

CHAPTER 9
AB INITIO AND DENSITY FUNCTIONAL METHODS
OUTLINE

Homework Questions Attached

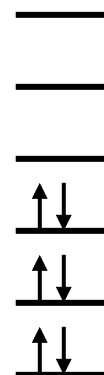
SECT	TOPIC
-------------	--------------

- | | |
|----|--|
| 1. | Atomic Orbitals (Slater Type Orbitals: STOs) |
| 2. | Basis Sets |
| 3. | LCAO-MO-SCF Theory for Molecules |
| 4. | Examples: Hartree-Fock Calculations on H ₂ O and CH ₂ =CH ₂ |
| 5. | Post Hartree-Fock Treatment of Electron Correlation |
| 6. | Density Functional Theory |
| 7. | Computational Times |
| 8. | Some Applications of Quantum Chemistry |

Chapter 9 Homework

1. Qualitative Questions (see PowerPoint slides and class notes for answers)
 - (a) Why are STOs simulated by fixed combinations of GTOs in most basis sets?
 - (b) What is the purpose of adding polarization functions to atoms in quantum mechanical calculations?
 - (c) What is the purpose of adding diffuse functions to atoms in quantum mechanical calculations?
 - (d) What is the difference between a “Double Zeta” basis set and a “Doubly Split Valence” basis set?
 - (e) Explain why the Coulomb ($J_{\mu\nu}$) and Exchange ($K_{\mu\nu}$) integrals are described as “two-electron four-center” integrals. Why is it difficult to evaluate these integrals using STOs? What is usually done to overcome this difficulty.
 - (f) Why is the Hartree-Fock method called a “Self-Consistent Field (SCF)” method?
 - (g) What is the correlation energy? Why don't the energies calculated by the Hartree-Fock method include the correlation energy?
 - (h) What are the three methods commonly used to perform correlation energy corrections to the Hartree-Fock energies?
 - (i) Consider the CCSD(T) method to correct the Hartree-Fock energy for electron correlation. What does each letter signify?
 - (j) In Density Functional Theory (DFT), what are gradient corrected exchange-correlation functionals?
 - (k) In Density Functional Theory (DFT), what are hybrid exchange-correlation functionals?
 - (l) Are bond lengths of second row atoms computed at the HF/6-31G(d) level generally too long or too short? Explain your answer.
 - (m) What does it mean if it is stated that a quantum mechanical energy is computed at the MP4/6-311G(d,p) // HF/6-31G(d) level? Why is this an acceptable procedure?
 - (n) What is/are the purpose(s) of the 0.95 scale factor in MP2/6-31G(d) vibrational frequencies.
 - (o) What is/are the purpose(s) of the 0.90 scale factor in HF/6-31G(d) vibrational frequencies.
 - (p) What are the 3 corrections that must be added to the computed quantum mechanical energy of a molecule to obtain the enthalpy of the molecule.
 - (q) If a computed enthalpy of a reaction, ΔH^0 , is too **high** (i.e. the error is positive), would you expect the calculated equilibrium constant of the reaction to be too **high** or too **low**?

- (r) If a nucleophilic addition to an unsaturated molecule is **orbitally** controlled, what would you look at to predict the site of attack?
- (s) If a nucleophilic addition to an unsaturated molecule is **charge** controlled, what would you look at to predict the site of attack?
2. (a) The STO-3G basis set is a minimal basis set. Describe the Slater Type Orbitals on each atom in PH_2F using the STO-3G basis.
- (b) How many Molecular Orbitals will be formed in PH_2F using the STO-3G basis set? How many will be occupied orbitals and how many will be unoccupied orbitals?
- (c) What do the 3, 2 and 1 in the 3-21G basis set represent?
- (d) Describe the Slater Type Orbitals on each atom in PH_3 using the 6-31G(2d,p) basis set.
- (e) Describe the Slater Type Orbitals on each atom in PH_3 using the 6-311++G basis set.
3. The diagram at the right a Molecular Orbital diagram containing three occupied and three unoccupied orbitals.
- (a) Show a singly excited electron configuration.
- (b) Show a doubly excited electron configuration.
- (c) Show a triply excited electron configuration.
- (d) What does CISD stand for? Which of the above configurations would be used in CISD?



4. Consider the chemical equilibrium: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) = 2 \text{NH}_3(\text{g})$

The data in the table below represent the electronic energies (and correction terms), in a.u. and the entropies, in J/mol-K, of N_2 , H_2 and NH_3 computed at 400 °C (673 K) at the QCISD(T)/6-311++G(3df,2pd)//HF/6-31G(d) level.

Molecule	E_{el}	$E_{\text{ZPE(vib)}}$	E_{therm}	PV (=RT)	S^0
	a.u.	a.u.	a.u.	a.u.	J/mol-K
N_2	-109.372	0.006	0.005	0.002	215.1
H_2	-1.171	0.009	0.005	0.002	153.7
NH_3	-56.471	0.033	0.007	0.002	233.3

Use the data in this table to calculate the following:

- (a) The entropy change for this reaction, ΔS^0 , in kJ/mol, at 400 °C.
- (b) The enthalpy change for this reaction, ΔH^0 , in J/mol-K, at 400 °C
- (c) The equilibrium constant, K_{eq} , for this reaction, at 400 °C

Chapter 9

***Ab Initio* and Density Functional Methods**

Slide 1

Outline

- **Atomic Orbitals (Slater Type Orbitals: STOs)**
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
- Post Hartree-Fock Treatment of Electron Correlation
- Density Functional Theory
- Computation Times
- Some Applications of Quantum Chemistry

Slide 2

Atomic Orbitals: Slater Type Orbitals (STOs)

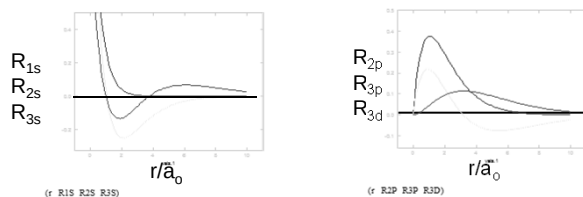
When performing quantum mechanical calculations on molecules, it is usually assumed that the Molecular Orbitals are a Linear Combination of Atomic Orbitals (LCAO).

The most commonly used atomic orbitals are called Slater Type Orbitals (STOs).

Hydrogen atomic orbitals

$$\psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \cdot Y_{lm}(\theta, \varphi)$$

The radial function, $R_{nl}(r)$ has a complex nodal structure, dependent upon the values of n and l .



Slide 3

Slater Type Orbitals

The radial portion of the wavefunction is replaced by a simpler function

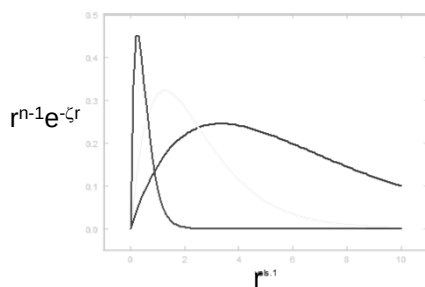
of the form: $r^{n-1}e^{-\zeta r/na_0}$ or $r^{n-1}e^{-\zeta r/n}$

SI

AU

$$S_{nlm}(r, \theta, \varphi) = N r^{n-1} e^{-\zeta r} \cdot Y_{lm}(\theta, \varphi)$$

The value of ζ ("zeta") determines how far from the nucleus the orbital extends.



(r R1 R2 R3)

Slide 4

The Problem with STOs

$$S_{nlm}(r, \theta, \varphi) = N r^{n-1} e^{-\zeta r} \cdot Y_{lm}(\theta, \varphi)$$

Slater Type Orbitals represent the radial distribution of electron density very well.

In molecules, one often has to evaluate numerical integrals of the product of 4 different STOs on 4 different nuclei (aka four centered integrals).

This is very time consuming for STOs.

Gaussian Type Orbitals (GTOs)

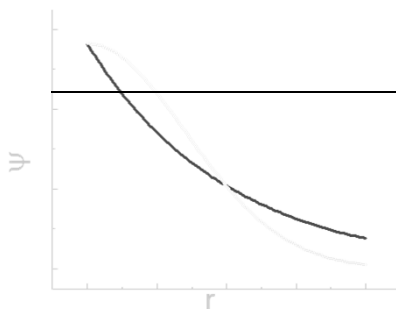
The integrals can be evaluated MUCH more quickly for “Gaussian” functions (aka Gaussian Type Orbitals, GTOs):

$$G(r, \theta, \varphi) = N x^a y^b z^c e^{-\alpha r^2} \cdot Y_{lm}(\theta, \varphi)$$

The problem is that GTOs do not represent the radial dependence of the electron density well at all.

Slide 5

GTO vs. STO representation of 1s orbital



$$1s \text{ STO: } S_{1s} = A e^{-\zeta r}$$

An electron in an atom or molecule is best represented by an STO. However, multicenter integrals involving STOs are very time consuming.

$$1s \text{ GTO: } G_{1s} = A e^{-\alpha r^2}$$

It is much faster to evaluate multicenter integrals involving GTOs. However, a GTO does not do a good job representing the electron density in an atom or molecule.

Slide 6

The Problem

Multicenter integrals of GTOs can be evaluated very efficiently, but STOs are much better representations of the electron density.

The Solution

One fits a fixed sum of GTOs (usually called Gaussian “primitive” functions) to replicate an STO.

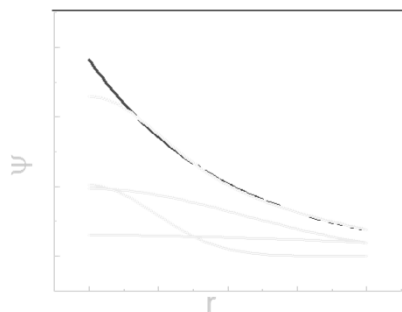
$$S(r, \theta, \varphi) \approx \sum a_i G_i(r, \theta, \varphi)$$

e.g. An STO may be approximated as a sum of 3 GTOs

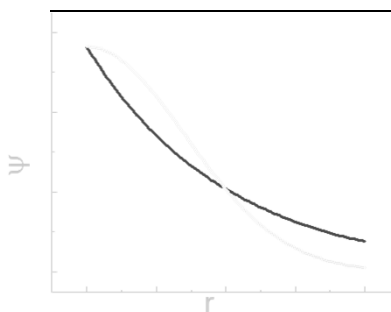
$$S(r, \theta, \varphi) \approx a_1 G_1(r, \theta, \varphi) + a_2 G_2(r, \theta, \varphi) + a_3 G_3(r, \theta, \varphi)$$

It requires more GTOs to replicate an STO with large ζ (close to nucleus) than one with a smaller ζ (further from nucleus)

Slide 7



An STO approximated as the sum of 3 GTOs



An STO approximated by a single GTO

Generally, more GTOs are required to approximate an STO for inner shell (core) electrons, which are close to the nucleus, and therefore have a large value of ζ .

Slide 8

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- **Basis Sets**
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H₂O and CH₂=CH₂
- Post Hartree-Fock Treatment of Electron Correlation
- Density Functional Theory
- Computation Times
- Some Applications of Quantum Chemistry

Slide 9

Basis Sets

Within the Linear Combination of Atomic Orbital (LCAO) framework, a Molecular Orbital (ϕ_i) is taken to be a linear combination of "basis functions" (χ_j), which are usually STOs (composed of sums of GTOs).

$$\phi_i = \sum_j c_{ij} \chi_j = c_{i1} \chi_1 + c_{i2} \chi_2 + c_{i3} \chi_3 + \dots$$

The number and type of basis functions (χ_j) used to describe the electrons on each atom is determined by the "Basis Set".

There are various levels of basis sets, depending upon how many basis functions are used to characterize a given electron in an atom in the molecule.

Slide 10

Minimal Basis Sets

A minimal basis set contains the minimum number of STOs necessary to contain the electrons in an atom.

First Row (e.g. H): $\chi_{1s_H}(\zeta_{1s_H})$

Second Row (e.g. C): $\chi_{1s_C}(\zeta_{1s_C})$
 $\chi_{2s_C}(\zeta_{2s_C})$
 $\chi_{2px_C}(\zeta_{2p_C}), \chi_{2py_C}(\zeta_{2p_C}), \chi_{2pz_C}(\zeta_{2p_C})$

Third Row (e.g. P): $\chi_{1s_P}(\zeta_{1s_P})$
 $\chi_{2s_P}(\zeta_{2s_P})$
 $\chi_{2px_P}(\zeta_{2p_P}), \chi_{2py_P}(\zeta_{2p_P}), \chi_{2pz_P}(\zeta_{2p_P})$
 $\chi_{3s_P}(\zeta_{3s_P})$
 $\chi_{3px_P}(\zeta_{3p_P}), \chi_{3py_P}(\zeta_{3p_P}), \chi_{3pz_P}(\zeta_{3p_P})$

Slide 11

The STO-3G Basis Set

This is the simplest of a large series of "Pople" basis sets.

It is a minimal basis set in which each STO is approximated by a fixed combination of 3 GTOs.

How many STOs are in the STO-3G Basis for CH_3Cl ?

