Molecular Density Functional Theory and its coupling with the N body quantum problem

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Résumé

The computational cost of the most advanced quantum methods used to study chemical systems tends to become rapidly prohibitive when the number of electrons increase. 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. Because of the computational cost, its usage remains limited to a few hundreds of atoms for a few ps.

To overcome this computational 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 a classical force field, this is the so-called QM/MM technique. Another popular approach is to describe the solvent by a dielectric continuum. The latter has the advantage of keeping the computational cost comparable to a vacuum quantum calculation but it lacks molecular description of the solvent. In the former, it is still necessary to sample the phase space of solvent degrees of freedom and the computational cost is still several orders of magnitude larger than the in-vaccum calculation.

The purpose of this presentation is to introduce a liquid theory technique that might be a good alternative to tackle this problem: the molecular DFT. I will introduce the classical DFT framework [1, 2] and the approximations made to derive the MDFT formalism [3, 4]. I will illustrate its relevance to study classical solvation problems. Finally, I will present some preliminary work on the coupling between MDFT and QM techniques.

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Mots-Clés: Molecular DFT, Solvation, QM/MM