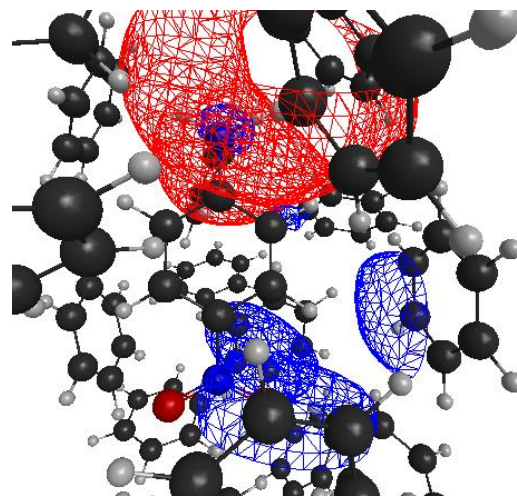


Excited state dynamics with the Effective Fragment Potential method?

Lyudmila V. Slipchenko

Department of Chemistry, Purdue University

- Effective Fragment Potential method (EFP)
- Beyond polarizable embedding
- Prospects for excited state dynamics



Methodology:

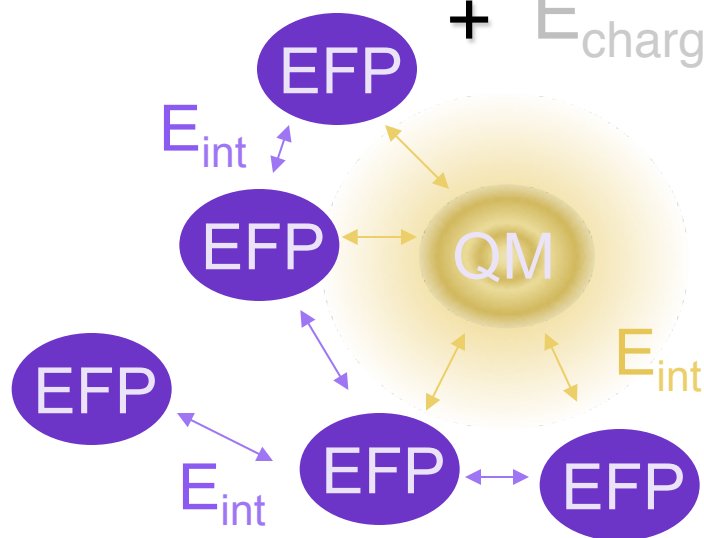
Effective Fragment Potential method (EFP)

Perturbation theory applied to non-interacting fragments

$$\begin{aligned} E_{\text{interaction}} = & E_{\text{coulomb}} \\ & + E_{\text{polarization}} \\ & + E_{\text{dispersion}} \\ & + E_{\text{exchange-repulsion}} \\ & + E_{\text{charge-transfer}} \end{aligned}$$

long-range perturbation theory

short-range perturbation theory



*distributed approach
used for all terms*

Day et al, *J. Chem. Phys.* **1996**, *105*, 1968-1986;
Gordon et al, *Phys. Chem. A* **2001**, *105*, 293-307;
Gordon et al, *Ann. Rep. Comp. Chem.*, **2007**, *3*, 177-193;
Ghosh et al, *J. Phys. Chem. A* **2010**, *114*, 12739-12754

EFP set-up

1. Preparation of EFP fragment parameters

general fragment: MAKEFP run (GAMESS)

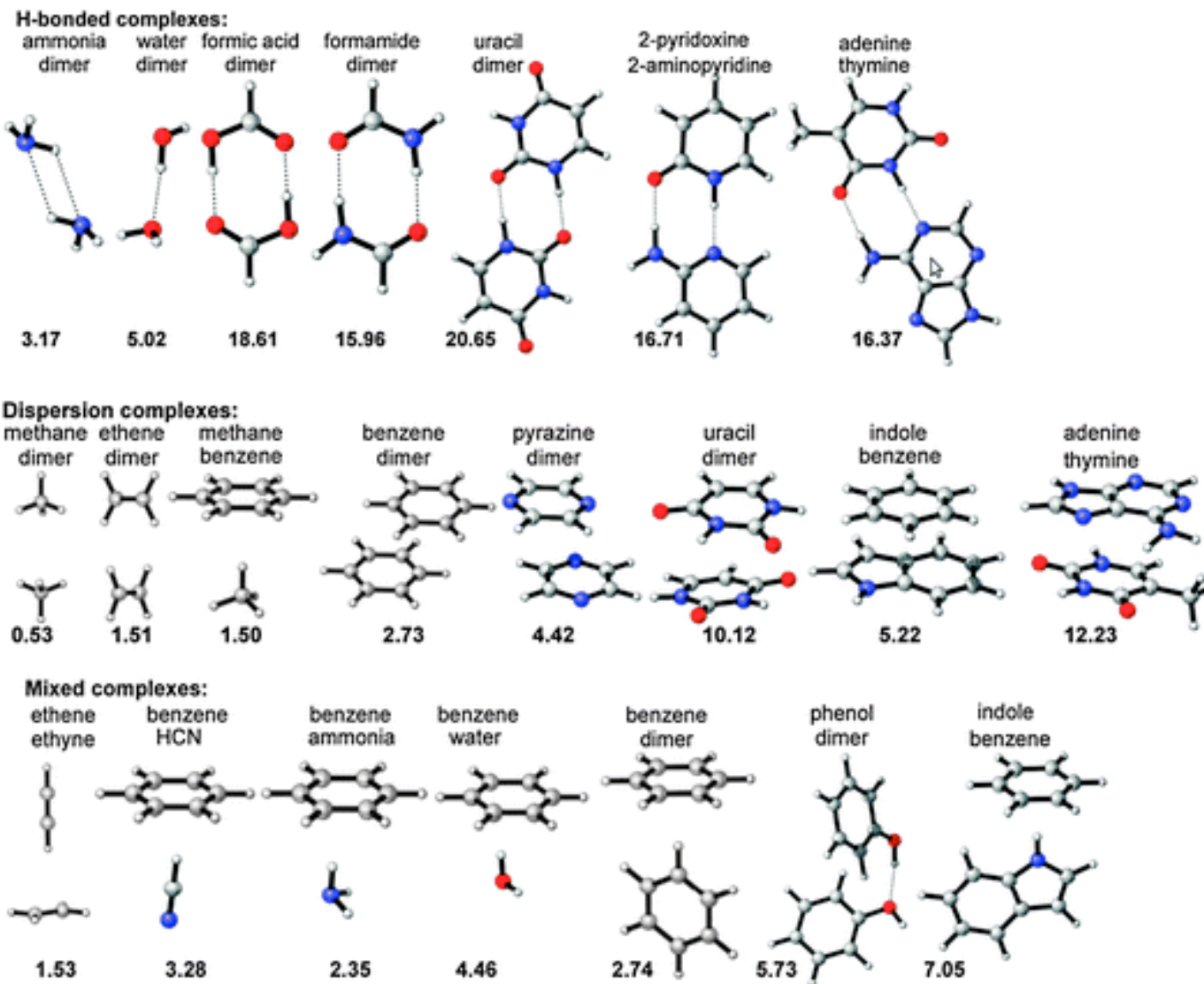
a set of ab initio calculations on each unique fragment

- **Coulomb:** set of point multipoles (DMA)
- **Polarization:** static polarizability tensors at LMO (coupled HF)
- **Dispersion:** dynamic polarizability tensors at LMO (TDHF)
- **Exchange-repulsion:** wave function & Fock matrix (HF)

2. EFP calculation (energy, optimization, MD, MC, ...)

- EFP-EFP interactions by (semi)-classical formulas
- QM-EFP interactions via 1-electron terms in QM Hamiltonian

S22 dataset of intermolecular interactions

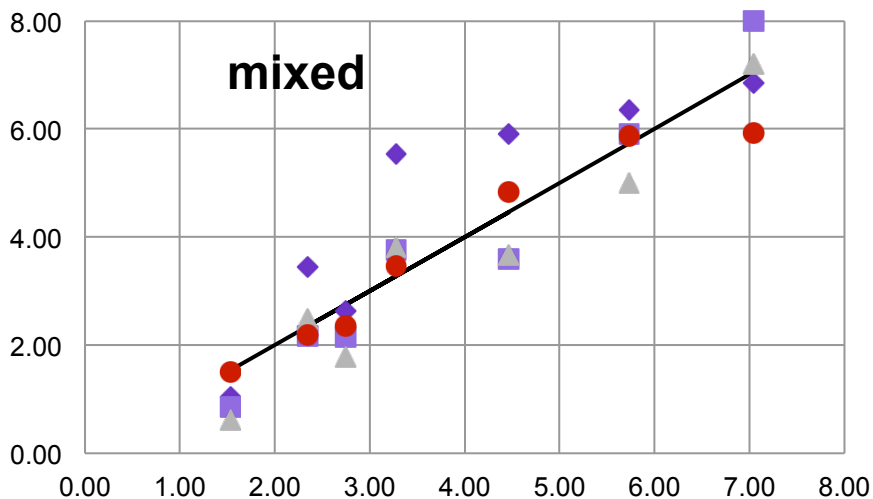
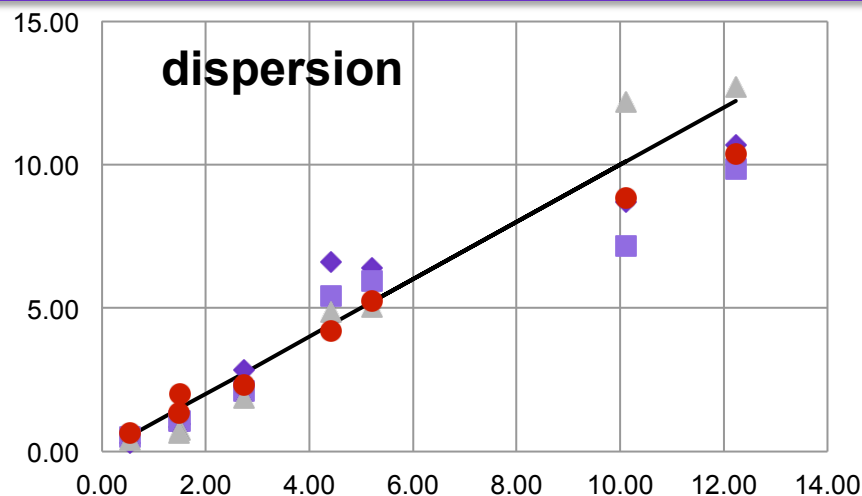
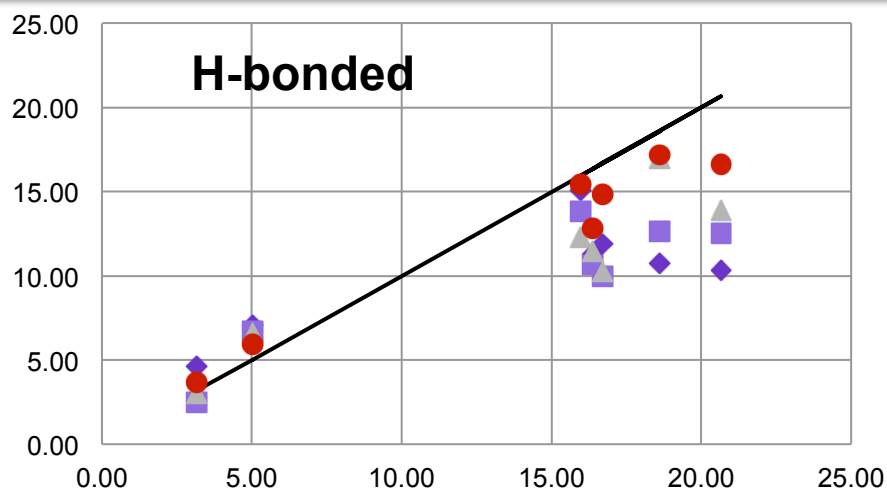


S22: performance of popular methods

**MAD,
kcal/mol**

	HB	disp	mixed	overall
HF	3.29	7.24	3.15	4.56
B3LYP	1.77	6.22	2.64	3.54
PBE	1.13	4.53	1.66	2.44
M06	0.89	0.99	0.67	0.85
M06-2X	0.73	0.36	0.32	0.47
ω B97X-D	0.27	0.30	0.42	0.33
MP2	0.24	1.69	0.61	0.88
SCS-MP2	1.54	0.55	0.37	0.80
SCS-CCSD	0.40	0.23	0.08	0.24
Amber	4.64	0.98	0.89	2.12
OPLSAA	4.45	1.07	0.56	1.98
MMFF94	3.61	0.73	0.60	1.61
EFP	1.82	0.57	0.35	0.89
10% error	1.38	0.48	0.39	0.74

S22: performance of force fields



- ◆ Amber
- ▲ MMFF94
- OPLSAA
- EFP



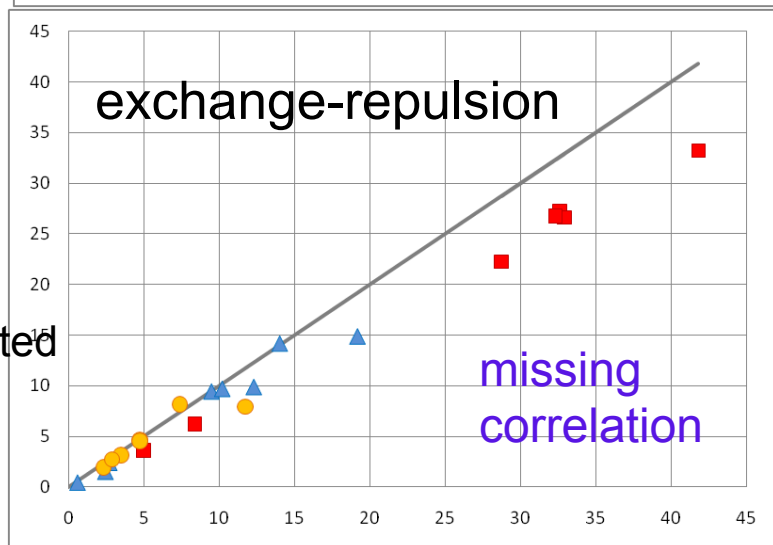
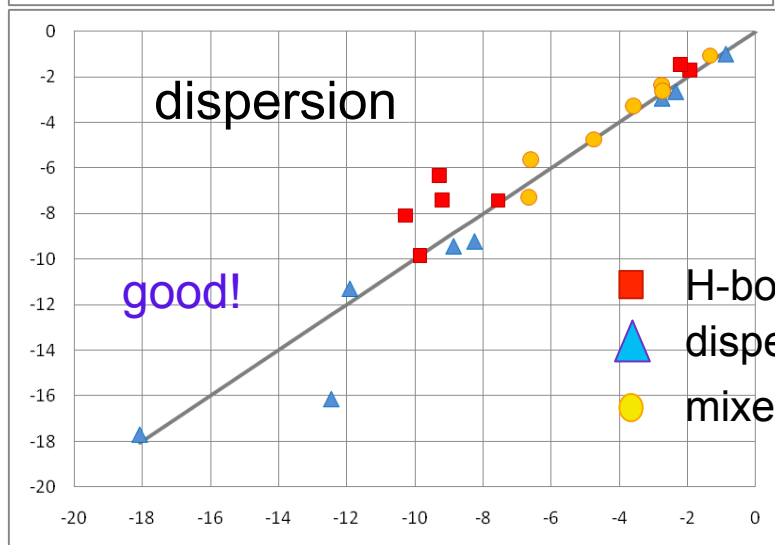
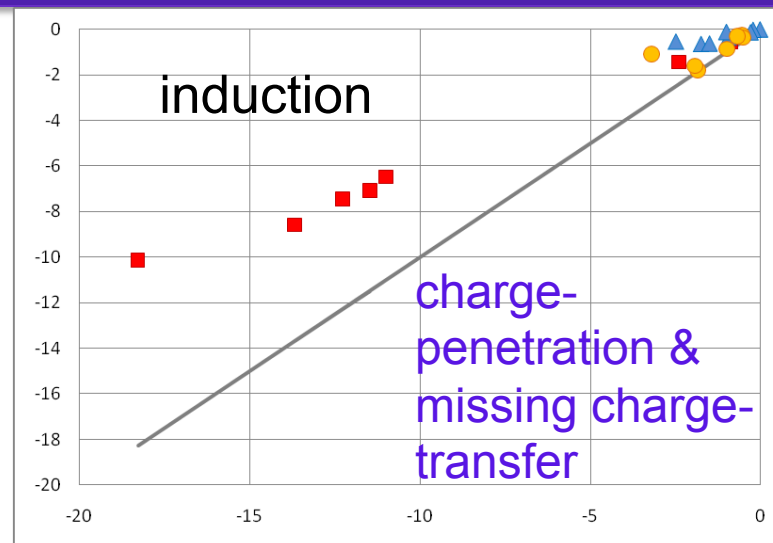
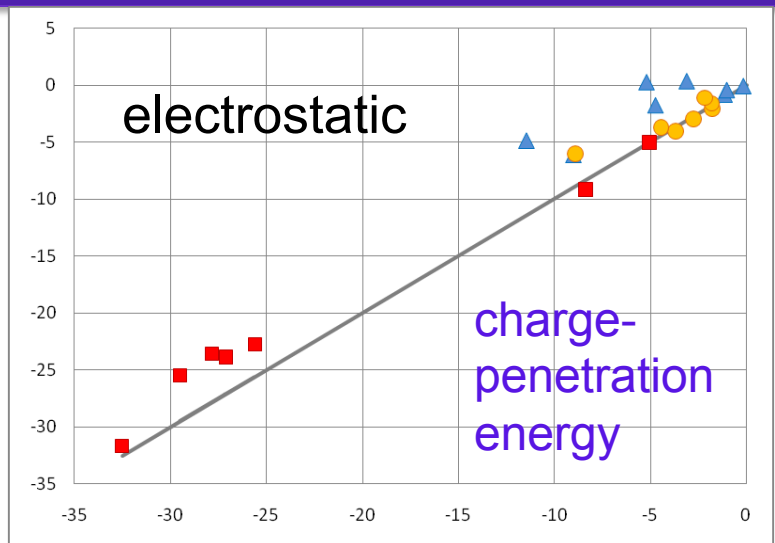
Dr. Dmytro Kosenkov



