Solvation Modeling and Computational Electrochemistry

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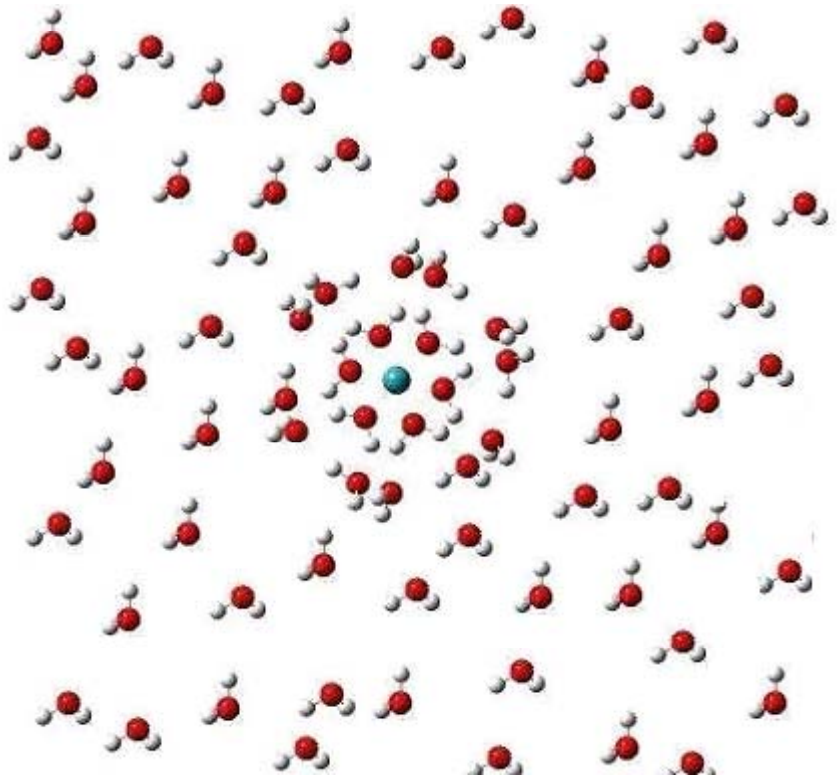
Outline

- **Solvation and charge models**
- **Energetics and dynamics in solution**
- **Computational electrochemistry**
- **Future plans**

Solvation Modeling

- ***Explicit solvation models***



- ***Implicit solvation models***
  - **Poisson equation**
  - **Generalized Born equation**
    - ✓**Partial atomic charges**

