

# Q-Chem Program: Innovative Methods for Post-HF, Excited States, and Properties

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G2 database Calculations with B3LYP in kcal/mol.  
Target basis is always 6-311++G(3df,3pd).

Small basis	single basis	dual basis
6-311G	MAD = 24.3	MAD = 4.0
6-311G*	MAD = 7.0	MAD = 2.2
6-311G**	MAD = 4.9	MAD = 2.2
6-311++G(3df,3pd)	MAD = 2.2	MAD = 2.2

- Ground states - CCSD(T), CCSD(2), OD
- Ground states - Efficient multireference schemes
- Excited states - EOM-XX-CCSD schemes
- Excited states – various schemes for larger structures
- Linear-scaling NMR chemical shifts
- QM/MM capability

- CCSD energy and gradient
- CCSD(T) energy
- CCSD(2) energy
- OD – Optimized orbital CCD, no HF ref required

*Van Voorhis, Head-Gordon @ berkeley.edu*

## Active-Space Models

### - Alternatives to CASSCF

- PP – Perfect pairing
- IP – Imperfect pairing
- RCC – Restricted Pairing
- Gradient implemented

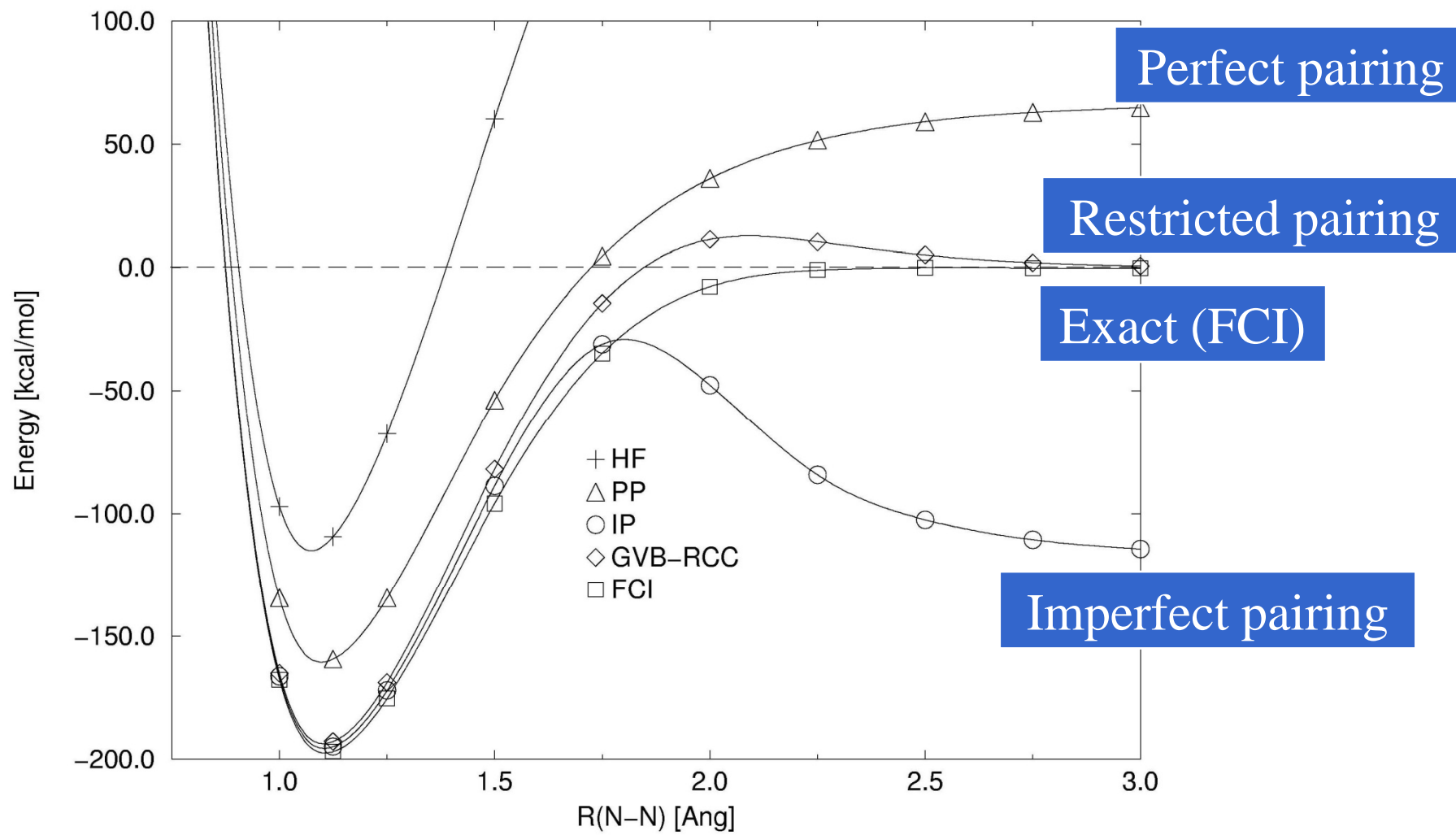
Perfect pairing (PP)  $\hat{T} \equiv \sum_i t_i \hat{a}_{i^*}^\dagger \hat{a}_{\bar{i}^*}^\dagger \hat{a}_i \hat{a}_{\bar{i}}$

