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Los Angeles

**Development of Methods for Reducing the Cost of
Density Functional Theory and Time-Dependent
Density Functional theory**

A dissertation submitted in partial satisfaction
of the requirements for the degree
Doctor of Philosophy in Chemistry

By

Samuel Hernandez

2015

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ABSTRACT OF THE DISSERTATION

Development of Methods for Reducing the Cost of Density Functional Theory
and Time-Dependent Density Functional theory

by

Samuel Hernandez

Doctor of Philosophy in Chemistry

University of California, Los Angeles, 2015

Professor Daniel Neuhauser, Chair

Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TDDFT) are powerful methods for solving a variety of problems, including ground state electronic structure, electron dynamics, and the absorbance cross section of molecules and materials. DFT is used to calculate the ground state electron configuration, whereas TDDFT is used to solve for the absorption cross section of excited systems. These techniques are not without their challenges. DFT requires the solution of Kohn-Sham orbitals through the diagonalization of the one electron Hamiltonian, which scales as $O(N^3)$ where N signifies the number of orbitals in a simulation. TDDFT has its challenges as well. Each orbital must be propagated every time step, but since a single TDDFT simulation requires thousands of time steps, it is very costly. In this dissertation, we present methods that were developed to circumvent the limitations of DFT and TDDFT.

One method for decreasing the cost of DFT and TDDFT is direct delocalization, which was used to calculate the electron transfer rate of a fullerene derivative dimer. Specifically, a common way of determining the electron transfer rate is through the use of Marcus theory, which relies on the dimer having symmetric environments. In nature this is usually the case because the dimer is surrounded by other molecules, thus creating a locally homogeneous environment. In theoretical simulations this is much more difficult to achieve. One way is to add solvating molecules, but this can be extremely costly. Instead we were able to use, in Chapter 1, a modified version of Marcus theory, which applies a bias across the Fock-matrix. This modified version of the Marcus theory allows us to solve for the electron transfer rate using one DFT calculation, because it eliminates the need to solvate the dimer to balance out the environments. The electron transfer rate was calculated to qualitatively determine the factors which lead to a good acceptor in an organic solar cell, as is important for creating an efficient solar cell.

In Chapter 2, we present a method for solving for the coupling constant of a dimer without having to balance the environments with solvating molecules. The coupling constant is used in Marcus theory to determine the electron transfer rate. To avoid the balancing we apply an electric field to the system, mimicing the effect that the solvating molecules have on the dimer. The method presented in Chapter 2 is cheaper than the preceding approaches as it limits the size of the system.

The final method we developed was the stochastic paradigm for DFT and TDDFT. The stochastic methods that are described in Chapters 3 and 4 reduce the cost of large-scale calculations by replacing the Kohn-Sham orbitals with stochastic orbitals. The density function is determined by a statistical average of the stochastic orbitals. This method enables the calculation of the absorption cross section of large systems such as 9-(4-Mercaptaphenylethynyl)anthracene (MPEA)

chemisorbed onto a gold surface, and large gold nanoclusters. Both these systems, which contain thousands of electrons, are expensive to simulate using conventional TDDFT, but the stochastic approach we use, stochastic TDDFT (TDsDFT) makes these calculations feasible since it scales moderately (sublinearly) with the number of electrons in the system.

The dissertation of Samuel Hernandez is approved.

Peter M. Felker

Rowan Killip

Daniel Neuhauser, Committee Chair

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2015

This dissertation is dedicated to my friends who supported me, my family who encouraged me,
and to my mom and dad who gave me my first science book and taught me to love science.

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Chapter 1

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Chapter 2

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Chapter 3

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Chapter 4

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Arntsen, C.A.; Reslan, R.; Hernandez, S.; Gao, Y.; Neuhauser, D. Direct Delocalization for Calculating Electron Transfer in Fullerenes, *Int. J. Quant. Chem.*, 2013, 113, 1885-1889

Aguirre, J.C.; Arntsen, C.; Hernandez, S.; Huber, R.; Nardes, A.M.; Hamil, M.; Kilbride, D.; Rubin, Y.; Tobert, S.H.; Kopidakis, N.; Schwartz, B.J.; Neuhauser, D. Understanding Local and Macroscopic Electron Mobilities in the Fullerene Network of Conjugated Polymer-based Solar Cells: Time-Resolved Microwave Conductivity and Theory, *Adv. Func. Mater.*, 2014, 117, 5407-5415

Introduction

Modern quantum chemistry revolves around quantum mechanics. In quantum chemistry, one describes a system through the time-independent Schrödinger equation:

$$\hat{H}\Psi = E\Psi, \quad (0.1)$$

where Ψ represents the wavefunction of the system, which is an eigenfunction of Hamiltonian $\hat{H}$, and the total energy is defined as E . Solving the Schrödinger equation can be very difficult for system containing multiple particles because the many-body interactions do not allow for an independent solution of a wavefunction for each particle separately.

Consider the Hamiltonian, in atomic units, for a many body system containing electrons and nuclei:

$$\hat{H} = -\frac{1}{2} \sum_A m_A^{-1} \nabla_A^2 - \frac{1}{2} \sum_i \nabla_i^2 - \sum_{Ai} \frac{Z_A}{|r_A - r_i|} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|r_A - r_B|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}, \quad (0.2)$$

where A and B designate nuclei and i and j represent electrons. In practice we assume that the mass of the nuclei is much greater than the mass of an electron. In general the velocity of a particle as a function of kinetic energy is $v = \sqrt{2T/m}$, where T represents the kinetic energy of a particle, and m its mass. Since the mass of the nuclei is much larger than that of an electron, given the same kinetic energy the velocities of the nuclei should be much smaller than of the electrons so the nuclei seem “frozen” compared with the relatively fast movements of the electrons. This assumption allows us to ignore the kinetic energy of the nuclei and is known as the Born-Oppenheimer approximation.

Using the Born-Oppenheimer approximation the nuclei are stationary, and the electronic Hamiltonian is then:

$$\hat{H}_{ele} = -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_{Ai} \frac{Z_A}{|R_A - r_i|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|r_i - r_j|}, \quad (0.3)$$

where R represent a stationary position of a nucleus. The electronic states of the system are solutions of:

$$\hat{H}_{ele} \Psi_{ele} = E_{ele} \Psi_{ele}, \quad (0.4)$$

where the total energy of the system is:

$$E = E_{ele} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{|R_A - R_B|}, \quad (0.5)$$

The use of the electronic Hamiltonian is so common, that it is usually (and here, henceforth) referred to as the Hamiltonian $\hat{H}$ of the system. This Hamiltonian is extremely expensive to solve for large systems.

Many approximate methods use one-electron operators. An example is the Hartree-Fock method, where the a one-electron Fock operator is:

$$\hat{F} = \hat{T} + \sum_A \frac{Z_A}{|R_A - r|} + v_{HX}(r), \quad (0.6)$$

where $\hat{T} = -(1/2)\nabla^2$ stands for the general kinetic energy operator in atomic units. The Hartree-Fock potential $v_{HX}(r) = v_H[n(r)] + v_X[n(r)]$ (where the electronic density function is represented by $n(r)$) contains two different parts. The Coulomb potential $v_H[n(r)]$:

$$v_H[n(r)] = \int \frac{n(r')}{|r - r'|} dr, \quad (0.7)$$

represents the electrostatic repulsion of the electrons. The second term is the exchange potential $v_X[n(r)]$, which represents a correction where two electrons can exchange eigenstates. In the Hartree-Fock paradigm, the wavefunction is defined as a Slater determinant:

$$\Psi(r_1, r_2, \dots, r_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \psi_1(r_1) & \psi_1(r_2) & \cdots & \psi_1(r_{N_e}) \\ \psi_2(r_1) & \psi_2(r_2) & \cdots & \psi_2(r_{N_e}) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_{N_e}(r_1) & \psi_{N_e}(r_2) & \cdots & \psi_{N_e}(r_{N_e}) \end{vmatrix}, \quad (0.8)$$

where N_e is the number of electrons, r_j the position of electron j , and $\psi_i(r)$ is an eigenfunction of the Fock Operator:

$$\hat{F}\psi_i = \varepsilon_i\psi_i. \quad (0.9)$$

Note however that the sum of the eigenvalues ε_i does not equal the electronic energy. The electronic density is determined as:

$$n(r) = 2 \sum_i^N |\psi_i(r)|^2, \quad (0.10)$$

where the factor of two is included because two electrons occupy each orbital, as we consider the system a closed shell system. In Hartree-Fock, the electronic energy becomes:

$$E_{HF} = \sum_{ij} \langle \psi_i | \hat{F} - (1/2)v_{HX}(r) | \psi_j \rangle. \quad (0.11)$$

The Fock operator does not take into account fully the movement of the electrons, so the exact energy of a system will be:

$$\mathcal{E} = E_{HF} + E_{corr}, \quad (0.12)$$

where E_{corr} is the correlation energy, which takes into account the correlation in the movement of the electrons, as well as other type of interactions which are not included the Hartree Fock potential.

Kohn-Sham Density functional theory formally does take into account the correlation energy, and has a one-electron Hamiltonian of:

$$\hat{h}_{KS} = \hat{T} + v_{KS}(r), \quad (0.13)$$

where the Kohn-Sham potential is $v_{KS}(r) = v_{ne}(r) + v_H[n(r)] + v_{XC}[n(r)]$, again $v_{ne}(r)$ is the nucleus-electron potential, $v_H[n(r)]$ is the Coulomb potential, and $v_{XC}[n(r)]$ is the exchange-correlation potential.

One fundamental difference between KS-DFT and other methods like Hartree-Fock is that the exchange-correlation potential is calculated using functionals. A function takes in a value, and creates another value. For example, the nucleus-electron potential will tell you what the potential energy between the electron and nucleus, when the electron is at the position of r . A functional is similar, except that it tells you what function you will get from another function, e.g., an exchange-correlation functional takes in the density function, and tells you what the exchange-correlation potential function is. In theory, KS-DFT can be an exact method if one can determine the exact exchange-correlation potential, but in practice, approximations are used since we do not know the exact functional.

Most approaches for solving the electronic structure of the ground state use self-consistent field methods (SCF). In SCF, first the electronic density is used to construct the potential field. The

potential field is then added to the Hamiltonian, which is diagonalized to create the wavefunctions. Finally, the wavefunctions are used to construct a new electronic density, and then this process repeats until the potential field is converges. In this scheme, the most expensive step is often the diagonalization of the Hamiltonian to create the wavefunctions, where the number of operations required to complete this step scales as $O(N^3)$. The cost of diagonalizing the Hamiltonian can make solving of the electronic structure difficult for large number of electrons. In this dissertation, four different studies are presented, each with the intent of cost reduction of specific calculations. These studies are ordered by the date they were, or will be, published.

Chapter 1 is a paper that describes the direct delocalization method for calculating the electronic transfer rate. The organic solar cells industry is growing, and currently there is a need for a method of producing cheap and efficient solar cells. There has been great interest in organic photovoltaic devices (OPV). Most OPVs use fullerene derivative acceptors, like phenyl-C₆₁-butyric acid methyl ester (PCBM). One of the challenges of designing efficient solar cells is producing a bulk heterojunction (BHJ), which has morphology that aids the electron transfer. In essence,

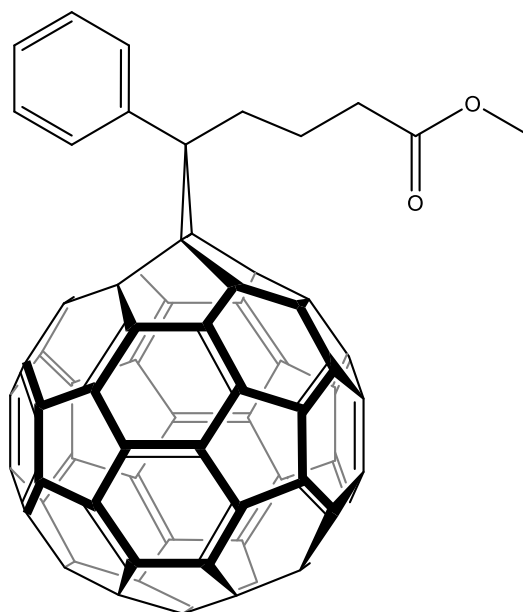


Figure 0.1. Structure of phenyl-C₆₁-butyric acid methyl ester (PCBM)

the problem can be reduced to two main factors. First is how close the exciton (excited electron-hole pair) is to the acceptor-donor interface. Typically the exciton has to be within 9 nm of the acceptor-donor interface to efficiently transfer to electron before it undergoes (electron-hole) recombination. The other factor is the mobility of the electron, i.e., how freely it can move to the

accepter-donor interface. Having a good electron transfer rate is essential for improving the efficiency of the OPV. Quantum chemistry provides valuable insight on these processes and can aid in the creation of more efficient acceptor/donors, for example through the calculation of the electron transfer rate. The electron transfer rate calculations narrow down the class of molecules will aid in the transport of the exciton. The faster the transfer rate, the greater the chance the electron will be transported to and from the acceptor-donor interface before recombination occurs. This helps in determining why certain molecules perform better than others.

One common method for calculating the electron transfer rate is by the Marcus formula:

$$k_{MT} = \frac{2\pi}{\hbar} |J_{ij}|^2 (4\pi\lambda k_B T)^{\frac{1}{2}} \exp\left(-\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right), \quad (0.14)$$

where J_{ij} is the transfer integral of the donor and acceptor, ΔE_{ij} is the difference between the initial and final states, and λ is the reorganization energy.

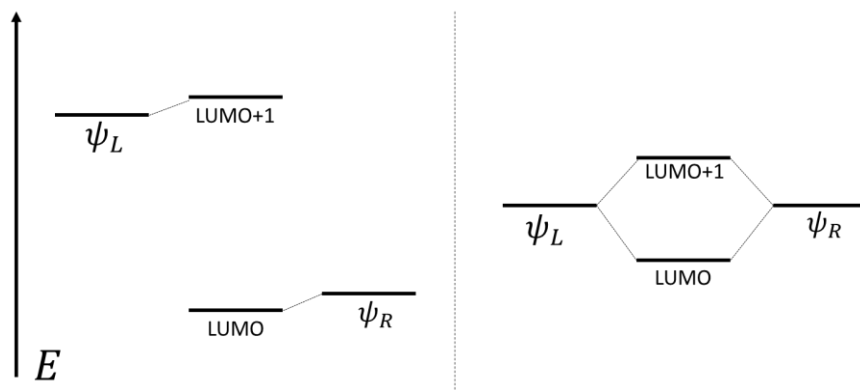


Figure 0.2. Energy level diagram a dimer with a non-symmetric environment (left), and a symmetric environment (right). The dashed lines indicate which wavefunctions are hybridize.

Consider an isolated dimer, where each molecule's LUMO, ψ_L and ψ_R for the left and right molecule respectively, can combine. Fig. 0.2 shows the resulting energy diagram for a non-

symmetric dimer (left) and a symmetric dimer (right). In the case of the non-symmetric dimer, the two orbitals will undergo slight mixing, but remain localized on each molecule. Then, when the electron gets excited to the LUMO, there is only a small chance that the electron will transfer from left to right, despite the fact that the right side has a lower energy. In the case of the symmetric dimer (Fig. 0.2 right), the LUMO is a mixture of both the left and right molecular orbitals. This means that the electron can easily move from left to right because of the delocalized LUMO and LUMO+1 states.

In nature these donor and acceptor molecules are usually surrounded, or “solvated,” by many other molecules causing even asymmetric dimers to have a locally quasi-homogeneous environment. The challenge is that for large molecules simulating the solvation can be very expensive. There are two ways to simulate solvation and balance the environments. One method is to solvate the dimer by placing other molecules around it, where the solvating molecules are represented by Mulliken point charges, self-consistently determined. Creating the environment can be, however, quite arduous, especially if the system requires a large amount of solvating molecules. The second option is to apply an electric field across the two molecules, which will delocalize the electron across both molecules. When an electric field is applied, the eigenvalues of each individual molecule are shifted because it causes the electrons to move from an area of high potential to low potential. If the electric field is adjusted correctly, the eigenvalues will be similar, mimicking the homogenous environment caused by solvation.

In Chapter 1, we propose a third method where we apply a bias directly to the Fock-Matrix using a modified Marcus theory. In this modified version of Marcus theory, the electron transfer rate is defined as:

$$k'_{MT} = \frac{2\pi}{\hbar} \sum_{ij} f(\epsilon_i - \mu_L) |J_{ij}|^2 (4\pi\lambda k_B T)^{-\frac{1}{2}} \exp\left(\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda k_B T}\right), \quad (0.15)$$

and the Fermi Dirac occupation of the donor states is defined as:

$$f(\epsilon_i - \mu_0) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu_0)}}, \quad (0.16)$$

and ϵ_i is the energy of the donor state. In practice the electron transfer rate is determined as the inverse of the Marcus theory rate:

$$\tau = \frac{1}{k_{MT}}. \quad (0.17)$$

Overall, the modified Marcus theory is straightforward; however the calculations of the rearrangement energy can be extensive. In the paper presented in Chapter 1, we instead use a range of rearrangement energies between 0.1 and 0.15 eV, close to the rearrangement energy of PCBM of 0.136 eV.

Another aspect of solving for the electron exchange rate, is the calculation of the transfer integral. This is done through the flux-operator:

$$\tilde{J} = i[\tilde{F}, \tilde{\theta}], \quad (0.18)$$

where we introduce the Fock operator $\tilde{F}$ and the left-theta operator $\tilde{\theta}$. The tilde symbol on the matrices indicates that they refer to an orthogonal basis. The orthogonal basis can be created from a non-orthogonal one using the overlap matrix S , which is used to orthogonalize the Fock and left-theta operator as:

$$\begin{aligned}\tilde{F} &= S^{-\frac{1}{2}}FS^{-\frac{1}{2}}, \\ \tilde{\theta} &= S^{-\frac{1}{2}}\theta S^{-\frac{1}{2}}.\end{aligned}\tag{0.19}$$

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

$$\begin{aligned}\theta_{ij} &= g(i)S_{ij}g(j), \\ g(i) &= \begin{cases} 1 & \text{if } i \in \text{left(donor)fragment,} \\ 0 & \text{otherwise.} \end{cases}\end{aligned}\tag{0.20}$$

The chemical potentials of the neutral (μ_0) and charged species (μ_{-1}) were determined self-consistently, such that the following conditions were met:

$$\begin{aligned}2\text{tr}[f(\tilde{F} - \mu_0)] &= \sum_{j=1}^N f(\epsilon_j - \mu_0) = N_e, \\ 2\text{tr}[f(\tilde{F} - \mu_{-1})] &= N_e + 1,\end{aligned}\tag{0.21}$$

where N represents the number of orbitals, and N_e represents the number of electrons. The factor of 2 is due to the doubly occupied orbitals of the closed shell system.