Charge Models and Classes

Class I

- *classical mechanics (e.g., for diatomics)*

Class II

- *population analysis (e.g., Löwdin)*

Class III

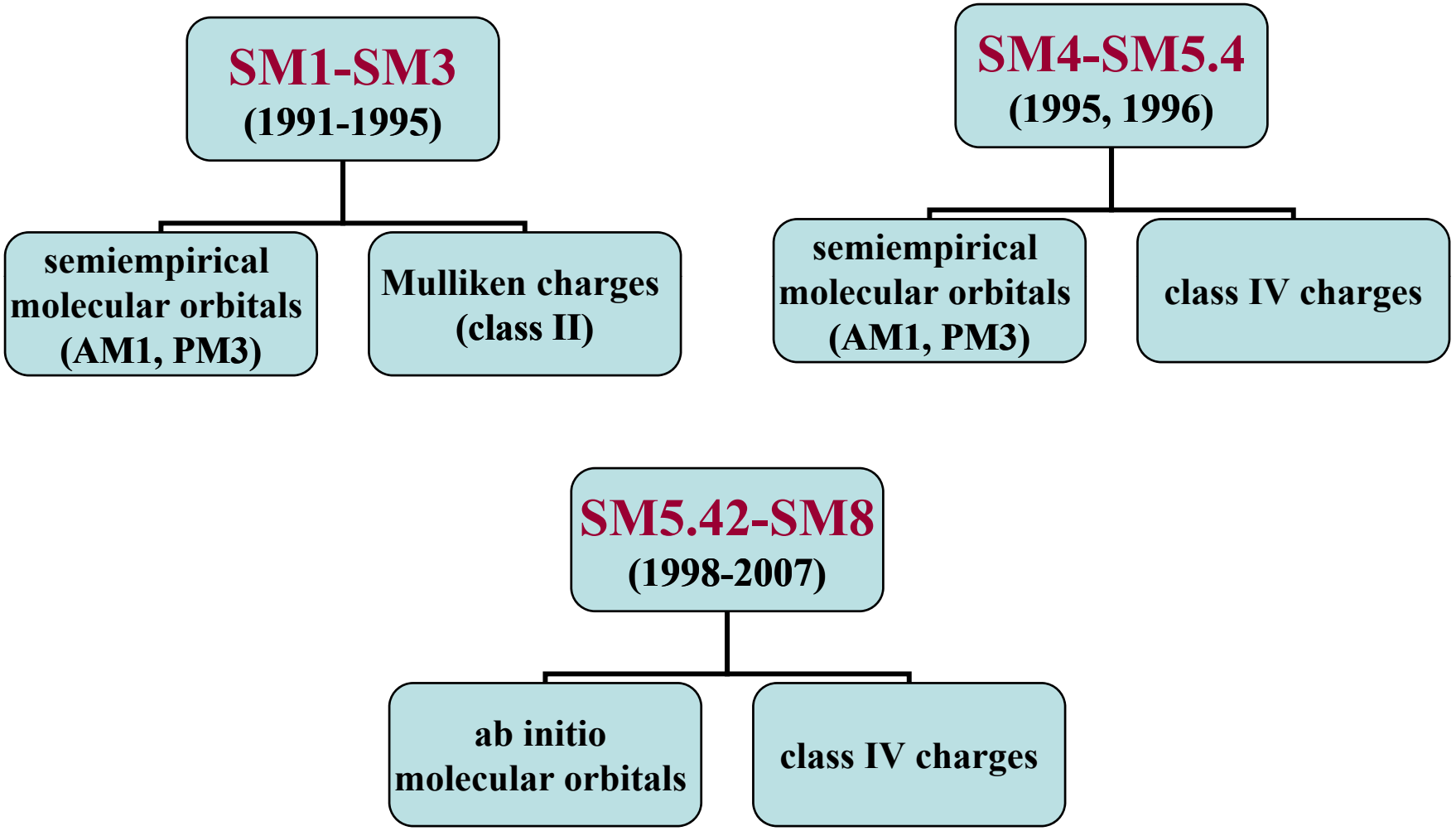
- *reproducing computed properties (e.g., dipole moments)*

Class IV

- *reproducing observed properties (e.g., dipole moments)*

charge models
CM1, CM2, CM3, CM4

The Family History of SM*x*



Recent Solvation Models

SM5.42 **(aqueous, nonaqueous)**
based on Charge Model 2 (CM2)

SM5.43 **(aqueous, nonaqueous)**
based on Charge Model 3 (CM3)

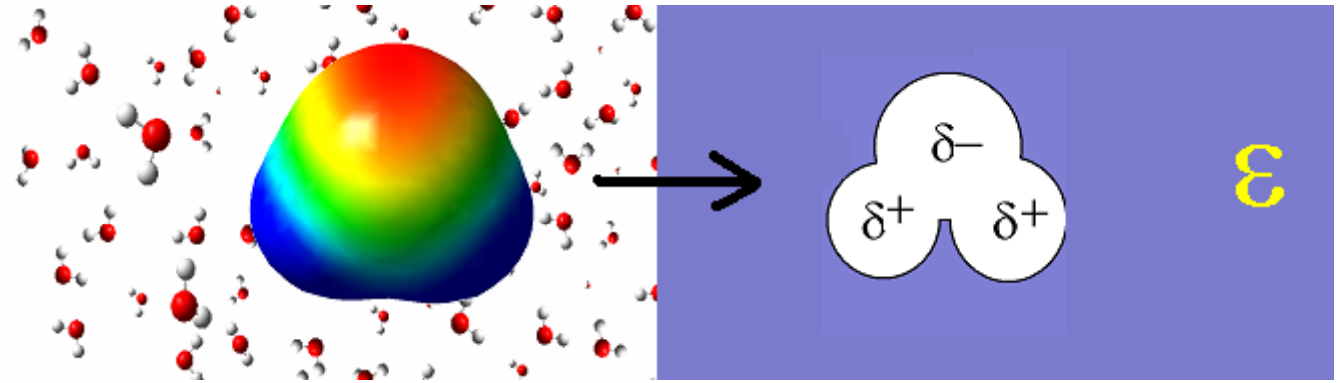
SM6 **(only aqueous)**
based on Charge Model 4 (CM4)

