Final Report
Award DE-SC0016501

Post-Marcus Theory and Simulation of Interfacial Charge Transfer Dynamics in Organic Semiconducting Materials

Kent State University
2017-2022
(Submitted Dec. 2022)

Margaret S. Cheung[1], Barry D. Dunietz[2], Eitan Geva[3]

1. University of Washington, WA; 2. Kent State University, OH; 3. University of Michigan, MI

The goal of the research program is to develop, validate and apply predictive computational protocols for calculating charge transfer (CT) rates in complex molecular systems, including molecular dyads and triads in liquid solution and solid-state organic semiconducting (OSC) materials. We have established a transformative computational scheme, that goes beyond widely used simplifications, to achieve realistic descriptions of CT processes. The approach properly addresses the effects of molecular environment at ambient conditions on CT processes. Our approach achieves unique insight on CT processes in relevant experimental efforts.

The investigated processes span multiple scales in space and time, a challenge that we have overcome by developing an integrative approach. The collaborative team includes three principal investigators (PIs), with complimentary expertise in classical molecular dynamics (MD) simulations and data science (Cheung), state-of-the-art electronic structure calculations (Dunietz), and cutting-edge theory and simulation techniques for modeling energy, charge and coherence transfer dynamics in molecular systems (Geva). The computational efforts are pursued in collaborations with relevant experimental studies of material design, device fabrication and spectroscopy studies. See the general framework of the collaborative activity introduced in Figure 1.

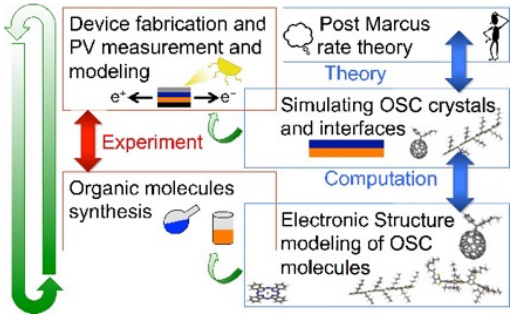

Figure 1: A multiscale and multi PI computational program to investigate charge transfer and transport in experimentally relevant molecular interfaces. Our program combines state-of-the-art electronic structure calculations, molecular dynamics simulations in the framework of quantum dynamical hierarchy of approaches with direct interpretation of experimental efforts pursued by external collaborators performing spectral studies, material design and synthesis and optoelectronic device measurements.

Our framework to calculated rates is guided by the working hypothesis that a detailed understanding of the relationship between CT rates and the underlying molecular and electronic structure is key to improving the efficiency in derived applications. The level of complexity and inherent heterogeneity of OSC materials necessitates a multiscaling approach. More specifically, we combine MD simulations for determining interfacial structures and the distributions of donor-acceptor (D-A) geometries they give rise to, electronic structure calculations for determining ground and excited state energies, charge distributions, and electronic coupling coefficients, and feasible, robust and transferable rate theory and simulation techniques for calculating CT rates from ab-initio and MD inputs. Here we briefly outline several advances achieved by our computational research program:

In one thrust, we developed a polarization consistent electronic structure framework, where we combine range-separated hybrid (RSH) functionals with polarizable continuum model (PCM). Our approach achieves physically relevant frontier orbitals with electron removal and addition energies that reproduce well measured energies in the condensed phase. The success stems from invoking the same

dielectric screening in the long-range part of the functional as invoked in the PCM treatment. In Figure 2 we demonstrate the success of our approach by following averaged energies over a benchmark set of molecular crystals, where our screened RSH-PCM (SRSH-PCM) frontier orbital energies are in excellent agreement with the measured ionization potentials (IPs) and electron affinities (EAs). *J. Chem. Theory Comput.* **14** (2018) 6287). SRSH-PCM was benchmarked in studying CT (*J. Chem. Theory Comput.* **15** (2019) 4305), and triplet (*J. Chem. Theory Comput.* **16** (2020) 3287) excitations and in several spectral studies of various chromophores. Recently it was employed successfully in the context of quantum embedding in studying the optical gap of cis-trans isomers of solvated azobenzene derivative (*J. Phys. Chem. Lett.* **13** (2022) 4849).

