

Ultrafast Quantum/Molecular Mechanics Monte Carlo Simulations

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A very fast and accurate quantum/molecular mechanics (QM/MM) method is presented for determining thermodynamic averages in solutions (or for active sites within a flexible environment such as in a protein). The solute is described quantum mechanically and held fixed during averaging over the MM solvent/environment configurations. Instead of repeating the quantum calculations, the response of the system to the long range electric field of the solvent is precalculated using generalized polarizabilities (GPs). The latter describe the response of the system to a spatially modulated electric field. The electric potential of the solvent is represented as a linear combination of mathematically simple (e.g., sine wave) potentials. Avoiding the recalculation of the QM wavefunction speeds up the simulations typically by 4 orders or more while retaining the full accuracy of the QM/MM calculations ([1] and Fig. 1). Unlike the usual QM/MM enzyme models, polarizability (induction) contributions of the QM system are included. This is essential to reproduce full QM/MM accurately. The Generalized Polarizability method has been implemented in a Monte Carlo program attached to the PQS suite and works with a number of water force fields. The AMBER protein force field has also been implemented. Gradient implementation is in progress.

Current applications focus in the behavior of halide ions near the air/water interface [2], the calculation of solvent effects on NMR spectra [3], and S_N2 reactions in water ([4] and Fig. 2.)

[1] Janowski, T.; Wolinski, K.; Pulay, P. *Chem. Phys. Lett.* 530: 1-9, 2012 (Frontiers article).

[2] Yamada, T.; Janowski, T.; Pulay, P.; Dupuis, M. *J. Chem. Phys.* in preparation.

[3] Janowski, T.; Wolinski, K.; Pulay, P., to be published.

[4] (a) Uner, O.; Janowski, T.; Pulay, P., in preparation (b) Uner, O. *M.S. Thesis*, U. of Arkansas, 2013.

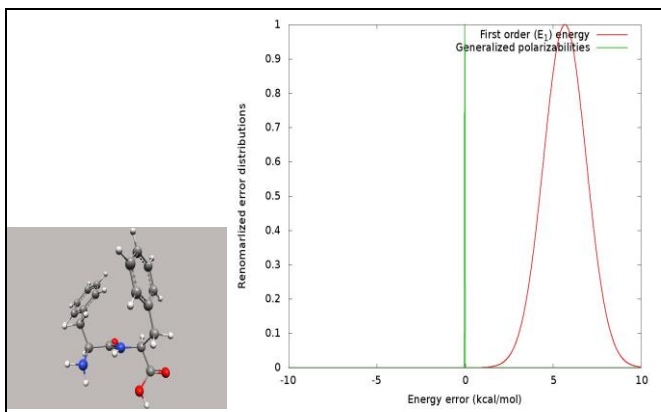


Fig. 1.

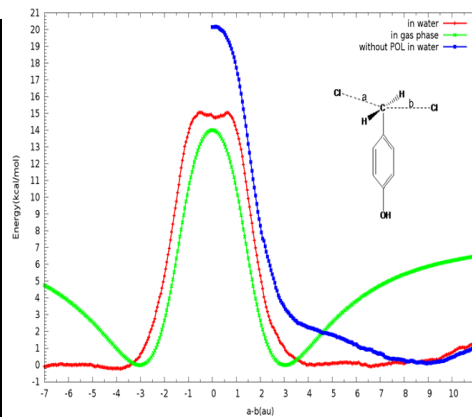


Fig. 2