SM8 **(aqueous, nonaqueous)**
based on CM4

J. Chem. Theory Comp. **2007 (Polarization issue)**

http://dx.doi.org/10.1021/ct7001418

Implicit Solvation



The free energy of solvation is a change in a solute's free energy upon passing the solute from the gas phase into solution

$$\Delta G_S^o = \Delta E_N + \Delta E_E + G_P + G_{CDS}$$

nuclear relaxation | **electronic reorganization** | **polarization energy** | **cavity dispersion solvent structure**

ΔG_{ENP} ← **both long- and short-range electrostatic effects are treated as bulk electrostatics using a *self-consistent reaction field* procedure**

G_{CDS} ← **semiempirical correction for non-bulk electrostatic effects proportional to a solute's solvent accessible surface area (SASA)**

The Generalized Born Approximation

$$G_{\mathrm{P}} = -\frac{1}{2}\left(1-\frac{1}{\varepsilon}\right)\sum_{k,\,k'} q_k \gamma_{kk'} q_{k'}$$

ε is the dielectric constant of the solvent.

q_k is the partial atomic charge of atom k.

$\gamma_{kk'}$ is a Coulomb integral involving atoms k and k'. It depends on intrinsic atomic Coulomb radii.

Parametrization of SM8

- **332 solvation free energies for *223 ions* in**
  - *water*
  - *acetonitrile*
  - *dimethyl sulfoxide*
  - *methanol*
- **2346 solvation free energies for *318 neutrals* in**
  - *water*
  - *90 organic solvents*
- **143 transfer free energies for *93 neutrals* between**
  - *water*
  - *15 organic solvents*

