TEXAS A&M HIGH PERFORMANCE RESEARCH COMPUTING

Introduction to Quantum Mechanics Short Course

Lecture 6 of 6

TEXAS A&M UNIVERSITY
Division of Research

Solvation

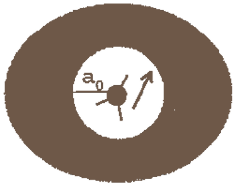
- The Problem:
    - Traditional quantum calculations are carried out in the **gas-phase**
    - Most reaction chemistry is performed in **solution**
    - Gas-phase calculations fail to properly describe the energetics of charged and/or neutral polar molecules involved in a reaction that occurs in solution.

Solvation

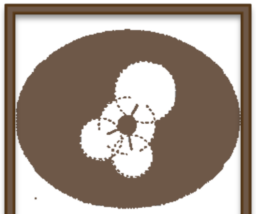
- Possible Solutions:
  - Explicit Solvation - include explicit solvent molecules.
    - Computationally expensive
    - Convergence problems
    - Can overestimate solvent interaction if an inadequate number of solvent molecules are included
  - Implicit Solvation - estimate the effect of the solvent molecules using an implicit solvation model.
    - Gives reasonable results for bulk polar solvent effects.
    - Fails if the solvent molecule is directly involved in the reaction chemistry (ie strong H-bonding, coordinated, etc).

Continuum Solvation Models

- Onsager Model (scrf=dipole) – requires you to provide the radius of the sphere used to represent the solute cavity.
- PCM – Polarizable Continuum models by Tomasi and coworkers
  - Integral Equation Formalism Model (scrf=PCM or scrf=IEFPCM)
  - IPCM (scrf=ipcm)
  - SCIPCM (scrf=scipcm)
- SMD – IEFPCM calculation using radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model.



Onsager (Dipole & Sphere) Model
SCRF=Dipole

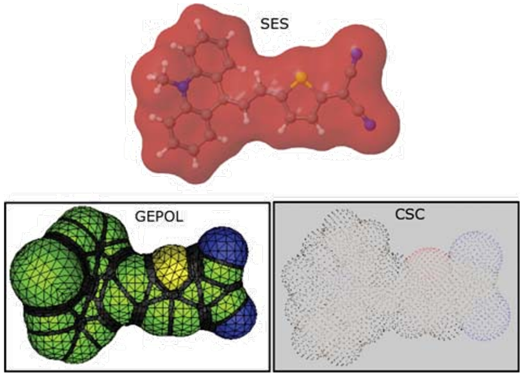


Tomasi's PCM Model
SCRF=PCM

Isodensity Model
SCRF=IPCM

Self-consistent Isodensity Model
SCRF=SCIPCM

Continuum Solvation Models



Wiley Interdisciplinary Reviews: Computational Molecular Science
Volume 2, Issue 3, pages 386-404, 17 JAN 2012 DOI: 10.1002/wcms.1086
http://onlinelibrary.wiley.com/doi/10.1002/wcms.1086/full#fig2

- $G_{sol} = G_{es} + G_{disp} + G_{rep} + G_{cav}$
  - G_{es} = elecrostatic
  - G_{disp} = dispersion
  - G_{rep} = repulsion
  - G_{cav} = cavitation
- By default in G09/16 PCM models only include G_{es}
  - To include non-electrostatic term you must use the scrf=(PCM,read) keyword and have an additional input section with the keywords: dis, rep, and cav
- To calculate ΔG_{solv} Gaussian suggest the use of SMD which includes the non-electrostatic terms

Continuum Solvation Models

- $G_{sol} = G_{el} + G_{disp} + G_{rep} + G_{cav}$
  - $\sigma(s)$ – surface charge
  - $\rho M(r)$ - solute charge distribution
  - $\varepsilon(r)$ - general position-dependent permittivity
  - V_{ai} - electrostatic potential of the electrostatic field due to the transition charge distribution ρ_{ai} computed at each surface tessera of area a_k
  - E_{ai} – normal component of the electrostatic field due to the transition charge distribution ρ_{ai} computed at each surface tessera of area a_k
  - n_{el} indicates the number of electrons in the solute
  - s_k – tesserae surface element position
  - ρ_s - density of the solvent
  - A_i - contribution of atom i to the surface of the cavity
  - R_i – radius of sphere i

$$G^{\mathrm{el}} = \frac{1}{2}\int_{\Gamma} \sigma(\vec{s}) \left[\int_V \frac{\rho_{\mathrm{M}}(\vec{r})}{|\vec{r} - \vec{s}|} d^3 r \right] d^2 s$$

$$G^{\mathrm{disp}} = -\frac{\beta}{2} \sum_k \sum_{\mathrm{ia}} V_{\mathrm{ai}}(\vec{s}_k) E_{\mathrm{ai}}(\vec{s}_k) a_k$$

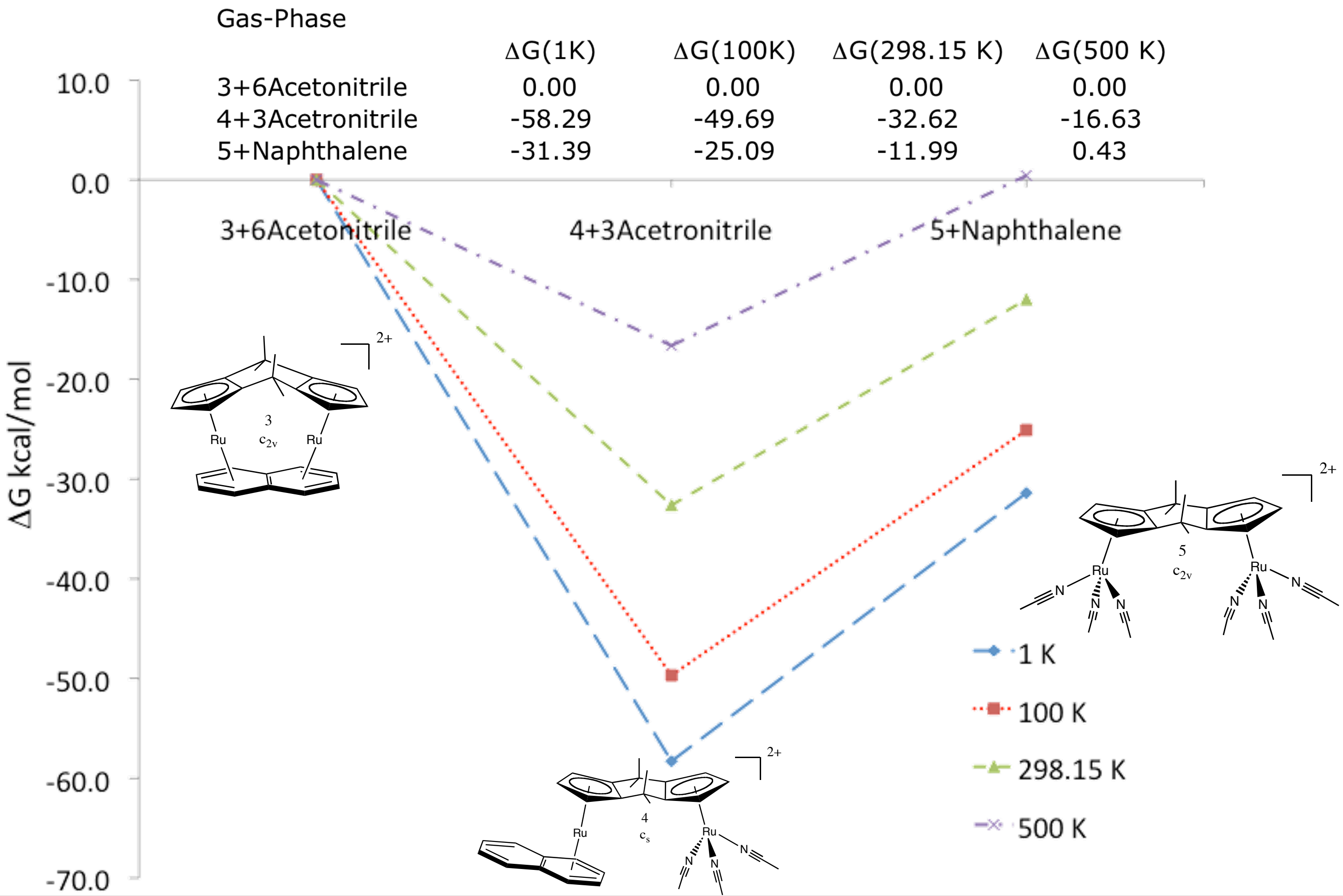
$$G^{\mathrm{rep}} = \alpha \left(n_{el} + \frac{1}{4\pi} \sum_k \sum_{\mathrm{ia}} E_{ai}(\vec{s}_k) a_k \right)$$