Joanna Flick

Paton et al, *J. Chem. Inf. Model.* 2009, 49, 944–955

EFP vs SAPT



J. Chem Theory Comp., 8 (8), 2835–2843 (2012)

EFP in a nutshell



- rigid-geometry fragment-based polarizable force field
- all EFP force field parameters are obtained from a separate *ab initio* calculation: **no fitted parameters**
- provides physical insight into intermolecular interaction
- **accuracy: 10-15% relative error in interaction energies** (similar to MP2, better than many DFT functionals, superior to classical force fields)
- accuracy can be further improved

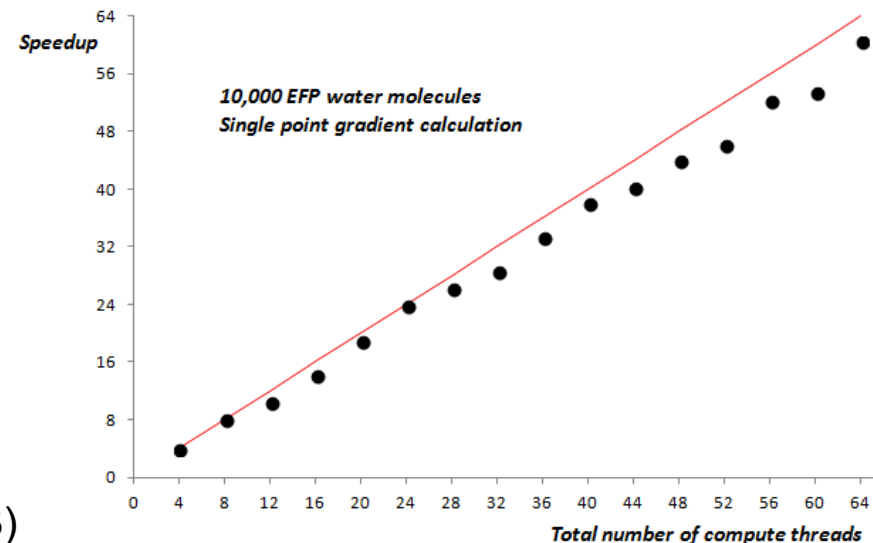
LibEFP: stand-alone EFP implementation

- written in standard C99
- uses native EFP data format generated by GAMESS
- 2-clause BSD license
- uses BLAS wherever possible for better performance
- available as a shared or static library
- parallelization across multiple nodes using hybrid MPI/OpenMP

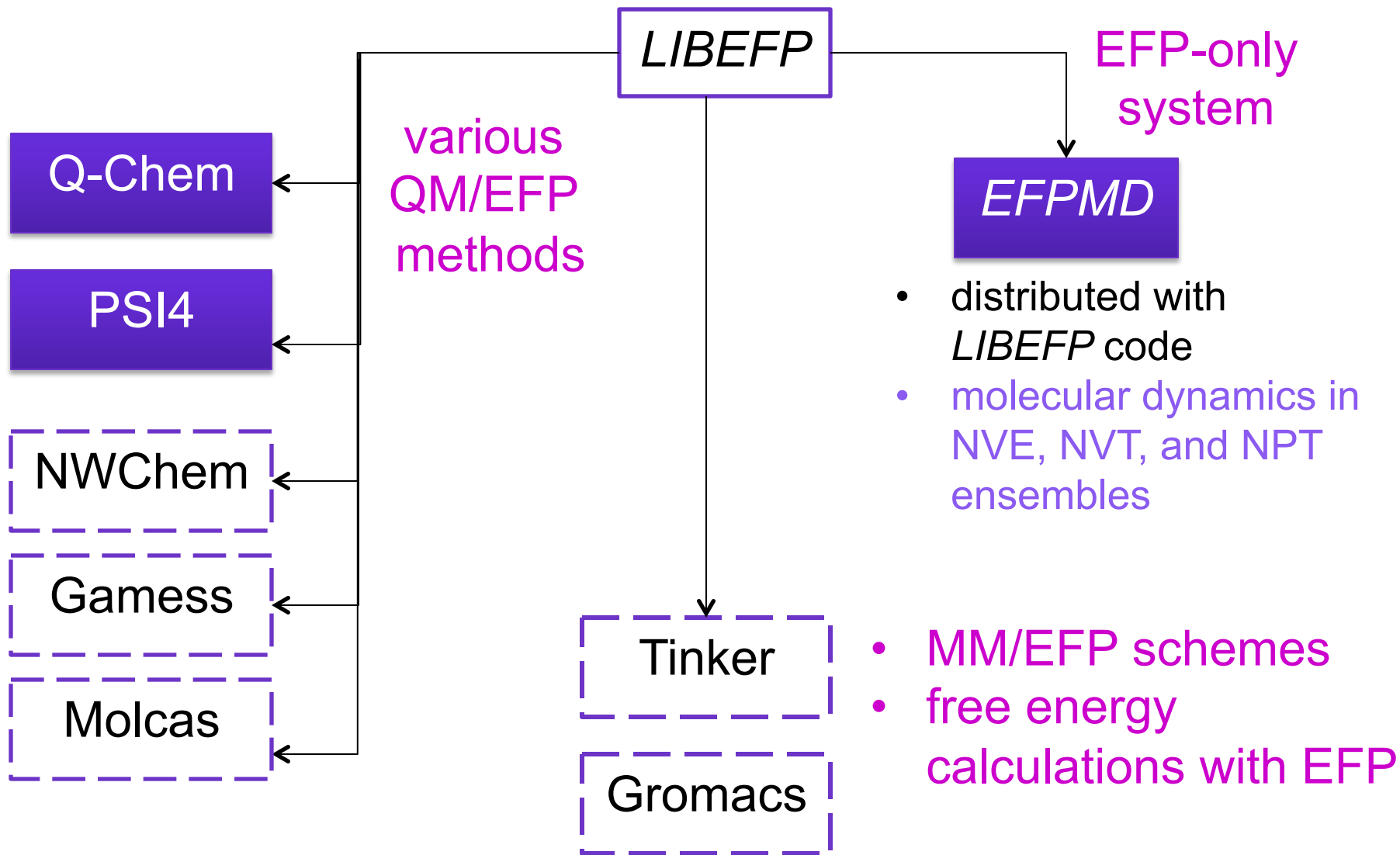
Kaliman and Slipchenko, JCC 34, 2284 (2013)
Kaliman and Slipchenko, JCC 36, 129 (2015)

