Recent development of the effective fragment potential method in Q-Chem

Lyudmila V. Slipchenko
Purdue University
• chemistry in the condensed phase
• effective fragment potential (EFP) method
• development of EFP in Q-Chem
• QM/EFP for excited states
• Applications:
  ▪ formaldehyde-water clusters
  ▪ p-nitroaniline-water clusters
Real chemistry happens in solution!

**Solvent effects:**

- Electronic properties of the solute
  - Dipole moment
- Conformational space of the solute
- Spectroscopic properties
  - Shifts in electronic, vibrational, and rotational spectra
- Tautomerization, acidity/basicity
- Chemical reactions
Electronic structure in environment

Environment can:

- modify PES and coupling of solute electronic states or even create new electronic state (CTTS)
- change localization of electronic states
- create complex dynamics

Solvatochromism:

differential solvation of the ground and excited states of chromophore

Fig. 1: Absorption spectra of 4-(4'-hydroxystyryl)-N-methyl-pyridinium-iodide in n-butanol (1), n-propanol (2), methanol (3), water (4)
Photocycle in PYP

a

resting state (pG)

Tyr$^{42}$

Glu$^{46}$

Arg$^{52}$

torsion a

torsion b

thioester bond

Cys$^{69}$

b

after isomerization (pR)
Smart models for big problems

- Implicit solvent
  - Self-consistent reaction field
  - Polarizable continuum model
  - Langevin dipoles (Warshel)
- Explicit solvent: QM/MM
  - Force-fields, EFP
  - ONIOM (Morokuma)
- Separation techniques
  - Fragment molecular orbitals (FMO) (Kitaura)
  - Divide-and-Conquer (Merz)
- Car-Parinello MD: plane-wave DFT
- Local correlation methods
- Linear scaling methods
QM/MM

• Quantum mechanics / molecular mechanics (QM/MM) approach

• Solute: accurate *ab initio* methods
  - Ground electronic state: MP2, CCSD, CCSD(T)
  - Excited electronic states: CI, EOM-CC family, TD-DFT

• Solvent: accurate *ab initio*-based (no fitted parameters!) force field method
  - EFP
Effective Fragment Potential method

Perturbation theory applied to non-interacting fragments

\[ E_{\text{interaction}} = E_{\text{coulomb}} + E_{\text{polarization}} + E_{\text{dispersion}} + E_{\text{exchange-repulsion}} + E_{\text{charge-transfer}} \]

long-range perturbation theory

short-range perturbation theory
Long-range perturbation theory

\[ H^0 = H^A + H^B \]
\[ H' = \int \frac{\rho_A \rho_B}{R_{12}} dv_1 dv_2 \]
\[ E^0 = E^A + E^B \]
\[ E' = \langle 00 \mid H' \mid 00 \rangle \]
\[ E'' = -\sum \frac{\langle 00 \mid H' \mid mn \rangle \langle mn \mid H' \mid 00 \rangle}{E_{mn}^0 - E^0} \]

\[ E_{ind}^A = -\sum_{m \neq 0} \frac{\langle 00 \mid H' \mid m0 \rangle \langle m0 \mid H' \mid 00 \rangle}{E_m^A - E^A} \]
\[ E_{ind}^B = -\sum_{n \neq 0} \frac{\langle 00 \mid H' \mid 0n \rangle \langle 0n \mid H' \mid 00 \rangle}{E_n^B - E^B} \]
\[ E_{disp} = -\sum_{m \neq 0, n \neq 0} \frac{\langle 00 \mid H' \mid mn \rangle \langle mn \mid H' \mid 00 \rangle}{E_m^A - E_n^B - E^A - E^B} \]
Densities overlap at short distances: wave functions should be antisymmetrized

\[ \Psi = \frac{1}{\sqrt{2(1 - S^2)}} |a(1)b(2) - a(2)b(1)| \]

new term appears:
exchange-repulsion energy
expressed as a series in orders of \( S \), truncated at \( S^2 \)

\[ E_{ex-rep} = f(S) \]

charge-transfer energy - interaction of occupied orbitals in A with virtuals in B and visa versa
also expressed as a series of \( S \)
1. MAKEFP (produces EFP parameters)
   
a set of ab initio calculations on each unique fragment
   - Electronic density ➔ set of point multipoles (DMA)
   - Static polarizability tensors at LMO (coupled HF)
   - Dynamic polarizability tensors at LMO (TDHF)
   - Wave function & Fock matrix (HF)

2. EFP calculation
   - EFP-EFP interactions by semi-classical formulas using EFP parameters
   - QM-EFP interactions as 1-electron terms in QM Hamiltonian, using EFP parameters
Effective fragment potential method