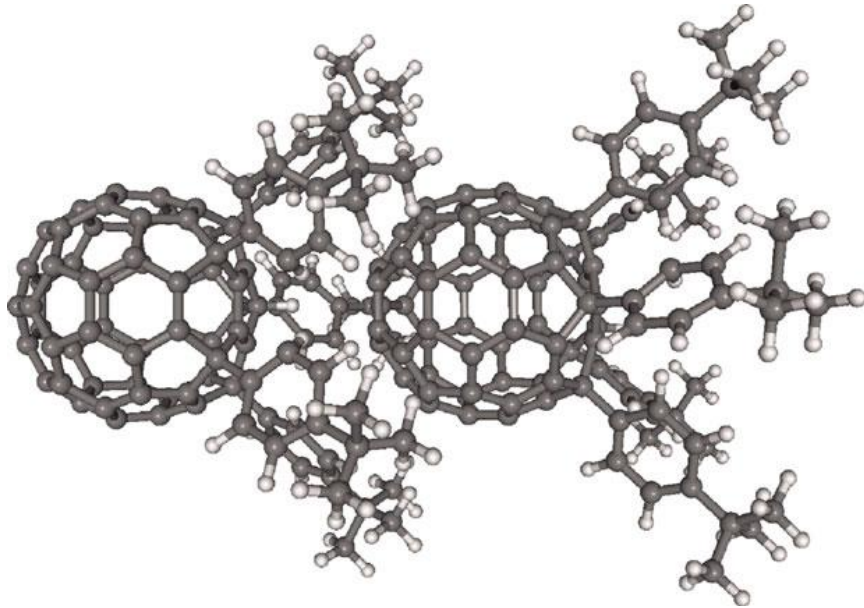


Figure 0.3. A molecular model of penta-(p-t-butylC₆H₄)-1-hydro-C₆₀ (TBP) dimer

The direct delocalization method was compared to methods where the dimer is solvated, and to application of a bias. The electron transfer rates determined from the direct delocalization method is comparable to that of the conventional methods. The conventional methods require multiple DFT simulations, whereas the direct delocalization method requires only one. The direct decocalization method can therefore be used in place of conventional methods with reasonable accuracy. Table 0.1 shows a comparison of the results for penta-(p-t-butylC₆H₄)-1-hydro-C₆₀ (TBP). A TBP dimer is shown above in Fig. 0.3.

Table 0.1. Results for the variety of methods for TBP				
Reorganization energy:		$\lambda = 0.1$ eV		$\lambda = 0.15$ eV
Dimer	Multiple-state transfer time (fs)	LUMOs transfer time(fs)	Multiple-state transfer time (fs)	LUMOs transfer time (fs)
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	1370,000

Direct delocalization helped us reduced the cost of determining the electron transfer rate by reducing the amount of simulations needed. This was done by applying the electric field directly to the Fock-matrix, instead of applying it self-consistently. Since the electric field was applied directly to the Fock-matrix, there was no need to run multiple DFT calculations.

Chapter 2 deals with the electron mobility in fullerene networks. In this paper, we analyzed multiple fullerene derivative molecules. One of the most common used acceptors is PCBM, which has a high electron transfer rate. In an attempt to improve the solar cell efficiency, four fullerene derivatives were analyzed, and the coupling coefficients where measured and simulated.

In polymer/fullerene solar cells, electron mobility locally amounts to charge transfer between neighboring fullerene acceptors. To understand how different fullerene derivatives affect the transfer rate, we developed a DFT-based protocol to calculate the electronic coupling between pairs of fullerene molecule in a variety of geometries. The electron transfer of a left molecule (L) and the right molecule (R) is:



The fundamental quantity of interest is the coupling constant γ between the L and R molecules. The coupling constant for these two molecules is defined as:

$$\gamma(L \rightarrow R) = |\langle \psi_L | \hat{H} | \psi_R \rangle|, \quad (0.23)$$

where $\hat{H}$ is the total Hamiltonian and ψ_i is the localized wavefunction of the transferred electron on each molecule (i.e., the LUMO of the neutral molecule). The Hamiltonian and the wavefunctions are calculated by DFT, with the B3LYP functional and an STO-3G basis set. Direct calculations of γ are problematic because when two molecules form a dimer, they can experience two different environments. One method we used to create symmetry among the environment was to apply an electric field to the system (Fig. 0.4).

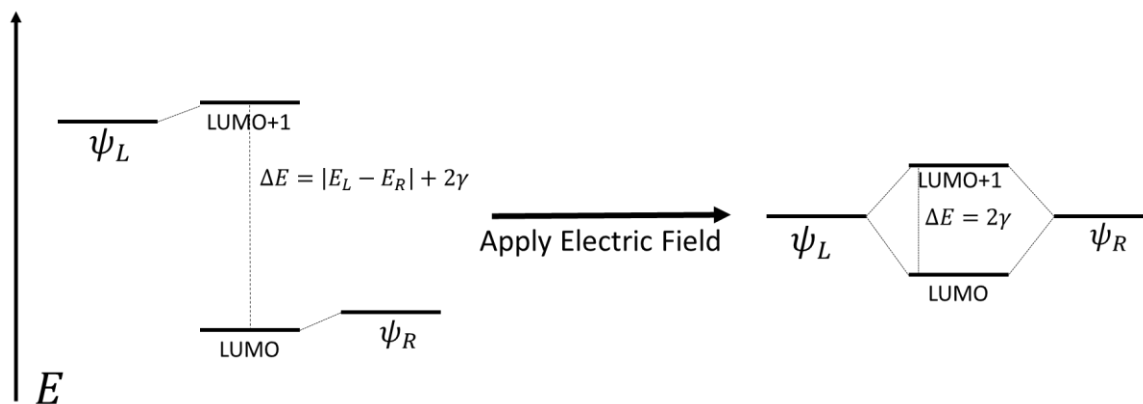


Figure 0.4. Energy diagram showing the effect that the electric field will have on the system. The electric field was altered until the LUMO and LUMO+1 energy gap was minimized. This value was determined as the coupling constant. Another method is adding solvating molecules, which are point charges with values that were determined self-consistently as the Mulliken charges around the dimer. Then an electric field was applied to this system, and the LUMO and LUMO+1 energy gap was minimized to find the coupling constant. These two methods were compared to each other in order to verify that they gave similar results.

In this study, we determined the coupling constant for PCBM, 6,9,12,15,18-pentakis(4-tert-butylphenyl)-1-hydro[60]fullerene (4-tBu), and 6,9,12,15,18-pentakis(4-methylphenyl)-1-hydro[60]fullerene (4-Me) dimers in different configurations (Fig. 0.5).

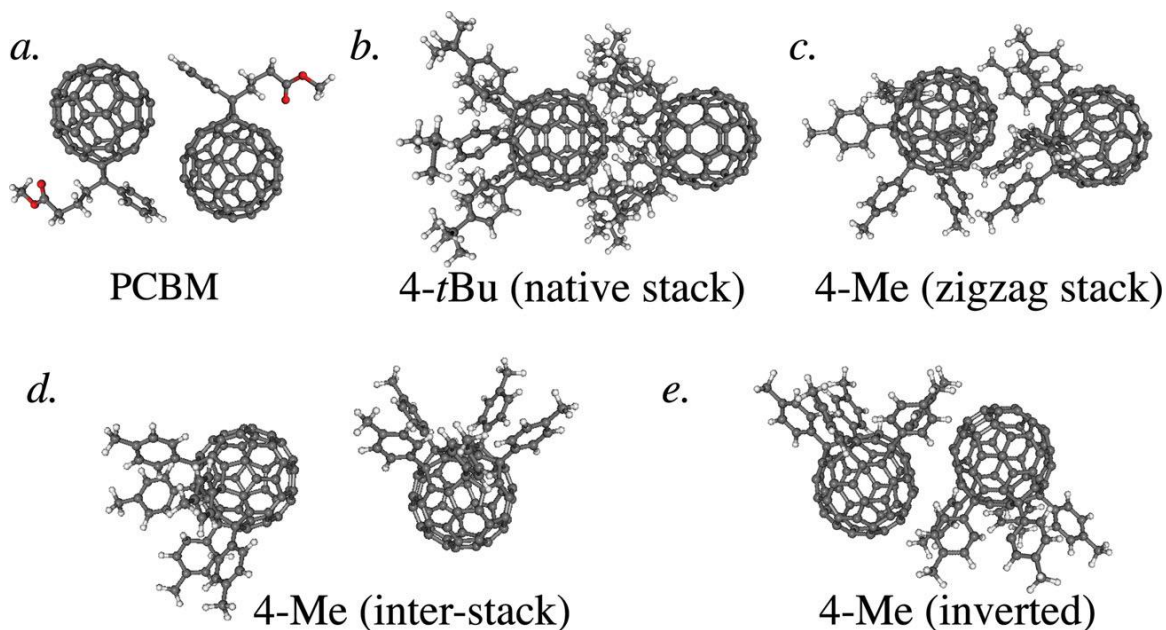


Figure 0.5. The structures of the fullerene derivatives' dimers in different configurations. The coupling constants for the systems shown here are given in Table 0.2. The coupling constants determined for both methods were shown to be the similar. Therefore we could just apply an electric field to the system itself, without having to worry about solvating the dimer. This reduces the time of running such calculations because we avoid solving for the Mulliken charges. However, such calculations are still arduous, requiring multiple simulations. For further information on the study, see Chapter 2.

Chapters 3 and 4 are two studies implementing stochastic density functional theory (sDFT) and time-dependent stochastic density function theory (TDsDFT) for very large systems with thousands of electrons. In sDFT and TDsDFT, the Kohn-Sham orbitals (KS orbitals) are replaced with purified stochastic orbitals (sP orbitals), which eliminate the need to solve for eigenstates of large matrices. The stochastic method can be implemented at a lower cost, and is easily run using parallel processing. Since this method is used in both Chapters 3 and 4, the next paragraphs overview the stochastic paradigm for DFT and TDDFT.

KS-DFT is a common method used to calculate the ground state electronic structure and energy. One challenge in KS-DFT is that the number of operations scales as $O(N^3)$. This is because in

order to solve for the density function, one must first diagonalize the Kohn-Sham Hamiltonian to get the KS orbitals. This makes the application of KS-DFT to large systems problematic. sDFT solves this problem by eliminating the need to solve for the KS-orbitals. This is achieved by replacing the Kohn-Sham orbitals with purified stochastic orbitals:

$$\xi_\mu(r) = \langle r | \sqrt{\hat{\theta}_\beta(\mu - \hat{H})} | \zeta \rangle, \quad (0.24)$$

where μ represents the chemical potential of the system, $\beta = 1/T$ represents the inverse temperature such that $E_g\beta \gg 1$, in which E_g represents the energy bandgap, and $\theta_\beta(E) = (1/2)\text{erfc}(-E)$ is a smooth Heaviside function, which projects the stochastic orbital $\zeta(r)$ onto the occupied space. In sDFT, the density function is defined as:

$$n_\mu(r) \approx 2 \left\langle |\xi_\mu(r)|^2 \right\rangle_\zeta, \quad (0.25)$$

where $\langle \dots \rangle_\zeta$ represents a statistical average of N_ζ stochastic orbitals. The two is included because we use a closed shell system, in which each occupied orbital contains two electrons. The stochastic orbital is defined as

$$\zeta(r) = e^{i\phi(r)}, \quad (0.26)$$

where $\phi(r)$ represents a uniform random phase, with the range of $[0, 2\pi]$. The purified stochastic orbitals are then solved as:

$$\xi_\mu(r) = \sum_i^{N_c} \rho_i(\mu) \zeta_i(r), \quad (0.27)$$

where $\rho_i(\mu)$ is the Chebyshev expansion coefficient which corresponds to μ , $\hat{H}^N = (\hat{H} - \bar{H})/\Delta H$ is the normalized Hamiltonian, and $\zeta_0(r) = \zeta(r)$, $\zeta_1(r) = \hat{H}^N \zeta_0(r)$, and $\zeta_i(r) = 2\hat{H}^N \zeta_{i-1}(r) - \zeta_{i-2}(r)$. Finally, the average energy is defined as $\bar{H}$, and the energy spectral range is defined as ΔH .

The chemical potential of the system is determined as:

$$N_e = \int dr n_\mu(r), \quad (0.28)$$

where μ is adjusted until the integral of $n_\mu(r)$ gives us the correct number of electrons for the system. In Chapter 4, we use sDFT to calculate the Kohn-Sham potential, defined as before as:

$$v_{KS}(r) = v_{ne}(r) + v_{HXC}[n(r)]. \quad (0.29)$$

The total energy is calculated as:

$$E = 2\langle \xi_\mu(r) | \hat{T} | \xi_\mu(r) \rangle_\zeta + \int v_{KS}(r) n_\mu(r) dr. \quad (0.30)$$

The general procedure of applying sDFT is:

- (i) Compute the KS potential for the density.
- (ii) Generate stochastic orbitals, in a grid (or plane wave) using Eq. 0.26, then project the stochastic orbitals to the occupied space using Eq. 0.27, through the Chebyshev polynomial.
- (iii) Determine $n_\mu(r)$ from Eq. 0.25 for several values of μ . Linearly extrapolate μ to find the correct chemical potential using Eq. 0.28.
- (iv) Reiterate until the chemical potential converges.

It is important to use the same set of stochastic orbitals throughout the self-consistent procedure. This method is exact for an infinite number of stochastic orbitals, but in practice we used a limited number of stochastic orbitals.

Time-dependent density functional theory (TDDFT) is a powerful method that is often used to calculate cross-sectional absorption as well as correlation energy corrections to DFT. In TDDFT, the closed-shell time-dependent electronic density function is defined as:

$$n(r, t) = 2 \sum_i |\psi_i(r, t)|^2, \quad (0.31)$$

where $\psi_i(r, t)$ are the time-dependent KS orbitals which follow the time-dependent Schrodinger equation:

$$i \frac{\partial}{\partial t} \psi_i(r, t) = \hat{H} \psi_i(r, t), \quad (0.32)$$

where $\hat{H}$ is a time-dependent Hamiltonian, defined as:

$$\hat{H} = \hat{T} + v_{ne}(r) + v_{HXC}[n(r, t)]. \quad (0.33)$$

The electron-electron potential $v_{HXC} = v_H + v_{XC}$ is solved for in the same way as DFT, and the potential is calculated at each time-step from the instantaneous electron density. The orbitals are propagated as:

$$\psi_i(r, t) = e^{-i\hat{H}t} \psi(r, t = 0). \quad (0.34)$$

In practice, each orbital is propagated by multiple small time steps. Each orbital could require thousands of time steps in order to reach the desired time scale. Thus systems containing thousands of electrons would require millions of propagations steps. Time-dependent stochastic density functional theory (TDsDFT) addresses this problem.

Using a given initial Kohn Sham potential $v_{KS}(r)$, the electronic structure of a system at its ground state is calculated first from Eq. 0.29. Each purified stochastic orbital, ξ_μ , is then the starting point for a time dependent stochastic orbital:

$$-i\hbar \frac{\partial}{\partial t} |\eta_\mu(t)\rangle = \hat{h}_{KS} |\eta_\mu(t)\rangle, \quad (0.35)$$

where

$$\hat{h}_{KS} = \hat{T} + v_{KS}(r) + v_{HXC}[n(r, t)] - v_{HXC}[n(r, t = 0)], \quad (0.36)$$

and $|\eta_\mu(t = 0)\rangle = \exp(-i\gamma\hat{v}/\hbar)|\xi_\mu\rangle$, and $\hat{v}$ is here the initial disturbance discussed below. The electronic density function is calculated as:

$$n(r, t) = 2 \left\langle |\eta_\mu(r, t)|^2 \right\rangle. \quad (0.37)$$

The number of pS orbitals required to solve for TDsDFT can be less than the number of occupied orbitals in TDDFT, because as the the number of electrons in a system rises, the number of pS orbitals required to get accurate results decreases due to self-averaging. For example, a system containing 3000 electrons will require the propagation of 1500 orbitals for a closed shell system. This system can be solved using TDsDFT with only ~ 200 -500 pS orbitals. This means that we can reduce the number of times we propagate the orbitals. This leads to a sub-linear cost for TDsDFT.

The general TDsDFT scheme is

- (i) Starting from an initial Kohn-Sham potential $v_{KS}(r)$, create N_ζ stochastic orbitals using Eq. 0.26 to form $\zeta(r)$, then project $\zeta(r)$ onto the occupation space using Eq. 0.27 to get $\xi(r)$.
- (ii) Solve for $n(r, t)$ using Eq. 0.37
- (iii) Solve for $\hat{h}_{KS}(t)$ using Eq. 0.36
- (iv) Propagate the stochastic orbitals using Eq. 0.35
- (v) Repeat ii to iv until the desired time has been reached.

The absorption spectrum is solved as

$$\sigma(\omega) = \frac{e^2}{3\epsilon_0 c} \omega \operatorname{Im} \int dr dr' r \cdot \tilde{\chi}(r, r', \omega) \cdot r', \quad (0.38)$$

where ω is the angular frequency of the absorbed photon, and $\tilde{\chi}(r, r', \omega)$ is the density susceptibility function which is determined using TDDFT. Specifically, the linear density response ($\delta n(r, t)$) to a small external time-dependent potential perturbation ($v(r', t')$) is described by the integral:

$$\delta n(r, t) = \int_0^t dt' \int dr' \chi(r, r', t - t') \delta v(r', t'), \quad (0.39)$$

where the susceptibility function is as:

$$\chi(r, r', t) = (i\hbar)^{-1} \theta(t) \langle 0 | [\hat{n}(r, t), \hat{n}(r', 0)] | 0 \rangle, \quad (0.40)$$

$\hat{n}(r, t)$ is the density operator at position r and time t , and $\theta(t)$ equals to 1 when $t \geq 0$, and 0 otherwise.

