Molecular Dynamic Simulation in Organic Semiconductor Investigation

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Abstract—The details of charge transfer events inside the organic semiconductor puzzled researchers for many years. This paper focuses on the simulation method’s capability to investigate on polaron’s properties and insights about charge transfer events inside the organic semiconductors. The paper adopts a molecular dynamic simulation method called LMD simulation from the journal of chemical science to model the charge transfer between pairs of fullerene molecules. By performing the simulation, the paper analyzes and evaluates the results it gained and concludes, by showing a large-scale investigation capability and accurate details for a single event, the molecular simulation is capable to study the charge transfer events of semiconductors.

1. Introduction
Photovoltaic is an electronic device that uses photoelectrical effect to produce electricity. The invention of organic semiconductors provides new facilitation of photovoltaic. The organic semiconductor has various advantages like much lower cost, ease of fabrication process and applicability of flexible elements. However, the inefficiency of charge transfers heavily interrupts its application on the photovoltaic. To investigate the charge movement inside the organic semiconductor, in a conventional way, scientists need to solve enormous complex quantum mechanical equations. Due to the variation of circumstances, solving equations is nearly impossible in many cases. Thus, the utilization of the molecular dynamic simulation method debuts. Molecular dynamics (MD) uses computational methods to measure and simulate the physical movements of atoms and molecules in a given system for a period of time. The molecular dynamics can help researchers to investigate the properties of complex systems, reveal the systems’ evolution and simulate the condition that cannot carry out in the laboratory at a much lower cost than conventional methods and can simulate a quite large scale the experiment at the same time. In this paper, we research a special attempt that uses LMD simulation to investigate the properties of polaron, particles that formed by charges due to strong coupling with lattice degree with freedom and investigate the insights of charge transfer events between fullerene molecules to test the capability of LMD simulation in the investigation of micro molecular behaviors. Moreover, this paper also analyzes, evaluates, and compares the results of simulation with other investigation methods. By observing a great accuracy in a single event simulation and a large-scale simulation capability, this research confirms that we can utilize molecular dynamic simulation to investigate the micro properties of molecular behaviors. This outcome is beneficial because it means we can use a much lower cost and quicker time to simulate the charge transfer event inside the organic semiconductor. Thus, by applying the appropriate model, scientists can simulate the charge movement much quicker and with a significantly lower cost. Hence, researchers can advance the invention and modification of photovoltaic significantly and improve the solar power conversion rate. More importantly, this research also shows a new possibility to investigate
charge transfer events from a simpler way which can help scientists to investigate the effects of multiple parameters on the charge transfer for lower cost both in financial and time. Besides, the validity of the molecular dynamic simulation method that is certified in the paper can apply in other areas that relates to electricity. By investigating the charge transfer event inside the devices microscopically, it can provide more insights for scientists for the origin of electricity and their electrical behaviors.

2. The molecular dynamic experiment in semiconductor

2.1. The purpose and methods used in the experiment

The development of organic semiconductors is an improvement in electric engineering. Organic semiconductors can be used to manufacture flexible devices and printing technology. Nowadays, scientists are still working on the revelation of the charge transportation inside organic semiconductors. The revelation of charge transportation can help researchers to deduce the mechanism and prevail the organic semiconductors in a wide range of applications. Yet, the vast number of atoms and complex conditions inside obstruct the research. Nevertheless, an article published in the journal Chemical Science issue 4 2017 provides a new way to investigate this sophisticated process.\(^1\)

The article suggests that the development of theoretical methods that accurately models charge transport would represent a major contribution to the optimization of this promising renewable energy technology.\(^1\) The scientist group used Langevin molecular dynamics (LMD) to carry out the entire experiment. Besides, the scientists assert that they present a multiscale approach grounded in constrained density functional theory (DFT) is a type of electronic structure calculation that has rapidly gained popularity.\(^2\) (CDFT) 29 calculations.\(^1\) They present that once a set of CDFT is conducted to a potential energy surface to the LMD transfer, the process can be modeled at a negligible cost which can be helpful to simulate the transferring process easier. The scientists apply their model to phenyl-C61-butyric acid methyl ester (PCBM) molecules\(^1\) because the recent study exhibited that the excess charges will mostly locate on a single PCBM molecule.

