



THE UNIVERSITY *of* TEXAS

HEALTH SCIENCE CENTER AT HOUSTON

SCHOOL *of* HEALTH INFORMATION SCIENCES

## Quantum Chemistry II

For students of HI 6327 “Biomolecular Modeling”

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<http://biomachina.org/courses/modeling/12.html>

# Overview

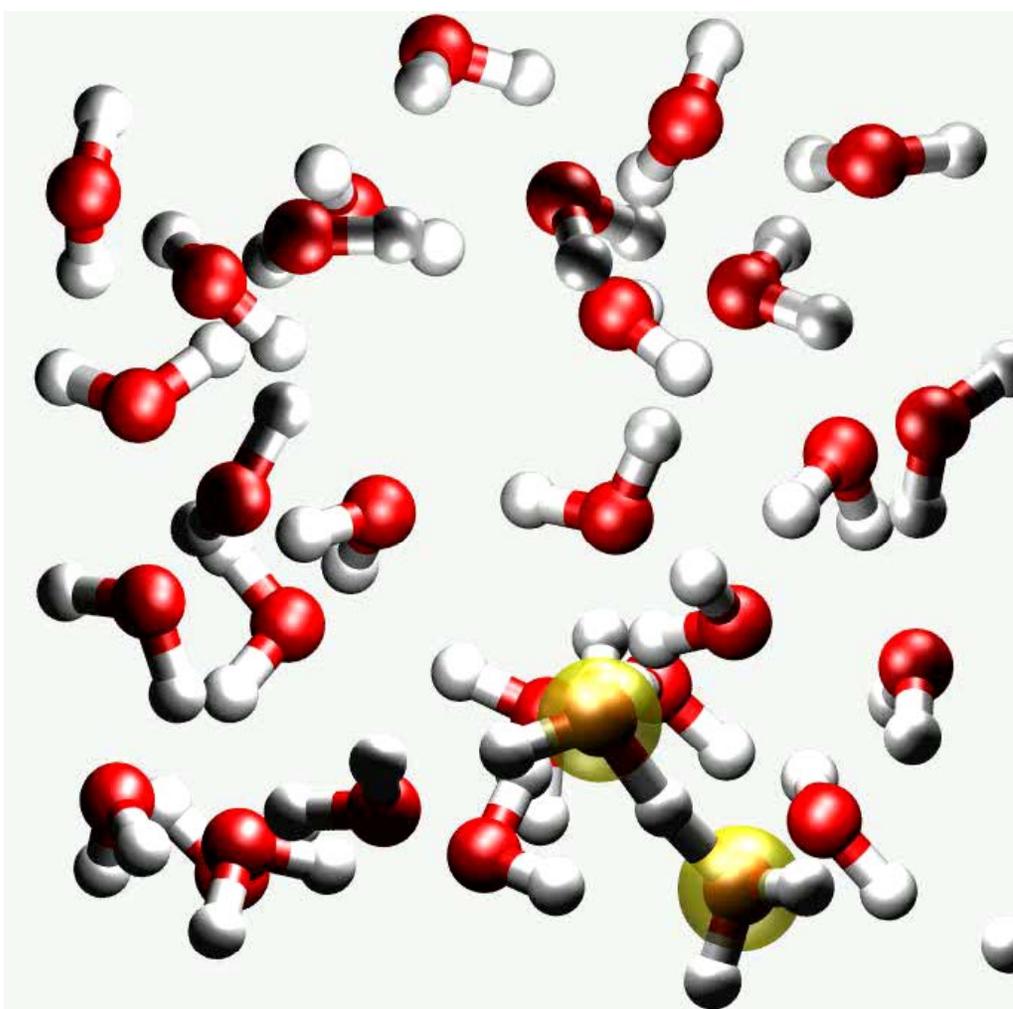
- Car-Parrinello (brief)
- QM/MM embedding
- The HSE DFT functional
- Accuracy of various QC methods
- Calculating molecular properties
- Force field parameterization
- A case study

# Car-Parrinello MD

CPMD is a DFT method based on the following idea:

Small perturbations in the positions of the nuclei only produce a small change in the solution of the SCF procedure.

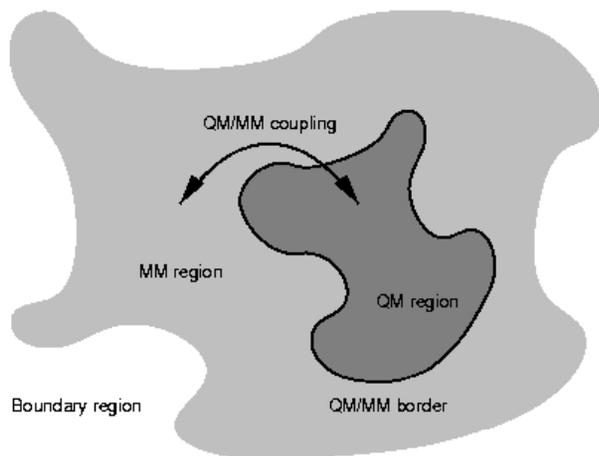
→ Evolve atom positions and the wave function simultaneously



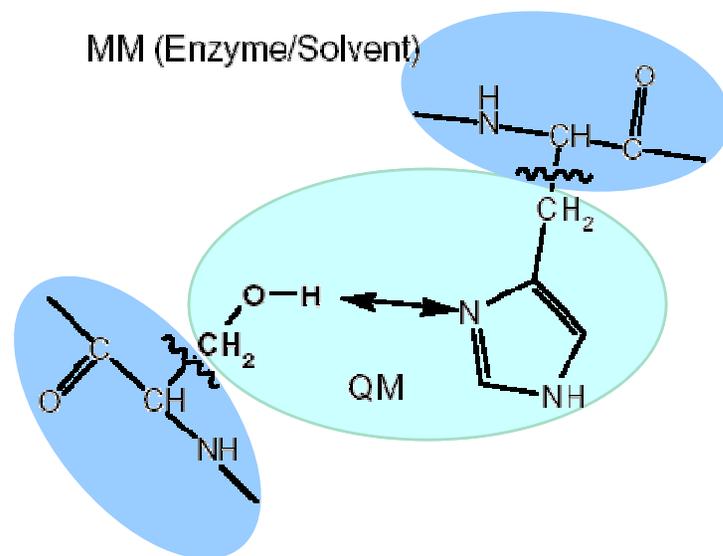
# Quantum Mechanics/Molecular Mechanics (QM/MM)

Goal: Investigate chemical reactions in condensed phase environments.

Exploit explicit treatment of electrons with QM approach in combination with computationally inexpensive MM approach to treat condensed phase environment.



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# Embedding Approaches

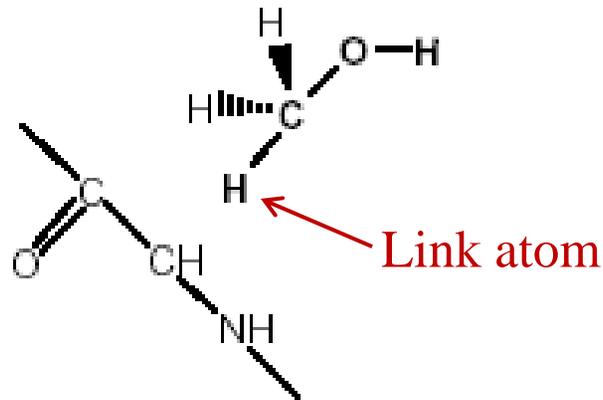
$$E = E_{\text{QM}} + E_{\text{MM}} + E_{\text{QM/MM}}$$

The tough part – how do QM and MM interact?

- Steric embedding
- Charge embedding
- Link atom
- Covalent embedding

# Link Atom Approach

- 1) Include hydrogen to fill valence (or fluorine or methyl).
- 2) Maintain QM to MM covalent terms (bonds, angles, and dihedrals)
- 3) QM sees all MM atoms (as charges) and vice versa. Omission of link atom to MM atom interactions leads to poor results due to polarization of link atom - carbon bond. This is caused by the carbon “feeling” the MM field while the link atom does not.



Apply constraints to keep link atom along the C-CH bond.

# Link-Atom Embedding: Problems

## ◆ Potential Problems with Link Atom Idea

- Extra degrees of freedom which somehow need to be removed; i.e. the link atom somehow needs to be connected to the MM part of the simulation
- Electronic structure at boundary will be very different if H and the atom it replaces do not have similar electronegativities

# Selection of QM Region

- In solution: Reactants being treated by QM are surrounded by MM waters: no covalent bonds between QM atoms and MM atoms
- Enzyme active site: Necessity of including amino acid or coenzyme functional groups in QM region requires treatment of covalent link between QM and MM regions (frontier region).
- Valences of the frontier atoms of QM region must be filled:
  - Link Atoms
  - Frontier Orbitals
- Other guidelines:
  - 1) Perform test calculations using different QM/MM partitions to see if the charge distribution reproduces full QM values in the gas phase.
  - 2) ALWAYS place QM/MM frontier (link atom or orbital) at an aliphatic carbon as it is desirable to have the smallest possible charge distribution at the frontier.

Questions: QM/MM?

Next: Density Functional Theory (cont.)

# Density Functional Theory

- Hohenberg and Kohn (1964)

$$E = E[\rho]$$

- The energy is composed of several parts

$$E_{tot} = T_e + V_{ne} + J_{ee} + E_{XC}$$

# Exchange and Correlation Functionals

$$E_{XC} = E_{XC}[\rho]$$

Local spin density  
approximation (LSDA)

$$E_{XC} = E_{XC}[\rho, \nabla\rho]$$

Generalized gradient  
approximation (GGA)

BLYP, PBE, ...

$$E_{XC} = E_{XC}[\rho, \nabla\rho, \tau]$$

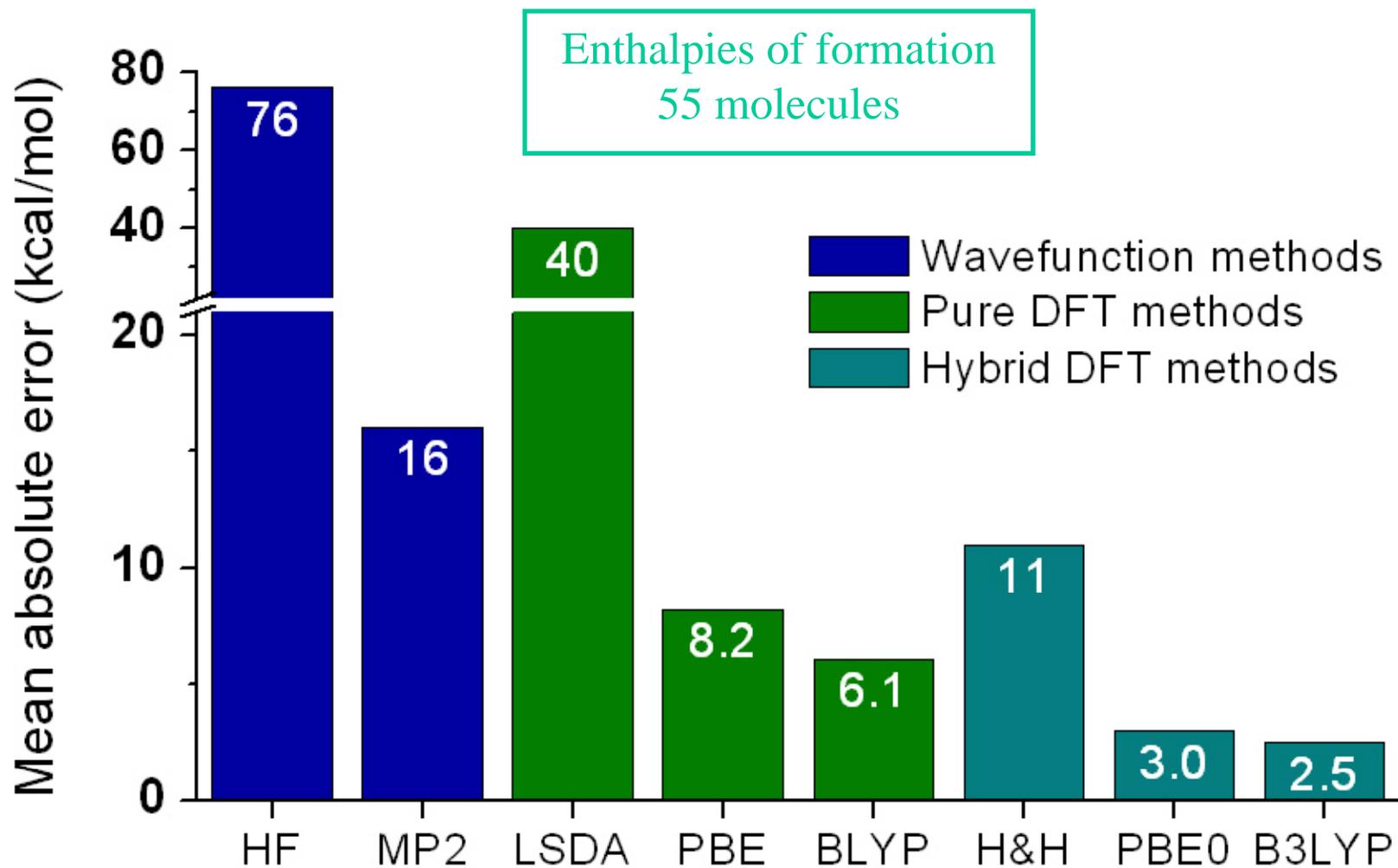
Meta-generalized gradient  
approximation (mGGA)

VSXC, TPSS, ...

