Explicitly unraveling the roles of counter ions, solvent molecules, and electron correlation in homogeneous reaction mechanisms

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ABSTRACT: Widely used continuum solvation models are an efficient, practical, and straightforward way to study molecules in homogeneous solvents. However, these models do not account for explicit intermolecular interactions that may be critically important when studying reaction pathways and mechanisms. We prescribe a computational approach to obtain nuclear coordinates for explicitly solvated minimum energy pathways that are amenable to treatments with high levels of quantum chemistry theory. We demonstrate this approach using CO₂ reduction by NaBH₄ and NaBH₃OH in aqueous solution as test cases. We show that the entire first solvation shell around reacting atoms as well as explicit counter ions can play significant roles influencing reaction energies of electronically adiabatic hydride transfers. Depending on the chemical process, the level of quantum chemistry theory used beyond that treated by standard GGA exchange correlation functionals can play a far less significant role.