Coupling Molecular Density Functional Theory with Wave-Function methods to study excited states in aqueous solution

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Most of the chemical properties of a molecule are governed by its electronic structure. This is why electronic structure calculations play a central role in theoretical and computational chemistry. However, most chemical processes occur in solution rather than in a vacuum. Furthermore, the solvent significantly impacts chemical reactions or solute properties. Yet, precise quantum chemistry calculations are often conducted in vacuum, neglecting the solvent's role, or using a continuum solvent model that overlooks its molecular nature. A more direct approach to accounting for solvent effects while retaining a molecular description is to explicitly include solvent molecules in quantum (QM) calculations[1]. However, this substantially increases computational costs, scaling polynomially with the number of electrons.

When the solvent does not react with the solute, a common strategy involves treating solvent molecules with molecular mechanics (MM) using a classical force field. This method reduces computational costs for the bulk of the system while maintaining a QM description of the crucial part: the solute. This approach is known as QM/MM. Molecular Dynamics (MD) is often chosen as the MM method for such studies, but it is the most expensive MM method. Another QM-MM strategy involves liquid state theories (LST), particularly Classical Density Functional Theory (cDFT). In brief, cDFT computes the grand-potential and equilibrium liquid density by minimizing a functional of the solvent density. Like its electronic counterpart, cDFT is theoretically sound, but practical utilization requires approximations in selecting the functional describing particle interactions, in this case, solvent molecules.

In the present work, we propose coupling quantum calculations with the hybrid continuum/molecular description of the solvent provided by molecular density functional theory (MDFT). Two crucial features of our method include computing both electronic and molecular densities self-consistently and considering electrostatic interactions as point charges. We validate this new framework by computing excited state properties of two molecules, water, and formaldehyde, in both vacuum and aqueous solvent. Then, we compare our method with state-of-the-art approaches using a coupled cluster (CC) level of theory for the QM part and a molecular[2] or continuum[3] description of the solvent. Our results demonstrate that even in the simple case of the water molecule, our approach yields results closer to the molecular description of the solvent than pure continuum approaches. Additionally, we investigate the impact of the level of theory used to describe the QM part in the MDFT calculation. To rationalize predicted excitation energies, we also compute the dipole moment of both ground and excited states in vacuum and solution.

Keywords: Solvation, QM/MM, Wave-Function Methods, DFT, Excited States.

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