers in noncentrosymmetric dimers experience different chemical environments, so that the dimers do not necessarily represent bulk-like molecules. Therefore, we apply a delocalizing bias directly to the Fock matrix of the dimer system, and verify that

this is almost as accurate as self-consistent solvation. As large molecules like fullerenes have a plethora of excited states, the initially excited state orbitals are thermally populated, so that the rate is obtained as a thermal average over Marcus thermal transfers. © 2013 Wiley Periodicals, Inc.

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Introduction

Organic solar cells have gained much attention lately as an inexpensive alternative to inorganic cells, as they are getting closer to being economically viable.^[1] However, little is understood about what fundamentally makes one type of organic solar cell more efficient than another.^[2,3] One main bottleneck in many solar cells is the extraction of free electrons, that is, even if the electron-hole separation is facile the diffusion of the free electrons to the electrodes could be a limiting factor.^[4] This issue is especially important in fullerene-based solar cells. In this study, we therefore study electron transfer of several fullerene derivatives of the type most commonly used as electron acceptors in organic solar cells, and present a simple method for calculating the transfer rates.

The most popular electron acceptors in organic photovoltaic devices (OPVs) are fullerene derivatives, most notably [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM).^[5] Due to the large size of fullerene molecules, it is necessary to apply a computationally efficient method for the study of transfer rates. In recent works, we advocated a simple methodology for calculating the coupling between identical molecules in dimeric systems of fullerene derivatives [C. Arntsen, R. Reslan, S. Hernandez, D. Kilbride, K. Lopata, N. Govind, Y. Gao, S. Tolbert, B. Schwartz, Y. Rubin, A. N. Nardes, N. Kopidakis, D. Neuhauser, in preparation]. In spite of the fact that the dimers are chemically identical when they are not placed in a centrosymmetric fashion, the chemical environment seen by each of the individual molecules is different (e.g., see Fig. 1). Because of this, the order of the frontier orbitals involved in electron transfer (primarily the LUMO and LUMO+1 orbitals) could be misplaced, for example, in an isolated dimer calculation (where no delocalizing potential is applied), both LUMO and LUMO+1 could be located on the same molecule. In that case, a dimer calculation will show little transfer between the molecules.

To overcome the different-environment problem in isolated dimer calculations, we delocalize the LUMO and LUMO+1 across the two molecules using one of two methods. The first

method involves "solvating" the dimer with surrounding molecules. Because the systems are so large, it would be too computationally expensive to explicitly treat solvating molecules; therefore, we solvate the dimer with point charges. The values of the point charges are set self-consistently to equal the Mulliken charges on the atoms of the dimer. Solving for the values of the point charges is relatively arduous, so we have also shown that the same results can be achieved by applying an electric field to the system to delocalize the frontier orbitals. This method, which we label Delocalizing Field, is much simpler in that one can sweep across a wide range of electric fields to see where the ideal delocalization occurs. However, due to the cost of density functional theory (DFT) simulations on large molecules, the delocalizing field method, while more simple than solvation, is still computationally expensive because it involves a potentially large number of DFT calculations.

We present a substantially more efficient method here. Rather than delocalizing the frontier orbitals with an electric field, we perform a single DFT calculation on a dimer system (here using the B3LYP functional). We then apply a bias directly to the post-self-consistent field (SCF) Fock matrix until the extra electron is balanced evenly between the two molecules in the dimer. We are then able to calculate the transfer rate according to Marcus theory. We show that the new method gives similar results and identical trends to the more complicated methods mentioned above.

The balance of the article is as follows. We present a more detailed description of the methodology in the next section; followed by the Results section, and finally the Discussion section.

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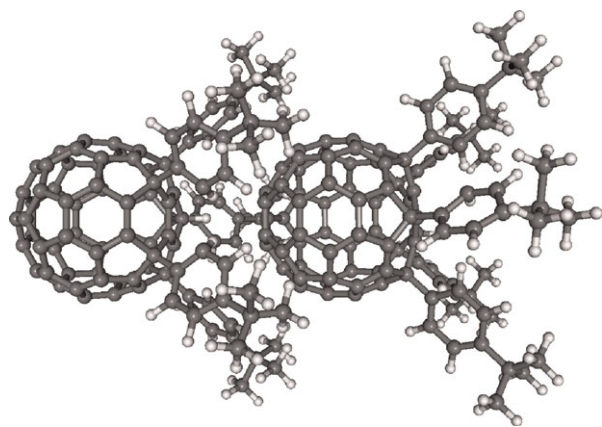


Figure 1. TBP dimer. Note the 'cap' on the left molecule is exposed, whereas the cap on right molecule is solvated by the adducts of its neighbor.