2.2. The experiment process and results shown

The scientists’ group use 7 steps to summarize and introduce the experiment’s implementations: (1) Perform CDFT calculations, as well as unconstrained DFT calculations, to find the optimized geometries of the initial state, final state, and transition state, (2) Perform single-point CDFT calculations for a series of geometries along with the reaction coordinate. There are two sets of single-point CDFT calculations., (3) Use diabatic PESs to compute the adiabatic PESs. The lower adiabat is then used to create our PES for LMD, (4) This adiabatic PES, like the diabatic PESs, is a function of the reaction coordinate. However, we wish to obtain a pseudo-atom PES as a function of the spatial coordinate (5) Effective mass and friction are assigned, (6) The spatial-coordinate PES, the effective mass, and the friction are then used as input for our LMD simulations, (7) LMD results are then analyzed to compute charge transfer rates and examine the details of polaron movement through space.\(^1\)

First, the optimization of CDFT and reaction coordinates can illustrate the initial state and the final state of moving charge by conducting an extra charge constrained to only one of the two molecules participating in charge transfer events. Notably, the charge can be constrained to the entire PCBM molecules or only the C60 molecules. The optimized geometric graph can be represented by R which each molecule contains coordinates XYZ in PCBM molecules. The geometric graph corresponding to the reaction coordinates R is extracted from the charge transporting event including initial state(R1), transition state (Rt) and final state(R2). This gradual change can be described by the following interpolation suggested by Wu et al.;\(^3\)

\[
R_\alpha = \frac{q(q+1)}{2} R_1 - (q - 1)(q+1)R_t + \frac{q(q-1)}{2} R_2
\]  

(1)
Second, we create diabats by conducting CDFT single-point energy calculations for a series of PCBM geometries along with the reaction coordinate $R_q$. \[1\] The energy is shown by each point along the diabats. The set of nuclear positions corresponds to the charge constrained to the fullerene 1 and charge constrained to the fullerene 2.

Third, the diabats and their coupling can be used to derive adiabats (a system that cannot exchange heat with its surroundings. \[8\]) PES in LMD simulation. Because the adiabats represent a charge that gradually moves along the reaction coordinate, it is the natural choice for a PES in LMD simulation. The shapes of these diabats capture the coupling between adiabats. \[1\] A low peak is produced by a high coupling while a low coupling will produce a strong peak. A full dimensional PES is essential in the construction of a full-dimensional LMD. The scientists suggest a simple measure to obtain the full-dimensional graph. They perform an LMD simulation to simulate a charge that transfers in a straight line from one molecule to another molecule. Thus, a 1-dimensional PES can be used.

![Figure 1 The diabatic and adiabatic PES obtained from CDFT calculation \[1\]](image)

The graph shows that the initial adiabatic state energy is not equivalent to the final adiabatic state energy. This asymmetry is due to the removal of the outlying points mentioned above. The researchers mention that asymmetry is the real state that happens inside organic semiconductors because the molecules are usually in disorder inside the system. Moreover, the disorder causes a great variation in PESs between different pairs of molecules and the scientists only want to find one reasonable PES for the improvement and testification for the LMD model.

Fourth, the scientists state that converting the adiabatic coordinates to spatial coordinates is essential for an LMD simulation to indicate the movement of particles in space. First, researchers use an equation that is shown in Figure 1 to derive the reaction coordinates $R_q$ from $R_1$, $RT$ and $R_2$. Then, the researchers compute the spatial coordinates $X_{sp}$ by using multiple equations: 1. $X_{sp} = A_1 X_1 + A_2 X_2$ 2. $A_1 = C_{12}/C_{12} + C_{22}$ $A_2 = C_{22}/C_{12} + C_{22}$. $X_1$ and $X_2$ are the positions of fullerenes, $C_1$ and $C_2$ describe the contribution of each diabat to the adiabat at a given point on the reaction coordinate and $A_1$ and $A_2$ give the contributions of diabats #1 and #2 to the adiabat at each point on the reaction coordinate \[1\]. Afterwards, the adiabats PES shows as a function of space. The curve is mirrored and expanded in one-dimensional space to create a full PES for LMD simulation. The bellowing graph show specific steps to derive the full PES from optimized geometries.
Fifth, the authors propose that calculations of effective mass or friction are more challenging tasks because there are no methods for deriving mass that widely apply in organic semiconductors. Thus, scientists investigate the relationship that each variable has on the transfer rate and adopt the value of effective mass and friction that show consistency with experiment observation. Therefore, scientists could formulate the properties of quasi-particle (describes a physical concept, which treats elementary excitations in solids, like spin waves, as particles. As the particles do not consist of matter, they are called quasiparticles. [5]) from this method. The scientists use values of meff from $7.22 \times 10^{-2}$ to $7.22 \times 10^{3}$ amu $^{[1]}$. The effective mass is not the mass of electron nor the mass of nuclei. The scientists state that exploring the wide range of effective mass is essential to the development of the model and comparison to the benchmark. The friction is much more complex in this case, the scientists conclude the formula to calculate the friction $\gamma = p \gamma D$, the magnitude of $p$ is varied from $3.6, 0.36$ and $0.036$$^{[1]}$ and the $\gamma D$ is proportional to the square root of meff.

Sixth, due to the random nature of the simulation, the ensemble of orbits is essential for an accurate prediction. The researchers use the average time to obtain the rate of transfer. The velocity of molecules is distributed randomly that has a mean of 0 and standard deviation of $(KT/meff)^{0.5}$, each point in the meff/$\gamma$ parameter will perform a 500 times calculation. The calculation that has an average time shorter than 5ns will not be adopted because it corresponds to charge mobility several orders of magnitude lower than that needed for a functional OPV device $^{[1]}$.