# Exchange Functionals and Hartree-Fock Exchange

- DFT exchange functionals perform well for systems with slowly varying densities
- HF exchange is exact but difficult to pair with a DFT correlation functional
- Hybrid exchange functionals mix DFT and HF
- Hybrids can describe systems with rapid variations in electron density

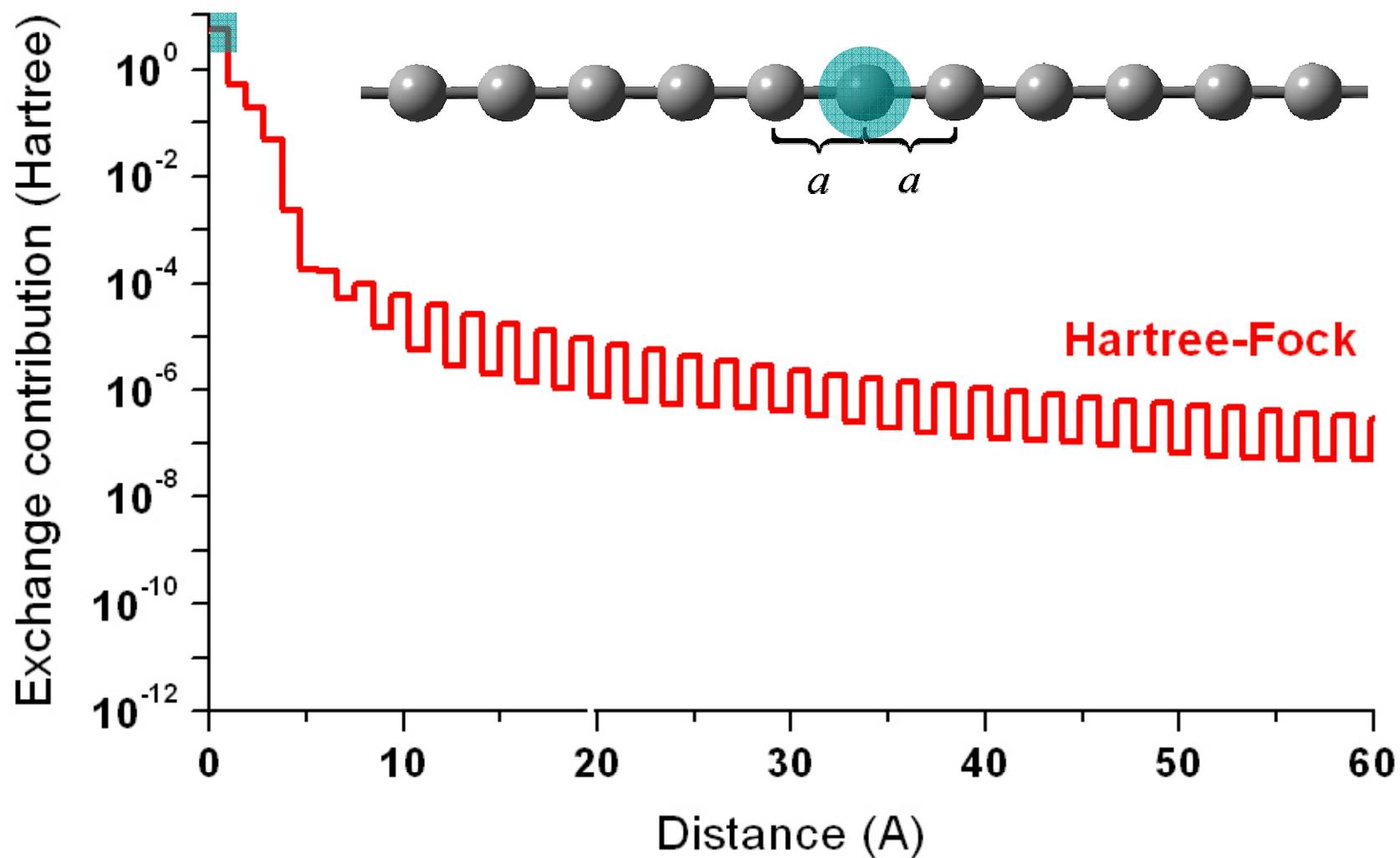
# Why Do We need Exact (HF) Exchange?



## Why not always use hybrids?

- Pure DFT scales linearly with system size
- HF exchange is computationally expensive
- Linear scaling methods for evaluating exact exchange depend strongly on the HOMO-LUMO (or band) gap
- Truncation schemes often lead to errors of unknown magnitude and can complicate the self-consistent field convergence

# Infinite Carbon Atom Chain



# The Central Idea

Let the exchange potential delocalize,  
but only among **near neighbors!**

# Partitioning the Coulomb Operator

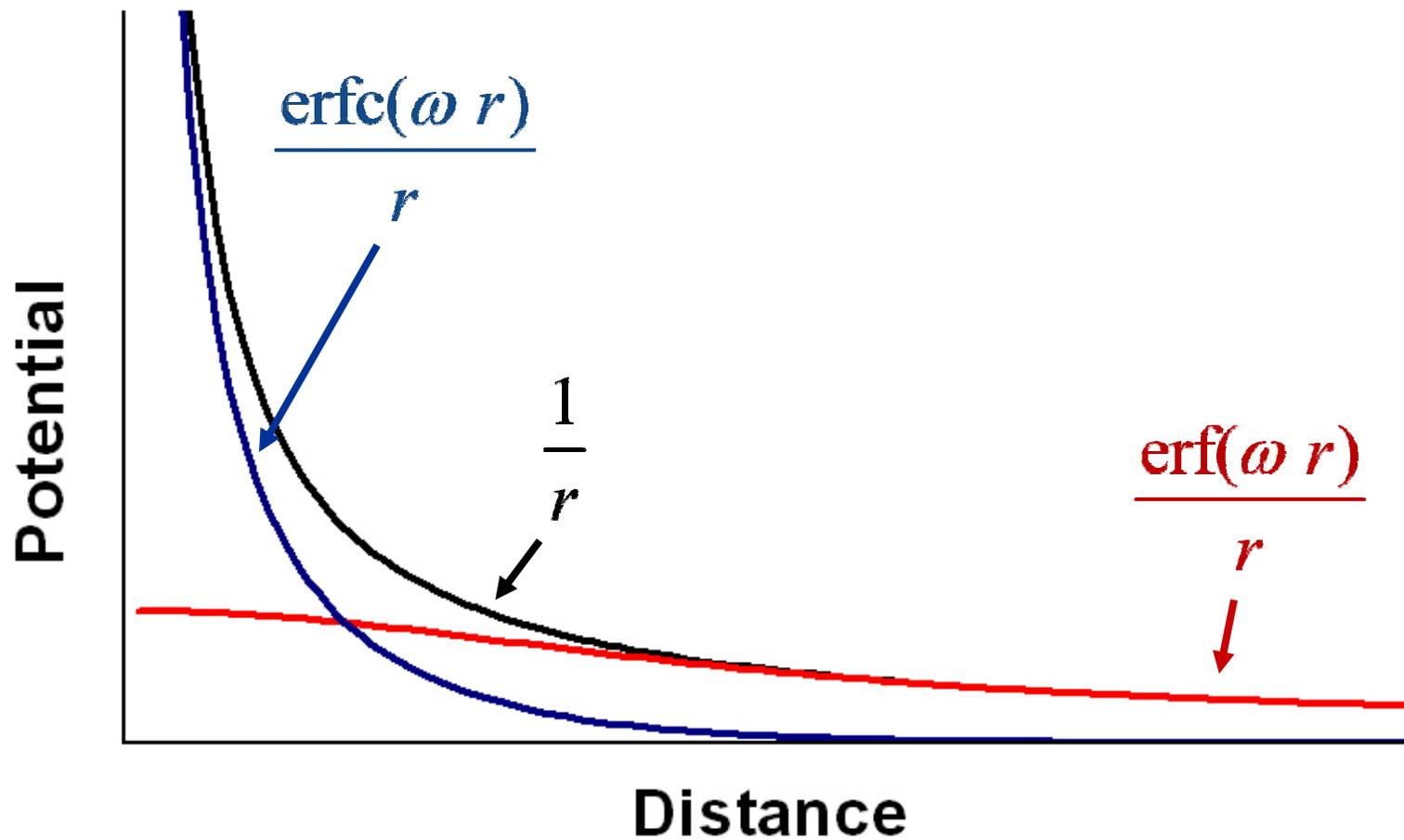
The Coulomb operator can be separated as follows:

$$\frac{1}{r} = \frac{\operatorname{erfc}(\omega r)}{r} + \frac{\operatorname{erf}(\omega r)}{r} \quad \omega \geq 0$$

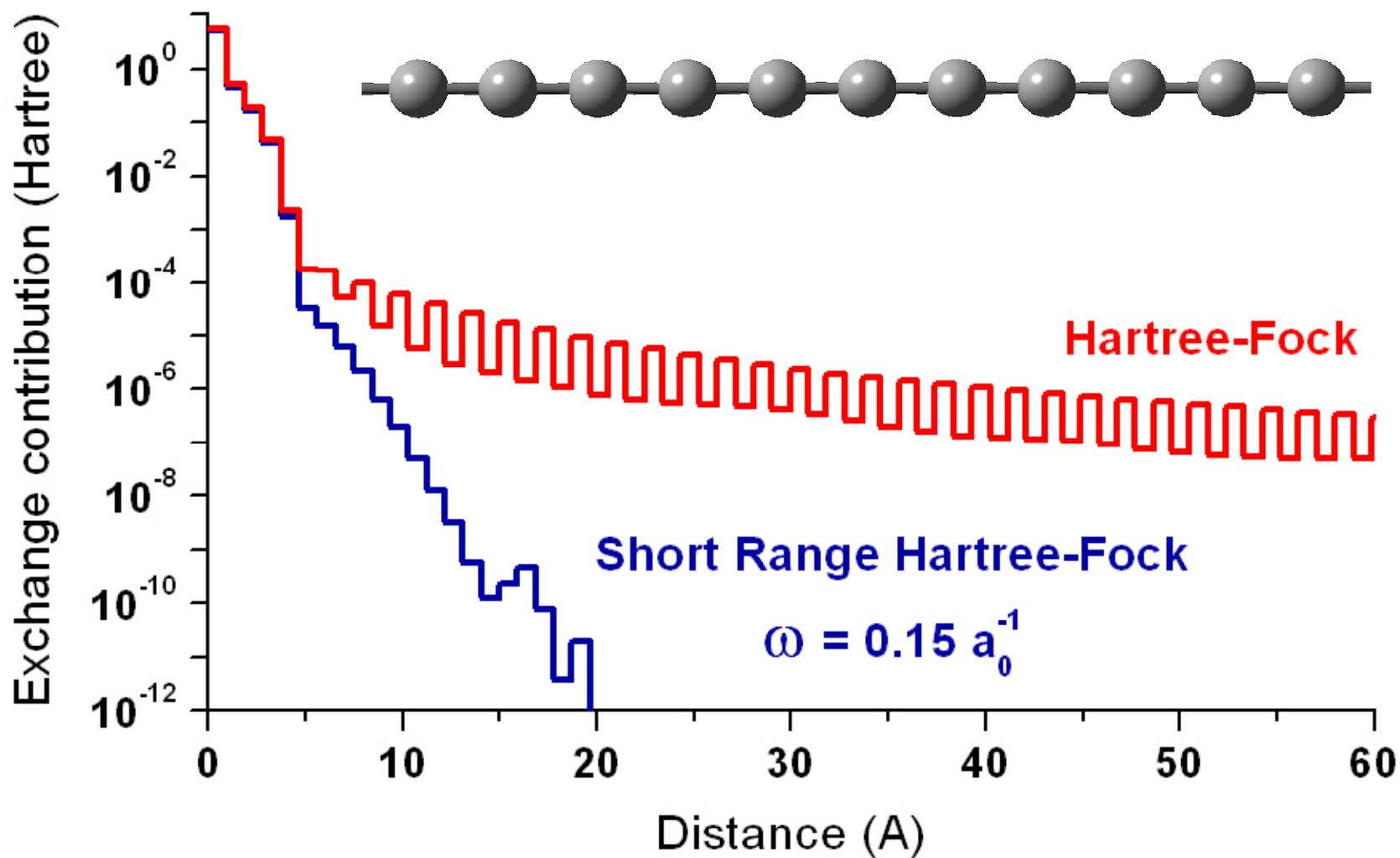
**Short Range**      **Long Range**

The parameter  $\omega$  controls the splitting into short and long range.

