Time-dependent Vibrational Electronic Coupled Cluster (VECC) theory for the non-adiabatic nuclear dynamics

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Non-adiabatic dynamics is associated with many photo-electron chemical processes where the nuclear wavefunction is strongly coupled with the electronic wavefunction near the conical intersection of the potential energy surface (PES). In this work we present the Vibrational Electronic Coupled Cluster (VECC) method which provides a compact time-dependent representation of the wavefunction for non-adiabatic vibronic models. The wave function is parameterize using a second quantized representation for the vibrational degrees of freedom, and diabatic electronic labels. This representation can be used to calculate time-correlation functions and hence vibronic spectra. This work builds on the general formulation of the Thermal Normal Ordered Exponential (TNOE) ansatz [1]. By introducing this compact representation, the time-dependent and thermal properties can be determined by solving a set of coupled cluster equation of motions (CC-EOMs). The computational complexity to solve the CC-EOMs has a polynomial scaling as the number of the normal mode of the vibronic models. In this way, our approach is more efficient comparing to the conventional basis set based approaches that have an exponential scaling.

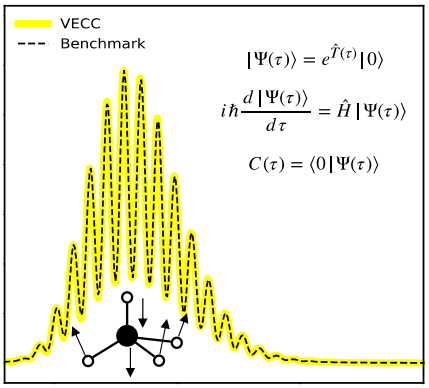

Illustration of the VECC method

[1] M. Nooijen; S. Bao; *molecular physics,* **119**, 21-22, (2021)