Imperfect Perfect pairing (IP)

$$\hat{T} = \sum_{ij} \left( t_{ij}^{i^* j^*} \hat{E}_{ii^*} \hat{E}_{jj^*} + t_{ij}^{j^* i^*} \hat{E}_{ij^*} \hat{E}_{ji^*} \right)$$

Restricted CC: eliminates the 4-electron terms responsible for incorrect dissociation from imperfect pairing.

- Pairs automatically chosen
- Cost effective – same scaling as HF
- Can handle as big as C<sub>30</sub>H<sub>62</sub> (182 active orbitals)
- Versus CASSCF up to 14 active orbitals
- Dynamic correlation for PP with perturbation





## EOM-XX-CCSD

*Slipchenko, Levchenko, Wang, Krylov @ usc.edu*

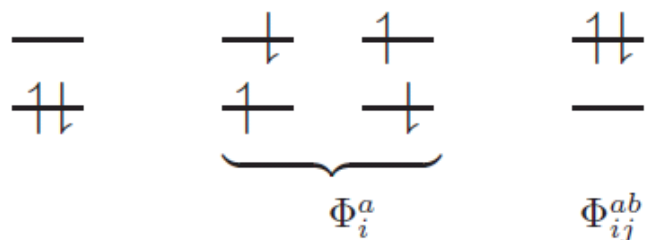
- **XX** = **EE** – electronically excited
- **XX** = **IP** – ionic potential  
= **EA** – electron attachment

*Ground and excited states of doublet radicals*

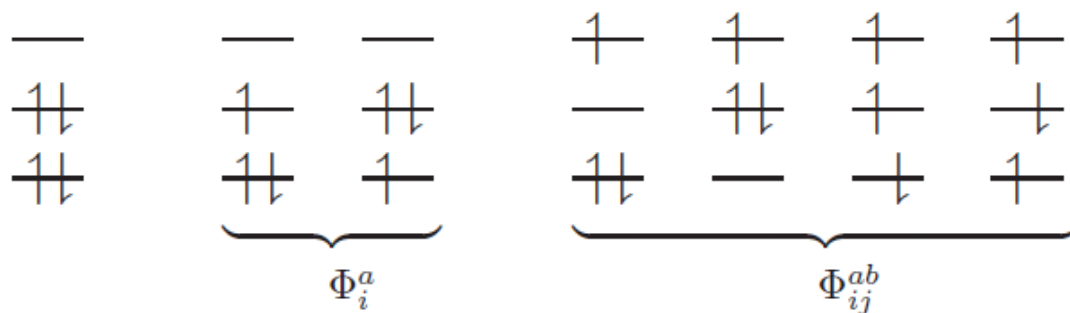
- **XX = SF** (spin-flip)