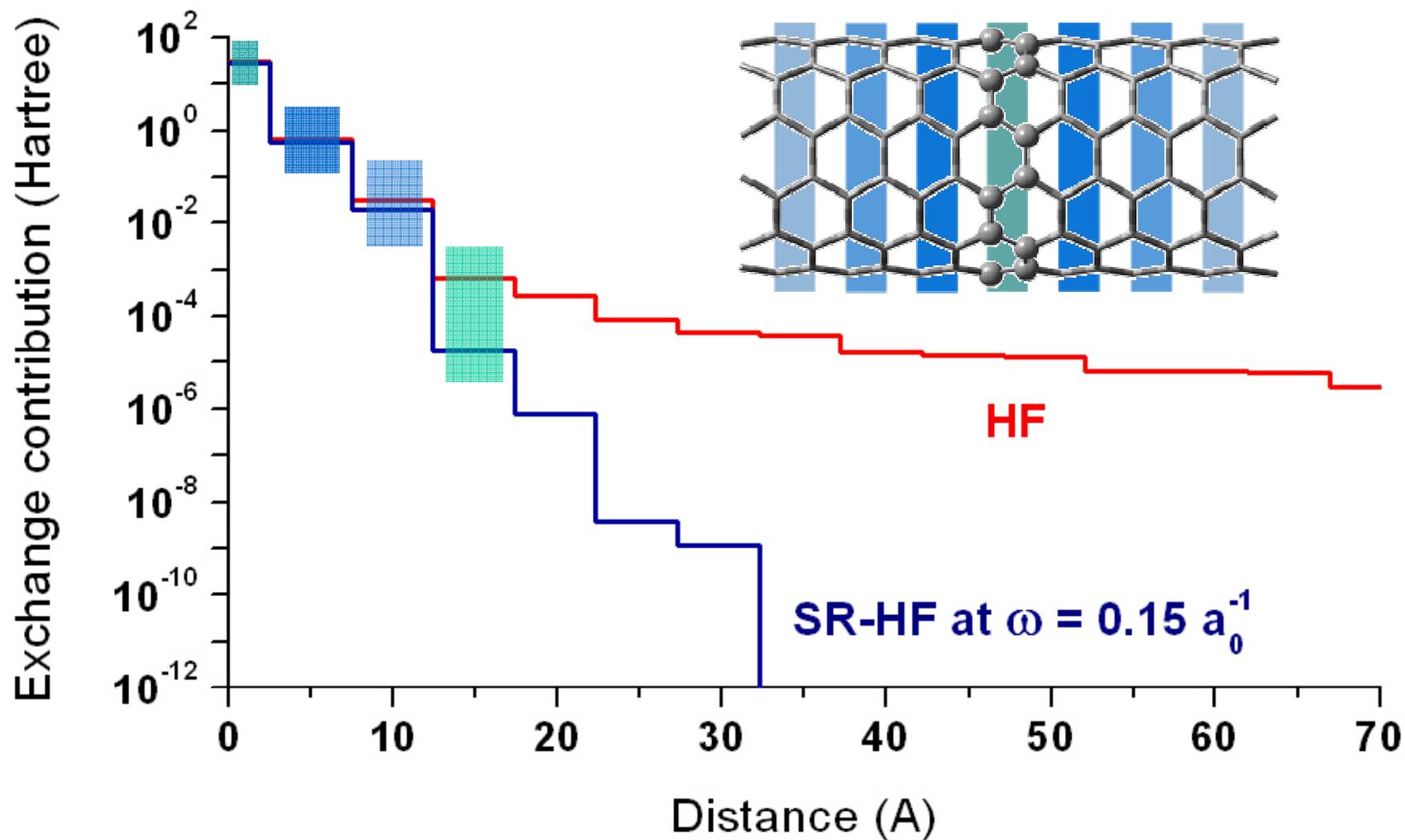
# Partitioning the Coulomb Operator



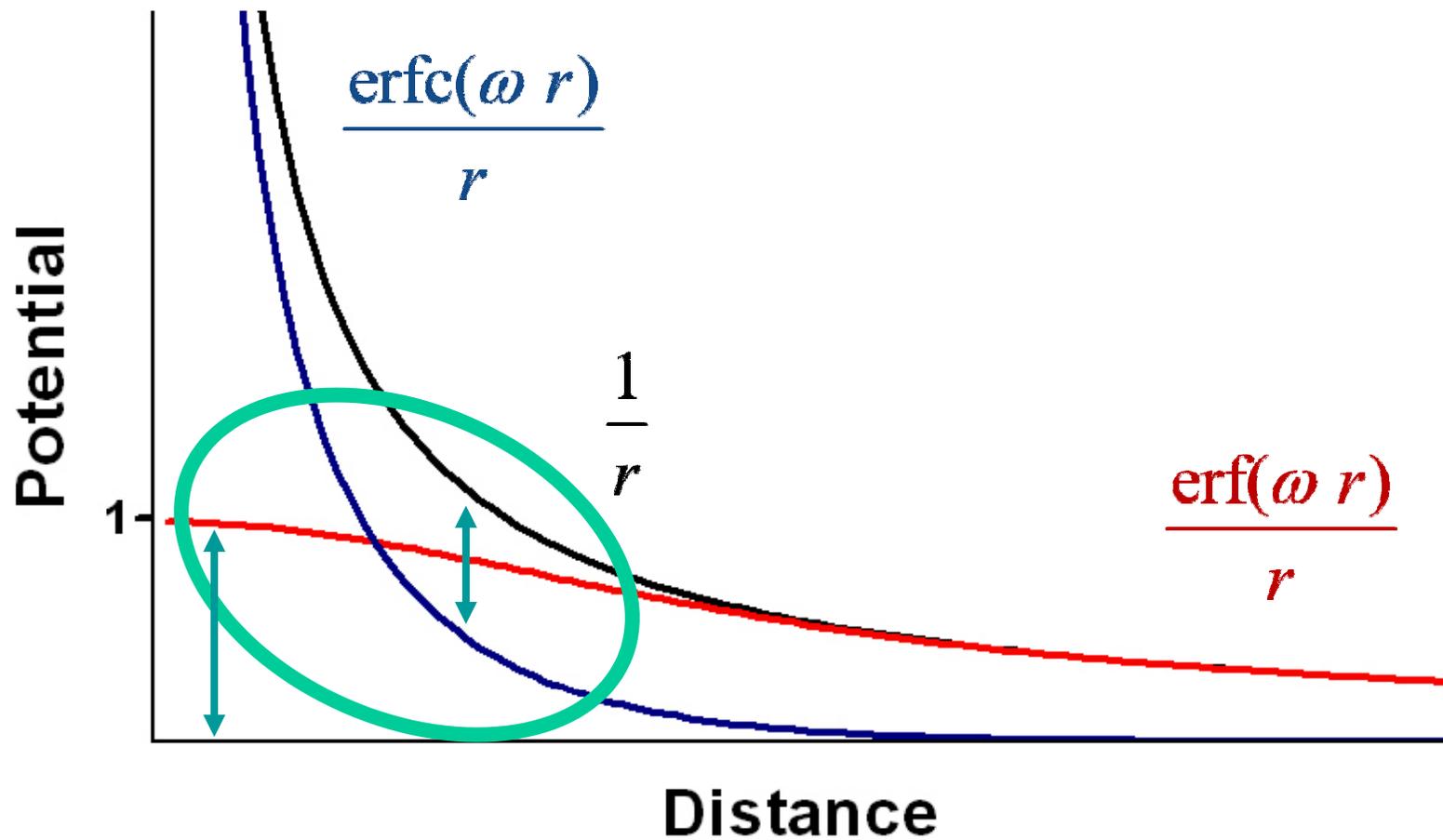
# Infinite Carbon Atom Chain



# (6,6) Carbon Nanotube: Decay of the Exchange Interaction



# Partitioning the Coulomb Operator



# Heyd-Scuseria-Ernzerhof Hybrid Functional

Starting from the standard PBE0 hybrid

$$E_{XC}^{\text{PBE0}} = a \cdot E_X^{\text{HF}} + (1-a) \cdot E_X^{\text{PBE}} + E_C^{\text{PBE}} \quad a = 1/4$$

$$E_X = a \cdot E_X^{\text{HF}} + (1-a) \cdot E_X^{\text{DFT}}$$

$$E_X = a \cdot E_X^{\text{HF,SR}}(\omega) + a \cdot E_X^{\text{HF,LR}}(\omega) + (1-a) \cdot E_X^{\text{DFT,SR}}(\omega) \\ + E_X^{\text{DFT,LR}}(\omega) - a \cdot E_X^{\text{DFT,LR}}(\omega)$$

assumed to cancel

$$\rightarrow E_{XC}^{\text{HSE}} = a \cdot E_X^{\text{HF,SR}}(\omega) + (1-a) \cdot E_X^{\omega\text{PBE,SR}}(\omega) \\ + E_X^{\omega\text{PBE,LR}}(\omega) + E_C^{\text{PBE}}$$

$a = 1/4$
$\omega = 0.15$

Questions: HSE?

Next: DFT performance on various  
systems

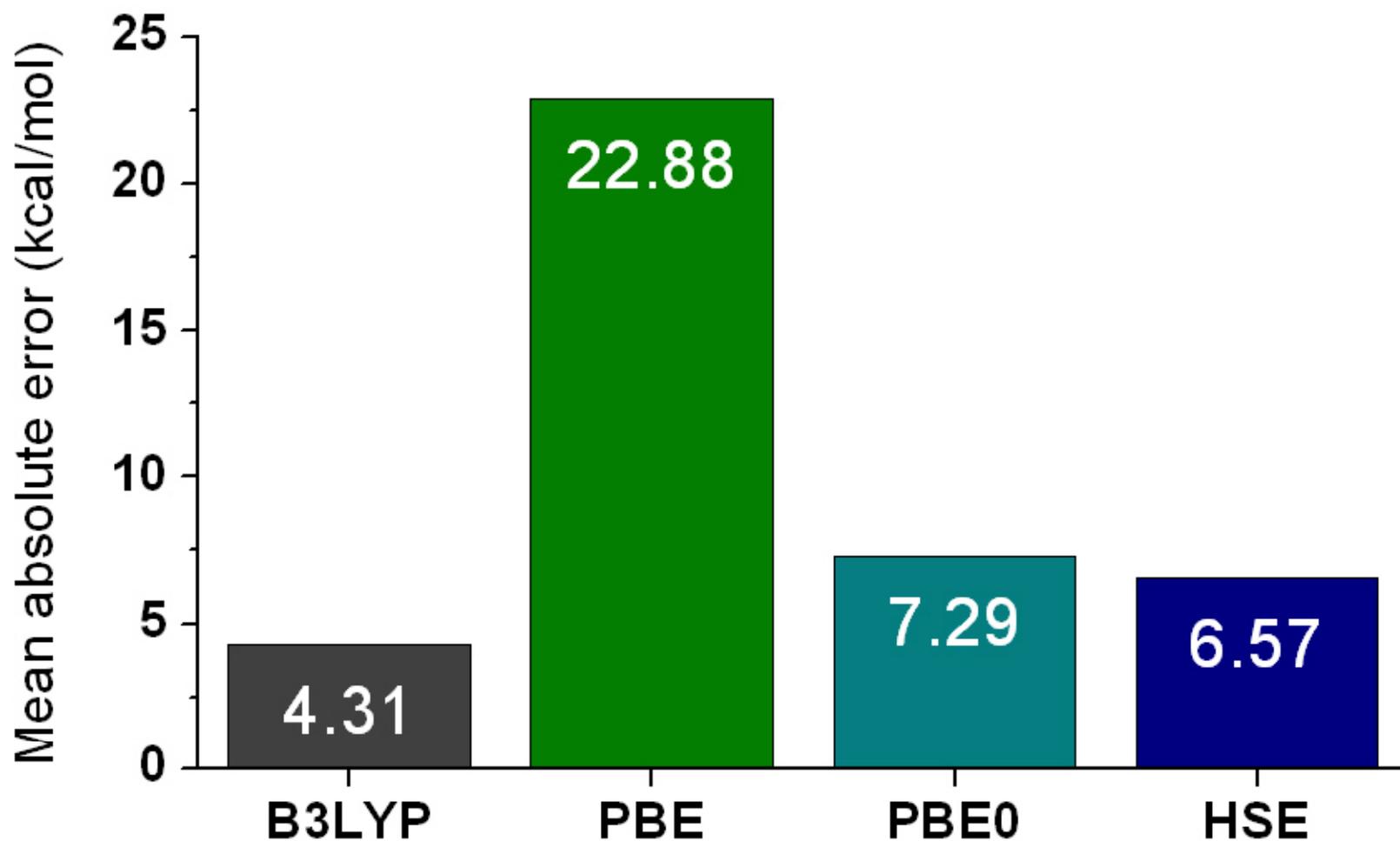
# Atomization Energies:

## Basis set dependence for a set of 55 molecules

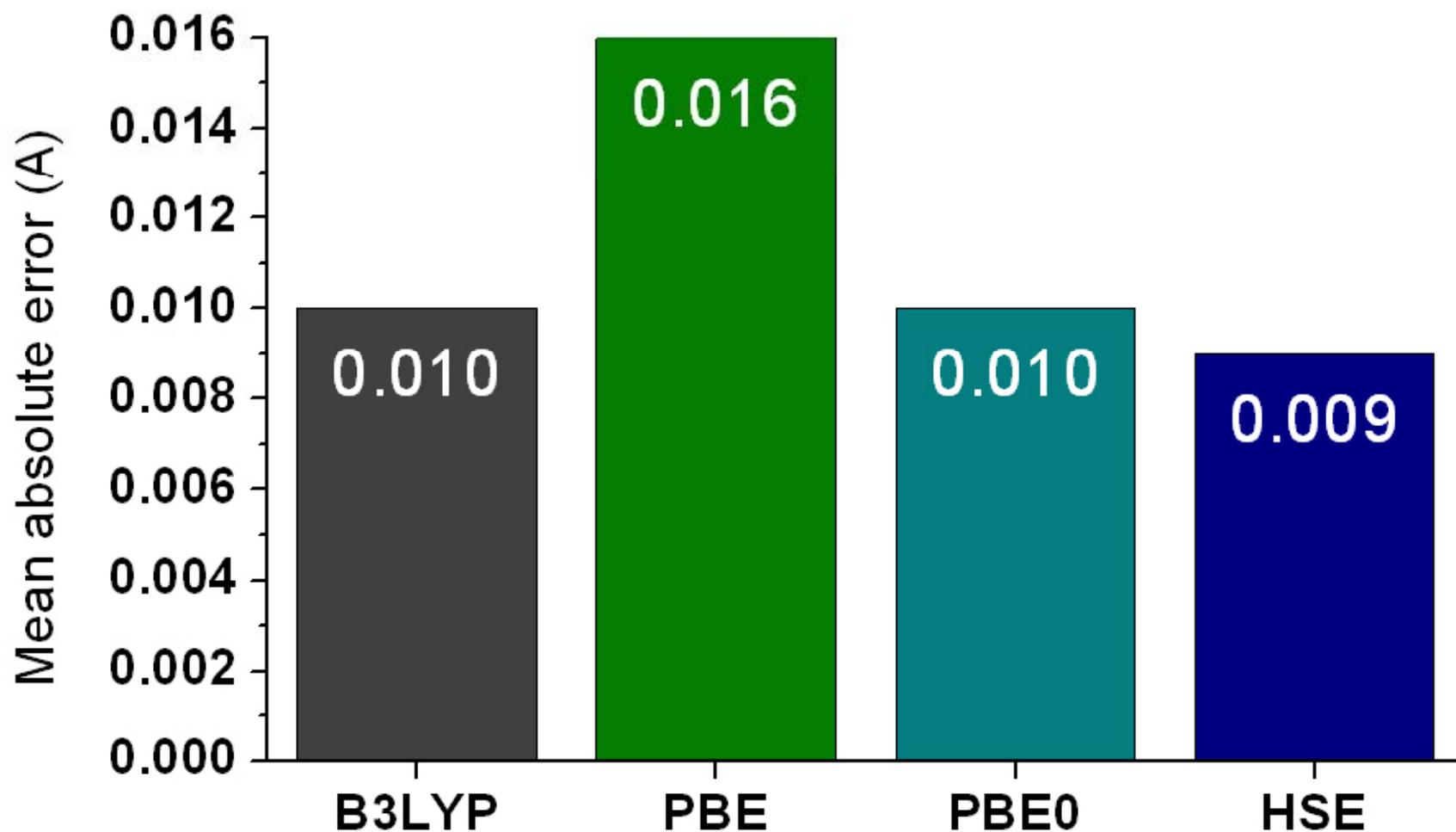
<b>Basis Set</b>	<b>PBE</b>	<b>PBE0</b>	<b>HSE</b>
<b>3-21G</b>	<b>12.94</b>	<b>22.56</b>	<b>17.91</b>
<b>6-31G*</b>	<b>7.23</b>	<b>6.94</b>	<b>6.40</b>
<b>6-311G**</b>	<b>6.14</b>	<b>6.47</b>	<b>4.88</b>
<b>6-311++G(3df,3pd)</b>	<b>5.92</b>	<b>3.49</b>	<b>3.38</b>

