Dark Doubly Excited States and Non-adiabatic Mixed Quantum-Classical Dynamics: New Frontiers for Equationof-motion Coupled Cluster Methods

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The coupled cluster method and its excited state extension, equation-of-motion coupled cluster (EOM-CC) are benchmark methods for studying energies and other properties of small molecular systems. However, there are still many challenges to overcome, including high computational expense and the treatment of strongly correlated systems. In this talk, I will present our work on two such challenges in treating excited states using the EOM-CC family of methods. One is the treatment of states that are not of dominant single excitation character; in such cases, EOM-CCSD fails to provide a reliable calculation of excitation energies. We present an assessment of the performance of the newly introduced EOM-DCSD and pair CCD-based tailored coupled cluster.

In the second part of this talk, we present results from a joint experimental-theoretical study on ultrafast photofragmentation of dimethyl disulphide which is one of the smallest organic molecule with a sulphur-sulphur bond and serves as a model to study the stability of proteins in the presence of UV light. The theoretical study we present complements ultrafast electron diffraction experiments performed at the Linac Coherent Light Source, Stanford to study the non-adiabatic dynamics of dimethyl disulfide after photoexcitation at 200 nm. We employ nonadiabatic mixed quantum-classical (NA-MQC) dynamics with trajectory surface hopping, including spin-orbit coupling. Our joint theoretical and experimental study charts the intricate dynamics of this model system with disulfide linkage and proposes novel excited state pathways to fragmentation, including ultrafast intersystem crossing.

References

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