Dr. Ilya Kaliman

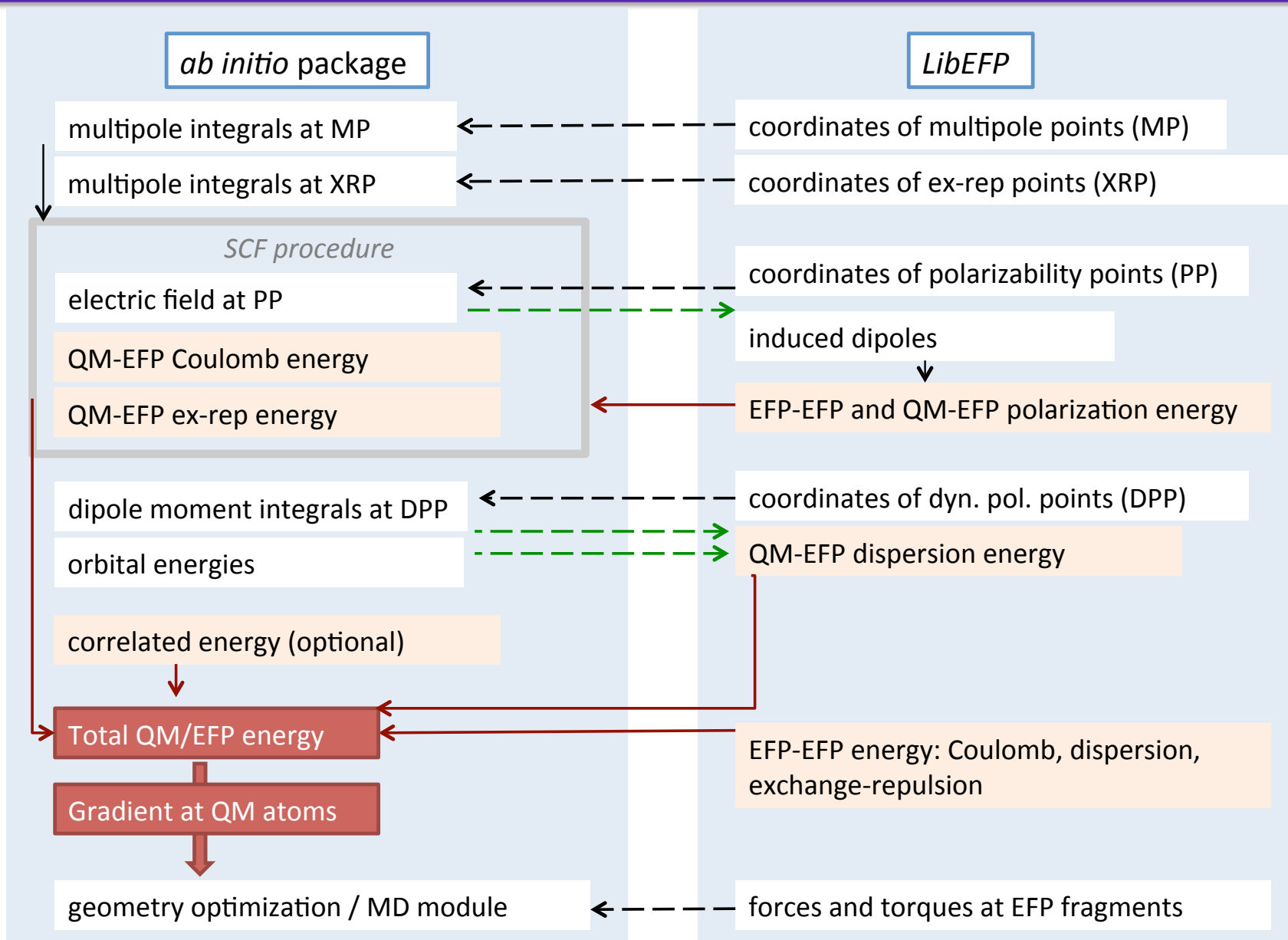
<http://www.libefp.org/>



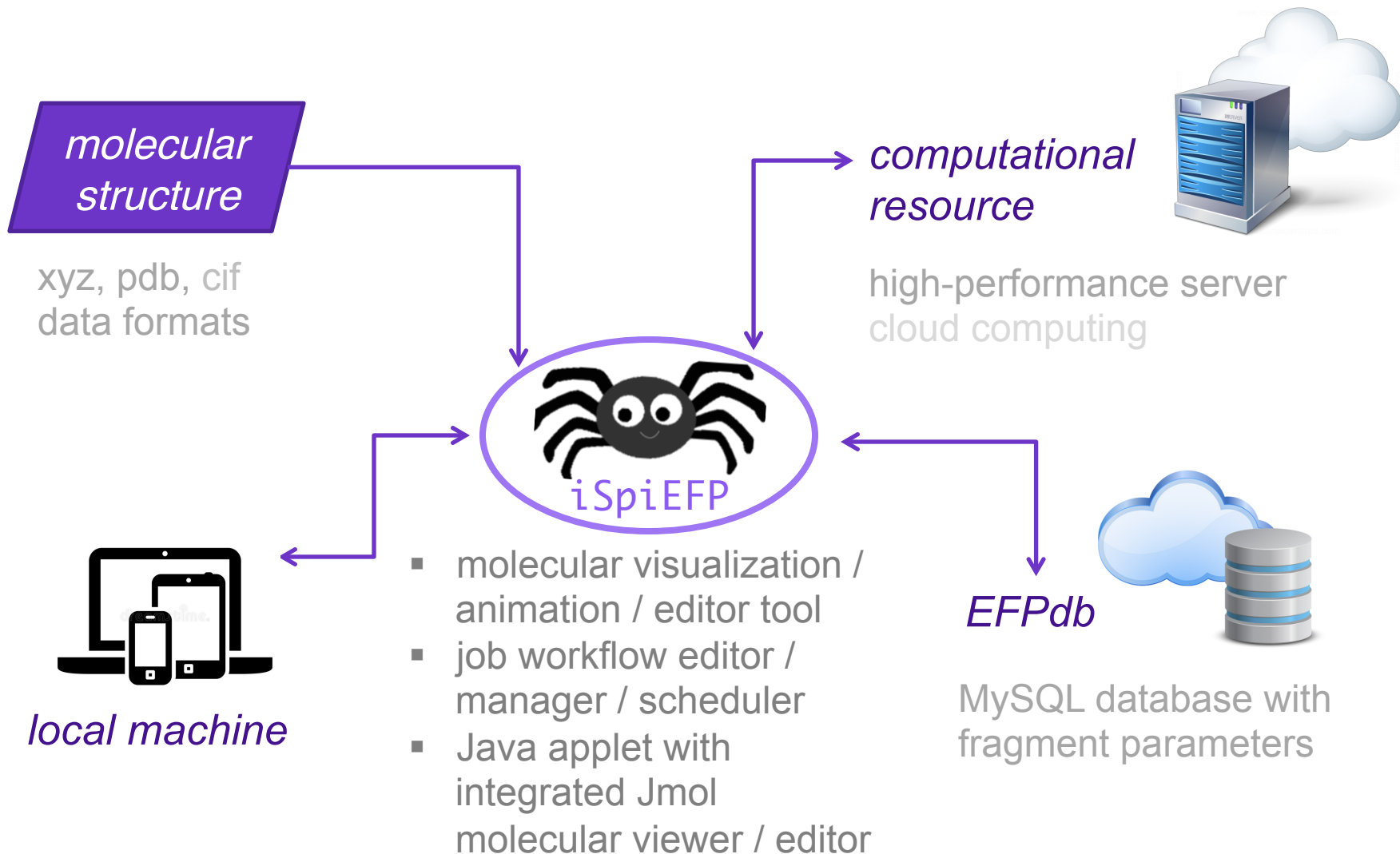
LibEFP



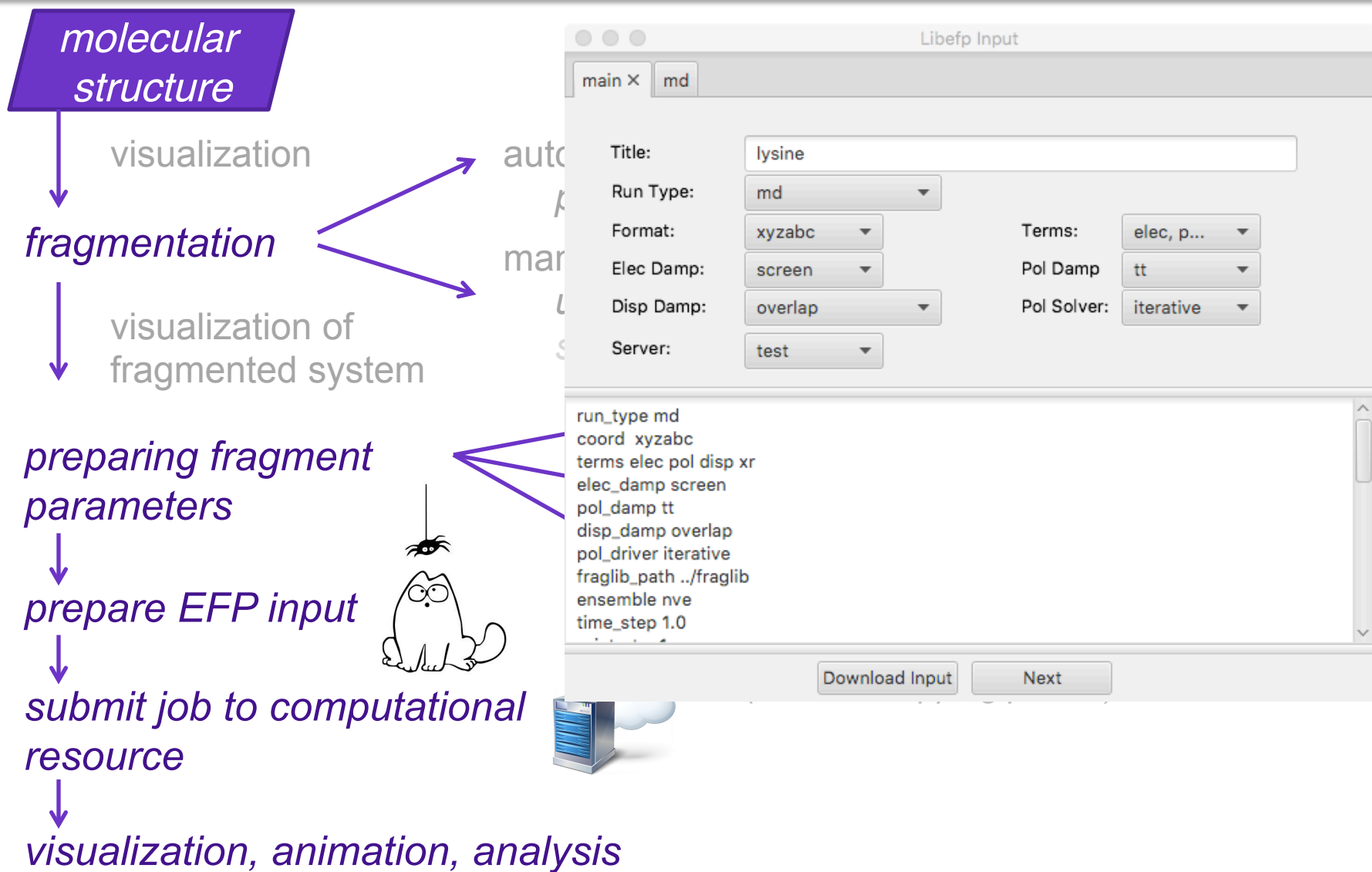
QM-LibEFP interface



iSpiEFP: GUI and job manager



iSpiEFP: EFP workflow



Fragmentation of covalent systems

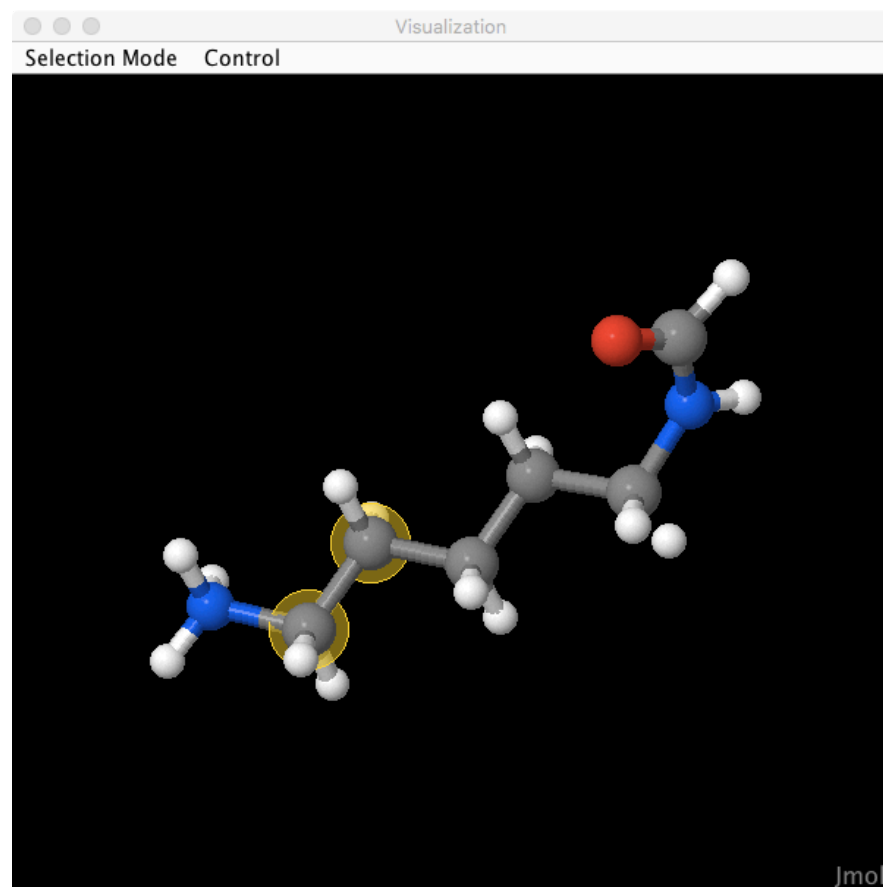
automatic

proteins, DNA, fatty acids

manual

user-defined fragmentation

smart substructure search



Fragmentation of covalent systems

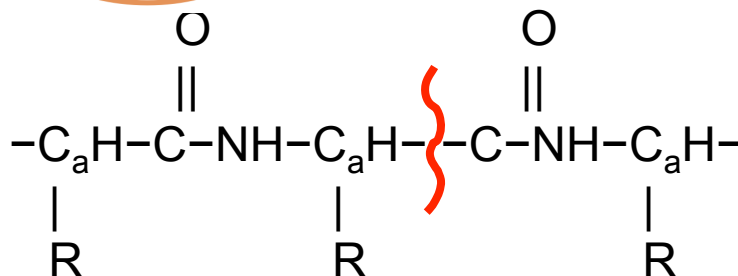
automatic

proteins, DNA, fatty acids

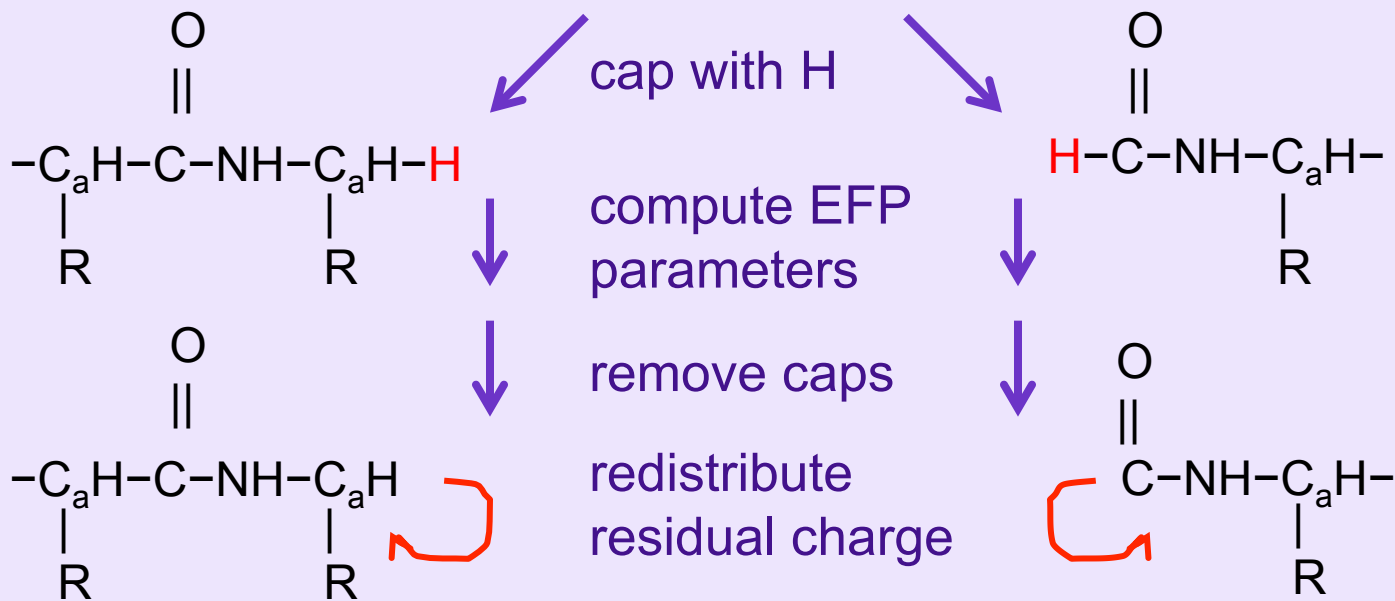
manual

user-defined fragmentation

smart substructure search



automated



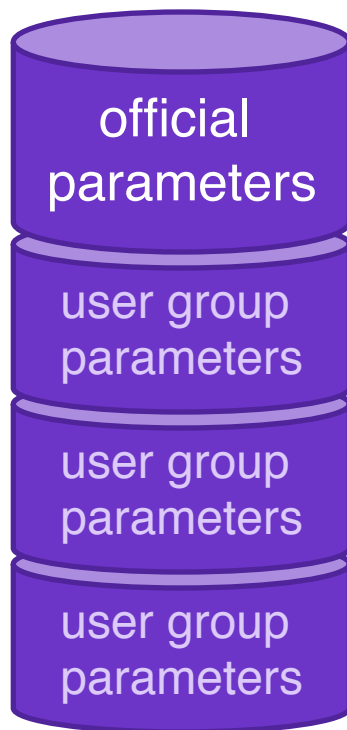
EFPdb parameter database



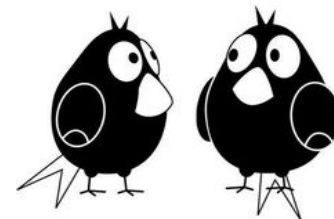
MySQL database with fragment parameters

Fragment info

- name
- chemical formula
- smile string
- EFP terms
- basis set used
- status (official / unofficial)
- structure (xyz format)
- parameters for each term



official parameters
open to the world



user group parameters
open to users within
the group

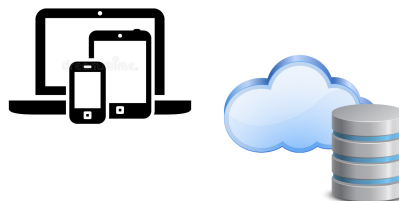
* group is defined during
GUI registration



Fragment search

search local directories

search EFPdb database

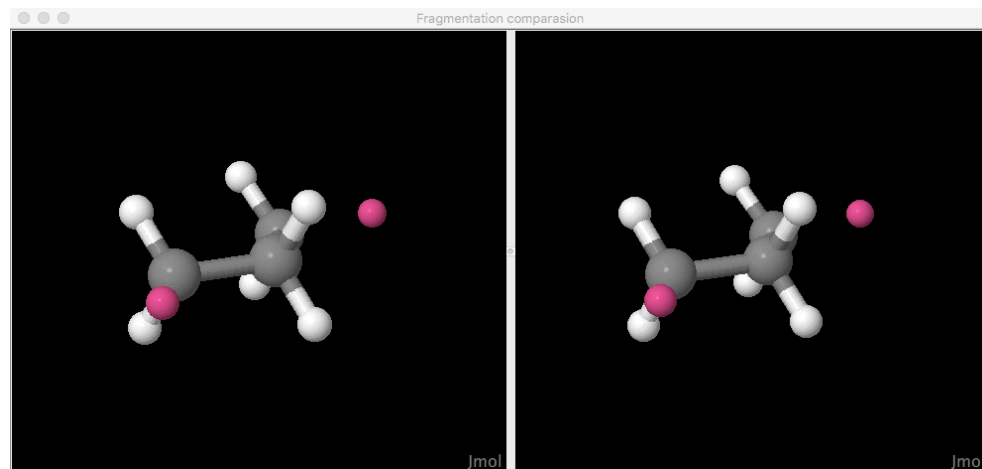
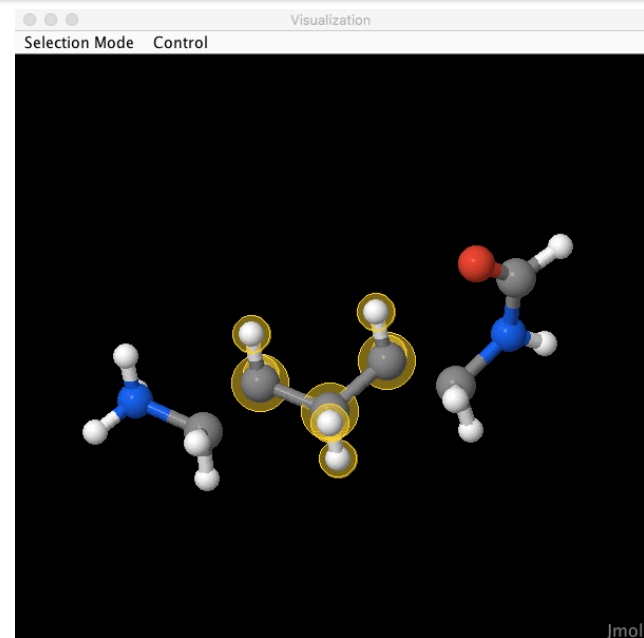


- Search is based on:
1. *Chemical formula (ordered)*
 2. *Connectivity map (distinguishing between structural isomers)*
 3. *RMSD between atom positions*

a list of fragments with user-defined tolerance on RMSD

visualization of all fragments in the list

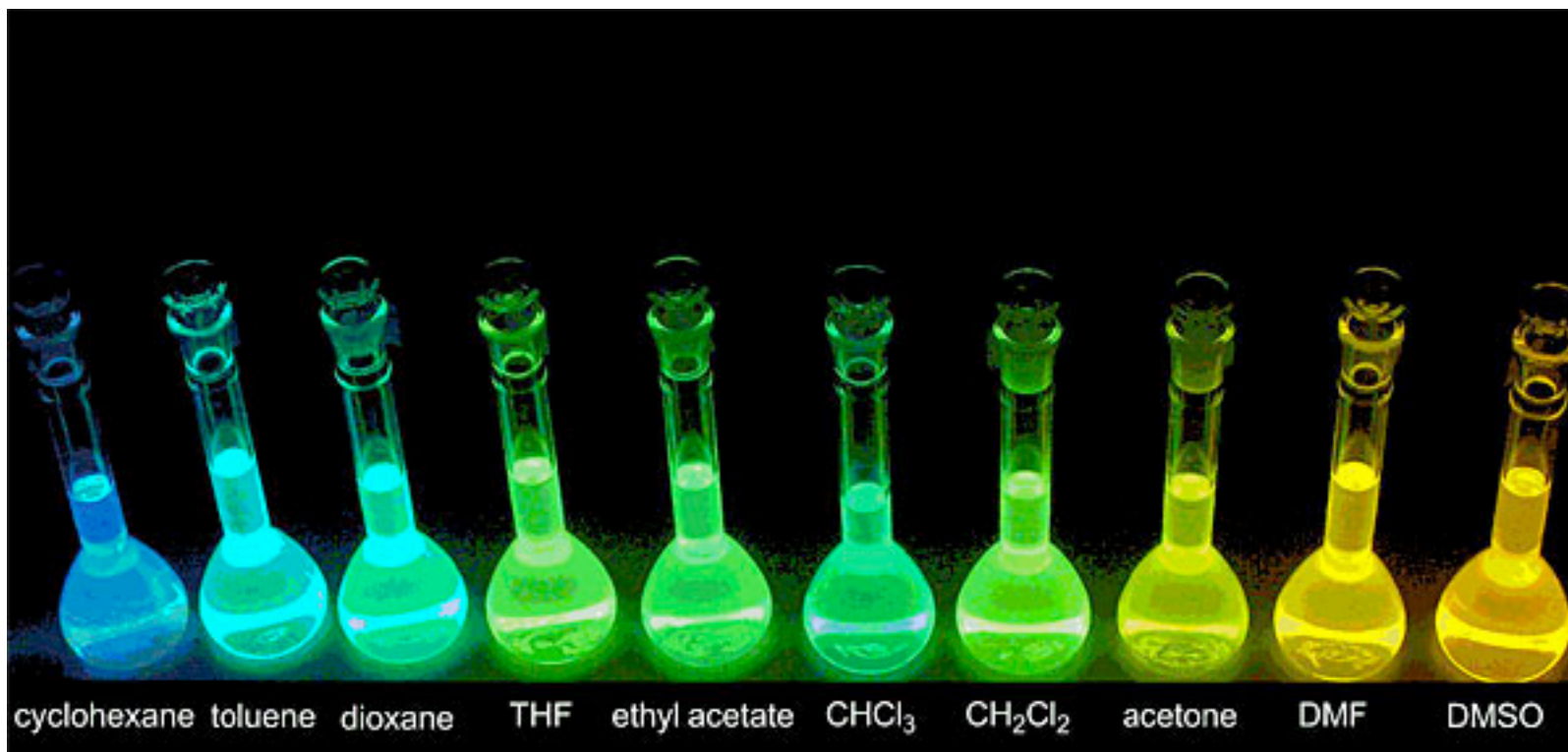
selection of a fragment
default: smallest RMSD