H: 3x1 STO

C: 5 STOs

Cl: 9 STOs

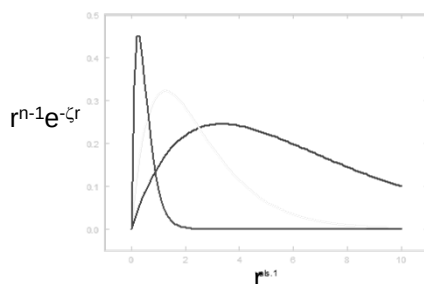
Total: 17 STOs

Slide 12

Double Zeta Basis Sets

A single STO (with a single value of ζ) to characterize the electron in an atomic orbital lacks the versatility to describe various different types of bonding.

One can gain versatility by using two (or more) STOs with different values of ζ for each atomic orbital. The STO with a large ζ can describe electron density close to the nucleus. The STO with a small ζ can describe electron density further from the nucleus.



Large ζ
Intermediate ζ
Small ζ

Slide 13

First Row (e.g. H): $\chi_{1s_H}^a(\zeta_{1s_H}^a)$ $\chi_{1s_H}^b(\zeta_{1s_H}^b)$

Second Row (e.g. C): $\chi_{1s_C}^a(\zeta_{1s_C}^a)$ $\chi_{1s_C}^b(\zeta_{1s_C}^b)$
 $\chi_{2s_C}^a(\zeta_{2s_C}^a)$ $\chi_{2s_C}^b(\zeta_{2s_C}^b)$
 $\chi_{2px_C}^a(\zeta_{2p_C}^a)$, $\chi_{2py_C}^a(\zeta_{2p_C}^a)$, $\chi_{2pz_C}^a(\zeta_{2p_C}^a)$
 $\chi_{2px_C}^b(\zeta_{2p_C}^b)$, $\chi_{2py_C}^b(\zeta_{2p_C}^b)$, $\chi_{2pz_C}^b(\zeta_{2p_C}^b)$

Third Row (e.g. P): $\chi_{1s_P}^a(\zeta_{1s_P}^a)$ $\chi_{1s_P}^b(\zeta_{1s_P}^b)$
 $\chi_{2s_P}^a(\zeta_{2s_P}^a)$ $\chi_{2s_P}^b(\zeta_{2s_P}^b)$
 $\chi_{2px_P}^a(\zeta_{2p_P}^a)$, $\chi_{2py_P}^a(\zeta_{2p_P}^a)$, $\chi_{2pz_P}^a(\zeta_{2p_P}^a)$
 $\chi_{2px_P}^b(\zeta_{2p_P}^b)$, $\chi_{2py_P}^b(\zeta_{2p_P}^b)$, $\chi_{2pz_P}^b(\zeta_{2p_P}^b)$
 $\chi_{3s_P}^a(\zeta_{3s_P}^a)$ $\chi_{3s_P}^b(\zeta_{3s_P}^b)$
 $\chi_{3px_P}^a(\zeta_{3p_P}^a)$, $\chi_{3py_P}^a(\zeta_{3p_P}^a)$, $\chi_{3pz_P}^a(\zeta_{3p_P}^a)$
 $\chi_{3px_P}^b(\zeta_{3p_P}^b)$, $\chi_{3py_P}^b(\zeta_{3p_P}^b)$, $\chi_{3pz_P}^b(\zeta_{3p_P}^b)$

Slide 14

Split Valence Basis Sets

Inner shell (core) electrons don't participate significantly in bonding.

Therefore, a common variation of the multiple zeta basis sets is to use two (or more) different STOs only in the valence shell, and a single STO for core electrons.

STO-6-31G (aka 6-31G)

This is a "Pople" doubly split valence (DZV – for double zeta in the valence shell).

6-31G

Core electrons are characterized by a single STO, composed of a fixed combination of 6 GTOs.

Two STOs with different values of ζ are used for valence:

The "inner" STO (higher ζ) is composed of 3 GTOs.

The "outer" STO (lower ζ) is composed of a single GTO.

Slide 15

STO-6-31G (aka 6-31G)

First Row (e.g. H): $\chi_{1s_H}^a(\zeta_{1s_H}^a)$ $\chi_{1s_H}^b(\zeta_{1s_H}^b)$

Second Row (e.g. C): $\chi_{1s_C}^a(\zeta_{1s_C}^a)$
 $\chi_{2s_C}^a(\zeta_{2s_C}^a)$ $\chi_{2s_C}^b(\zeta_{2s_C}^b)$
 $\chi_{2p_{x_C}}^a(\zeta_{2p_C}^a)$, $\chi_{2p_{y_C}}^a(\zeta_{2p_C}^a)$, $\chi_{2p_{z_C}}^a(\zeta_{2p_C}^a)$
 $\chi_{2p_{x_C}}^b(\zeta_{2p_C}^b)$, $\chi_{2p_{y_C}}^b(\zeta_{2p_C}^b)$, $\chi_{2p_{z_C}}^b(\zeta_{2p_C}^b)$

Third Row (e.g. P): $\chi_{1s_P}^a(\zeta_{1s_P}^a)$
 $\chi_{2s_P}^a(\zeta_{2s_P}^a)$
 $\chi_{2p_{x_P}}^a(\zeta_{2p_P}^a)$, $\chi_{2p_{y_P}}^a(\zeta_{2p_P}^a)$, $\chi_{2p_{z_P}}^a(\zeta_{2p_P}^a)$
 $\chi_{3s_P}^a(\zeta_{3s_P}^a)$ $\chi_{3s_P}^b(\zeta_{3s_P}^b)$
 $\chi_{3p_{x_P}}^a(\zeta_{3p_P}^a)$, $\chi_{3p_{y_P}}^a(\zeta_{3p_P}^a)$, $\chi_{3p_{z_P}}^a(\zeta_{3p_P}^a)$
 $\chi_{3p_{x_P}}^b(\zeta_{3p_P}^b)$, $\chi_{3p_{y_P}}^b(\zeta_{3p_P}^b)$, $\chi_{3p_{z_P}}^b(\zeta_{3p_P}^b)$

Slide 16

The Advantage of Doubly Split Valence or Double Zeta Basis Sets

Consider a carbon atom in the following molecules or ions:

CH_4 , CH_3^+ , CH_3^- , CH_3F etc.

$$\begin{aligned}\varphi_{MO} = & c_1 \chi_{1s_C}^a (\zeta_{1s_C}^a) \\ & + c_2 \chi_{2s_C}^a (\zeta_{2s_C}^a) + c_3 \chi_{2s_C}^b (\zeta_{2s_C}^b) \\ & + c_4 \chi_{2p_C}^a (\zeta_{2p_C}^a) + c_5 \chi_{2p_C}^a (\zeta_{2p_C}^a) + c_6 \chi_{2p_C}^a (\zeta_{2p_C}^a) \\ & + c_7 \chi_{2p_C}^b (\zeta_{2p_C}^b) + c_8 \chi_{2p_C}^b (\zeta_{2p_C}^b) + c_9 \chi_{2p_C}^b (\zeta_{2p_C}^b) \\ & + \text{Basis Functions on other atoms}\end{aligned}$$

Having two different STOs for each type of valence orbital (i.e. $2s, 2p_x, 2p_y, 2p_z$) gives one the flexibility to characterize the bonding electrons in the carbon atoms in the very different types of species given above.

Slide 17

Triply Split Valence Basis Set: 6-311G

Core electrons are characterized by a single STO (composed of a fixed combination of 6 GTOs).

Valence shell electrons are characterized by three sets of orbitals with three different values of ζ .

The inner STO (largest ζ) is composed of 3 GTOs. The middle and outer STOs are each composed of a single GTO.

$$\text{First Row (e.g. H): } \chi_{1s_H}^a (\zeta_{1s_H}^a) \quad \chi_{1s_H}^b (\zeta_{1s_H}^b) \quad \chi_{1s_H}^c (\zeta_{1s_H}^c)$$

$$\begin{aligned}\text{Second Row (e.g. C): } & \chi_{1s_C}^a (\zeta_{1s_C}^a) \\ & \chi_{2s_C}^a (\zeta_{2s_C}^a) \quad \chi_{2s_C}^b (\zeta_{2s_C}^b) \quad \chi_{2s_C}^c (\zeta_{2s_C}^c) \\ & \chi_{2p_C}^a (\zeta_{2p_C}^a), \chi_{2p_C}^a (\zeta_{2p_C}^a), \chi_{2p_C}^a (\zeta_{2p_C}^a) \\ & \chi_{2p_C}^b (\zeta_{2p_C}^b), \chi_{2p_C}^b (\zeta_{2p_C}^b), \chi_{2p_C}^b (\zeta_{2p_C}^b) \\ & \chi_{2p_C}^c (\zeta_{2p_C}^c), \chi_{2p_C}^c (\zeta_{2p_C}^c), \chi_{2p_C}^c (\zeta_{2p_C}^c)\end{aligned}$$

Slide 18

Polarization Functions

Often, the electron density in a bond is distorted from cylindrical symmetry. For example, one expects the electron density in a C-H bond in $\text{H}_2\text{C}=\text{CH}_2$ to be different in the plane and perpendicular to the plane of the molecule.

To allow for this distortion, "polarization functions" are often added to the basis set. They are STOs (usually composed of a single GTO) with the angular momentum quantum number greater than that required to describe the electrons in the atom.

For hydrogen atoms, polarization functions are usually a set of three 2p orbitals (sometimes a set of 3d orbitals are thrown in for good measure)

For second and third row elements, polarization functions are usually a set of five** 3d orbitals (sometimes a set of f orbitals is also used)

** In some basis sets, six (Cartesian) d orbitals are used, but let's not worry about that.

Slide 19

6-31G(d): A set of d orbitals is added to all atoms other than hydrogen.
[aka 6-31G*]

6-31G(d,p): A set of d orbitals is added to all atoms other than hydrogen.
[aka 6-31G**]

A set of p orbitals is added to hydrogen atoms.

6-311G(3df,2pd): Three sets of d orbitals and one set of f orbitals are added to all atoms other than hydrogen.

Two sets of p orbitals and one set of d orbitals is added to hydrogen atoms.

Slide 20

What are the STOs on each atom (and the total number of STOs) in CH_3Cl using a 6-311G(2df,2p) basis set?

Hydrogens: 3 1s STOs (triply split valence)
2 x 3 2p STOs (polarization functions)
Each hydrogen has 9 STOs

Carbon: 1 1s STO (core)
3 2s STOs (triply split valence)
3 x 3 2p STOs (triply split valence)
2 x 5 3d STOs (polarization functions)
7 4f STOs (polarization functions)
The carbon has 30 STOs

Slide 21

Chlorine: 1 1s STO (core)
1 2s STO (core)
3 2p STOs (core)
3 3s STOs (triply split valence)
3 x 3 3p STOs (triply split valence)
2 x 5 3d STOs (polarization functions)
7 4f STOs (polarization functions)
The chlorine has 34 STOs

Total Number of STOs: $3 \times 9 + 30 + 34 = 91$

Slide 22

Diffuse Functions

Molecules (a) with a negative charge (anions)
(b) in excited electronic states
(c) involved in Hydrogen Bonding

have a significant electron density at distances further from the nuclei than most ground state neutral molecules.

To account for this, “diffuse” functions are sometimes added to the basis set.

For hydrogen atoms, this is a single ns orbital with a very small value of ζ (i.e. large extension away from the nucleus)

For atoms other than hydrogen, this is an ns orbital and 3 np orbitals with a very small value of ζ .

Slide 23

6-31+G



All atoms other than hydrogen have an s and 3 p diffuse orbitals.

6-31++G



All atoms other than hydrogen have an s and 3 p diffuse orbitals.

In addition, each hydrogen has an s diffuse orbital.

Slide 24

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- **LCAO-MO-SCF Theory for Molecules**
 - Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
 - Post Hartree-Fock Treatment of Electron Correlation
 - Density Functional Theory
 - Computation Times
 - Some Applications of Quantum Chemistry

Slide 25

LCAO-MO-SCF Theory for Molecules

Translation: LCAO = Linear Combination of Atomic Orbitals

MO = Molecular Orbital

SCF = Self-Consistent Field

In 1951, Roothaan developed the LCAO extension of the Hartree-Fock method.

This put the Hartree-Fock equations into a matrix form which is much easier to use for accurate QM calculations on large molecules.

I will outline the method. You are **not** responsible for any of the equations, only for the qualitative concept.

Slide 26

Outline of the LCAO-MO-SCF Hartree-Fock Method

1. The electrons in molecules occupy Molecular Orbitals (ϕ_i).

There are two electrons in each molecular orbital.
One has α spin and the second has β spin.

2. The total electronic wavefunction (ψ) can be expressed as a Slater Determinant (antisymmetrized product) of the MOs.

If there are a total of N electrons, then $N/2$ MOs are needed.

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1\alpha & \phi_1\beta & \phi_2\alpha & \phi_2\beta & \cdots & \phi_{N/2}\beta \end{vmatrix}$$

Slide 27

3. Each MO is assumed to be a linear combination of Slater Type Orbitals (STOs).

$$\phi_k = \sum_v c_{kv} \chi_v$$

e.g. for the first MO: $\phi_1 = c_{11}\chi_1 + c_{12}\chi_2 + c_{13}\chi_3 + \cdots$

There are a total of n_{bas} basis functions (STOs)

Note: The number of MOs which can be formed by n_{bas} basis functions is n_{bas}

e.g. if there are a total of 50 STOs in your basis set, then you will get 50 MOs.

However, only the first $N/2$ MOs are occupied.

Slide 28

4. In the Hartree-Fock approach, the MOs are obtained by solving the Fock equations.

$$\hat{f}_k \phi_k = \varepsilon_k \phi_k$$

The Fock operator is the Effective Hamiltonian operator, which we discussed a little in Chapter 8.