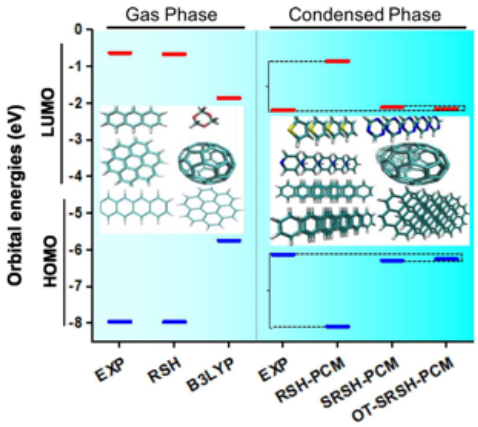

Figure 2: Averaged frontier orbital (HOMO and LUMO) energies, in eV, calculated in the gas phase and in various combinations with a PCM compared to the averaged benchmark IP and EA energies in gas and thin-film forms (Exp.). The SRSH-PCM and OT-SRSH-PCM present excellent agreement with the measured values in the crystal phase (*J. Chem. Theory Comput.* **14** (2018) 6287). Followup benchmark studies show the success of the SRSH-PCM framework in calculating charge transfer states ((*J. Chem. Theory Comput.* **15** (2019) 4305), and triplet excitations (*J. Chem. Theory Comput.* **16** (2020) 3287).

In the second thrust, we develop and implement a hierarchy of approximations based on the linearized semiclassical (LSC) method for CT rate constants in complex molecular systems. In particular the triad system is used to test our LSC hierarchy of methodologies that range from a semi-classical (Marcus-like approach) to a Fermi-Golden rule level, where the molecular environment is probed by MD simulations. Our approach combines all-atom molecular dynamics simulations with explicit solvent and electronic-state-specific force fields. The validity of the second-order cumulant approximation, which leads to a Marcus-like expression for the rate constant is established by comparing the rate constants calculated with and without resorting to this approximation. We also studied the CT process in the triad with a non-equilibrium extension of the Fermi golden rule rate expression introducing an instantaneous Marcus expression to describe evolving rates following a perturbation representing electronic state population induced by photoexcitation (*J. Phys. Chem. B*, **124**, (2020) 9579). See the results summarized in Figure 3.

We reported several additional new tools for modeling quantum dynamics that go beyond the perturbative equilibrium Fermi's golden rule level. One such tool is the generalized quantum master equation (GQME), which allows to simulate the CT dynamics for electronic

coupling of arbitrary strength (*J. Chem. Phys*., **160** (2019) 034101). Another such tool is based on representing the electronic degrees of freedom in terms of mapping variables with a well defined classical limit and simulating the dynamics of the overall (electronic + nuclear) system within the framework of LSC. (*J. Chem. Phys*., **151** (2019) 074103.)

In the third research thrust, we developed and implemented the computational framework to study CT processes in systems related to actual experiments. For example, in considering the interface of SubPC and C_{60}, D-A materials that are widely studied, we resolve the molecular interfaces and describe their effect on CT rates using the newly developed computational framework. (*Phys. Rev. App.* **13** (2020) 054075). In Figure 4 we introduce the algorithmic workflow as implemented by CTRAMER an open source software package that takes as input atomic coordinates of the considered materials and generates a distribution of CT rates in the condensed phase consisting of thin films made of the same organic materials (J. Chem. Phys. **154** (2021) 214108).

Using the computational tool, we benchmarked the choices of the density functional and of the force field, finding that a range-separated hybrid functional provides superior performance in reproducing experimental CT rates, whereas employing B3LYP appears to overstate the importance of selecting a polarizable force field to represent the molecular environment (J. Chem. Theory Comput., **16** (2020) 6481).

