Wang and Truhlar – NSF research, Feb. 2011

Computations on complex systems are a current frontier of theoretical chemistry, and much work is accomplished using combined quantum mechanical/molecular mechanical methods where a critical subsystem is treated by QM and its environment by MM.

This group is carrying out fundamental studies to improve the way that the two subsystems are combined, especially with regard to electrostatics. Dramatic progress has been made, as delineated on the next two slides.

Slide 2 is concerned with a QM/MM boundary that passes through a covalent bond (as is required to treated biopolymers, solid-state catalysts, and nanoparticles.

Slide 3 is concerned with a QM/MM boundary that passes between molecules as required to treat many processes in liquids.

New Treatment of Boundary and Coulomb Interactions in Combined Quantum Mechanical and Molecular Mechanical Methods

Bo Wang and Donald G. Truhlar

MM Region

QM Region

Tuned Pseudoatom

Balanced (Smeared) Redistributed Charges

Tuned and Balanced (Smeared) Redistributed Charge Algorithms

A tuned pseudoatom scheme with balanced (smeared) redistributed charge algorithms is developed to treat the QM/MM boundary across polar covalent bonds more realistically. We tested 25 molecules with 13 different kinds of bonds at a QM–MM boundary, including C–C, N–C, O–C, S–C, C–N, O–N, C–O, Al–O, Si–O, C–Si, O–Si, C–S, and S–S bonds. The mean unsigned error (MUE) of the QM/MM deprotonation energy is reduced *from around 20 kcal/mol in conventional methods to 1.3 kcal/mo*l in the new scheme.
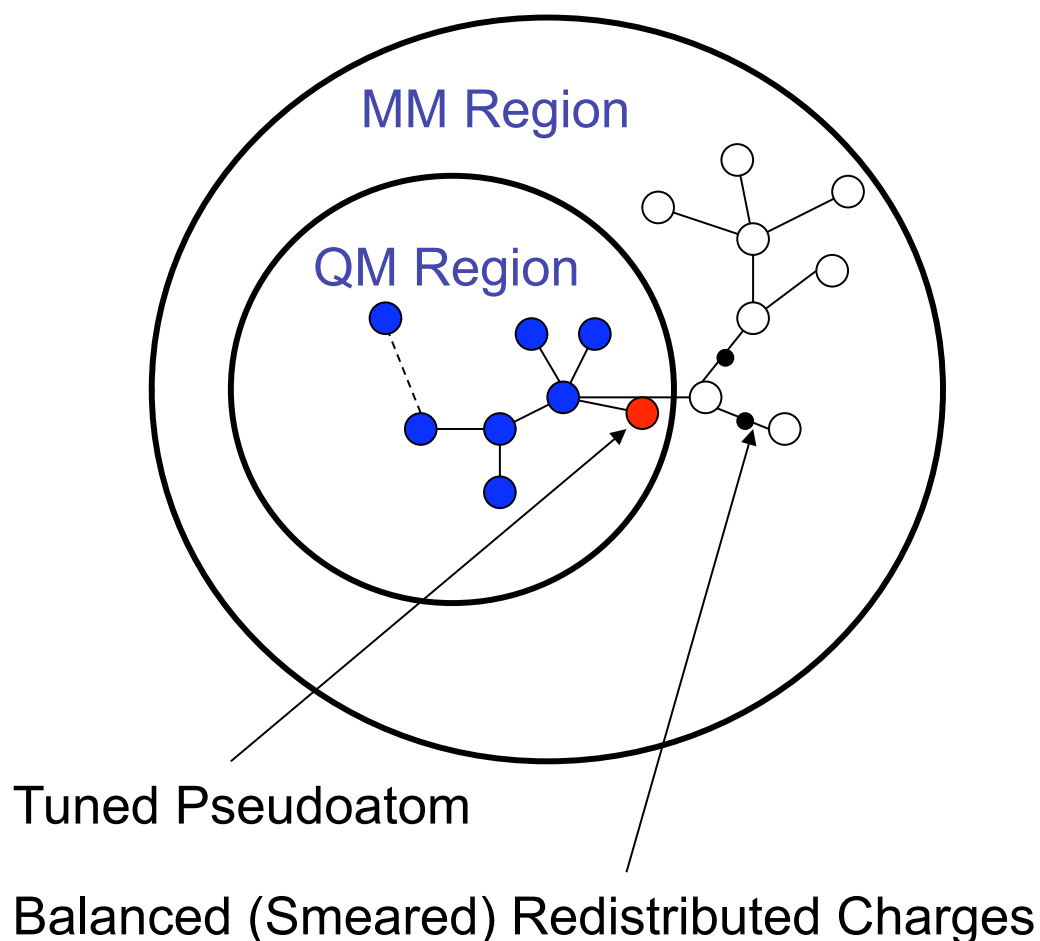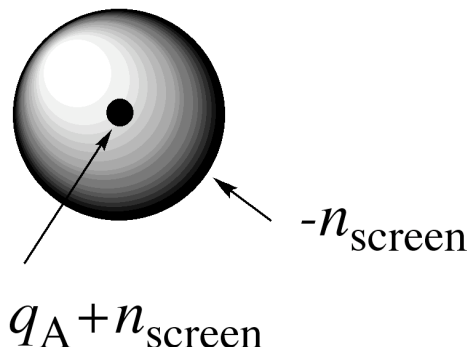
1. Wang, B.; Truhlar, D. G. submitted to *Phys. Chem. Chem. Phys.*
2. Wang, B.; Truhlar, D. G. *J. Chem. Theory Comput.*, **2010**, *6*, 359-369

Screened charge model

The MM charge is represented as a point charge for the nucleus, core electrons, and inner valence electrons and a smeared charge for the outer valence electron density in a Slater-type orbital

$$q_A^* = q_A + n_{\text{screen}} f(\zeta r)\exp(-2\zeta r)$$

ζ is a single parameter for each element. The method is tested against a test suite including 40 dimers, which contain H, C, N, O, F, Na, Al, Si, P, S, Cl, and Br elements.

q_A

$q_A + n_{\text{screen}}$

$-n_{\text{screen}}$

(a)

(b)

Comparison between (a) point charge model and (b) screened charge model

Charge penetration effects are taken into account in the screened charge model. Compared with the point charge scheme, the MUE of QM/MM electrostatic interactions between QM and MM regions is reduced *from 8.1 kcal/mol to 2.8 kcal/mol*, and the MUE of QM/MM induction interactions is reduced from 1.9 kcal/mol to 1.4 kcal/mol.

3. Wang, B.; Truhlar, D. G. *J. Chem. Theory Comput.*, **2010**, 6, 3330-3342