5. When the LCAO of STOs is plugged into the Fock equations (above), one gets a series of n_{bas} homogeneous equations..

$$\begin{array}{c} \hat{f}_k \phi_k = \varepsilon_k \phi_k \quad + \quad \phi_k = \sum_v c_{kv} \chi_v \\ \downarrow \\ \sum_v (f_{\mu v} - \varepsilon S_{\mu v}) c_v = 0 \end{array}$$

We'll discuss the matrix elements a little bit (below).

Slide 29

5. In order to obtain non-trivial solutions for the coefficients, c_v , the Secular Determinant of the Coefficients must be 0.

$$\sum_v (f_{\mu v} - \varepsilon S_{\mu v}) c_v = 0 \quad \longrightarrow \quad |f_{\mu v} - \varepsilon S_{\mu v}| = 0$$

Although this may all look very weird to you, it's actually not too much different from the last Chapter, where we considered the interaction of two atomic orbitals to form Molecular Orbitals in H_2^+ .

$$\psi = c_a 1s_a + c_b 1s_b$$



Linear Equations

Secular Determinant

$$\begin{array}{l} (H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b = 0 \\ (H_{ab} - \langle E \rangle S_{ab}) c_a + (H_{bb} - \langle E \rangle) c_b = 0 \end{array} \quad \longrightarrow \quad \begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

We then solved the Secular Determinant for the two values of the energy, and then the coefficients for each energy.

Slide 30

The Matrix Elements: $f_{\mu\nu}$ and $S_{\mu\nu}$

$$|f_{\mu\nu} - \varepsilon S_{\mu\nu}| = 0$$

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

No Big Deal!!

Overlap Integral

$$f_{\mu\nu} = h_{\mu\nu} + 2J_{\mu\nu} + K_{\mu\nu}$$

$$h_{\mu\nu} = \langle \chi_\mu(1) | -\frac{1}{2} \nabla_1^2 - \sum_\alpha \frac{Z_\alpha}{r_{1\alpha}} | \chi_\nu(1) \rangle$$

Core Energy Integral One electron (two center) integral
A Piece of Cake!!

$$J_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \langle \chi_\mu(1) \chi_\sigma(2) | \frac{1}{r_{12}} | \chi_\nu(1) \chi_\lambda(2) \rangle$$

Coulomb Integral A **VERY** Big Deal!!

$$K_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \langle \chi_\mu(1) \chi_\sigma(2) | \frac{1}{r_{12}} | \chi_\lambda(1) \chi_\nu(2) \rangle$$

Exchange Integral

Slide 31

$$|f_{\mu\nu} - \varepsilon S_{\mu\nu}| = 0 \quad f_{\mu\nu} = h_{\mu\nu} + 2J_{\mu\nu} + K_{\mu\nu}$$

$$J_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \langle \chi_\mu(1) \chi_\sigma(2) | \frac{1}{r_{12}} | \chi_\nu(1) \chi_\lambda(2) \rangle$$

Coulomb Integral

$$K_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \langle \chi_\mu(1) \chi_\sigma(2) | \frac{1}{r_{12}} | \chi_\lambda(1) \chi_\nu(2) \rangle$$

Exchange Integral

The Coulomb and Exchange Integrals cause 2 Big Time problems.

1. Both $J_{\mu\nu}$ and $K_{\mu\nu}$ depend on the MO coefficients.
Therefore, the Fock Matrix elements, $F_{\mu\nu}$, in the Secular Determinant also depend on the coefficients
2. Both $J_{\mu\nu}$ and $K_{\mu\nu}$ are "2 electron, 4 center" integrals. These are extremely time consuming to evaluate for STOs.

Slide 32

- Both $J_{\mu\nu}$ and $K_{\mu\nu}$ depend on the MO coefficients.
Therefore, the Fock Matrix elements, $F_{\mu\nu}$, in the Secular Determinant also depend on the coefficients

Solution: Employ iterative procedure (same as before).

1. Guess orbital coefficients, c_{ij} .
2. Construct elements of the Fock matrix
3. Solve the Secular Determinant for the energies, and then the simultaneous homogeneous equations for a new set of orbital coefficients
4. Iterate until you reach a Self-Consistent-Field, when the calculated coefficients are the same as those used to construct the matrix elements

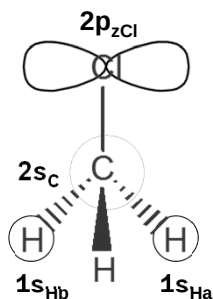
Slide 33

- Both $J_{\mu\nu}$ and $K_{\mu\nu}$ are "2 electron, 4 center" integrals. These are extremely time consuming to evaluate for STOs.

$$J_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \left\langle \chi_\mu(1) \chi_\sigma(2) \left| \frac{1}{r_{12}} \right| \chi_\nu(1) \chi_\lambda(2) \right\rangle$$

For example, in CH_3Cl , one would have integrals of the type:

$$\left\langle \chi_{1s_{\text{Ha}}}(1) \chi_{2p_{z\text{Cl}}}(2) \left| \frac{1}{r_{12}} \right| \chi_{2s_{\text{C}}}(1) \chi_{1s_{\text{Hb}}}(2) \right\rangle$$



Thus, in molecules with 4 or more atoms, one has integrals containing the products of 4 different functions centered on 4 different atoms.

This is **not** an appetizing position to be in.

Slide 34

$$J_{\mu\nu} = \sum_j \sum_\sigma \sum_\lambda c_{j\lambda} c_{j\sigma} \left\langle \chi_\mu(1) \chi_\sigma(2) \left| \frac{1}{r_{12}} \right| \chi_\nu(1) \chi_\lambda(2) \right\rangle \quad \text{4 Center Integrals}$$

The Solution

Slater Type Orbitals (STOs) are much better at representing the electron density in molecules.

However, multicenter integrals involving STOs are **very** difficult.

Because of some mathematical simplifications, multicenter integrals involving Gaussian Type Orbitals (GTOs) are **much** simpler (i.e. faster).

That's why the majority of modern basis sets use STO basis functions, which are composed of fixed combinations of GTOs.

Slide 35

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- **Examples: Hartree-Fock Calculations on H₂O and CH₂=CH₂**
- Post Hartree-Fock Treatment of Electron Correlation
- Density Functional Theory
- Computation Times
- Some Applications of Quantum Chemistry

Slide 36

Example 1: Hartree-Fock Calculation on H₂O

To illustrate Hartree-Fock calculations, let's show the results of a HF/6-31G calculation on water.

To obtain quantitative data, one would perform a higher level calculation. But this calculation is fine for qualitative discussion

The total number of basis functions (STOs) is:

O	– 9 STOs
H ₁	– 2 STOs
H ₂	– 2 STOs
Total:	13 STOs

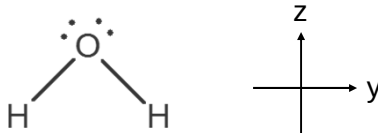
Therefore, the calculation will generate 13 MOs

H₂O has 10 electrons.

Therefore, the first 5 MOs will be occupied.

Slide 37

As we learned in General Chemistry, the Lewis Structure of water is:



Therefore, we expect the 5 pairs of electrons to be distributed as follows:

1. One pair of 1s Oxygen electrons
2. Two pairs of O-H bonding electrons
3. Two pairs of Oxygen lone-pair electrons

Yeah, right!!

If you believe that, then you must also believe
in Santa Claus and the Tooth Fairy.

Slide 38

		1	2	3	4	5
		(A1)--0	(A1)--0	(B2)--0	(A1)--0	(B1)--0
EIGENVALUES --		-20.55347	-1.35260	-0.72644	-0.54826	-0.49831
1	1 0 1S	0.99577	-0.21312	0.00000	-0.07138	0.00000
2	2S	0.02202	0.47005	0.00000	0.17057	0.00000
3	2PX	0.00000	0.00000	0.00000	0.00000	0.64018
4	2PY	0.00000	0.00000	0.50448	0.00000	0.00000
5	2PZ	-0.00202	-0.10590	0.00000	0.56058	0.00000
6	3S	-0.00805	0.47958	0.00000	0.28973	0.00000
7	3PX	0.00000	0.00000	0.00000	0.00000	0.51155
8	3PY	0.00000	0.00000	0.26243	0.00000	0.00000
9	3PZ	0.00179	-0.05640	0.00000	0.41873	0.00000
10	2 H 1S	0.00005	0.14092	0.26551	-0.13455	0.00000
11	2S	0.00201	-0.00852	0.11472	-0.07515	0.00000
12	3 H 1S	0.00005	0.14092	-0.26551	-0.13455	0.00000
13	2S	0.00201	-0.00852	-0.11472	-0.07515	0.00000

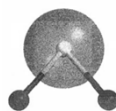
Above are the MOs of the 5 occupied MOs of H₂O at the HF/6-31G level.

The energies (aka eigenvalues) are shown at the top of each column.

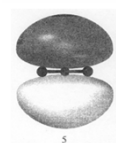
The numbers represent simple numbering of each type of orbital; e.g. O 1s means the the "1s" orbital (only a single STO) on O. Both O 2s and O 3s are the doubly split valence "2s" orbitals on O.

Slide 39

		1	2	3	4	5
		(A1)--0	(A1)--0	(B2)--0	(A1)--0	(B1)--0
EIGENVALUES --		-20.55347	-1.35260	-0.72644	-0.54826	-0.49831
1	1 0 1S	0.99577	-0.21312	0.00000	-0.07138	0.00000
2	2S	0.02202	0.47005	0.00000	0.17057	0.00000
3	2PX	0.00000	0.00000	0.00000	0.00000	0.64018
4	2PY	0.00000	0.00000	0.50448	0.00000	0.00000
5	2PZ	-0.00202	-0.10590	0.00000	0.56058	0.00000
6	3S	-0.00805	0.47958	0.00000	0.28973	0.00000
7	3PX	0.00000	0.00000	0.00000	0.00000	0.51155
8	3PY	0.00000	0.00000	0.26243	0.00000	0.00000
9	3PZ	0.00179	-0.05640	0.00000	0.41873	0.00000
10	2 H 1S	0.00005	0.14092	0.26551	-0.13455	0.00000
11	2S	0.00201	-0.00852	0.11472	-0.07515	0.00000
12	3 H 1S	0.00005	0.14092	-0.26551	-0.13455	0.00000
13	2S	0.00201	-0.00852	-0.11472	-0.07515	0.00000



Orbital #1 contains the Oxygen 1s pair. Check!!



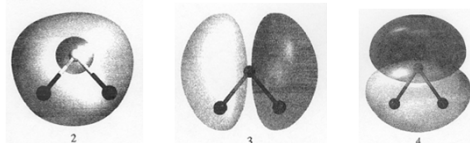
Orbital #5 contains one of the Oxygen's lone pairs. Double Check!!

Let's keep going. We're on a roll!!!

Let's find the second Oxygen lone pair and the two O-H bonding pairs of electrons.

Slide 40

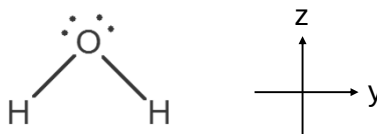
				1	2	3	4	5
				(A1) --0	(A1) --0	(B2) --0	(A1) --0	(B1) --0
EIGENVALUES --				-20.55347	-1.35260	-0.72644	-0.54826	-0.49831
1	1	0	1S	0.99577	-0.21312	0.00000	-0.07138	0.00000
2			2S	0.02202	0.47005	0.00000	0.17057	0.00000
3			2PX	0.00000	0.00000	0.00000	0.00000	0.64018
4			2PY	0.00000	0.00000	0.50448	0.00000	0.00000
5			2PZ	-0.00202	-0.10590	0.00000	0.56058	0.00000
6			3S	-0.00805	0.47958	0.00000	0.28973	0.00000
7			3PX	0.00000	0.00000	0.00000	0.00000	0.51155
8			3PY	0.00000	0.00000	0.26243	0.00000	0.00000
9			3PZ	0.00179	-0.05640	0.00000	0.41873	0.00000
10	2	H	1S	0.00005	0.14092	0.26551	-0.13455	0.00000
11			2S	0.00201	-0.00852	0.11472	-0.07515	0.00000
12	3	H	1S	0.00005	0.14092	-0.26551	-0.13455	0.00000
13			2S	0.00201	-0.00852	-0.11472	-0.07515	0.00000



Oops!! Orbitals #2, 3 and 4 all have significant contributions from both the Oxygen and the Hydrogens.

Where's the second Oxygen lone pair??

Slide 41



Well!!! So much for Gen. Chem. Bonding Theory.

The problem is that, whereas the Oxygen $2p_x$ orbital belongs to a different symmetry representation from the Hydrogen 1s orbitals,

- 1) The $2p_y$ belongs to the same representation as the antisymmetric combination of the Hydrogen 1s orbitals.
- 2) The O 2s & $2p_z$ orbitals belongs to the same representation as the symmetric combination of the Hydrogen 1s orbitals.

However, don't sweat the symmetry for now.

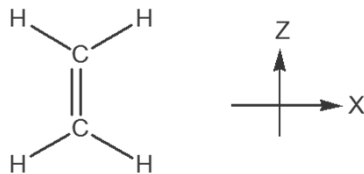
Just remember that life ain't as easy as when you were a young, naive Freshman.