- polarizable force field
- all EFP force field parameters are obtained from a separate $ab\ initio$ calculation: no fitted parameters
- computationally cheap
- covers all major types of intermolecular forces
- accuracy of EFP can be further improved
- in present implementation, accuracy of EFP is similar to accuracy of MP2
- gives physical insight
EFP: studied systems (GAMESS)

- H-bonding systems:
  - dynamics of water
  - bonding of polar solvents
  - water-alcohol mixing
  - solvation of aminoacids
  - aqueous reactions
  - hydration of ions

- $\pi-\pi$ interactions:
  - complexes of benzene and benzene derivatives
  - benzene-water interactions
  - complexes of styrene
QM/EFP approach: HF level

Ground state calculations (HF level)
EFP terms appear as 1-electron integrals in the *ab initio* Hamiltonian

\[
\hat{H}_{QM/MM} = \hat{H}^{el} + \hat{H}^{pol} + \hat{H}^{disp} + \hat{H}^{exch-rep}
\]

Under development, currently - classically
\[ \hat{H}^{el} = \sum_p \sum_q \sum_{k \in A} \left( \sum_{p} d_{pq} \langle p | V^e_k q \rangle + \sum_{I \in A} \langle p | \frac{Z_I}{R} | q \rangle \right) \]

\[ \langle p | V^e_k q \rangle = \langle p | \frac{q^k}{R} | q \rangle + \langle p | \sum_{a} \frac{\mu^k_a a}{R^3} | q \rangle \]

\[ + \langle p | \sum_{a,b} \frac{\Theta^k_{ab}(3ab - R^2 \delta_{ab})}{3R^5} | q \rangle \]

\[ + \langle p | \sum_{a,b,c} \frac{\Omega^k_{abc}(5abc - R^2(a\delta_{bc} + b\delta_{ac} + c\delta_{ab}))}{5R^7} | q \rangle \]

integral code:
Christopher Williams
& John Herbert
Induced dipole: \( \mu_\gamma = \alpha_{\gamma\alpha} F_{\alpha}^{\text{total}} \)

Total field:

\[
F^{\text{total}} = \sum (F^{\text{mult}} + F^{\text{ind}}) + F^{ai} + F^{ai-nuc}
\]

Polarizability:

\[
E^{\text{pol}} = -\frac{1}{2} \sum \mu F^{\text{mult}} + \frac{1}{2} \sum \mu F^{ai}
\]
Polarization within HF cycle

\[
\begin{align*}
\mu &= 0 \\
\Psi &= \text{guess()}
\end{align*}
\]

Compute \(\Psi\)

Compute \(F_\psi\)

Compute \(F_\mu\)

Compute \(\mu\)

Is \(\Psi\) converged?

Is \(\mu\) converged?

Exit
### EFP in Q-Chem: summary

<table>
<thead>
<tr>
<th>term</th>
<th>MAKEFP</th>
<th>EFP-EFP</th>
<th>HF-EFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrostatics</td>
<td>+</td>
<td>energy</td>
<td>energy</td>
</tr>
<tr>
<td>polarization</td>
<td>+</td>
<td>energy</td>
<td>energy</td>
</tr>
<tr>
<td>dispersion</td>
<td>-</td>
<td>energy</td>
<td>classically</td>
</tr>
<tr>
<td>exchange-repulsion</td>
<td>+</td>
<td>energy</td>
<td>classically</td>
</tr>
<tr>
<td>charge-transfer</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Vitalii Vanovschi & Anna Krylov
Correlated methods and EFP

- **Ground state** - approach “0”: use modified by EFP terms HF Hamiltonian in CC procedure, no or “static” EFP corrections

- **Excited states** - generally, each excited state will have different density & charge distribution and get different response from environment
  Preferably, all QM/EFP interactions should be recalculated for each excited state
  Currently, implemented for electrostatic and polarization interactions
Electrostatics for excited states

• Approach 1: classical
difference between the ground and excited states can be estimated at the MM-MM level:

  density -> DMA ->
interaction of classical point multipoles between solute and solvent

• Approach 2: quantum
using one-particle density $P$ of the excited state

$$\Delta E^{el} = (P_{ex} - P_{gr})H^{el}$$
Induced dipoles were iterated until self-consistency with the ground state wave function. What to do for the excited state?