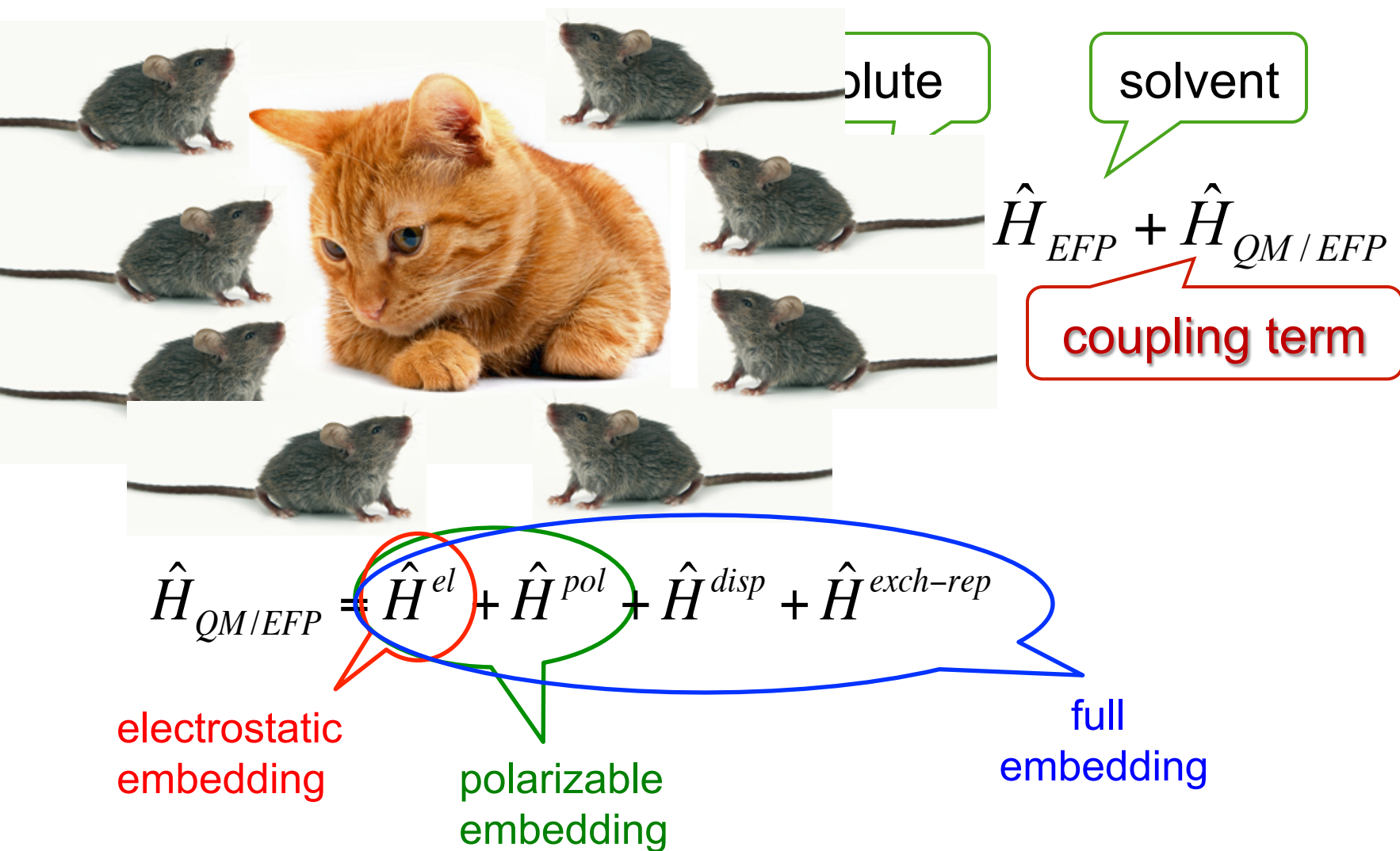
Solute-solvent tete-a-tete

Solvatochromism = differential solvation of the ground and excited states of a chromophore

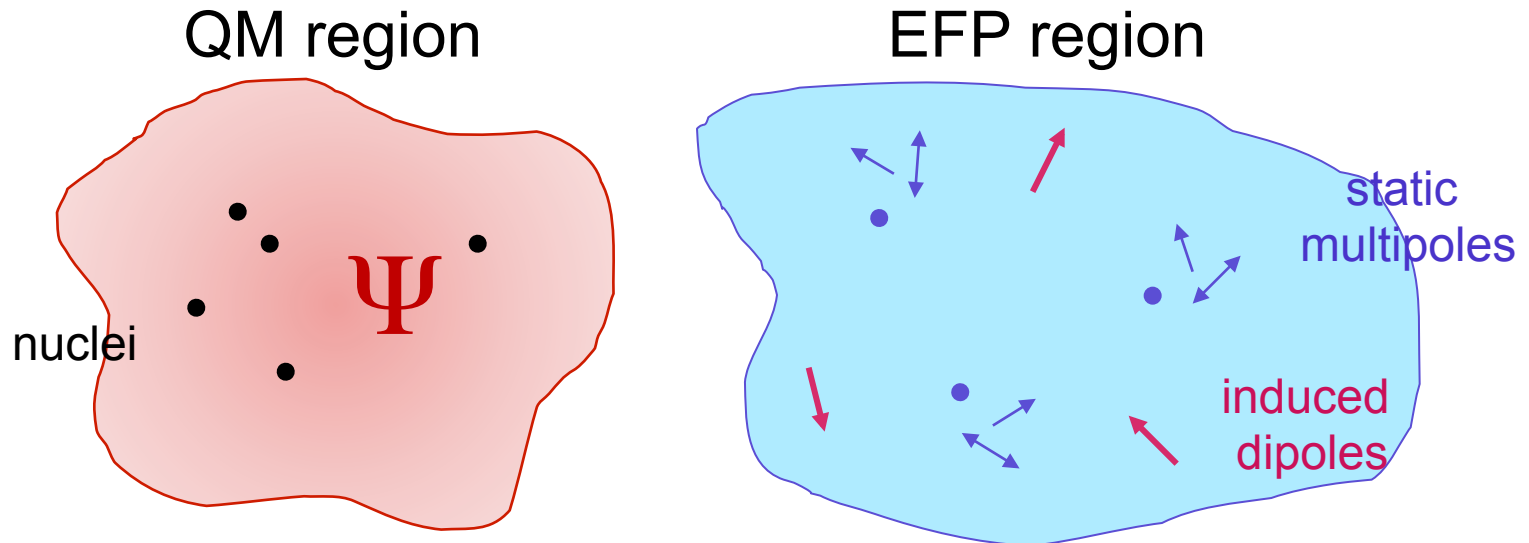
Influence of solvent on properties of solute



QM / EFP



Self-consistent polarization



Induced dipole

$$\mu_{\gamma} = \alpha_{\gamma\alpha} F_{\alpha}^{total}$$

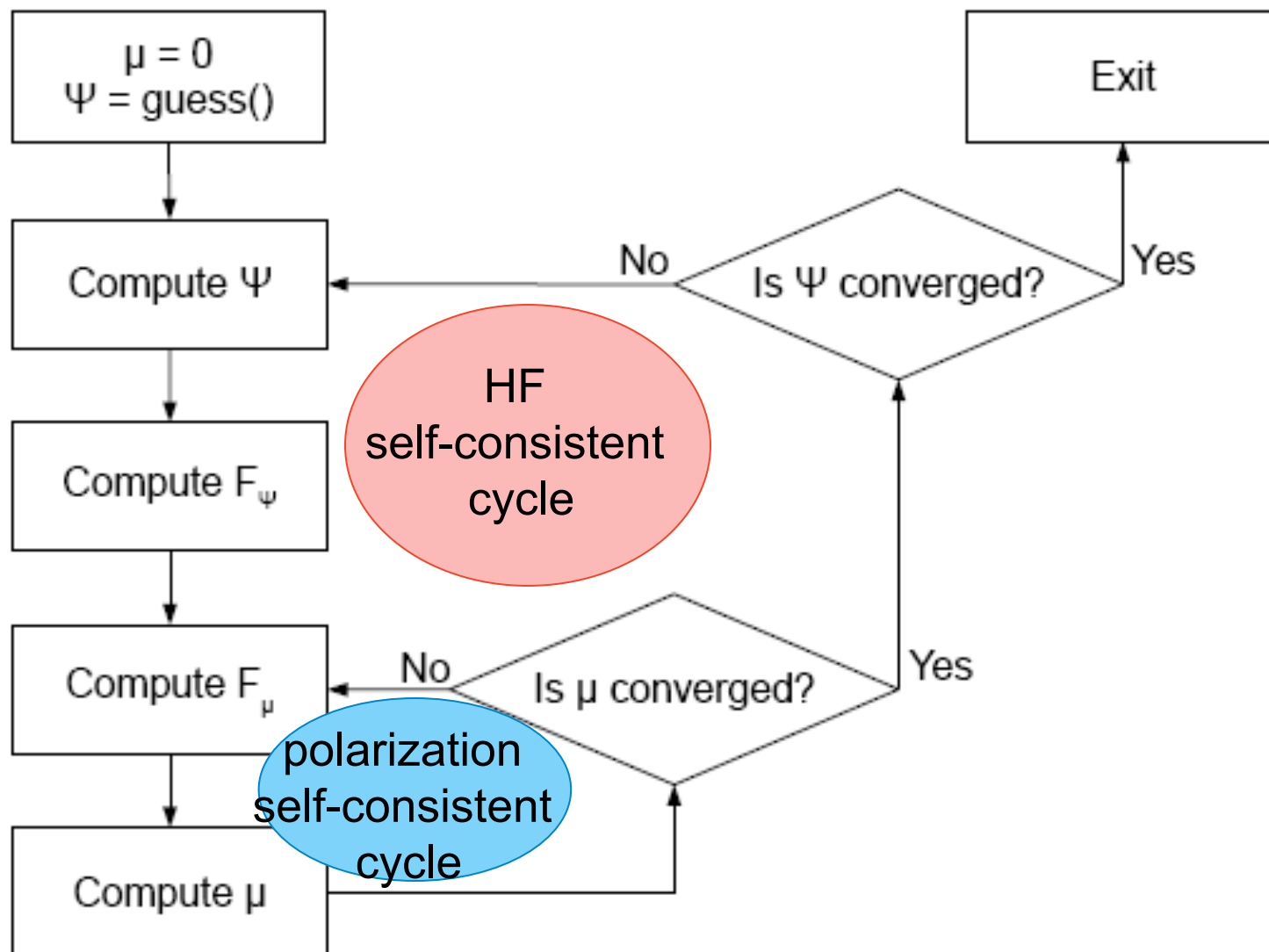
total field

polarizability tensors

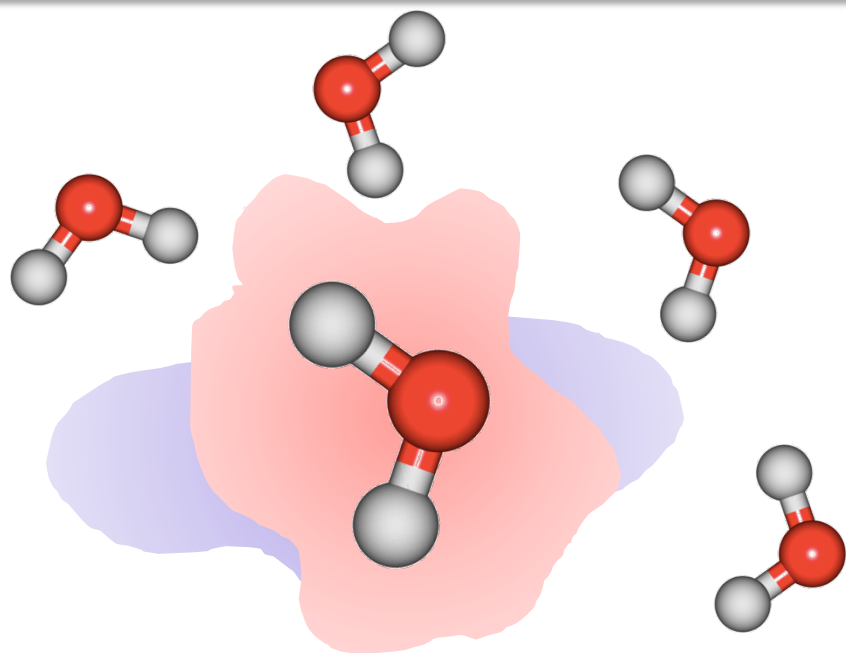
$$F^{total} = \sum (F^{mult} + F^{ind}) + F^{ai} + F^{ai-nuc}$$

$$E^{pol} = -\frac{1}{2} \sum \mu (F^{mult} + F^{ai-nuc}) + \frac{1}{2} \sum \mu F^{ai}$$

Polarization within HF cycle



QM/EFP for the electronic excited states



Generally, each excited state has different electron density & charge distribution \rightarrow different response from environment \rightarrow **state-specific perturbative treatment**

Polarization correction to the excitation energy due to polarizable environment (using one-electron **excited state density**):

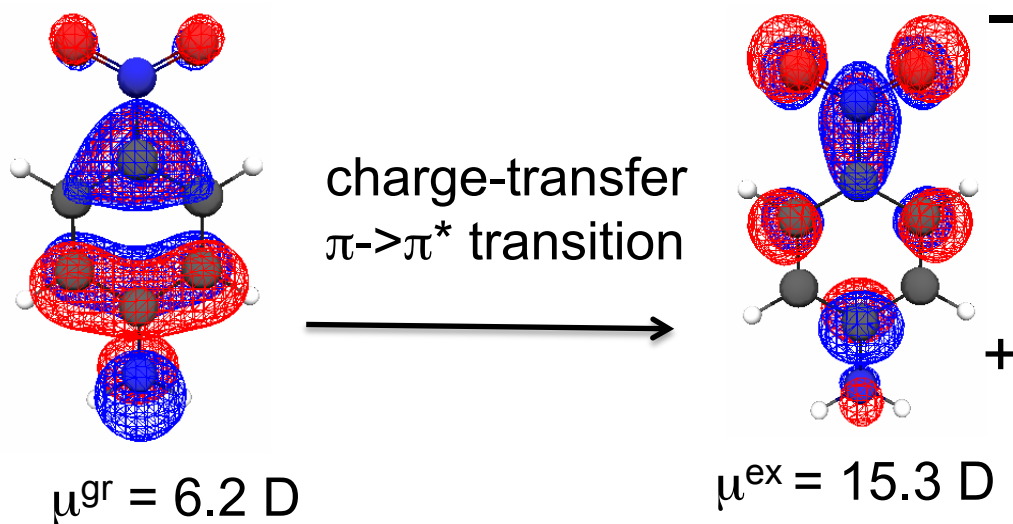
$$\Delta E^{pol} = E^{pol,ai}(\mu^{ex}) - E^{pol,gr}(\mu^{gr}) - \underbrace{\sum (\mu^{ex} - \mu^{gr}) F^{ai,ex}}_{\text{leading correction to the interaction between } \mu^{ex} \text{ and } \Psi^{ex}}$$

