VISTA Seminar

Seminar 2

10:00 – 11:30 am EDT / 2:00 – 3:30 pm GMT

TOC:

Ehrenfest Dynamics with Decoherence and Detailed Balance

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Abstract The Ehrenfest (mean-field) method provides one the most fundamental and simplest descriptions of quantum-classical dynamics. Based on the Ehrenfest theorem [1] of quantum mechanics, which shows that quantum expectation values follow classical-like equations of motions, the method couples classical variables to quantum averages; hence, the mean-field nature of the approximation. The Ehrenfest method has been derived in multiple ways, tested with various models and applied to numerous systems. (A small number of references on the derivation is provided here [2-11].) Applications to condensed phase and nanoscale problems has identified two major deficiencies of the Ehrenfest approach, i.e. lack of detailed balance [12] and decoherence. Detailed balance between transitions upward and downward in energy ensures that the system reaches Boltzmann equilibrium in the long-time limit. This is essential for studying relaxation dynamics in large systems. Decoherence is important to obtain correct transition rates [13]. If a quantum system, e.g. electrons, is coupled to a quantum bath, e.g. vibrations, the system loses coherence between superpositions of quantum states. This effect is missing if the bath is treated classically. Decoherence can be incorporated into the Ehrenfest method stochastically, leading to surface hopping (SH) type dynamics [14-15]. SH is also known to satisfy detailed balance [16]. However, SH requires sampling of multiple stochastic realizations, which creates significant computational cost, especially in large systems. In comparison, the Ehrenfest method is fully deterministic, and therefore, requires about two orders of magnitude fewer trajectories than SH. The talk will discuss our "Ehrenfest with decoherence and detailed balance" (Ehrenfest-DDB) method [17]. Decoherence is included using the coherence penalty functional approach [18], with the decoherence rates estimated as pure-dephasing times of the optical response theory [19]. Detailed balance is introduced using a nonlinear modification of the Schrodinger equation [20] with the nonadiabatic couplings scaled according to a semiclassical correction to the time-correlation functions [21]. The method has been implemented within real-time time-dependent density functional theory [17,22] and is illustrated by application to tip-induced luminescence in a porphyrin [23,24].

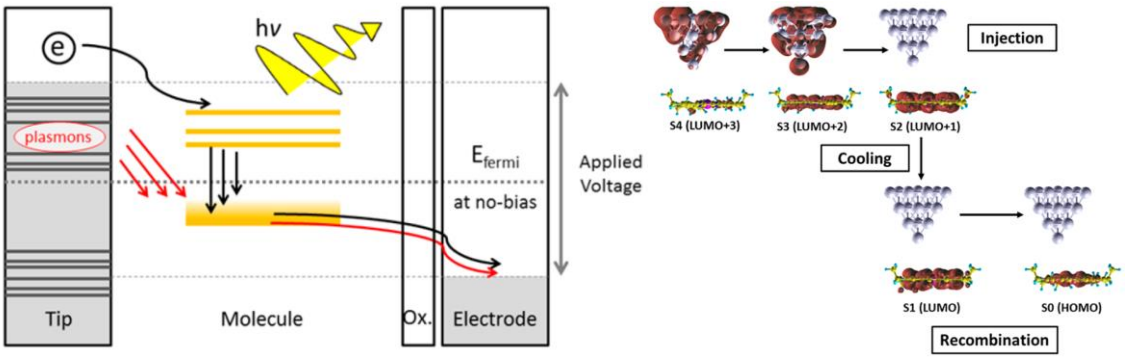

Figure 1. Model of luminescence in a porphyrin molecule induced by an STM tip.

References

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