Absorption Spectra and Thermal Properties for non-adiabatic systems using Vibrational-Electronic Coupled Cluster Theory (VECC)

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A general discussion of the calculation of thermal properties and time-dependent properties will be presented, for both electronic and vibronic problems. Two related approaches are considered: Normal ordered exponentials (NOE) and Thermofield approaches. Both approaches share an exponential ansatz in second quantization. The NOE approach uses both annihilation and creation operators, which are not (anti)commuting, and normal ordering is vital. In thermofield approaches an ancillary space is introduced and one can formally use single reference like Couped Cluster approaches to evolve a state in the combined (fictitious) Hilbert space.

The approach is developed for non-adiabatic vibronic problems for which second quantization is highly effective for bosonic degrees of freedom and no basis set needs to be introduced. The so-call Vibrational-Electronic Coupled Cluster (VECC) approach allows calculation of vibronic spectra from time-correlation functions and thermal averages using methods that essentially scale like classical (non-quantum) approaches.

The VECC approach in a Singles-Doubles-Triples truncation is mature for vibronic problems and can be applied to large molecules (e.g. 50 normal modes) and a fair number of coupled electronic states (e.g. 10). To date this is our most successful application of the general theory. Applications to thermal free energies for non-adiabatic manifolds will be discussed also.