Differential Geometry based solvation models

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Introduction

Solvation is an elementary process in nature and is of paramount importance to more sophisticated chemical, biological and biomolecular processes. The understanding of solvation is an essential prerequisite for the quantitative description and analysis of biomolecular systems.
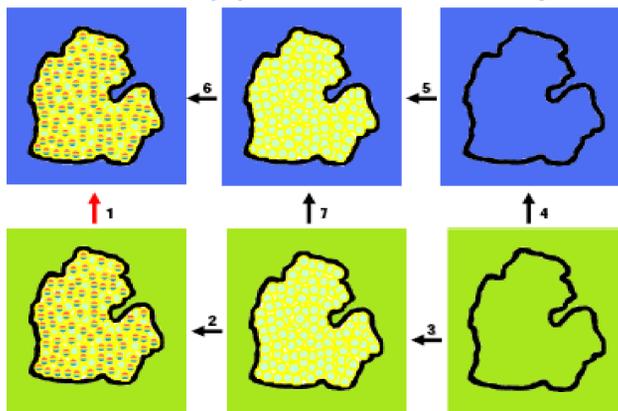

Figure 1: Solvation free energy cycle: the total solvation energy is decomposed into several steps: The energy associated with Step (7) is generally termed a ``nonpolar solvation energy'' while the difference in energies associated with Steps (1) and (6) is generally considered as ``polar solvation energy''

Theory and model

We propose a multiscale total free energy functional for solvation

$$G_{total}[S,\Phi,n] = \int_{\Omega} \left\{ \gamma|\nabla S| + pS + (1-S)\rho_0 U_{ss} + S\left[\rho_{total}\Phi - \frac{1}{2}\varepsilon_m|\nabla\Phi|^2\right] \right.$$
$$+ (1-S)\left[-\frac{1}{2}\varepsilon_s|\nabla\Phi|^2 - k_B T \sum_{i=1}^{N_c} n_i^0 (e^{-\Phi Q_i/k_B T} - 1)\right]$$
$$\left. + S\left[\sum_j \frac{\hbar^2}{2m}|\nabla\psi_j|^2 + E_{XC}[n]\right]\right\}dr \qquad (1)$$

where Φ is the electrostatic potential, n(r) represents electronic charge density, and a function S(r) is used to characterize the overlapping solvent-solute boundary. The first three terms describe the nonpolar energy functional. The last two terms represents the electronic energy functional, and the rest terms count for the electrostatic energy functional. By using the Euler–Lagrange variation, we derive the generalized Poisson-Boltzmann equation (2) for electrostatic potential, the generalized Laplace-Beltrami equation (LB) (3) for solvent-solute interface, and the Kohn-Sham equation (KS) (4) for electronic structure.

$$-\nabla\bullet(\varepsilon(S)\nabla\Phi) - (1-S)\sum_{i=1}^{N_c} Q_i n_i^0 e^{-\Phi Q_i/k_B T} = S\rho_{total} \qquad (2)$$

$$\frac{\partial S}{\partial t} = |\nabla S|\left[\nabla\bullet(\gamma\frac{\nabla S}{|\nabla S|}) + V_{LB}\right] \qquad (3)$$

$$\left(\frac{\hbar^2}{2m}\nabla^2 + V_{KS}\right)\psi_j = E_j\psi_j \qquad (4)$$

where V_{LB} and V_{KS} are effective LB and KS potentials, respectively .
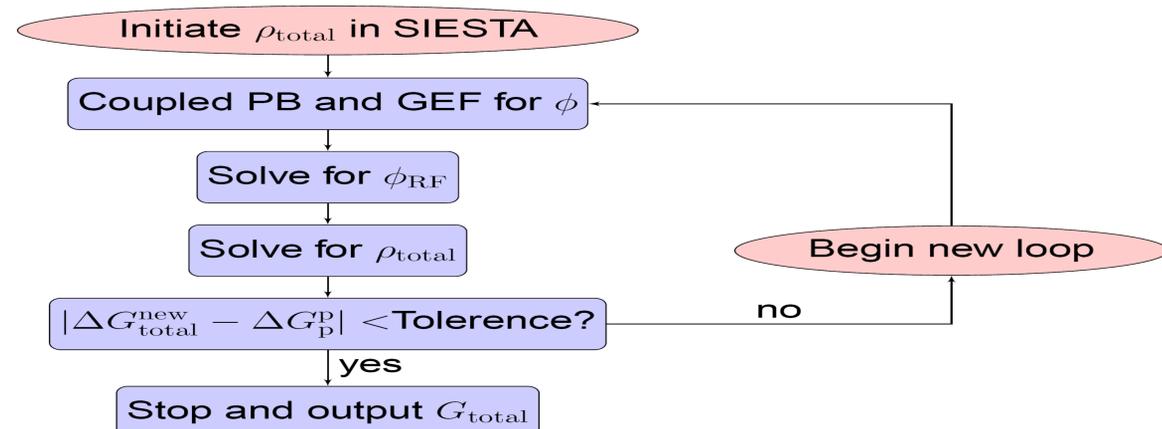
Implementation

Figure 2: Flowchart of the numerical solution of the coupled PDES
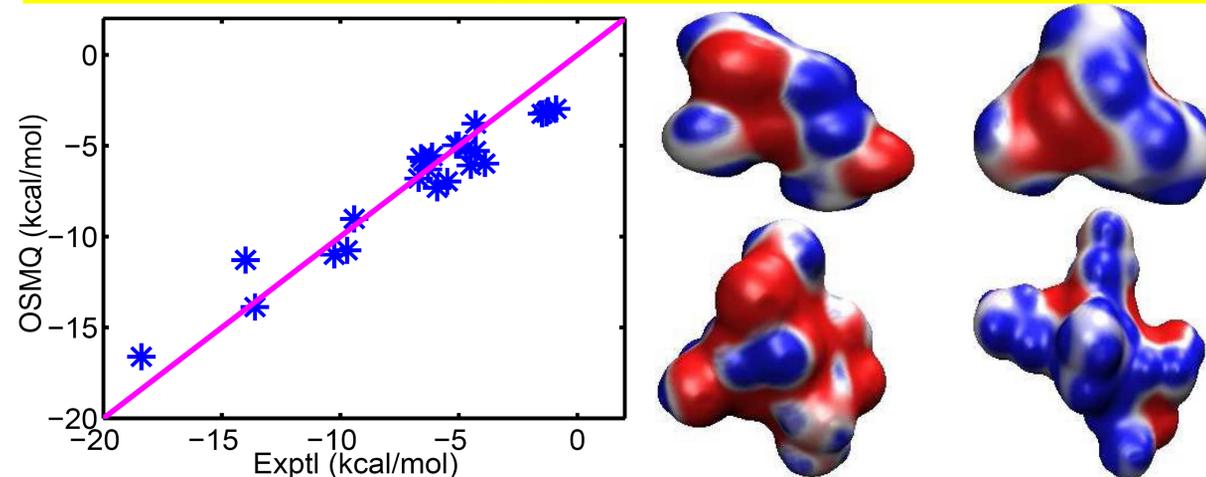
Applications

Figure 3: Left: Correlation between experimental data and the calculated in solvation free energy of 24 small molecules; Right: Illustration of surface electrostatic potential at their corresponding isosurface of S=0.50

Conclusion

We construct a new multiscale total energy functional which not only consists of polar and nonpolar solvation contributions, but also the electronic kinetic and potential energies. By using variational principle, we derive coupled equations. Appropriate iterative procedure is designed for solution. Our model is validated with experimental data.

References

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Acknowledgments