Rather than computing $\chi(r, r', t)$ directly, which will be time consuming for large systems, a more practical method to solve for $\delta n(r, t)$ using a sudden perturbation, i.e. $\delta v(r', t') = \gamma v(r') \delta(t')$:

$$\delta n(r, t) = \gamma \int dr' \chi(r, r', t) v(r'). \quad (0.41)$$

The linear density response is therefore computed by applying a perturbation $e^{-i\gamma\hat{v}/\hbar}$ and propagating the perturbed ground state

$$\delta n(r, t) = \langle 0 | e^{i\gamma\hat{v}/\hbar} n(r, t) e^{-i\gamma\hat{v}/\hbar} | 0 \rangle - n_0(r), \quad (0.42)$$

where $\hat{v} = \int v(r') \hat{n}(r') dr'$. In order to obtain $\delta n(r, t)$, one must solve the many-electron time dependent Schrödinger equation, which can be difficult. Starting from the KS system of non-

interacting electrons having the ground-state density $n_0(r) = 2 \sum_{j \in occ} |\phi_j(r)|^2$, one perturbs the KS eigenstates $\phi_j(r)$ at $t = 0$:

$$\psi_j(r, t = 0) = e^{-i\gamma v(r)/\hbar} \phi_j(r), \quad (0.43)$$

and then propagates in time according to the TDKS equations

$$i\hbar \frac{\partial \psi_j(r, t)}{\partial t} = \hat{h}(t) \psi_j(r, t), \quad (0.44)$$

where $\hat{h}(t)$ depends on the propagated density function $n_\gamma(r, t) = \sum_{j \in occ} |\psi_j(r, t)|^2$. The density response is obtained from:

$$\int dr' \chi(r, r', t) v(r') = \frac{1}{\gamma} (n_\gamma(r, t) - n_{\gamma=0}(r, t)) \equiv \Delta n(r, t). \quad (0.45)$$

These equations state that the integral of the susceptibility and the potential $v(r)$ can be computed from the difference between the perturbed and unperturbed density functions. This relationship holds true for the Fourier transform of Eq. 0.45. ($\tilde{f}(\omega) = \int_0^\infty dt e^{i\omega t} f(t)$):

$$\int dr' \tilde{\chi}(r, r', \omega) v(r') = \frac{1}{\gamma} (\tilde{n}_\gamma(r, \omega) - \tilde{n}_{\gamma=0}(r, \omega)) = \Delta \tilde{n}(r, \omega). \quad (0.46)$$

This is easily solved using TDDFT. Expanding r' in the full equation of $\sigma(\omega)$

$$\sigma(\omega) = \frac{e^2}{3\epsilon_0 c} \omega \int dr r \cdot [\Delta \tilde{n}_x(r, \omega) + \Delta \tilde{n}_y(r, \omega) + \Delta \tilde{n}_z(r, \omega)], \quad (0.47)$$

where the subscript of $\Delta n_x(r, \omega)$, $\Delta n_y(r, \omega)$, and $\Delta n_z(r, \omega)$ signifies the type of perturbation used for the density response function. Finally

$$\sigma(\omega) = \frac{e^2}{3\epsilon_0 c} \omega [\tilde{d}_{xx}(\omega) + \tilde{d}_{yy}(\omega) + \tilde{d}_{zz}(\omega)], \quad (0.48)$$

where $\tilde{d}_{xx}(\omega)$, $\tilde{d}_{yy}(\omega)$, and $\tilde{d}_{zz}(\omega)$ are the Fourier transform of the dipole response function defined as:

$$\begin{aligned}
d_{xx}(t) &= \int x \Delta n_x(r, t) dr, \\
d_{yy}(t) &= \int y \Delta n_y(r, t) dr, \\
d_{zz}(t) &= \int z \Delta n_z(r, t) dr.
\end{aligned} \tag{0.49}$$

This leads us to the cross sectional absorption being:

$$\sigma(\omega) = \sigma_x(\omega) + \sigma_y(\omega) + \sigma_z(\omega), \tag{0.50}$$

where $\sigma_x(\omega)$, $\sigma_y(\omega)$, and $\sigma_z(\omega)$ is the absorption contribution of x, y, and z polarized light, defined as:

$$\begin{aligned}
\sigma_x(\omega) &= \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \tilde{d}_{xx}(\omega), \\
\sigma_y(\omega) &= \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \tilde{d}_{yy}(\omega), \\
\sigma_z(\omega) &= \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \tilde{d}_{zz}(\omega).
\end{aligned} \tag{0.51}$$

These equations are the dipole response functions. Depending on the symmetry of the system, it is possible to reduce the number of TDsDFT propagations..

Chapter 3 discusses the implementation of TDsDFT to calculate the absorption cross section of 9-(4-mercaptophenylethynyl)anthracene (MPEA) (Fig. 0.6) chemisorbed onto an Au{111} surface. This study focuses on the effect that the Au{111} surface has on the absorption cross section of the organic molecule. The calculation simulates an experiment employing Scanning Tunneling Microscopy (STM), a powerful technique that has nanoscale resolution.

STM works through the tunneling of an electron from a metallic surface to the STM tip, or vice versa. In STM, an electric field is applied, and the current caused by the tunneling electron is measured. From the measured current, STM creates an image of the topography of a surface.

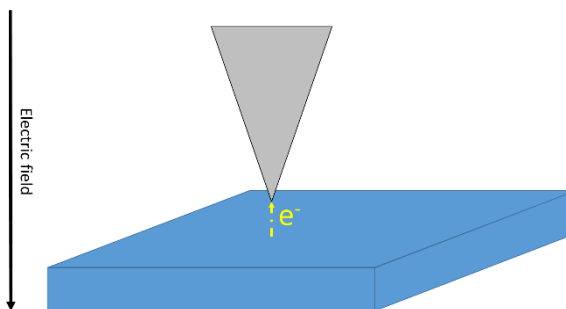


Figure 0.6. Schematic of the setup of a STM

One possible application for STM is the detection of defects on a surface that has been coated with a substrate, usually a self-assembled monolayer. If there is a defect, there is a change in the current in the local area of the defect. This change in current could be difficult to detect if it is too small. MPEA can be introduced to the surface and will chemisorb to the surface of these defects, offering a way to detect them. This can then be measured by using laser-assisted STM (ls-STM). The laser is used to photo-excite an electron in MPEA into an excited state, which will then readily tunnel into the STM tip. One of the challenges is determine the wavelength that corresponds to the HOMO-LUMO energy gap of MPEA, because one has to take into account the environment that MPEA is in.

One challenge is that the HOMO-LUMO bandgap of MPEA is affected by the gold surface. The effect of the gold surface can be gauged by measuring the spectrum of an isolated MPEA vs. the chemisorbed MPEA. There are two difficulties in this prescription. Determining the spectra of an isolated MPEA is difficult because MPEA will have to be in low enough concentrations such that the interaction with other MPEAs is negligible. Further, the absorption of the chemisorbed MPEA is tiny compare to that of the gold surface, and could be difficult to detect. One way to determine the effect of the gold surface on the HOMO-LUMO energy gap of MPEA is to use DFT to calculate the bandgap of isolated and chemisorbed MPEA. But using DFT to determine the effect of the

gold surface is difficult because the movement of the electrons affects this energy bandgap. A better approach is to use TDDFT to calculate the spectrum.

In Chapter 3, we calculate the spectra of an isolated MPEA, an isolated MPEA where the hydrogen bonded to the sulfur was removed (dubbed tMPEA), MPEA which is chemisorbed (cMPEA) onto an Au{111} surface, and a bare gold surface (BAuS). Fig. 0.7 shows MPEA, tMPEA, and cMPEA/AuS.

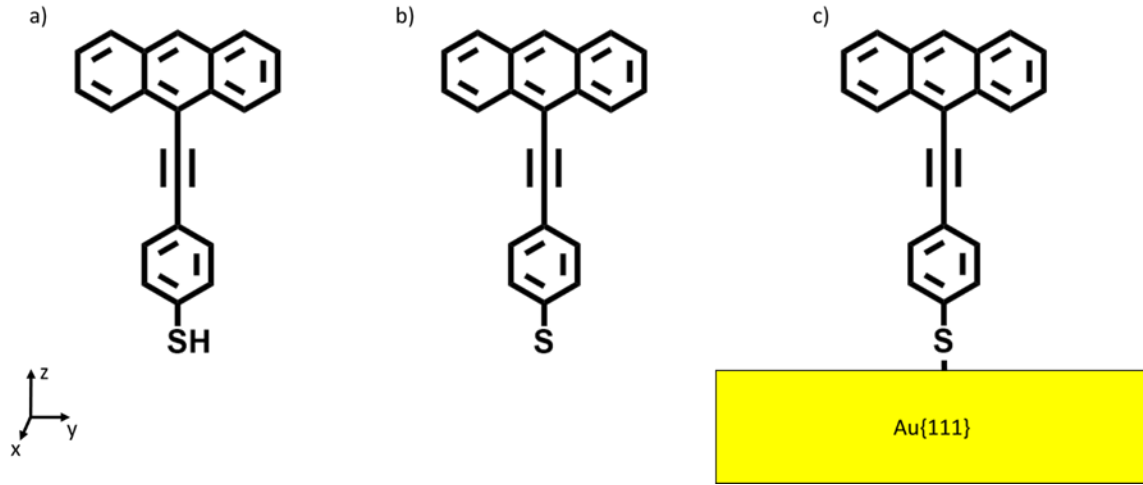


Figure 0.7. Schematic of a) MPEA, b) tMPEA, and c) cMPEA/AuS. The arrows represents the x, y and z axis. MPEA is aligned to the YZ plane.

One of the outcomes of this research is the development a way to extract the spectrum of cMPEA. Instead of measuring the dipole response of the entire system, we select a region of space where we sample the dipole response using a selective integration. This leads to a selective dipole response $d^s(t)$, defined as:

$$d_{xx}^s(t) = \int dr \, x \, S(r) \, \Delta n_x(r, t), \quad (0.52)$$

where $d_{yy}^s(t)$, and $d_{zz}^s(t)$ are determined similarly. $S(r)$, dubbed the selective space function, is defined as

$$S(r) = \begin{cases} 1 & \text{when } r \text{ is within the sample space,} \\ 0 & \text{everywhere else.} \end{cases} \quad (0.53)$$

This allows us to measure the spectra of that area as the imaginary dipole response

$$\sigma^S(\omega) = \sigma_x^S(\omega) + \sigma_y^S(\omega) + \sigma_z^S(\omega), \quad (0.54)$$

where the dipole response is replaced with the selective dipole response. Fig. 0.8 shows the results of this study. The anthracene portion contributes most of the absorption of the system. For further details, see Chapters 3.

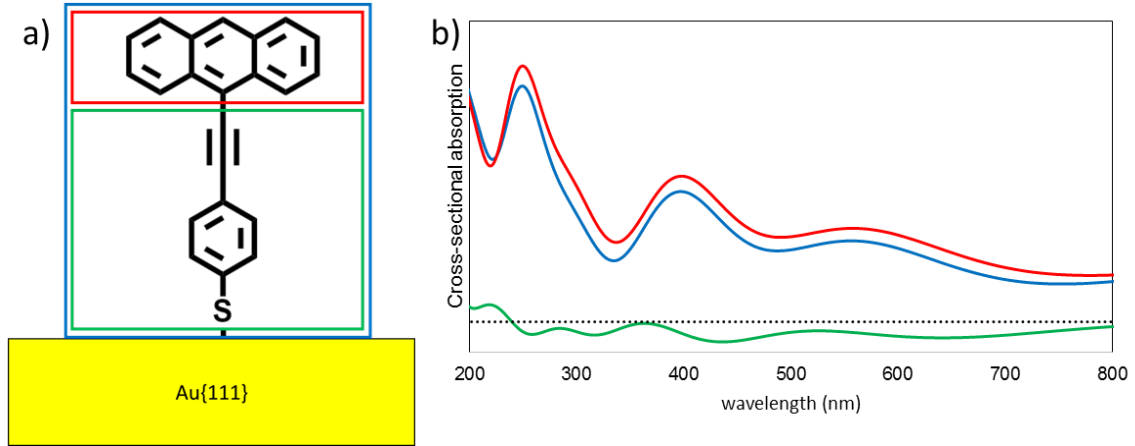


Figure 0.8. a) Area relevant for the b) the spectra. Blue is the spectrum determined for the full cMPEA, red is the spectrum of the top portion of cMPEA, and green is the spectrum of the bottom part.

In Chapter 4, we discuss the TDsDFT simulations of octahedral gold nanoclusters. Fig. 0.9 shows an octahedral shaped gold nanocluster (Au_{670}), which is the biggest gold nanocluster that was studied. This particular system is very challenging, as it contains over 7000 electrons. Such calculations would be expensive using KS-DFT and TDDFT. Instead we first use sDFT to determine the Kohn-Sham potential of octahedral Au_{344} and Au_{670} . Then the spectra was determined using TDsDFT.

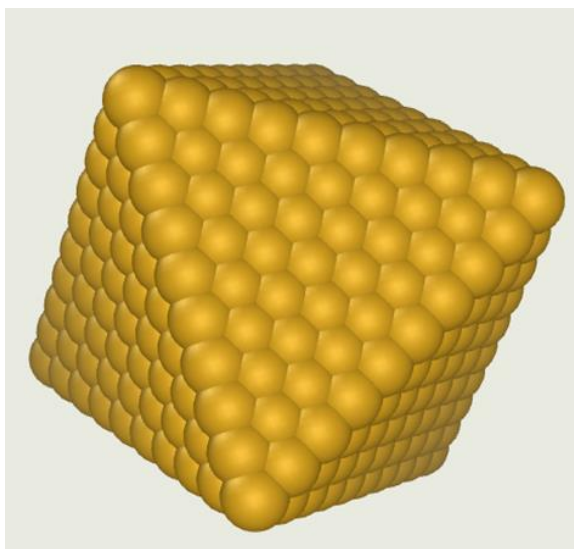


Figure 0.9. Image of octahedral Au_{670} .

Due to symmetry of the system, the entire absorption cross section is:

$$\sigma(\omega) = 3\sigma_x(\omega). \quad (0.55)$$

Fig. 0.10 shows show a comparison of the spectra of Au_{44} using DFT/TDDFT and DFT/TDsDFT. As the number of stochastic orbitals grows, the absorption cross-section approaches that calculated using DFT/TDDFT.

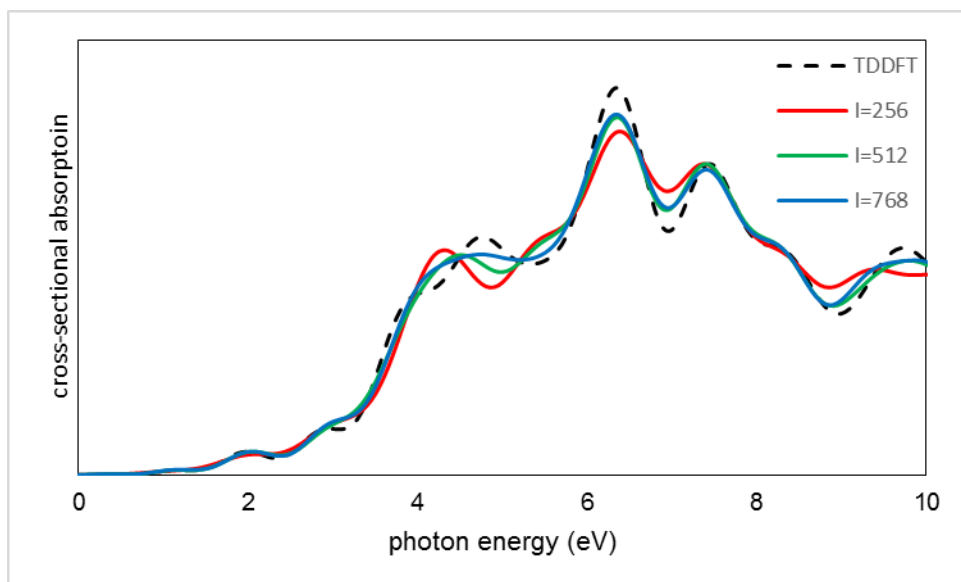


Figure 0.10. Comparison of the absorption cross section for Au_{44} using TDDFT and TDsDFT. The Kohn-Sham potential was calculated using TDDFT (dashed black line), and using TDsDFT with 256 (red), 512 (green) and 768 (blue) stochastic orbitals.

In previous studies, both sDFT and TDsDFT have been shown to be more accurate and require relatively less resources for larger systems, and our study demonstrates and uses this fact to tackle giant systems. For more details, see Chapter 4.

Chapter 1

Direct Delocalization for Calculating Electron

Transfer in Fullerenes

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 non-centrosymmetric 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. Since large molecule 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.

1.1 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, i.e., 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 fullerenes 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.⁶ 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 Figure 1.1). 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 paper is as follows. We present a more detailed description of the methodology in Section II; results follow in Section III, and discussion in Section IV.

