Photoreactions With Quantum Treatment of Coupled Electronic, Photonic, and Nuclear Degrees of Freedom

Landon Johnson[1,2], Dmitri Kilin[3]

[1]North Dakota State University, Materials and Nanotechnology Program

[2]North Dakota State University, Department of Mathematics

[3]North Dakota State University, Department of Chemistry and Biochemistry

The goal of this project is to create distributable software capable of simulating photoreactions. This software will treat the electronic, photonic, and nuclear degrees of freedom quantum mechanically, while including coupling between all of them. We expect this to be a useful way to explore photochemistry and thereby how to bypass activation barriers during reactions. For example, this software will be directly applicable to laser assisted chemical vapor deposition (LCVD) processes as well as the study of exciton and phonon polaritons[1]. Our plan of implementation is based on reducing the dimensionality of our system and rigorously testing each individual component under our developed regime, e.g. reducing spatial dimensions to an internuclear distance, using radial vs. plane-wave basis sets for electronic wavefunctions, etc. As this project lies largely in uncharted territory, it is currently unclear what the "best" approaches are. Once we have individual pieces working, we will combine them and continue testing in order to assess the accuracy and computational speed of various approximations and numerical methods so that we may document the effectiveness of various approaches. We are currently developing the capability to model H_2^+ inside of an optical resonator. Even with the symmetry of this system, it still presents several challenges. For example, the phase accumulation for off-resonant subsystems require very fine time steps for dynamical systems. Unless this software becomes surprisingly efficient, it will be necessary to devise a reasonable approximation to track this accumulation over larger time steps. Another challenge comes from the fact this this software will ultimately be utilizing dissociative potentials, which renders the eigenvalue approach unusable. When the software can sufficiently handle such a symmetric system, we will move on to break the symmetry in various ways that test how well our methods can be generalized to more complicated systems. This will include asymmetric diatomic molecules and molecules with more than two atoms such as $LaCp_3$, which are of particular interest to LCVD. Such expansions to this software will also be applicable to modeling chemical lasers such as HF and photoisomerization processes.

This research is supported by NSF CHE-1944921

(1) Hu, D.; Mandal, A.; Weight, B. M.; Huo, P. Quasi-Diabatic Propagation Scheme for Simulating Polariton Chemistry. *The Journal of Chemical Physics* **2022**, *157* (19), 194109. https://doi.org/10.1063/5.0127118.