Thompson & Schenter, JPC 99, 6374 (1995)

leading correction to the interaction between μ^{ex} and Ψ^{ex}

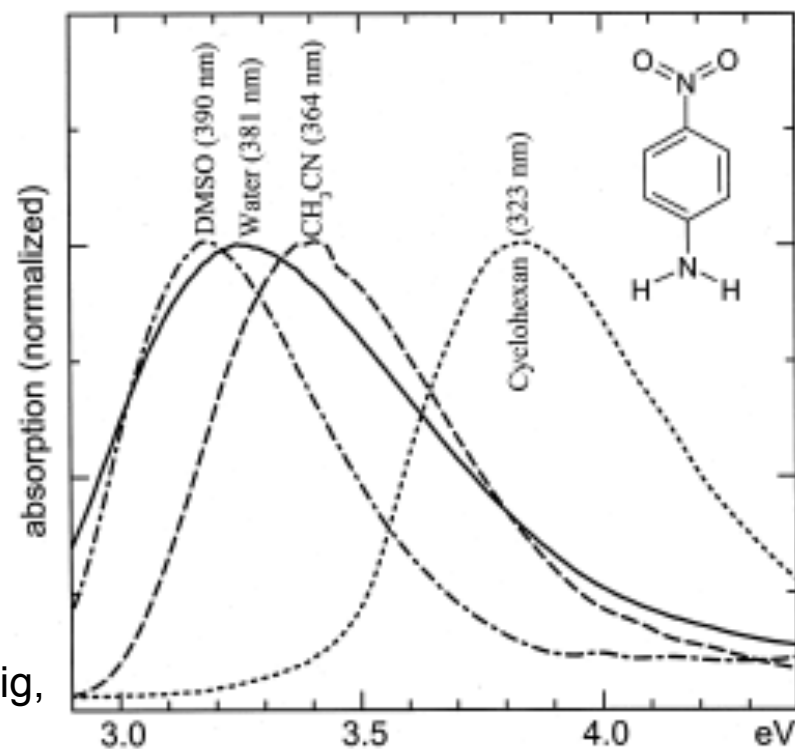
Solvatochromism in para-nitroaniline

Para-nitroaniline (pNA) – a chromophore with bright low-lying charge-transfer state



Kovalenko, Schanz, Farztdinov, Hennig, Ernsting, CPL 323, 312 (2000)

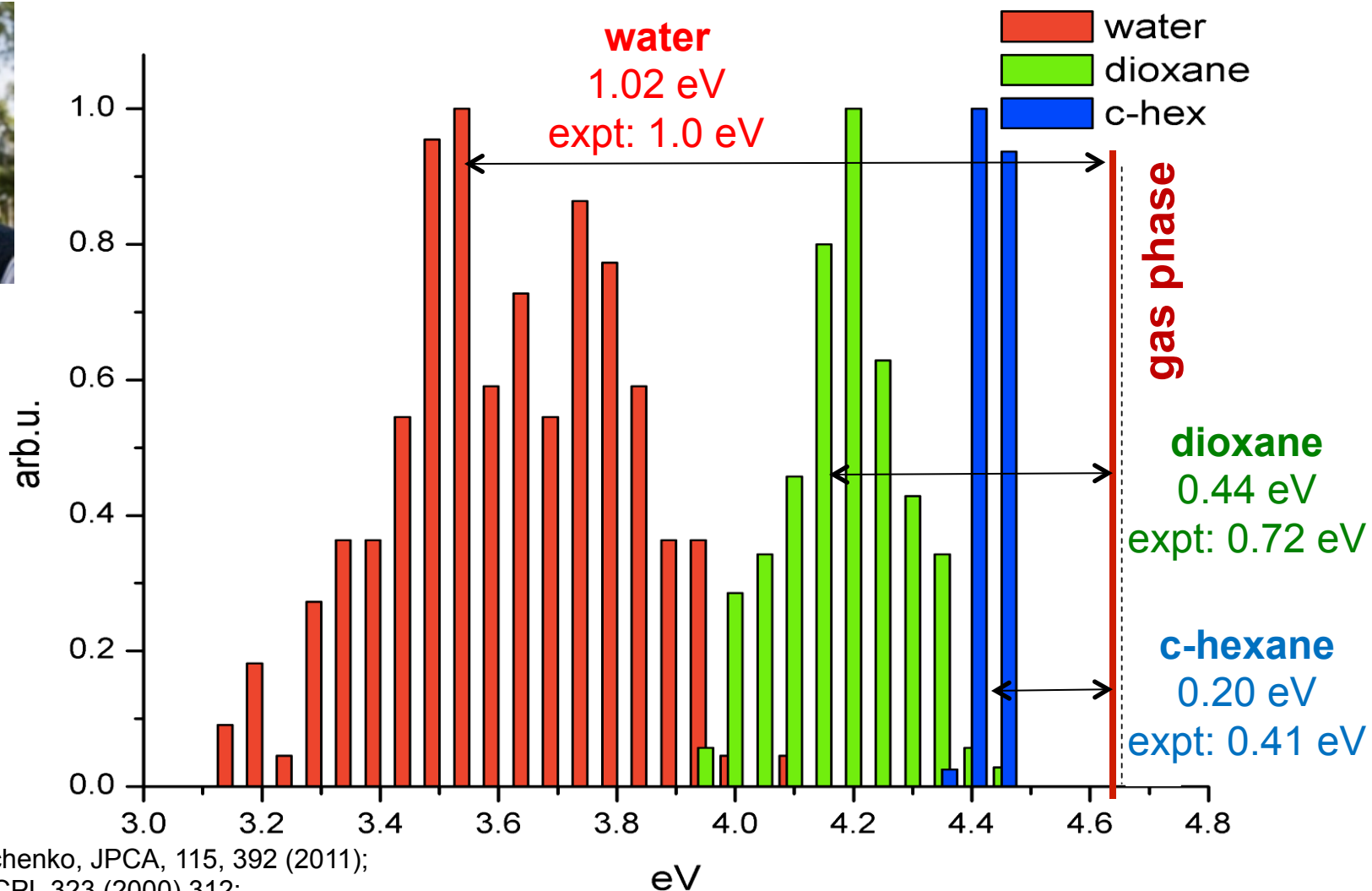
absorption spectrum



Solvatochromic shifts in pNA



Dr. Dmytro Kosenkov

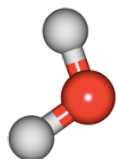
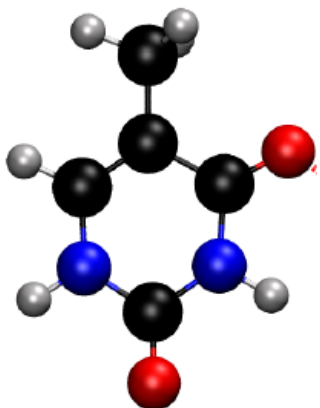


Kosenkov & Slipchenko, JPCA, 115, 392 (2011);
Kovalenko et al, CPL 323 (2000) 312;
Morgan et al, JCP 115 (2001) 912

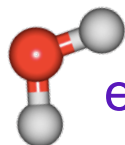
Vertical ionization energy of hydrated thymine



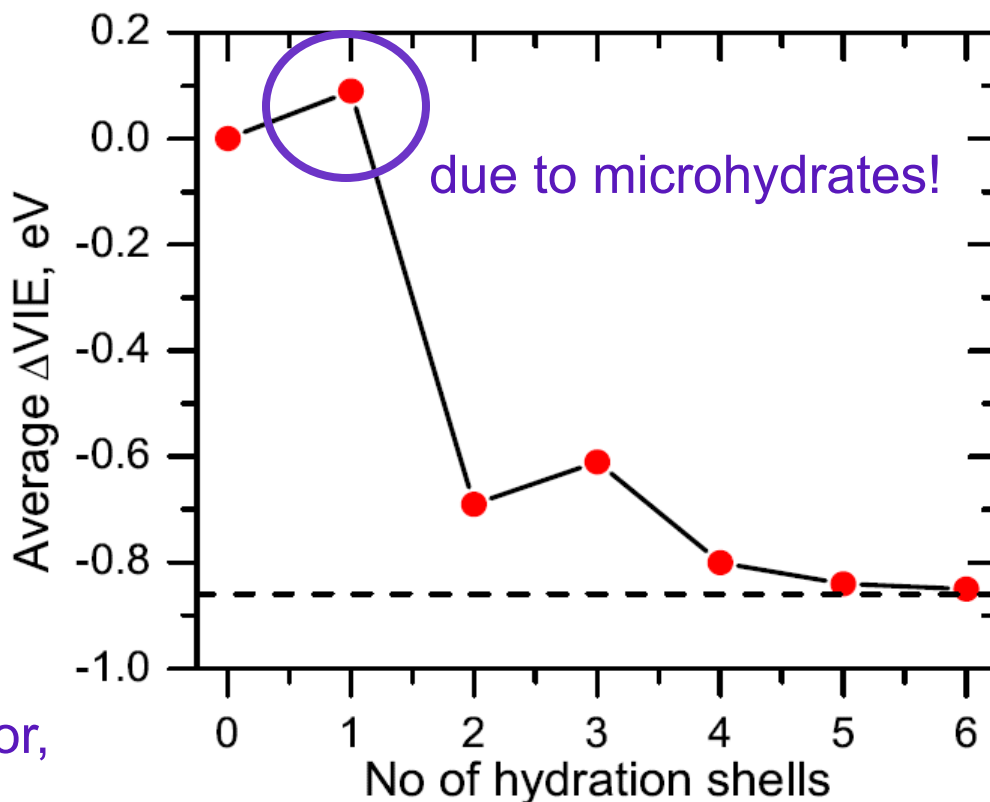
Dr. Debashree Ghosh



electron acceptor,
increases VIE



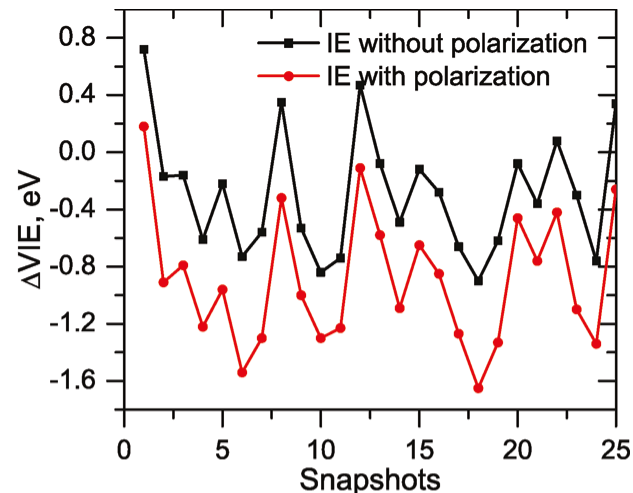
electron donor,
decreases VIE



EOM-IP-CCSD/EFP

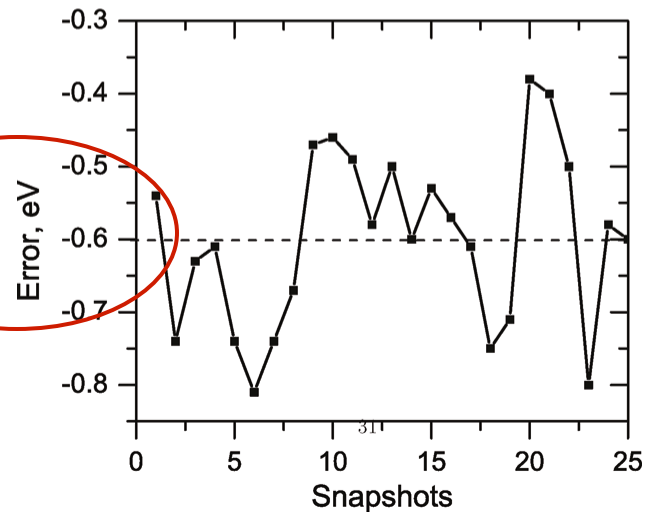
Ghosh, Isayev, Slipchenko, Krylov,
JPCA **115**, 6028 (2011)

VIE of hydrated thymine



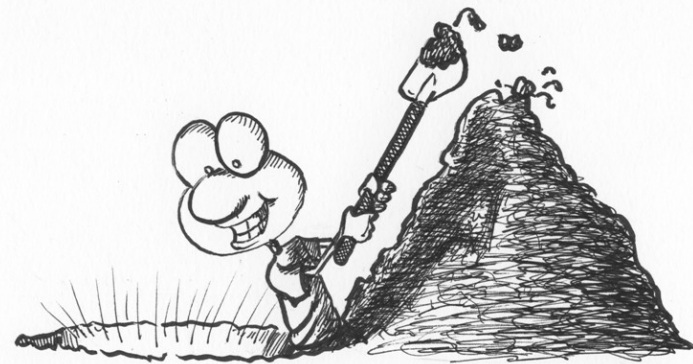
(a)

Polarization of environment is extremely important!



(b)

A closer look at solvatochromism

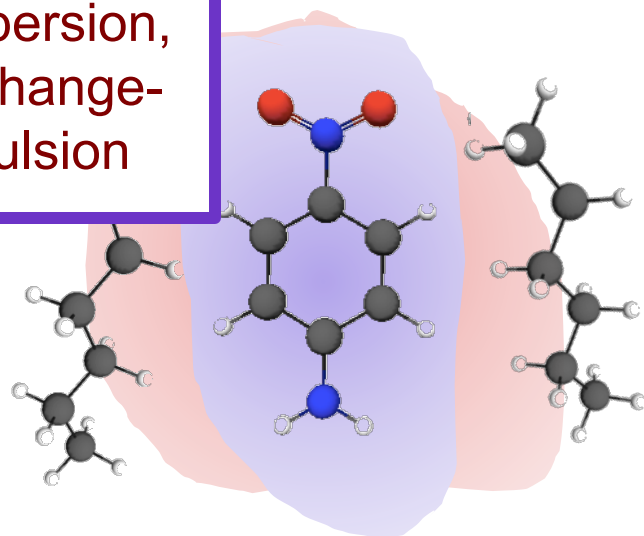
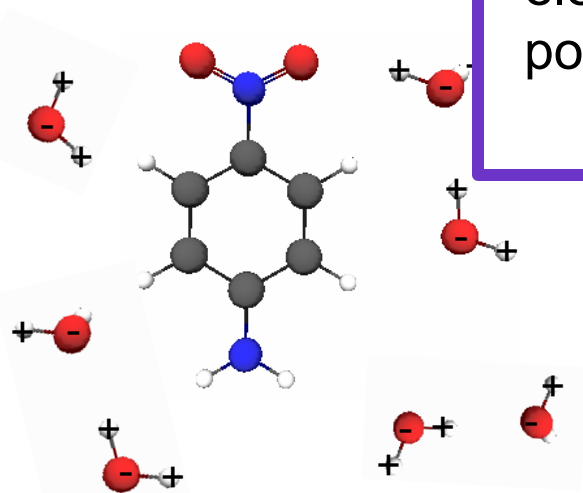
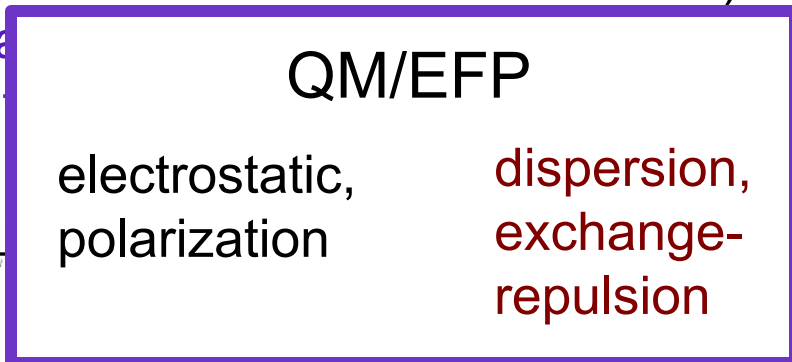


Electrostatic terms (dominant in polar or polarizable solvents) - stabilize the electronic state

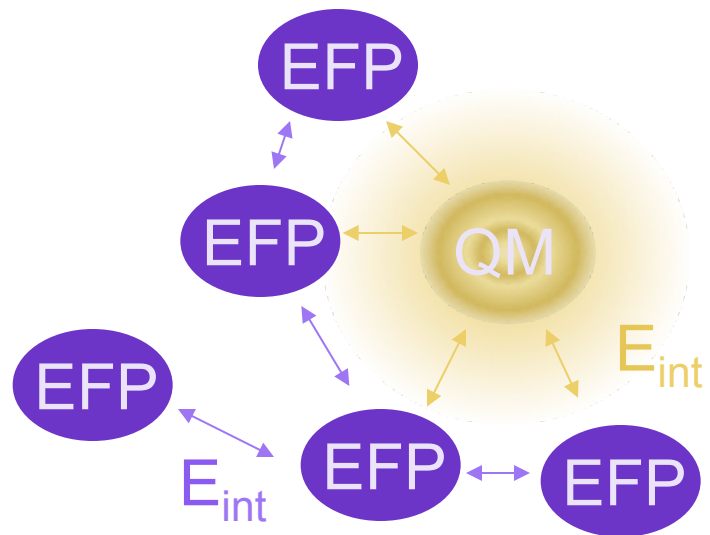
with larger partial charges
larger dipole moments

Short-range "cavity terms" (dominant in non-polar solvents)

the electronic state of
size



QM / EFP: toward full embedding



solute

solvent

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{EFP} + \hat{H}_{QM/EFP}$$

coupling term

$$\hat{H}_{QM/EFP} = \hat{H}^{el} + \hat{H}^{pol} + \hat{H}^{disp} + \hat{H}^{exch-rep}$$

Smith, Ruedenberg, Gordon,
Slipchenko, JCP 136, 244107 (2012);