Methodology

Typically, the electron transfer rate is calculated for symmetric organic molecules from the Marcus theory expression,

$$k_{MT} = \frac{2\pi}{\hbar} |J_{ij}|^2 (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda\kappa_B T}\right) \quad (1)$$

where "i" and "j" denote the initial and final states, located on the donor and acceptor, respectively, J is the transfer integral, ΔE_{ij} is the energy difference between the initial and final states, and λ is the reorganization energy. This expression is appropriate when the electronic states within both the donor and acceptor are well-isolated; however, for large molecules such as fullerenes the distance between electronic states in the valence band is quite small, below 0.1 eV, so that a sum over all initial excited states is required; these initial states will each have its own rearrangement energies due to different coupling to the environment vibrational states. Furthermore, in large molecules one does not really calculate the true electronic states but instead uses a single particle (or RPA/TDDFT) approximation, making the degrees of freedom of the other electrons into an effective bath (not necessarily linearly coupled); these can actually enhance the transfer for symmetric systems, unlike vibrational degrees of freedom.

Here we, therefore, use a modified Marcus formalism,^[6] whereby we sum over all initial states to calculate the total electron transfer rate:

$$k'_{MT} = \frac{2\pi}{\hbar} \sum_{ij} f(\epsilon_i - \mu_L) |J_{ij}|^2 (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda\kappa_B T}\right) \quad (2)$$

where we introduced the Fermi Dirac occupation of the donor states, defined as

$$f(\epsilon_i - \mu_0) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu_0)}} \quad (3)$$

and ϵ_i is the energy of the donor state. In practice, we report the rate in terms of the transfer time, defined as

$$\tau = \frac{1}{k'_{MT}} \quad (4)$$

For the most part, Eq. (2) is a straightforward generalization of the Marcus formula for a single pair of states. However, as stated above, each of these combinations of donor and acceptor states should in principle have a particular rearrangement energy. It is computationally demanding to calculate the reorganization energies for all the initial states, and the whole concept of transfer energy becomes questionable when there are many low lying states; so to simplify, we calculate the transfer rates for a range of values. According to MacKenzie et al.,^[7] the rearrangement energy for electron transfer in $C_{61}H_2$, that is, a fullerene with the same linker group as PCBM, was calculated to be 0.136 eV when ignoring the outer sphere contribution to the reorganization. We, therefore, present results for which the reorganization energy was assumed to be 0.1 and 0.15 eV. These choices bracket the relevant range of values and take into account minor differences in the individual couplings and in the outer sphere contribution. While solvent effects are certainly important in electron transfer processes, for computational efficiency, we rely on the reorganization term in the Marcus theory formalism to account for these effects based on prior use of Marcus theory in electron transfer of large molecules (e.g., see Ref. [7]).

The computationally nontrivial aspect of the calculation is the transfer integral. Formally, the flux-operator has the form:

$$\tilde{J} = i[\tilde{F}, \tilde{\theta}] \quad (5)$$

where we introduced the Fock operator and the left-theta operator (identity on the left-fragment space, zero on the right); the tilde symbol on the matrices indicates that they refer to an orthogonal basis.

In practice, the calculations are performed by first generating the Fock and overlap matrices, F and S in a nonorthogonal basis using DFT, which has been shown to give good accuracy within the Marcus framework.^[8-13] The NWChem software package was used for calculations.^[14] The matrices were calculated using the B3LYP functional and STO-3G basis set for neutral and anionic systems. Results for both neutral and anionic systems were similar (i.e., the choice of which Fock operator was used is immaterial in this basis set), and in the results section we use the neutral systems and anionic systems in PCBM, which are in good agreement, and the neutral systems for the other molecules.