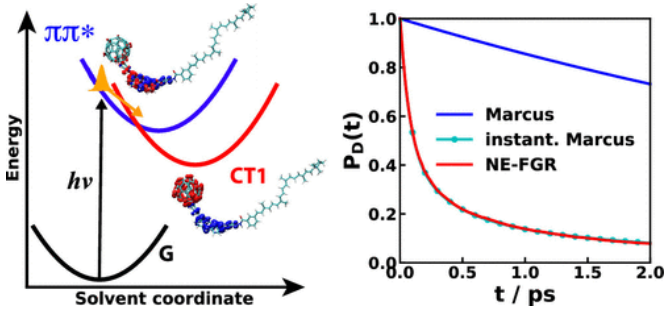

Figure 3: In earlier work a Marcus-like expression, based on the second order cumulant approximation, was validated for an experimentally-relevant triad system. Strong dependence of CT dynamics on the triad' s conformation is demonstrated, where the bent→linear conformational change is found to the rate-determining step for CT in this system. The CT in the solvated molecular triad was found to be driven by the solvent, which highlights the important role that interactions with the host can have on CT kinetics. (*J. Phys. Chem. C*. **122** (2018) 11288-11299). Here we extend the formulation to non-equilibrium form of Fermi Golden rule and introduce an instanteous Marcus rate expression.

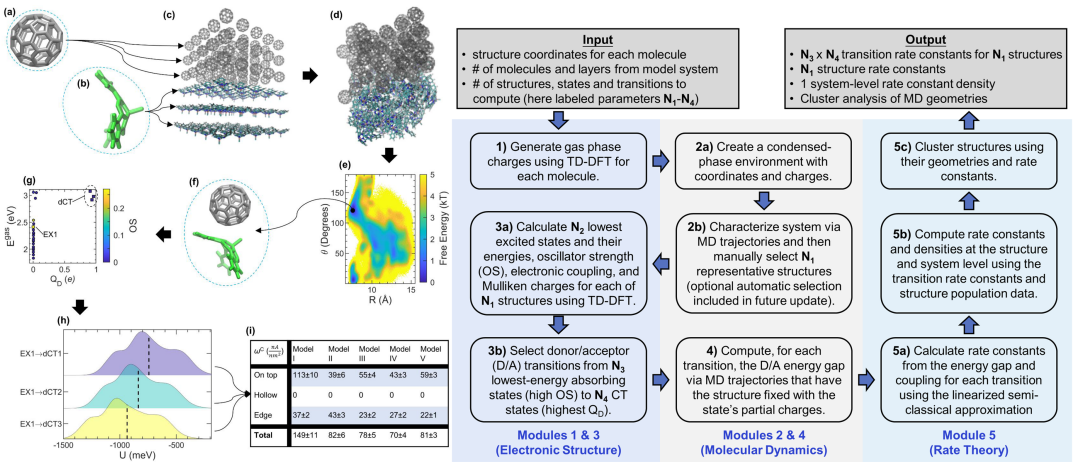

Figure 4: CTRAMER: A software package to calculate the interfacial charge transfer rates demonstrated on thin films consisting of SubPC-C_{60}.

Grants: DE-SC0004924, DE- FG02-10ER16174, and DE-SC0016501

Postdoc(s): Alexander Schubert, Atsushi Yamada, Qinguo Feng, Arun Manna, Huseyin Aksu, Buddhadev Maiti, Jaebeom Han, Pengzhi Zhang, Xing Gao, Chandrima Chakrabarty, Bikash Mandal

Student(s): Srijana Bhandari, Jacob Tinnin, Ellen Mulvihill, Yudan Liu, Khadiza Begam

Products, peer-reviewed publications acknowledging the award:

1. Solvent Dependent Nuclear Magnetic Resonance Molecular Parameters Based on a Polarization Consistent Screened Range Separated Hybrid Density Functional Theory Framework K Begam, L Cohen, G Goobes, BD Dunietz J. Chem. Theory Comput. **18** (2022) 5259-5266 https://doi.org/10.1021/acs.jctc.2c00275

2. Role of Dielectric Screening in Calculating Excited States of Solvated Azobenzene: A Benchmark Study Comparing Quantum Embedding and Polarizable Continuum Model for representing the solvent C Chakravarty, H Aksu, JA Martinez B, P Ramos, M Pavanello, B. D. Dunietz *J. Phys. Chem. Lett.* , **13** (2022) 4849 https://doi.org/10.1021/acs.jpclett.2c00982

3. Correlating Interfacial Charge Transfer Rates with Interfacial Molecular Structure in the Tetraphenyldibenzoperiflanthene/C70 Organic Photovoltaic System J. Tinnin, S. Bhandari, P. Zhang, E. Geva, B. D. Dunietz, X. Sun, M. S. Cheung *J. Phys. Chem. Lett.* , **13** (2022) 763 https://doi.org/10.1021/acs.jpclett.2c00982

4. Enhancing fluorescence and lowering the optical gap through C=P doping of a pi-conjugated molecular backbone: A computational-based design approach
S. Sarkar, P. Durairaj, J. D. Protasiewicz, B. D. Dunietz *J. Photochem. Photobio*. **8** (2021) 100089 https://doi.org/10.1016/j.jpap.2021.100089

5. Electronic Spectra of C-60 Films Using Screened Range Separated Hybrid Functionals Chandrima Chakravarty, Huseyin Aksu, Buddhadev Maiti, Barry D. Dunietz, *J. Phys. Chem. A.* , **125** (2021) 7625 https://doi.org/10.1021/acs.jpca.1c04908

6. Intersystem Crossing in Tetrapyrrolic Macrocycles. A First-Principles Analysis
Srijana Bhandari, Sunandan Sarkar, Alexander Schubert, Atsushi Yamada, Jameson Payne, Marcin Ptaszek, Eitan Geva, Barry D. Dunietz, *J. Phys. Chem. C*. **125** (2021) 13493-13500 https://doi.org/10.1021/acs.jpcc.1c03696

7. Three-state harmonic models for photoinduced charge transfer
Dominikus Brian, Zengkui Liu, Barry D. Dunietz, Eitan Geva, and Xiang Sun *J. Chem. Phys*. **154** (2021) 174105 https://doi.org/10.1063/5.0050289

8. Heat flow enhancement in a nanoscale plasmonic junction induced by Kondo resonances and electron-phonon coupling Hussyein Aksu, Barry D Dunietz Ali Goker *Physica E: Low-dimensional Systems and Nanostructures* **127** (2021) 11453 https://doi.org/10.1016/j.physe.2020.114536

9. Achieving Predictive Description of Negative Differential Resistance in Molecular Junctions Using a Range-Separated Hybrid Functional Srijana Bhandari, Atsushi Yamada, Austin Hoskins, Jameson Payne, Huseyin Aksu,and Barry D. Dunietz Adv. Theory Simul., (2021) 200016 https://doi.org/10.1002/adts.202000016

10. CTRAMER: An open source software package for correlating interfacial charge transfer rate constants with donor/acceptor geometries in organic photovoltaic materials J Tinnin, H. Aksu, Z. Tong, P. Zhang, E. Geva, B. D. Dunietz, X. Sun, M. S. Cheung *J. Chem. Phys.,* **154** (2021) 214108 https://doi.org/10.1063/5.0050574

11. Cyanide Bridged Platinum-Iron Complexes as Cisplatin Prodrug Systems: Design and Computational Study Ariela W. Kaspi-Kaneti, Srijana Bhandari, Alexander Schubert, Songping Huang, Barry D Dunietz *ChemPhysChem* **22** (2020) 106 https://doi.org/10.1002/cphc.202000748