• Approach 1: exact
  ➢ environment response is calculated at each Davidson iteration (i.e., induced dipoles are recalculated) -> consistent with environment excited state

  ... will converge? Probably not 😞 - or some tricks in the Davidson algorithm are required
Polarization for excited states (cont)

- **Approach 2:**
  - HF, the ground state **solvent response** (induced dipoles)
  - Davidson @ this (ground state) solvent response => ex. state (one-particle) density
  - calculate environment response for the given **excited state density** (reinduce dipoles)

\[
\Delta E^{\text{pol}} = E^{\text{pol}}(\mu^{\text{ex}}) - E^{\text{pol}}(\mu^{\text{gr}}) - \sum (\mu^{\text{ex}} - \mu^{\text{gr}}) F_{ai, \text{ex}}
\]

Leading correction to the interaction between \(\mu^{\text{ex}}\) and \(\Psi^{\text{ex}}\)

• Electrostatic and polarization environmental response is calculated for the excited states

• One-particle excited state density is required

• Any number of the excited states can be treated simultaneously

• Q-Chem: currently implemented for CI and EOM-CC excited state methods which have one-particle properties (CIS, CIS(D), EOM-CCSD and their SF counterparts)
Formaldehyde in water

n -> $\pi^*$ transition

Gas phase ex. state energy (expt): 4.07 eV
$\mu^{gr} = -1.04$ D
$\mu^{ex} = -0.55$ D

solvatochromic blue shift in absorption in polar solvents

Robin, *Higher excited states of polyatomic molecules*, 1985
Formaldehyde-water clusters

Full EOM: 4.28 eV  
EOM/EFP: 4.41 eV

EOM/EFP: 4.40 eV  
EOM/EFP: 4.69 eV

gas phase: 4.13 eV

Why disagreement?
• basis set size
• dispersion & exchange-repulsion effects

6-31+G*
Excitation energy components

Excitation energy, eV

- gas-phase $S_0 \rightarrow S_1$
  - 4.137 eV

- electrostatics: solvent destabilizes $S_1$
  - 0.260 eV

- polarization: solvent stabilizes $S_1$
  - -0.016 eV

- solvent stabilizes $S_0$
  - 0.309 eV
P-nitroaniline in water

Gas phase ex. state energy (expt): 4.24 eV
\( \mu^{gr} = 6.2 \text{ D}; \quad \mu^{ex} = 15.3 \text{ D} \)

solvatochromic red shift in absorption depends on a polarity of solvent

Kovalenko, Schanz, Farztdinov, Hennig, Ernsting, CPL 323, 312 (2000)
Electronic states of PNA

EOM-CCSD/
CIS(D):
3.579 eV
3.960 eV

6-31+G*
### PNA-water complexes

<table>
<thead>
<tr>
<th></th>
<th>Full CIS(D)</th>
<th>CIS(D)/EFP</th>
<th>CT triplet</th>
<th>CT singlet</th>
<th>gas phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.91 eV</td>
<td>3.92 eV</td>
<td>3.88 eV</td>
<td>3.88 eV</td>
<td>4.01 eV</td>
</tr>
<tr>
<td></td>
<td>4.32 eV</td>
<td>4.18 eV</td>
<td>4.42 eV</td>
<td>4.32 eV</td>
<td>4.04 eV</td>
</tr>
</tbody>
</table>

**CT triplet**

- Full CIS(D): 3.91 eV
- CIS(D)/EFP: 3.92 eV
- 3.88 eV
- 4.01 eV

**CT singlet**

- Full CIS(D): 4.32 eV
- CIS(D)/EFP: 4.18 eV
- 4.42 eV
- 4.34 eV

**Gas phase:**

- 3.93 eV
- 4.65 eV
CT singlet state

Excitation energy, eV

- gas-phase $S_0 \rightarrow S_{CT}$: 4.654 eV
  - electrostatics: solvent stabilizes $S_{CT}$ (-0.106 eV)
  - polarization: solvent destabilizes $S_{CT}$ (0.002 eV)

- solvent destabilizes $S_0$ (-0.268 eV)
Summary: formaldehyde and PNA

• Major contribution to the environmental response to the excited states comes from the “indirect” term – correction of the ground state density by the EFP potential

• Electrostatic contribution to the excited states is important, polarization contribution is much smaller

• Importance of cavity terms – dispersion and exchange-repulsion – needs to be investigated
Conclusions

• QM/EFP methods for electronic excitations in the condensed phase are developed in Q-Chem
• main advantages of the new methodology:
  ▪ first-principle-based
  ▪ detailed knowledge of solvent-solute interactions for the excited state
• work to be done:
  ▪ completing quantum QM-EFP interface (dispersion and exchange repulsion terms)
  ▪ implementing analytic gradients for QM/EFP
Acknowledgements

USC:
Dr. Vitalii Vanovschi
Prof. Anna Krylov

Ohio State:
Dr. Christopher Williams
Prof. John Herbert

Iowa State:
Pooja Aurora
Prof. Mark Gordon

Q-Chem Inc.:
Dr. Yihan Shao
Dr. Ryan Steele

Purdue University
Frank Emmert