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Variational state specific solvent models for excited states from time dependent self-consistent field methods JOSIAH BJORGAARD, KIRILL VELIZHANIN, SERGEI TRETIAK, Los Alamos National Laboratory — The effect of a dielectric environment on a molecule can be profound, causing changes in nuclear configuration and electronic structure. Quantum chemical simulation of a solute-solvent system can be prohibitively expensive due to the large number of degrees of freedom attributed to the solvent. To remedy this, the solvent can be treated as a dielectric cavity. Mutual polarization of the solute and solvent must be considered for accurate treatment of an optically excited state (ES) with a state-specific solvent model (SSM). In vacuum, time dependent self-consistent field (TD-SCF) methods (e,g, TD-HF, TD-DFT) give variational excitation energies. With the well known Z-vector equation, a variational ES energy is used to explore the ES potential energy surface (PES) with analytical gradients. Modification of the standard TD-SCF eigensystem to accommodate a SSM creates a nonlinear TD-SCF equation with non-variational excitation energies. This prevents analytical gradients from being formulated so that the ES PES cannot be explored. Here, we show how a variational formulation of existing SSMs can be derived from a Lagrangian formalism and give numerical results for the variability of calculated quantities. Model dynamics using SSMs are showcased.

Josiah Bjorgaard
Los Alamos National Laboratory

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