12. Photoinduced Charge Transfer in Zn(II) and Au(III)-Ligated Symmetric and Asymmetric Bacteriochlorin Dyads: A Computational Study Aksu, H. and Maiti, B. and Ptaszek, M. and Dunietz, B. D. *J. Chem. Phys.* **153** (2020) 134111 https://doi.org/10.1063/5.0023609

13. Photoinduced Charge Transfer Dynamics in the Carotenoid–Porphyrin–C60 Triad via the Linearized Semiclassical Nonequilibrium Fermi's Golden Rule Z. Hu, Z. Tong, M. S. Cheung, B. D. Dunietz, E. Geva, X. Sun *J. Phys. Chem. B*, **124** (2020) 9579 https://doi.org/10.1021/acs.jpcb.0c06306

14. How Well Does a Solvated Octa-acid Capsule Shield the Embedded Chromophore? A Computational Analysis Based on an Anisotropic Dielectric Continuum Model Huseyin Aksu, Suranjan K. Paul, John M. Herbert, and Barry D. Dunietz *J. Phys. Chem. B* **124** (2020) 6998 https://doi.org/10.1021/acs.jpcb.0c04032

15. On the Interplay Between Electronic Structure and Polarizable Force Fields When Calculating Solution-Phase Charge Transfer Rates J. Han, P Zhang, H. Aksu, B. Maiti, X. Sun, E. Geva, B. D. Dunietz, M. S. Cheung, *J. Chem. Theory Comput*., **16** (2020) 6481 https://doi.org/10.1021/acs.jctc.0c00796

16. Charge Transfer Rate Constants for the Carotenoid-Porphyrin-{C60} Molecular Triad Dissolved in Tetrahydrofuran: {The} Spin-Boson Model vs the Linearized Semiclassical Approximation Z. Tong, X. Gao, M. S. Cheung, B. D. Dunietz, E. Geva, X. Sun, *J. Chem. Phys*., **153** (2020) 044105 https://doi.org/10.1063/5.0016160

17. Discovery and characterization of an acridine radical photoreductant A. MacKenzie, L. Wang, N. P. R. Onuska, O. F. Williams, K. Begam, A. M. Moran, B. D. Dunietz & D. A. Nicewicz, *Nature*, **580** (2020) 76-80. https://doi.org/10.1038/s41586-020-2131-1

18. Molecular-Level Exploration of the Structure-Function Relations Underlying Interfacial Charge Transfer in the Subphthalocyanine C_{60} Organic Photovoltaic System J. Tinnin, S. Bhandari, P. Zhang, H. Aksu, B. Maiti, E. Geva, B. D. Dunietz, X. Sun, M. S. Cheung *Phys. Rev. App.,* **13** (2020) 054075. https://doi.org/10.1103/PhysRevApplied.13.054075

19. Efficient Charge Generation via Hole Transfer in Dilute Organic Donor–Fullerene Blends Y. Song, A. Schubert, X. Liu, S. Bhandari, S. R. Forrest, B. D. Dunietz, E. Geva, J. P. Ogilvie *J. Phys. Chem. Lett.,* **11** (2020) 2203-2210 https://doi.org/10.1021/acs.jpclett.0c00058

20. Screened Range-Separated Hybrid Functional with Polarizable Continuum Model Overcomes Challenges in Describing Triplet Excitations in the Condensed Phase Using TDDFT K. Begam, S. Bhandari, B. Maiti, B. D. Dunietz *J. Chem. Theory Comput.,* **16** (2020) 3287. https://doi.org/10.1021/acs.jctc.0c00086

21. On the Role of the Special Pair in Photosystems as a Charge Transfer Rectifier Aksu, H. and Schubert, A. and Bhandari, S. and Yamada, A. and Geva, E. and Dunietz, B. D. *J. Phys. Chem. B.*, **124** (2020) 1987 https://doi.org/10.1021/acs.jpcb.9b11431

