QM:QM approach: Efficient tool in photochemical and electrochemical calculations

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In only limited number of quantum chemical calculations, solvent molecules may be included at the full quantum level. In other cases, both efficient and reliable way of solvent modeling is sought. There are many wide-spread approaches, e.g. surrounding the molecule or microsolvated cluster by polarizable continuum (possibly combined with microsolvation) or modeling the solvent at the molecular mechanical level (QM/MM).

In this contribution, alternative technique of QM:QM division of the system [1] is presented in context of excitation and ionization calculations for vertical and adiabatic processes, i.e. for purposes of both photochemistry and electrochemistry. In the QM:QM methodology, molecular system is divided into subsystems which are all treated at the quantum level. The mutual subsystem interactions are however only electrostatic. In this way, polarization of the system is accounted for, in contrary to the conventional QM/MM approach. Furthermore, by including additional charge centers into the subsystems, even charge transfer phenomenon (which is in fact only extreme case of polarization) may be treated. The QM:QM method is very efficient as the computational time scales linearly with number of included solvent molecules.

The performance of the QM:QM methodology is demonstrated on the vertical ionization of highly-charged PO_4^{3-} ion in water solvent. Here, four water layers (about 600 water molecules) are shown to be necessary to approach the experimental ionization potential and the importance of the long-range polarization is thus revealed. In the electrochemical context, redox properties of the novel helquats molecules [2] are investigated.

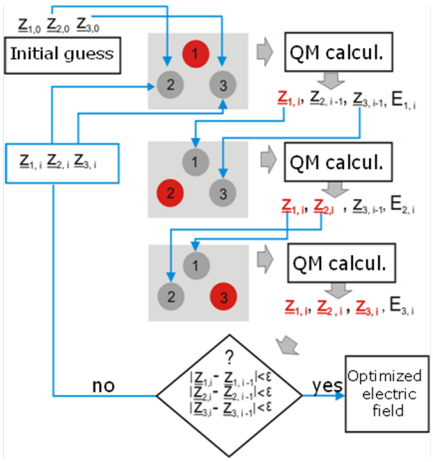

Figure 1: QM:QM calculation scheme for system divided into three parts.

References

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