Let's look at a simpler example: Ethylene

Slide 42

Example 2: Hartree-Fock Calculation on C_2H_6

The Lewis Structure of ethylene is:

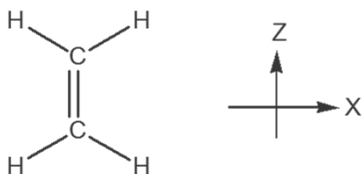


There are a total of $2 \times 6 + 4 \times 1 = 16$ electrons

We expect the 8 pairs of electrons to be distributed as follows:

1. Two pairs of 1s Carbon electrons
2. Four pairs of C-H bonding electrons
3. One pair of C-C σ bonding electrons
4. One pair of C-C π bonding electrons

Slide 43



We will use the STO-3G Basis Set

The total number of basis functions (STOs) is:

C_1	– 5 STOs
C_2	– 5 STOs
H_1	– 1 STO
H_2	– 1 STO
H_3	– 1 STO
H_4	– 1 STO
Total:	14 STOs

Therefore, there will be a total of 14 MOs generated.

Only the first 8 MOs will be occupied.

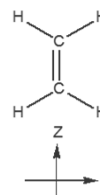
The remaining 6 MOs will be unoccupied (or “Virtual”) MOs.

Slide 44

The results below were obtained at the HF/STO-3G level.

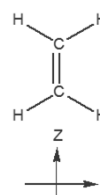
		1	2	3	4	5
		0	0	0	0	0
EIGENVALUES --		-11.02171	-11.02067	-0.98766	-0.74572	-0.60562
1	1 C 1S	0.70178	0.70145	-0.17953	-0.13564	0.00000
2	2S	0.02001	0.03160	0.46805	0.41005	0.00000
3	2PX	0.00000	0.00000	0.00000	0.00000	0.39688
4	2PY	0.00000	0.00000	0.00000	0.00000	0.00000
5	2PZ	0.00204	-0.00451	-0.11950	0.20333	0.00000
6	2 C 1S	0.70178	-0.70145	-0.17953	0.13564	0.00000
7	2S	0.02001	-0.03160	0.46805	-0.41005	0.00000
8	2PX	0.00000	0.00000	0.00000	0.00000	0.39688
9	2PY	0.00000	0.00000	0.00000	0.00000	0.00000
10	2PZ	-0.00204	-0.00451	0.11950	0.20333	0.00000
11	3 H 1S	-0.00475	-0.00492	0.11196	0.22358	0.25659
12	4 H 1S	-0.00475	-0.00492	0.11196	0.22358	-0.25659
13	5 H 1S	-0.00475	0.00492	0.11196	-0.22358	0.25659
14	6 H 1S	-0.00475	0.00492	0.11196	-0.22358	-0.25659

		6	7	8	9	10
		0	0	0	V	V
EIGENVALUES --		-0.54024	-0.45805	-0.33550	0.32832	0.61879
1	1 C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
2	2S	-0.01685	0.00000	0.00000	0.00000	0.00000
3	2PX	0.00000	0.39337	0.00000	0.00000	0.69821
4	2PY	0.00000	0.00000	0.63196	0.81757	0.00000
5	2PZ	0.49997	0.00000	0.00000	0.00000	0.00000
6	2 C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
7	2S	-0.01685	0.00000	0.00000	0.00000	0.00000
8	2PX	0.00000	-0.39337	0.00000	0.00000	0.69821
9	2PY	0.00000	0.00000	0.63196	-0.81757	0.00000
10	2PZ	-0.49997	0.00000	0.00000	0.00000	0.00000
11	3 H 1S	0.21698	0.35062	0.00000	0.00000	-0.62630
12	4 H 1S	0.21698	-0.35062	0.00000	0.00000	0.62630
13	5 H 1S	0.21698	-0.35062	0.00000	0.00000	-0.62630
14	6 H 1S	0.21698	0.35062	0.00000	0.00000	0.62630

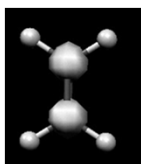


Slide 45

		1	2	3	4	5
		0	0	0	0	0
EIGENVALUES --		-11.02171	-11.02067	-0.98766	-0.74572	-0.60562
1	1 C 1S	0.70178	0.70145	-0.17953	-0.13564	0.00000
2	2S	0.02001	0.03160	0.46805	0.41005	0.00000
3	2PX	0.00000	0.00000	0.00000	0.00000	0.39688
4	2PY	0.00000	0.00000	0.00000	0.00000	0.00000
5	2PZ	0.00204	-0.00451	-0.11950	0.20333	0.00000
6	2 C 1S	0.70178	-0.70145	-0.17953	0.13564	0.00000
7	2S	0.02001	-0.03160	0.46805	-0.41005	0.00000
8	2PX	0.00000	0.00000	0.00000	0.00000	0.39688
9	2PY	0.00000	0.00000	0.00000	0.00000	0.00000
10	2PZ	-0.00204	-0.00451	0.11950	0.20333	0.00000
11	3 H 1S	-0.00475	-0.00492	0.11196	0.22358	0.25659
12	4 H 1S	-0.00475	-0.00492	0.11196	0.22358	-0.25659
13	5 H 1S	-0.00475	0.00492	0.11196	-0.22358	0.25659
14	6 H 1S	-0.00475	0.00492	0.11196	-0.22358	-0.25659

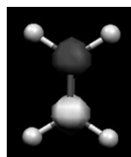


#1



Orbitals #1 and #2 are both Carbon 1s orbitals.

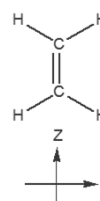
#2



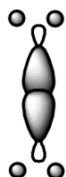
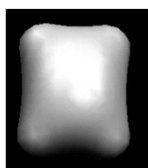
In the Table and Figures, you see both in phase and out-of-phase combinations of the two orbitals. However, that's artificial when the orbitals are degenerate.

Slide 46

			1	2	3	4	5
			0	0	0	0	0
EIGENVALUES	--		-11.02171	-11.02067	-0.98766	-0.74572	-0.60562
1	1	C 1S	0.70178	0.70145	-0.17953	-0.13564	0.00000
2		2S	0.02001	0.03160	0.46805	0.41005	0.00000
3		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
4		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
5		2PZ	0.00204	-0.00451	-0.11950	0.20333	0.00000
6	2	C 1S	0.70178	-0.70145	-0.17953	0.13564	0.00000
7		2S	0.02001	-0.03160	0.46805	-0.41005	0.00000
8		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
9		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
10		2PZ	-0.00204	-0.00451	0.11950	0.20333	0.00000
11	3	H 1S	-0.00475	-0.00492	0.11196	0.22358	0.25659
12	4	H 1S	-0.00475	-0.00492	0.11196	0.22358	-0.25659
13	5	H 1S	-0.00475	0.00492	0.11196	-0.22358	0.25659
14	6	H 1S	-0.00475	0.00492	0.11196	-0.22358	-0.25659



#3

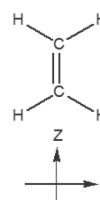


Orbital #3 is primarily a C-C σ bonding orbital, involving 2s and $2p_z$ orbitals on each carbon .

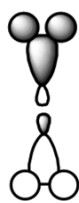
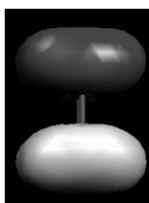
There is also a small bonding component from the hydrogen 1s orbitals.

Slide 47

			1	2	3	4	5
			0	0	0	0	0
EIGENVALUES	--		-11.02171	-11.02067	-0.98766	-0.74572	-0.60562
1	1	C 1S	0.70178	0.70145	-0.17953	-0.13564	0.00000
2		2S	0.02001	0.03160	0.46805	0.41005	0.00000
3		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
4		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
5		2PZ	0.00204	-0.00451	-0.11950	0.20333	0.00000
6	2	C 1S	0.70178	-0.70145	-0.17953	0.13564	0.00000
7		2S	0.02001	-0.03160	0.46805	-0.41005	0.00000
8		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
9		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
10		2PZ	-0.00204	-0.00451	0.11950	0.20333	0.00000
11	3	H 1S	-0.00475	-0.00492	0.11196	0.22358	0.25659
12	4	H 1S	-0.00475	-0.00492	0.11196	0.22358	-0.25659
13	5	H 1S	-0.00475	0.00492	0.11196	-0.22358	0.25659
14	6	H 1S	-0.00475	0.00492	0.11196	-0.22358	-0.25659



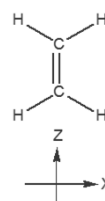
#4



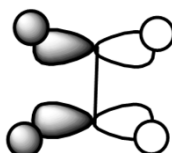
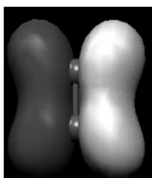
Orbital #4 represents C-H bonding of the Hydrogen 1s with the Carbon 2s and $2p_z$ orbitals.

Slide 48

			1	2	3	4	5
			0	0	0	0	0
EIGENVALUES --			-11.02171	-11.02067	-0.98766	-0.74572	-0.60562
1	1	C 1S	0.70178	0.70145	-0.17953	-0.13564	0.00000
2		2S	0.02001	0.03160	0.46805	0.41005	0.00000
3		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
4		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
5		2PZ	0.00204	-0.00451	-0.11950	0.20333	0.00000
6	2	C 1S	0.70178	-0.70145	-0.17953	0.13564	0.00000
7		2S	0.02001	-0.03160	0.46805	-0.41005	0.00000
8		2PX	0.00000	0.00000	0.00000	0.00000	0.39688
9		2PY	0.00000	0.00000	0.00000	0.00000	0.00000
10		2PZ	-0.00204	-0.00451	0.11950	0.20333	0.00000
11	3	H 1S	-0.00475	-0.00492	0.11196	0.22358	0.25659
12	4	H 1S	-0.00475	-0.00492	0.11196	0.22358	-0.25659
13	5	H 1S	-0.00475	0.00492	0.11196	-0.22358	0.25659
14	6	H 1S	-0.00475	0.00492	0.11196	-0.22358	-0.25659



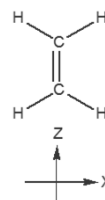
#5



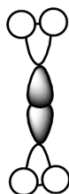
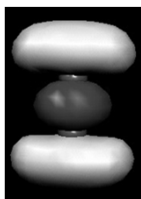
Orbital #5 represents C-H bonding between the Hydrogen 1s and Carbon 2p_x orbitals.

Slide 49

			6	7	8	9	10
			0	0	0	V	V
EIGENVALUES --			-0.54024	-0.45805	-0.33550	0.32832	0.61879
1	1	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
2		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
3		2PX	0.00000	0.39337	0.00000	0.00000	0.69821
4		2PY	0.00000	0.00000	0.63196	0.81757	0.00000
5		2PZ	0.49997	0.00000	0.00000	0.00000	0.00000
6	2	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
7		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
8		2PX	0.00000	-0.39337	0.00000	0.00000	0.69821
9		2PY	0.00000	0.00000	0.63196	-0.81757	0.00000
10		2PZ	-0.49997	0.00000	0.00000	0.00000	0.00000
11	3	H 1S	0.21698	0.35062	0.00000	0.00000	-0.62630
12	4	H 1S	0.21698	-0.35062	0.00000	0.00000	0.62630
13	5	H 1S	0.21698	-0.35062	0.00000	0.00000	-0.62630
14	6	H 1S	0.21698	0.35062	0.00000	0.00000	0.62630



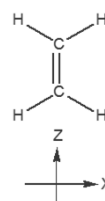
#6



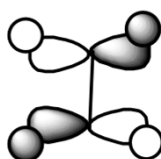
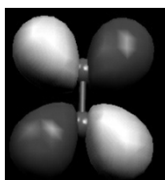
Orbital #6 represents C-H bonding of the Hydrogen 1s with the Carbon 2p_z orbitals. There are also a C-C σ bonding interaction through the 2p_z orbitals.

Slide 50

			6	7	8	9	10
			0	0	0	V	V
EIGENVALUES --			-0.54024	-0.45805	-0.33550	0.32832	0.61879
1	1	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
2		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
3		2PX	0.00000	0.39337	0.00000	0.00000	0.69821
4		2PY	0.00000	0.00000	0.63196	0.81757	0.00000
5		2PZ	0.49997	0.00000	0.00000	0.00000	0.00000
6	2	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
7		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
8		2PX	0.00000	-0.39337	0.00000	0.00000	0.69821
9		2PY	0.00000	0.00000	0.63196	-0.81757	0.00000
10		2PZ	-0.49997	0.00000	0.00000	0.00000	0.00000
11	3	H 1S	0.21698	0.35062	0.00000	0.00000	-0.62630
12	4	H 1S	0.21698	-0.35062	0.00000	0.00000	0.62630
13	5	H 1S	0.21698	-0.35062	0.00000	0.00000	-0.62630
14	6	H 1S	0.21698	0.35062	0.00000	0.00000	0.62630



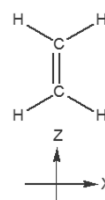
#7



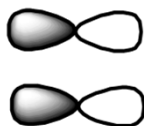
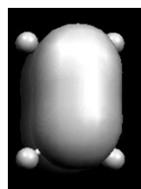
Orbital #7 represents C-H bonding between the Hydrogen 1s and Carbon 2p_x orbitals.

