Electron transfer with TD-Split, a linear response time-dependent method

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We present a simple method, time-dependent split (TD-Split) for A → B electron transfer by a TD evaluation of the lowest excitation energy from the ground state of the combined (AB) system. As an example, we study transfer between substituted fullerenes, primarily PCBM. Electron transfer in such fullerene systems is important as it is often the bottleneck in organic solar cells. The TD-Split method is described in detail, including numerical linearization which reduces the number of required iterations, and comparison to other possible approaches. We also compare to other molecules such as C60Me5H, and find similar trends as experiment.

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1. Introduction

Electron transport is an established problem which continues to attract significant attention as it is both seemingly simple and physically and technologically important. In fact many of the challenges associated with devices such as photovoltaic devices are due to electron transport [1], making theoretical guidance desirable. An example is transport between fullerenes, which is a bottleneck in several fullerene-polymer solar energy architectures.

For small molecules, the treatment of electron transport of the isolated-Density Functional Theory, is generally more appropriate for accurate for electronically excited states. TD-DFT, Time Dependent-Density Functional Theory, is generally more appropriate for excitations, so it is tempting to use it also for transport [2–6].

Both TD-DFT and DFT present other challenges, primarily in determining what is the proper initial and final state. Specifically, the fundamental electronic structure overlap integral in the Marcus formalism is the transfer integral:

\[ J = |\langle \phi_L | H | \phi_R \rangle|^2, \]  

(1)

which refers to the left and right (initial and final) states, and \( H \) is the coupling Hamiltonian. The fundamental challenge is to properly define such initial and final states. It is possible to use an isolating potential to define these states [3]. However, unless the system is extremely large, the localization of the charge on one side influences the charge distribution on the other side, thereby influencing the transport; i.e., once the localization constraint is removed, then even when the charge is not yet transported from reactant to product (A to B in our example), there will be significant charge relaxation in both reactant and product and therefore apparent dynamics which is not due to the actual electron transfer, but has to do with the removal of the localization constraint.

In this paper we therefore present a different approach, which is inherently linear-response [7,8] in form. The linear response nature of the method is numerically useful, as discussed later. We label the method TD-Split.

TD-Split is based on a response formula of the generic form:

\[ \delta A(t) \equiv \langle \Psi(t)|A|\Psi(t) \rangle, \]  

(2)

where \( |\Psi(t)\rangle \) is a perturbed ground state of the complete system (i.e., with the electron delocalized over the donor and the acceptor); \( A \) is a perturbation operator as defined below. This formula has the inherent advantage that it has a very well defined initial state and any time-dependent dynamics is directly associated with the transport.

Physically, in the TD-Split approach, the initial state is the ground static density matrix associated with the whole (donor + acceptor) charged system. A time-dependent excitation is then applied; the response to this excitation peaks at a frequency which together with its amplitude determines the electron transfer rate. This approach is therefore inherently a linear response method, so that practically the very efficient numerical tools developed for linear response in time-dependent approaches are immediately available.

The fundamental attraction in using the simple transport formula based on a symmetric case rather than a localized approach
is apparent if we qualitatively view the system as a single electron being transported while the others act as a background. In this way of viewing the system, the initial state can be viewed as an electron transition-state, i.e., all the electrons arrange themselves so that one electron delocalizes as much as possible over the whole system.

The approach presented here is simplest to understand and to apply in a case where there is an isolated single pair of conducting molecular orbitals (i.e., with significant amplitude on the acceptor and donor). This case is very common in many practical applications, such as transport (hopping) between fullerene or other symmetric or quasi-symmetric molecules. The method is however quite general to apply and will be useful in other circumstances, as explained below. For other time-dependent approaches in this context, see Refs. [9–11].

The linear-response simulations use here a semi-empirical approach, TD-PM3 (Time Dependent-Parametric Model 3) [12]. An attractive feature of TD-PM3 is that as in TD-HF (Time-Dependent Hartree-Fock), TD-PM3 has no self-energy in explicit open shell treatment, and reduced self-energy in a closed shell treatment. TD-PM3 is very efficient, both in scaling and in the use of a minimal basis set, and allows the treatment of realistic large organic systems. The methodology is general and applicable to other methods, primarily TD-DFT, which we plan to pursue in future work.