Slipchenko, Ruedenberg, Gordon,
JPCA 2017, 121, 9495-9507

Long-range perturbation theory

$$H^0 = H^A + H^B$$

$$H' = \int \frac{\hat{\rho}^A(r)\hat{\rho}^B(r')}{4\pi\epsilon_0|r-r'|} drdr'$$

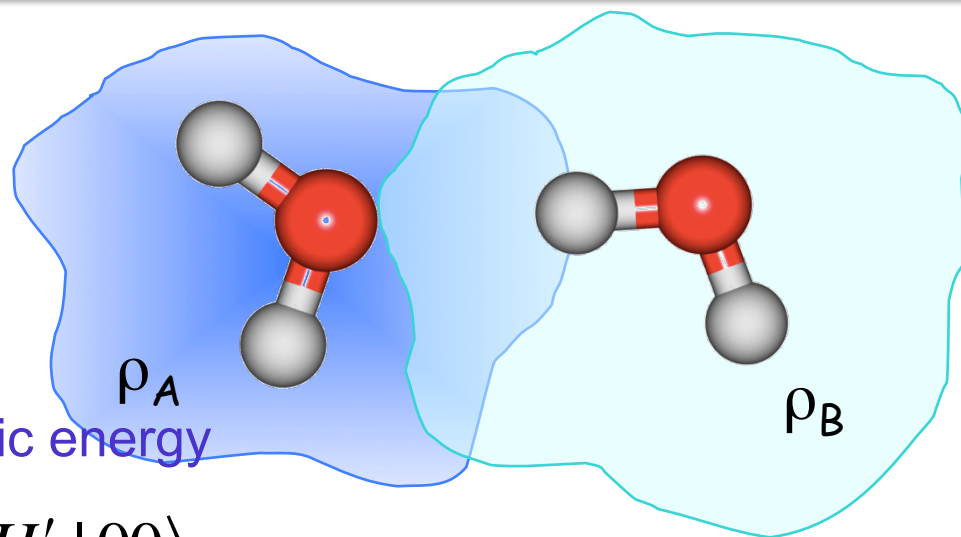
$$E^0 = E^A + E^B$$

$$E' = \langle 00 | H' | 00 \rangle \quad \text{electrostatic energy}$$

$$E'' = - \sum \frac{\langle 00 | H' | mn \rangle \langle mn | H' | 00 \rangle}{E_{mn}^0 - E^0}$$

polarization (induction)
energy

dispersion energy



$$E_{ind}^A = - \sum_{m \neq 0} \frac{\langle 00 | H' | m0 \rangle \langle m0 | H' | 00 \rangle}{E_m^A - E^A}$$

$$E_{ind}^B = - \sum_{n \neq 0} \frac{\langle 00 | H' | 0n \rangle \langle 0n | H' | 00 \rangle}{E_n^B - E^B}$$

$$E_{disp} = - \sum_{\substack{m \neq 0 \\ n \neq 0}} \frac{\langle 00 | H' | mn \rangle \langle mn | H' | 00 \rangle}{E_m^A - E_n^B - E^A - E^B}$$

Dispersion energy between EFP fragments

Applying **multipole expansion** to classical **fragments A and B**, the perturbation H' becomes:

$$H' = Tq^A q^B + T_\alpha (q^A \hat{\rho}_\alpha^B - \hat{\rho}_\alpha^A q^B) - T_{\alpha\beta} \hat{\rho}_\alpha^A \hat{\rho}_\beta^B + \dots$$

T , T_α and $T_{\alpha\beta}$ are the electrostatic tensors of zero, first, and second rank

The leading term (C6):

$$E^{disp} = - \sum_{m,n \neq 0} T_{\alpha\beta}^{AB} T_{\gamma\delta}^{AB} \frac{\langle 0^A | \hat{\rho}_\alpha^A | m \rangle \langle m | \hat{\rho}_\gamma^A | 0^A \rangle \langle 0^B | \hat{\rho}_\beta^B | n \rangle \langle n | \hat{\rho}_\delta^B | 0^B \rangle}{E_{m0}^A + E_{n0}^B}$$

Introducing Casimir-Polder identity: $\frac{1}{A+B} = \frac{2}{\pi} \int_0^\infty \frac{AB}{(A^2 + \omega^2)(B^2 + \omega^2)} d\omega$

and notation
dynamic po

$$T_{\alpha\beta} = \nabla_\beta \nabla_\alpha \left(\frac{1}{R} \right) = \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{R^5} \quad 2 \sum_m \frac{\omega_{m0} \langle 0 | \hat{\rho}_\alpha | m \rangle \langle m | \hat{\rho}_\beta | 0 \rangle}{\hbar(\omega_{m0}^2 - \omega^2)}$$

**Principal
fragment-fragment
energy**

$$E_6^{disp} = - \frac{\hbar}{2\pi} \sum_{\alpha\beta\gamma\delta}^{x,y,z} T_{\alpha\beta}^{AB} T_{\gamma\delta}^{AB} \int_0^\infty \alpha_{\alpha\gamma}^A(i\omega) \alpha_{\beta\delta}^B(i\omega) d\omega$$

Approximations in EFP-EFP dispersion term

- Distributed polarizabilities (on LMOs):
- Isotropic and spherical-atom approximation for polarizabilities:
- EFP-EFP C6 coefficient computed using 12-point quadrature:
- Damping function using inter-fragment overlap integrals:
- 4/3 factor to account for higher-order terms

$$\alpha_{bd}^B(i\omega) \rightarrow \sum_{j \in B} \alpha_{bd}^j(i\omega)$$

$$\alpha_{ab}(i\omega) = \bar{\alpha}(i\omega)\delta_{ab}$$

$$C_{6,kj} = \sum_{i=1}^{12} w_i \frac{2v_0}{(1-t_i)^2} \bar{\alpha}^k(i\omega) \bar{\alpha}^j(i\omega)$$

$$f_S^6 = 1 - S^2(1 - 2\ln|S| + 2\ln^2|S|)$$

$$E_{EFP-EFP}^{disp} = -\frac{4}{3} \sum_{k \in A, j \in B} \frac{f_{kj}^6 C_{kj}^6}{R_{kj}^6}$$

Amos et al, *J. Phys. Chem.* **1985**, 89, 2186-2192;
Adamovic & Gordon, *Mol. Phys.* **2005**, 103, 379-387;
Slipchenko and Gordon, *Mol. Phys.*, 107, 999 (2009)

QM-EFP dispersion

Applying **multipole expansion** to classical **fragment B**, while **A remains quantum**, the perturbation H' is:

$$H' = \int T_\alpha \mu_\alpha^B \rho^A(r) dr$$

$$E^{disp} = - \sum_{m,n \neq 0} \frac{\langle 0 | T_\alpha \rho^A | m \rangle \langle m | T_\beta \rho^A | 0 \rangle \langle 0 | \mu_\alpha^B | n \rangle \langle n | \mu_\beta^B | 0 \rangle}{E_{m0}^A + E_{n0}^B}$$

Again, using Casimir-Polder identity and gathering terms for dynamic polarizability tensor on fragment B:

$$E_{QM-EFP}^{disp} = -\frac{1}{\pi} \sum_{m \neq 0} \sum_{\alpha\beta}^{x,y,z} \langle 0 | T_\alpha \rho^A | m \rangle \langle m | T_\beta \rho^A | 0 \rangle \int_0^\infty \frac{\omega_{m0}^A}{(\omega_{m0}^A)^2 + \omega^2} \alpha_{\alpha\beta}^B(i\omega) d\omega$$

Approximating the sum-over-state expression by the orbital-based summation, obtain the principal expression:

$$E_{QM-EFP}^{disp} = -\frac{1}{\pi} \sum_{j \in B} \sum_k^{occ} \sum_r^{vir} \sum_{\alpha\beta}^{x,y,z} \langle k | T_\alpha | r \rangle \langle r | T_\beta | k \rangle \int_0^\infty \frac{\omega_{rk}^A}{(\omega_{rk}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega$$

QM-EFP dispersion

$$E_{QM-EFP}^{disp} = -\frac{1}{\pi} \sum_{j \in B} \sum_k^{occ} \sum_r^{vir} \sum_{\alpha\beta}^{x,y,z} \langle k | T_\alpha | r \rangle \langle r | T_\beta | k \rangle \int_0^\infty \frac{\omega_{rk}^A}{(\omega_{rk}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega$$

$$T_\alpha = \nabla_\alpha \left(\frac{1}{R} \right) = -\frac{R_\alpha}{R^3}$$

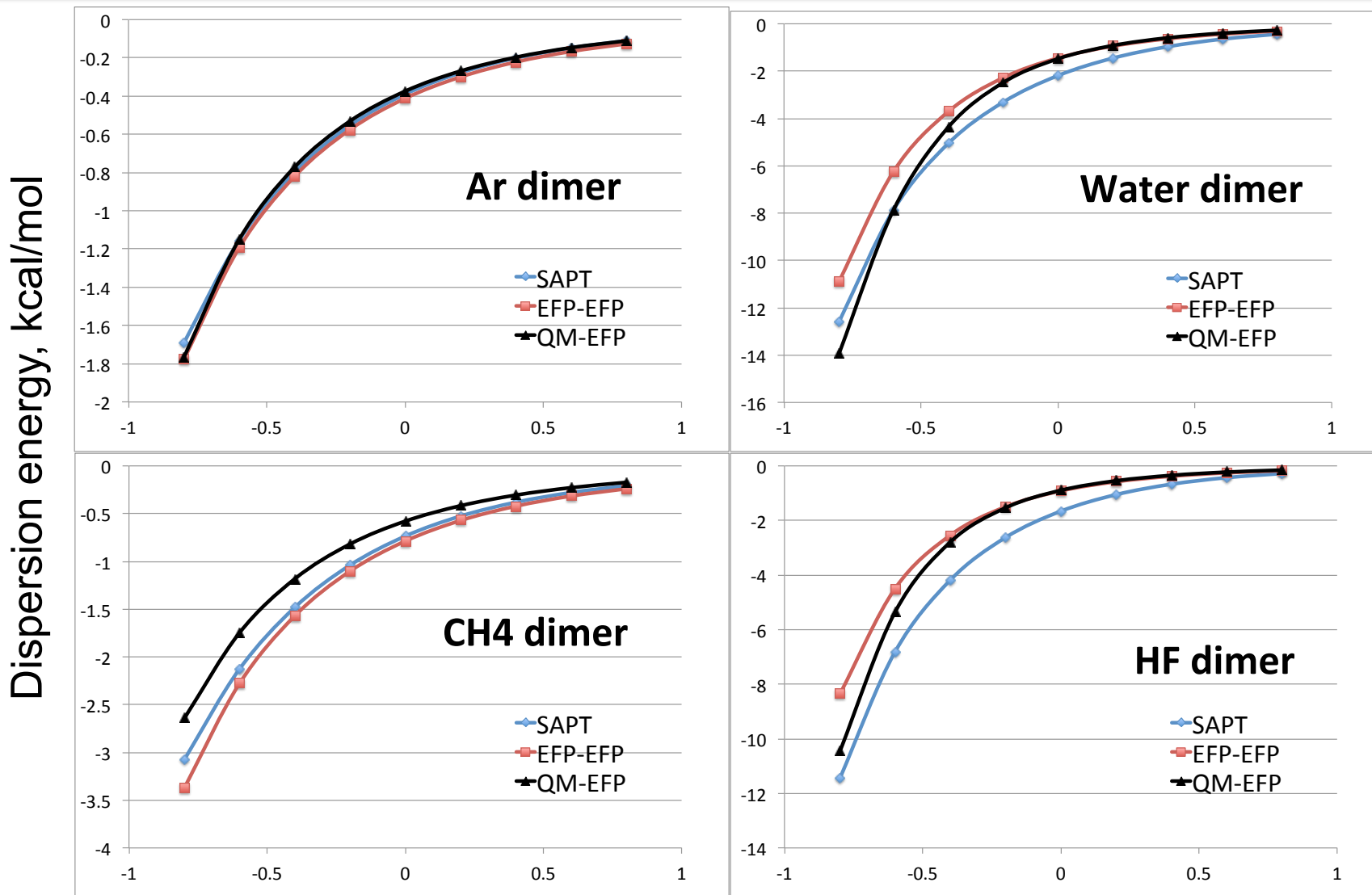
electric field integrals in occupied-virtual block ("transition" electric field)

computed using 12-point quadrature

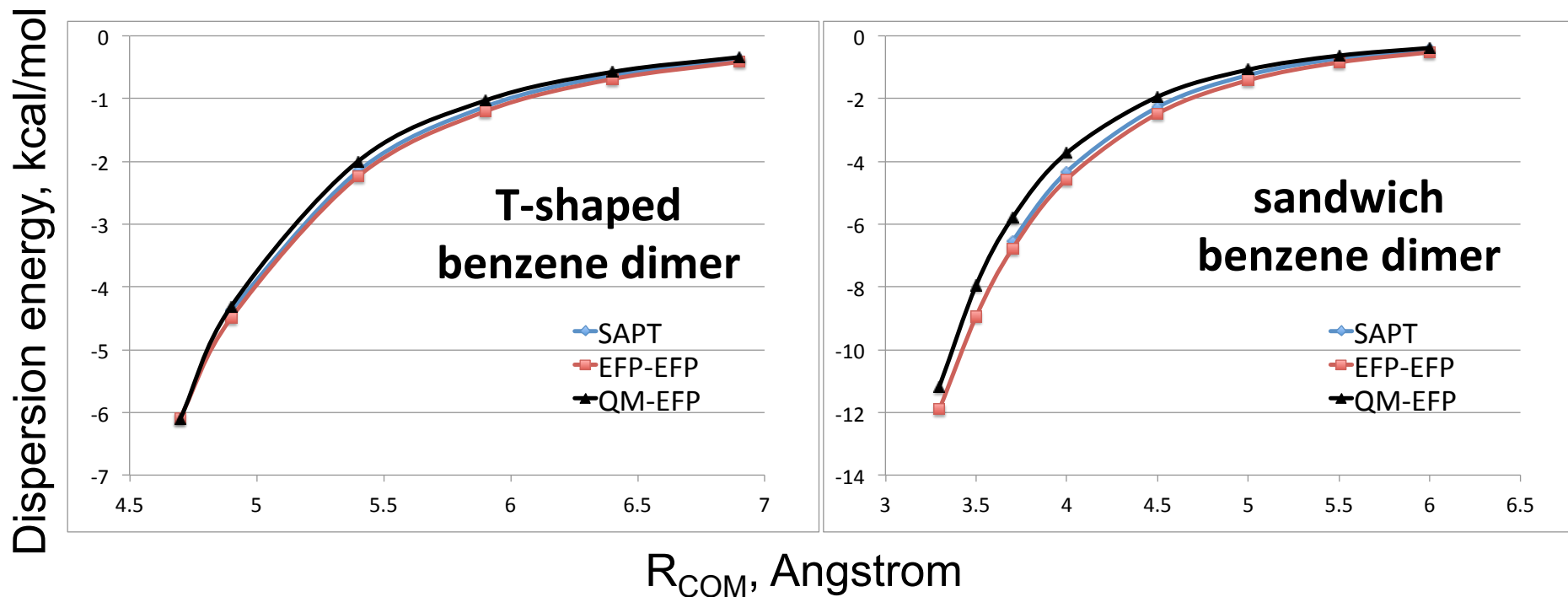
- Distributed polarizability tensors (on fragments) are used
- Information from the QM subsystem: electric field integrals, orbital energies
- Additive correction to SCF energy of the QM-EFP system