$$G^{\mathrm{cav}} = \rho_s \sum_i \frac{A_i}{4\pi R_i^2} G^{\mathrm{cav}}(R_i)$$

PCM Atomic Radii for PCM methods

- **UFF – All atom default Radii in G09/G16.**
- UA0 – United Atom Topological Model (Was the default in G03)
- UAHF – United Atom Topological Model developed from HF/6-31G(d) calculations.
- UAKS – United Atom Topological Model developed from PBE1PBE/6-31G(d) calculations.
- Pauling – Pauling atomic radii – all atom
- Bondi – Bondi atomic radii – all atom
- note: SMD uses its own set of radii therefore, you shouldn't specify what radii to use.

3 + 6Acetonitrile ➛ 4 + 3Acetonitrile ➛ 5 + Naphthalene



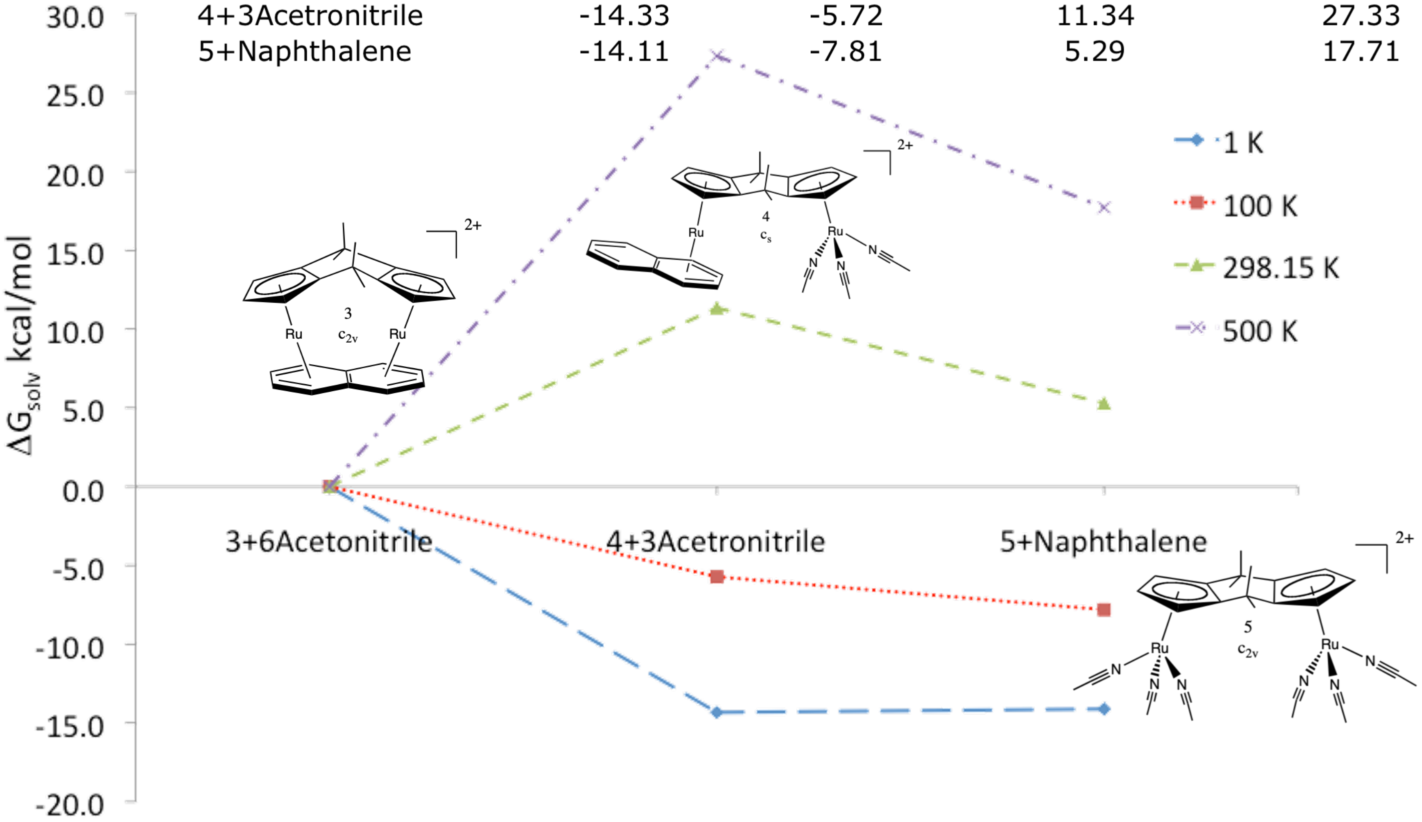
Gas-Phase

	ΔG(1K)	ΔG(100K)	ΔG(298.15 K)	ΔG(500 K)
3+6Acetonitrile	0.00	0.00	0.00	0.00
4+3Acetronitrile	-58.29	-49.69	-32.62	-16.63
5+Naphthalene	-31.39	-25.09	-11.99	0.43

3 + 6Acetonitrile ➛ 4 + 3Acetonitrile ➛ 5 + Naphthalene

Solvation (smd) water

	ΔG_{solv}(1K)	ΔG_{solv}(100K)	ΔG_{solv}(298.15 K)	ΔG_{solv}(500 K)
3+6Acetonitrile	0.00	0.00	0.00	0.00
4+3Acetronitrile	-14.33	-5.72	11.34	27.33
5+Naphthalene	-14.11	-7.81	5.29	17.71