*Diradicals, triradicals, bond-breaking*

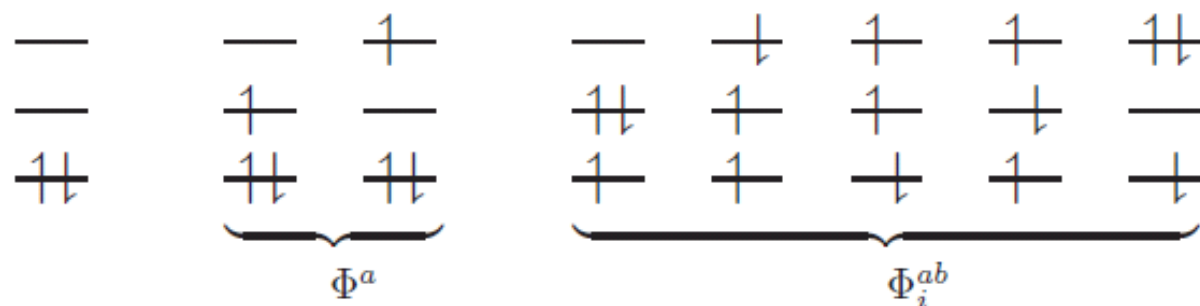
**EOM-EE**  $\Psi(M_s = 0) = R(M_s = 0)\Psi_0(M_s = 0)$



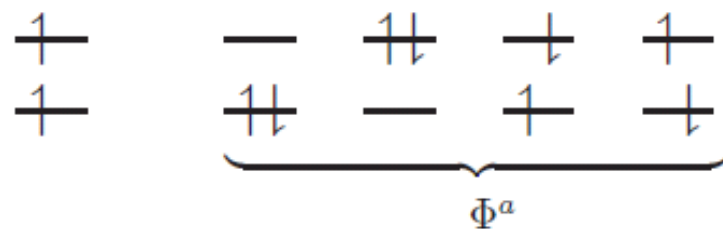
**EOM-IP**  $\Psi(N) = R(-1)\Psi_0(N + 1)$