Atomization Energy MAE in kcal/mol

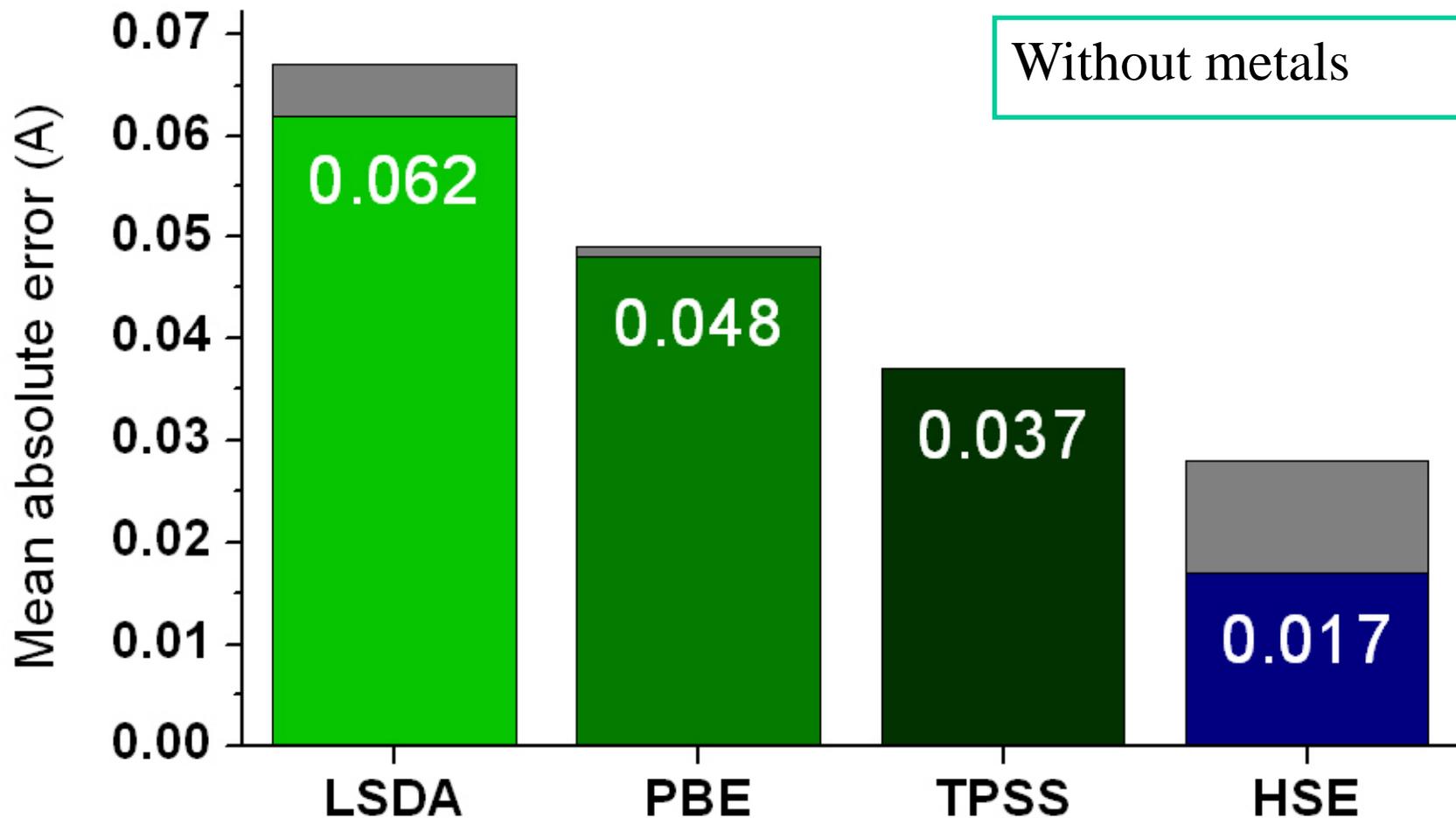
# Enthalpies of Formation: G3 Test Set (223 Molecules)



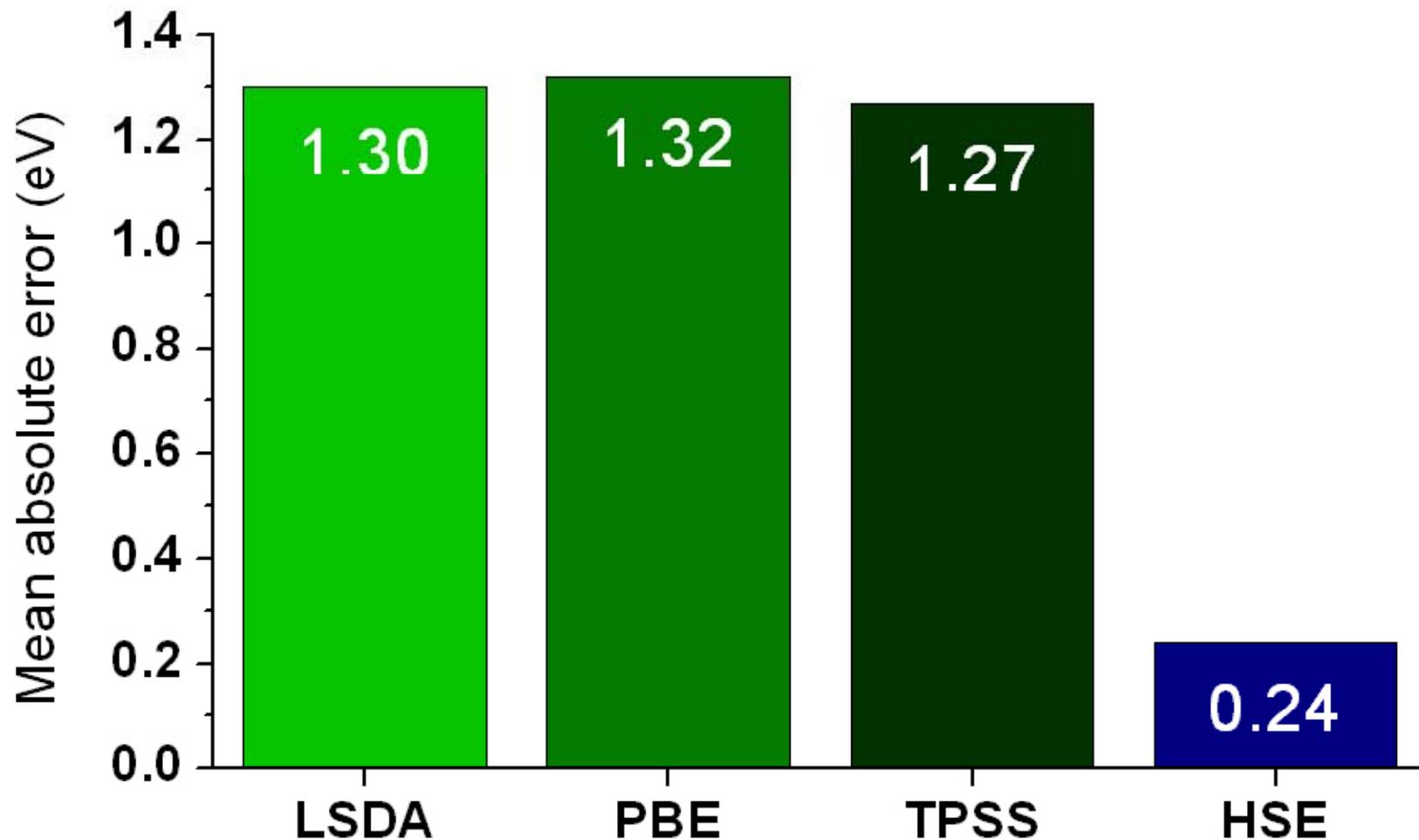
# Optimized Bond Lengths: T-96R Test Set (96 Molecules)



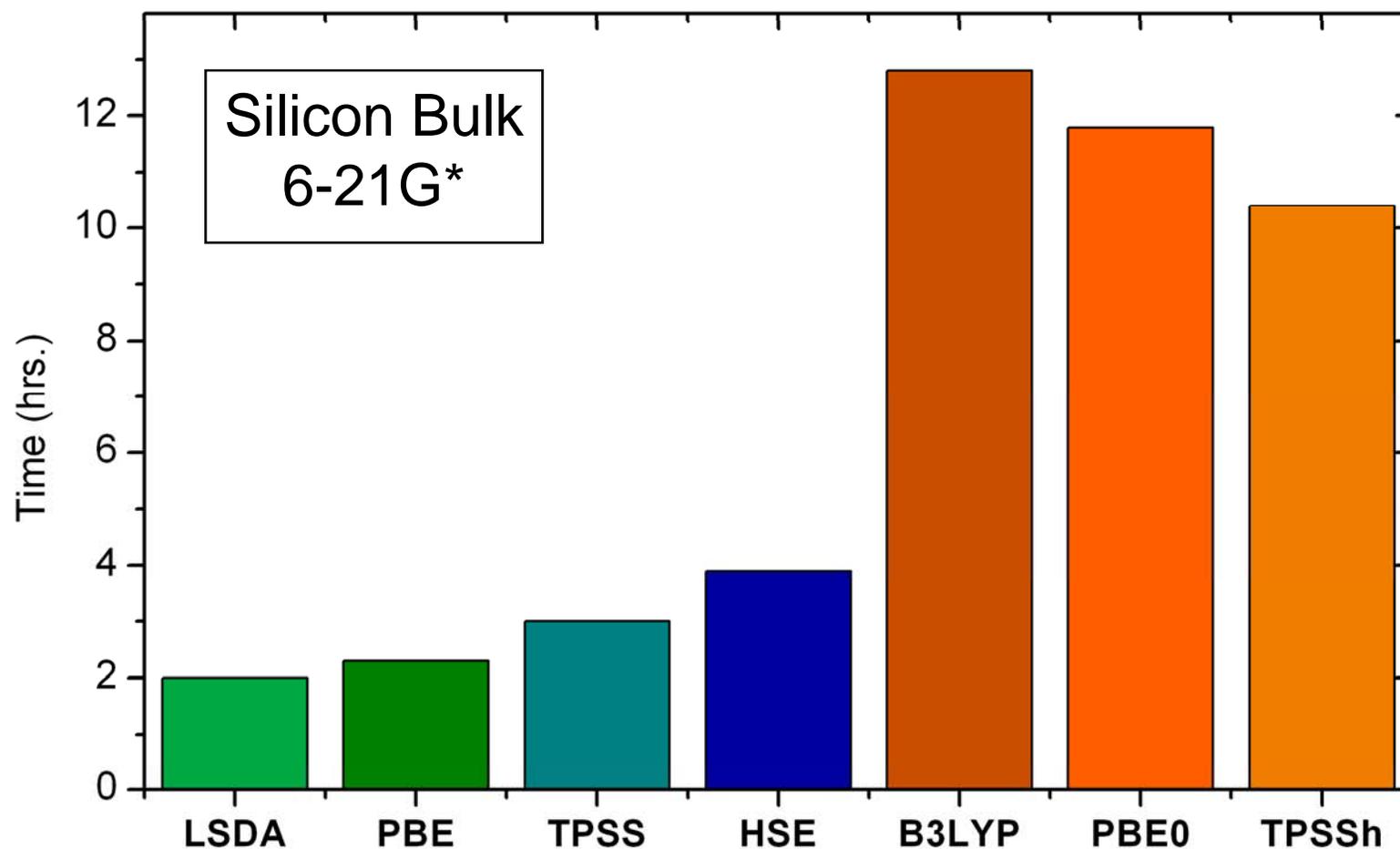
# Lattice Constants



# Band Gaps (Semi-Conductors)



# Time Per Complete SCF



Questions: DFT?

