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Cluster Expansion Method for Solvation Free Energy Calculations: Theoretical Development

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Abstract: The cluster expansion approach was used by McMillan and Mayer in the forties for the development of imperfect gas theory [1]. An interesting advantage of the method is that configurational integrals are relevant only in regions where the gas molecules are close. Considering the possibility of taking advantage of this property, a cluster-like expansion method for computation of the solvation free energy difference was developed in this work. Based on pairwise potentials, a Mayer-like function involving variation in the solute-solvent potential energy was used. Thus, considering solute-solvent initial potential energy U^0 and a new potential energy U^1, the related solvation free energies of the solute "S" are given by:

$$\Delta G^1_{solv}(S) = \Delta G^0_{solv}(S) - kTln[1 + \rho\bar{B}_2 + \rho^2\bar{B}_3 + \cdots] \qquad (1)$$

In this proposal, the series expansion remains inside the logarithm and is a finite series. The first correction term, $\bar{B}_2$, is given by:

$$\bar{B}_2 = \int f_{s,1} e^{-\beta\Delta W^0(r_1)} \boldsymbol{dr_1} \qquad (2)$$

The $f_{s,1}$ is the Mayer-like function, using the difference in the potential energy, and the ΔW^o is the potential of mean force for the position of the solvent molecule around the solute. The integral in equation (2) is meaningful only for configurations of the solvent close to the solute. The method can be applied for improving hybrid QM/MM calculations. In this case, the reference potential is classical and the new potential is calculated by quantum mechanics. Thus, equations (1) and (2) can be applied in the case that classical solvent molecules are transformed in quantum molecules. Further manipulation of equation (2) can be done for application in hybrid discrete/continuum approach.[2]

Key-words: free energy perturbation, cluster-continuum, single ions solvation, continuum method
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References:
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