Solvation Calculations

- Geometry Optimization and frequency performed in the gas Gas Phase

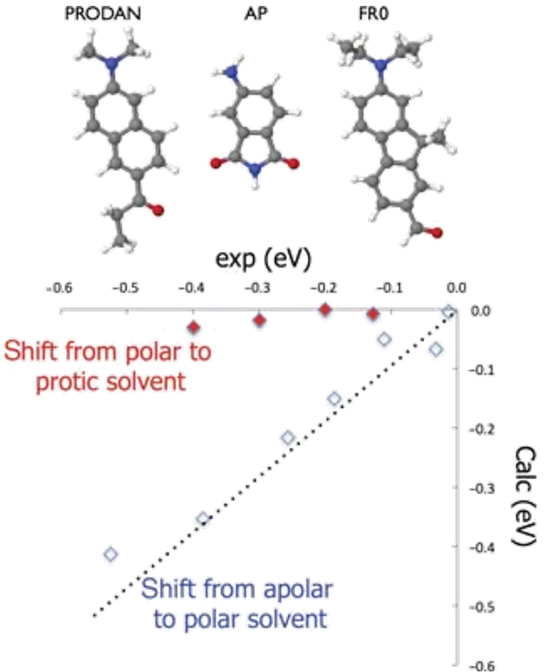
```
Zero-point correction=                           0.010473 (Hartree/Particle)
Thermal correction to Energy=                    0.012833
Thermal correction to Enthalpy=                  0.013777
Thermal correction to Gibbs Free Energy=        -0.000995  Gcorr
Sum of electronic and zero-point Energies=              -1.122035
Sum of electronic and thermal Energies=                 -1.119674
Sum of electronic and thermal Enthalpies=               -1.118730
Sum of electronic and thermal Free Energies=            -1.133503
```

- Single point PCM calculation

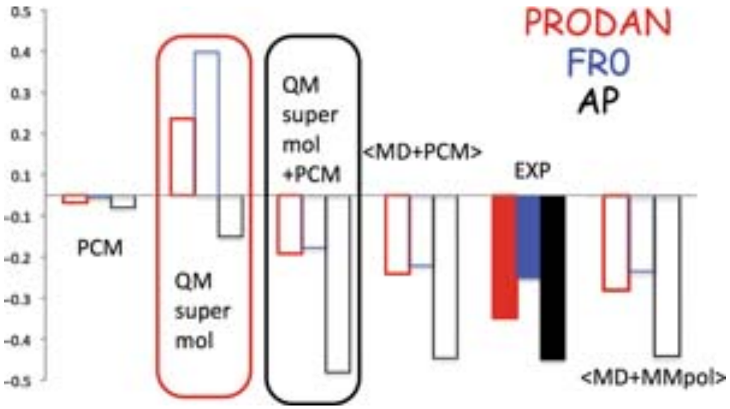
```
Error on total polarization charges =  0.00644
SCF Done:  E(RB3LYP) =  -113.306376503     A.U. after    9 cycles     (Esolv)
            Convg  =    0.7227D-09              -V/T =  2.0112
KE= 1.120524010887D+02 PE=-3.076682289508D+02 EE= 6.113684744058D+01
```

$G_{solv} = E_{solv} + G_{corr} = -113.306376503 + -0.000995$ hartrees

TD-DFT and PCM



TD CAMB3LYP/6-311+G(d,p)/PCM results of shifts in the absorption and emission energies (eV) of AP, PRODAN, and FR0 moving from an apolar (cyclohexane for AP, dioxane for PRODAN and FR0) to a polar (acetonitrile for AP, dimethylsulfoxide for PRODAN and FR0) solvent. Experimental results are from Ref 65 for AP and Ref 66 for PRODAN and FR0.



TD CAMB3LYP/6-311+G(d,p)/PCM results of shifts (in **eV**) of the emission energies of AP, PRODAN, and FR0 moving from a polar (acetonitrile for AP and dimethylsulfoxide for PRODAN and FR0) to a protic polar (**water** for AP and PRODAN, **methanol** for FR0) solvent. Experimental results are from Ref 65 for AP and Ref 66 for PRODAN and FR0.

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http://onlinelibrary.wiley.com/doi/10.1002/wcms.1086/full#fig2

Partial Charges

- Mulliken Population Analysis (MPA)
- Natural Population Analysis (NPA)
- Löwdin Population Analysis
- Atomic Polar Tensors (APT)
- Atoms in Molecules (AIM)
- Molecular Electrostatic Potential (MEP/ESP)
    - Merz-Singh-Kollman (MK)
    - CHELP
    - CHELPG

Mulliken Population Analysis (MPA)

$$N = \sum_{j}^{n} \langle \psi_j | \psi_j \rangle = \text{Number of electrons}$$

$$= \sum_{j}^{n} \sum_{r,s} \langle c_{jr}\sigma_r | c_{js}\sigma_s \rangle$$

$$= \sum_{j}^{n} \left(\sum_{r} c_{jr}^{2} + \sum_{r,s,r \neq s} c_{jr} c_{js} S_{rs} \right)$$

$$diagonal \quad off-diagonal$$

$$N_k = \sum_{j}^{n} \left(\sum_{r \in k} c_{jr}^{2} + \sum_{r,s \in k, r \neq s} c_{jr} c_{js} S_{rs} + \frac{1}{2} \sum_{r \in k, s \notin k} c_{jr} c_{js} S_{rs} \right)$$

$$q_k = Z_k - N_k = \text{Mulliken partial charge for atom } k$$

- MPA splits the shared electron density equally between the atoms involved
- MPA charges are reported with SPE or higher calculations by default.
- MPA charges tend not to converge with increasing basis-set size
- MPA does not conserve the dipole moment

Atomic Polar Tensors (APT)

$$q_k = \frac{1}{3}\left(\frac{\partial \mu_x}{\partial x_k} + \frac{\partial \mu_y}{\partial y_k} + \frac{\partial \mu_z}{\partial z_k}\right)$$

- APT charges require 2nd derivatives (freq)
- APT charges converge quickly with basis set size
- APT conserves the dipole moment
- APT charges are sensitive to the level of theory (ie electron correlation)
- Also called GAPT (Generalized atomic polar

Atoms in Molecules (AIM)

$$q_k = Z_k - \int_{\Omega_k} \rho(r)dr$$

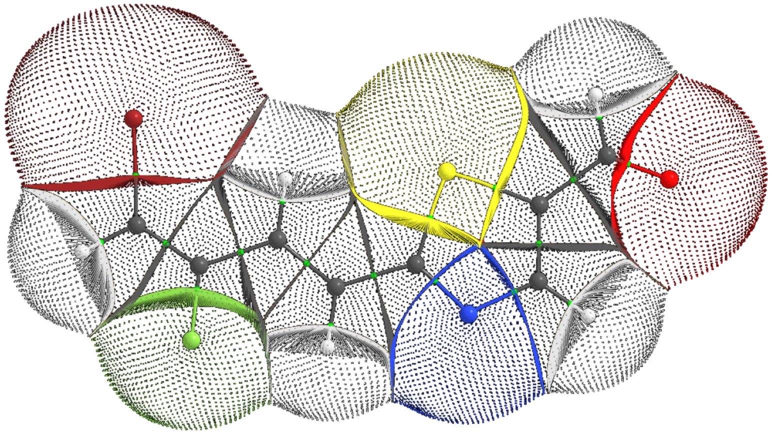
Ω_k = spatial volume encompassed

by the zero-flux surface of atoms k

zero-flux surface = points in space

where, $\nabla\rho \bullet n = 0$ n is a unit vector

perpendicular to the surface



http://aim.tkgristmill.com/index.html

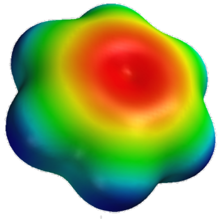
- AIM charges are:
  - intuitive
  - Dependent on the quality of y
  - should converge with increasing basis set
  - tend to overestimate charges in polar bonds
  - do not conserve the dipole moment

