Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

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This project worked towards developing a predictive and practical method for electron-ion dynamics, to model processes involved in solar energy conversion, using time-dependent density functional theory (TDDFT) for electrons, and semiclassical dynamics for nuclei, capturing trajectory branching and relaxation in a more theoretically sound way than current methods. Properties of the exchange-correlation functional required for full transfer of charge, as opposed to merely a calculation of charge-transfer excitation spectra, were identified and, dynamical steps in the potential were found that are missing in all currently used approximations. These features, hard to model in approximations, can be dampened with a judicious choice of initial Kohn-Sham state. We found a new exact condition on the exchange-correlation functional that has general implications for dynamics. When a field driving a system is turned off, the Kohn-Sham potential typically continues evolving, yielding time-dependent Kohn-Sham frequencies. The exchange-correlation kernel must cancel this time-dependence, yielding an exact condition, but this is typically violated by approximations. The violation is behind inaccuracies in the predictions of dynamics, and suggests that the condition should be imposed in some way. With regards to the coupling to nuclear motion, we have begun to develop a formalism based on the "exact factorization" approach, which gives rigorous expressions for the forces acting on nuclei when coupled to electronic dynamics. In any practical approach, these forces need to be approximated, and we used simple models of charge-transfer dynamics for which exact solutions are available, to find features of the exact potential that correctly approximate such non-adiabatic effects. Some features resemble forces in surface-hopping but our approach overcomes the over-coherence problems that surface-hopping suffers from. These models will be used to validate the mixed semiclasssical-quantum approach we are developing. The kind of fundamental research described above is important for building reliable and practical methods for energy materials discovery.

Several postdocs were trained under this grant, providing salary for Johanna Fuks, as well as for Ali Abedi and Elham Khosravi on a shorter term. The funding provided by the grant enabled the PI, postdocs, and students in the group to present our results at many national and international conferences, to hold mini-workshops at CUNY with other researchers working in non-adiabatic dynamics, and to host a visit from collaborators Michael Ruggenthaler (Vienna) and Robert van Leeuwen (Jyväskyla).

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4. E. Khosravi, A. Abedi, and N. T. Maitra, *The exact potential driving the electron dynamics in enhanced ionization,* Physical Review Letters **115** (2015).
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