Several methods for extracting the information are discussed. In addition to direct time-dependent simulations, we discuss time-dependent linear response using Chebyshev propagation. Within the latter method, significant savings result when we use Filter-Diagonalization, which is a method for extracting frequency-resolved information from a short-time section of the results (or, in the Chebyshev case, from few iterations). The need for the method is however acute in weakly coupled homogenous systems, because the splitting can be small so that a direct propagation or iterative methods would require long propagation times (as the propagation time is, in most methods, proportional to the inverse of the splitting). We show that with Filter-Diagonalization, few iterative steps (few thousands at most) are required.

The main example used here is a dimer of PCBM molecules. PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) has been the primary fullerene acceptor in organic solar cells for more than a decade; a dimer of PCBM molecules has a fairly large coupling of the LUMO levels of each PCBM. In addition to the PCBM dimer, we also investigated another example, transport within a C60Me3H dimer.

In the remainder of the paper we discuss the propagation approaches (Section 2), discuss the numerical techniques used for the presented method (Section 3), and show sample results (Section 4) on PCBM and C60Me3H. Conclusions follow in Section 5.

2. Theory

2.1. Simplified treatment

One approach for electronic transport is to apply a voltage or a bias in order to hold an electron or a portion of it in one of the molecules [13]. The bias is then relaxed and the change in charge distribution over both molecules is examined over time. This method will be referred to as release of bias.

Another method is derived from a simpler one-body problem where a single electron is transferred from a left molecule (donor) to a right molecule (acceptor). In a localized basis (left and right) the Hamiltonian governing this simple system is:

\[
H = \begin{pmatrix}
\varepsilon_L & \eta \\
\eta & \varepsilon_R
\end{pmatrix},
\]

where \(\varepsilon_L\) is essentially equivalent to the energy of the LUMO in the left molecule (\(\psi_L\)) and \(\varepsilon_R\) is associated with energy of the LUMO in the right molecule (\(\psi_R\)). \(\eta\) is the coupling constant.

The eigenvalues of the Hamiltonian are denoted as \(\lambda_+\) and \(\lambda_-\), associated with the symmetric and antisymmetric orbitals. The symmetric (+) and antisymmetric (−) eigenstates of the combined system can be described as combinations of \(\psi_L\) and \(\psi_R\) as follows:

\[
\psi_+ = a_{\psi_L} + b_{\psi_R},
\]

\[
\psi_- = b_{\psi_L} - a_{\psi_R},
\]

which are normalized so \(a^2 + b^2 = 1\), and equivalently:

\[
\phi_L = a_{\psi_L} - b_{\psi_-},
\]

\[
\phi_R = b_{\psi_L} + a_{\psi_-}.
\]

The coefficients \(a\) and \(b\) indicate how localized the transport is. If \(a\) and \(b\) are the same, then the molecular orbitals are very delocalized; but if \(a = 1\) and \(b = 0\), then there is no delocalization and there will be very little transport. As long as \(\varepsilon_L\) and \(\varepsilon_R\) are different by less than the coupling strength, \(a\) and \(b\) will be reasonably large. In that case, good electron transport is determined through having a large coupling strength. For degenerate initial states, the coupling is determined from the splitting parameter, labeled as \(\gamma\):

\[
\gamma = \lambda_+ - \lambda_- = 2\eta.
\]

The splitting can be obtained by calculating the static energy difference between the two eigenstates.

The straightforward extension of this approach to interacting electronic systems uses the neutral combination (AB), and determines the splitting between the LUMO and LUMO + 1 so that both levels are unoccupied and there is no inconsistency to the treatment. This method will be referred to as static-split.

2.2. TD excitation

Finally, we suggest to obtain the splitting \(\gamma\) from a TD treatment, rather than from the static splitting. To obtain a time-dependent expression for \(\gamma\), we revert back to the one-electron problem. The transition can be viewed as starting a wavefunction in one molecule and watching the transition to the other molecule; fundamentally this will then be:

\[
Q(t) \equiv |\langle \psi_L | \psi_R(t) \rangle|^2.
\]

The time-evolution of the symmetric and antisymmetric eigenstates is:

\[
\psi_+(t) = e^{-i\lambda t} |\psi_+\rangle,
\]

\[
\psi_-(t) = e^{-i\lambda t} |\psi_-\rangle.
\]

Substituting into Eq. (7) and simplifying, we get:

\[
Q(t) = 4a^2b^2 \sin \left( \frac{\lambda}{2} t \right).
\]

A Fourier transform of \(Q(t)\) will give \(\gamma/2\) by the location of the maximum and the magnitude will give \(4a^2b^2\).