The Fock matrix and theta operator are then converted to a local orthogonal basis:

$$\begin{aligned} \tilde{F} &= S^{-\frac{1}{2}} F S^{-\frac{1}{2}} \\ \tilde{\theta} &= S^{-\frac{1}{2}} \theta S^{-\frac{1}{2}} \end{aligned} \quad (6)$$

and the theta operator determines whether the orbital of interest is on the left or the right molecule:

$$\theta_{ij} = g(i) S_{ij} g(j) \quad (7)$$

where

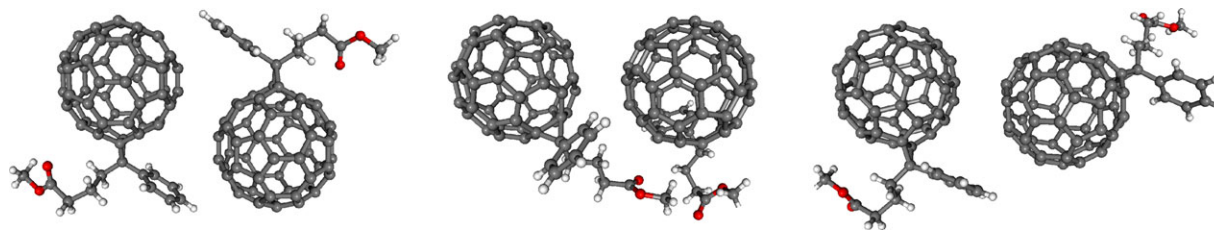


Figure 2. The three PCBM orientations studied in this article, denoted in the results section PCBM-1, PCBM-2, and PCBM-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$g(i) = \begin{cases} 1 & \text{if } i \in \text{left(donor)fragment} \\ 0 & \text{otherwise} \end{cases} \quad (8)$$

We then self-consistently calculate the chemical potential of the neutral and charged species, μ_0 and μ_{-1} , such that the following conditions are met:

$$2\text{Tr}[f(\tilde{F} - \mu_0)] = \sum_{j=1}^{N_0} f(\epsilon_j - \mu_0) = N \quad 2\text{Tr}[f(\tilde{F} - \mu_{-1})] = N + 1 \quad (9)$$

where N is the number of electrons in the neutral system, N_0 is the number of orbitals and f is now a Fermi–Dirac operator

$$f(\tilde{F} - \mu_0) = \frac{1}{1 + e^{\beta(\tilde{F} - \mu_0)}} \quad (10)$$

The factor 2 in Eq. (9) above is due to spin.

We then apply a local bias w to the Fock matrix,

$$\tilde{F} \rightarrow \tilde{F} + w\tilde{\theta} \quad (11)$$

such that the extra electron is delocalized evenly between the two fragments. This is essentially the same as applying an external electric field on the system; however, as mentioned, there is significant time saving since the DFT calculation is only done once, post SCF convergence.

To calculate the transfer integral, we convert the theta operator into the molecular orbital basis,

$$\tilde{\theta}^E = V^T \tilde{\theta} V \quad (12)$$

where V is the eigenvector matrix of the orthogonal-basis Fock matrix, \tilde{F} . The transfer integral becomes:

$$J_{ij} = (\epsilon_i - \epsilon_j) \tilde{\theta}_{ij}^E \quad (13)$$

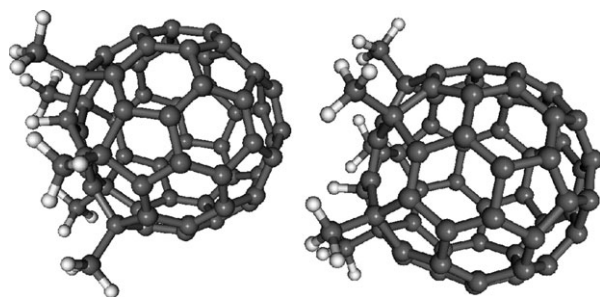


Figure 3. $C_{60}Me_5H$ dimer.

The transfer integral is then used to calculate the extended Marcus-theory rate, Eq. (2), summing over all initial states.