Molecular Electrostatic Potential (MEP)

- Partial charges may be calculated to approximately reproduce the MEP
  - MK (Merz-Singh-Kollman)
  - CHELP
  - CHELPG

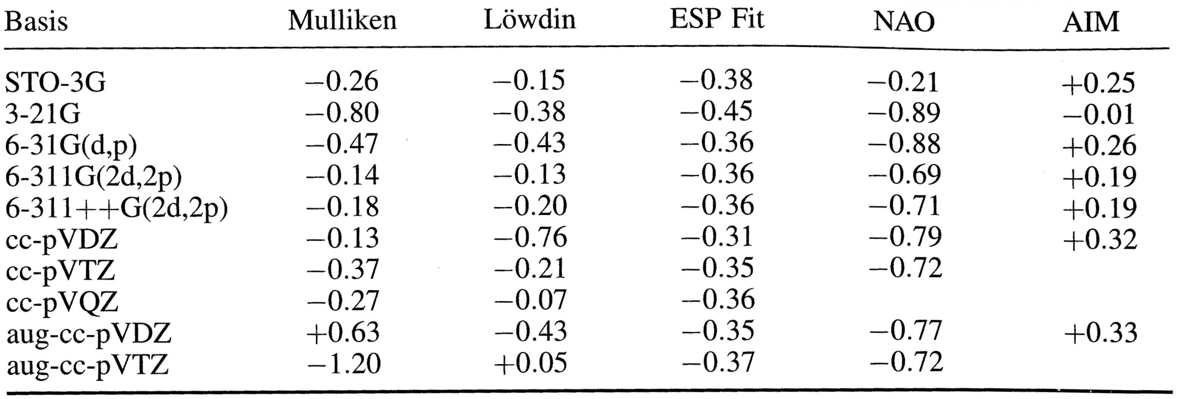
$$V_{MEP}(r) = \sum_{k}^{Nuclei} \frac{Z_k}{|r - r_k|} - \int \frac{|\psi(r_i)|^2}{|r - r_i|} dr_i$$

$$V_{ESP}(r) \approx \sum_{k}^{Nuclei} \frac{q_k}{|r - r_k|}$$


MEP (ESP) of benzene

- Upon request, the schemes above can be set to conserve the dipole of the molecule.
- ESP fitting methods are normally used to calculate partial charges for Molecular Mechanics calculations.

Partial Charges for C in CH_4



Basis	Mulliken	Löwdin	ESP Fit	NAO	AIM
STO-3G	−0.26	−0.15	−0.38	−0.21	+0.25
3-21G	−0.80	−0.38	−0.45	−0.89	−0.01
6-31G(d,p)	−0.47	−0.43	−0.36	−0.88	+0.26
6-311G(2d,2p)	−0.14	−0.13	−0.36	−0.69	+0.19
6-311++G(2d,2p)	−0.18	−0.20	−0.36	−0.71	+0.19
cc-pVDZ	−0.13	−0.76	−0.31	−0.79	+0.32
cc-pVTZ	−0.37	−0.21	−0.35	−0.72	
cc-pVQZ	−0.27	−0.07	−0.36		
aug-cc-pVDZ	+0.63	−0.43	−0.35	−0.77	+0.33
aug-cc-pVTZ	−1.20	+0.05	−0.37	−0.72	

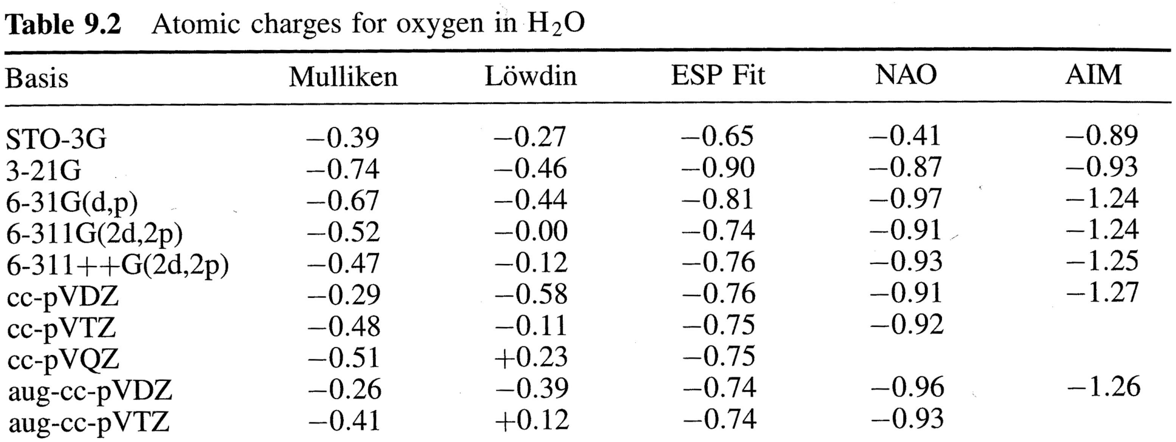


Table 9.2 Atomic charges for oxygen in H_2O

Basis	Mulliken	Löwdin	ESP Fit	NAO	AIM
STO-3G	−0.39	−0.27	−0.65	−0.41	−0.89
3-21G	−0.74	−0.46	−0.90	−0.87	−0.93
6-31G(d,p)	−0.67	−0.44	−0.81	−0.97	−1.24
6-311G(2d,2p)	−0.52	−0.00	−0.74	−0.91	−1.24
6-311++G(2d,2p)	−0.47	−0.12	−0.76	−0.93	−1.25
cc-pVDZ	−0.29	−0.58	−0.76	−0.91	−1.27
cc-pVTZ	−0.48	−0.11	−0.75	−0.92	
cc-pVQZ	−0.51	+0.23	−0.75		
aug-cc-pVDZ	−0.26	−0.39	−0.74	−0.96	−1.26
aug-cc-pVTZ	−0.41	+0.12	−0.74	−0.93	