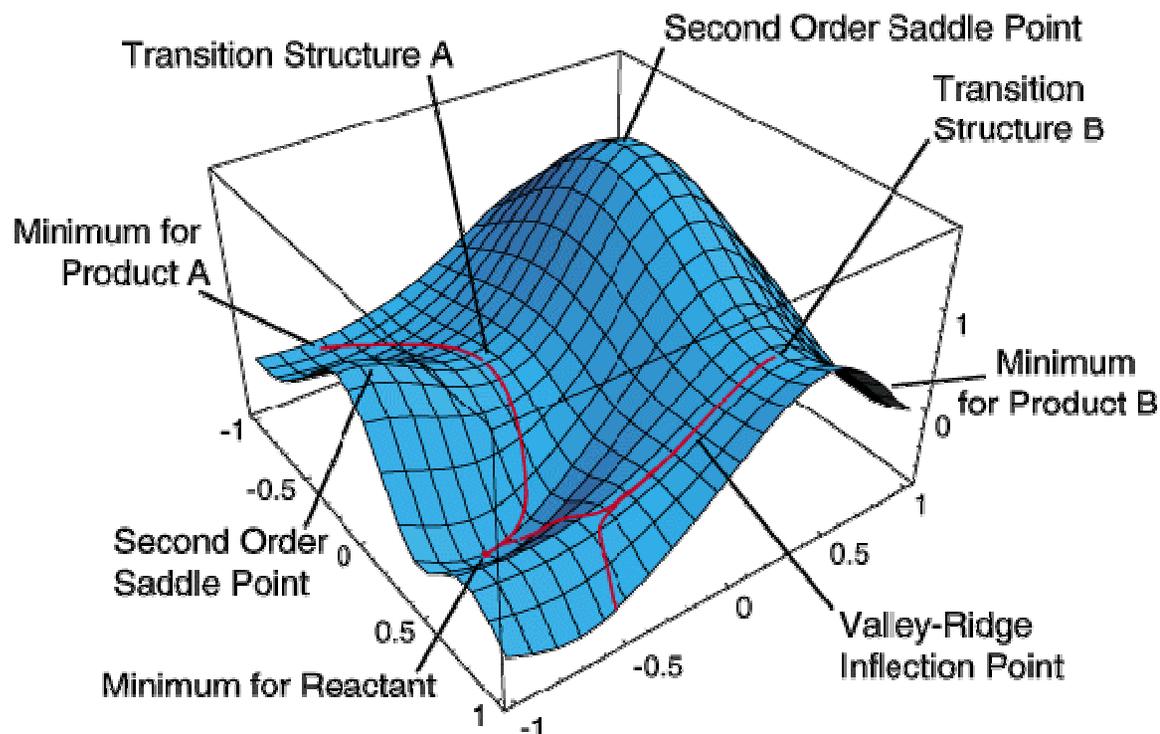
Next: Calculating Molecular Properties

# Calculating Molecular Properties

All molecular properties are derivatives of either the energy or the electronic density / wavefunction.

- Molecular geometry
- Vibrational frequencies
- Electron density and HOMO/LUMO
- Partial charges
- Electrostatic potential

# Potential Energy Surfaces



- Equilibrium molecular structures correspond to the positions of the minima in the valleys on a PES
- Energetics of reactions can be calculated from the energies of the minima for reactants and products
- A reaction path connects reactants and products through a mountain pass
- A transition structure is the highest point on the lowest energy path
- Reaction rates can be obtained from the height and profile of the potential energy surface around the transition structure

# Important Points

- Normally, only look for stationary points

$$\left. \frac{\partial E(\vec{R})}{\partial \vec{R}} \right|_{\vec{R}_{stationary}} = 0$$

- These geometries may be local minima, global minima, transition states or higher order saddle points
- How to check?
  - Build and diagonalize the "Hessian" matrix

$$\begin{pmatrix} \frac{\partial^2 E}{\partial R_1^2} & & \frac{\partial^2 E}{\partial R_1 \partial R_N} \\ & \ddots & \\ \frac{\partial^2 E}{\partial R_N \partial R_1} & & \frac{\partial^2 E}{\partial R_N^2} \end{pmatrix}$$

- Count negative eigenvalues
  - 0 → local minimum
  - 1 → saddle point
  - >1 → useless

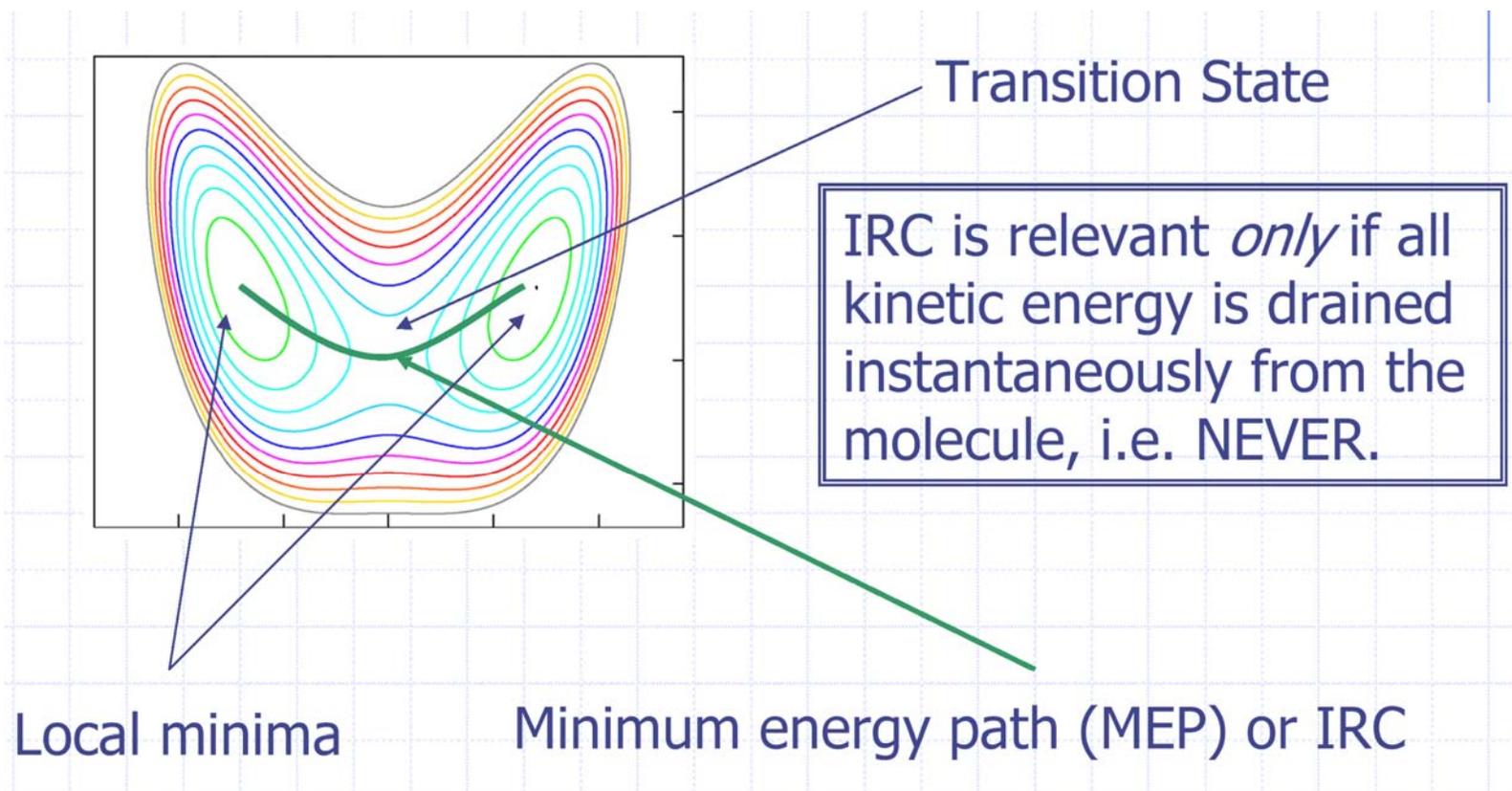
# Calculation of Harmonic Vibrational Frequencies

Harmonic vibrational frequencies can be calculated via the second derivative of the energy with respect to the atomic coordinates.

Important uses:

- Characterization of transition states
- Calculation of IR and Raman spectra

# Intrinsic Reaction Coordinate (IRC)



# Electron Density, HOMO and LUMO

- The electron density is the probability distribution of finding an electron at a specific point in space.
- The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are important tools to understand molecular reactivity.

# Population Analysis

- Population analysis methods partition the electron density between the nuclei so that each nucleus has a number of electrons associated with it.
- There is no quantum mechanical operator for the atomic charge and so any partitioning scheme must be arbitrary.
- Many methods have been devised, such as: Mulliken and Löwdin analysis, Bader's theory of atoms in molecules, natural population analysis
- Mulliken method: All the electron density ( $P_{\mu\mu}$ ) in an orbital is allocated to the atom on which  $\phi_{\mu}$  is located.
  - For each element  $\phi_{\mu}\phi_{\nu}$  of the density matrix, half of the density is assigned to the atom on which  $\phi_{\mu}$  is located and half to the atom on which  $\phi_{\nu}$  is located
  - The net charge on atom A is calculated by subtracting the number of electrons from the nuclear charge,  $Z_A$

$$q_A = Z_A - \sum_{\mu=1; \mu \text{ on A}}^K P_{\mu\mu} + \sum_{\mu=1; \mu \text{ on A}}^K \sum_{\nu=1; \nu \neq \mu}^K P_{\mu\nu} S_{\mu\nu}$$

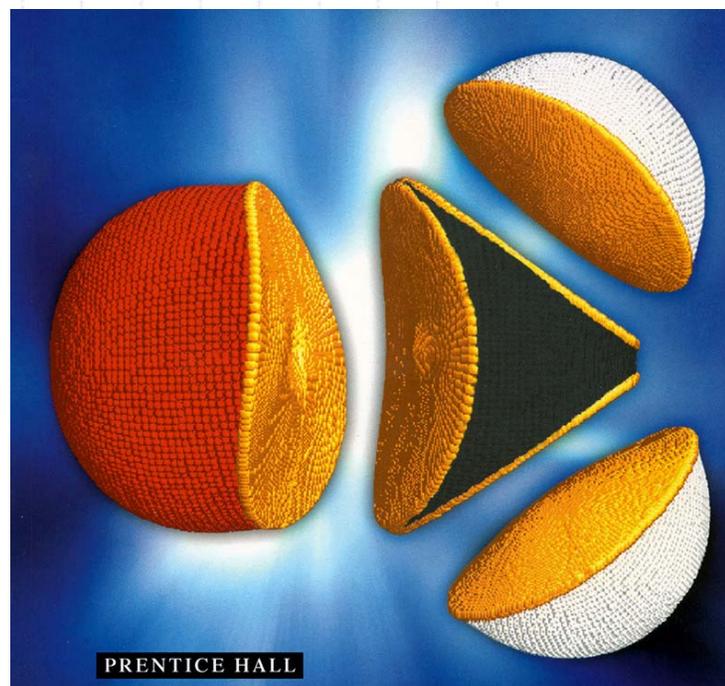
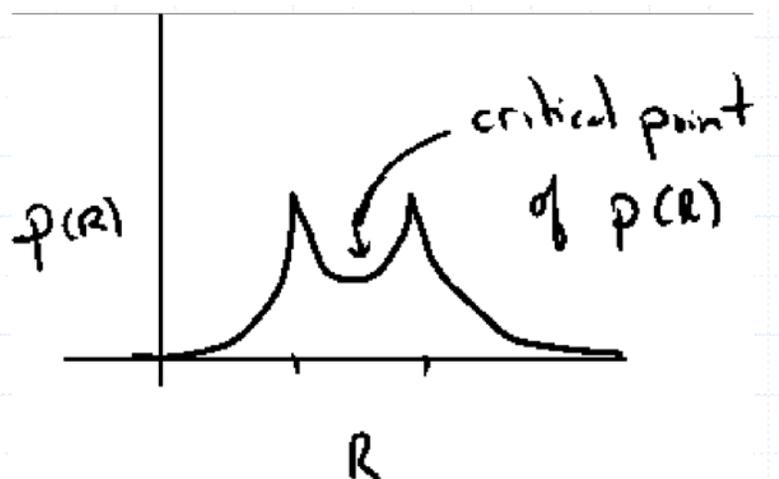
# Partial Atomic Charges

- ◆ “Atoms” are not well-defined in molecules – there is no quantum mechanical operator corresponding to an atom.
- ◆ This leads to ambiguity in the definition of an atomic charge
- ◆ Population Analysis Schemes
  - Basically, sum over all electrons using the basis functions of a given atom
  - Depends on the atom-centered nature of the basis set
  - Breaks down as the basis functions become more delocalized – results do not usually converge with increasing basis set!

# Atoms in Molecules

## ◆ Atoms-in-molecules

- Atoms are defined by “critical points” of the charge density
- More stable than Mulliken/Lowdin schemes with respect to basis set expansion
- Implemented in Gaussian
- Not clear whether stable=“correct”



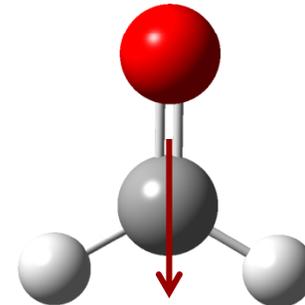
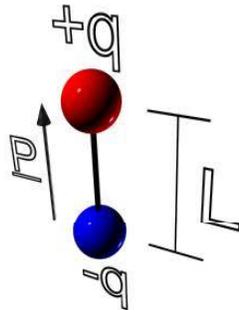
# Dipole Moment

- The electric multipoles reflect the distribution of charge in a molecule, i.e. it is a measure of the asymmetry in the molecular charge distribution
- The simplest electric moment is the dipole.
- The dipole moment of a distribution of charges  $q_i$  located at positions  $l_i$  is given by

$$\sum q_i l_i$$

- The dipole moment of a complex molecule can be represented approximately in the form of the vectorial sum of the moments belonging to the individual bonds.

$$p = ql$$



- The quadrupole is the next electric moment. A molecule has a non-zero electric quadrupole moment when there is a non-spherically symmetrical distribution of charge.