Slipchenko, Ruedenberg, Gordon,
JPCA 2017, 121, 9495–9507

Simple tests

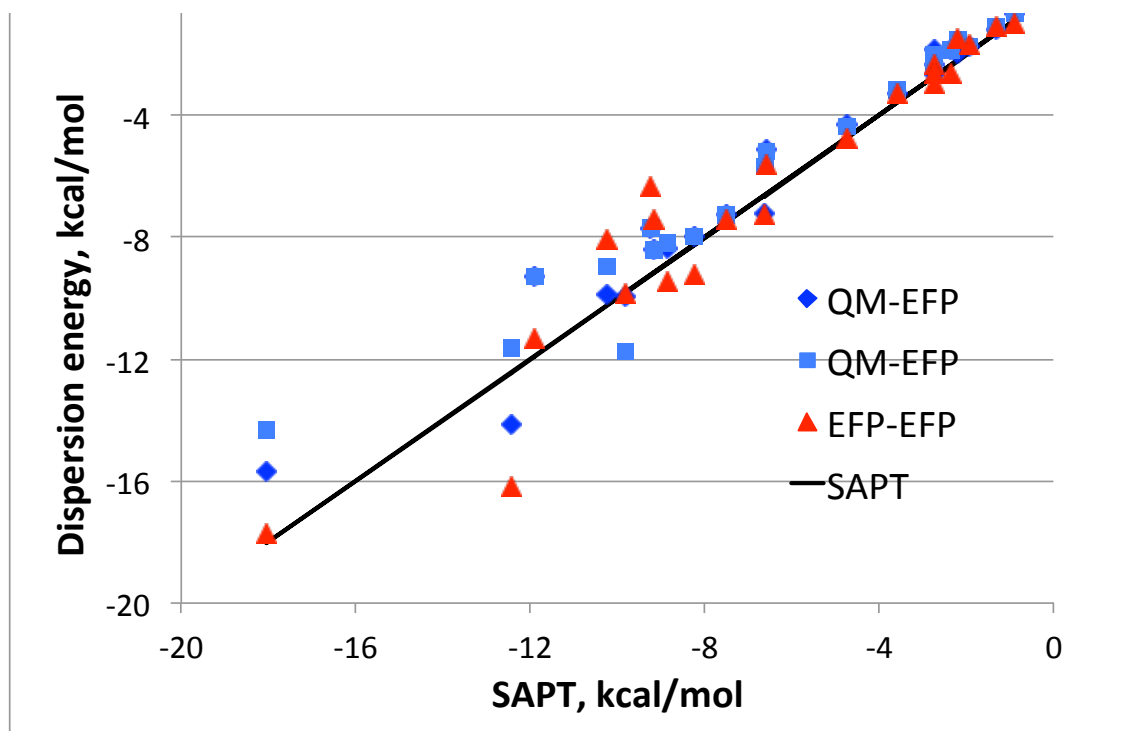


Favorite test: benzene dimer



Benchmarking on S22 dataset

	QM-EFP			EFP-EFP		
	MSE	MUE	Rel. error	MSE	MUE	Rel. error
H-bonded	0.43	0.73	0.10	1.12	1.13	0.16
dispersion	0.87	1.08	0.13	-0.62	0.85	0.10
mixed	0.54	0.62	0.15	0.20	0.38	0.09
all	0.63	0.82	0.13	0.20	0.79	0.12

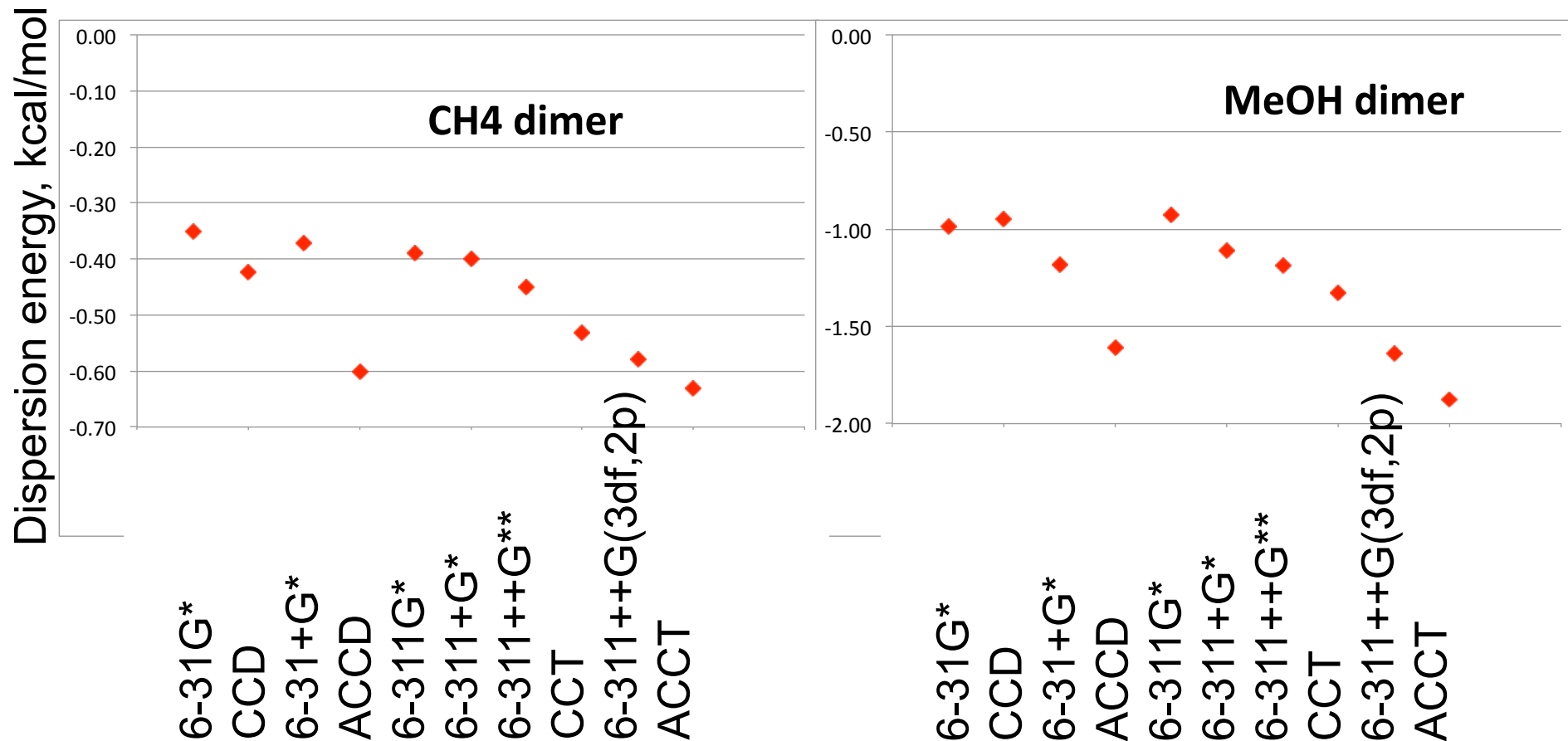


values in kcal/mol

QM-EFP and
EFP-EFP
dispersion terms
perform similarly

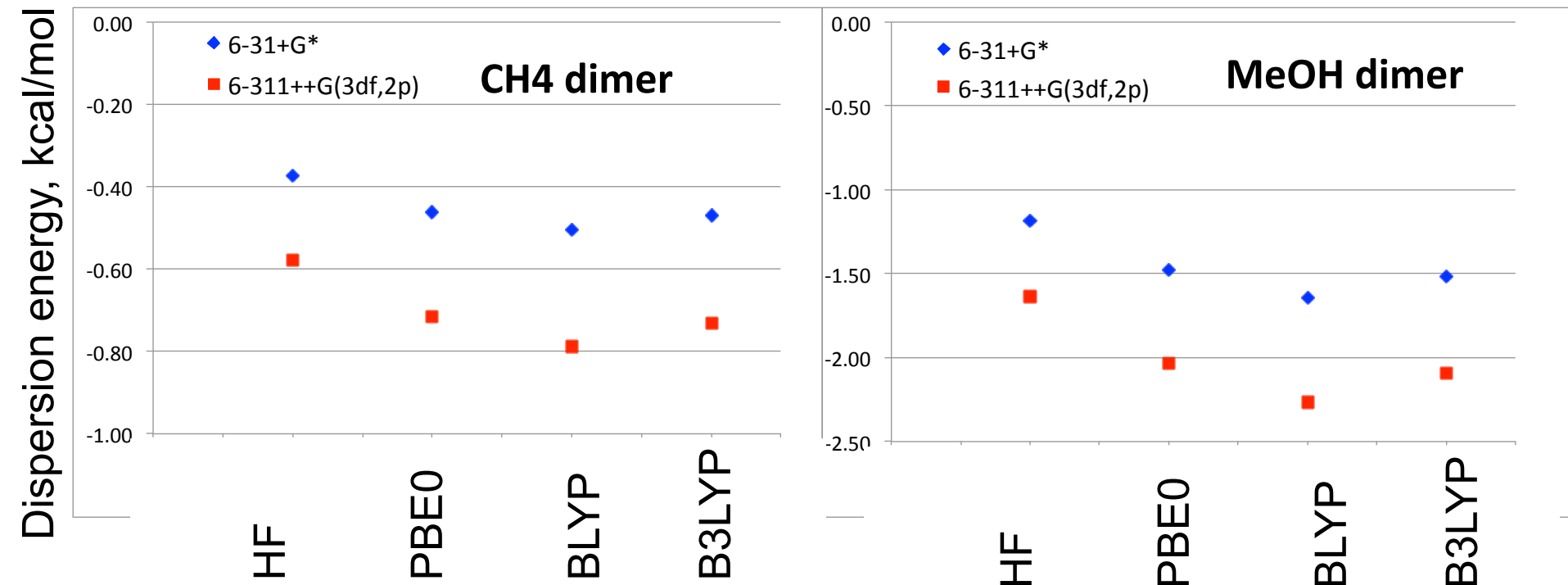
Practical aspects of using QM/EFP dispersion

Dependence on QM basis set



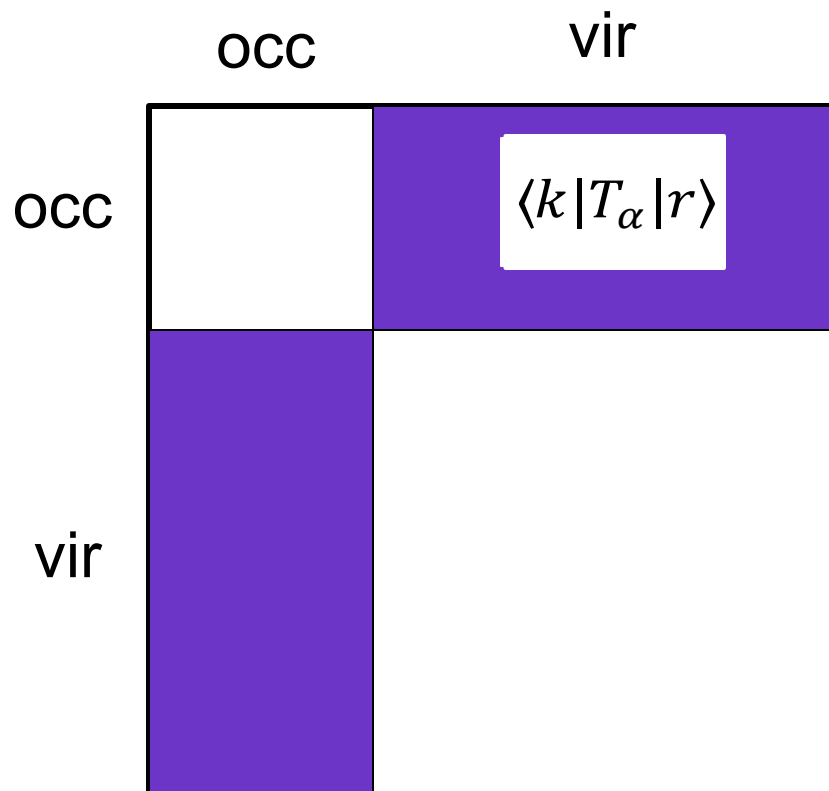
Practical aspects of using QM/EFP dispersion

Dependence on DFT functional



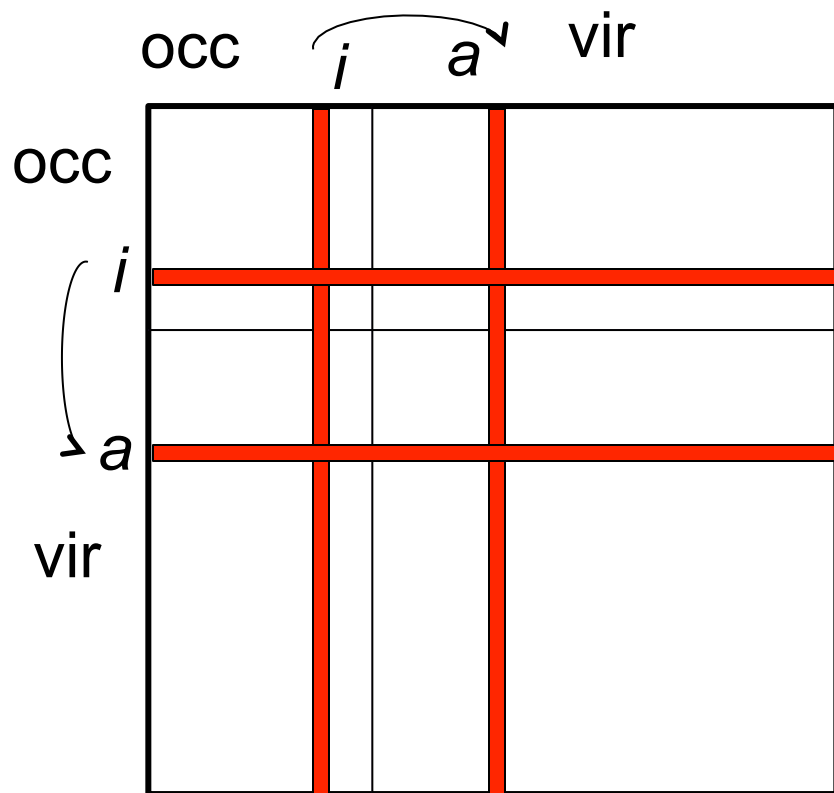
Dispersion for the ground electronic state

$$E_{QM-EFP}^{disp} = -\frac{1}{\pi} \sum_{j \in B} \sum_k^{occ} \sum_r^{vir} \sum_{\alpha\beta}^{x,y,z} \langle k | T_\alpha | r \rangle \langle r | T_\beta | k \rangle \int_0^\infty \frac{\omega_{rk}^A}{(\omega_{rk}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega$$



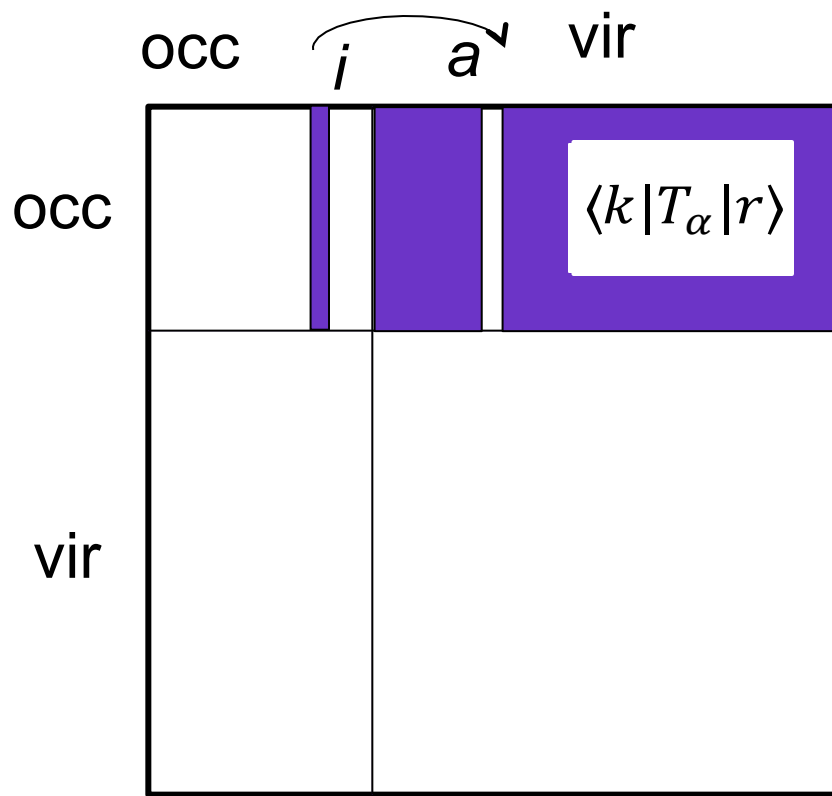
Dispersion for the excited electronic state