Slide 51

			6	7	8	9	10
			0	0	0	V	V
EIGENVALUES --			-0.54024	-0.45805	-0.33550	0.32832	0.61879
1	1	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
2		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
3		2PX	0.00000	0.39337	0.00000	0.00000	0.69821
4		2PY	0.00000	0.00000	0.63196	0.81757	0.00000
5		2PZ	0.49997	0.00000	0.00000	0.00000	0.00000
6	2	C 1S	0.01489	0.00000	0.00000	0.00000	0.00000
7		2S	-0.01685	0.00000	0.00000	0.00000	0.00000
8		2PX	0.00000	-0.39337	0.00000	0.00000	0.69821
9		2PY	0.00000	0.00000	0.63196	-0.81757	0.00000
10		2PZ	-0.49997	0.00000	0.00000	0.00000	0.00000
11	3	H 1S	0.21698	0.35062	0.00000	0.00000	-0.62630
12	4	H 1S	0.21698	-0.35062	0.00000	0.00000	0.62630
13	5	H 1S	0.21698	-0.35062	0.00000	0.00000	-0.62630
14	6	H 1S	0.21698	0.35062	0.00000	0.00000	0.62630



#8



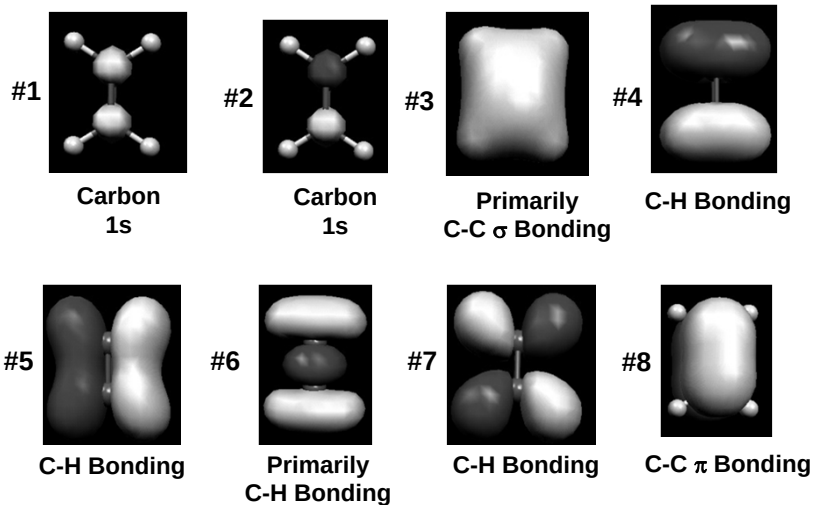
Orbital #8 is the C-C π bond between the 2p_y orbitals on each Carbon.

→ y

The y-axis has been rotated into the plane of the slide for clarity.

Slide 52

Ethylene: Orbital Summary



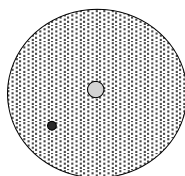
Slide 53

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
- **Post Hartree-Fock Treatment of Electron Correlation**
- Density Functional Theory
- Computation Times
- Some Applications of Quantum Chemistry

Slide 54

Post Hartree-Fock Treatment of Electron Correlation



Recall that the basic assumption of the Hartree-Fock method is that a given electron's interactions with other electrons can be treated as though the other electrons are "smeared out".

The approximation neglects the fact that the positions of different electrons are actually **correlated**. That is, they would prefer to stay relatively far apart from each other.

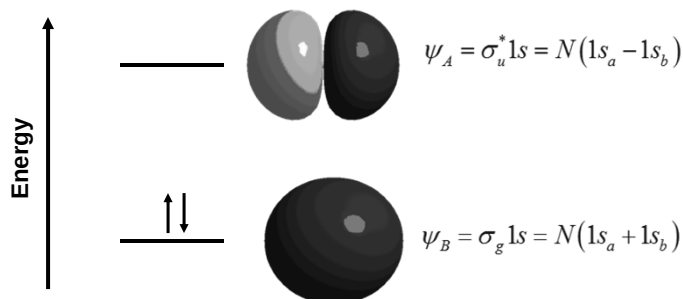
High
Energy
Not favored

Low
Energy
Favored

Slide 55

Excited State Electron Configurations

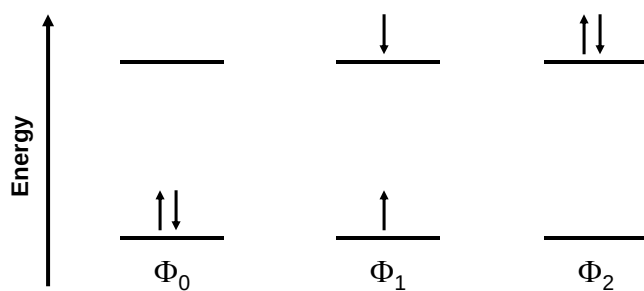
Recall that when we studied the H_2^+ wavefunctions (in Chapter 10), it was found that the antibonding wavefunction represents a more localized electron distribution than the bonding wavefunction.



There are several methods by which one can correct energies for electron correlation by "mixing in" some excited state electron configurations, in which the electron density is more localized.

Slide 56

Electron Configurations in H₂



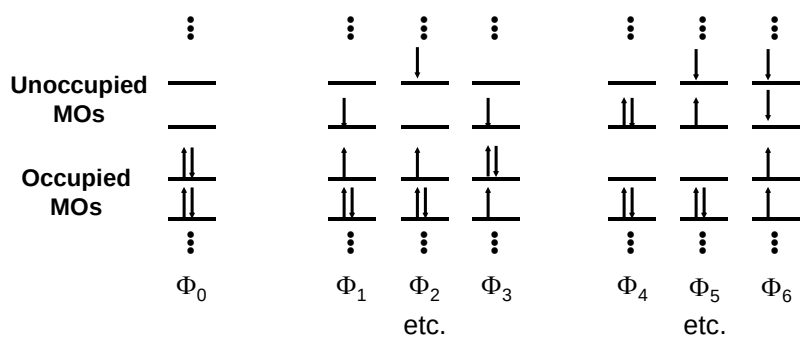
Φ_0 represents the ground state configuration: $(\sigma_g 1s)^2$

Φ_1 represents the singly excited state configuration: $(\sigma_g 1s)^1(\sigma_u^*)^1$

Φ_2 represents the doubly excited state configuration: $(\sigma_u^*)^2$

Slide 57

Electron Configurations in General



Some singly excited configurations

Some doubly excited configurations

There are also triply excited configuration, quadruply excited configurations, ...

One can go as high as "N-tuply excited configurations", where N is the number of electrons.

Slide 58

Møller-Plesset n-th order Perturbation Theory: MPn

This is an application of Perturbation Theory to compute the correlation energy.

Recall that in the Hartree-Fock procedure, the actual electron-electron repulsion energies are replaced by effective repulsive potential energy terms in forming effective Hamiltonians.

The zeroth order Hamiltonian, $H^{(0)}$, is the sum of effective Hamiltonians.

The zeroth order wavefunction, $\psi^{(0)}$, is the Hartree-Fock ground state wavefunction.

The perturbation is the sum of actual repulsive potential energies minus the sum of the effective potential energies (assuming a smeared out electron distribution).

Slide 59

First order perturbation theory, MP1, can be shown not to furnish any correlation energy correction to the energy.

Second Order Møller-Plesset Perturbation Theory: MP2

The MP2 correlation energy correction to the Hartree-Fock energy is given by the (rather disgusting) equation:

$$E(MP2) = \sum_{i < j}^{\text{Occ Orbs}} \sum_{a < b}^{\text{Unocc Orbs}} \frac{\langle \Phi_0 | H' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | H' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

Φ_0 is the wavefunction for the ground state configuration

Φ_{ij}^{ab} is the wavefunction for the doubly excited configuration in which an electron in Occ. Orb. i is promoted to Unocc. Orb. a and an electron in Occ. Orb. j is promoted to Unocc. Orb. b.

Slide 60

$$E(\text{MP2}) = \sum_{i < j}^{\text{Occ Orbs}} \sum_{a < b}^{\text{Unocc Orbs}} \frac{\langle \Phi_0 | H' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | H' | \Phi_0 \rangle}{E_0 - E_{ij}^{ab}}$$

The most important aspect to this equation is that MP2 energy corrections mix in excited state (i.e. localized electron density) configurations, which account for the correlated motion of different electrons.

It's actually not as hard to use the above equation as one might think. You type in "MP2" on the command line of your favorite Quantum Mechanics program, and it does the rest.

MP2 corrections are actually not too bad. They typically give ~80-90% of the total correlation energy.

To do better, you have to use a higher level method.

Slide 61

Fourth Order Møller-Plesset Perturbation Theory: MP4

From what I've heard, the equation for the MP4 correction to the Hartree-Fock energy makes the MP2 equation (above) look like the equation of a straight line.

There are some things in life that are better left unseen.

The important fact about the MP4 correlation energy is that it also mixes in triply and quadruply excited electron configurations with the ground state configuration.

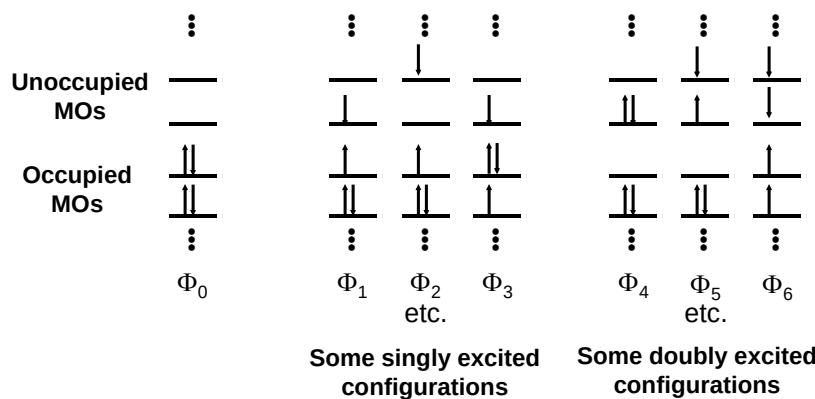
The use of the MP4 method to calculate the correlation energy isn't too difficult. You replace the "2" by the "4" on the program's command line; i.e. type: MP4

The MP4 method typically will get you 95-98% of the correlation energy.

The problem is that it takes *many* times longer than MP2 (I'll give you some relative timings below).

Slide 62

Configuration Interaction: CI



A second method is to calculate the correlation energy correction by mixing in excited configurations "Configuration Interaction".

It is assumed that the complete wavefunction is a linear combination of the ground state and excited state configurations.

Slide 63

$$\psi = \sum_{\text{configs}} c_j \Phi_j = c_0 \Phi_0 + c_1 \Phi_1 + c_2 \Phi_2 + \dots$$

Φ_0 is the ground state configuration and the other Φ_j are the various excited state configurations; singly, doubly, triply, quadruply, ... excited configurations.

The Variational Theorem is used to find the set of coefficients which gives the minimum energy.

This leads to an MxM Secular Determinant which can be solved to get the energies.

Slide 64

A Not So Small Problem

Recall that one can have up to N -tuply excited configurations, where N is the number of electrons.

For example, CH_3OH has 18 electrons. Therefore, one has excited state configurations with anywhere from 1 to 18 electrons transferred from an occupied orbital to an unoccupied orbital.

For a CI calculation on CH_3OH using a 6-31G(d) basis set, this leads to a total of $\sim 10^{18}$ (that's a billion-billion) electron configurations.

Solving a $10^{18} \times 10^{18}$ Secular Determinant is most definitely **not** trivial. As a matter of fact, it is quite impossible.

CI calculations can be performed on systems containing up to a few billion configurations.

Slide 65

Truncated Configuration Interaction

We absolutely **MUST** cut down on the number of configurations that are used. There are two procedures for this.

1. The "Frozen Core" approximation
Only allow excitations involving electrons in the valence shell
2. Eliminate excitations involving transfer of a large number of electrons.
CISD: Configuration Interaction with only single and double excitations
CISDT: Configuration Interaction with only single, double and triple excitations

For medium to larger molecules, even CISDT involves too many excitations to be done in a reasonable time.

Slide 66

A final note on currently used CI methods.

You will see calculations in the literature using the following CI methods, and so I'll comment briefly on them.

QCISD: There is a problem with truncated CI called "size consistency" (don't worry about it). The Q represents a "quadratic correction" intended to minimize this problem.

QCISD(T): We just mentioned that QCISDT isn't feasible for most molecules; i.e. there are too many triply excited excitations.

The (T) indicates that the effects of triple excitations are approximated (using a perturbation treatment).

Slide 67

Coupled Cluster (CC) Methods

In recent years, an alternative to Configuration Interaction treatments of electron correlation, named Coupled Cluster (CC) methods, has become popular.

The details of the CC calculations differ from those of CI. However, the two methods are very similar. Coupled Cluster is basically a different procedure used to "mix" in excited state electron configurations.

In principle, CC is supposed to be a superior method, in that it does not make some of the approximations used in the practical application of CI.

However, **in practice**, equivalent levels of both methods yield very similar results for most molecules.

Slide 68

CCSD: Coupled Cluster including single and double electron excitations.

$$\text{CCSD} \approx \text{QCISD}$$

CCSD(T): Coupled Cluster including single and double electron excitations + an approximate treatment of triple electron excitations.

$$\text{CCSD(T)} \approx \text{QCISD(T)}$$

Slide 69

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
- Post Hartree-Fock Treatment of Electron Correlation
- **Density Functional Theory**
- Computation Times
- Some Applications of Quantum Chemistry

Slide 70

Density Functional Theory: A Brief Introduction

Density Functional Theory (DFT) has become a fairly popular alternative to the Hartree-Fock method to compute the energy of molecules.