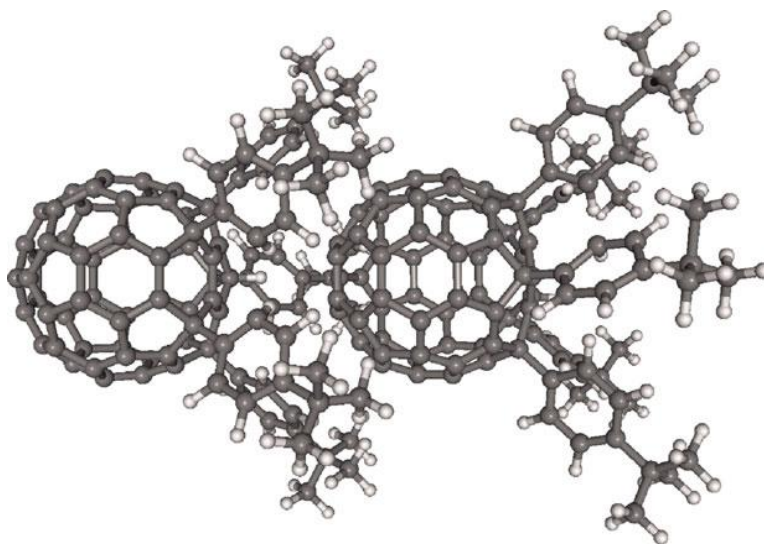


Figure 1.1. TBP dimer. Note the “cap” on the left molecule is exposed, whereas the cap on right molecule is solvated by the adducts of its neighbor

1.2 Methodology

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

$$k_{MT} = \frac{2\pi}{\hbar} |J_{ij}|^2 (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda\kappa_B T}\right), \quad (1.1)$$

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. Further, 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,⁷ whereby we sum over all initial states to calculate the total electron transfer rate:

$$k'_{MT} = \frac{2\pi}{\hbar} \sum_{ij} f(\epsilon_i - \mu_L) |J_{ij}|^2 (4\pi\lambda\kappa_B T)^{-\frac{1}{2}} \exp\left(\frac{(\Delta E_{ij} + \lambda)^2}{4\lambda\kappa_B T}\right), \quad (1.2)$$

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

$$f(\epsilon_i - \mu_0) = \frac{1}{1 + e^{\beta(\epsilon_i - \mu_0)}}, \quad (1.3)$$

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

$$\tau = \frac{1}{k'_{MT}}. \quad (1.4)$$

For the most part, Eq. (1.2) 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 many low lying states, so to simplify we calculate the transfer rates for a range of values. According to MacKenzie et al,⁸ the rearrangement energy for electron transfer in C₆₁H₂, i.e. 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 0.1 eV 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 (see Ref. 8, for example).

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

$$\tilde{J} = i[\tilde{F}, \tilde{\theta}], \quad (1.5)$$

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 non-orthogonal basis using DFT, which has been shown to give good accuracy within the Marcus framework.⁹⁻¹⁴ The NWChem software package was used for calculations.¹⁵ The matrices were calculated using the B3LYP functional and STO-3G basis set for neutral and anionic systems. Results for both neutral and anionic system 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:

$$\begin{aligned} \tilde{F} &= S^{-\frac{1}{2}} F S^{-\frac{1}{2}}, \\ \tilde{\theta} &= S^{-\frac{1}{2}} \theta S^{-\frac{1}{2}}, \end{aligned} \quad (1.6)$$

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

$$\theta_{ij} = g(i) S_{ij} g(j), \quad (1.7)$$

where

$$g(i) = \begin{cases} 1 & \text{if } i \in \text{left(donor) fragments} \\ 0 & \text{otherwise} \end{cases} \quad (1.8)$$

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:

$$2Tr[f(\tilde{F} - \mu_0)] = \sum_{j=1}^{N_o} f(\epsilon_j - \mu_0) = N, \quad (1.9)$$

$$2Tr[f(\tilde{F} - \mu_{-1})] = N + 1,$$

where N is the number of electrons in the neutral system, N_o is the number of orbitals and f is now a Fermi-Dirac operator:

$$f(\tilde{F} - \mu_0) = \frac{1}{1 + e^{\beta(\tilde{F} - \mu_0)}}. \quad (1.10)$$

The factor 2 in Eq. (1.9) above is due to spin.

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

$$\tilde{F} \rightarrow \tilde{F} + w\tilde{\theta}, \quad (1.11)$$

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:

$$\tilde{\theta}^E = V^T \tilde{\theta} V, \quad (1.12)$$

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

$$J_{ij} = (\epsilon_i - \epsilon_j) \tilde{\theta}_{ij}^E, \quad (1.13)$$

The transfer integral is then used to calculate the extended Marcus-theory rate, Eq. (1.2), summing over all initial states.

1.3 Results

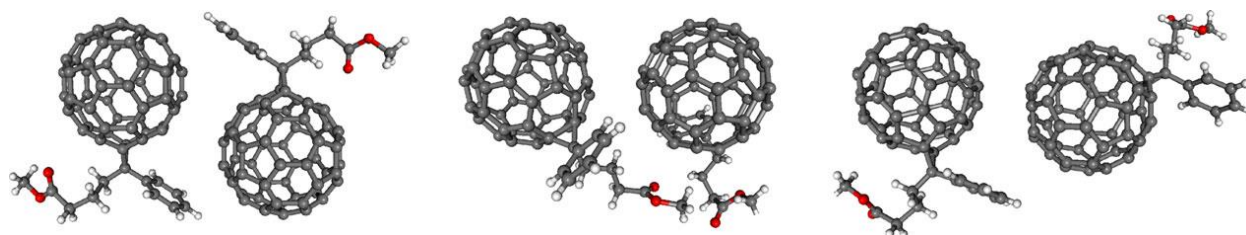


Figure 1.2. The three PCBM orientations studied in this article, denoted in the results section PCBM-1, PCBM-2, and PCBM-3.

We have studied several molecules, as follows: PCBM (Fig. 2), penta-(p-t-butylC₆H₄)-1-hydro-C₆₀ (denoted TBP) (Fig. 1.1), and pentamethyl-monohydro-C₆₀ (denoted C₆₀Me₅H) (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 C₆₀Me₅H 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 heterojunction solar cells.

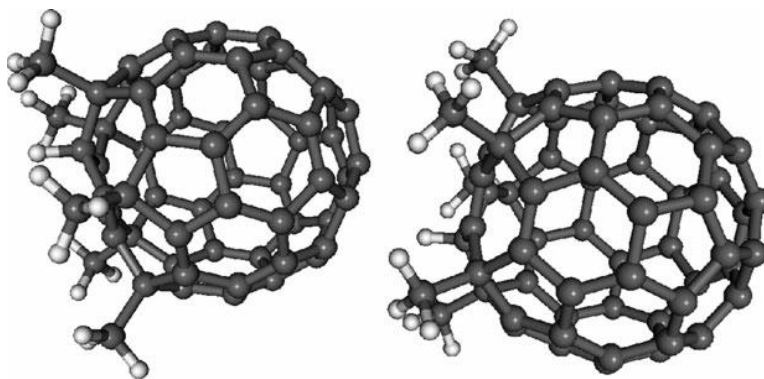


Figure 1.3. C₆₀Me₅H dimer.

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 $i, j = \text{LUMO}, \text{LUMO}+1$ (and vice versa) in the sum in Eq. (1.2). The results for the transfer time, τ , with the present formalism for the alignment potential w (i.e. satisfying Eq.(1.9)) are shown in Table 1.1. 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. (1.2) and (1.1), respectively.

Table 1.1. 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 ₅ H	24,200	38,800	43,200	60,500

Table 1.2 presents the electron transfer times for PCBM where we calculated the Fock using several methods: neutral system 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 shows similar results for the three methods, and in the interest of computational time, have shown results for neutral systems throughout.

Table 1.2. Comparison of transfer times with neutral and anionic systems in PCBM.				
Reorganization energy:	$\lambda = 0.1$ eV		$\lambda = 0.1$ eV	
	Multiple-State transfer time (fs)	LUMOs transfer time (fs)	Multiple-state Transfer time (fs)	LUMOs transfer time (fs)
B3LYP neutral	335	531	527	950
PBE neutral	370	747	595	1300
PBE anionic	433	1100	680	2000

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 Fig. 1.2, 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. 1.4), 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 eV 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 eV and 0.10 eV above the LUMO. This energy difference results in a much more substantial contribution from the LUMO+2.

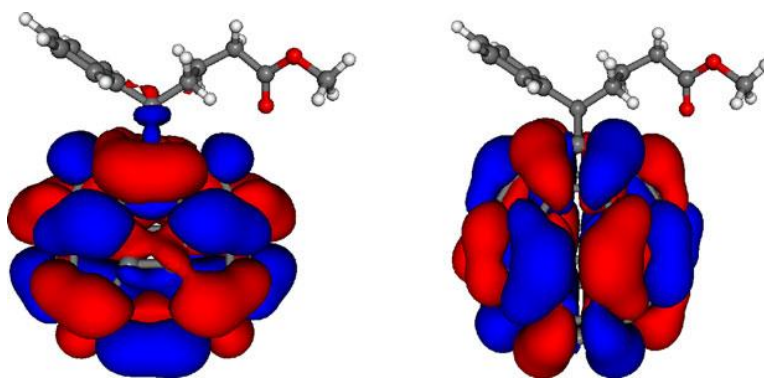


Figure 1.4. Frontier orbitals of PCBM. The LUMO is shown on the left, and LUMO+1 on the right.

The results for the variety of methods for TBP is shown in Table 1.3. Comparing the three methods, we note that the total 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, i.e., the LUMO,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.

Table 1.3. 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	1370,000

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 that 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 133000 fs and 210000 fs for reorganization energies of 0.1 eV and 0.15 eV,

respectively. This is in good agreement with our direct delocalization times of the unsolvated dimer.

1.4 Conclusions

We present a simple method to efficiently calculate electron transfer rates between molecular dimers. The method handles 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 (PCE) versus 1.5% for TBP. 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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Chapter 2

Understanding Local and Macroscopic Electron Mobilities in the Fullerene Network of Conjugated Polymer-based Solar Cells: Time-Resolved Microwave Conductivity and Theory

The efficiency of bulk heterojunction (BHJ) organic photovoltaics is sensitive to the morphology of the fullerene network that transports electrons through the device. This sensitivity makes it difficult to distinguish the contrasting roles of local electron mobility (how easily electrons can transfer between neighboring fullerene molecules) and macroscopic electron mobility (how well-connected is the fullerene network on device length scales) in solar cell performance. In this work, a combination of density functional theory (DFT) calculations, flash-photolysis time-resolved microwave conductivity (TRMC) experiments, and space-charge-limit current (SCLC) mobility estimates are used to examine the roles of local and macroscopic electron mobility in conjugated polymer/fullerene BHJ photovoltaics. The local mobility of different pentaaryl fullerene derivatives (so-called 'shuttlecock' molecules) is similar, so that differences in solar cell efficiency and SCLC mobilities result directly from the different propensities of these molecules to self-assemble on macroscopic length scales. These experiments and calculations also demonstrate that the local mobility of phenyl-C₆₀ butyl methyl ester (PCBM) is an order of magnitude higher than that of other fullerene derivatives, explaining why PCBM has been the acceptor of choice for conjugated polymer BHJ devices even though it does not form an optimal macroscopic network. The DFT calculations indicate that PCBM's superior local mobility comes from the near-spherical nature of its molecular orbitals, which allow strong electronic coupling between adjacent molecules. In combination, DFT and TRMC techniques provide a tool for screening new fullerene

derivatives for good local mobility when designing new molecules that can improve on the macroscopic electron mobility offered by PCBM.

2.1 Introduction

There are a number of factors that can limit the power conversion efficiency (PCE) of organic photovoltaics, including the efficiency of exciton generation and separation,^[1-4] the mobilities of the subsequently generated electrons and holes,^[5-8] and the nanometer-scale morphology of the bulk heterojunction (BHJ) network that determines how easily carriers can reach the electrodes or recombine.^[9-14] The importance of the network morphology can be seen in the fact that a number of organic electron donors and acceptors with seemingly optimally matched energy levels produce poorly performing solar cells because they have an improper degree of phase segregation when blended together.^[15,16] Because of this, there has been a great deal of effort to use processing conditions to control BHJ morphology, including the use of solvent additives,^[17-19] post-fabrication thermal annealing,^[20-22] and sequential deposition of the donor and acceptor layers.^[23-30] All of these techniques greatly increase the parameter space for optimizing power conversion efficiency, which is detrimental when most of the progress in increasing PCE for a given set of materials is made via exploring this parameter space through trial-and-error.

In previous work, we developed a method to control the nanometer-scale morphology of the BHJ network in polymer/ fullerene photovoltaics using pentaaryl-substituted fullerenes that self-assemble into one-dimensional stacks.^[31-33] The idea is that pentaaryl substitution creates fullerene molecules with a self-complementary shape that promotes stacking; because of their shape, we (and others^[34-37]) have referred to this class of fullerene derivatives as 'shuttlecocks' (SCs). When exploring the behavior of SCs in photovoltaic blends with poly(3-hexylthiophene) (P3HT), we

found that the SCs that formed 1-dimensional stacks had significantly improved photovoltaic performance compared with nearly identical fullerenes that had meta substitution on the SC 'feathers' that inhibited the ability to stack.^[31] Subsequently, we worked to control the propensity for stacking by varying the size of alkyl substituents in the para position of the SC feathers. We found using X-ray diffraction and atomic force microscopy that varying the functionalization of the pentaaryl feather substituents by a single methyl group lead to dramatic differences in nanoscale morphology in blends with P3HT.^[32] This is because SCs with shorter alkyl feather substituents tend to stack less easily than those with longer substituents^[33]; non-stacking SCs prefer to phase separate from the donor polymer, whereas the more self-assembling fullerene derivatives preserve the desired blended nanoscale architecture.^[32] As a result, the PCE of devices based on fullerene self-assembly was improved due both to enhanced charge separation and an increase in electron mobility throughout the assembled fullerene network.^[31]

Even though we were able to demonstrate that self-assembly produces a fullerene network that leads to improved photovoltaic performance, the power conversion efficiency of devices based on SCs fell well short of those utilizing the well-studied [6,6]-phenyl-C₆₀ -butyric acid methyl ester (PCBM) fullerene derivative as the electron acceptor. Since PCBM does not self-assemble into one-dimensional stacks, the fact that PCBM devices perform better than SC-based devices indicates that network formation is not the only factor contributing to electron mobility in a BHJ device. This suggests that there are (at least) two length scales over which electron mobility is determined in the fullerene network: the macroscopic length scale (i.e., the active layer thickness) over which the electrons must move to be extracted from the device, and a shorter-ranged molecular length scale over which the probability for an electron to hop from one fullerene molecule to the adjacent one is determined. Although a high local electron mobility does not

guarantee high macroscopic mobility (since macroscopic mobility can be limited by grain boundaries, the fractal nature of the network etc.), poor local mobility clearly limits the macroscopic performance of a device. It is therefore plausible that molecules like PCBM have local electron mobilities that are so high compared to those of SC derivatives that SC-based devices do not perform as well PCBM-based devices, even though SCs form a better macroscopic network.

Although there are many methods for measuring the macroscopic mobility of the carriers in organic photovoltaics, it is less clear how to measure the role that local mobility plays in device performance. Thus, in this paper we aim to ascertain how device-wide network formation and local molecular arrangements collectively determine electron extraction from polymer/fullerene solar cells. We start by developing a density functional theory (DFT)-based computational technique to examine the electronic coupling between adjacent fullerene molecules, providing a theoretical estimate of the 'local' electron mobility. To verify that our calculation protocol makes physical sense, we then turn to time-resolved microwave conductivity (TRMC) experiments that directly measure local conductivities in P3HT/fullerene blend films. We find that the experimentally-measured TRMC local mobilities correlate well with the theoretical predictions. Taken together, the two techniques are able to explain general features of organic photovoltaic device performance, including why PCBM is the acceptor of choice for most polymer-based solar cells even though it does not form the best macroscopic network. The fact that the theoretical predictions are validated by experiment also indicates that we can use such calculations to determine 'design rules' for new fullerene acceptors that could potentially outperform PCBM. And perhaps more importantly, the fact that most fullerene acceptors (including PCBM) do not form networks that simultaneously optimize both the local and macroscopic electron mobilities indicates that there is still significant room for improvement in the fullerene component of polymer/fullerene solar cells.

1.2 Results and Discussion

1.2.1 Electronic Coupling Determined through Density Functional Theory Calculations

In polymer/fullerene solar cells, electron mobility at the local level consists of charge transfer between neighboring fullerene acceptors. To understand how the local rate of electron transfer varies between different fullerene derivatives, we developed a DFT-based protocol to calculate the electronic coupling between pairs of fullerene molecules in a variety of geometries. The electron transfer problem we consider consists of moving charge between two fullerene molecules, which we label left (L) and right (R):



The fundamental quantity of interest is the electronic coupling γ between the L and R molecules, which has the form:^[39,40]

$$\gamma(L \rightarrow R) = |\langle \Psi_L | H | \Psi_R \rangle|, \quad (2.2)$$

where H is the total Hamiltonian and Ψ_i is the localized wavefunction of the transferred electron on molecule i (i.e., the LUMO of the neutral molecule). In our case, the Hamiltonian and wavefunctions are calculated with DFT, which has been shown to give good accuracy within the Marcus theory framework,^[41-46] using the B3LYP functional and STO-3G basis set. Direct calculation of γ , however, can be problematic. This is because if the effects of the environment are ignored, the electron can be artificially localized on an individual molecule due to asymmetry in the system. To overcome this problem, when calculating γ we apply an electric field to delocalize the excited states across the two-molecule system. This is because in a real BHJ system, each fullerene molecule sees, on average, an identical chemical environment; our application of an external field in effect 'equilibrates' the system and allows the electron to delocalize between the

two molecules the way it would in the bulk system. This means that with the application of the field, the LUMO and LUMO+1 orbitals are not localized on the same molecule, so we can easily calculate γ from the energy splitting between these two orbitals. More specifically, in a two-level system, the coupling between the two levels is equal to the half-splitting of the levels in the diagonal basis. Therefore, we rotated the two-level Hamiltonian into the diabatic basis, and found the coupling simply from the off-diagonal elements; the details of how we perform these calculations are described in the Supporting Information (SI).

To tie in with our previous work on self-assembling fullerenes, we started by examining the coupling between two SC molecules, 6,9,12,15,18-pentakis(4-tert-butylphenyl)-1-hydro[60] fullerene (4-tBu) and 6,9,12,15,18-pentakis(4-methylphenyl)-1-hydro[60]fullerene (4-Me). We chose these two SC fullerenes because they present a sharp contrast in their ability to self-assemble. Previously, we found that 4-tBu was a 'universal stacker', assembling into one-dimensional stacks when crystallized from essentially every solvent we explored,^[33] which in turn lead to the best solar cell performance of all the SC fullerenes we examined.^[32] In contrast, the 4-Me molecule, which is electronically identical to 4-tBu, appeared to show little propensity for columnar self-assembly,^[33] which resulted in poor device performance.^[32] Finally, to understand how local mobility among the fullerenes influences overall device performance, we also elected to examine coupling between molecules of the well studied PCBM. The chemical structures of the 4-tBu, 4-Me and PCBM fullerene derivatives, as well as the geometries we used for calculating the electronic coupling between pairs of these molecules, are shown in Figure 2.1 (and the precise coordinates used in our calculations are given in the SI).

