10.675 LECTURE 9

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1. TODAY

$\rightarrow$ Finish basis sets
$\rightarrow$ zeta basis set
$\rightarrow$ BSSE
$\rightarrow$ explanation of test of basis sets
$\rightarrow$ correlation (CI and MP)

2. BASIS SETS

Zeta $= (\frac{(2\zeta)^{n+1/2}}{[(2n)!]^{1/2}})r^{n-1}e^{\frac{-\zeta r}{a_o}}Y_l^n(\theta, \phi)$
Zeta's CC-PV*Z, AUC-CC-PV*Z
AUG $\rightarrow$ diffuse functions
* $\rightarrow$ variable... D double, T triple, Q quadruple, 5 quintuple.
double means use 2 gaussians to describe each set
p $\rightarrow$ polarization
cc $\rightarrow$ correlation consistent (electrons optimized) to reproduce atoms energies
(CISD).

3. BASIS SET SUPERPOSITION ERROR - BSSE

"localized" LCAO
2 atoms A and B... Individually, they are an incomplete system (which we will
say is a combination of the two).
incompleteness if compensated in the molecule due to the other molecule. The
isolated incomplete basis sets complete/help each other.
The problem: Bond energy over predicted due to change in completeness from A
+B $\rightarrow$ AB independent of method.
Basis Set Limit: extrapolation to the max # of basis sets to still minimize energy.
Solution, use both incomplete orbitals on each atom (named Counter Poise
Correction).
Include the basis function, but no nuclei of the other molecule. This
overcompensates arbitrarily.
Try bigger basis sets to confirm if "average" is 1/2

4. CORRELATION

- Correction beyond mean field approximation
- exchange is a correction to the mean field
- HF exchange
- HF correlation

Date: Fall 2004.

- Non-relativistic

5. HF Approximations

1 - No correlation
2- BO approximation
3 - Incomplete Basis Set
4- Non Relativistic

6. Correlation II

$E^{corr} = \epsilon_o - E^{HF}$ $\epsilon_o =$ exact non-relativistic energy of the system $E^{HF} =$ Hartree-Fock energy in the basis set limit $E^{corr} =$ is essentially the correlation or "error" of the hartree-fock energy.

7. Experimental Comparisons

$\rightarrow$HF generally overestimates the vibrational frequencies by 10% - heuristic rule.
We can correct via scale factor, which is typically set to 0.84.
HF geometries are generally pretty good to within 0.01 Å
HF typically not very good with bond energies.

Molecule	pieces		$6-31G**$	Experimental
$H_3C - CH_3$	H_3C .	$.CH_3$	69	97
$HO - OH$	OH .	$.OH$	0	55
F_2	F .	$.F$	-33	38

Lack of correlation is killing HF
Dipole moments are often incorrect
Some molecules will not bond when they should.

8. Correction

Configuration Interaction (CI)
$\{\phi_i(x)\}$ complete set basis functions then any function $\Phi(x_i)$ described by
$\sum_i a_i \phi_i(x_i)$ coefficients.
What about $\Phi(x_1, x_2) = \sum_i a_i(x_2)\phi_i(x_i)$
$= \sum_i \sum_j b_{ij}\phi_j(x_2)\phi_i(x_1)$
Φ must have proper antisymmetric behavior $\Phi(x_1, x_2) = -\Phi(x_2, x_1)$
$b_{ij} = -b_{ji}$
$\Phi(x_1, x_2) = \sum_i \sum_j b_{ij}\phi_i(x_1)\phi_j(x_2) - \phi_j(x_1)\phi_i(x_2)$
Can expand $\Phi(x_1, x_2)$ in terms of determinants formed from a complete set of 1-variable functions.
New variational problem, find the coefficients. If the basis set is complete, then the lowest eigenvalue of Φ is the exact non-relativistic solution.
CI is extremely costly.

9. Perturbation Theory

$H\Phi_i = (H_o + V)\Phi_i = \epsilon_i\Phi_i$
Where V is the perturbation or "correction" to the HF hamiltonian $V \rightarrow \lambda V$
$V = \sum_i^N \sum_{i<k}^N \frac{1}{r_{ij}} \sum_i (j_i - k_i)$
We know that $H_o\Phi_i = E_i^o\Psi_i^o$

Now we perform a Taylor Series expansion.

$\epsilon_i = E_i^o + \lambda E_i^1 + \lambda^2 E_i^2 + ...$

$\Phi_i = \Phi_i^o + \lambda \Phi_i^1 + \lambda^2 \Phi_i^2$

Plugin and solve.

$\Phi = c_o \Phi_o + \sum_{r_a} c_a^r \Phi_a^r + \sum_{a<b,r<s} c_{ab}^{rs} \Phi_{ab}^{rs} + ...$

Which are the ground, singlet, and doublet states...

$(H + \lambda V)(\Psi_i^o + \lambda^1 \Psi_i^1 + \lambda^2 \Psi_i^2) = (E_o^i + \lambda E_i^1 + \lambda^2 E_i^2)(\Psi_i^o + \lambda \Psi_i^1 ...)$

equate coefficients of λ

$\lambda = 0 \quad H_o \Psi_i^o = E_i^o \Psi_i^o$

$\lambda = 1 \quad H_o \Psi_i^1 + V \Psi_i^o = E_i^o \Psi_i^1 + E_i^1 \Psi_i^o$

$\lambda = 2 \quad H_o \Psi_i^2 + V \Psi_i^1 = E_i^o \Psi_i^2 + E_i^1 \Psi_i^1 + E_i^2 \Psi_i^o$