Its chief advantage is that one can compute the energy **with correlation corrections** at a computational cost similar to that of H-F calculations.

In DFT, it is assumed that the energy is a **functional** of the electron density, $\rho(x,y,z)$.

What is a “Functional”?

A functional is a function of a function.

Slide 71

The electron density is a **function** of the coordinates (x, y and z)

$$\rho = \rho(x, y, z)$$

The energy is a **functional** of the electron density.

$$E = E[\rho] = E[\rho(x, y, z)]$$

Types of Electronic Energy

1. Kinetic Energy, $T(\rho)$
2. Nuclear-Electron Attraction Energy, $E_{ne}(\rho)$
3. Coulomb Repulsion Energy, $J(\rho)$
4. Exchange and Correlation Energy, $E_{xc}(\rho)$

Slide 72

The DFT expression for the energy is:

$$E_{DFT}(\rho) = T(\rho) + E_{ne}(\rho) + J(\rho) + E_{xc}(\rho)$$

The major problem in DFT is deriving suitable formulas for the Exchange-Correlation term, $E_{xc}(\rho)$.

The various formulas derived to compute this term determine the different “flavors” of DFT.

Gradient Corrected Methods

The Exchange-Correlation term is assumed to be a functional, not only of the density, ρ , but also the derivatives of the density with respect to the coordinates (x,y,z).

Slide 73

Two currently popular exchange-correlation functions are:

LYP: Derived by Lee, Yang and Parr (1988)

PW91: Derived by Perdew and Wang (1991)

Hybrid Methods

Another currently popular “flavor” involves mixing in the Hartree-Fock exchange energy with DFT terms.

Among the best of these hybrid methods were formulated by Becke, who included 3 parameters in describing the exchange-correlation term.

The 3 parameters were determined by fitting their values to get the closest agreement with a set of experimental data.

Slide 74

Currently, the two most popular DFT methods are:

B3LYP: Becke's 3 parameter hybrid method using the Lee, Yang and Parr exchange-correlation functional

B3PW91: Becke's 3 parameter hybrid method using the Perdew-Wang 1991 functional

The Advantage of DFT

One can calculate geometries and frequencies of molecules (particularly large ones) at an accuracy similar to MP2, but at a computational cost similar to that of basic Hartree-Fock calculations.

Slide 75

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
- Post Hartree-Fock Treatment of Electron Correlation
- Density Functional Theory
- **Computation Times**
- Some Applications of Quantum Chemistry

Slide 76

Computation Times

Method / Basis Set

Generally (although not always), one can expect better results when using: (1) a larger basis set

(2) a more advanced method of treating electron correlation.

However, the improved results come at a price that can be very high.

The computation times increase very quickly when either the basis set and/or correlation treatment method is increased.

Some typical results are given below. However, the actual increases in times depend upon the size of the system (number of "heavy atoms" in the molecule).

Slide 77

Effect of Method on Computation Times

The calculations below were performed using the 6-31G(d) basis set on a Compaq ES-45 computer.

Method	Pentane	Octane
HF	1 (24 s)	1 (43 s)
B3LYP	1.9	1.8
MP2	1.6	2.5
MP4	44	394
QCISD	23	101
QCISD(T)	72	547

Note that the percentage increase in computation time with increasing sophistication of method becomes greater with larger molecules.

Slide 78

Effect of Basis Set on Computation Times

The calculations below were performed on Octane on a Compaq ES-45 computer.

Basis Set	# Bas. Fns.	HF	MP2
6-31G(d)	156	1 (39 s)	1 (102 s)
6-311G(d,p)	252	1.7	7.2
6-311+G(2df,p)	380	35	53

Note that the percentage increase in computation time with increasing basis set size becomes greater for more sophisticated methods.

Slide 79

Computation Times: Summary

- Increasing either the size of the basis set or the calculation method can increase the computation time very quickly.
- Increasing both the basis set size and method together can lead to **enormous** increases in the time required to complete a calculation.
- When deciding the method and basis set to use for a particular application, you should:
 - (1) Decide what combination will provide the desired level of accuracy (based upon earlier calculations on similar systems.
 - (2) Decide how much time you can "afford";
i.e. you can perform a more sophisticated calculation if you plan to study only 3-4 systems than if you plan to investigate 30-40 different systems.

Slide 80

Outline

- Atomic Orbitals (Slater Type Orbitals: STOs)
- Basis Sets
- LCAO-MO-SCF Theory for Molecules
- Examples: Hartree-Fock Calculations on H_2O and $\text{CH}_2=\text{CH}_2$
- Post Hartree-Fock Treatment of Electron Correlation
- Density Functional Theory
- Computation Times
- **Some Applications of Quantum Chemistry**

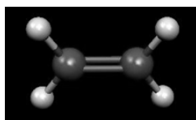
Slide 81

Some Applications of Quantum Chemistry

- Molecular Geometries
- Vibrational Frequencies
- Bond Dissociation Energies
- Thermodynamic Properties
- Enthalpies of Reaction
- Equilibrium Constants
- Reaction Mechanisms and Rate Constants
- Orbitals, Charge and Chemical Reactivity
- Some Additional Applications

Slide 82

Molecular Geometry

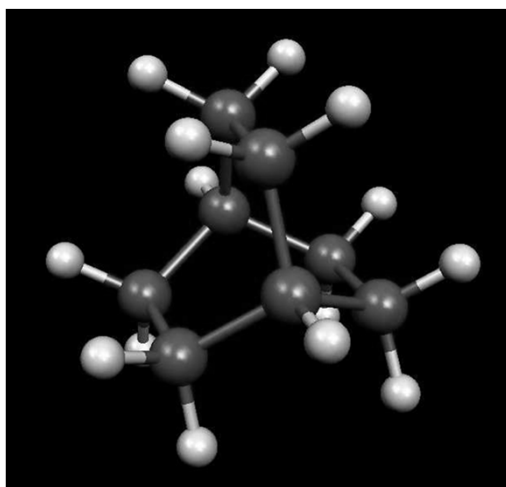


Method	R_{CC}	R_{CH}	$\angle HCH$
Experiment	1.338 Å	1.087 Å	117.5°
HF/6-31G(d)	1.317	1.076	116.4
MP2/6-31G(d)	1.336	1.085	117.2
QCISD/6-311+G(3df,2p)	1.332	1.083	117.0

- Hartree-Fock bond lengths are **usually** too short.
Electron correlation will usually lengthen the bonds so that electrons can stay further away from each other.
- MP2/6-31G(d) and B3LYP/6-31G(d) are very commonly used methods to get fairly accurate bond lengths and angles.
- For bonding of second row atoms and for hydrogen, bond lengths are typically accurate to approximately ± 0.02 Å and bond angles to $\pm 2^\circ$

Slide 83

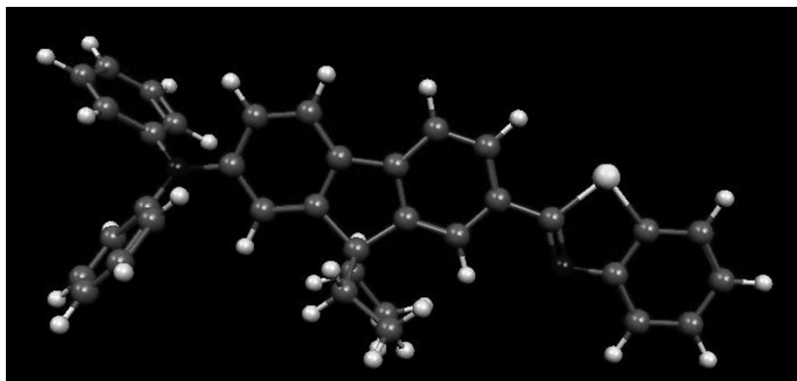
A Bigger Molecule: Bicyclo[2.2.2]octane



HF/6-31G(d): Computation Time ~3 minutes

Slide 84

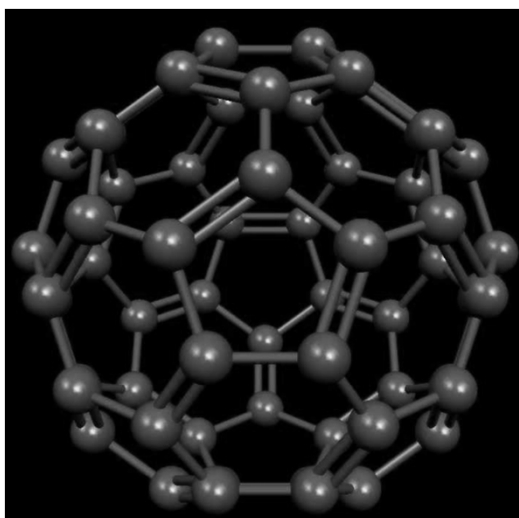
Bigger Still: A Two-Photon Absorbing Chromophore



HF/6-31G(d): Computation Time ~5.5 hours

Slide 85

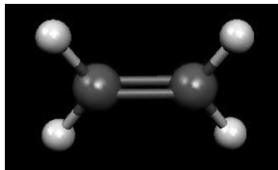
One More: Buckminsterfullerene (C₆₀)



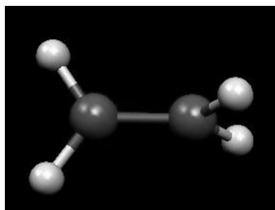
HF/STO-3G: 4.5 minutes

Slide 86

Excited Electronic States: $\pi \rightarrow \pi^*$ Singlet in Ethylene



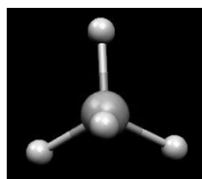
Ground State



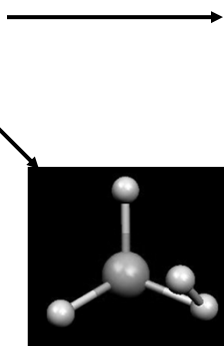
$\pi \rightarrow \pi^*$ Singlet

Slide 87

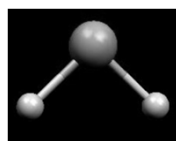
Transition State Structure: H_2 Elimination from Silane



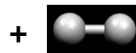
Silane



Transition State



Silylene



+

Slide 88

Two Level Calculations

As we'll learn shortly, it is often necessary to use fairly sophisticated correlation methods and rather large basis sets to compute accurate energies.

For example, it might be necessary to use the QCISD(T) method with the 6-311+G(3df,2p) basis to get a sufficiently accurate energy.

A geometry optimization at this level could be **extremely** time consuming, and furnish little if any improvement in the computed structure.

It is very common to use one method/basis set to calculate the geometry and a second method/basis set to determine the energy.

Slide 89

For example, one might optimize the geometry with the MP2 method and 6-31G(d) basis set.

Then a "Single Point" high level energy calculation can be performed with the geometry calculated at the lower level.

An example of the notation used for such a two-level calculation is:

QCISD(T) / 6-311+G(3df,2p) // MP2 / 6-31G(d)

↑	↑	↑	↑
Method for "Single Point" Energy Calc.	Basis set for "Single Point" Energy Calc.	Method for Geometry Optimization	Basis set for Geometry Optimization

Slide 90

Vibrational Frequencies

Applications of Calculated Vibrational Spectra

- (1) Aid to assigning experimental vibrational spectra
One can visualize the motions involved in the calculated vibrations
- (2) Vibrational spectra of transient species
It is usually difficult to impossible to experimentally measure the vibrational spectra in short-lived intermediates.
- (3) Structure determination.
If you have synthesized a new compound and measured the vibrational spectra, you can simulate the spectra of possible proposed structures to determine which pattern best matches experiment.

Slide 91

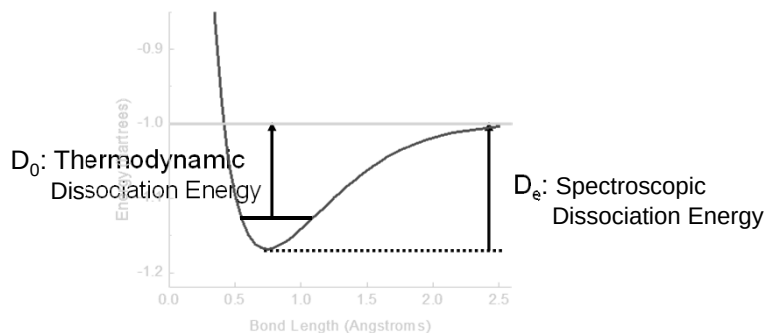
An Example: Vibrations of CH₄

Expt. [cm ⁻¹]	MP2/6-31G(d) [cm ⁻¹]	Scaled (0.95) MP2/6-31G(d) [cm ⁻¹]	HF/6-31G(d) [cm ⁻¹]	Scaled (0.90) HF/6-31G(d) [cm ⁻¹]
3019	3245	3083	3302	2972
2917	3108	2953	3197	2877
1534	1625	1544	1703	1532
1306	1414	1343	1488	1339

- Correlated frequencies (MP2 or other methods) are typically ~5% too high because they are “harmonic” frequencies and haven’t been corrected for vibrational anharmonicity.
- Hartree-Fock frequencies are typically ~10% too high because they are “harmonic” frequencies and do not include the effects of electron correlation.
- Scale factors (0.95 for MP2 and 0.90 for HF) are usually employed to correct the frequencies.