It is necessary to obtain a form that can be used with TD-PM3. This will be done by introducing the following:

\[
B(t) \equiv |\langle \psi_- | \theta k e^{i\theta k} e^{-i\theta k} |\psi_+\rangle|
\]

Here, \(\theta_k\) and \(\theta_{\bar{k}}\) are step functions; \(\theta_k\) is 1 on the left and 0 on the right, and the opposite for \(\theta_{\bar{k}}\). Formally,

\[
\theta_k |\psi_L\rangle = |\psi_L\rangle,
\]

\[
\theta_{\bar{k}} |\psi_R\rangle = 0,
\]

\[
\theta_k |\psi_R\rangle = 0.
\]
serves the same purpose as Eq. (19), giving:

\[ B(t) = \langle \psi_i | \hat{H} e^{i \hat{H} t} | \psi_i \rangle. \]

Now let:

\[ I = |\psi_i \rangle \langle \psi_i | + |\psi_\perp \rangle \langle \psi_\perp |. \]

Inserting Eq. (13) into Eq. (12) gives:

\[ B(t) = \langle \psi_i | \hat{H} e^{i \hat{H} t} | \psi_\perp \rangle + \langle \psi_\perp | \hat{H} e^{i \hat{H} t} | \psi_i \rangle, \]

so

\[ B(t) = \langle \psi_i | \hat{H} e^{i \hat{H} t} | \psi_\perp \rangle + e^{-i \hat{H} t} \langle \psi_\perp | \hat{H} e^{i \hat{H} t} | \psi_i \rangle. \]

Substituting with Eq. (4) gives

\[ B(t) = a^2 b^2 (1 - e^{-2t}). \]

This is analogous to Q(t) and taking the Fourier transform of both will yield a similar spectrum of similar magnitude.

To make Eq. (10) more applicable for use in TD-PM3, it is written as

\[ B(t) = \text{Tr} \left( |\psi_i \rangle \langle \psi_i | \hat{H} e^{i \hat{H} t} | \psi_i \rangle \langle \psi_i | \right), \]

or

\[ B(t) = \text{Tr} \left( P_0 e^{i \hat{H} t} \right). \]

Here, \( P_0 \) is the initial density matrix taken in the symmetric state, \( P_0 = |\psi_i \rangle \langle \psi_i |. \)

Eq. (19) is in a form that can be usable in TD-PM3 or TD-DFT. To turn it into a form that can be used with efficient numerical methods, first recognize that:

\[ 2i \text{Im}(B(t)) = \text{Tr} \left( P_0 e^{i \hat{H} t} \right) - \text{Tr} \left( e^{i \hat{H} t} P_0 e^{i \hat{H} t} \right). \]

But since

\[ i \omega_i = \frac{\partial |\psi_i \rangle \langle \psi_i |}{\partial \omega} \bigg|_{\omega=0}, \]

we get

\[ \text{Im}(B(t)) = \frac{1}{2} \frac{\partial}{\partial \omega} \left( \text{Tr}(e^{i \hat{H} t} e^{-i n \omega} P_0 e^{i n \omega} e^{i \hat{H} t}) \right) \bigg|_{\omega=0}. \]

To simplify, let

\[ P_s(t) = e^{-i \omega t} P_0 e^{i n \omega}, \]

and also

\[ P_s(t) = e^{-i \omega t} P_s(0) e^{i n \omega}. \]

The above can then be inserted into Eq. (22) to become

\[ \text{Im}(B(t)) = \frac{1}{2} \frac{\partial}{\partial \omega} \left( \text{Tr}(P_s(t) \omega) \right) \bigg|_{\omega=0}. \]

TD-PM3 or TD-DFT can be used to obtain the time evolution of \( P_s(t) \). The derivative with respect to \( \omega \) can be obtained using numerical methods. Some efficient numerical methods to be used are described in the next section.

3. Practical evolution

Here we outline the practical evolution of the transmission.

3.1. Initial state

The first stage is the preparation of an initial ground state; for large systems, we will likely choose between Hartree–Fock, a semi-empirical method (PM3, etc.), or DFT, although the same formalism is useful if other methods, such as MP2, are applied to the ground-state calculation. Eventually, the ground state of the complete system density \( |\psi_0 \rangle \) or initial wavefunction/orbitals \( |\psi_0 \rangle \) is obtained.