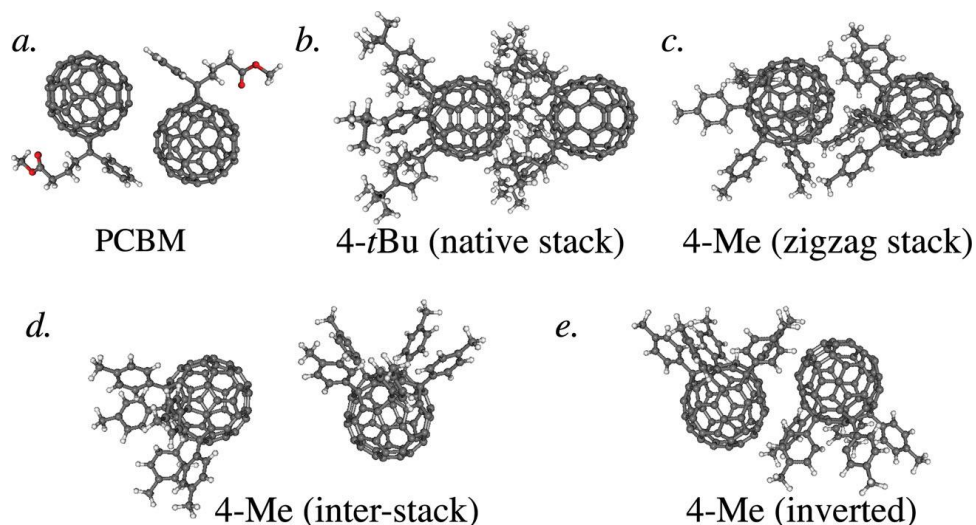


Figure 2.1. Chemical structures of the fullerene derivatives considered in this work and the geometries of the fullerene pairs used in our DFT calculations. a) PCBM, taken from the crystal structure in Ref. [38]; b) the 4-*t*Bu shuttlecock molecule in its stacked orientation, taken from the crystal structure in Ref. [33]; c) the 4-Me shuttlecock in its native crystal structure, taken from Ref. [33]: note the 4-Me molecules crystallize in a 'zigzag stack' motif rather than the linear 'ball-in-cup' exhibited by 4-*t*Bu; d) the 4-Me molecule in its interstack geometry over which we varied the separation distance of the individual molecules; e) 4-Me molecules in a head-to-tail ('inverted stack') geometry similar to that of PCBM molecules, taken from Ref. [33]. The red color in PCBM denotes oxygen atoms; none of the other molecules contain any hetero-atoms. See SI for details.

Although we do not know the distribution of geometries of pairs of fullerene molecules in a working BHJ device, it seems reasonable that on molecular length scales, the spatial relationship between adjacent fullerene molecules should be similar to that in single crystals. Thus, we chose geometries for our calculations for the 4-Me and 4-*t*Bu derivatives from the crystal structures found in our previous work.^[33] For the electronic coupling in 4-*t*Bu dimers, we considered only the linearly stacked orientation found in the crystals derived from most different organic solvents (Figure 2.1b). For pairs of 4-Me molecules, we calculated the electronic coupling in a 'zigzag stack' geometry taken from crystals formed in toluene (Figure 2.1c) and a head-to-tail 'inverted' geometry taken from crystals formed in methanol (Figure 2.1e). For completeness, we also calculated the coupling between 4-Me dimers at their 'interstack' geometry (Figure 2.1d). In the

native crystal, the interstack 4-Me orientation contains interstitial solvent molecules, which prevent the 4-Me molecules from residing close together. Since there likely is not any solvent present between fullerene molecules in a BHJ device, to calculate the electron transfer probability between 4-Me molecules in this orientation, we eliminated the solvent from the crystal structure and repeated the calculation over intermolecular distances ranging from 11.2 Å to 15.2 Å center-to-center fullerene separation (the lower end of this range is limited by van der Waals contact between the 4-Me molecules, while the upper end is what is found in the native crystal with interstitial solvent molecules). Finally, for the electronic coupling between PCBM molecules (Figure 2.1a), we took the geometry from the PCBM crystal structure in Reference [38].

Using these geometries and our DFT-based method, which is outlined above and in the SI, we calculated the electronic coupling between multiple pairs of fullerene molecules and obtained the results summarized in Table 2.1. For the SC fullerene derivatives, we find that both the 4-Me and 4-tBu molecular pairs have essentially the same electronic coupling (within 10%) when placed in their respective 'stacking' orientations; this result makes sense given that 4-Me and 4-tBu have an identical electronic structure, so the overlap of their LUMOs is about the same when adjacent molecules are forced to have similar geometries. When the SC molecules are not in the desired stacked geometry, the electronic coupling varied strongly (roughly exponentially) with the average distance between the fullerene balls. At the closest possible non-stacked distance (limited by steric hindrance of the alkyl substituents), the coupling is actually slightly higher than that in the stacked geometry. Thus, even though we do not know the precise geometry between neighboring SC fullerene molecules in BHJ devices, we can conclude that as long as these molecules stay in close van der Waals contact, the electronic coupling of the pentaaryl fullerenes is comparable in any geometry, lying in the range of 10^{-4} to low 10^{-3} eV.

Table 2.1. Calculated electron couplings for fullerene molecular dimers with the geometries shown in Figure 2.1. Couplings were calculated using the DFT-based methods outlined in the SI.

Molecule	Center-to-Center Distance [Å]	Coupling [eV]
4-tBu (native stack)	10.8	2.95×10^{-4}
4-Me (zigzag stack)	10.9	2.64×10^{-4}
4-Me (interstack)	11.2–15.2	$1.75 \times 10^{-7} - 4.15 \times 10^{-4}$
4-Me (inverted)	9.9	1.45×10^{-3}
PCBM	10.2	1.00×10^{-2}

The fact that the molecular length-scale coupling between pentaaryl fullerenes is similar in nearly every geometry has important implications for solar cells built from these materials. Since the local coupling of these molecules is the same because the molecules have identical electronic structure (i.e., identical HOMO and LUMO levels with similar orbitals), the large differences in device performance we observed for these two molecules^[32] must be the result of differences in the macroscopic geometry of the fullerene network. This makes sense given that 4-tBu shuttlecocks self-assemble into long stacks, creating a much better macroscopic fullerene network throughout the active layer than 4-Me molecules, which phase segregate from the polymer into unconnected islands.^[32] Thus, self-assembly can indeed improve the macroscopic network of polymer-fullerene BHJ solar cells, as we demonstrated experimentally in previous work.^[31]

Also shown in Table 2.1 are the results of the electronic coupling calculation for a pair of PCBM molecules. We find that the electronic coupling between neighboring PCBM molecules is roughly two orders of magnitude larger than the average coupling between the SC fullerenes. This explains why devices built from the SC fullerenes perform so much more poorly than devices built with PCBM, even though the assembled macroscopic 4-tBu fullerene network is likely better than the

random PCBM network: electrons are simply more efficiently moved between PCBM molecules than between SC molecules.

Why is the electronic coupling so much higher between PCBM molecules than other fullerenes? For PCBM, the LUMO and LUMO+1 orbitals are highly delocalized around the molecule in a nearly spherically symmetric fashion, as shown in Figure 2.2a. This allows for greater orbital overlap between neighboring molecules no matter what their relative geometry. In contrast, the frontier orbitals of the 4-*t*Bu and 4-Me shuttlecocks are fairly localized, with the electron density avoiding the regions near and inside the pentaaryl feathers, as illustrated in Figure 2.2b. This means that when the SC molecules are stacked, there is relatively

poor overlap of the orbitals on the neighboring molecules: the electron density on the ball of one SC has little overlap with the electron density in the 'bowl' of the next SC in the stack. The non-spherical orbital distribution of the SCs also explains why the electronic coupling in the non-stacking direction is roughly equivalent to that in the stacked direction, since the electronic overlap in this geometry is equally as poor.

In summary, our calculations suggest that even though pentaaryl fullerenes self-assemble into excellent macroscopic BHJ networks, the electron mobility of these compounds is limited at the

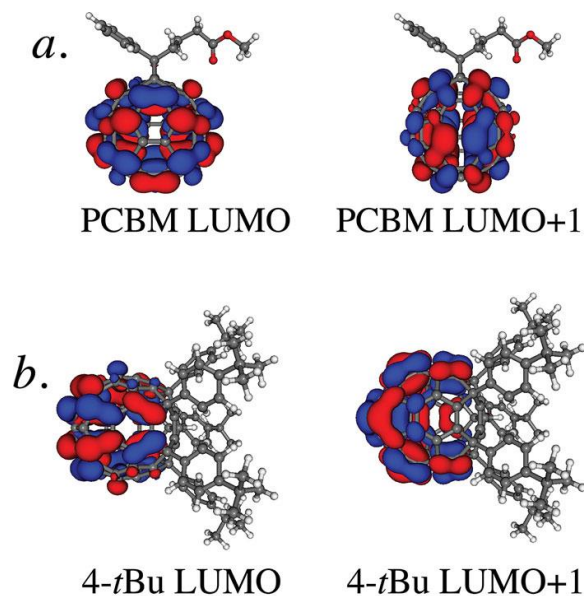


Figure 2.2. Kohn-Sham orbitals from our DFT calculations corresponding to the LUMO and LUMO+1 of the isolated fullerene molecules: a) PCBM, and b) 4-*t*Bu. The orbitals were calculated using the B3LYP functional and STO-3G basis set (see SI for details).

local, molecular length scale. Moreover, our calculations also suggest that PCBM is a champion electron acceptor for organic photovoltaics because the electron transfer rate between PCBM molecules is not only outstanding, but also is roughly independent of the molecular geometry. In the next section, we turn to time-resolved microwave conductivity (TRMC) to provide an experimental verification of these ideas concerning local mobility. But most importantly, what these calculations tell us is that if one wishes to create new self-assembling fullerene acceptors, a key design goal must be to have strong orbital overlap between adjacent fullerenes.

2.2 Local Electron Mobility Determined through Time-Resolved Microwave Conductivity

Although there are numerous methods for estimating the mobility of the carriers in organic photovoltaic devices (e.g., fitting space-charge-limited current models to single-carrier diodes built from the active materials,^[47] building field effect transistors from the materials,^[48] various transient photovoltage and photocurrent experiments,^[49-52] etc.) all of these methods measure carrier motion only at the macroscopic, device length scale. Moreover, most of these methods also are sensitive to the nature of the contacts between the electrodes and the active material(s). To experimentally probe the local mobility of photogenerated carriers, it is necessary to turn to an electrodeless pump-probe method. Flash photolysis TRMC provides exactly such a method,^[53,54] and thus offers the perfect testbed for comparing our calculations in the previous section to an experimental measure of local electron mobility; the TRMC technique has been used previously to comparing local and network-wide hole mobility in samples of P3HT.^[55]

The flash photolysis TRMC technique measures the time-dependent change of the microwave power in a cavity that contains the sample following the photogeneration of charges in that sample. The microwave power absorbed is directly related to the photoconductance of the sample, which is proportional to the yield of photogenerated carriers per photon absorbed (ϕ) and the (sum of the) high-frequency (local) effective mobility ($\sum\mu$) of those carriers.^[56] For TRMC experiments, the measured photoconductance peak ($\sum G_{peak}$) is given by:

$$\Delta G_{peak} = \beta q_e d (n\mu_e + p\mu_h), \quad (2.3)$$

where β is the ratio of the interior dimensions of the microwave waveguide (2.2 for our experimental set-up), q_e is electronic charge, d is the sample thickness, and n and p are the density of the photogenerated electrons and holes, respectively. Since it is difficult to measure the densities of the individual carriers, Equation (2.3) is usually rewritten as:

$$\Delta G_{peak} = \beta q_e I_0 F_A (\mu_e + \mu_h), \quad (2.4)$$

where I_0 is the incident flux of photons used to excite the sample to create photoconducting carriers, and F_A is the fraction of those photons that are absorbed, given by $F_A = 1 - 10^{-OD}$, where OD is the optical density of the sample at the excitation wavelength. Since β , q_e , I_0 , and F_A are all easily measured (as described in the SI), the TRMC experiment directly yields the product of the yield (or quantum efficiency) of free carriers per absorbed photon (ϕ) and the sum of their mobilities, $\mu_e + \mu_h$, or $\phi\sum\mu$.

To understand the nature of the local mobility for the molecules we examined theoretically in the previous section, we prepared BHJ films of P3HT with both the 4-Me and 4-tBu shuttlecock molecules and with PCBM. For some samples, we prepared the BHJ blends in a manner identical to our previous work studying photovoltaic devices made from these materials using equimolar

ratios of PCBM, 4-tBu, and 4-Me (polymer:fullerene weight ratios of 1:0.8, 1:0.45 and 1:0.35, respectively);^[32] for others, we used very low loadings of the different fullerenes (P3HT:fullerene weight ratios of 1:0.0015 and 1:0.0013 for 4-tBu and 4-Me respectively), as described in the SI. Figure 2.3 shows how the $\phi\Sigma\mu$ product-the carrier yield times the effective mobility-varies in all of our samples as a function of absorbed photon flux. Although Equation (2.4) predicts a linear relationship between ΔG_{peak} and $I_0 F_A$, there is a sublinear relationship at higher light intensities observed in Figure 2.3 that is due to exciton-charge annihilation, which causes the carrier concentration (ϕ) to drop at high excitation intensities.^[56] Since our experimental apparatus cannot measure the absorbed microwave power at intensities low enough to be entirely in the linear regime, we fit the data using the formalism described in the SI (see Equation S3) to extract an extrapolated low-light-intensity value of $\phi\Sigma\mu$. These extrapolated values are summarized in Table 2.2.

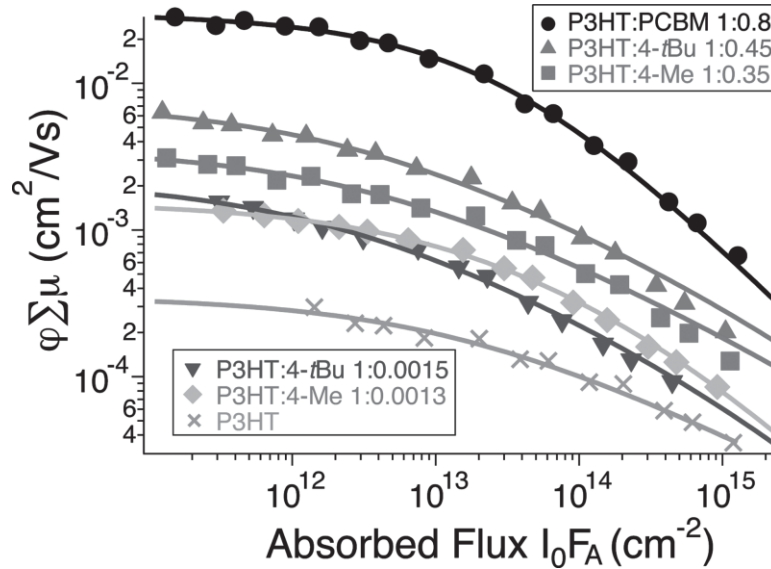


Figure 2.3. The dependence of $\phi\Sigma\mu$, calculated from the measured TRMC photoconductance via Equation 1, on absorbed photon flux ($I_0 F_A$) for pure P3HT and blends with different fullerenes. The solid curves are fits to Equation S3 in the SI.

The first thing that is clear from Figure 2.3 and Table 2.2 is that the BHJ samples with low loadings of fullerene show increased photoconductivity compared to pure P3HT. This results from the fact that the presence of even a limited number of fullerene acceptors greatly increases the number of photogenerated carriers relative to pure P3HT.^[57,58] We find that at these low acceptor loadings, the photoconductance of both the 4-tBu and 4-Me pentaaryl fullerenes are fairly similar to each other, although different from what has been measured previously for low concentrations of PCBM in P3HT.^[57] Since we expect the mobility of the holes on P3HT to be independent of the choice of fullerene when the fullerenes are isolated at such low concentrations, most of the difference in photoconductance we measure must result from differences in the number of photogenerated carriers when different fullerenes are used. We will use this difference in carrier yields for different fullerenes, in combination with photoluminescence quenching experiments, to extract the local mobility of electrons among the network of different fullerenes present at device loadings, as described further below.

Table 2.2. Summary of low-light-intensity photoconductance and average exciton lifetimes in different P3HT:fullerene blends.

Sample	$\phi \Sigma \mu$ ^{a)}	Exciton Lifetime ^{b)}	PL Quenching Carrier Yield	TRMC Carrier Yield	ns/ps Yield Ratio	'Corrected' ns Yield	Hole mobility ^{c)}	Calculated electron mobility ^{c)}
P3HT:4-Me 1:0.0013	0.15	121	41%	11%	0.26	NA	1.4	0
P3HT:4-tBu 1:0.0015	0.21	128	37%	15%	0.40	NA	1.4	0
P3HT:4-Me 1:0.35	0.30	78	62%	NA	0.26 ^{d)}	16%	1.4	0.44
P3HT:4-tBu 1:0.45	0.60	43	79%	NA	0.40 ^{d)}	32%	1.4	0.49
P3HT:PCBM 1:0.8	2.79	47	77%	NA	NA	77%	1.4	2.2
Pure P3HT	0.02	204	NA	1.4%	NA	NA	1.4	NA ^{a)}

a) 10^{-2} cm²/Vs; b) ps; c) 10^{-2} cm²/Vs $\phi \Sigma \mu$ values were determined via Equation 2.1 from the TRMC measurements in Figure 2.3 (see SI). Exciton lifetimes determined from deconvoluting the PL decay data in Figure 2.4; d) Yield ratio values taken from samples with low fullerene loading.