Slide 92

Bond Dissociation Energies: Application to Hydrogen Fluoride



Recall from Chapter 5 that D_e represents the Dissociation Energy from the bottom of the potential curve to the separated atoms.

Slide 93



Method/Basis	E _{HF}	E _H	E _F
HF/6-31G(d)	-100.003	-0.498	-99.365
HF/6-311++G(3df,2pd)	-100.058	-0.500	-99.402
MP2/6-311++G(3df,2pd)	-100.332	-0.500	-99.602
QCISD(T)/6-311++G(3df,2pd)	-100.341	-0.500	-99.618

HF/6-31G(d) calculation of D_e

$$D_e = E_H + E_F - E_{HF} = -0.498 - 99.365 - (-100.003)$$

$$= 0.140 \text{ au} \cdot \frac{2625 \text{ kJ/mol}}{\text{au}} = 367 \text{ kJ/mol}$$

Slide 94


Method/Basis
 D_e

Experiment 591 kJ/mol

HF/6-31G(d) 367

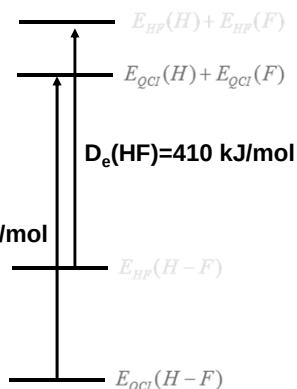
HF/6-311++G(3df,2p) 410

MP2/6-311++G(3df,2p) 604

QCISD(T)/6-311++G(3df,2p) 586

Hartree-Fock calculations predict values of D_e that are too low.

This is because errors due to neglect of the correlation energy are greater in the molecule than in the isolated atoms.



Slide 95

Thermodynamic Properties (Statistical Thermodynamics)

We have learned in earlier chapters how Statistical Thermodynamics can be used to compute the translational, rotational, vibrational and (when important) electronic contributions to thermodynamic properties including: Internal Energy (U)

Enthalpy (U)

Heat Capacities (C_v and C_p)

Entropy (S)

Helmholtz Energy (A)

Gibbs Energy (G)

For gas phase molecules, these calculations are so exact that the values computed from Stat. Thermo. are generally considered to be **THE** experimental values.

Slide 96

Enthalpies of Reaction

The energy determined by a quantum mechanics calculation at the equilibrium geometry is the Electronic Energy at the bottom of the potential well, E_{el} .

To convert this to the Enthalpy at a non-zero (Kelvin) temperature, typically 298.15 K, one must add in the following additional contributions:

1. Vibrational Zero-Point Energy
2. Thermal contributions to E (translational, rotational and vibrational)
3. PV (=RT) to convert from E to H

$$\begin{aligned} H(298.15\text{ K}) &= E_{el} + E_{ZPE}(vib) + E_{therm}(298.15\text{ K}) + PV \\ &= E_{el} + E_{ZPE}(vib) + E_{therm}(298.15\text{ K}) + RT \end{aligned}$$

Slide 97

Vibrational Zero-Point Energy

$$E_{ZPE}^{vib} = \frac{1}{2} N_A \sum_{i(vibs)} h\nu_i = \frac{1}{2} N_A \sum_{i(vibs)} hc\tilde{\nu}_i$$

Thermal Contributions to the Energy

$$E_{trans}(T) = \frac{3}{2} RT$$

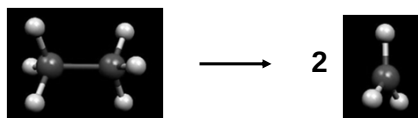
$$E_{rot}(T) = RT \quad (\text{Linear molecules})$$

Does not include vibrational ZPE

$$E_{therm}^{vib}(T) = R \cdot \sum_{i(vibs)} \frac{\Theta_{vib,i}}{e^{\Theta_{vib,i}/T} - 1} \quad \Theta_{vib,i} \equiv \frac{hc\tilde{\nu}_i}{k}$$

Slide 98

Ethane Dissociation



HF/6-31G(d)
Data

Molecule	E(el)	E _{ZPE(vib)}	E _{therm}	PV (=RT)	H(298.15)
C ₂ H ₆	-79.2288	0.0712	0.0035	0.0009	-79.1530
CH ₃	-39.5590	0.0277	0.0033	0.0009	-39.5271

$$\Delta E_{el} = 2E_{el}(\text{CH}_3) - E_{el}(\text{C}_2\text{H}_6) = 2 \cdot (-39.5590) - (-79.2280)$$

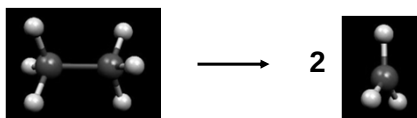
$$= 0.110 \text{ au} \cdot \frac{2625 \text{ kJ/mol}}{\text{au}} = 289 \text{ kJ/mol}$$

$$\Delta H = 2H(\text{CH}_3) - H(\text{C}_2\text{H}_6) = 2 \cdot (-39.5271) - (-79.1530)$$

$$= 0.0988 \text{ au} \cdot \frac{2625 \text{ kJ/mol}}{\text{au}} = 259 \text{ kJ/mol}$$

Note that there is a significant difference between ΔE_{el} and ΔH .

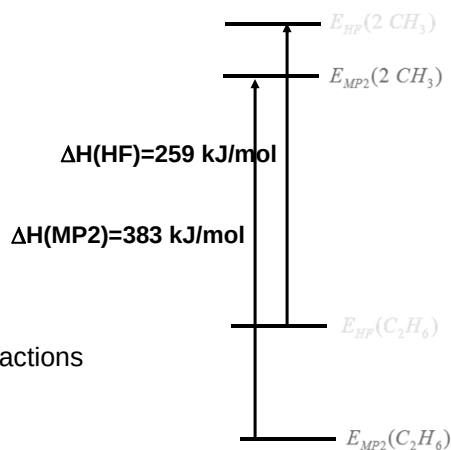
Slide 99



Method	ΔH
Experiment	375 kJ/mol
HF/6-31G(d)	259
HF/6-311++G(3df,2p)	243
MP2/6-311++G(3df,2p)	383

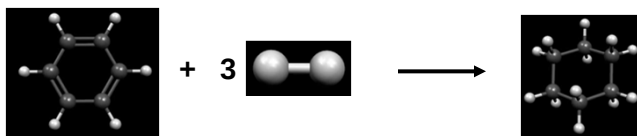
Hartree-Fock energy changes for reactions are usually **very** inaccurate.

The magnitude of the correlation energy in C₂H₆ is greater than in CH₃.



Slide 100

Hydrogenation of Benzene



Method	ΔH
Experiment	-206 kJ/mol
HF/6-31G(d)	-248
HF/6-311G(d,p)	-216
MP2/6-311G(d,p)	-211

We got lucky !!

Errors in HF/6-311G(d,p) energies cancelled.

Slide 101

Reaction Equilibrium Constants

Reactants $\rightleftharpoons$ Products

$$\Delta G^0 = -RT \ln(K_{eq}) \quad + \quad \Delta G^0 = \Delta H^0 - T\Delta S^0$$

↓

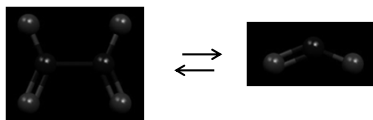
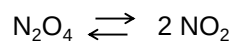
$$\ln(K_{eq}) = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \text{or} \quad K_{eq} = e^{-\frac{\Delta G^0}{RT}} = e^{\frac{\Delta S^0}{R}} e^{-\frac{\Delta H^0}{RT}}$$

Quantum Mechanics can be used to calculate enthalpy changes for reactions, ΔH^0 .

It can also be used to compute entropies of molecules, from which one can obtain entropy changes for reactions, ΔS^0 .

Slide 102

Application: Dissociation of Nitrogen Tetroxide



Experiment

T	$K_{\text{eq}}(\text{Exp})$
25 °C	0.15
100	15.1

Slide 103

K_{eq} at 25 °C

Calculations were performed at the MP2/6-311G(d,p) // MP2/6-31G(d) level

Molecule	H^0	S^0
	[au]	[J/mol-K]
N_2O_4	-409.300	308.2
NO_2	-204.639	244.8

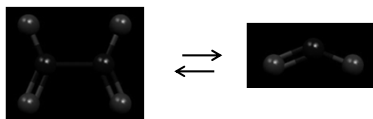
$$\begin{aligned} \Delta H^0 &= 2H^0(\text{NO}_2) - H^0(\text{N}_2\text{O}_4) = 2(-204.639) - (-409.300) \\ &= +0.022 \text{ au} \cdot 2625 \text{ kJ/mol au} = 57.75 \text{ kJ/mol} \end{aligned}$$

$$\Delta S^0 = 2S^0(\text{NO}_2) - S^0(\text{N}_2\text{O}_4) = 2(244.8) - 308.2 = 181.4 \text{ J/mol-K}$$

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0 = 5.775 \times 10^4 \text{ J/mol} - (298 \text{ K})(181.4 \text{ J/mol-K}) \\ &= 3690 \text{ J/mol} \end{aligned}$$

$$K = e^{-\Delta G^0/RT} = e^{-3690/(8.314 \cdot 298)} = 0.23$$

Slide 104



T	$K_{eq}(\text{Exp})$	$K_{eq}(\text{Cal})$
25 °C	0.15	0.23
100	15.1	34.5

The agreement is actually better than I expected, considering the **Curse of the Exponential Energy Dependence**.

Slide 105

Curse of the Exponential Energy Dependence

$$K = e^{-\frac{\Delta G}{RT}} = e^{\frac{\Delta S}{R}} e^{-\frac{\Delta H}{RT}}$$

Energy (ΔE) and enthalpy (ΔH) changes for reactions remain difficult to compute accurately (although methods are improving all of the time).

Because $K \propto e^{-\Delta H/RT}$, small errors in ΔH_{cal} create much larger errors in the calculated equilibrium constant.

We illustrate this as follows. Assume that (1) there is no error between the calculated and experimental entropy change: $\Delta S_{cal} = \Delta S_{exp}$, and (2) that there is an error in the enthalpy change: $\Delta H_{cal} = \Delta H_{exp} + \delta(\Delta H)$

$$K_{cal} = e^{\frac{\Delta S_{cal}}{R}} e^{-\frac{\Delta H_{cal}}{RT}} = e^{\frac{\Delta S_{exp}}{R}} e^{-\frac{\Delta H_{exp} + \delta(\Delta H)}{RT}} = e^{\frac{\Delta S_{exp}}{R}} e^{-\frac{\Delta H_{exp}}{RT}} e^{-\frac{\delta(\Delta H)}{RT}} = K_{exp} e^{-\frac{\delta(\Delta H)}{RT}}$$

Slide 106

$$K_{cal} = K_{exp} e^{-\frac{\delta(\Delta H)}{RT}} \longrightarrow \frac{K_{cal}}{K_{exp}} = e^{-\frac{\delta(\Delta H)}{RT}}$$

At room temperature (298 K), errors of ± 5 kJ/mol and ± 10 kJ/mol in ΔH will cause the following errors in K_{cal} .

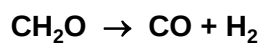
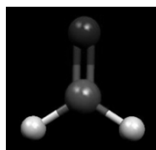
$\delta(\Delta H)$	K_{cal}/K_{exp}
+10 kJ/mol	0.02
+5	0.13
-5	7.5
-10	57

One can see that relatively small errors in ΔH lead to much larger errors in K .

That's why I noted that the results for the N_2O_4 dissociation equilibrium (within a factor of 2 of experiment) were better than I expected.

Slide 107

The Mechanism of Formaldehyde Decomposition

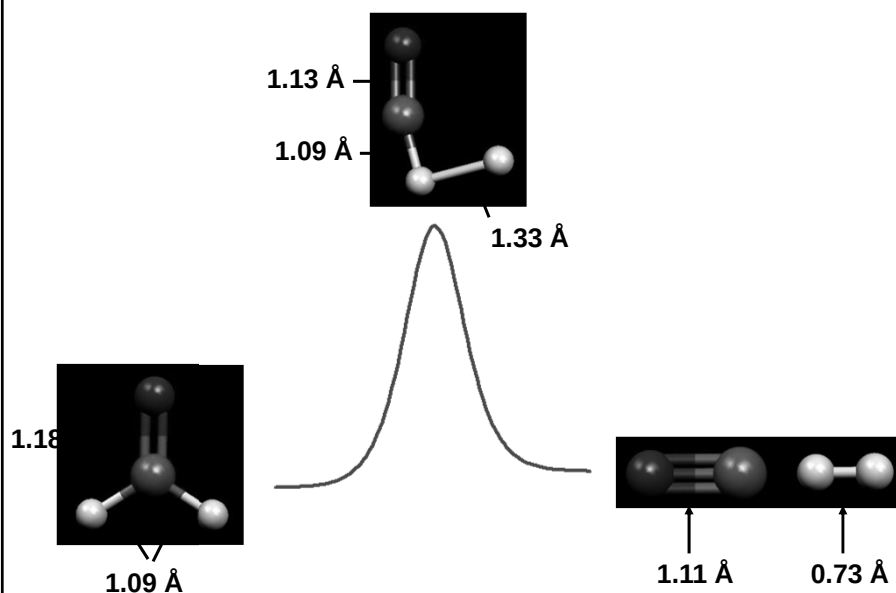


How do the two hydrogen atoms break off from the carbon and then find each other?

