

VISTA Seminar

Seminar 40

July 20, 2022

10:00 am – 11:30 am EDT / 3:00 – 4:30 BST / 4:00 pm – 5:30 pm Paris

TOC:

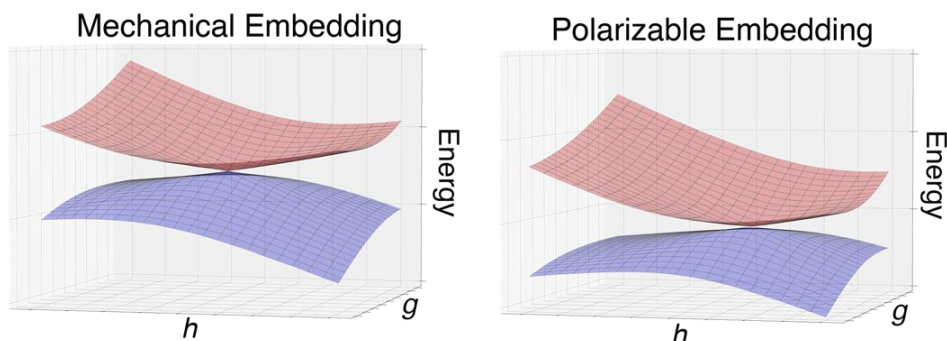
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Conical intersections in solution with polarizable embedding: integral-exact direct reaction field

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A popular strategy to exploring the molecular properties and reactivity of complex systems is to use quantum mechanics/molecular mechanics (QM/MM) embedding, wherein a QM region is defined and treated with electronic structure theory and the remainder of the system is treated with a forcefield. Equally important to the level of electronic structure theory and quality of forcefield is the treatment of the coupling between the QM and MM subsystems, i.e. how the QM region is embedded in the MM system. The state-of-the-art is to use a polarizable forcefield for the MM region and mutually couple the QM wavefunction and MM induced dipoles, in addition to the usual electrostatic embedding, yielding a polarizable embedding (QM/MM-Pol) approach. However, extensions to electronic excited states are less well developed, and we showed previously that current QM/MM-Pol approaches have problems of root flipping and/or incorrect descriptions of electronic crossings in multistate calculations.¹

Here we demonstrate a solution to the above problems with an integral-exact reformulation of the Direct Reaction Field approach of Thole and Van Duijnen (QM/MM-IEDRF).^{2,3} The resulting embedding potential includes one- and two-electron operators, and many-body dipole-induced dipole interactions, and thus includes a natural description of the screening of electron-electron interactions by the MM induced dipoles. In addition, since the MM dipoles are entangled with the QM system, state-dependent QM-MM polarization interactions are captured, and the method correctly describes electronic state crossings. We describe a graphical processing unit implementation of the method and its analytical gradients that enables application to systems of hundreds of QM and MM particles at the HF, DFT, CIS, TDDFT, CASCI, and CASSCF levels.³ We furthermore demonstrate that QM/MM-IEDRF correctly predicts asymmetry in the charge-transfer pathways of the purple bacteria reaction center (L-branch versus M-branch), and that protein polarization plays a dominant role in selecting the L-branch.⁴

References

- ¹ M. A. Hagras & W. J. Glover, *J. Chem. Theory Comput.* **14**, 2137 (2018)
- ² X. Liu, A. Humeniuk, W. J. Glover, *ChemRxiv* 10.26434/chemrxiv-2022-15cjt (2022)
- ³ A. Humeniuk, W. J. Glover, *ChemRxiv* 10.26434/chemrxiv-2022-j8rgj (2022)
- ⁴ A. Humeniuk, A. S. P. Paz, Y. Cao, W. J. Glover, *ChemRxiv* 10.26434/chemrxiv-2022-mkffd (2022)

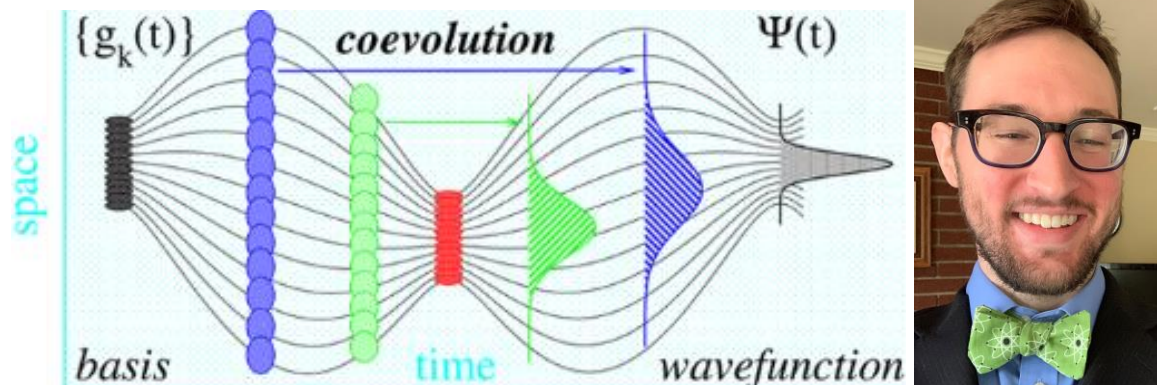
The QTAG Approach to Nonadiabatic Dynamics

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The broad role of nonadiabatic phenomena in chemical systems has spawned much attention in recent years, particularly in the fields of photochemistry and laser-induced processes. These effects are tied to reaction dynamics, and describe the interactions of electrons and nuclei in excited molecular systems. Often neglected in ground-state chemical calculations, the role of nuclei is of particular importance in these systems, as their motions frequently mediate de-excitation pathways. From a theoretical perspective, performing exact quantum dynamics calculations on these systems is intractable beyond a dozen or so degrees of freedom; however, this has in turn motivated the development of a wealth of trajectory-based approximate methods capable of tackling larger systems (see for example, [1]). Many of these methods are rooted either in Tully's surface hopping (in which independent trajectories move classically along adiabatic surfaces with a chance of swapping) or in an Ehrenfest (trajectories move along a single 'average' surface) picture. While these techniques have been quite successful in a range of applications to date, they often do not capture nuclear quantum effects, which are at times critical to a correct description of molecular behavior.

Today I will present the groundwork for a formally exact method, actively in development in the Garashchuk research group and predicated on propagating Gaussian basis functions along quantum (Bohmian) trajectories. Abbreviated the QTAG -- Quantum Trajectory-guided Adaptable Gaussians -- method, this approach combines the advantages of the inherent quantum nature of Bohmian trajectories with the efficiency of a Gaussian basis representation to propagate a wavefunction smoothly in time [2]. Initially formulated for single-surface systems with quantum features, I will discuss the generalization to nonadiabatic systems in this talk.

References

- [1] WIREs Comput. Mol. Sci. 2019, 9, 5, 1-21
- [2] J. Chem. Theory Comput. 2020, 16, 18-34

How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 40

Time: Jul 20, 2022 10:00 AM Eastern Time (US and Canada)

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