Figure 2.3 and Table 2.2 also show that increasing the concentration of fullerenes in P3HT blend films to that present in typical photovoltaic devices further increases the photoconductance signal. Moreover, blend films containing 4-tBu show a higher photoconductance than samples utilizing

4-Me as the acceptor, and neither of the SC fullerenes gives a photoconductance as high as that in P3HT:PCBM blends. To understand where these differences in photoconductance come from at high loadings, we examined the photoconductance decay profiles of the different blends, which are shown in Figure 2.4. The difference we observe between the photoconductance decay profiles of the P3HT:PCBM blend and that of pure P3HT has been attributed in previous work to differences in the type of carrier that dominates the TRMC signal: the mobility of electrons in PCBM is higher than that of holes in P3HT, hence the electrons dominate the photoconductance in the P3HT:PCBM sample.^[57] The slow decay of G observed in this case is attributed to slow bimolecular recombination at low excitation intensities.^[57] In contrast, the photoconductance decays of the

P3HT:SC blends are similar to those of the pure P3HT sample, indicating that for these blends the dominant ΔG term arises from the holes in P3HT, which have distinctly different dynamics than the electrons.^[57] Although Figure 2.4 only shows representative transients at a specific excitation intensity, this observation holds at all the light intensities we used in this work. We therefore conclude that in P3HT:SC blends, the electron mobility in the SC domains is lower than the hole mobility in P3HT, and thus significantly lower than the electron mobility in PCBM.

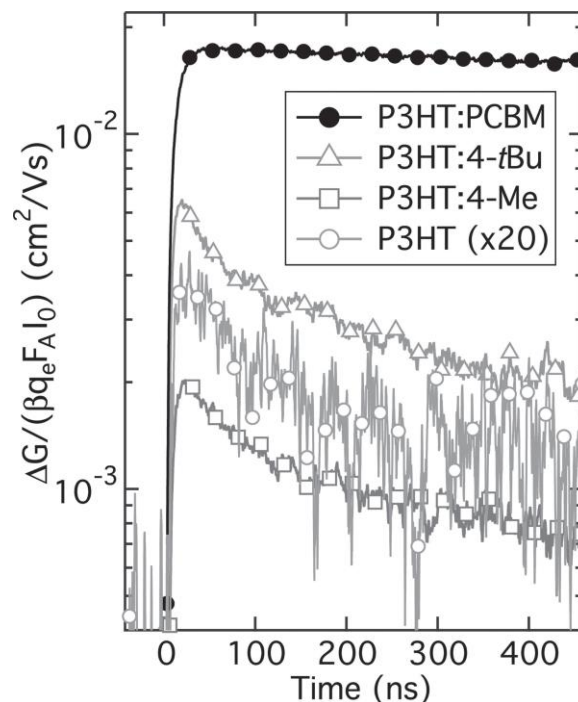


Figure 2.4. TRMC photoconductance transients (normalized for absorbed photon flux and physical constants, see Equation (2.4)) for P3HT-based samples at device loadings with different fullerenes. The photoexcitation wavelength was 500 nm, and the data shown are for an absorbed photon flux of 10^{12} cm^{-2} , which corresponds to a fluence of 0.56 mJ/cm^2 . The results were similar, however, at all photon fluxes examined in this work.

Even though the photoconductance decay profiles in Figure 2.4 show that the electrons on different fullerenes have different local mobilities, the data does not allow us to directly make quantitative mobility comparisons between the samples. This is because the overall carrier yield at high fullerene loadings not only depends on the fullerenes' intrinsic ability to split excitons, but also depends on the donor/acceptor interfacial area, which is sensitive to the degree of phase segregation between P3HT and the different fullerenes. Thus, to extract quantitative information about differences in local carrier mobility among the different fullerenes, we need to find a way to determine the carrier yields (ϕ) in the blend films with different fullerenes. We chose to estimate ϕ from the degree of fluorescence quenching observed via time-correlated single photon counting (TCSPC). Using the methods outlined in the SI, we excited each of our TRMC samples at 510 nm and monitored the decay of the photoluminescence (PL) at 720 nm, producing the TCSPC data shown in Figure 2.5. After deconvoluting the instrument response function and fitting the resulting PL transients to a sum of two exponentials (see SI), we obtained the PL lifetimes given in Table 2.2. Presuming that every quenched exciton produces carriers that survive on the TRMC time scale, fluorescence quenching provides a direct measure of the fraction of absorbed excitation photons that produce charge carriers. Unfortunately, not all of the carriers generated through exciton quenching survive to the ns time scales measured in TRMC. We can estimate how many carriers survive to this time scale, however, using our measurements on the dilute fullerene-containing samples. Since all of the measured photoconductance in these samples comes from hole mobility on P3HT, we can use the literature value for P3HT's TRMC hole mobility ($0.014 \text{ cm}^2/\text{Vs}$ ^[57,59,60]) to calculate ϕ for each of the different fullerenes on the TRMC time scale. We can then compare this value of ϕ to that determined from our PL quenching measurements to determine the ratio of carriers generated on the ps time scale to those that survive on the ns time scale.

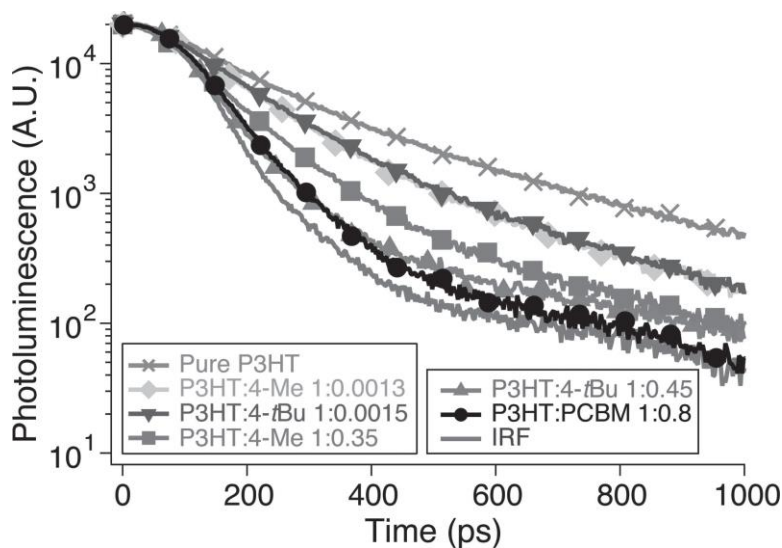


Figure 2.5. Fluorescence quenching of the polymer:fullerene blend samples used for the TRMC experiments shown in Figure 2.3 measured by time correlated single photon counting. Symbols have the same meaning as in Figure 2.3.

Using this procedure, we were able to determine the local electron mobilities of the 4-Me and 4-tBu SC fullerenes at device-level loadings. Table 2.2 shows that at high concentrations, the 4-tBu pentaaryl fullerene has a PL lifetime that is shorter than that of the 4-Me molecule, indicating that there is $\sim 30\%$ more PL quenching for P3HT:4-tBu blends than for P3HT:4Me blends. This result is in excellent agreement with steady-state fluorescence measurements in our previous work, and can be attributed to the enhanced phase separation of the nonstacking 4-Me molecule relative to the self-assembling 4-tBu.^[32] Thus, even though the photoconductance of the 4-tBu sample at device loadings is higher than that of the 4-Me sample, most of this difference results from changes in carrier yield. In fact, when we use the information from the dilute samples, we conclude that on the ns time scale of TRMC, the carrier yield for the 4-tBu sample is roughly twice as large as for the 4-Me sample. Since the measured photoconductance for these two samples also differs by a factor of two, this means that the local mobilities of these two SC fullerenes must be roughly similar, in accord with the DFT calculations presented in the previous section. This also implies

that the dramatic differences in device performance observed between BHJs with these two fullerenes^[32] must result from differences in the macroscopic mobility of the fullerene network, verifying that the self-assembling 4-tBu molecule forms a significantly better interpenetrating network than its non-assembling 4-Me analogue.

Also of interest in Figure 2.3 and Table 2.2 is the fact that the PL lifetimes of P3HT:4-tBu and P3HT:PCBM^[57] blends at device loadings (high weight ratios) are essentially identical, resulting in fairly similar carrier yields on the ps time scale of the TCSPC measurement. If we continue to assume that the hole mobility of P3HT does not change when increasing fullerene loading, then the difference in the TRMC-measured $\phi \Sigma \mu = \phi(\mu_e + \mu_h)$ product at higher fullerene loadings are caused both by a decreased ϕ and a decreased local electron mobility for the SCs relative to PCBM. We note that the value for the local electron mobility that we extract for PCBM at the 1:0.8 blend ratio is somewhat lower than previously reported,^[57] which is caused by the different processing conditions used here. Our analysis confirms, however, that the local electron mobility in PCBM is at least a factor of five higher than that in 4-tBu, as summarized in Table 2.2. This is also consistent with our DFT calculations in the previous section, and verifies that the reason PCBM is such a good electron acceptor for use in polymer blend solar cells is because it has outstanding local mobility due to the strong overlap of the LUMOs between adjacent molecules, even though it doesn't necessarily form the best macroscopic BHJ network.

Finally, to examine how the macroscopic fullerene network changes with the different SCs molecules, we constructed diodes out of films of the pure 4-tBu and 4-Me molecules; the details of the fabrication and construction of these fullerene-only diodes are given in the SI. We fit the measured current-voltage curves for these SC diodes to the Mott-Gurney law, and extracted the

space-charge limited macroscopic electron mobilities for these fullerenes of 3.9 and 0.7×10^{-6} cm^2/Vs for 4-tBu and 4-Me, respectively. Since the local electron mobilities of these two fullerenes are similar to each other (0.49 and 0.44×10^{-2} cm^2/Vs), this result verifies that the nature of the electron-conducting network is also important for macroscopic mobility/overall charge extraction. Although carriers may be able to move with similar ease between adjacent 4-tBu and 4-Me fullerene molecules, the global network formed with the 4-tBu fullerene is more than five times more effective at moving charges across macroscopic distances than the network formed by 4-Me fullerenes. It is important to emphasize that this conclusion was based on diodes fabricated from pure fullerene films, so the data is influenced only by the macroscopic connectivity of the fullerene network and not by polymer/fullerene phase separation. For comparison, it is worth noting that the space-charge limited electron mobility of both SC fullerenes is much lower than that of PCBM (2.0×10^{-4} cm^2/Vs ^[61]). Thus, as we have argued throughout this work, both network formation and good local electronic coupling are important to obtain efficient charge extraction from an organic photovoltaic device.

2.3 Conclusions

In this paper, we have used both theoretical and experimental techniques to better understand the distinction between the local mobility and the macroscopic mobility of electrons on the fullerene network of polymer-based BHJ photovoltaic devices. Our work shows that there are indeed two significant components to electron mobility: the intrinsic ability of electrons to move between adjacent fullerenes (local mobility), and the overall architecture and morphology of the fullerene network on device length scales (macroscopic mobility). The macroscopic mobility is what is typically measured in device physics experiments, and we have shown that a good understanding

of local mobility can be obtained from a combination of DFT calculations and TRMC experimental measurements.

To understand the differences between local and macroscopic mobility, we examined the behavior of BHJ blends of P3HT and a pair of pentaaryl fullerene derivatives that have an identical electronic structure but different propensities to self-assemble on macroscopic length scales. Our DFT calculations found that the coupling between adjacent molecules is quite similar for the self-assembling 4-tBu and non-assembling 4-Me shuttlecock fullerenes, so that with their nearly identical electronic structure, their local electron mobilities are also nearly identical. Our TRMC experiments on blends of these fullerenes show that the local electron mobilities on these are indeed comparable; the slightly higher net local mobility for the 4-tBu molecule is likely directly related to the fact that self-assembly can assist mobility even on the local length scales probed by TRMC. More importantly, however, photovoltaic devices fabricated with 4-tBu show dramatically better performance than those fabricated with 4-Me^[32] and diodes built from 4-tBu have a higher space-charge limited mobility than those built from 4-Me, verifying that changes in the macroscopic network morphology affect device performance even when the local mobilities are comparable.

We also used the idea of separate local and macroscopic electron mobilities to understand why PCBM is the fullerene of choice for nearly every polymer-based photovoltaic. Our DFT calculations show that the local electronic behavior of PCBM is nearly ideal for solar cells: the coupling between adjacent molecules is very high, and the delocalization of the frontier orbitals allows for efficient charge transfer in almost every orientation. This is in contrast to the SC fullerenes, whose frontier orbitals are perturbed by the presence of the pentaadducts, leading to

poorer electronic overlap. Our TRMC experiments verified that the local electron mobility on PCBM is significantly higher than that on the SC fullerenes, consistent with the fact that PCBM consistently produces the best photovoltaic devices.

Finally, all of our results suggest that there is further room for improvement in the fullerene component of polymer BHJ solar cells. Since self-assembly can produce macroscopic networks that dramatically improve device performance, it seems clear that designing new fullerenes that both self-assemble and have high local electron mobilities should produce devices that are even better than those using PCBM, particularly since it has been argued that electron mobility on the fullerene network is what limits overall device performance.^[62] Furthermore PCBM has a low LUMO compared to novel fullerene acceptors like ICBA.^[63,64] Future fullerene acceptors that utilize self-assembly and possess a higher lying LUMO will potentially lead to improvements in both open circuit voltage and short circuit current. The fact that our DFT calculations are corroborated by experiment means that we can design new fullerenes and test them for local mobility before synthesizing them. In combination with TRMC and other measurements, this should provide a way to explore new self-assembling fullerenes that are simultaneously optimized for both local and macroscopic electron mobility, thus helping polymer-based photovoltaic devices to reach their ultimate potential.

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Chapter 3

Time dependent stochastic density functional theory calculations of the spectrum of anthracene derivative chemisorbed to an Au{111} surface

3.1 Introduction

Scanning tunneling microscopy (STM) yields nanoscale real-space information. STM uses the inelastic tunneling of electrons from a surface to a tip, making it possible to study atoms in real-space. One of the advantages of STM is that it is not specific to the chemical composition of the analyte, yet a drawback is that it works best at low temperatures^[1-4] because the thermal movement of the particles makes it difficult for the STM tip to pinpoint its location. One method to circumvent this problem is the use of laser-assisted STM to photo-excite a molecular junction at room temperature, which is then able to induce an electron to tunnel into the STM tip.^[3,4] Laser-assisted STM improves the resolution by effectively increasing the contrast between the excited molecule and its background. Since the current caused from this photoexcited molecule will be greater than the background, the molecular position is easily resolved, even at room temperature.

One example is 9-(4-Mercaptaphenylethynyl)anthracene (MPEA).^[4] This molecule will chemisorb onto a gold surface, and a photon which matches the band gap will photoexcite it. When the electron of MPEA is excited from the HOMO to the LUMO, it tunnels into the STM, inducing a measurable current. This makes it possible to measure the location of MPEA as the difference between the current from the laser-assisted STM and the current from just STM (without the laser). One use of this method is to introduce MPEA to a surface that has been coated with a substrate. MPEA will chemisorb into any defects exposed on the gold surface and can be read with laser

assisted STM. It is important to note that MPEA cannot be used for every type of substrate, but similar molecules can be used for different substrates.

One challenge is determining the correct wavelength of light, which roughly corresponds to the HOMO-LUMO gap of the chemisorbed molecule.^[5-7] The gap is affected however by the environment. For example, the molecule can be affected by the polarity of the gold surface, the removal of the substituted hydrogen as it chemisorbs onto the surface, and the configuration the it has on the gold surface.

Theory can provide a valuable insight into the processes involved in the photoexcitation and tunneling of the electron from MPEA to the STM tip. One method used to determine the bandgap is to calculate energy states of the HOMO and LUMO with deterministic DFT.^[8] The problem is that the eigenvalues are determined for the system at its ground state, and not of an excited state. Such calculations often overestimate the bandgap.^[8] Another issue is that MPEA is chemisorbed to the gold surface, which affects the bandgap due to its polarity.^[6,7] When solving for the eigenstates of such a system, the molecular orbitals of the MPEA and gold surface combine, making it difficult to determine which corresponds to the HOMO and LUMO of MPEA alone.

One useful method for solving the energy gap is to calculate the absorption spectrum of MPEA using time dependent density functional theory.^[9,10] We excite the system using a perturbing potential, and then measure the oscillation in the polarity. This determines which frequencies of light are absorbed, yielding the HOMO-LUMO bandgap. In this paper, we use time dependent stochastic density functional theory (TDsDFT)^[10] to solve the spectrum of MPEA when it is chemisorbed onto the gold surface. We calculate the spectra of an isolated MPEA (Fig. 3.1a), an

isolated trim MPEA (tMPEA, Fig. 3.1b), a chemisorbed MPEA (cMPEA) attached to the gold surface (cMPEA/AuS, Fig. 3.1c), and a bare gold surface (BAuS).

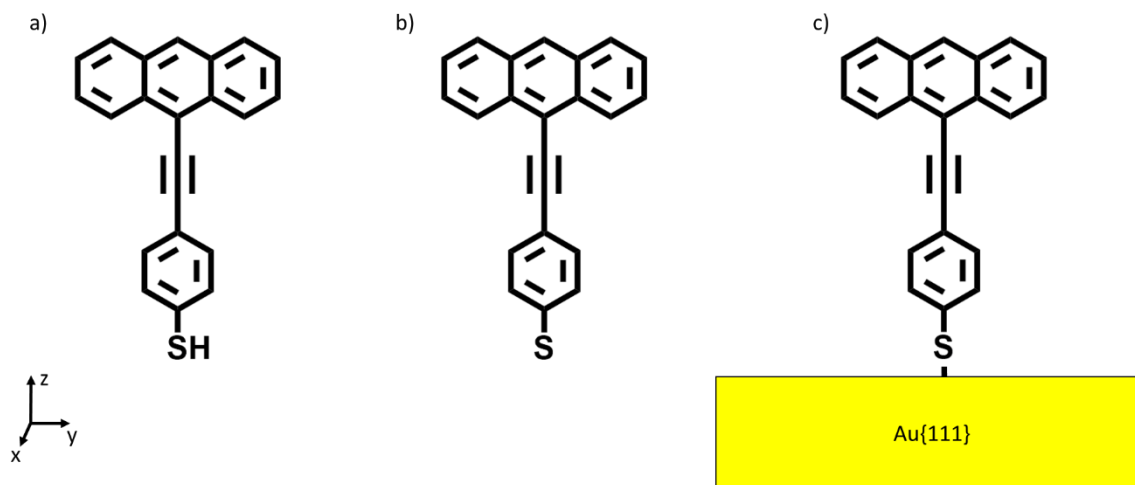


Figure 3.1. Schematic of a) MPEA, b) tMPEA, and c) cMPEA/AuS. The arrows represents the x, y and z axis. MPEA is aligned to the yz plane.

The spectrum of cMPEA was determined from the spectrum of cMPEA/AuSurf by first subtracting the spectrum of BAuS, as well as a more extensive method in which we determine the spectra from a local area.