Quantum mechanics can be used to determine the structure of the reactive transition state (with the lowest energy) leading from reactants to products.

Slide 108

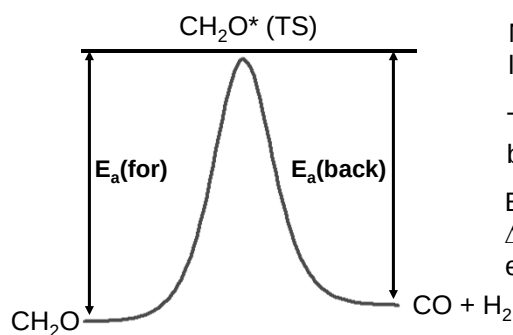
Geometries calculated at the HF/6-31G(d) level



Slide 109

The Energy Barrier (aka "Activation Energy")

Method	Energies in au's				Barriers in kJ/mol	
	CH ₂ O	CH ₂ O* (TS)	CO	H ₂	E _a (For)	E _a (Back)
HF/6-31G*	-113.866	-113.694	-112.738	-1.127	454	449
HF/6-311+G(d,p)	-113.903	-113.740	-112.771	-1.132	427	428
MP2/6-31G*	-114.165	-114.009	-113.018	-1.144	411	403
MP2/6-311+G(d,p)	-114.240	-114.094	-113.077	-1.160	383	374



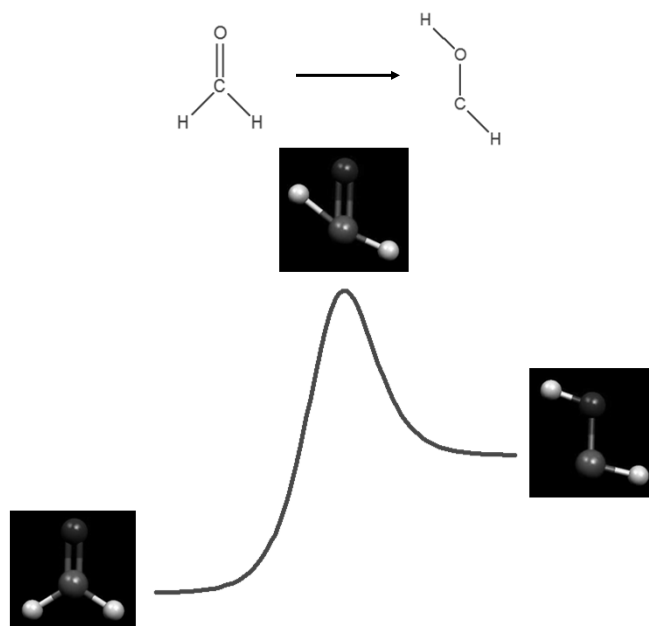
Note that HF barriers (even with large basis set) are too high.

The above are "classical" energy barriers, which are $\Delta E_{el}^\ddagger$.

Barriers can be converted to $\Delta H^\ddagger$ in the same manner shown earlier for reaction enthalpies.

Slide 110

Another Reaction: Formaldehyde 1,2-Hydrogen shift

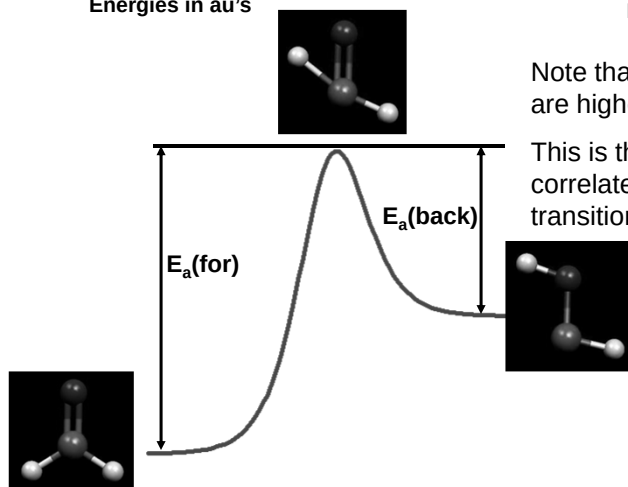


Slide 111

Method	CH_2O	TS	HCOH	$E_a(\text{For})$	$E_a(\text{Back})$
HF/6-31G(d)	-113.86633	-113.69964	-113.78352	438	220
HF/6-311+G(d,p)	-113.90274	-113.74315	-113.82478	419	214
MP2/6-31G(d)	-114.16527	-114.01936	-114.07021	383	133
MP2/6-311+G(d,p)	-114.24005	-114.10227	-114.15315	362	134

Energies in au's

Barriers in kJ/mol



Note that, as before, H-F barriers are higher than MP2 barriers.

This is the norm. One **must** use correlated methods to get accurate transition state energies.

Slide 112

Reaction Rate Constants

The Eyring Transition State Theory (TST) expression for reaction rate constants is:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

$\Delta G^\ddagger$ is the free energy of activation.

It is related to the activation entropy, $\Delta S^\ddagger$, and activation enthalpy, $\Delta H^\ddagger$, by: $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

$$\text{where } \Delta H^\ddagger = H^{TS} - H^{Rct}$$

$$\Delta S^\ddagger = S^{TS} - S^{Rct}$$

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}$$

Slide 113

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}} \quad \text{where } \Delta H^\ddagger = H^{TS} - H^{Rct}$$

$$\Delta S^\ddagger = S^{TS} - S^{Rct}$$

Quantum Mechanics can be used to calculate $\Delta H^\ddagger$ and $\Delta S^\ddagger$, which can be used in the TST expression to obtain calculated rate constants.

QM has been used successfully to calculate rate constants as a function of temperature for many gas phase reactions of importance to atmospheric and environmental chemistry.

The same as for equilibrium constants, the calculation of rate constants suffers from the **curse of the exponential energy dependence**.

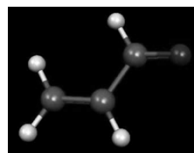
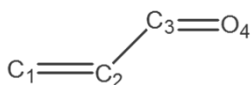
A calculated rate constant within a factor of 2 or 3 of experiment is considered a success.

Slide 114

Orbitals, Charge and Chemical Reactivity

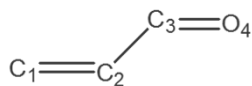
One can often use the frontier orbitals (HOMO and LUMO) and/or the calculated charge on the atoms in a molecule to predict the site of attack in nucleophilic or electrophilic addition reactions

For example, acrolein is a good model for unsaturated carbonyl compounds.



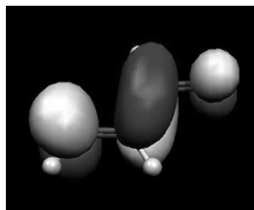
Nucleophilic attack can occur at any of the carbons or at the oxygen.

Slide 115



Nucleophiles add electrons to the substrate. Therefore, one might expect that the addition will occur on the atom containing the largest LUMO coefficients.

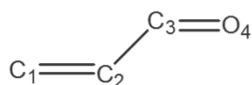
Acrolein
LUMO



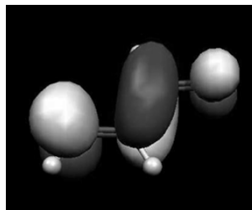
Let's tabulate the LUMO's orbital coefficient on each atom (C or O). These are the coefficients of the p_z orbital.

Based upon these coefficients, the nucleophile should attack at C_1 .

Slide 116



Acrolein
LUMO



Based upon these coefficients, the nucleophile should attack at C_1 .

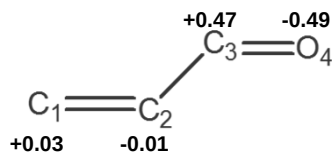
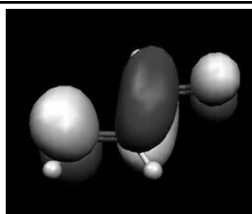
This prediction is *usually* correct.

“Soft” nucleophiles (e.g. organocuprates) attack at C_1 .

However “hard” (ionic) nucleophiles (e.g. organolithium compounds) tend to attack at C_3 .

Slide 117

Acrolein
LUMO



Let's look at the calculated (Mulliken) charges on each atom (with hydrogens summed into heavy atoms).

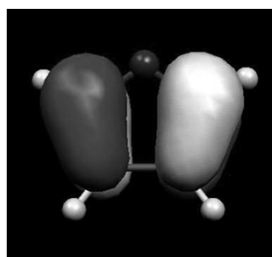
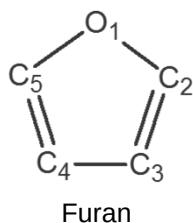
Indeed, the charges predict that a hard (ionic) nucleophile will attack at C_3 , which is found experimentally.

These are examples of: Orbital Controlled Reactions
(soft nucleophiles)
Charge Controlled Reactions
(hard nucleophiles)

Slide 118

Another Example: Electrophilic Reactions

An electrophile will react with the substrate's frontier electrons. Therefore, one can predict that electrophilic attack should occur on the atom with the largest HOMO orbital coefficients.



HOMO

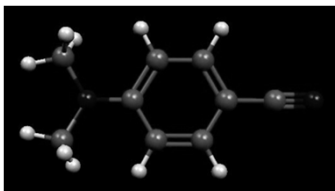
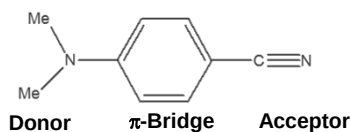
The HOMO orbital coefficients in Furan predict that electrophilic attack will occur at the carbons adjacent to the oxygen.

This is found experimentally to be the case.

Slide 119

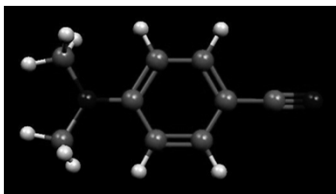
Molecular Orbitals and Charge Transfer States

Dimethylaminobenzonitrile (DMAB-CN) is an example of an aromatic Donor-Acceptor system, which shows very unusual excited state properties.



Slide 120

Ground State: $\mu \approx 6 \text{ D}$

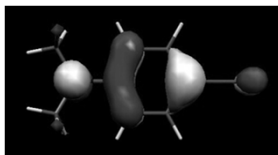


Excited State: $\mu \approx 20 \text{ D}$

Slide 121

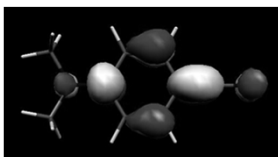
The basis for this enormous increase in the excited state dipole moment can be understood by inspection of the frontier orbitals.

HOMO



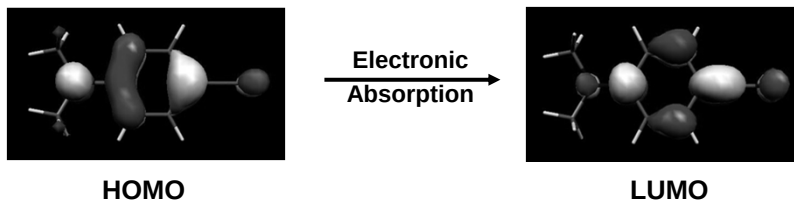
Electron density in the HOMO lies predominantly in the portion of the molecule nearest the electron donor (dimethylamino group)

LUMO



Electron density in the LUMO lies predominantly in the portion of the molecule nearest the electron acceptor (nitrile group)

Slide 122



Excitation of the electron from the HOMO to the LUMO induces a very large amount of charge transfer, leading to an enormous dipole moment.

This leads to very large Electrical “Hyperpolarizabilities” in these electron Donor/Acceptor complexes, leading to anomalously high “Two Photon Absorption” cross sections.

These materials have potential applications in areas ranging from 3D Holographic Imaging to 3D Optical Data Storage to Confocal Microscopy.

Slide 123

NMR Chemical Shift Prediction

Compound	$\delta(^{13}\text{C})$ Expt.	$\delta(^{13}\text{C})$ Calc.
Ethane	8 ppm	7 ppm
Propane (C_1)	16	16
Propane (C_2)	18	16
Ethylene	123	123
Acetylene	72	64
Benzene	129	129
Acetonitrile (C_1)	118	109
Acetonitrile (C_2)	0	0
Acetone (C_1)	31	28
Acetone (C_2)	207	206

B3LYP/6-31G(d) calculation. D. A. Forsyth and A. B. Sebag,
J. Am. Chem. Soc. **119**, 9483 (1997)

Slide 124

Dipole Moment Prediction

Method	H ₂ O	NH ₃
Experiment	1.85 D	1.47 D
HF/6-31G(d)	2.20	1.92
HF/6-311G(d,p)	1.74	2.14
HF/6-311++G(3df,2pd)	1.98	1.57
MP2/6-311G(d,p)	2.10	1.75
MP2/6-311++G(3df,2pd)	1.93	1.56
QCISD/6-311++G(3df,2pd)	1.93	1.55

The quality of agreement of the calculated with the experimental Dipole Moment is a good measure of how well your wavefunction represents the electron density.

Note from the examples above that computing an accurate value of the Dipole Moment requires a large basis set and treatment of electron correlation.

Slide 125

Some Additional Applications

- Ionization Energies
- Electron Affinities
- Electronic Excitation Energies and Excited State Properties
- Potential Energy Surfaces
- Enthalpies of Formation
- Solvent Effects on Structure and Reactivity
- Structure and Bonding of Complex Species (e.g. TM Complexes)
- Others

Slide 126