Next, a perturbation operator is found. In practice, several perturbation operators are potentially useful (possibly in combination, as described below). The first is \( \hat{B}_1 \) from Eq. (11). A second is:

\[ A = |\phi \rangle \langle \phi | - |\phi_\perp \rangle \langle \phi_\perp |. \]

A third option is simply:

\[ A' = |\phi_{\text{homo}} \rangle \langle \phi_{\text{homo}} | + c.c. \]

The last (third) transition operator will not yield the correct amplitude for the transitions (the equivalent of \( 4a^2 b^2 \)) unless the system is close to symmetric, so \( a \sim b \sim 1/\sqrt{2} \).

3.2. Linear-response evolution

Next is the evolution in time. In the methods we consider the Fock operator is used to propagate a density matrix (or a set of orbitals); these methods includes TD-HF, TD-DFT, and TD-PM3. The details of the Fock operator depend on the method used; for TD-PM3, for example, see Refs. [14,15], but briefly it is formally similar to Hartree–Fock:

\[ F = h_0 + \sum_{ij} V_{ij} P_{ij}, \]

except that now \( h_0 \), \( V_{ij} \) are semiempirical matrix elements, and each \( V_{ij} \) vanishes unless it is a two center integral, i.e., the only non-zero elements are:

\[ V(i_s,j_s,k_s,l_s), \quad V(i_s,j_k,k_s,l_k), \quad V(i_s,j_s,k_l,l_k), \]

where \( i_s, k_s \) for example, refers to a basis function “i” localized on atom “a”.

One option would have been to use explicit time-dependent propagation. Then, starting at \( P_0 \) include the perturbation to get:

\[ P(t = 0^+) = P_0 - \eta |A, P_0| \]

After that, propagate forward the Fock equation,

\[ \frac{idP}{dt} = [F(P), P], \]

where \( F \) is the density-dependent Fock operator.

Another option pursued here is to use the linear response time-dependent Chebyshev approach [7,16]; briefly, in the approach one first constructs residues:

\[ R_n = \text{Tr} (B X_n), \]

where the modified Chebyshev series is defined as:

\[ X_0 = -i [A, P_0], \]

\[ X_1 = \frac{1}{\Delta H} LX_0, \]

\[ X_n = \frac{2}{\Delta H} LX_{n-1} + X_{n-2}, \]

and \( \Delta H \) is a numerical parameter characterizing the spectrum of the Fock operator (typically chosen as \( \sim 75 \text{ eV} \) for TD-PM3 applications) and the Liouville operator is defined as:

\[ LP = \frac{1}{\zeta} [F(P_0 + \zeta P), P_0 + \zeta P] - [F(P_0), P_0], \]

where \( \zeta \) is a small number chosen to ensure the linear response; for clarity, we denote the explicit density dependence of the Fock operator.
From the modified Chebyshev series and the residues there are three options. One is to construct explicitly the time-dependent signal,

$$\delta B(t) = \sum_n (2 - \delta_{00}) R_n(t) \Delta H R_n,$$

and then Fourier transform the above signal. A more efficient option is to directly Fourier transform the Chebyshev series elements, leading to

$$B(\omega) = \sum_n b_n(\omega) R_n,$$

where

$$b_n(\omega) = (2 - \delta_{00}) \int_0^\infty e^{\omega t} f(t) R_n(t) \Delta H dt,$$

and the damping function is

$$f(t) = e^{-\alpha t}.$$

3.3. Filter-Diagonalization

The third option for extracting the eigenvalues is Filter-Diagonalization [17]. Briefly, this is a method to expand a general series, $C_n$, as made from (initially unknown) complex frequencies and weights $(c_n, p_n)$ as:

$$C_n = \sum_k p_k e^{i\omega_k n}.$$

In its most relevant form for this problem [18], Filter-Diagonalization becomes an approach to extract the frequencies and weights directly from the Chebyshev series. Filter Diagonalization extracts the coefficients and eigenvalues directly from such a series in fewer terms than a Fourier transform will (i.e., with fewer elements than necessary in a series such as the one in Eq. (36) to develop well-isolated peaks). In this context, this is based on formally writing the initial modification to the density matrix (i.e., its linear response part) as:

$$X_0 = \sum_k p_k A_k,$$

where each $A_k$ is a separate density matrix that is an eigenstate of the Liouville operator, i.e.,

$$L A_k = i \omega_k A_k,$$

and

$$T r(A_k A_k) = \delta_{\omega_k}$$

so

$$p_k = T r(X_0 A_k).$$

(Note that $\omega_k$ are the transition frequencies.) Then, each residue is formally:

$$R_0 = \sum_k p_k \cos(nz_k),$$

where

$$z_k = \cos^{-1} \left( \frac{\omega_k}{2\Delta} \right).$$

Eq. (44) has the form of a harmonic series, i.e., a sum of a series of exponential terms.