Frank Jensen, Introduction to Computation Chemistry

Partial Charges

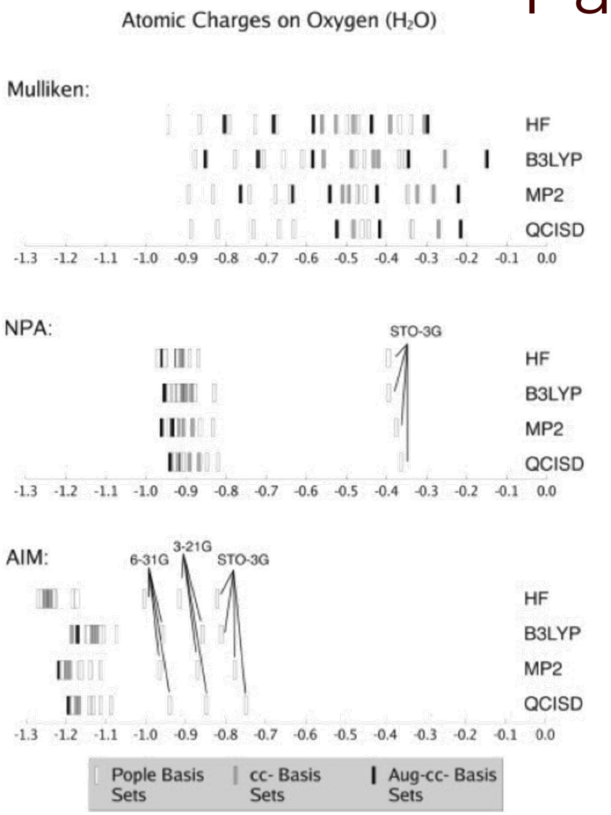


Figure 1. Oxygen partial charges calculated with the Mulliken, the NPA, and the AIM population analysis methods for water.

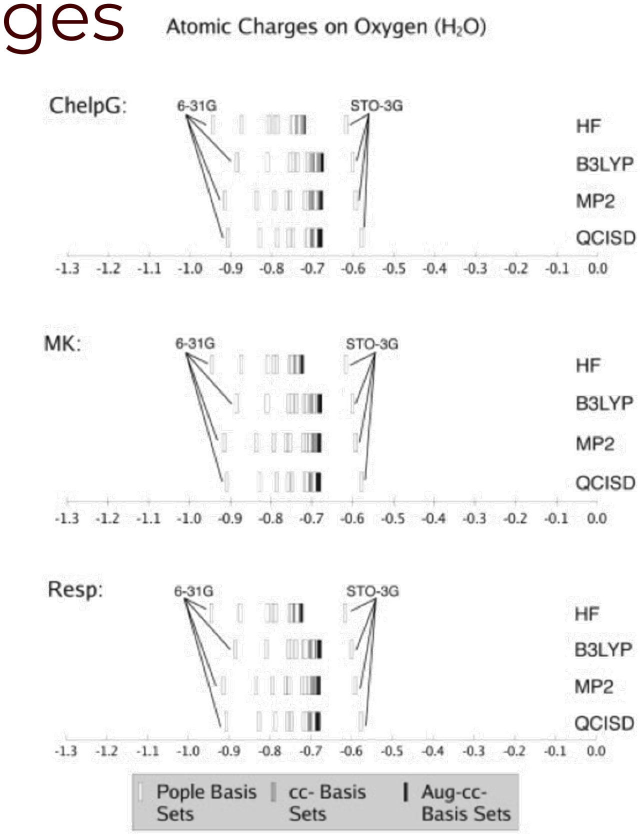
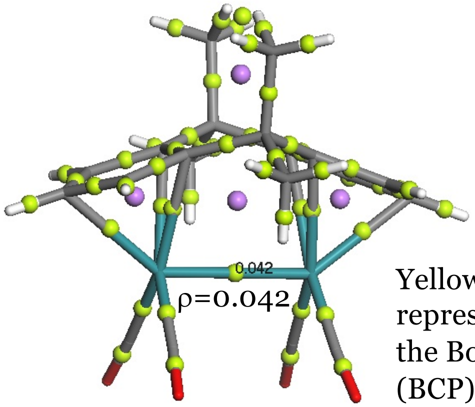
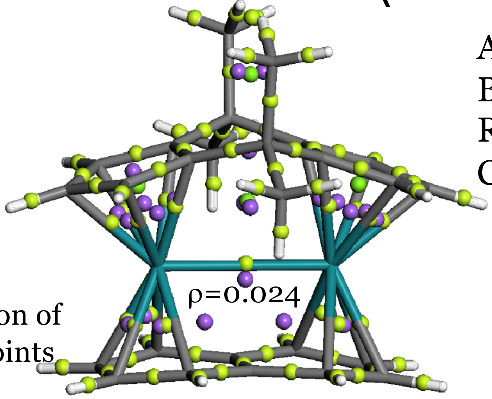


Figure 2. Oxygen partial charges calculated with the CHELPG, the MK, and the Resp schemes for water.

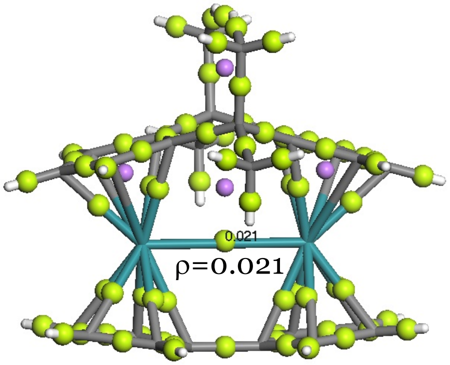
Martin, F. and Zipse, H. (2005) J. Comput. Chem., 26: 97–105. doi: 10.1002/jcc.20157

Atoms in Molecules (AIM) Analysis

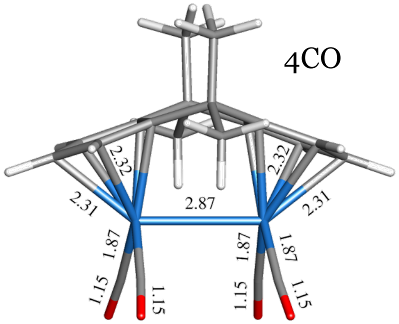




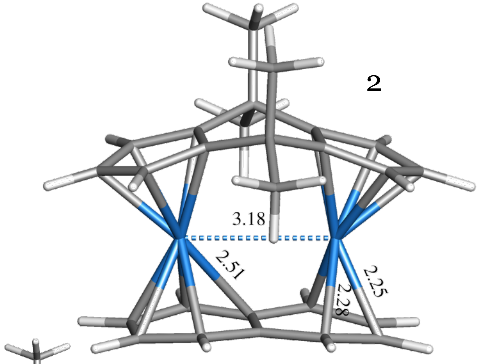
Atom CP (3, -3)
Bond CP (3, -1)
Ring CP (3, +1)
Cage CP (3, +3)



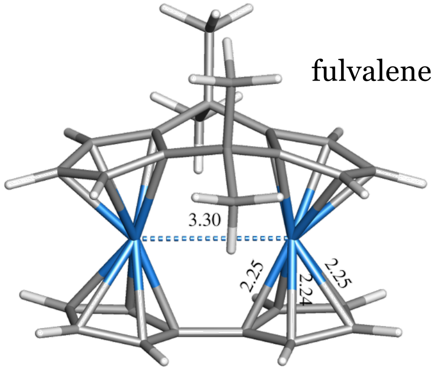
Yellow Spheres represent the location of the Bond Critical Points (BCP)



4CO

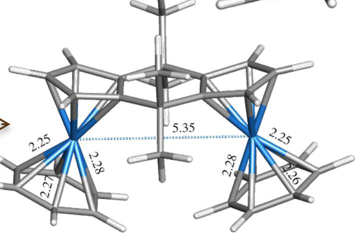


2



fulvalene

AIM analysis does not calculate a BCP between the Ru atoms in the 2benzene complex.



