PHYSICAL CHEMISTRY COLLOQUIUM: Theory and Linear Scaling Implementation of a Polarizable QM/AMOEBA/Continuum Embedding

Filippo Lipparini
Department of Chemistry & Industrial Chemistry
University of Pisa

Date:
9/10/2021

Time:
10:30 AM- 11:50 AM

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Please contact snsgradstaff@ucmerced.edu for the Zoom information.

Abstract:

Combining the strengths of an atomistic QM/MM description in dealing with anisotropic, specific interactions with the natural ability of polarizable continuum models to treat long-range electrostatics is a natural idea in quantum chemistry. However, while the idea itself is straightforward, formulating and implementing such a model for a polarizable MM embedding[1], where therefore all three layers mutually polarize each other, comes with several theoretical and numerical challenges.

Formulating a fully coupled scheme can be cumbersome and making sure that all the interactions are present and not double counted requires a very careful derivation of the equations. Things are even more complicated when the polarizable models are not variational, as in the latter case arguments of classical electrostatics can not be used in a straightforward manner to guide the formulation.

From a computational point of view, a three-layer, polarizable embedding represents a formidable bottleneck, as the need to achieve mutual polarization results in large sets of linear equations that need to be solved. The size of such equations can easily be 50-100 times the number of atoms in the system, which, for even not-too-large biological systems, makes the use of dense linear algebra impossible and even the use of a quadratic-scaling iterative solution too costly.

In this contribution, we address both problems in the case of two non-variational embedding models: the AMOEBA polarizable force field[2] and the domain-decomposition formulation of the Conductor-like Screening Model[3] (ddCOSMO). After briefly sketching a completely general theory for polarizable embedding models and their coupling, the AMOEBA/ddCOSMO coupled equations are presented and the calculation of analytical derivatives – including the embedding contributions to the Fock/Kohn-Sham matrix and forces – is discussed.
We show how linear scaling in cost and memory requirements can be achieved by using the Fast Multipole Method to compute all the relevant electrostatic quantities[4] and ddCOSMO as a naturally linear scaling method.

Finally, we show some pilot applications of the newly implemented strategy and discuss its potentials, limitations, and required further developments.

[1] M. Bondanza, M. Nottoli, L. Cupellini, F. Lipparini, B. Mennucci, Phys. Chem. Chem. Phys. 2020, 22, 14433-14448
[2] Ren, P.; Ponder, J. W. J. Phys. Chem. B 2003, 107, 5933–5947
[3] B. Stamm et al., Int. J. Quantum Chem. 2019, 119, e25669
[4] F. Lipparini, J. Chem. Theory Comput. 2019, 15, 4312–4317