Results

We have studied several molecules, as follows: PCBM (Fig. 2), penta-(*p*-*t*-butyl C_6H_4)-1-hydro- C_{60} (denoted TBP) (Fig. 1), and pentamethyl-monohydro- C_{60} (denoted $C_{60}Me_5H$) (Fig. 3). PCBM is the most commonly used fullerene in organic solar cells, and consists of a phenyl group and butyric acid methyl ester group attached to the fullerene ball via a methano-linker. Here, we study three dimer orientations of PCBM, each derived from a crystal structure. TBP and $C_{60}Me_5H$ are penta-substituted fullerenes, with *tert*-butyl phenyl and methyl adducts, respectively; each has an additional hydrogen atom bonded to the fullerene ball to compensate for the breaking of a double bond. The allure of these molecules from a device fabrication perspective is that they tend to self-assemble into columns, which could enhance optimal phase separation in bulk hetero-junction solar cells.

We present data for the extended Marcus theory formalism, that is, summation over all initial states (labeled as “multiple-state transfer time,” as well as the traditional Marcus theory formalism, which typically only considers the coupling between the lowest states (LUMOs) on the left and right, which in our language amounts to including only the $ij = \text{LUMO, LUMO}+1$ (and vice versa) in the sum in Eq. (2).

The results for the transfer time, τ , with the present formalism for the alignment potential w [i.e., satisfying Eq. (9)] are shown in Table 1. Note that in the table we refer to “Multiple-state transfer time,” and to “LUMO-transfer time”; these refer to the inverse of the rates in eqs. (2) and (1), respectively.

Table 2 presents the electron transfer times for PCBM where we calculated the Fock using several methods: neutral system

Table 1. Results of transfer times with the present formalism.

Reorganization energy:	$\lambda = 0.1 \text{ eV}$		$\lambda = 0.15 \text{ eV}$	
	Multiple-state transfer time (fs)	LUMOs transfer time (fs)	Multiple-state transfer time (fs)	LUMOs transfer time (fs)
Dimer:				
PCBM-1	335	531	527	950
PCBM-2	322	1710	478	3060
PCBM-3	147	170	251	305
TBP	140,000	773,000	220,000	1,370,000
$C_{60}Me_5H$	24,200	33,800	43,200	60,500

Table 2. Comparison of transfer times with neutral and anionic systems in PCBM.

Reorganization energy:	$\lambda = 0.1$ eV		$\lambda = 0.15$ eV	
	Multiple-state transfer time (fs)	LUMOs transfer time (fs)	Multiple-state transfer time (fs)	LUMOs transfer time (fs)
Method				
B3LYP neutral	335	531	527	950
PBE neutral	370	747	595	1300
PBE anionic	433	1100	680	2000

with B3LYP functional, neutral system with PBE functional, and anionic system with PBE functional (we ignore the anionic system with B3LYP functional as B3LYP has been shown to give inadequate results for charged systems). The data show similar results for the three methods, so henceforth we employ the B3LYP functional for neutral species.

Several things in particular stand out about the data. First, we demonstrate that for all the molecules presented, a two-level Marcus formula is insufficient to fully capture the electron transfer behavior. This is because for very large molecules such as fullerene derivatives, the excited states are sufficiently low that they can be thermally excited. Therefore, many levels can be thermally populated and can contribute to electron transfer.

We also note that for all relative orientations of PCBM, shown in Figure 2, electron transfer rates are very high. Due to the spherical symmetry of the LUMO and LUMO+1 orbitals about the fullerene units in PCBM (shown in Fig. 4), the molecule conducts well in a variety of directions, and the rate of transfer is primarily a function of separation between these units. The variation in transfer times and the importance of summing over all initial states is primarily a result of the energy difference between the higher order state and the LUMO. For example, only a minor improvement in transfer time is seen in the third PCBM dimer; in this system, the LUMO+1 and LUMO+2 orbitals are 0.04 and 0.12 eV above the LUMO, respectively. Therefore, the standard Marcus transfer handles this system quite well. Alternatively, in the second PCBM dimer, the LUMO+1 and LUMO+2 are 0.07 and 0.10 eV above the LUMO. This energy difference results in a much more substantial contribution from the LUMO+2.