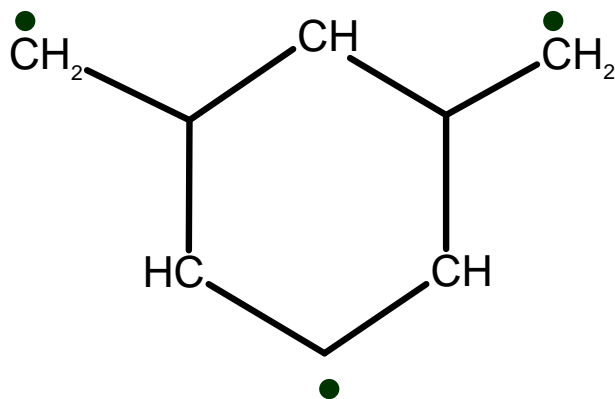
EOM-EA  $\Psi(N) = R(+1)\Psi_0(N-1)$

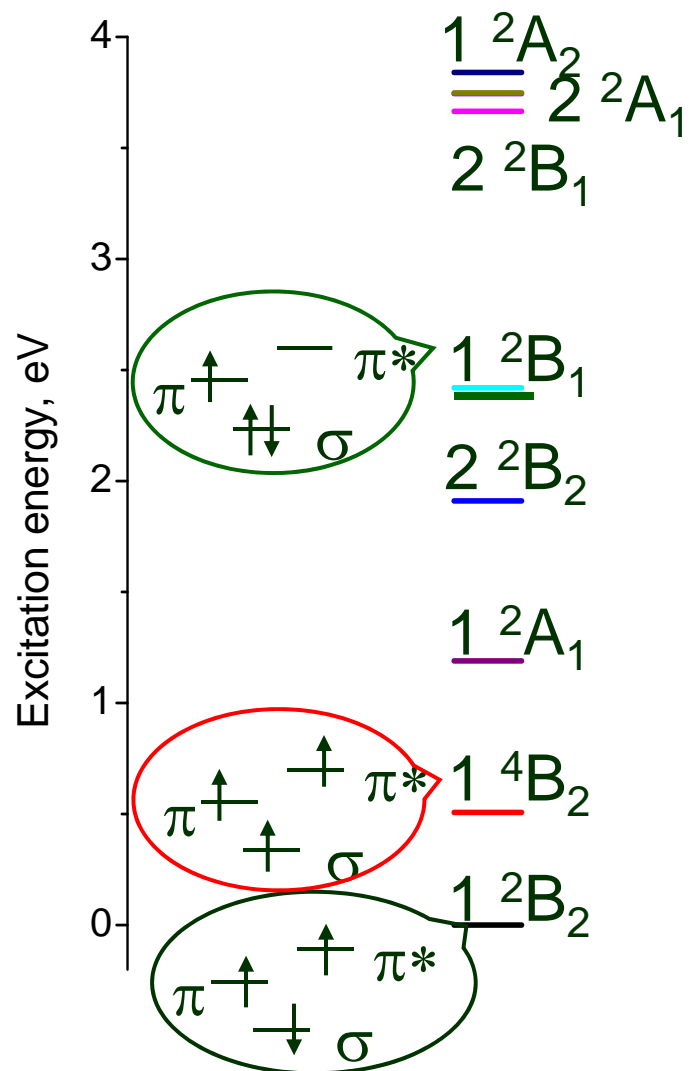
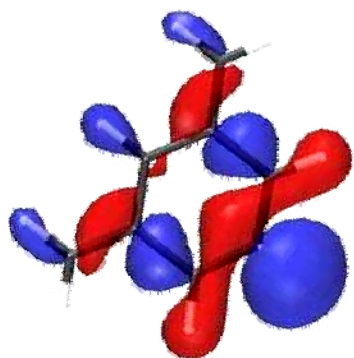
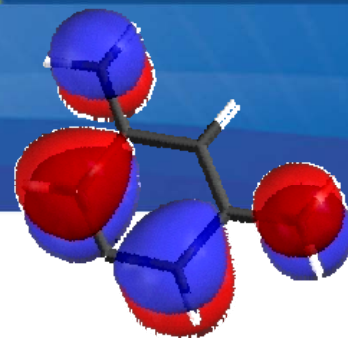
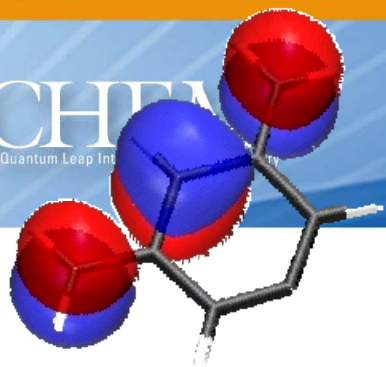


EOM-SF  $\Psi(M_s = 0) = R(M_s = -1)\Psi_0(M_s = 1)$



The *first* example of an organic molecule  
with an *open-shell doublet* ground state





## Type of Reference:

- Energy: RHF, ROHF, UHF
- Analytical gradient: RHF, UHF

- TDDFT energy
- Spin-flip DFT for diradicals and triradicals
  - gradient available

## XCIS (extended CIS)

- Problem: ROHF-CIS is worse than closed-shell CIS
- Solution: Including a few double excitations