Parametrization of SM8

Step I

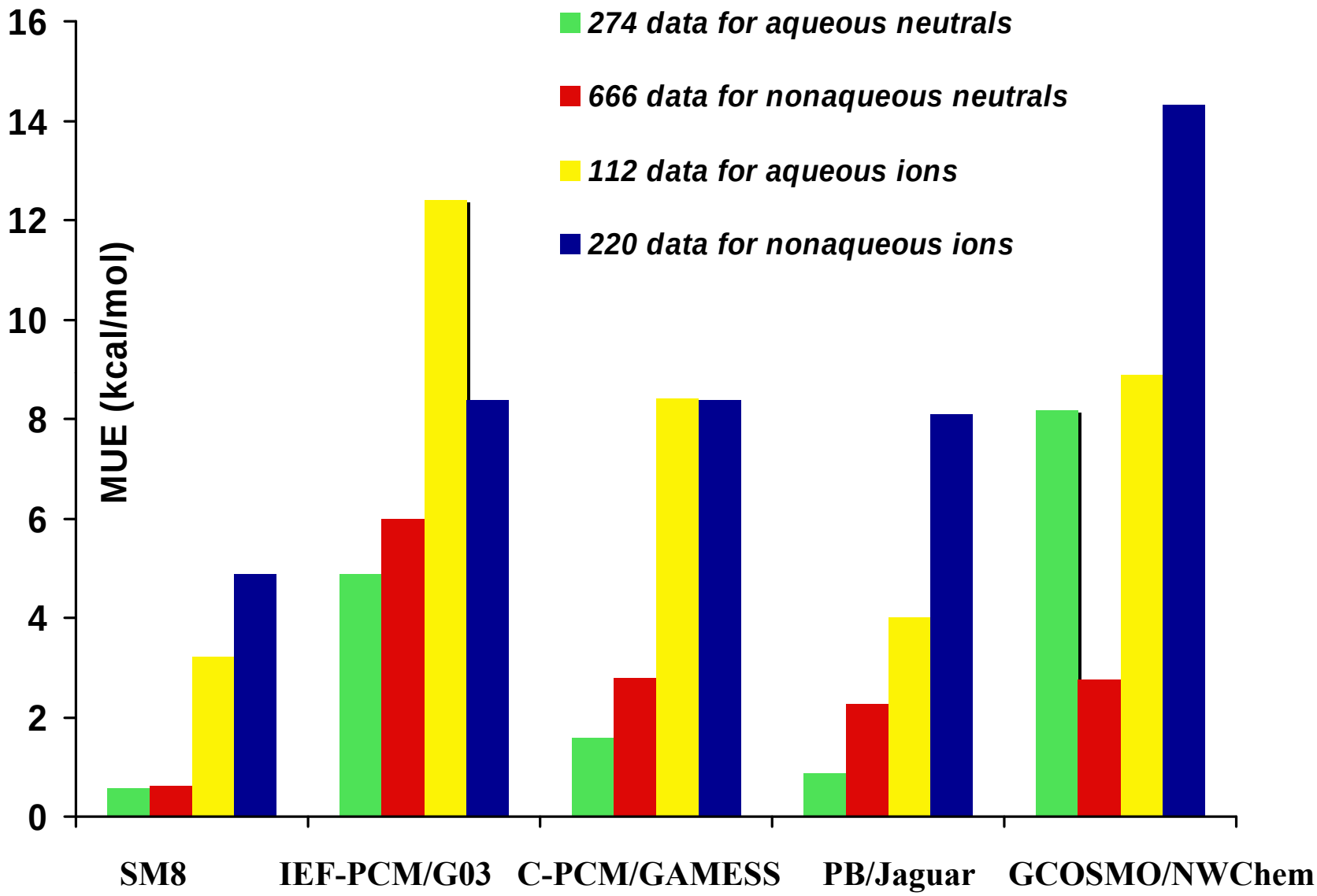
Optimization of atomic Coulomb radii that determine the bulk *electrostatic* component of ΔG_S (using ions)

- *Each radius is a function of the solvent hydrogen bond acidity parameter*

Step II

Optimization of the atomic surface tension parameters that determine the *non-bulk-electrostatic* component of ΔG_S (using neutrals)

- *54 parameters*


274 data for aqueous neutrals
666 data for nonaqueous neutrals
112 data for aqueous ions
220 data for nonaqueous ions
MUE (kcal/mol)
16
14
12
10
8
6
4
2
0
SM8
IEF-PCM/G03
C-PCM/GAMESS
PB/Jaguar
GCOSMO/NWChem

Conclusions on SM8

- **SM8 is a universal continuum solvation model for**
  - ***Ions and neutrals in aqueous and nonaqueous solutions***

- **It is applicable to any solvent or liquid medium using a few key descriptors such as**
  - ***Dielectric constant***
  - ***Abraham's hydrogen bond acidity and basicity***
  - ***Refractive index***
  - ***Macroscopic surface tension***
  - ***Carbon aromaticity and electronegative halogenicity***

- **It may be used with any level of theory as long as accurate partial charges can be computed for that level**

Applications

- **Electronic dynamics in solution**
  - ***electronic relaxation***
  - ***charge transfer***
  - ***polarization effects***

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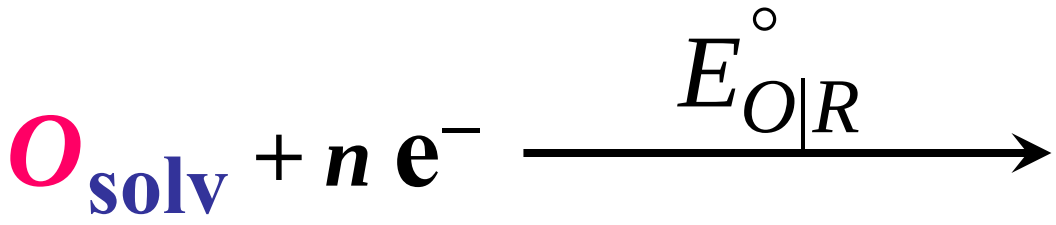
http://dx.doi.org/10.1021/ct7001539