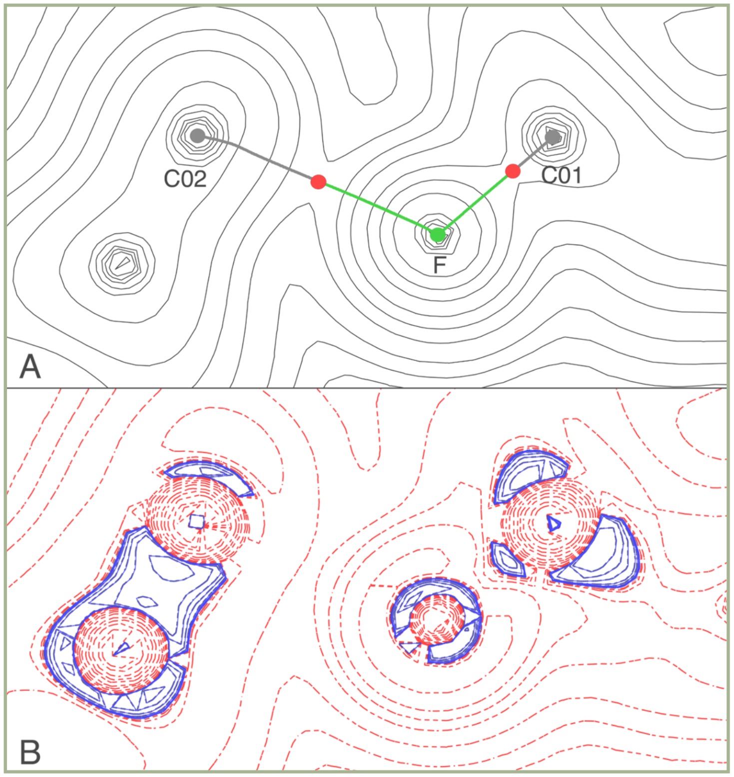
Critical Point $\nabla\rho=0$

Critical Point (σ, λ)

σ= rank, # of non-zero eigenvalues of $\nabla^2\rho$

λ= signature, algebraic sum of the diagonal terms

Wavefunction Analysis - Laplacian

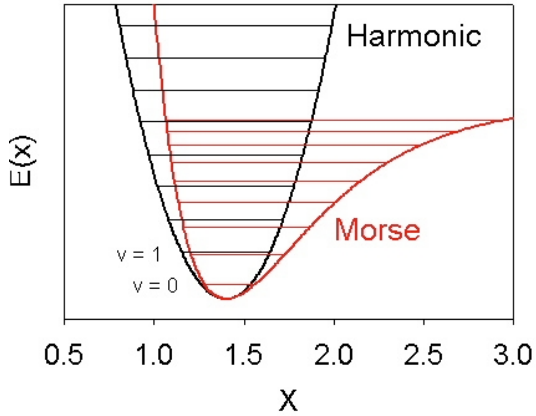


A) Contour plot of the electron density of [1-F]+ showing the short and long C-F bonds. The plane was selected to contain the C02, F, and C01 atoms. B) Contour plot of $-1/4\nabla^2\rho(r)$ for [1-F]+ illustrating the covalent nature of the short C-F bond and the dative nature of the long C-F bond. Positive and negative values are shown with blue solid and red dashed lines, respectively.

IR Spectra

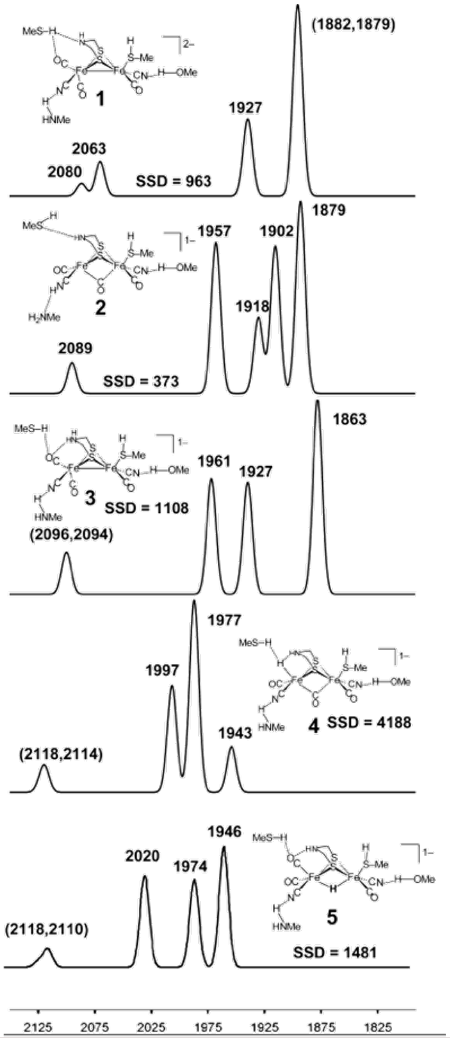
$$\text{IR Intensity} \propto \left(\frac{\partial \mu}{\partial q}\right)^2 \propto \left(\frac{\partial^2 E}{\partial R \partial F}\right)^2$$

- μ - Dipole Moment
- *q* - Normal Coordinates
- *E* - Energy
- *R* - Nuclear Coordinates
- *F* - External Electric Field

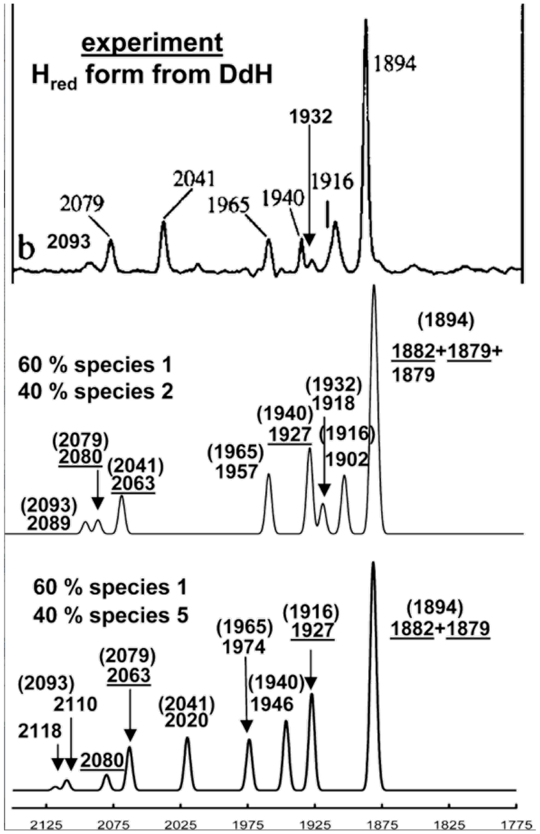


- Calculated by default for frequency calculations in Gaussian.
- First order approximation (double harmonic) therefore only fundamental bands with have an intensity different from zero (allowed).
- Correct frequencies with a scaling factor (DFT ~ 0.98)

IR Spectra



Predicted infrared spectra for various structural candidates for the H_{red} form of the [FeFe]H_2ase enzyme derived from DdH (species **1**–**5**).