The results for the variety of methods for TBP are shown in Table 3. Comparing the three methods, we note that the total

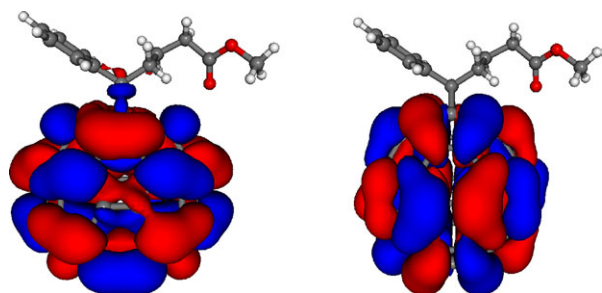


Figure 4. Frontier orbitals of PCBM. The LUMO is shown on the left, and LUMO+1 on the right. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvation method gives transfer rates about 40% faster than the electric field delocalization and direct delocalization, which give very similar results. This is a result of several things. First, the addition of solvating molecules causes the frontier orbitals to have a much greater overlap, that is, the LUMO and LUMO+1 matrix element of the theta operator in the molecular orbital basis is much larger. Second, in the solvation method, the higher order frontier orbitals are closer to the LUMO than in the electric field and direct delocalization methods. For example, in direct delocalization, the LUMO+1 and the LUMO+2 are 5.94×10^{-4} eV and 3.06×10^{-2} eV above the LUMO, respectively; whereas when solvated, these orbitals are 5.10×10^{-4} eV and 2.57×10^{-2} eV above the LUMO. Additionally, excited states higher than the LUMO+2 play only a minor role in electron transfer, as the energy gap above the LUMO prevents significant population. We also note that the transfer times are also more greatly enhanced when one compares the multiple-state method to the LUMOs method. This is due to the higher level orbitals being closer to the LUMO. While the results presented for the several methods for calculating transfer times in TBP vary, we would argue that the solvation method provides the most accurate treatment of the system. The presence of point charges around the dimer, while not explicit treatment of neighboring molecules, most thoroughly mimics the bulk environment of the system. Nonetheless, the direct delocalization method provides a qualitative picture for comparing possible performance device of a number of molecules.

We also investigated the solvent effects of using the polarizable continuum model to solvate a TBP dimer, using the COSMO method in NWChem. We find that similar to calculations on an isolated dimer, the excited state orbitals are localized on a single fragment, and, therefore, no electron transfer is observed. We believe that this unphysical and the polarizable continuum model does not sufficiently capture the electronic behavior of the system. To compare the transfer rates of such a system, we applied the direct delocalization method and find that the multiple-state transfer times are 133,000 and 210,000 fs for reorganization energies of 0.1 and 0.15 eV, respectively. This is in good agreement with our direct delocalization times of the unsolvated dimer.

Conclusions

We present a simple method to efficiently calculate electron transfer rates between molecular dimers. The method handles

Table 3. Results for the variety of methods for TBP.

Reorganization energy:	$\lambda = 0.1$ eV		$\lambda = 0.15$ eV	
	Multiple-state transfer time (fs)	LUMOs transfer time (fs)	Multiple-state transfer time (fs)	LUMOs transfer time (fs)
Dimer:				
Solvated TBP	84,000	3,500,000	141,000	6,220,000
Electric field delocalization	128,000	1,120,000	208,000	1,980,000
Direct delocalization	140,000	773,000	2,200,000	1,370,000

vastly asymmetric-placed dimers, where each individual molecule sees a different chemical environment. Additionally, the method is useful in molecules for which higher excited states interact with the frontier orbitals of the system. The proposed method is also highly efficient as it does not require additional DFT calculations.

Of the molecules studied, PCBM and TBP have been fabricated to make OPV devices. According to experiment, PCBM makes significantly more efficient devices than TBP, 5–6% power conversion efficiency versus 1.5% for TBP.^[15–17] Our study is, therefore, qualitatively consistent with experiment and can be used to screen new molecules. While our study does not take into account the morphological behavior of these molecules, it gives a good basis for the types of molecules that would make efficient devices. We mention in the Results section, for example, the spherical symmetry of the LUMOs about the fullerene cage provides multidirectional pathways for electron transfer.

The work presented indicates several important factors relevant in the design of fullerenes for the use of organic solar cells. First, the methano-substituted motif, as in PCBM, conducts electrons well due to the spherical symmetry of the frontier orbitals. Additionally, substitutional motifs that retain this spherical symmetry about the fullerene unit would also make for high transfer rates. We should note, however, that this would not necessarily lead to a top performing cell as the energetics would still need to match those of the electron donor. Nonetheless, the particular motif seems highly efficient.

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Keywords: organic solar cells • Marcus theory • electron transfer • fullerene • density functional theory

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