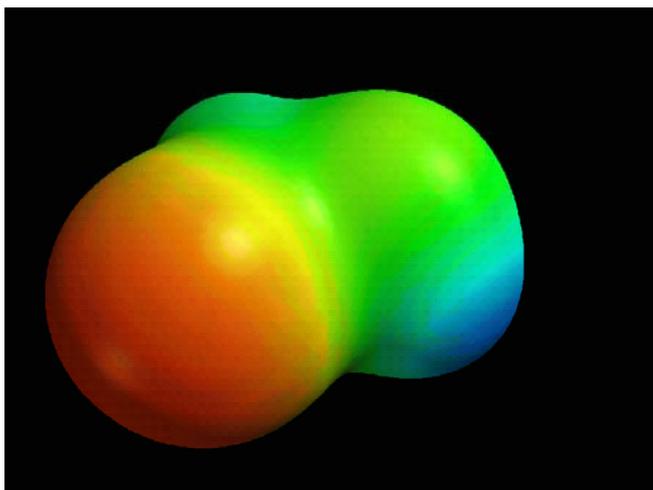
# Electrostatic Potential

- The electrostatic potential at point  $r$ ,  $\phi(r)$ , is defined as the work done to bring unit positive charge from infinity to the point.
- the electrostatic interaction energy between a point charge  $q$  located at  $r$  and the molecule equals  $q\phi(r)$
- The electrostatic potential  $V(r)$  that is produced at any point  $r$  by the electrons and nuclei (A) of the system is given by

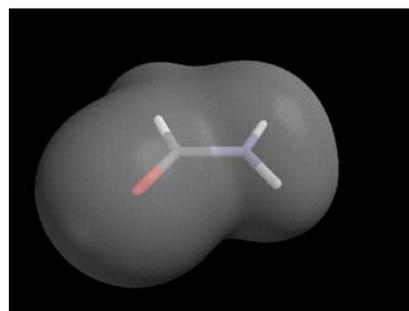
$$V(r) = \sum_A \frac{Z_A}{|r - R_A|} - \int \frac{dr' \rho(r')}{|r' - r|}$$

- The electrostatic potential is particularly useful for rationalising the interactions between molecules and molecular recognition processes. The electrostatic force is primarily responsible for long-range interactions between molecules.
- Electrostatic potential contours can be used to propose where electrophilic attack might occur; electrophiles are often attracted to regions where the electrostatic potential is most negative.

# Electrostatic Potential

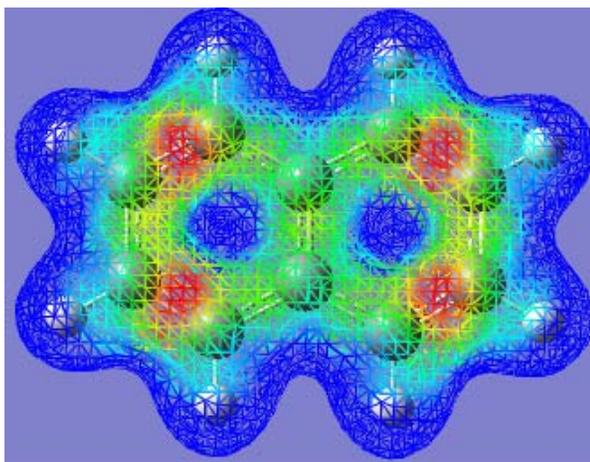


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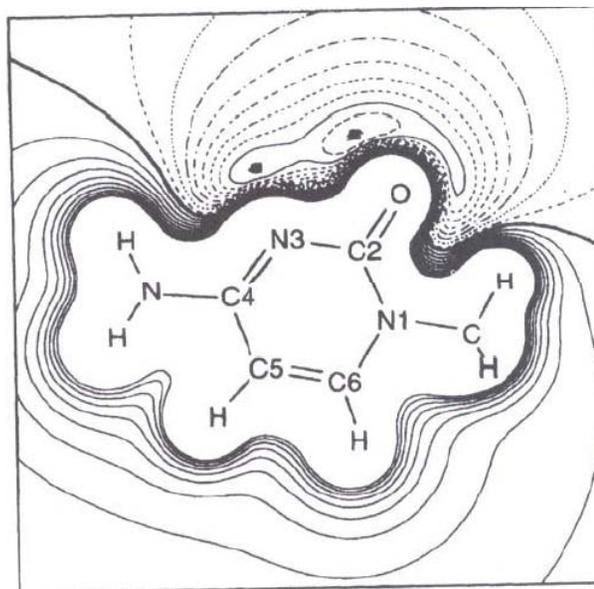


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Electrostatic potential mapped onto the electron density surface of formamide. Red indicates negative electrostatic potential and blue is positive potential.



Naphthalene MEP © Gaussian Inc.



Electrostatic potential contours around cytosine. Negative contours are dashed, the zero contour is bold. The minima near N3 and O are marked.

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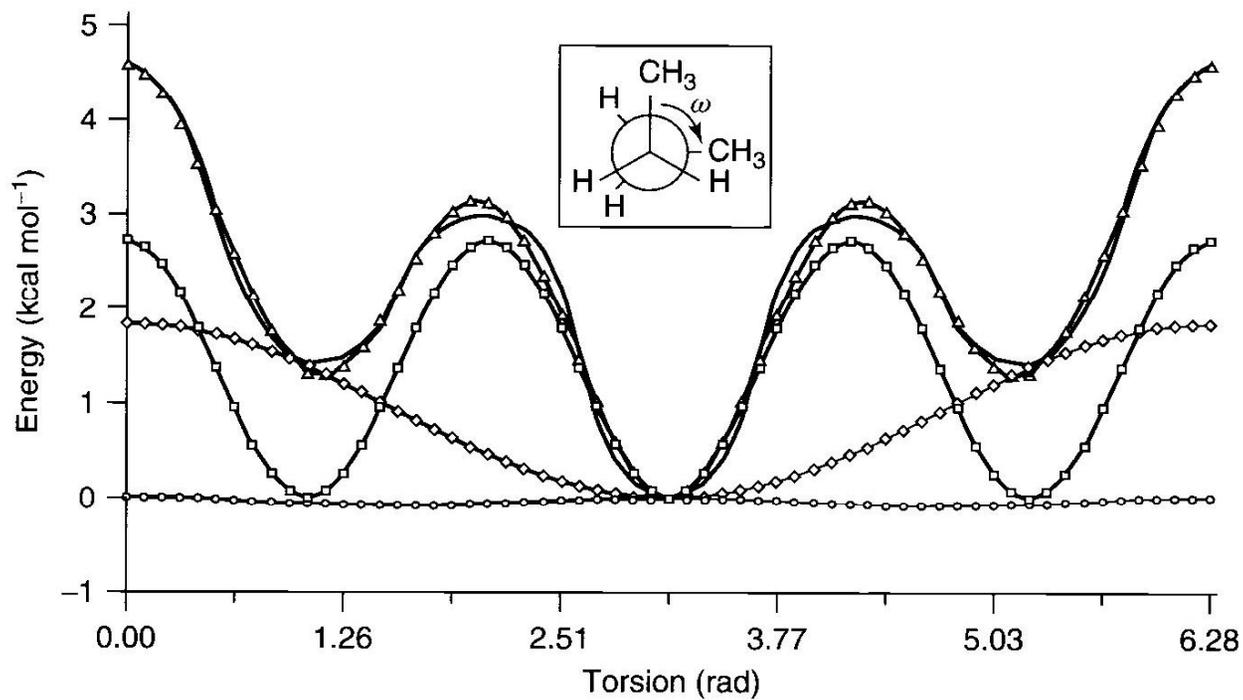
Questions: Calculating Molecular  
Properties?

Next: Parametrizing Potentials

# Force-Field Parameterization

- These parameters have to be chosen against some model of *reality*. Traditionally this is taken from experimental data. For other classes of molecules data is more scarce. Even when experimental data is available, some force field parameters can be hard to determine from it.
- Bond lengths and angles can be determined from crystallography. Van der Waals can be determined from crystal structures. **However, torsional potentials can be hard to determine, as are atomic charges.**
- Recently some force fields have been parameterized using data from electronic structure calculations. This allows the determination of force field parameters for molecules where little or no data exists.
- It also allows the **determination of parameters in a consistent fashion**. Whereas experimental data relevant to one set of parameters may be available in the gas phase, while that for another may be available for a solid, parameters from electronic structure calculations can all be found from the same phase (usually the gas phase). This can be important as there can be large differences in molecular structure in different phases.
- Full torsional potentials can be determined from electronic structure calculations. Partial atomic charges can also be found from calculations. However, there are several different methods to find charges, with little agreement between them.

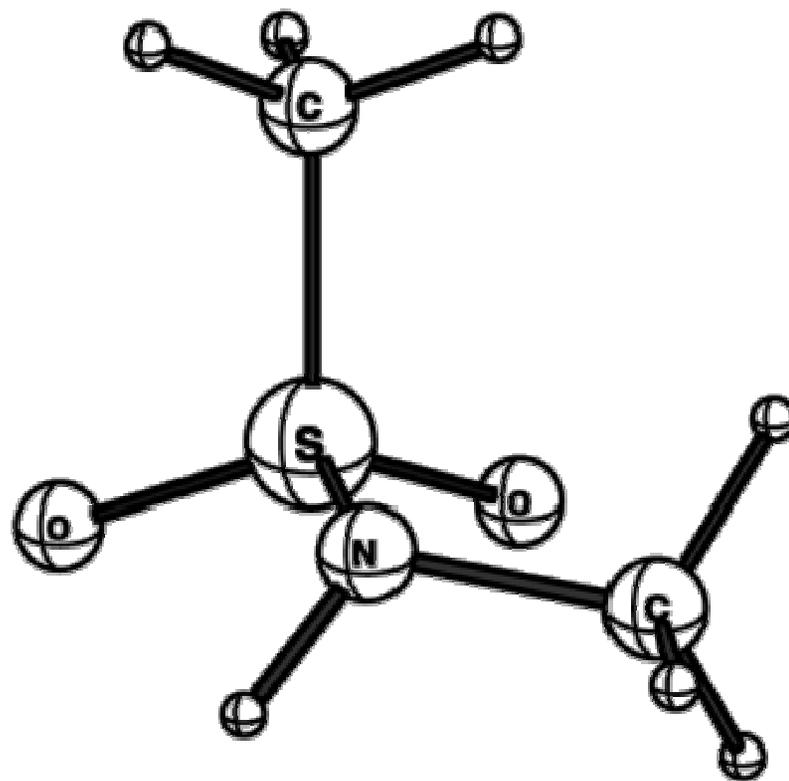
# Torsional Potential Terms



$$E_{\text{tors}} = \sum \{ V_i \cos[(\theta - \theta_0)] + V'_i \cos[2(\theta - \theta_0)] + V''_i \cos[3(\theta - \theta_0)] \}$$

# Di-Methyl-Sulfonamide (DMSA): A Case Study

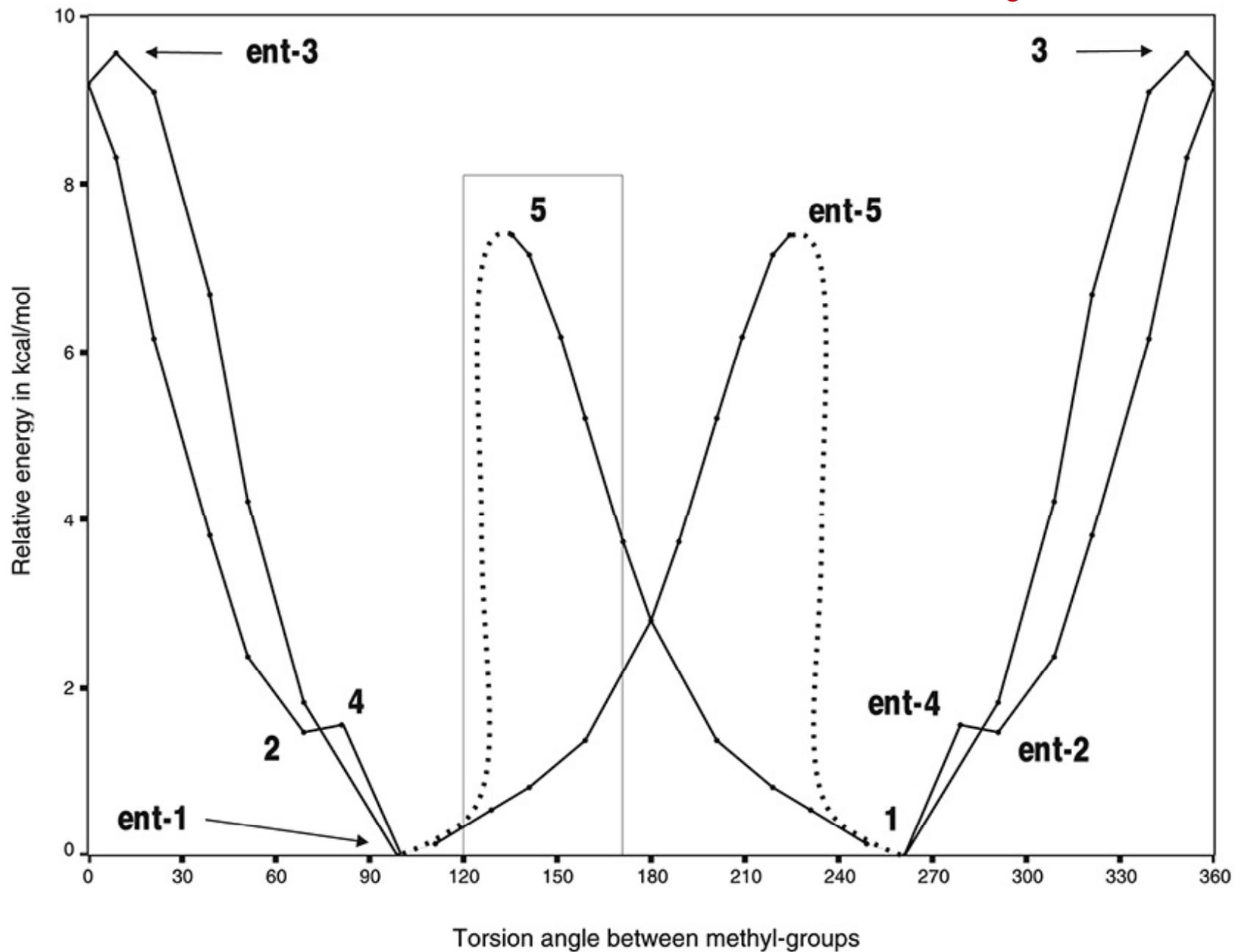
- Sulfonamides are important in medicine for treating infections
- A medical company needed force field parameters
- How do we proceed?

