Exploring the Combination of Linear Response and State Specific Approaches for a More Accurate Description of Excited States in Solution

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Time-Dependent Density Functional Theory (TD-DFT) has emerged as the method affording the best compromise between accuracy and computational cost, for the study of molecular excited states [1]. For the same reason, the Polarizable Continuum Model (PCM) [2] has become the preferred approach for the description of solvent effects on the structure and the electronic properties of molecular solutes. The combination of TD-DFT and PCM with the goal of providing an accurate picture of excited states in solution is – however – less than straightforward. One of two approaches is usually chosen: in the linear-response approach solvation effects arise from the electric transition dipole, while in the state-specific approach the change in the molecular dipole associated with the electronic transition modifies the self-consistent reaction field established for the ground state. In addition, while both approaches can be used to describe non-equilibrium solvent effects on absorption, only the state-specific one provides a consistent description of a non-equilibrium emission process. By itself, each one of the linear-response or the state-specific approach provides a partial picture of the actual physical phenomenon. The solvent effect on a very bright transition not associated with a significant change in the molecular electric dipole is unlikely to be well described by the state-specific approach. On the other hand, the linear-response approach seems ill-suited to describe the solvent effect on a dark transition which nevertheless involves a redistribution of charge. In this contribution, we present a compact implementation of a method that combines the two approaches in an effective and useful way. The usual linear-response approach and the state-specific Vertical Excitation Model (VEM) [3] are combined with user-defined weights, with the goal of providing the best description of each electronic transition based on its characteristics. Moreover, if the orbital relaxation terms are excluded from the VEM, the analytic gradient of the combined approach is readily available [4,5], allowing for the study of the excited state potential energy.

References
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