2.3 The analysis and conclusions of the experiment
Step 7 includes the interpretation, analysis of the data and results present in the experiment. The authors divide the analysis part of the LMD result into 3 sections.

First, the scientist states that using a defined estimate rate of transfer can modify the model. Researchers use the diffusion constant of material $D=KL^2/2$ and mobility $= eD/KBT$ derive from
Einstein relation to calculate the mobility range in PCBM is from $0.001–0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$\[^6\]. The $k$ value is from $k = 5.14 \times 10^9 \text{ s}^{-1}$ to $k = 4.11 \times 10^{11} \text{ s}^{-1}$.

Second, scientists compare the results of LMD simulation with other theories. First, the researchers compare the LMD simulation results with Kramers’ theory. Figure 3 shows the results from LMD simulation and Kramers’ theory\[^1\].

The researchers suggest 2 possibilities that cause this discrepancy. First, the Kramers’ theory relied on the theory of friction, but the LMD simulation does not make any simplification of the model. Second, Kramers’ theory does not contain all information on the PES. On the other hand, LMD simulation incorporates the complete shape of all regions of the PES.

The second comparison is made between LMD simulation and Marcus theory (a method for calculating rates of electron transfer in outer-sphere processes\[^7\]). The results show a big discrepancy that the outcome of Marcus’s theory is 2 magnitudes larger than the LMD simulation. Scientists suggest that this difference is due to the rate of reorganization of polaron transfer. The Marcus theory relied on the assumption that the rate of reorganization is quicker than the rate of reaction. However, in the condition of a low reorganization rate, the accuracy of Marcus’s theory decreases rapidly.

In conclusion, researchers state that the Marcus theory is applicable in low friction conditions while Kramers’ theory is applicable in high friction circumstances. On the other hand, the LMD simulation is not constrained by the level of friction and can choose the right friction and effective mass for the experiment interest.

Last, the LMD simulation also provides an approach for scientists to investigate when and why the transfer occurs. For instance, the scientists show an experiment by using a different mass of pseudo-atom to show their discrepancy in transfer events.

The graphs exhibit below show that the pseudo-atoms with lower effective mass have a more frequent oscillation pattern and hop over the barrier slower than the pseudo-atoms with larger effective mass. In contrast, the pseudo-atoms with larger effective mass hop over the barrier quickly and have a relatively slow oscillation pattern.
Figure 4 The movement of pseudo-atoms with different effective mass in 500ps time span [1]

3. The future of semiconductor and molecular dynamics

Molecular dynamics have a serious drawback. For example, the time span is too short for an experiment. The scale of molecular dynamics is usually in nanosecond and picoseconds. Though scientists are working on it to expand the scale to a higher time level, it will at least take researchers 15 years to expand the time limit to the micrometer level. Simulations of macromolecular assembly will also extend to include very large complexes [2] due to the rapid development of computer capability.

The future of semiconductors is also promising. The development of electronics facilitates the progress of semiconductors to be cheaper, efficient, and smaller. An organic conductor is a promising area in the future. They are flexible and widely used in printing technology. Yet, the low efficiency is the main obstacle to their further development. However, by using molecular dynamics to understand the mechanism in transporting charges through the organic semiconductor. The researchers can modify and improve the conductivity of organic semiconductors significantly. Besides, organic semiconductors are manufactured with multiple ingredients and compounds to minimize their production costs, so the organic semiconductors also have a huge potential in mass-scale production.

4. Conclusion

The scientists show that the main advantage of the LMD model was it can simulate the large scale of particles at a relatively low computational cost, allowing much larger volume simulation that is intractable in other simulation methods. The scientists patch a series of one-dimensional transportation events to simulate a three-dimensional transportation event. Though, there are multiple molecules adjacent to the molecules that charge reside. However, the simulation method can predict the results by utilizing the random numbers R(t) and accepting the particle that transfers most quickly to be the new position of pseudo-atom. The scientists show that morphology should be considered. The research group acknowledges that the PES was only performed by considering the orientation between 2 molecules. Yet, the overall morphology will have an effect on the molecules’ friction and effective mass.

The scientists use the LMD model to derive the polaron motions in the organic semiconductor. They note that the interaction between charges and surrounding vibration is an active area for researchers to investigate the multiple properties of polaron in organic semiconductors. Besides, they also conclude that the low computational cost is the most important advantage of this model. At last, they admit that the transport rate of charges in organic semiconductors is the most concerning problem in the development of organic semiconductor manufacturing.

The investigation has more important meaning. The experiment successfully measures the multi parameters of the process of charge transfer inside the organic semiconductor. The high accuracy of a
single event test and the capacity of large-scale experiments prove the capability of the molecular dynamic simulation in the research of semiconductor. The lower cost and more efficient and convenient operations will enable scientists to investigate the property and invent new organic semiconductor more quickly in the future.

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