- **Nuclear dynamics in solution**
  - ***liquid-phase geometry optimization for reagents and transition states***

- **Electrochemistry**
  - ***computation of reduction potential in solution***

J. Phys. Chem. C **2007, 111, 5783** **http://dx.doi.org/10.1021/jp066765w**

Theoretical prediction of reduction potential in solution

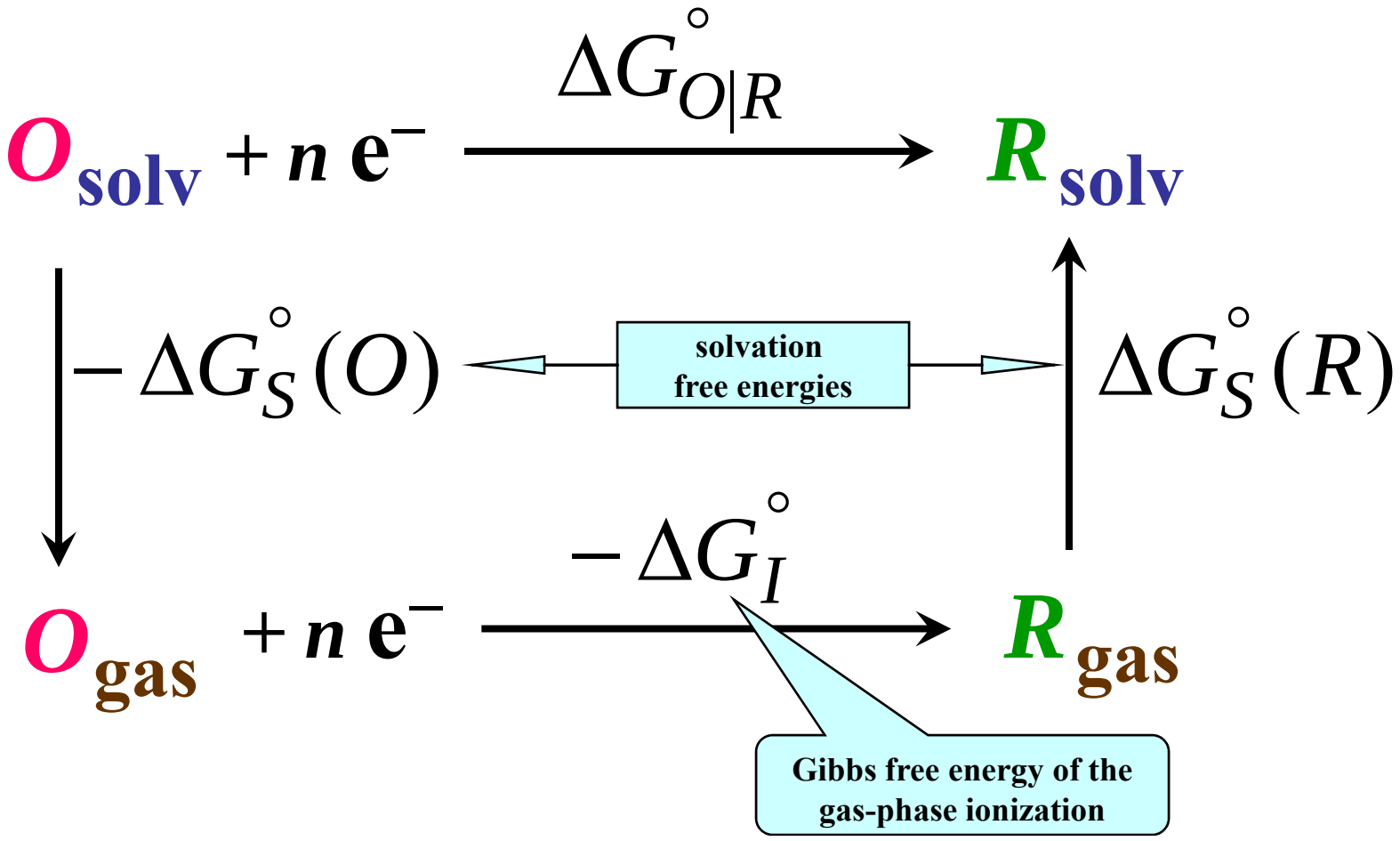


Gibbs free energy of the reduction reaction

Gibbs free energy of the standard hydrogen electrode