3.2 Method

Kohn Sham density function theory (KS-DFT) was used to determine the Kohn Sham potential of the ground states.^[11,12] We use the local density approximation (LDA) to calculate the exchange-correlation potential $v_{xc}[n(r)]$.^[13] The nuclear-electron potential ($v_{ne}(r)$) was the Trolier-Martins norm conserving pseudopotential.^[14] The Kohn Sham potential, $v_{KS}(r) = v_{ne}(r) + v_{HXC}[n(r)]$ was calculated with a self-consistent field method, where $v_{HXC}[n(r)]$ contains the Coulomb potential $v_H[n(r)] = \int dr n(r)/|r - r'|$ and the exchange-correlation potential. This

potential was used to determine the Kohn Sham Hamiltonian, $\hat{h}_{KS}(r) = \hat{T} + v_{KS}(r)$, where $\hat{T} = -(1/2)\nabla^2$ is the kinetic energy operator in atomic units. The Kohn-Sham potential was calculated for all systems self-consistently, until the electronic energy converged below of 1×10^{-6} eV.

TDDFT was used to calculate the spectra of MPEA and tMPEA. To calculate the spectra of the larger systems, TDsDFT was used. TDsDFT is similar to deterministic TDDFT,^[10] with the exception that all the Kohn Sham orbitals are replaced by purified stochastic orbitals. The stochastic orbitals are defined as:

$$\zeta_i(r) = \frac{e^{i\theta_i(r)}}{\sqrt{\delta V}}, \quad (3.1)$$

where $\theta_i(r)$ is uniform random phase $[0, 2\pi]$, δV is the volume element of our grid, and $i = 1, \dots, N_\zeta$ signifies the multiple stochastic orbitals. These stochastic orbitals are projected onto the occupied orbitals:

$$|\xi_i\rangle = \sqrt{\hat{\theta}_\beta} |\zeta_i\rangle, \quad (3.2)$$

where $\hat{\theta}_\beta = (1/2)\text{erfc}(-\beta(\mu - \hat{h}_{KS}))$ is a Heaviside operator, μ is the chemical potential, and $\hat{h}_{KS} = \hat{T} + v_{KS}(r)$. The temperature β was defined such that $\beta E_g \gg 1$, where E_g is the Fourier energy bandgap. The chemical potential μ is determined from:

$$N_e = 2\langle\langle \xi | \xi \rangle\rangle_\zeta, \quad (3.3)$$

where $\langle\langle \dots \rangle\rangle_\zeta$ denotes a statistical average of all the stochastic orbitals. Since ξ is a function of the chemical potential μ , the average number of electrons should equal N_e when the chemical potential is within the HOMO-LUMO band gap. The time dependent electron density is determined as:

$$n(r, t) = \langle |\xi(r, t)|^2 \rangle_\zeta = \frac{2}{N_\zeta} \sum_i^{N_\zeta} |\xi(r, t)|^2. \quad (3.4)$$

The time-dependent stochastic orbitals are propagated as:

$$i \frac{\partial}{\partial t} \xi(r, t) = \hat{h} \xi(r, t), \quad (3.5)$$

where $\hat{h} = \hat{h}_{KS} + v_{HXC}[n(r, t)] - v_{HXC}[n(r, t = 0)]$ is the time dependent one electron Hamiltonian, and at $t = 0$ the orbitals are perturbed by a dipole excitation. The advantage of TDSDF is that the number of orbitals required is lower, for large systems, than in conventional TDDFT. For our system, which contains over 2500 electrons, we use 480 stochastic orbitals, way lower than required for conventional TDDFT.^[10]

In order to calculate the absorption cross section, one must first determine the general susceptibility function $\chi(r, r', t)$.^[15] The absorption cross section is determined as the imaginary part of the susceptibility:

$$\sigma(\omega) = \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \int dr dr' r \cdot \chi(r, r', \omega) \cdot r', \quad (3.6)$$

where c is the speed of light. Solving for the susceptibility function can be problematic for large systems, but if we use a perturbing potential of $v(r) = x, y, \text{ or } z$, then the spectra as a summation becomes:

$$\sigma(\omega) = \sigma_x(\omega) + \sigma_y(\omega) + \sigma_z(\omega), \quad (3.7)$$

where $\sigma_x(\omega)$, $\sigma_y(\omega)$ and $\sigma_z(\omega)$ are the spectra one gets when using x, y, or z polarized light respectively, and $\sigma_x(\omega)$ is calculated as:

$$\sigma_x(\omega) = \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \int x \Delta \tilde{n}_x(r, \omega) d^3r, \quad (3.8)$$

$\Delta \tilde{n}_x(r, \omega)$ are the linear response densities.^[10] The other two spectra $\sigma_y(\omega)$, and $\sigma_z(\omega)$ are calculated in a similar maner.

Finally, we extracted the spectrum of cMPEA from the cMPEA/AuS simulation. This was done using a method we dubbed selective integration. Instead of measuring the dipole response of the entire system, we select a space in which we sample the dipole response selectively. This leads to a selective dipole response $d^S(t)$ defined as:

$$d_{xx}^S(t) = \int dr x S(r) \Delta n_x(r, t), \quad (3.9)$$

where $d_{yy}^S(t)$, and $d_{zz}^S(t)$ are determined similarly. $S(r)$, the selective space function, is defined as

$$S(r) = \begin{cases} 1 & \text{when } r \text{ is within the sample space,} \\ 0 & \text{everywhere else.} \end{cases} \quad (3.10)$$

The spectrum of the selective space is:

$$\sigma^S(\omega) = \sigma_x^S(\omega) + \sigma_y^S(\omega) + \sigma_z^S(\omega), \quad (3.11)$$

where the dipole responses of the entire system are replaced with the selective dipole response. This method was used to measure the spectrum of cMPEA from cMPEA/AuS. The spectra of the isolated MPEA and tMPEA were calculated using deterministic TDDFT, whereas the spectra of BAuS and cMPEA/AuS was calculated using TDsDFT with 480 time dependent stochastic orbitals. The spectrum of cMPEA was then determined using selective integration.

Results and discussion

The spectrum of MPEA is shown in Fig 3.2a. Experimental data suggests that there should be a peak at ~ 400 nm.^[4] This peak was not present for the isolated MPEA spectrum. This difference could be caused by the functional we used for the exchange-correlation potential, or the difference in environments between the experiment and the theory. Since a hydrogen is removed from MPEA as it is chemisorbed onto the gold surface, the spectra of tMPEA was calculated (Fig. 3.2b). Two peaks from the isolated MPEA (Fig 3.2a) peaks at ~ 300 and ~ 550 nm shift to ~ 400 and ~ 650 nm respectively, implying that the removal of the hydrogen had an effect on the spectrum. The effect the gold surface has on the spectrum was determined by comparing the spectrum of tMPEA to cMPEA, because tMPEA and cMPEA have similar compositions. The peak at 400 nm was used as a reference point for later calculations.

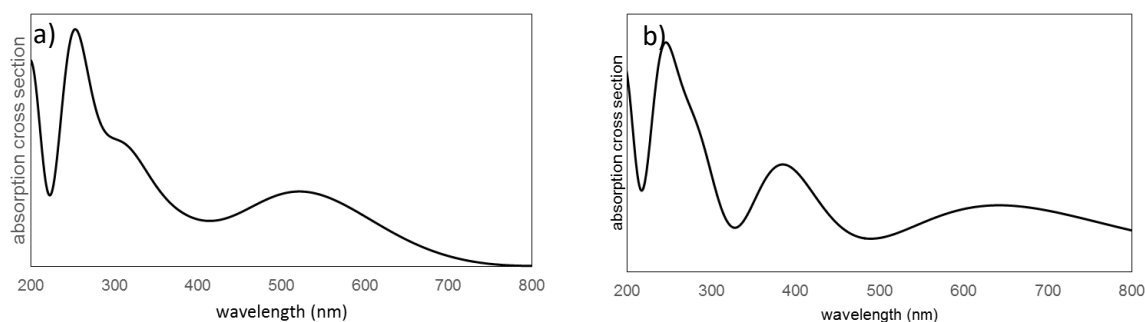


Figure 3.2. TDsDFT calculations of the cross-sectional absorption using TDDFT for a) an isolated MPEA, and b) an isolated tMPEA.

The spectra of cMPEA/AuS and BAuS were determined similarly to MPEA and tMPEA (Fig. 3.3). The absorption from the gold surface dominates the spectrum of cMPEA/AuS, which makes the two spectra of cMPEA (without the gold surface) difficult to see.

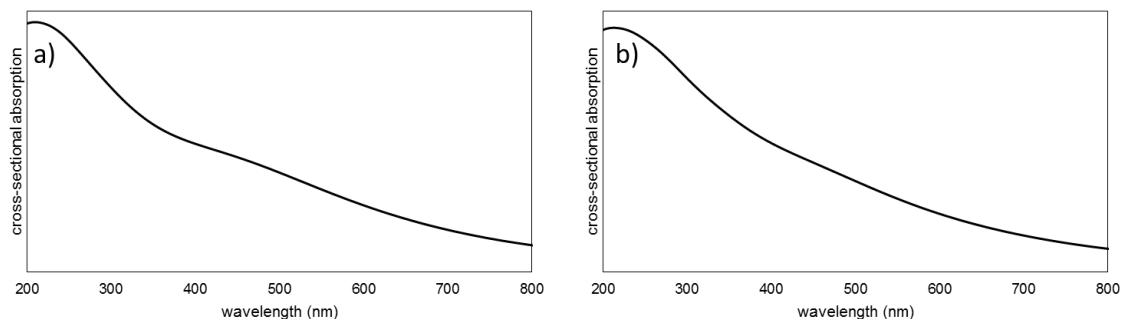


Figure 3.3. TDsDFT calculations of the cross-sectional absorption using 480 stochastic orbitals for a) cMPEA/AuS and b) AuS.

Using the spectra of cMPEA/AuS and BAuS, we determined the spectrum of cMPEA as the difference of the two. This resulted in a spectrum that has no resemblance to the isolated MPEA (Fig. 3.2a) or isolated tMPEA (Fig. 3.2b). The difference could be caused by the small amount of error caused by using TDsDFT. The randomness of the stochastic orbitals has the effect of introducing “noise” into the spectra. Since the spectrum of cMPEA/AuS is dominated by the gold surface, the signal of cMPEA will get lost in the noise. This “noise” makes it difficult to subtract out the spectrum of the gold surface. One alternative is to increase the number of stochastic orbitals, which could reduce the noise, but an easier method is to extract the spectrum directly from the system using selective integration.

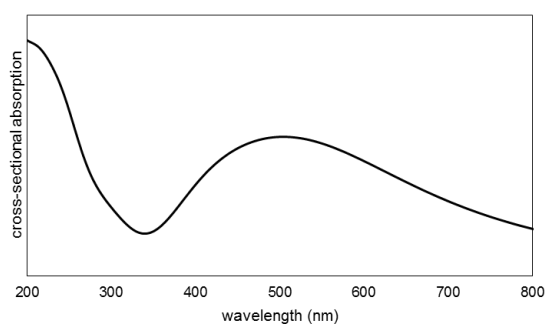


Figure 3.4. Cross-sectional absorption of cMPEA, which was determined from the difference of the spectra of cMPEA/AuS and AuS.

Heat maps of the magnitude of the imaginary portion of $\omega\Delta\tilde{n}(r, \omega)$ for $\omega = 3.1$ eV are shown in Fig.3.5. A photon energy of 3.1 eV was chosen because it corresponded to a wavelength of 400 nm, which matches the peak absorption in Fig. 3.2b. These maps were used to estimate the areas at which we can selectively integrate the system to get an “extracted spectrum.” The intensity of the Fourier density response functions is largest when $v(r) = z$ because the absorption of cMPEA is strongest for z polarized light. Finally, the magnitude of the response function seems to extend into the gold surface.

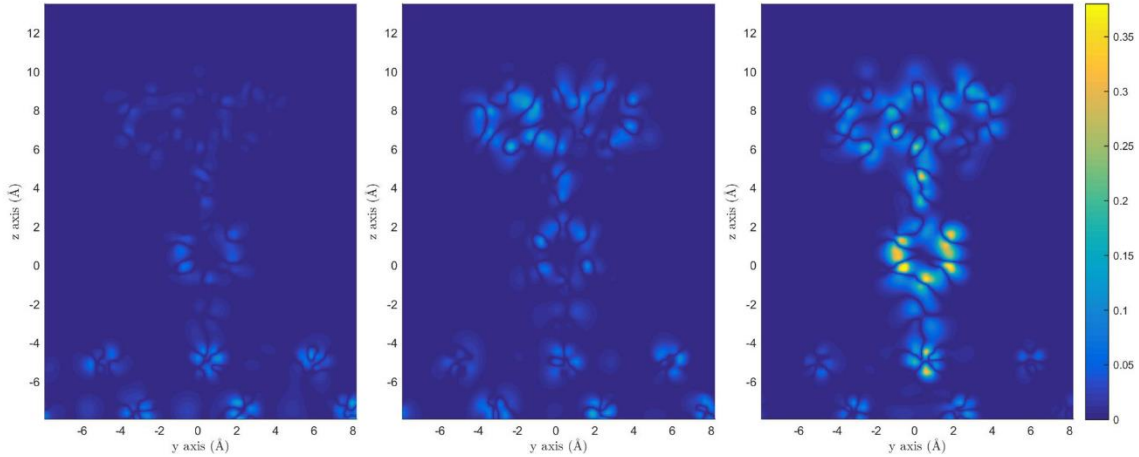


Figure 3.5. Heat maps of the magnitude of the imaginary portion of $\omega\Delta\tilde{n}(r, \omega)$ at 3.1 eV for x polarized (left), y polarized (middle) and z polarized (right) light. The red dashed line represents the boundary of the gold surface.

Three areas were chosen to integrate over (Fig 3.6a) with the corresponding spectra (Fig 3.6b). The first is the space just above the gold surface boundary (Fig. 3.6, blue). The spectrum of cMPEA, which was determined using selective integration, is similar to that of isolated tMPEA, indicating that the gold does not have a significant effect on its spectrum. The next area we focus on was the top portion, containing anthracene (Fig. 3.6, red). The spectrum extracted from this area is nearly identical to that of the full cMPEA, which indicates that the majority of the

absorption is coming from the anthracene portion of the molecule. The lack of absorption from the bottom portion of the molecule (Fig. 3.6b, green line) further supports the hypothesis that the anthracene portion of cMPEA is absorbing most of the light. Finally, the absence of the broad peak found in Fig. 3.4 (~ 500 nm) might indicate that the inclusion of cMPEA might cause extra absorption in the gold surface.

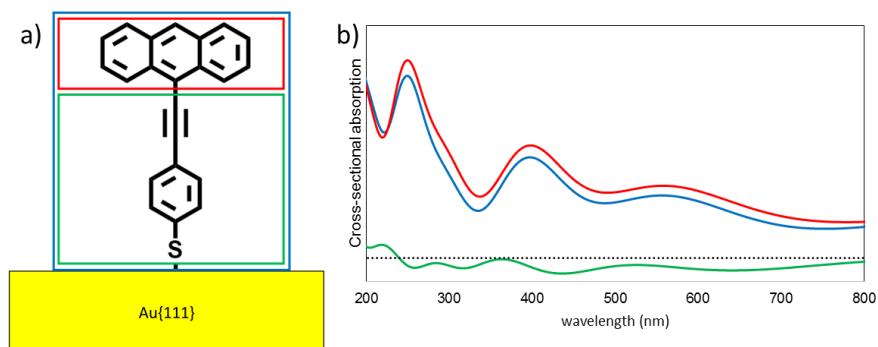


Figure 3.6. a) The areas which were used to create b) the spectra. Blue represents the spectrum determined for the full cMPEA, red represents the spectrum of the top portion of cMPEA, and green represents spectrum of the bottom of cMPEA.

Conclusions

We were able to determine the spectrum of cMPEA using TDsDFT. In order to accomplish this, we use a selective integration scheme to extract the spectrum of cMPEA directly from the cMPEA/AuS system. This method offers an improvement over the conventional approach, where the difference of cMPEA/AuS and BAuS is used to determine the spectrum of cMPEA, since it yields accurate results without running TDDFT calculations on the “background”, i.e. the BAuS system. This method is also more versatile than the conventional method since we can choose which areas to integrate over.

We also demonstrated that a majority of the absorption within the wavelengths of 200 and 800 nm comes from the anthracene portion of cMPEA, and that the spectrum of cMPEA is similar to that of tMPEA, which indicates that the gold surface has no effect on the HOMO-LUMO gap. The similarity in the spectra of tMPEA and cMPEA indicates that the sulfur-gold bond has no effect on the spectrum, since its spectrum is different from the spectrum of the isolated MPEA.

Finally, even though the spectrum of cMPEA is not affected by the gold surface, the spectrum determined from the difference of cMPEA/AuS and BAuS indicates that cMPEA has an effect on the spectrum of the gold surface. One possible explanation is that cMPEA acts as an impurity. This is further indicated by the response function of Fig. 3.5 (right figure). Further studies will have to be conducted to determine if the spectrum of the gold surface is influenced by the inclusion of cMPEA.

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Chapter 4

Time dependent stochastic density functional theory calculations of the absorption cross section of gold nanoclusters

4.1 Introduction

Time-dependent density functional theory (TDDFT)^[1] allows for the calculations of time evolving electronic densities under timed dependent perturbations. One common use for TDDFT is the calculations of the absorption cross-section of molecules,^[2,3] which often use approximations such as adiabatic, local/semi-local exchange-correlation, or time-dependent adiabatic generalized gradient approximations.

Through multiple advancements, TDDFT has become a cost effective means for solving the spectrum of a molecule, get correlation energy correction, as well as many other applications. There are still limitations precluding traditional TDDFT calculations for large systems with thousands of electrons. One of the major issues is overcoming the quartic ($O(N^4)$) scaling in the frequency formulation, or the quadratic ($O(N^2)$) limit achieved when propagating the time-dependent Kohn-Sham (TDKS) equations.^[3-6]

Here we use time-dependent stochastic density functional theory (TDsDFT),^[7] which addresses the scaling of TDDFT by eliminating the need for using Kohn-Sham orbitals (KS orbitals) and replaces them with purified stochastic orbitals (pSO). TDsDFT approximates the time-dependent density function as an ensemble of pSO, which can be propagated similarly to traditional deterministic time-dependent orbitals. TDsDFT scales sublinearly $O(N^{0.5})$ ^[7] because fewer pSO

orbitals are needed for larger systems. For large systems, the cost is often less or much less than in deterministic TDDFT, which requires propagation of all the occupied KS orbitals.