Jesse W. Tye *et al. Inorg. Chem.* **2008,** 47, 2380-2388. DOI: 10.1021/ic7013732

Raman Spectra

$$\text{Raman Intensity} \propto \left(\frac{\partial \alpha}{\partial q}\right)^2 \propto \left(\frac{\partial^3 E}{\partial R \partial F^2}\right)^2$$

- α - Polarizability
- q - Normal Coordinates
- E - Energy
- R - Nuclear Coordinates
- F - External Electric Field

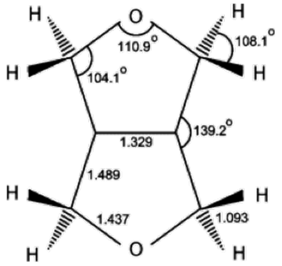
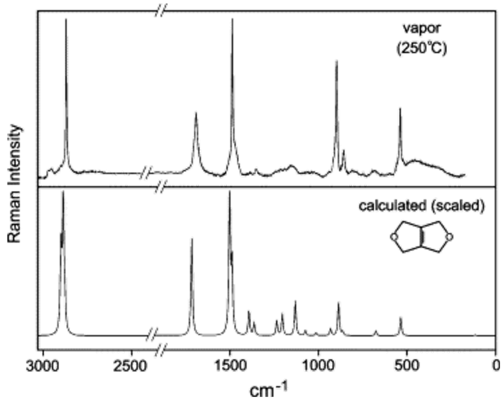


Fig. 2. Structure of DOBO from the MP2 calculation (MP2/CC-pVTZ).

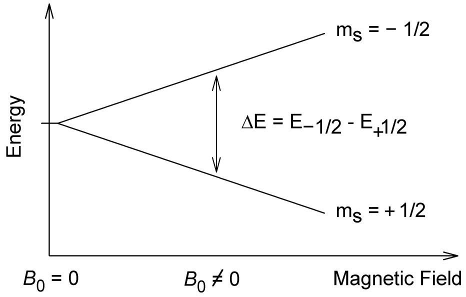


C. Mlynek et al. / Journal of Molecular Structure 742 (2005) 161–164
http://dx.doi.org/10.1016/j.molstruc.2004.09.036

- Raman intensity calculations require a numerical calculation for DFT, therefore they are not performed by default for frequency calculations in Gaussian. HF is analytical and performed by default.
- First order approximation (double harmonic) therefore only fundamental bands will have an intensity different from zero (allowed).
- Correct frequencies with a scaling factor (DFT ~ 0.96)

NMR Calculations

$$\text{NMR Shielding} \propto \left(\frac{\partial^2 E}{\partial B \, \partial I} \right)$$

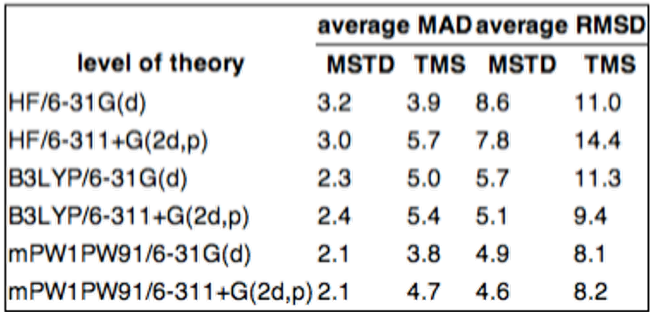


- E - Energy
- B - External Magnetic Field
- I - Nuclear Magnetic Moment (Nuclear Spin)

$$\text{Spin–Spin Coupling} \propto \left(\frac{\partial^2 E}{\partial^2 I} \right)$$

- Need to calculate the NMR standard molecule (ie TMS - Trimethylsilane) at the same level of theory as the molecule of interest.

Table 1. Comparison of Errors in ^{13}C Computed Chemical Shifts for a Set of 50 Organic Compounds Determined via Comparison with TMS and Methanol/Benzene (MSTD)[a]



level of theory	average MAD		average RMSD	
	MSTD	TMS	MSTD	TMS
HF/6-31G(d)	3.2	3.9	8.6	11.0
HF/6-311+G(2d,p)	3.0	5.7	7.8	14.4
B3LYP/6-31G(d)	2.3	5.0	5.7	11.3
B3LYP/6-311+G(2d,p)	2.4	5.4	5.1	9.4
mPW1PW91/6-31G(d)	2.1	3.8	4.9	8.1
mPW1PW91/6-311+G(2d,p)	2.1	4.7	4.6	8.2

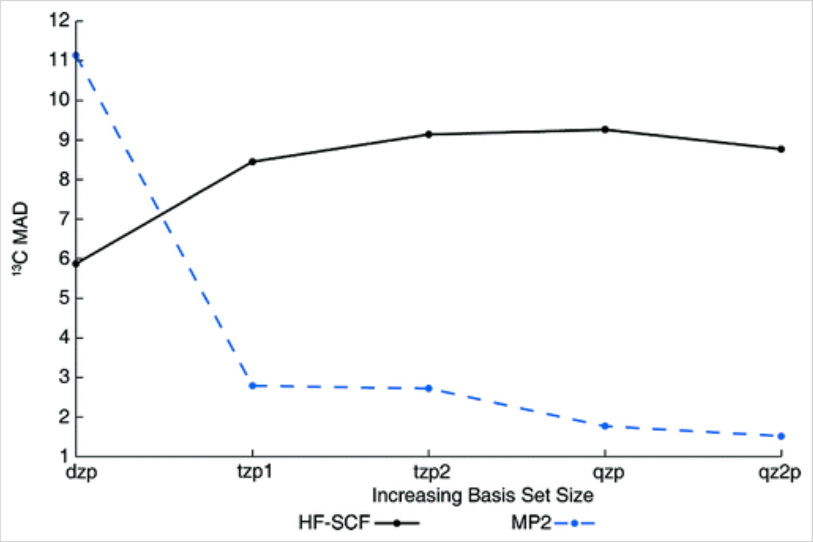
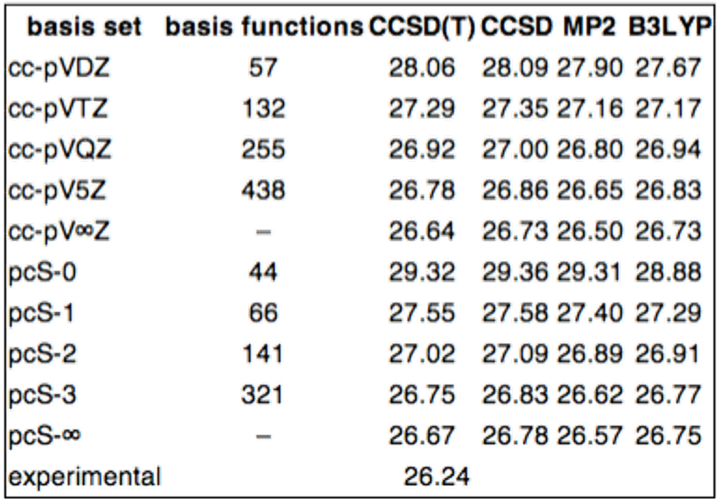


Table 21. Absolute Isotropic Shielding Constants (ppm) for the *cis*-*N*-Amide Proton of Formamide(238)