Suppose CIS formalism: $\Psi = \Phi_0 + \sum_{i,a}^{occ,virt} c_{ia} \Phi_i^a$



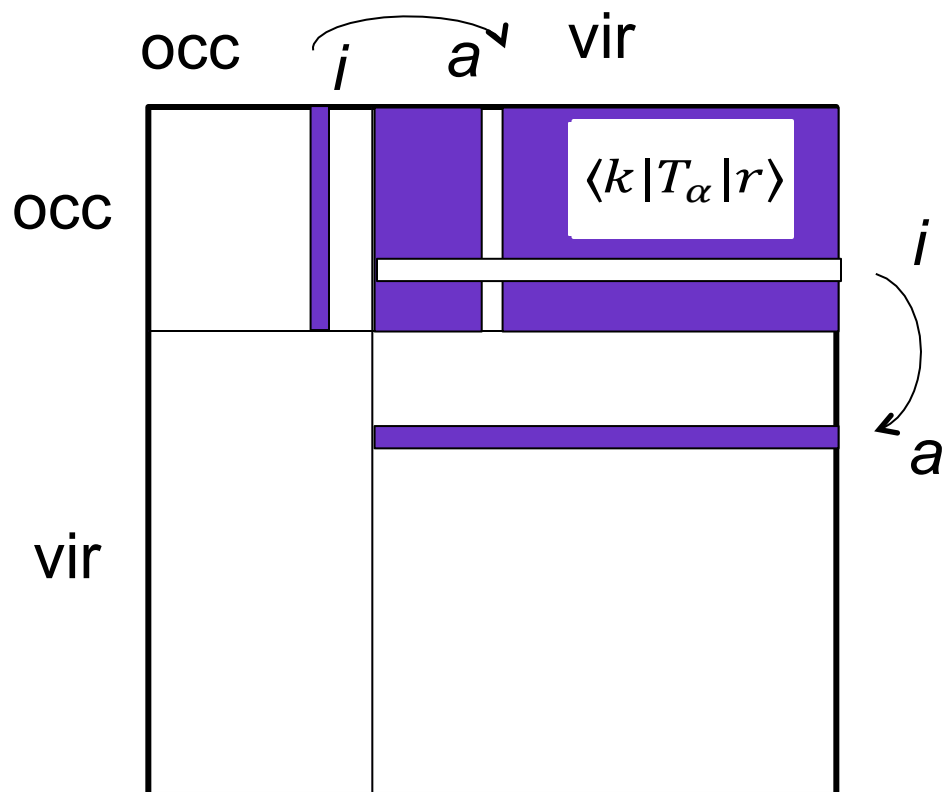
Dispersion for the excited electronic state

Suppose CIS formalism: $\Psi = \Phi_0 + \sum_{i,a}^{occ,virt} c_{ia} \Phi_i^a$



Dispersion for the excited electronic state

Suppose CIS formalism: $\Psi = \Phi_0 + \sum_{i,a}^{occ,virt} c_{ia} \Phi_i^a$



Dispersion for the excited electronic state

$$\begin{aligned}
 & E_{QM-EFP,ex}^{disp} \\
 &= -\frac{1}{\pi} \sum_{j \in B} \sum_{\alpha\beta}^{x,y,z} \sum_i^{occ} \sum_a^{vir} (C_{ia} C_{ai}) \left(-\sum_c^{vir} \langle i | T_\alpha^j | c \rangle \langle c | T_\beta^j | i \rangle \int_0^\infty \frac{\omega_{ci}^A}{(\omega_{ci}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega \right. \\
 &+ \sum_c^{vir} \langle a | T_\alpha^j | c \rangle \langle a | T_\beta^j | i \rangle \int_0^\infty \frac{\omega_{ca}^A}{(\omega_{ca}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega \\
 &+ \sum_k^{occ} \langle i | T_\alpha^j | k \rangle \langle k | T_\beta^j | i \rangle \int_0^\infty \frac{\omega_{ki}^A}{(\omega_{ki}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega \\
 &- \sum_k^{occ} \langle a | T_\alpha^j | k \rangle \langle k | T_\beta^j | a \rangle \int_0^\infty \frac{\omega_{ka}^A}{(\omega_{ka}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega \\
 &\left. + \langle i | T_\alpha^j | a \rangle \langle a | T_\beta^j | i \rangle \int_0^\infty \frac{\omega_{ai}^A}{(\omega_{ai}^A)^2 + \omega^2} \alpha_{\alpha\beta}^j(i\omega) d\omega \right)
 \end{aligned}$$

Does it work?

Dispersion energies, kcal/mol

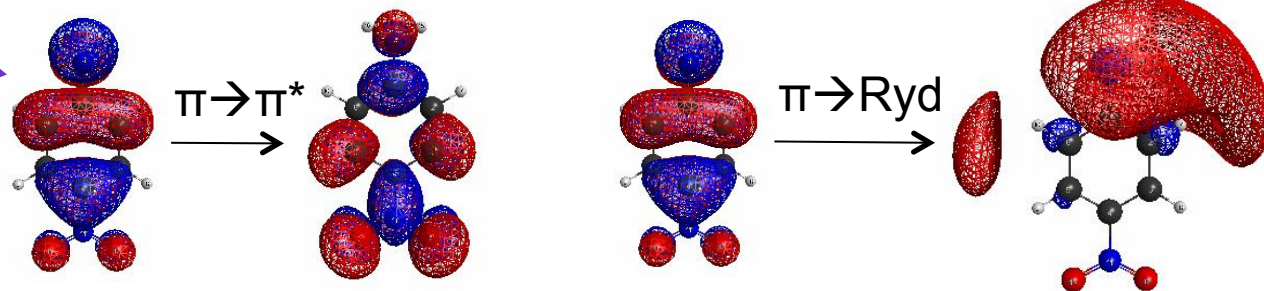
	Ground state	Triplet state	
		HF	CIS
Water dimer	-1.72	-2.94	-3.47
Ammonia dimer	-1.73	-3.58	-2.95
Ethene dimer	-2.03	-2.07	-1.89

Solvatochromism in pNA: revisited

QM/EFP: polarizable embedding + dispersion

QM/EFP dispersion in the ground state: -1.26 eV

eV	Excitation energy	Dispersion correction	Total energy
S_2	5.26	-0.29	4.97

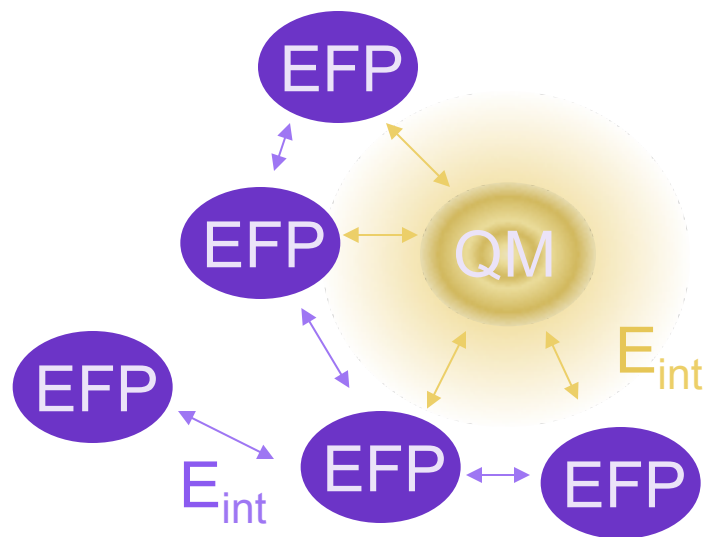


pNA in small
benzene cluster

CIS/6-31+G* //EFP

**Repulsion between QM and EFP regions
is a MUST!**

QM / EFP: toward full embedding



solute

solvent

$$\hat{H} = \hat{H}_{QM} + \hat{H}_{EFP} + \hat{H}_{QM/EFP}$$

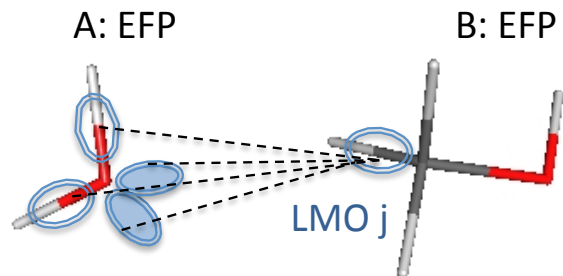
coupling term

$$\hat{H}_{QM/EFP} = \hat{H}^{el} + \hat{H}^{pol} + \hat{H}^{disp} + \hat{H}^{exch-rep}$$

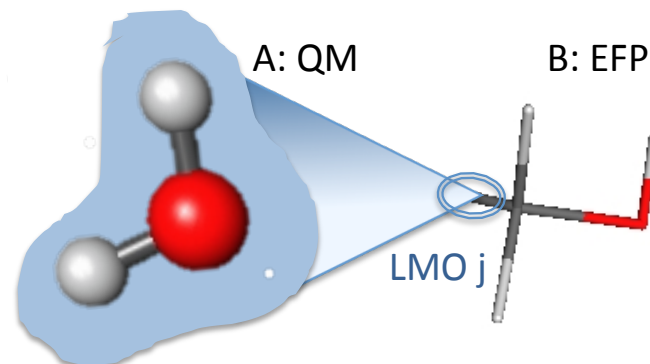
Annu. Rev. Phys. Chem., 64,
553-78 (2013);

Viquez-Rojas and
Slipchenko, *in prep*

QM-EFP exchange-repulsion



$$E^{EFP-EFP}(j) = \sum_{i \in A} E_{ij}^{exrep}$$



$$E^{QM-EFP}(j) = \langle \Psi | \beta_j \exp(-\alpha_j(r - R_j)^2) | \Psi \rangle$$

- 3-center-1-electron integrals are computed
- Need a pair of parameters for each unique LMO
- Parameterization is done based on comparison to SAPT0 ex-rep and total energies and EFP ex-rep energies for molecular clusters extracted from high-temperature MD trajectories
- Exchange-repulsion in QM/EFP1 (EFP1: water potential) is done similarly

Viquez-Rojas, Fine, Slipchenko, submitted to JCP



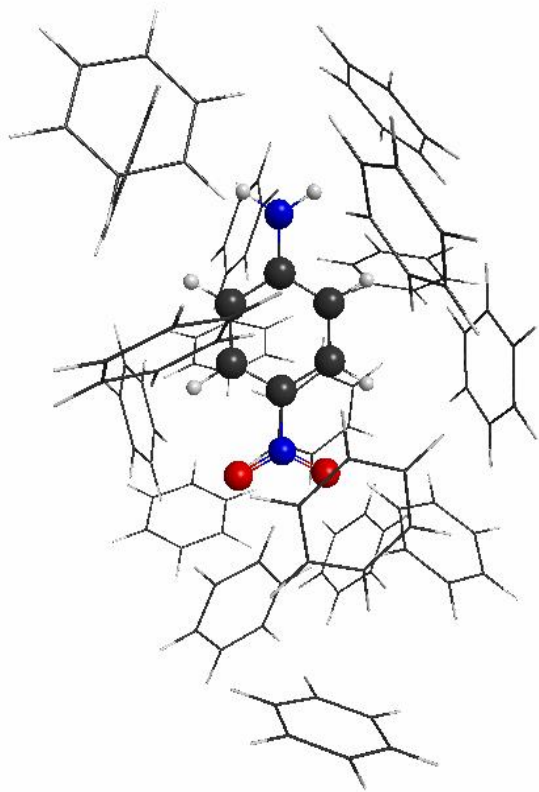
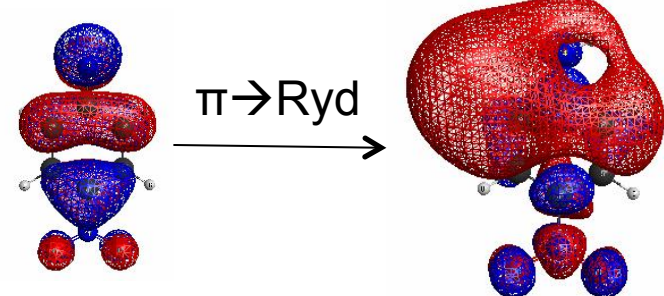
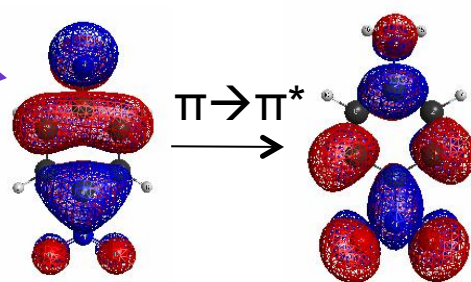
Claudia Viquez-Rojas

Solvatochromism in pNA: revisited 2

Full-embedded QM/EFP

QM/EFP dispersion in the ground state: -1.22 eV

eV	Excitation energy	Dispersion correction	Total energy
S ₂	5.35	-0.21	5.14
S ₈	7.97	-0.51	7.46

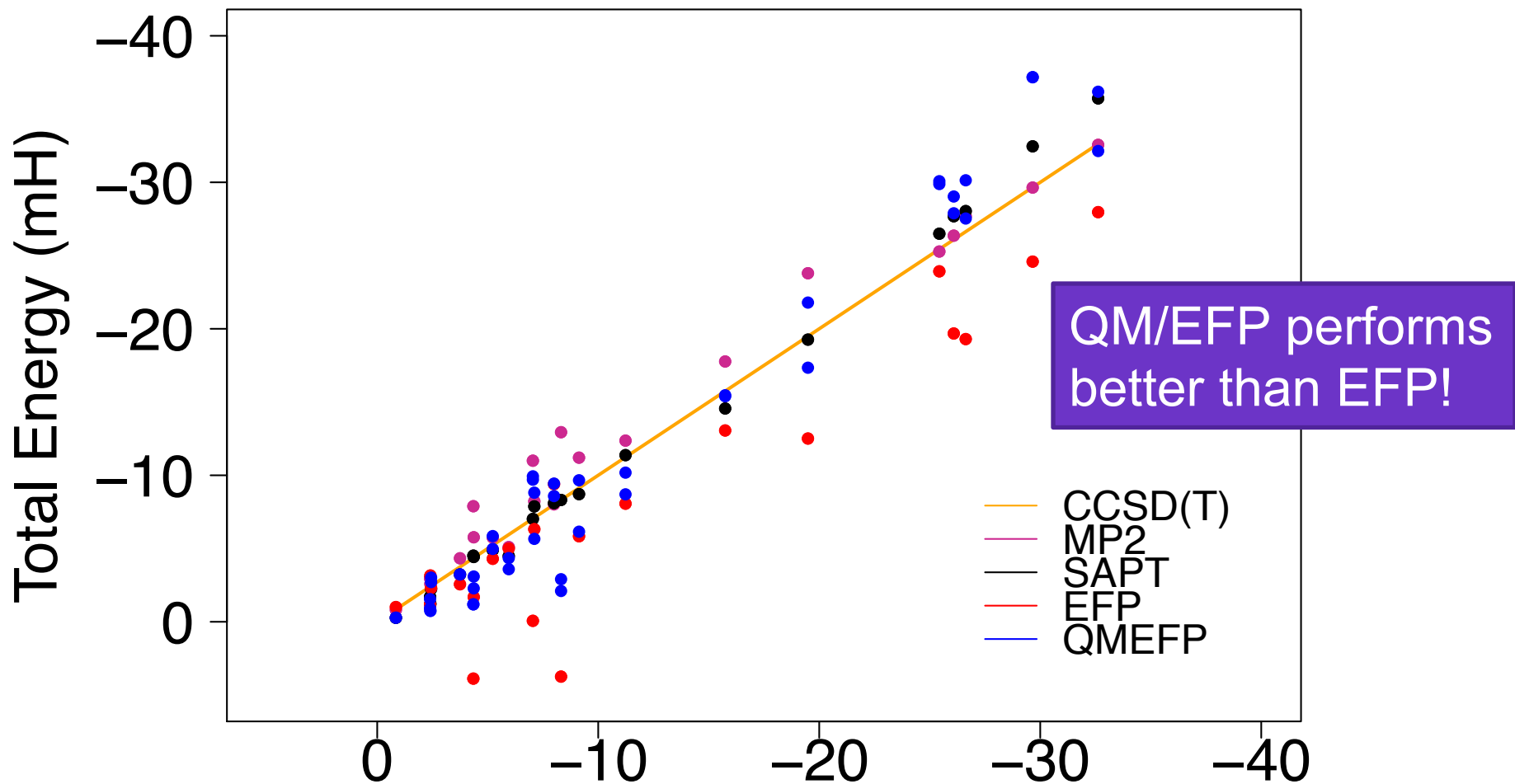


pNA in small benzene cluster

CIS/6-31+G* //EFP

Full-embedded QM/EFP provides qualitatively correct description of Rydberg states

Full QM/EFP energies for S22 dataset



Viquez-Rojas, Fine, Slipchenko, submitted to JCP

Conclusions

- EFP is first-principles based polarizable force field
- *LIBEFP* is a stand-alone EFP implementation designed for interfacing with ab initio and dynamics software
- QM/EFP: full embedding scheme for describing electronic structure in heterogeneous environments
- Excited state dynamics?
 - Missing analytic gradients: state-specific polarization and excited state dispersion contribution. Can they be ignored?
 - Need QM dynamics driver. Limited possibilities exist in GAMESS, Q-Chem,... We are interested in collaborations!

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Hanjjing Xu
Jia Lin Cheoh
Ryan DeRue

Group alumni:

Dr. Carlos Borca
Dr. Ilya Kaliman
Dr. Dmytro Kosenkov
Dr. Ben Nebgen
Dr. Mandy Green
Dr. Mike Hands
Dr. Frank Emmert

\$\$\$:

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