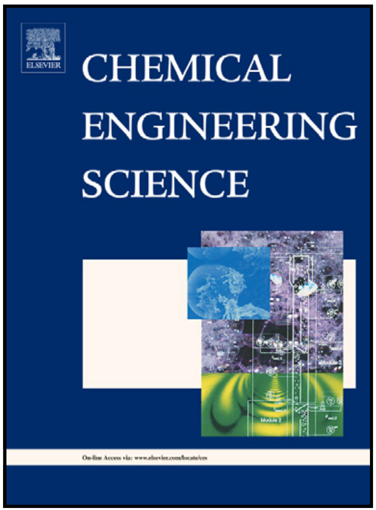

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Molecular density functional theory for multiscale modeling of hydration free energy

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ABSTRACT

Recent developments in physical and computer sciences enable quantitative predictions of chemical reactions and thermodynamic data from first principles by multiscale modeling. The hierarchical approach integrates different theoretical frameworks ranging from those describing phenomena at the electronic length and time scales to those pertinent to complex biomolecular systems and macroscopic phase transitions, promising broad applications to problems of practical concern. Whereas multiscale modeling has been emerging as a popular computational tool for engineering applications, the connection between calculations at different scales is far from being coherent, and the multiple choices of quantum/classical methods at each scale renders numerous combinations that have been rarely calibrated against extensive experimental data. In this work, we have examined a multiscale procedure for predicting the solvation free energies of a large set of small molecules in liquid water at ambient conditions. Using the experimental data for the hydration free energies as the benchmark, we find that the theoretical results are sensitive to the selection of quantum-mechanical methods for determining atomic charges and solute configurations, the assignment of the force-field parameters in particular the atomic partial charges, and approximations in the statistical-mechanical calculations. Because of significant uncertainties in quantum-mechanical calculations and the semi-empirical nature of force-field models, computational efficiency makes the classical density functional theory a valuable

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