VISTA Seminar

Seminar 78

October 30, 2024

10:00 am – 11:30 am EDT / 2:00 – 3:30 pm GMT London / 3:00 pm – 4:30 pm CET Paris / 10 pm – 11:30 pm CST Beijing

TOC:

Light emission in real-time molecular simulations

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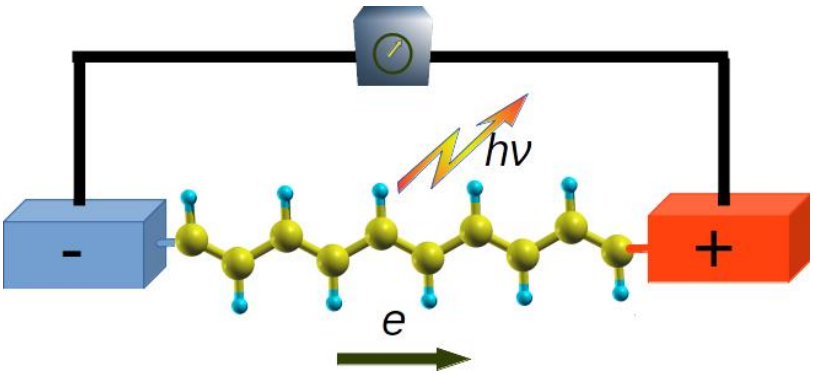

Electron dynamics methods for molecules and materials typically neglect electromagnetic emission: the radiative decay of an excited electronic state is not considered in usual treatments. In this talk we will present two approaches to this phenomenon. On one hand, a Lagrangian formulation where the radiation of the electronic density is approximated as the power emitted by a classical dipole, leading to a semiclassical dissipative equation of motion that quantitatively captures decay rates, natural broadening, and absorption intensities. On the other hand, we will introduce a Redfield type equation based on quantum-electrodynamics (QED), in which the evolution of the single-particle density matrix is coupled to a photon bath. Remarkably, one of the driving terms present in the QED equation of motion exactly matches the driving term of the semiclassical approximation. This coincidence highlights the missing piece in the semiclassical scheme, portraying two regimes: (i) weakly excited systems, where semiclassical dynamics dominate and emission power is controlled by the coherences; and (ii) strongly excited systems or eigenstates, where a full quantum treatment is mandatory to recover the power, controlled by the populations. We will show applications of these formalisms to model the electroluminescence of semiconducting polymers, and collective optical phenomena in molecules, as superradiance and subradiance.

References:

[1] *Phys. Rev. Lett.* 126, 087401 (2021)
[2] *J. Phys. Chem. Lett.* 13, 11601 (2022)
[3] *J. Chem. Phys.* 160, 214102 (2024)
[4] Tarasi, Todorov, Bustamante, Gadea, Stella, Apostolova, Scherlis, *under review in J. Chem. Phys.*

Simulating quantum dynamics and thermal equilibrium properties of vibronic coupling systems using the vibrational electronic coupled cluster (VECC) approach

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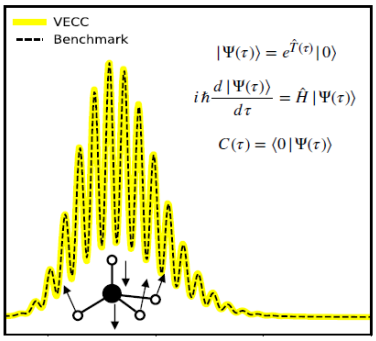

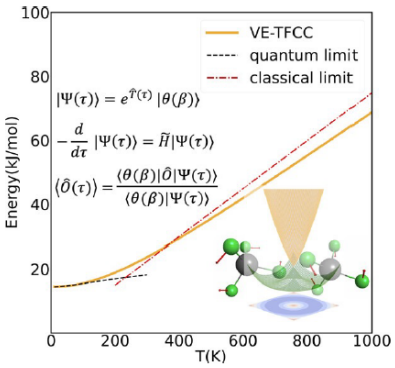

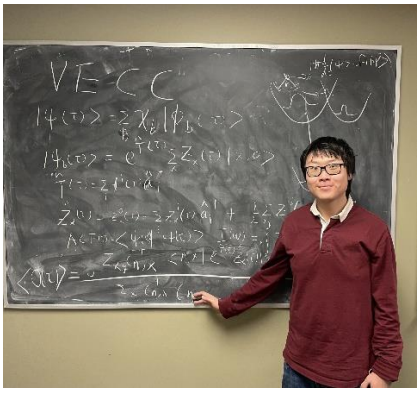

In this talk, I will introduce a novel class of methods called Vibrational Electronic Coupled Cluster (VECC) for simulating the quantum dynamics and thermal equilibrium properties of vibronic coupling systems.[1,2] This approach is based on the more general Thermal Normal Order Exponential (TNOE) framework, rooted in the quantum field theoretical formulation of statistical mechanics.[3] The core idea involves using a second quantized exponential ansatz to heuristically approximate the thermal state or time-dependent wavefunction, similar to the conventional coupled cluster method used for ground state electronic structures.

The thermofield formulation is utilized to represent the thermal state as a ”pure state” in a physical-ancillary dual space, and a Bogoliubov transformation is introduced to formulate the approach single-reference-like. I will demonstrate that the real-time formulation of this method effectively simulates non-adiabatic nuclear dynamics, including spectroscopy and diabatic state populations, with impressive efficiency and accuracy. Additionally, the imaginary time formulation, termed Vibrational Electronic-Thermofield Coupled Cluster (VE-TFCC), offers enhanced efficiency and accuracy in simulating the thermal properties of vibronic coupling systems compared to conventional methods.

Furthermore, I will discuss recent developments, including the use of GPU acceleration to enhance computational performance and the extension of the approach to incorporate finite temperature effects in spectroscopy simulations.

References:

[1] S. Bao, N. Raymond, M. Nooijen, J. Chem. Phys 160, 9 (2024).
[2] S. Bao, N. Raymond, T. Zeng, M. Nooijen, J. Chem. Theory Comput 20 14 (2024).
[3] M. Nooijen, S. Bao, Mol. Phys. 119 21-22 (2021).

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 78
Time: Oct 30, 2024 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting
https://buffalo.zoom.us/j/92579808027?pwd=0jx8AfN2KlENgYw6qaMpFAB0X2vxli.1

Meeting ID: 925 7980 8027
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