$$E^\circ_{O|R} = -\frac{\Delta G^\circ_{O|R} - \Delta G^\circ_{SHE}}{nF}$$

Thermochemical (Born-Haber) Cycle:



The $Ru^{3+}|Ru^{2+}$ Redox Couple in Aqueous Solution

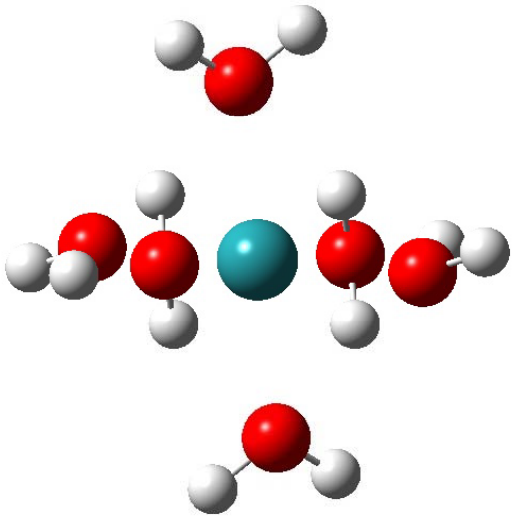
$$Ru^{3+} + e^- \rightarrow Ru^{2+}$$

Ru^{2+} and Ru^{3+} do not exist as bare ions.

$$[Ru(H_2O)_6]^{3+} + e^- \rightarrow [Ru(H_2O)_6]^{2+}$$

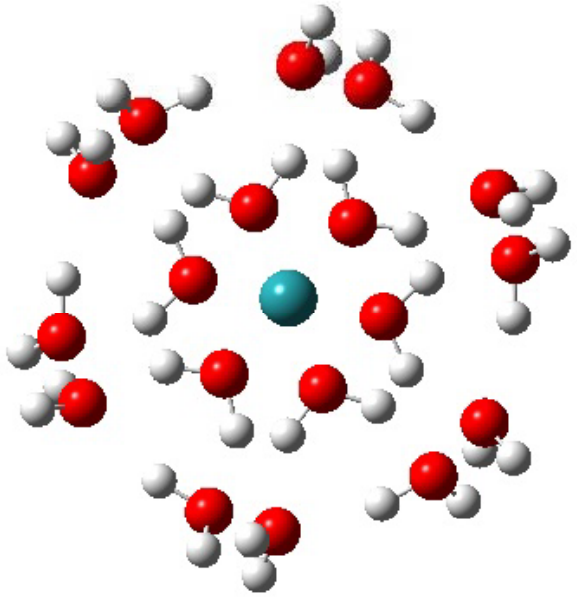
$$[Ru(H_2O)_{18}]^{3+} + e^- \rightarrow [Ru(H_2O)_{18}]^{2+}$$