## Correlations for CIS

- CIS(D) – MP2 for excited states
- SOS-CIS(D) – SOS-MP2 for excited states

*Shao @ q-chem.com, Woodcock @ nih.gov*

## Hybrid Methods

- MM code added
- ONIUM implemented
- Interface to CHARMM

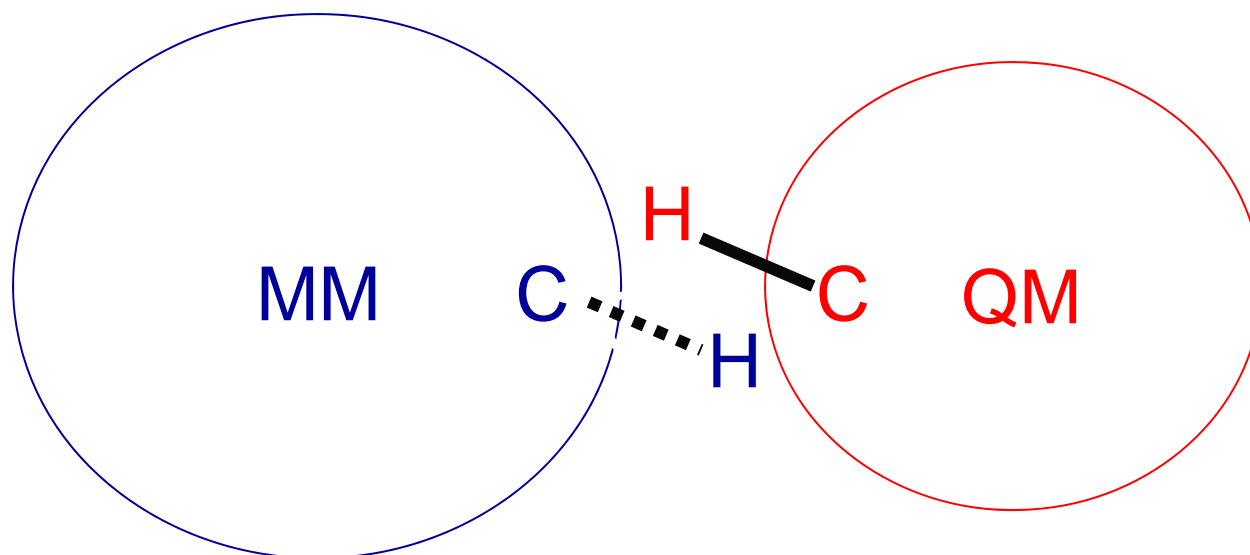
Developer: *Yihan Shao*

“qmmm\_interface yinyang”

“force\_field charmm27”

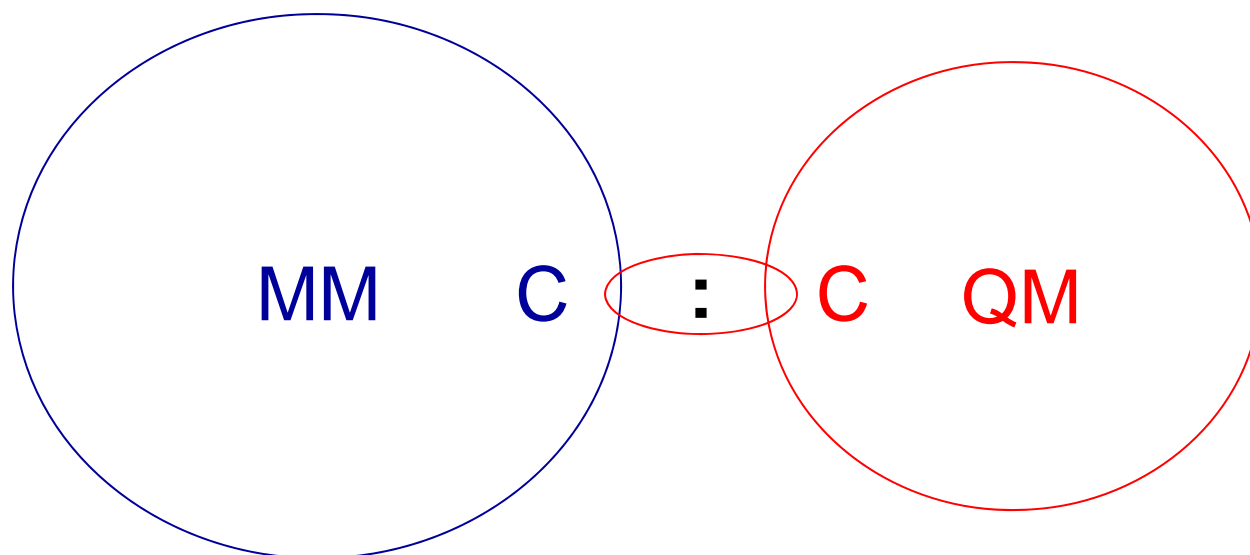
- Extremely simple: ONE parameter!
- Trivial to implement
- As accurate as any other model
- JPC A, *111*, 3661 (2007)

