

Coupling electronic and molecular Density Functional Theory

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ABSTRACT

The computational cost of the most advanced quantum methods used to study chemical systems tends to become rapidly prohibitive when the number of electrons increases. This is even worse when the solvation effects need to be taken into account. First, a large number of solvent molecules (i.e. a very large number of electrons) have to be considered. Second, it becomes necessary to sample the configuration space of the solvent since the meaningful quantity is free energy and not energy. Almost only one “ab-initio” method is used to study such problems: DFT-based Molecular Dynamics but its usage remains limited to a few hundreds of atoms for a few ps because of its computational cost.

To overcome this bottleneck, a natural choice is to adopt a more coarse description of the solvent. One common approach is to keep the explicit description of solvent molecules, but to describe their interaction with classical force fields, this is the popular QM/MM technique [1]. When the MM part is handled using molecular dynamics, it is still necessary to sample the phase space of solvent degrees of freedom and the computational cost remains several orders of magnitude larger than the in-vacuum calculation. Another popular approach is to describe the solvent by a dielectric continuum [2]. It keeps the computational cost comparable to a in vacuum quantum calculation but it lacks molecular description of the solvent.

I will present an alternative based on a quantum description of the solute using electronic density functional theory coupled with a classical grand-canonical treatment of the solvent using molecular density functional theory [3]. Unlike previous work, both densities are minimized self-consistently, accounting for mutual polarisation of the molecular solvent and the solute. The electrostatic interaction is accounted using the full electron density of the solute rather than fitted point charges. The introduced methodology represents a good compromise between QM/MD and continuum methods. The potential of the method is illustrated on two usual benchmark systems: a water solvated in water and the symmetrical nucleophilic substitution between chloromethane and chloride in water.

REFERENCES

- [1] Lin, H & Truhlar, D. G. “QM/MM: what have we learned, where are we, and where do we go from here?” *Theor. Chem. Acc.* **117**, 185. (2007)
- [2] Tomasi, J, Mennucci, B, & Cammi, R. “Quantum Mechanical Continuum Solvation Models.” *Chem. Rev.* **105**, 2999–3094. (2005)
- [3] Jeanmairat, G, Levesque, M, & Borgis, D. “Tackling solvent effects by coupling electronic and molecular Density Functional Theory. *Journal of Chemical Theory and Computation.*” **16**, 11, 7123–7134 (2020)

[1] Author "Title", Journal **vol**, pp (year)