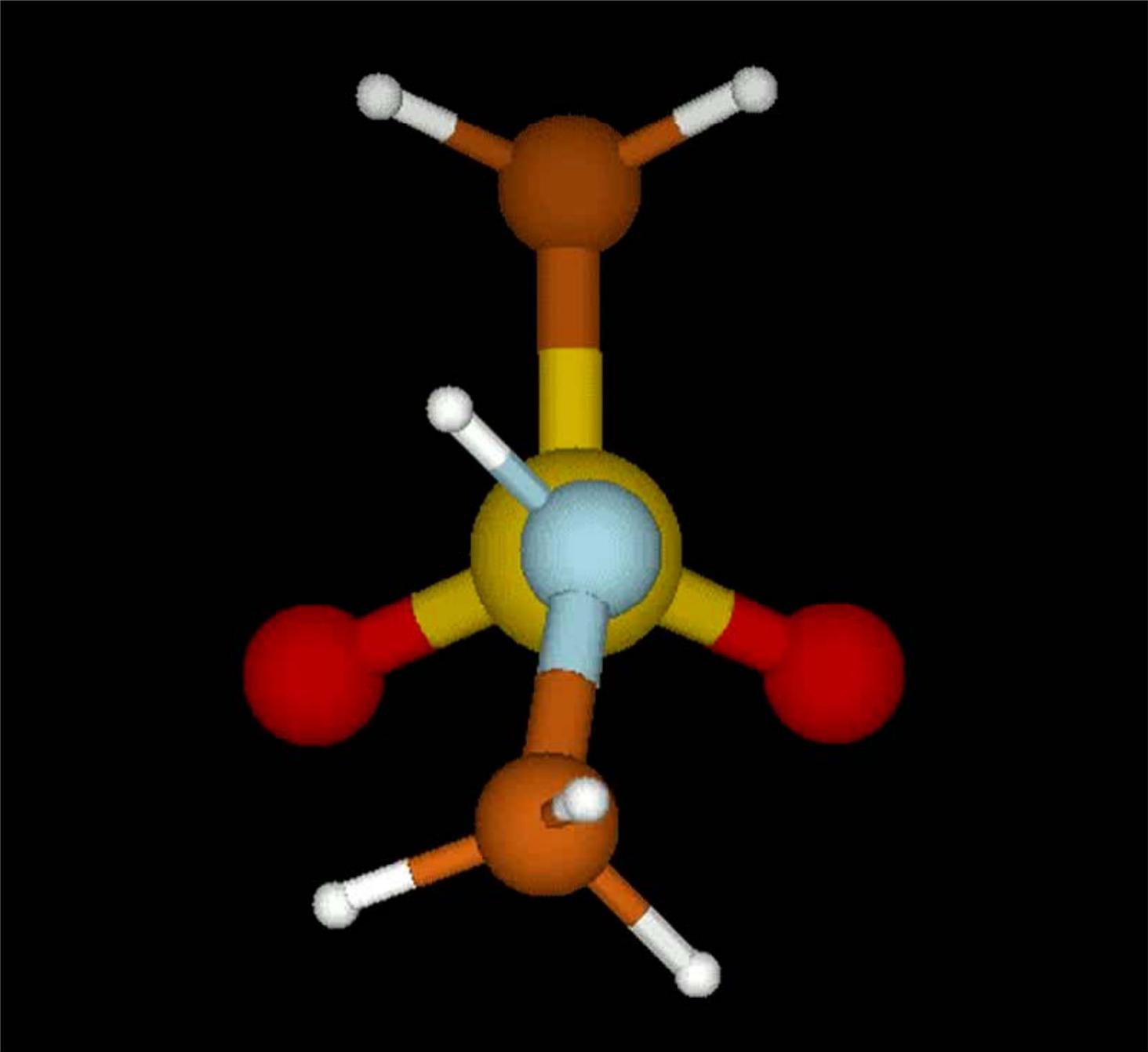


# DMSA: Computational Approach

1. Optimize the geometry
2. Scan the potential energy surface
3. Optimize transition states
4. Characterize transition states
5. Perform IRC run on transition states
6. Fit a torsional potential for use with the force field

# DMSA: The Full Story



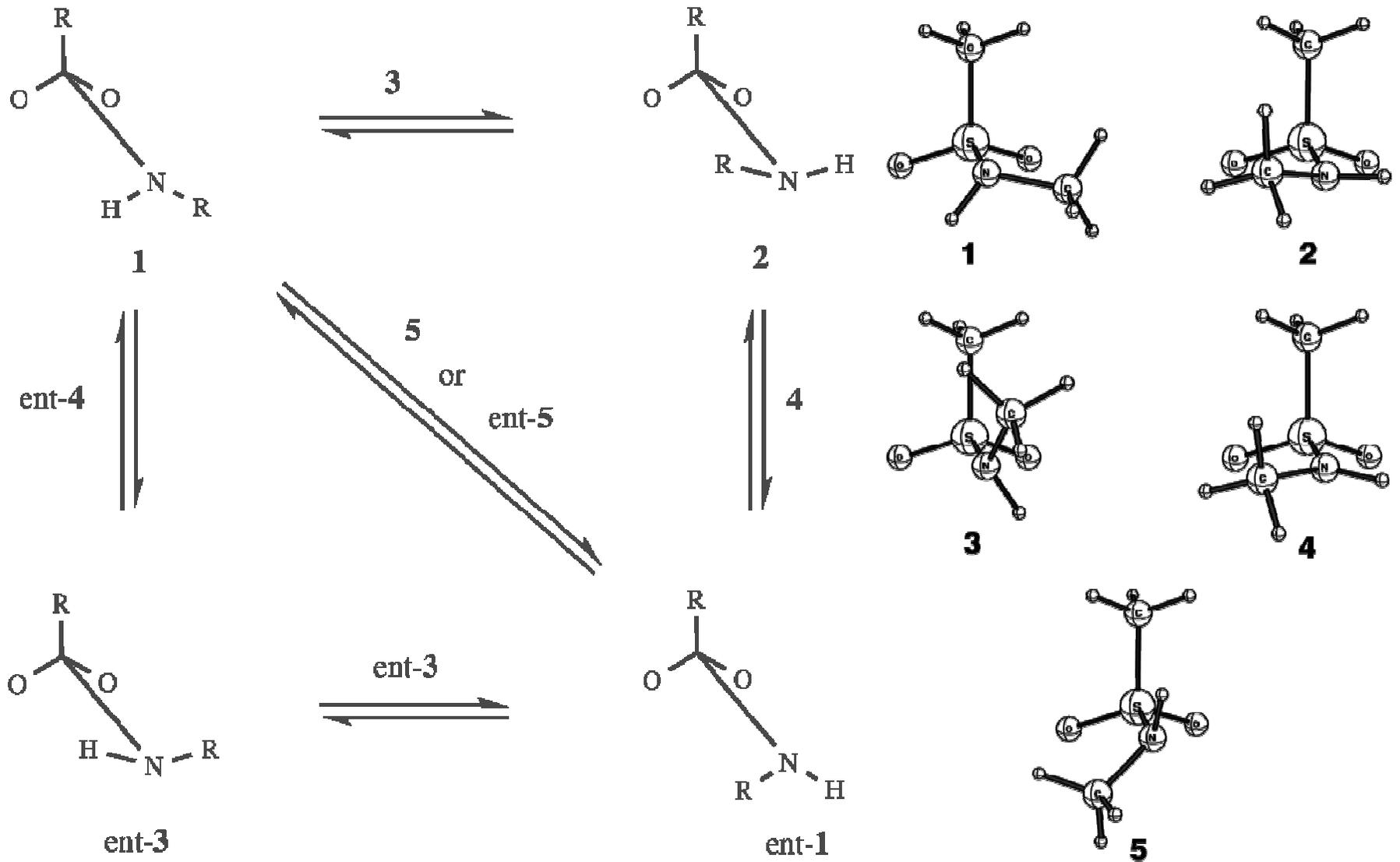


# DMSA: Comparison of Methods

	GS energy in HT's	$\Delta E$ of TS in $\frac{\text{kcal}}{\text{mol}}$	$\angle_{CN\text{SC},GS}$	$\angle_{CN\text{SC},TS}$	$\angle_{HN\text{SC},TS}$
HF/CEP-31G	not comp.	6.58	-104.62°	179.39°	-0.61°
HF/3-21G	-677.74974	15.94	-102.56°	170.40°	+1.22°
HF/6-31G*	-681.41657	7.39	-98.93°	135.63°	-4.69°
HF/6-311G**	-681.51363	7.41	-95.89°	136.68°	-4.06°
HF/6-311+G(2d,p)	-681.56260	7.41	-97.50°	133.86°	-2.66°
HF/6-311+G(2df,p)	-681.59221	7.16	-96.50°	139.45°	-3.70°
MP2/6-31G*	-682.34172	7.10	-98.23°	127.45°	-4.25°

J. Heyd, W. Thiel, and W. Weber, "Rotation and inversion barriers in N- methylmethanesulfonamide from ab initio calculations", *Theochem - J. Mol. Struc.* 391, 125 (1997)

# DMSA: The Full Story



# Resources and Further Reading

## WWW:

- Computational Chemistry List: <http://www.ccl.net>
- <http://educ.gaussian.com/visual/index.htm>

## Books:

- “Molecular Modeling-Principle and Application”, Andrew R. Leach, Chapter 2, 3
- “Exploring Chemistry with Electronic Structure Methods”, James B. Foresman, Eelen Frisch, Gaussian Inc.
- “Ab initio Molecular Orbital Theory”, W.J. Hehre, L. Radom, J.A. Pople, P.V.R. Schleyer
- “Combined Quantum Mechanical and Molecular Mechanical Methods”, J. Gao, M. A. Thompson (ed.), ACS Symposium Series no. 712, American Chemical Society, Washington 1998
- “Computer Modeling of Chemical Reactions in Enzymes and Solutions”, A. Warshel, John Wiley & Sons, New York 1991.
- “A Chemist’s Guide to Density Functional Theory”, W. Koch & M. C. Holthausen, WILEY-VCH, 2000.

## Papers:

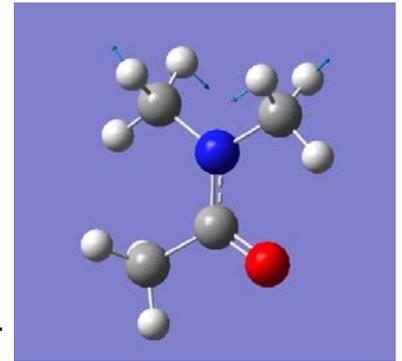
*Quantum Chemical Methods for Large Molecules*, Journal of Computational Chemistry, vol. 21, John Wiley & Sons, New York 2000

## Acknowledgements:

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- Alexander D. MacKerell Jr., University of Maryland at Baltimore
- Todd J. Martinez, University of Illinois at Urbana-Champaign
- G. Matthias Ullmann, Uni Heidelberg
- H. B. Schlegel, Wayne State University

# Additional Slides

# Calculation of Harmonic Vibrational Frequencies



The total energy of a molecule comprising  $N$  atoms near its equilibrium structure may be written as

$$E = T + V = \frac{1}{2} \sum_{i=1}^{3N} \dot{q}_i^2 + V_{\text{eq}} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{\text{eq}} q_i q_j. \quad (1)$$

Here, the mass-weighted cartesian displacements,  $q_i$ , are defined in terms of the locations  $x_i$  of the nuclei relative to their equilibrium positions  $x_{i,\text{eq}}$  and their masses  $M_i$ ,

$$q_i = M_i^{1/2} (x_i - x_{i,\text{eq}})$$

$V_{\text{eq}}$  is the potential energy at the equilibrium nuclear configuration, and the expansion (1) of the vibrational energy in terms of a power series is truncated at second order [16]. For such a system, the classical-mechanical equations of motion take the form

$$\ddot{q}_j = - \sum_{i=1}^{3N} f_{ij} q_i \quad j = 1, 2, \dots, 3N. \quad (2)$$

# Calculation of Harmonic Vibrational Frequencies

The  $f_{ij}$ , termed *quadratic force constants*, are the second derivatives of the potential energy with respect to mass-weighted cartesian displacements, evaluated at the equilibrium nuclear configuration, that is,

$$f_{ij} = \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right)_{\text{eq}}$$

The  $f_{ij}$  may be evaluated by numerical second differentiation,

$$\frac{\partial^2 V}{\partial q_i \partial q_j} \simeq \frac{\Delta(\Delta V)}{\Delta q_i \Delta q_j}$$

by numerical first differentiation of analytical first derivatives,

$$\frac{\partial^2 V}{\partial q_i \partial q_j} \simeq \frac{\Delta(\partial V / \partial q_j)}{\Delta q_i}$$

Equation (2) may be solved by standard methods [16] to yield a set of  $3N$  *normal-mode vibrational frequencies*. Six of these (five for linear molecules) will be zero as they correspond to translational and rotational (rather than vibrational) degrees of freedom.<sup>‡</sup>

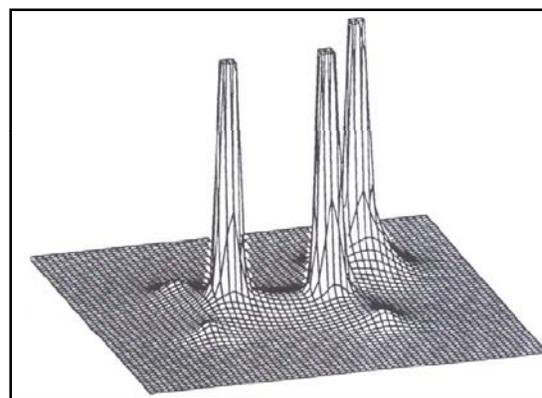
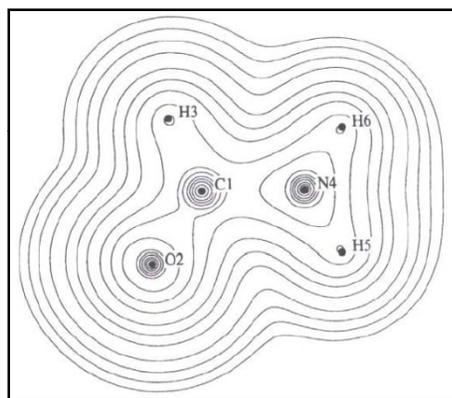
[16] E.B. Wilson, J.C. Decius, and P.C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.