Link atom

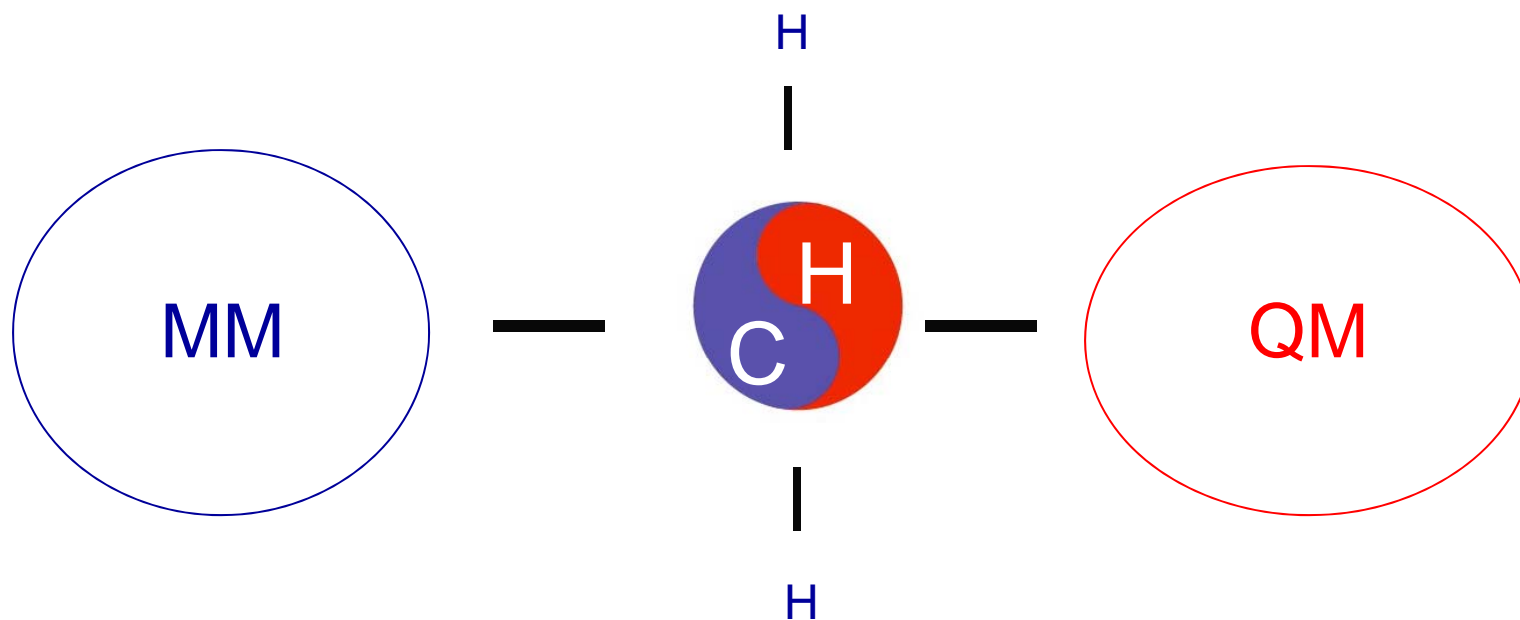


Onium, Amber, Charm, etc.

## Bond function



LSCF, FP, etc.