Molecular Structures



$[Ru(H_2O)_6]^{2+/3+}$

$[Ru(H_2O)_{18}]^{2+/3+}$



37 Tested Density Functionals

Generalized Gradient Approximation **(GGA)**

Meta GGA **(MGGA)**

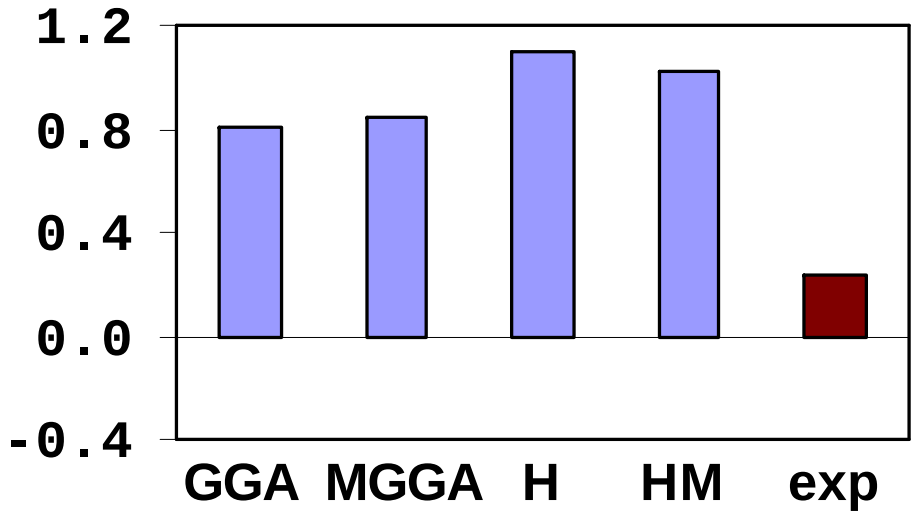
Hybrid **(H)**

Hybrid Meta **(HM)**

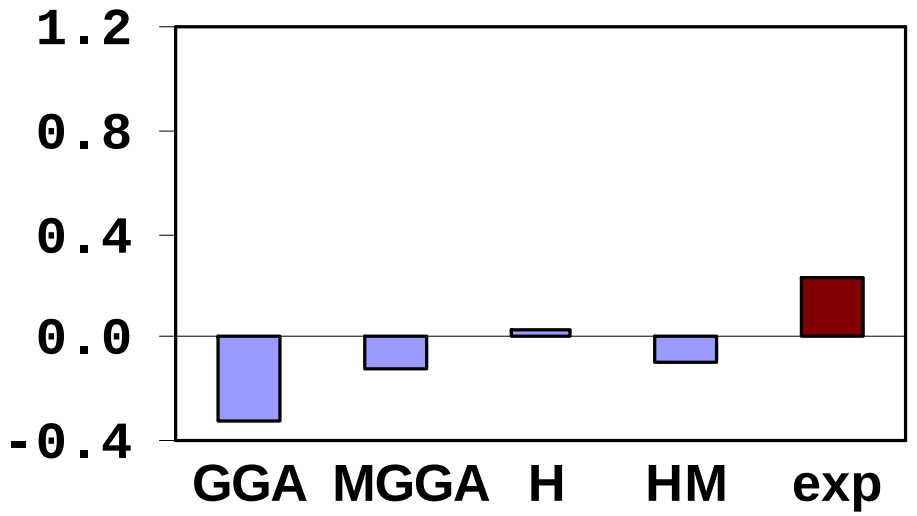
Reduction Potential E^o (in volts)

calculated with

One Hydration Shell



Two Hydration Shells



Future Plans

- **Parametrization of models based on the Poisson equation (without partial charge models)**
  - ***Solvent-dependent intrinsic atomic radii***
  - ***Cavity – dispersion – solvent structure formalism***

$$\nabla \cdot [\varepsilon(\vec{r})\ \nabla\phi(\vec{r})] = 4\pi\rho(\vec{r})$$

solute's charge density

solute's electrostatic potential

position-dependent dielectric constant

Future Plans

- **Extension of the generalized Born approximation to excited electronic states (e. g., for modeling *solvatochromism*)**
  - ***Equilibrium solvation: fast and slow polarization energy components***
  - ***Configuration interaction method***
  - ***Time-dependent density functional theory***
  - ***Hybrid explicit/implicit approaches***

Contributors

- **Ryan Olson**
- **Pablo Jaque**
- **Casey Kelly**
- **Adam Chamberlin (*temperature-dependent models*)**
- **Professors C. J. Cramer and D. G. Truhlar**

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