For the present application, we note that Filter-Diagonalization can be further improved because of the structure of the eigenvalues. The eigenvalues of the Liouville operator come here in pairs of negative and positive imaginary values, i.e., for each positive $\omega_k$ there is a negative one. We are interested in the pair with the lowest $|\omega_k|$, which we will denote as $\lambda_{\text{min}} - i\lambda_{\text{min}}$, each of which is associated with the HOMO–LUMO splitting frequency.

The usual Filter-Diagonalization technique will be challenged by the need to separate the pair of $\omega$’s that are associated with $\lambda_{\text{min}} - i\lambda_{\text{min}}$, which we will denote as $\lambda_{\text{min}} - i\lambda_{\text{min}}$ (and $\lambda_{\text{min}}$ is close to $\pi/2$). To circumvent this, we note that because of the pairing of the negative and positive eigenvalues, the odd terms will vanish

$$0 = R_1 = R_3 = \cdots = R_{2n+1}. \quad (46)$$

So that we define a new series

$$Q_n = R_{2n}, \quad n = 0, 1, 2, \ldots \quad (47)$$

and then use Filter-Diagonalization to fit it to

$$Q_n = \sum_k 2p_k \cos(2nz_k), \quad (48)$$

where now the sum is over half the eigenvalues, i.e., the $z_k$ associated with positive $\omega_k$. With this slight modification, Filter-Diagonalization is much more effective as it does not need to separate two very closely-spaced eigenvalues.

4. Results

The simulations were done on electron transport between two fullerene derivatives. The bulk of the simulations were done on a dimer of the PCBM fullerene derivatives. This system was constructed by taking a PCBM molecule and its nearest neighbor from the crystal structure of PCBM-1,2-C_6H_4Cl_2, as shown in Fig. 1 [19]. The PCBM dimer used here was chosen out of the other combinations in the crystal structure as it is relatively the closest, so its conductivity is assumed to be the highest of all the other combinations.

The rest of the simulations were done on a dimer of penta-methyl monohydro[60]fullerenes, which we will refer to as C_{60}Me_5H. The system was obtained by taking a molecule of C_{60}Me_5H and its nearest neighbor in a head-to-tail stacked arrangement from the crystal structure of C_{60}Me_5H-CS_2 [20], as shown in Fig. 2. The C_{60}Me_5H dimer was chosen as it provides a simple example of the stacking motif often observed in pentaaryl fullerenes, which have previously been evaluated as acceptors in bulk-heterojunction photovoltaic devices. Arranged in such a way, the contiguous $\pi$-electron systems are well separated and the dimer is thus expected to have a lower conductance, thereby exemplifying weakly conductive systems.

As a first stage in all methods, the ground state was found using the PM3 program in the MOPAC [21] package. Simulations were done on the PCBM dimer at the natural distance of 10.1 Å determined from the crystal structure of PCBM-1,2-C_6H_4Cl_2 and also at stretched distances.

In the simplest approach, static splitting, the orbital eigenvalues for the ground state were used to calculate the differences between the LUMO and LUMO + 1 of the neutral combination. One important point is that before calculation, it is necessary to ensure that the LUMO and LUMO + 1 are extended, i.e., do not localize on the fragments; otherwise, the splitting will be high but there will be no transition. To ensure that the LUMO and LUMO + 1 are delocalized, we apply a potential which is uniform on each fragment but is different between the fragments (similar results would have been obtained from applying an electric field). Such a potential is similar to a localization potential, but its role is to delocalize the orbitals.

In practice, the value of the potential enters the Marcus formulae, i.e., it is essentially part of the rearrangement energy – which is defined by the point where the two fragments have the same potential energy (here where the potential is delocalized). Results of the static splitting approach are shown in Fig. 3.
Next we show the results of calculating the time-dependent transmission by biasing the molecule, releasing the bias, and following the actual transfer of the electron (release of bias method). Specifically, first we obtain the ground state of the system in an ionic state using PM3 in the MOPAC package, with an extra electron inputted in the LUMO of the system. A bias is then applied and then released. The PCBM system is run with two choices:

- A bias that is large enough to initially keep the extra electron in one of the molecules and
- A small bias that initially keeps 60% of the extra electron in one of the molecules and 40% in the other.