Compare with full QM B3LYP/6-31G\*:  
structure and protonation



**MM:** Carbon parameters

**QM:** 6-31G, *Nuclear charge 0.82*

A single parameter to keep H-C distance

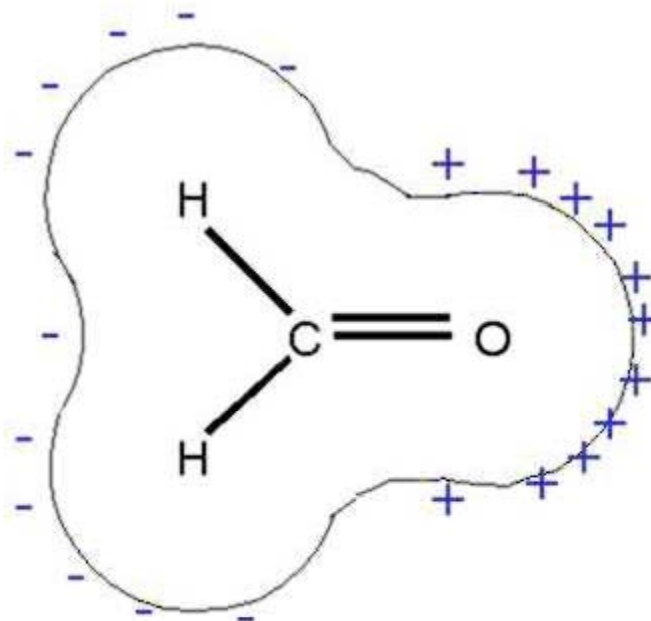
	bond			angle			Prot.	energy
	mean	rms	max	mean	rms	max	QM	QM/MM
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-0.004	0.006	-0.010	0.27	1.85	2.57		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH <sub>2</sub> <sup>+</sup>	-0.009	0.017	-0.039	0.72	3.08	5.60	196.20	197.02
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	-0.004	0.006	-0.010	0.42	1.80	2.63		
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>3</sub> <sup>+</sup>	-0.005	0.007	-0.013	0.32	2.04	3.75	231.32	233.37
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	-0.003	0.007	-0.014	0.13	1.74	2.49		
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH <sub>2</sub> <sup>+</sup>	-0.008	0.016	-0.038	0.50	2.74	-4.76	194.96	194.31
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>2</sub>	-0.004	0.007	-0.014	0.30	1.76	2.64		
HO-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -NH <sub>3</sub> <sup>+</sup>	-0.004	0.006	-0.013	0.14	1.81	-3.51	230.48	230.98



## Dielectric Continuum Solvation Models

- Onsager
- SM8
- Lagevin dipole
- SVP
- *Coming soon: COSMO*

## Self-Consistent Reaction Field



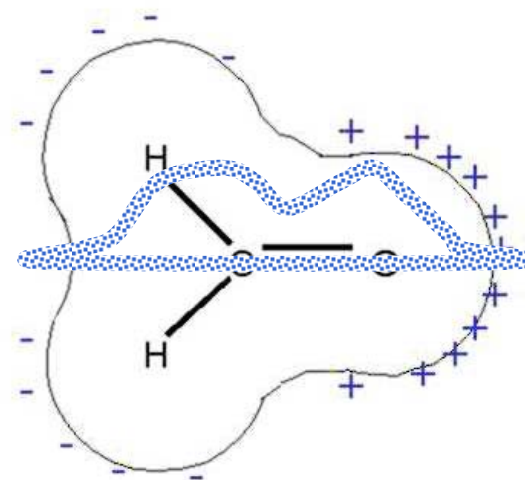
- Electrostatic
- Cavity and surface charge
- Dilute; solvent isotropic

- Solvent: homogenous dielectrics
- Solute: point dipole
- Spherical cavity
- Two parameters: dielectric constant and cavity radius

- From Crammer and Truhlar's groups at U of Minnesota
- Based on generalized Born model
- Born model: solvated point-charges and point dipoles  
(No explicit surface charges created)
- Additional treatment of the first shell
- Fitted to extensive properties and training sets
- Point charges important:
  - 6-31G\*, 6-31+G\*, 6-31+G\*\*
- Applicable to many solvents

## Surface and Simulation of Volume Polarization for Electrostatics

- Dan Chipman from Notre Dame U
- Explicit surface charge model
- Consider the escaped charges
- Isodensity surface
- Does particularly well for cations and anions



- Hybrid of continuum and discrete
- Created by Florian and Warshal at USC
- Water solution modeled by polarizable dipoles on a fixed grid
- Continuum model for the outer layers
- Detailed analysis:
  - LD electrostatic
  - Hydrophobic
  - vdW
  - Bulk correction

## Conductor-like Solvation Model

- Created by Klamt at CosmoLogic Inc.
- Surface charge model
- Single parameter to represent different solvents
- Outer layer correction
- As accurate as SM8