1.1 Method

4.1.1 Stochastic Density Function Theory

The Kohn-Sham potential, $v_{KS}(r) = v_{ne}(r) + v_H[n(r)] + v_{XC}[n(r)]$, was determined using either deterministic DFT (dDFT) or stochastic DFT (sDFT),^[8] where $v_{ne}(r)$ is the nucleus-electron Troullier-Martins norm conserving pseudopotential^[9] $v_H[n(r)] = \int dr n(r)/|r - r'|$ is the Coulomb potential, and the exchange-correlation potential $v_{XC}[n(r)]$ was calculated using the local density approximation (LDA).^[11] $n(r)$ is the ground state density function.

In dDFT, the density is defined as $n(r) = \sum_{i \in occ} |\psi_i(r)|^2$, where $\psi_i(r)$ are the KS orbitals. In contrast, sDFT replaces the KS orbitals with pS orbitals,^[8] which are defined as:

$$|\xi_\mu\rangle = \sqrt{\theta_\beta(\mu - \hat{H})} |\zeta\rangle, \quad (4.1)$$

where $\zeta(r) = e^{i\phi}/\sqrt{\delta V}$, $\phi(r)$ is a random phase within the range of $[0, 2\pi]$, and δV is the volume element of the grid. $\theta_\beta(E) = (1/2)\text{erfc}(-\beta E)$ is a smooth Heaviside function, which projects $|\zeta\rangle$ onto the occupied space. The chemical potential μ , and β is a temperature such that $\beta E_g \gg 1$, where E_g is the energy bandgap. The Heaviside function projects ζ directly to occupied space using Chebyshev polynomials:^[11-14]

$$\xi(r) = \langle r | \hat{\theta}_\beta | \zeta \rangle = \sum_i^{N_c} \rho_i(\mu) \zeta_i(r), \quad (4.2)$$

where $\rho_i(\mu)$ is the Chebyshev expansion coefficient which is μ dependent, $\zeta_0(r) = \zeta(r)$, $\zeta_1(r) = \hat{H}^N \zeta_0(r)$, and $\zeta_i(r) = 2\hat{H}^N \zeta_{i-1}(r) - \zeta_{i-2}(r)$, and $\hat{H}^N = (\hat{H} - \bar{H})/\Delta H$ is the normalized Hamiltonian, where $\bar{H}$ is the average energy, and ΔH is the energy spectral range. The density function is calculated as:

$$n_\mu(r) \approx 2 \left\langle |\xi_\mu(r)|^2 \right\rangle_\zeta, \quad (4.3)$$

where $\langle \dots \rangle_\zeta$ denotes a statistical average of the pS orbitals of N_ζ stochastic orbitals. The factor of two is due to the closed-shell representation, where each orbital is occupied by two electrons. The chemical potential μ is determined as:

$$N_e = \left\langle \langle \xi_\mu | \xi_\mu \rangle \right\rangle_\zeta, \quad (4.4)$$

The generalized procedure of sDFT is then

- (i) Compute the KS potential for the density.
- (ii) Generate stochastic orbitals, in a grid (or plane wave) using $\zeta = e^{i\phi}/\sqrt{\delta V}$, then project the stochastic orbitals to the occupation space using Eq. 4.2, by using the Chebyshev polynomial.
- (iii) Determine $n_\mu(r)$ from Eq. 4.3 for several values of μ . Linearly extrapolate μ to find the correct chemical potential using Eq. 4.4.
- (iv) Reiterate until the chemical potential converges.

In practice, one uses a finite amount of stochastic orbitals, where the density function should converge to the exact density function as the number of stochastic orbitals increases, with a statistical error (SE) that is proportional to $1/\sqrt{N_\zeta}$.

In this study, we used both time dependent dDFT (TDdDFT) and time dependent sDFT (TDsDFT).

In TDdDFT, the closed shell time-dependent electronic density function is defined as:

$$n(r, t) = 2 \sum_i \psi_i(r, t), \quad (4.5)$$

where $\psi_i(r, t)$ is the time-dependent KS orbitals, the stochastic orbitals are solved as:

$$i \frac{\partial}{\partial t} \psi_i(r, t) = \hat{H} \psi_i(r, t), \quad (4.6)$$

and $\hat{H}$ is a time-dependent Hamiltonian:

$$\hat{H} = \hat{T} + v_{ne}(r) + v_{HXC}[n(r, t)]. \quad (4.7)$$

The electron-electron potential $v_{HXC}[n(r, t)] = v_H[n(r)] + v_{XC}[n(r)]$ is calculated as in DFT, and the potential is calculated at each time-step for the current electron density function. TDdDFT requires that the Kohn-Sham orbitals of the ground states are all extracted. In contrast, TDsDFT only needs the KS potential for the ground state.

Using a given initial Kohn Sham potential $v_{KS}(r)$, the electronic structure of a system at its ground state is calculated using Eq. 4.7. This purified stochastic orbital can then be used to solve for the time dependent stochastic orbital:

$$-i\hbar \frac{\partial}{\partial t} |\eta_\mu(t)\rangle = \hat{h}_{KS} |\eta_\mu(t)\rangle, \quad (4.8)$$

where the time dependent Kohn-Sham potential $\hat{h}_{KS}$ is:^[7]

$$\hat{h}_{KS}(t) = \hat{T} + v_{KS}(r) + v_{HXC}[n(r, t)] - v_{HXC}[n(r, t = 0)], \quad (4.9)$$

and $|\eta_\mu(t = 0)\rangle = |\xi_\mu\rangle$. The electronic density function is calculated as:

$$n(r, t) = 2\langle |\eta(r, t)|^2 \rangle. \quad (4.10)$$

The number of pS orbitals required to solve for TDsDFT is less than in TDDFT for large systems. TDsDFT reduces the number of propagated orbitals, and since fewer orbitals are needed for larger systems the overall cost is sublinear in system size. The general TDsDFT scheme is:

- (i) Starting from an initial Kohn-Sham potential $v_{ks}(r)$, create N_ζ stochastic orbitals using $\zeta = e^{i\phi}/\sqrt{\delta V}$, then project $\zeta(r)$ onto the occupation space using Eq. 4.2 to get $\xi(r)$.
- (ii) Excite the stochastic orbitals with a dipole disturbance.
- (iii) The propagate the stochastic orbitals; In each step:
 - a. Solve for $n(r, t)$ using Eq. 4.10.
 - b. Solve for $\hat{h}_{KS}(t)$ using Eq. 4.9.
 - c. Propagate the orbital under the instantaneous Hamiltonian.
- (iv) Repeat iii until the desired time has been reached.

The absorption spectrum is the imaginary portion of the polarizability;

$$\sigma(\omega) = \frac{e^2}{3\epsilon_0 c} \omega \text{Im} \int dr dr' r \cdot \tilde{\chi}(r, r', \omega) \cdot r' \quad (4.11)$$

where ω is the angular frequency of the absorbed photon, and $\tilde{\chi}(r, r', \omega)$ is the density susceptibility function.^[15] The susceptibility function is difficult to solve for using traditional Many body methods. An alternative is to use TDDFT. The linear response of the density function is defined as:

$$\int dr' \chi(r, r', t) v(r') = \frac{1}{\gamma} \left(n_\gamma(r, t) - n_{\gamma=0}(r, t) \right) = \Delta n(r, t), \quad (4.12)$$

where $n_\gamma(r, t)$ represents the density of a system disturbed at time by a small perturbation potential $v(r)$ for a small time γ . $n_{\gamma=0}(r, t)$ represents the unperturbed density function. The Fourier transform of $\Delta n(r, t)$ yields:

$$\int dr' \tilde{\chi}(r, r', \omega) v(r') = \frac{1}{\gamma} \left(\tilde{n}_\gamma(r, \omega) - \tilde{n}_{\gamma=0}(r, \omega) \right) = \Delta \tilde{n}(r, \omega). \quad (4.13)$$

In this study, we determine the spectra of octahedral gold nanoclusters. Using the linear density response, we can simply solve for Eq. 4.11 as:^[7]

$$\sigma(\omega) = \frac{e^2}{\epsilon_0 c} \omega \text{Im } d_{xx}(\omega), \quad (4.14)$$

where $d_{xx}(\omega)$ is the Fourier transform of the density response function:

$$d_{xx}(t) = \int d^3r x \Delta n_x(r, t). \quad (4.15)$$

The number of simulations needed is reduced because each gold nanocluster has octahedral symmetry, such that $d_{xx}(t) = d_{yy}(t) = d_{zz}(t)$, so the spectra is obtained from only one TDDFT or TDsDFT calculation.

Results and Discussion

Figure 4.1 shows the absorption cross-section of Au₄₄ using TDDFT, and TDsDFT with 256, 512, and 768 stochastic orbitals. The Kohn-Sham potential was determined using DFT. The larger the number of stochastic orbitals, the more accurate the TDsDFT is. In theory, using an infinite number of stochastic orbitals should result in a spectrum that converges to TDDFT. In practice, the number of stochastic orbitals should be large enough to give accurate results, yet smaller than the number of the occupied Kohn-Sham orbitals. 512 stochastic orbitals were used for most TDsDFT simulations because this number is a good balance between accuracy and computational cost.

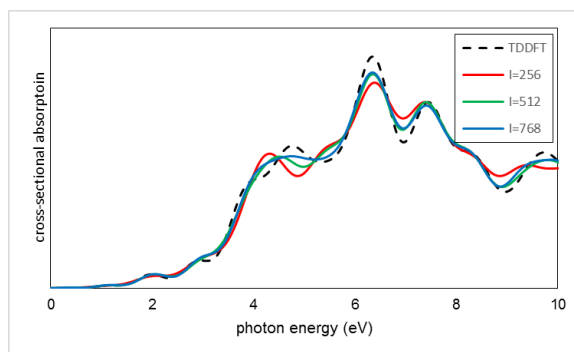


Figure 4.1. Comparison of the cross-sectional absorption for Au_{44} using TDDFT (dashed black), TDsDFT with 256 (red), 512 (green), and 768 (blue) stochastic orbitals. The Kohn-Sham potential was determined using DFT.

A study by Baer et al. has demonstrated that sDFT can often be used at a lower cost than DFT. Starting at Au_{344} , sDFT was used to calculate the Kohn-Sham potential. Figure 4.2 shows the effect that sDFT has on the spectrum. All spectra were calculated by TDsDFT with 512 stochastic orbitals. The dashed line is the spectrum using the Kohn-Sham potential, which was calculated from DFT. The red line represents the spectrum using sDFT (240 stochastic orbitals) with TDsDFT (256 stochastic orbitals). The green line represents the spectrum using sDFT (240 stochastic orbitals) with TDsDFT (512 stochastic orbitals). To prevent any variations in the spectrums, the TDsDFT was setup such that the same time-dependent stochastic orbitals were used for each simulation. The spectra for the DFT and sDFT containing 480 stochastic orbitals were closest to each other. For Au_{344} and Au_{670} , sDFT (480 stochastic orbitals) was used.

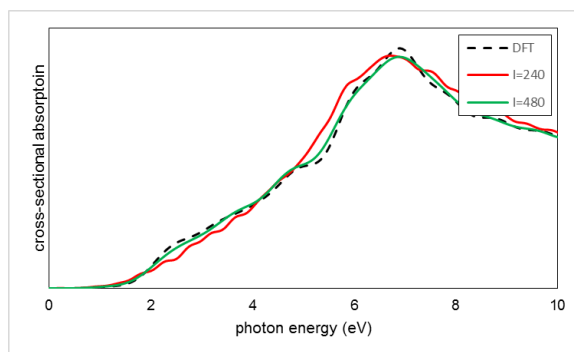


Figure 4.2. Comparison of the cross-sectional absorption for Au_{344} using TDsDFT with 512 stochastic orbitals, where the Kohn-Sham potential was determined using DFT (dashed black), and sDFT with 240 (red) and 480 (green) stochastic orbitals.

Table 1 shows the settings used to determine the final spectra. TDsDFT was used for Au_{44} and larger clusters. For the initial static portion, sDFT was used for the larger clusters, Au_{344} and Au_{670} . The temperature used for all methods was 0.03 a.u. and the grid spacing was 0.5 bohr.

Table 4.1. Parameters for each system studied				
System	grid dimensions	Method	Number of time-independent Stochastic orbitals	Number of time-dependent stochastic orbitals
Au_6	48x48x48	DFT/TDDFT		
Au_{44}	64x64x80	DFT/TDsDFT		512
Au_{146}	88x88x110	DFT/TDsDFT		512
Au_{344}	120x120x144	sDFT/TDsDFT	480	512
Au_{670}	144x144x180	sDFT/TDsDFT	480	512

The cross-sectional absorptions of all systems are shown below. As the number of gold atoms increases, the peaks become broader. Each spectrum has a peak around $\sim 6.5\text{-}7.0$ eV. As the number of stochastic orbitals increases, the accuracy increases.

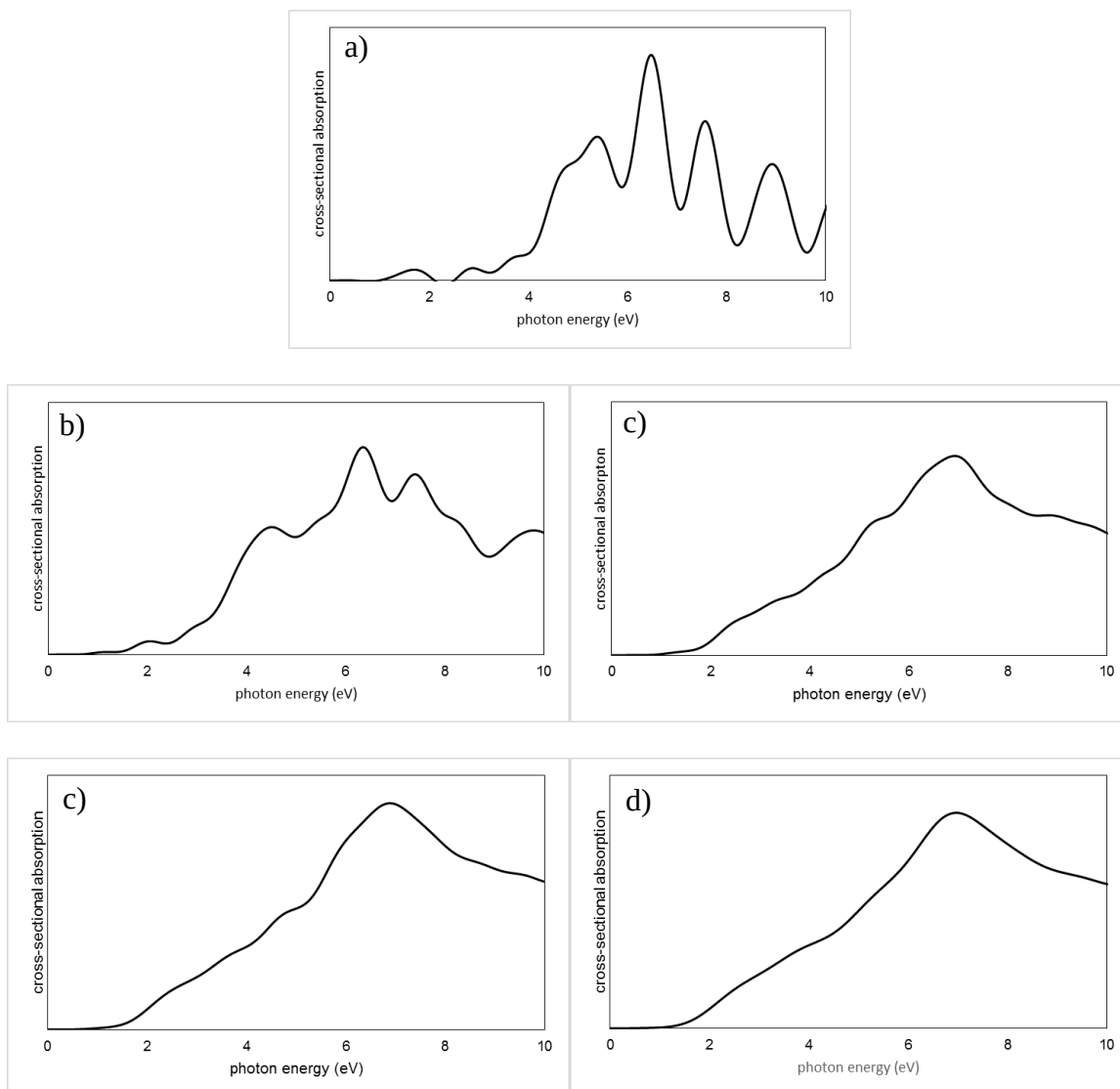


Figure 4.3. Cross sectional absorption of a) Au₆, b) Au₄₄, c) Au₁₄₆, d) Au₃₄₄, and e) Au₆₇₀ determined during this study. The method used for each molecule is explained in Table 4.1.

Conclusions

The present study demonstrates that calculating absorption cross-sections is possible with TDsDFT, and is especially advantageous for larger systems. Figure 4.1 shows the effect that the number of time-dependent stochastic orbitals have on the absorption cross section. Around 512 time-dependent stochastic orbitals are required to create a spectrum which closely resembles the DFT/TDDFT.

Spectra calculated using sDFT/TDsDFT also show promise. For systems containing thousands of electrons, DFT can be very expensive. Since TDsDFT requires only the Kohn-Sham potential of the ground state, sDFT is used for systems containing thousands of electrons. TDsDFT is applicable for systems with thousands of electrons. This study demonstrated that using a combination of sDFT and TDsDFT yields the absorption cross section for the larger gold nanoclusters, with reasonable accuracy.

In this study, we used a combination of sDFT and TDsDFT to produce accurate calculations of the absorption cross section. Figures 4.1 and 4.2 indicate the stochastic methods could reproduce results which are similar to DFT and TDDFT. The present stochastic method could be applied to even larger systems, which are very expensive to solve with conventional methods.

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