22. Combining the mapping Hamiltonian linearized semiclassical approach with the generalized quantum master equation to simulate electronically nonadiabatic molecular dynamics Mulvihill, E. and Gao, X. and Liu, Y. and Schubert, A. and Dunietz, B. D. and Geva, E. *J. Chem. Phys.*, **151** (2019) 074103 https://doi.org/10.1063/1.5110891

23. Quantitative Accuracy in Calculating Charge Transfer State Energies in Solvated Molecular Dimers Using Screened Range Separated Hybrid Functional Within a Polarized Continuum Model Bhandari, S. and Dunietz, B. D. *J. Chem. Theory Comput*, 15 (2019) 4305 10.1021/acs.jctc.9b00480

24. A modified approach for simulating electronically nonadiabatic dynamics via the generalized quantum master equation *J. Chem. Phys.* **150,** (2019) 034101 Ellen Mulvihill, Alexander Schubert, Xiang Sun, Barry D. Dunietz, and Eitan Geva https://doi.org/10.1063/1.5055756

25. Vibronic Structure of Photosynthetic Pigments Probed by Polarized Two-dimensional Electronic Spectroscopy and ab initio Calculations Song, Y. and Schubert, A. and Maret, E. and Burdick, R. K. and Dunietz, B. D. and Geva, E. and Ogilvie, J. P. *Chem. Sci.,* **10** (2019) 8143 10.1039/C9SC02329A

26. Gecko: Hierarchical heterogeneous portable shared memory abstraction M. Ghane, S. Chandrasekaran, M. S. Cheung, PMAM'19: Proceedings of the 10th International Workshop on Programming Models and Applications for Multicores and Manycores (2019) 21-30 10.1145/3303084.3309489 https://doi.org/10.1145/3303084.3309489

27. Pointerchain: Tracing Pointers to Their Root M. Ghane, M. S. Cheung, S. Chandrasekaran Parallel Computing **85** (2019) 190 https://doi.org/10.1016/j.parco.2019.04.007

28. Fundamental Gaps of Condensed-Phase Organic Semiconductors from Single-Molecule Calculations using Polarization-Consistent Optimally Tuned Screened Range-Separated Hybrid

Functionals S. Bhandari, M. Cheung, E. Geva, L. Kronik, and B. D. Dunietz *J. Chem. Theory Comput* **14** (2018) 6287 10.1021/acs.jctc.8b00876

29. Computational Study of Charge-Transfer Dynamics in the Carotenoid–Porphyrin–C60 Molecular Triad Solvated in Explicit Tetrahydrofuran and Its Spectroscopic Signature Xiang Sun, Pengzhi Zhang, Yifan Lai, Kyle L. Williams, Margaret S. Cheung, Barry D. Dunietz, and Eitan Geva *J. Phys. Chem. C.*, **122** (2018) 11288 10.1021/acs.jpcc.8b02697

30. A Comparative Study of Different Methods for Calculating Electronic Transition Rates Alexei A. Kananenka, Xiang Sun, Alexander Schubert, Barry D. Dunietz, and Eitan Geva *J. Chem. Phys.* , **148** (2018) 102304 10.1063/1.4989509

31. Conductance of junctions with acetyl-functionalized thiols: A first-principles-based analysis.
    A. Yamada, Q. Feng, Q. Zhou, A. Hoskins, K. M. Lewis, and B. D. Dunietz *J. Phys. Chem. C.*, **121** (2017) 10298 10.1021/acs.jpcc.7b02009

32. Enhancing charge mobilities in organic semiconductors by selective fluorination: a design approach based on a quantum mechanical perspective Buddhadev Maiti, Alexander Schubert, Sunandan Sarkar, Srijana Bhandari, Kunlun Wang, Zhe Li, Eitan Geva, Robert J. Twieg, and Barry D. Dunietz *Chem. Sci.* **8** (2017) 6947 10.1039/c7sc02491f