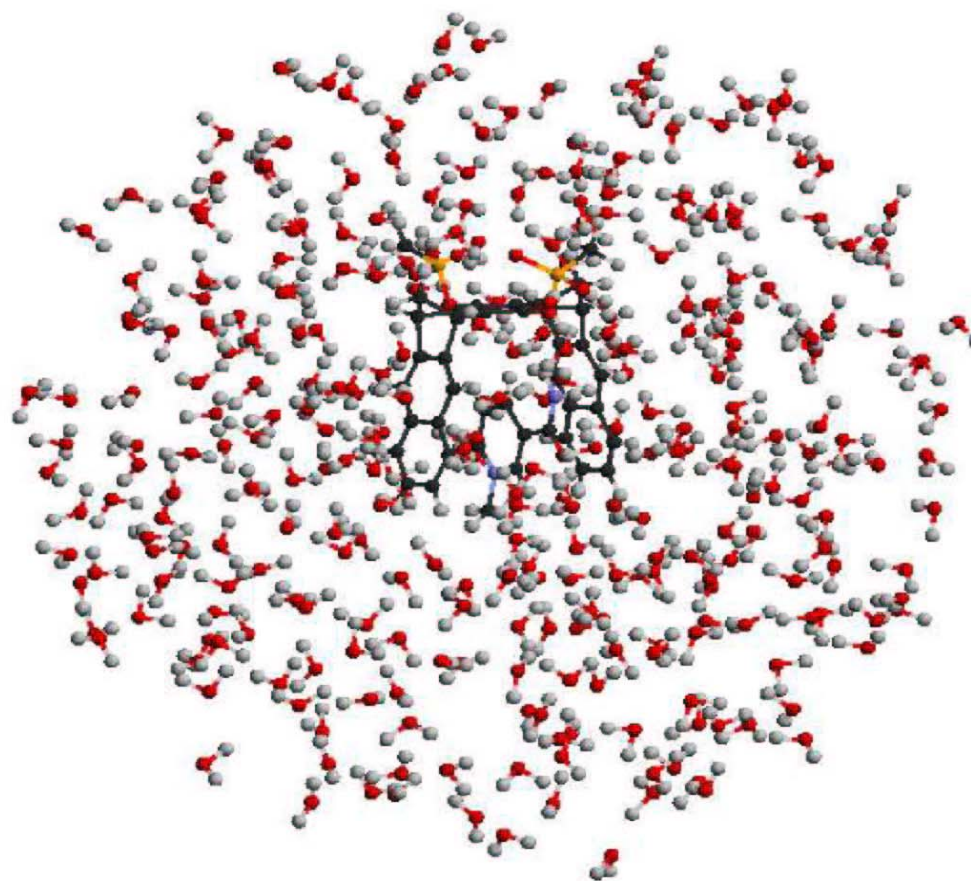
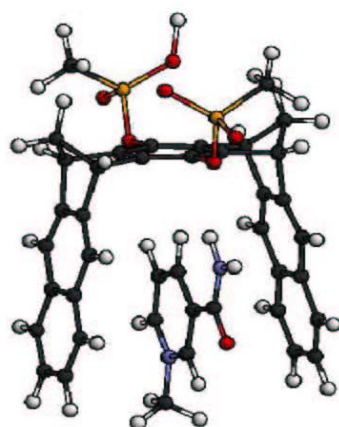
## O(N) NMR Chemical Shifts

*Ochsenfeld, Kussmann, Koziol @uni-tuebingen.de*

- Build on LinK and O(N) Coulomb
- Using sparse-matrix techniques
- Can treat much larger system than before



## Solvent Effects: Convergence of NMR Shieldings



Change in system size		Max. change
88	→ 169	1.3 ppm
169	→ 547	1.1 ppm
547	→ 1003	0.2 ppm

(1003 atoms, 8593 bf, GIAO-HF/6-31G\*\*)

C.Ochsenfeld, J.Kussmann, F.Koziol

Angew. Chem. Int. Ed. 43, 4485 (2004)

## Molecular Dynamics

*Herbert, Head-Gordon @ berkeley.edu*

- Born-Oppenheimer
- Car-Parrinello

谢谢 again!