Simulations were done on the PCBM system with the natural and stretched distances. The trace of the electron density on the
molecule that had the lesser density was calculated over time and shown in Fig. 4. Interestingly, for large bias the electron localizes, so that even after the bias is released the system does not fully oscillate (Fig. 4). This is because the system is initially not in an electronic transition state; i.e., the electrons on each side adjust their orbitals in the presence of the bias, and the release of the bias does not sufficiently force the electrons to redistribute.

In spite of the localization of the electron, it is possible to extract a form of a transfer frequency by taking a Fourier transform of the results shown in Fig. 4; the peak, as a function of the distance between the PCBM molecules, is shown in Fig. 5. As shown, the results depend on the bias. This is discussed in Section 5. However, since the amplitude of the oscillations is small, the frequency cannot be treated as a full electron oscillation.

Finally, we turn to the main method discussed here, TD-Split, where TD-PM3 is used to extract the HOMO–LUMO splitting for the ionic state without applying a bias on the neutral molecule. First, PM3 (again from MOPAC) was used, without applying a bias, to calculate the ground state. TD-PM3 was then used to propagate Eq. (25). The previously described Chebyshev and Filter-Diagonalization approaches (Eqs. (32)–(48)) were used to obtain the results.

Both a direct Chebyshev propagation (Eq. (36)) and Filter-Diagonalization gave comparable results. For the Chebyshev approach we typically used 25,000 iterations, while for Filter-Diagonalization typically 3000 total iterations were used. The Chebyshev method gives a continuous graph (Eq. (36)) of spectra vs. frequency, and the first peak yields the splitting, as shown in Fig. 6. Filter-Diagonalization gives the results as discrete values. The splitting determined from Chebyshev and Filter-Diagonalization is very similar, as shown in Fig. 7; the only difference between the two methods is found for a weakly interacting system, i.e., PCBM at very large distances where 25,000 Chebyshev iterations are not sufficient for convergence, but Filter-Diagonalization with 3000 iterations is ample.

Finally, these three methods discussed above are compared to each other in Fig. 8. The first method, static-split, involves finding the difference between the LUMO + 1 and the LUMO of the neutral molecules. This method is simple in that only a static PM3 or DFT calculation is required and so is the fastest. The results show that the splitting, and so the electron transfer, is reduced as the PCBM molecules are stretched apart, but is significantly smaller than the TD-PM3 results.

The second method, release of bias, which involves a bias that initially fixes the electron density and then releases it, generally follows the trend of decreasing conductance with increasing distance between the molecules, but the oscillation amplitude is too small when a large bias is used.

The third method, TD-Split, introduces TD-PM3 as a way to get the (charged-system) HOMO–LUMO split for the transferred molecule, from which we get the electron transfer rate. Similar methodology will work with TD-DFT. TD-PM3 allows for fast results, so the method can conceivably be used for combinatorial searches of improved transfer. Note that TD-Split can be considered as the limit of the 2nd approach (release of bias), when an infinitesimally small bias is used and then released.

Comparison with the first method (static split) shows that TD-Split gives significantly larger rates than the static version, at least...
when we used TD-PM3 and PM3. TD-Split best shows a trend of decreased electron transfer with increasing distance between the molecules. To further test the magnitude of the splitting produced by the TD-Split, simulations were done on C$_{60}$Me$_5$H and are compared with those of PCBM. The results are shown in Fig. 9. The equilibrium distance of C$_{60}$Me$_5$H is 10.0 Å. This graph shows how the C$_{60}$Me$_5$H dimer has much lower TD-based splitting than PCBM dimer (where in both cases the systems are negatively charged, to represent the transferred electron).

5. Conclusions

We have presented a TD-method to studying electron transfer between two molecules, TD-Split. We used here TD-PM3 due to its speed over TD-DFT, but either TD-DFT or alternately any other semiempirical method beyond PM3 could be used. This method was also compared with two other methods to study electron transfer, static-split and release of bias, and showed larger rates and consistent decay with transfer distance.

Future work involves improving on this proposed method. One is to use open-shell TD-PM3, rather than closed-shell. This should eliminate any residual self-energy and its effects. Another potential improvement is to use this method with TD-DFT rather than TD-PM3.

An interesting variant will be to study the flux–flux evolution in time, and see how polarization and time-dependent effects influence it; i.e., how the other electrons in the molecule “solvate” the transferred electrons.

Finally, the technique allows quantitative studies of the efficiency of transfer in different organic systems, and will be used to suggest theoretical guidance on the experimental transport of electrons in fullerenes. A follow-up paper will tackle this problem.

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