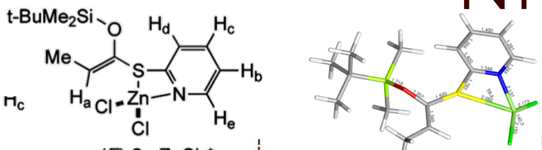


basis set	basis functions	CCSD(T)	CCSD	MP2	B3LYP
cc-pVDZ	57	28.06	28.09	27.90	27.67
cc-pVTZ	132	27.29	27.35	27.16	27.17
cc-pVQZ	255	26.92	27.00	26.80	26.94
cc-pV5Z	438	26.78	26.86	26.65	26.83
cc-pV∞Z	–	26.64	26.73	26.50	26.73
pcS-0	44	29.32	29.36	29.31	28.88
pcS-1	66	27.55	27.58	27.40	27.29
pcS-2	141	27.02	27.09	26.89	26.91
pcS-3	321	26.75	26.83	26.62	26.77
pcS-∞	–	26.67	26.78	26.57	26.75
experimental		26.24			

http://pubs.acs.org/doi/full/10.1021/cr200106v

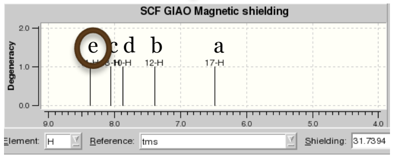
NMR Calculations

J. Am. Chem. Soc., 2012, 134 (6), pp 3084–3094 DOI: 10.1021/ja209163w

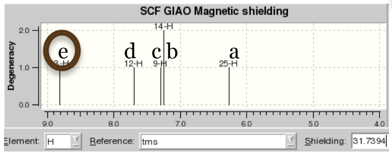


(E)-**2a**•ZnCl$_2$*

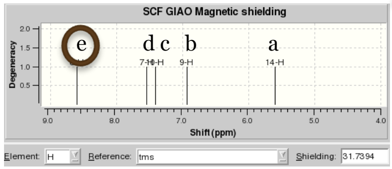
ΔG = **1.6** kcal/mol


SCF GIAO Magnetic shielding

Element: H
Reference: tms
Shielding: 31.7394

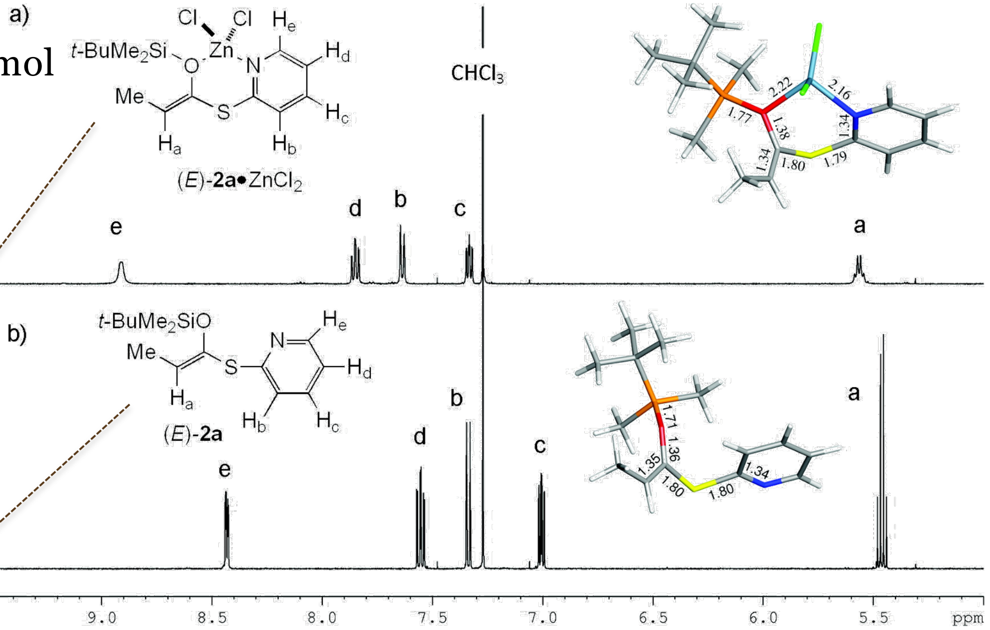

SCF GIAO Magnetic shielding

Element: H
Reference: tms
Shielding: 31.7394


SCF GIAO Magnetic shielding

Element: H
Reference: tms
Shielding: 31.7394

ΔG = = **0.00** kcal/mol



(E)-**2a**•ZnCl$_2$

(E)-**2a**

Upfield →

← Downfield

Quantum Mechanics

Time-independent Schrödinger Equation

$$\hat{H}\psi=E\psi$$

$\hat{H}$ = Hamiltonian Operator
ψ = Wavefunction (eigenfunction)
E = Energy of the system (eigenvalue)

Quantum Mechanics

- Wavefunction is represented by a Linear Combination of Atomic Orbitals (LCAO)
- Approximations made in the Hamiltonian:
    1) Neglect relativistic effect
    2) Neglect coupling of electronic states (adiabatic approximation)
    3) Neglect coupling of the electronic and nuclear motion (Born-Oppenheimer approximation)

Ab initio Summary

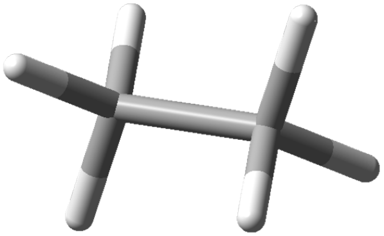
- HF<MP2<CISD<MP4(SDQ)~CCSD<MP4<CCSD(T)
    - note: MP4 includes less e^- correlation but more triple excitations than CCSD(T)
    - Hartree-Fock does not include dynamic e^- correlation
    - PROS:
        - Hierarchy which includes more e^- correlation as you move up the hierarchy
    - CONS:
        - Computational cost for post-scf calculations is high.
        - The accuracy of post-scf (post-HF) levels of theory are highly dependent on the quality of the basis set

Density Functional Theory Summary

- Pros:
  - Include dynamic electron correlation for about the same computational cost as Hartree-Fock
  - Often is more robust for systems with multi-reference character – transition metals, etc
  - Not as dependent on the quality of the basis set as *wave function methods*
- Cons:
  - No Hierarchy
  - Poor for dispersion

Overview - Getting Started

- Molecular Coordinates (atomic coordinates for all atoms to be included in the calculation, cartesian coordinates, internal coordinates (ie z-matrix), etc)
- Symmetry (Point Group)
- Charge (overall charge of the molecule/molecular system)
- Multiplicity (number of unpaired electrons)



C_2H_6
D_{3d}
Charge = 0
Multiplicity = 1

Overview

- Choose a level of theory
  - The level of theory determines the Hamiltonian (Ĥ) used to solve the Schrödinger/Kohn-Sham equation.
  - HF, MP2, MP3, CCSD, DFT (B3LYP, BP86, etc),etc
- Choose a basis set
  - The basis set is a set of coefficient and exponents for the equation used to describe the atomic orbitals that will be using to describe the wavefunction (ψ)
  - 6-31G(d), SDD, LANL2DZ, etc
- **Calibrate**
  - against experimental data
  - against benchmark calculations (CCSD(T), MRCI, etc)