Polarizable Embedding: Multireference embedding methods and large scale applications to optical properties in proteins

Erik Donovan Hedegård[1], Stefan Knecht[1,2], Nanna H. List[1], Hans Jørgen Aagaard Jensen[1], Jógvan Magnus Haugaard Olsen[1] and Jacob Kongsted[1]

[1] Institute for Physics, Chemistry and Pharmacy, University of Southern Denmark, Odense, Denmark

[2] ETH Zürich, Laboratorium für Physikalische Chemie, Zürich, Switzerland

edh@sdu.dk

Efficient algorithms have ensured that quantum mechanical methods are rapidly moving into the areas of biology and material sciences. A major part of this development has been driven by a divide-and-conquer strategy where large scale calculations have been parted into a focused region, treated by quantum mechanics and a remaining region (the environment) treated by a force field. These hybrids (QM/MM) methods have made it possible to obtain reliable structures for fast-lived intermediates, which can provide important insight in enzyme mechanisms. Yet, the interactions between the QM system and environment can be dramatic and for accurate prediction of molecular properties, higher accuracy than provided by the MM force field can be required. Notably most force field methods neglect the mutual polarization between environment and quantum mechanical regions.

Within the recent years our group has, with focus on molecular properties, developed an embedding scheme[1] using potentials derived from first-principles calculations for the environment. This strategy builds upon a multipole expansion of each site in the environment, adding also atom-centered polarizabilities on top. Most recently, this embedding scheme was extended to MC-SCF methods[2], including also the sr-DFT MCSCF hybrid method which allows dynamical and static correlation to be included simultaneously[3]. Here we present the new implementation, and emphasize the formal equality between the explicit polarizable embedding method and implicit continuum methods such as PCM. The effect of including dynamical correlation by the sr-DFT MCSCF hybrid scheme is discussed using small models and biological model complexes as examples. Furthermore, recent results for solvated systems and also for proteins with chromophores of significant multireference character is presented.

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