# Total Electron Density Distribution

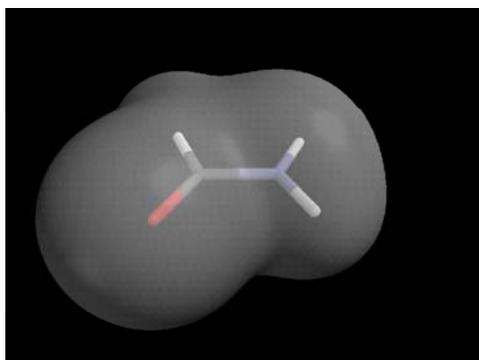
The integral of  $\rho(r)$  over all space equals the number of electrons in the system:

$$N = \int dr \rho(r) = \sum_{\mu=1}^K P_{\mu\mu} + 2 \sum_{\mu=1}^K \sum_{\nu=\mu+1}^K P_{\mu\nu} S_{\mu\nu}$$

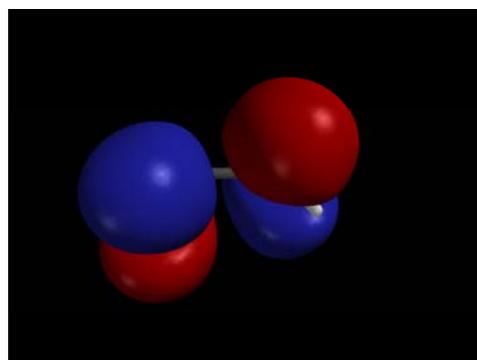
formamide



Isometric projection, height above the plane: magnitude of the electron density

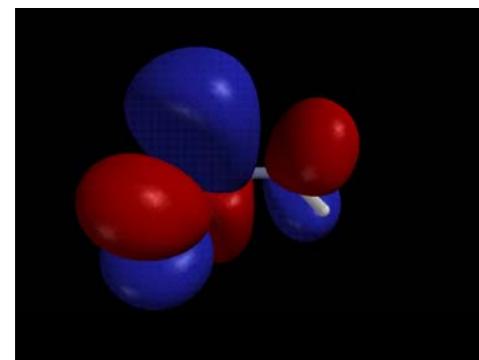


Surface, contour 0.0001 au



HOMO

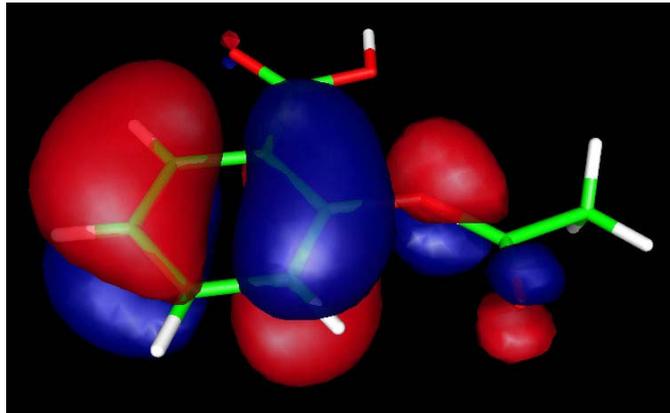
highest occupied molecular orbital



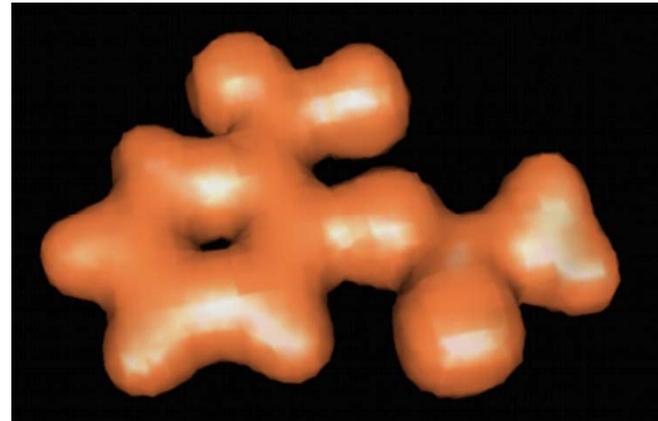
LUMO

lowest unoccupied molecular orbital

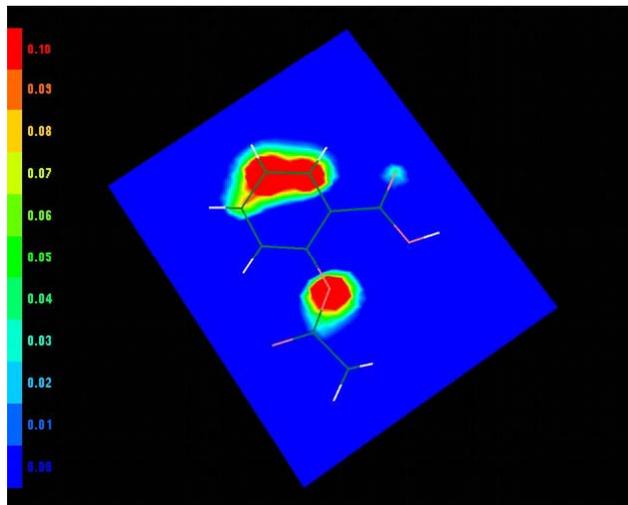
# Molecular Orbital & Electron Density



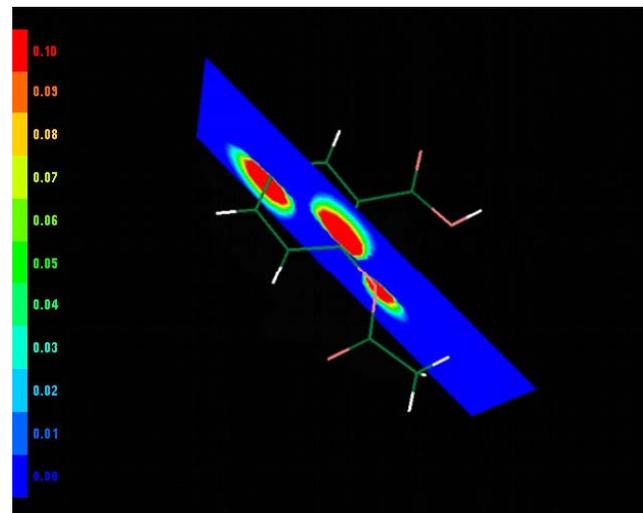
Molecule orbitals of aspirine



Electron density of aspirine



Cutplane at XY-plane of aspirine



Cutplane at XZ-plane of aspirine

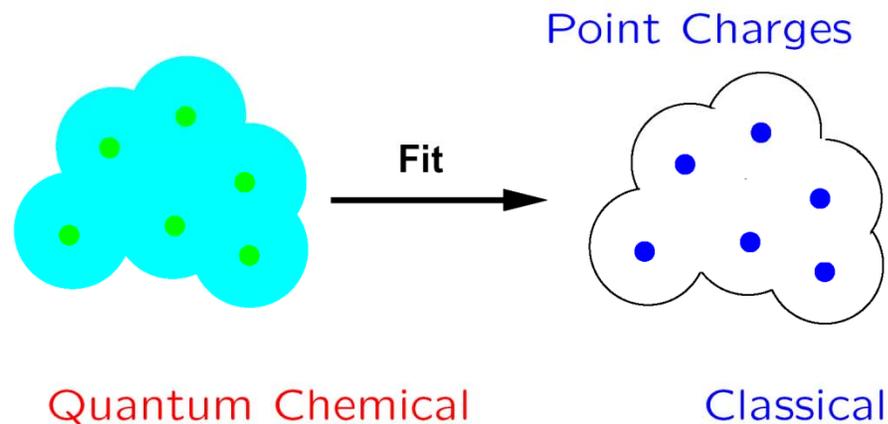
# Calculating Partial Atomic Charges

$$\phi_{\text{qm}}(\mathbf{r}) = \sum_{j=1}^{\text{Atoms}} \frac{Z_j}{|\mathbf{r} - \mathbf{R}_j|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

Nuclear  
Charges

Electron  
Density

$$\phi_{\text{classical}}(\mathbf{r}) = \sum_{j=1}^{\text{Atoms}} \frac{q_j}{|\mathbf{r} - \mathbf{R}_j|}$$



# Gaussian03(G03) - an *ab initio* Package

- Single Point Energy Calculation
- Geometry Optimization
- Frequency Calculation
- Chemical Reactions and Reactivity (TS, IRC, PES scan)
- Modeling Excited States
- Modeling Systems in Solution

# What Properties Can G03 Provide?

- Molecular orbital information
- Population analysis & atomic charges
- IR and Raman spectra
- NMR shielding tensors
- Multipole moments
- Electron affinities and ionization potentials
- Polarizabilities and hyperpolarizabilities

# G03 Basis Functions / Methods

<b>SCF methods</b>	<b>HF</b>	<b>Hartree-Fock</b>
	<b>CASSCF</b>	<b>Complete active space SCF</b>
<b>Post-SCF methods:</b>	<b>MP2,MP3,MP4</b>	<b>Møller-Plesset Pert. Theo.</b>
	<b>CI, QCISD</b>	<b>Configuration Interaction</b>
	<b>CCSD, QCISD</b>	<b>Couple cluster theory</b>
<b>DFT</b>	<b>BLYP, PW91</b>	<b>B3LYP, Backe-style 3-Parameter DFT (Lee-Yang-Parr correlation functional)</b>
<b>High Accuracy Energy</b>	<b>G1, G2, CBS-</b>	<b>Gaussian1, Gaussian2 Complete Basis Set Methods</b>
<b>Excited State</b>	<b>CIS</b>	
<b>Semi-empirical</b>	<b>CNDO, MINDO/3, AM1, PM3</b>	

# Input File Example

Method

Basis set

Key words

```
#HF/STO-3G opt  
[redacted]  
-- water opt --  
[redacted]  
0 1  
O  
H 1 r  
H 1 r 2 a }  
[redacted]  
r 0.99 }  
a 104.0 }  
[redacted]
```

Route section

Title section

Total charge &  
spin multiplicity

Molecule specifications

Variables

# Spin Multiplicity

The spin multiplicity  $M$  controls the spin state of your molecule.

<b>M</b>	<b>spin state</b>
1	singlet
2	doublet
3	triplet
4	quartet

→ No unpaired electrons (e.g. closed shell)

→ One unpaired electron

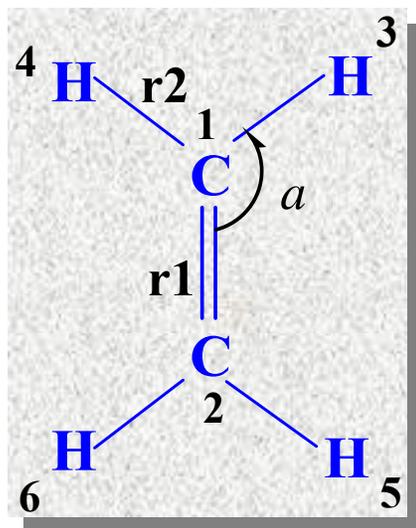
→ Two unpaired electrons of like spin

→ Three unpaired electrons of like spin

The spin multiplicity can be calculated from the quantum number  $S$  of the total spin or from the number  $n_u$  of unpaired electrons:

$$M = 2S + 1 = n_u + 1$$

# Internal Coordinates (Z-matrix)



**C**  
**1 C 1 r1**  
**2 H 1 r2 2 a**  
**3 H 1 r2 2 a 3 180.**  
**4 H 2 r2 1 a 3 0.**  
**5 H 2 r2 1 a 4 0.**  
**6**

**r1 1.31**  
**r2 1.07**  
**a 121.5**

Å, degree

# Population Analysis & Atomic Charge

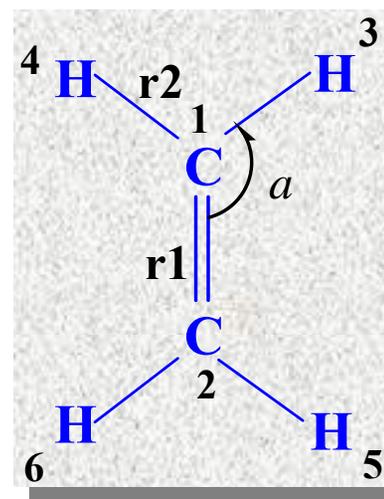
Condensed to atoms (all electrons):

	1	2	3	4	5	6
1 C	4.780096	0.612484	0.393153	0.393153	-0.025895	-0.025895
2 C	0.612484	4.780096	-0.025895	-0.025895	0.393153	0.393153
3 H	0.393153	-0.025895	0.596856	-0.024702	-0.005077	0.002118
4 H	0.393153	-0.025895	-0.024702	0.596856	0.002118	-0.005077
5 H	-0.025895	0.393153	-0.005077	0.002118	0.596856	-0.024702
6 H	-0.025895	0.393153	0.002118	-0.005077	-0.024702	0.596856

Total atomic charges:

	1
1 C	-0.127095
2 C	-0.127095
3 H	0.063548
4 H	0.063548
5 H	0.063548
6 H	0.063548

Sum of Mulliken charges= 0.00000



# Potential Energy Surface Scan

**#hf/6-31+g\* scan**

**--PES scan--**

**0 1**

**o**

**h 1 0.947**

**h 1 r 2 106.5**

**r 1.0 10 -0.01**

# Potential Energy Surface Scan

<b>N</b>	<b>r</b>	<b>SCF</b>
<b>1</b>	<b>1.0000</b>	<b>-76.01507</b>
<b>2</b>	<b>0.9900</b>	<b>-76.01595</b>
<b>3</b>	<b>0.9800</b>	<b>-76.01667</b>
<b>4</b>	<b>0.9700</b>	<b>-76.01722</b>
<b>5</b>	<b>0.9600</b>	<b>-76.01758</b>
<b>6</b>	<b>0.9500</b>	<b>-76.01774</b>
<b>7</b>	<b>0.9400</b>	<b>-76.01768</b>
<b>8</b>	<b>0.9300</b>	<b>-76.01739</b>
<b>9</b>	<b>0.9200</b>	<b>-76.01685</b>
<b>10</b>	<b>0.9100</b>	<b>-76.01605</b>
<b>11</b>	<b>0.9000</b>	<b>-76.01497</b>

