Quantum Chemistry I

For students of HI 6327 "Biomolecular Modeling"

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http://biomachina.org/courses/modeling/11.html

Quantum Mechanics

Is it possible to learn QM without math and atomic physics?

• Probably not very well.

• However, it is critical to start with quantum mechanics, because it is really the foundation of the "bottom-up" approach to biomolecular modeling.

• Goals for this lecture:

1. Provide an intuitive feel for quantum systems using model systems.

2. Introduce basics of electronic structure calculations, which are critical for force fields and docking calculations.

3. Understand the key scientific ideas behind the jargon (what does 6-31G* really mean, anyways?).

Fundamental QM Concepts

- Wave-Particle Duality:

  Matter and light both behave like waves and particles SIMULTANEOUSLY.

- Heisenberg Uncertainty Principle:

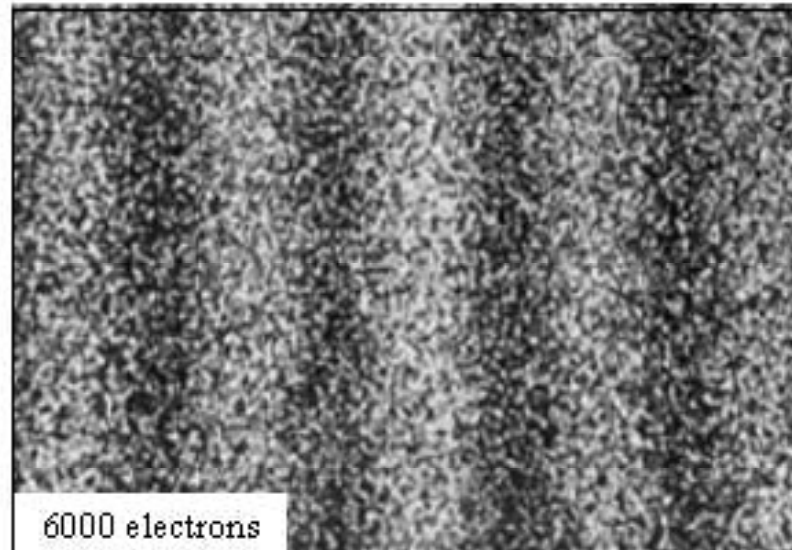 We can only know APPROXIMATELY how much energy a particle has, where it's located or what its speed has.

- Elementary particles (such as electrons) cannot be distinguished from each other.

The Two-Slit Experiment: Light

© http://commons.wikimedia.org/wiki/Image:YoungsDoubleSlit.png
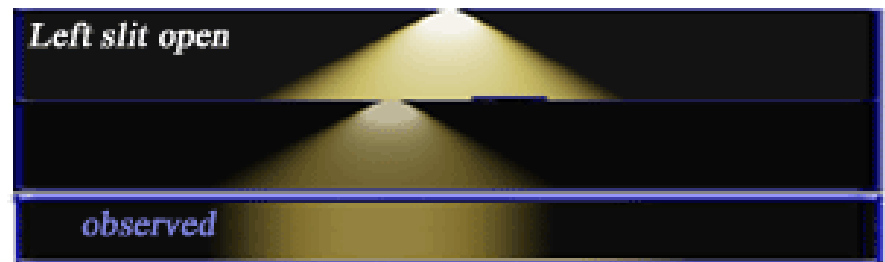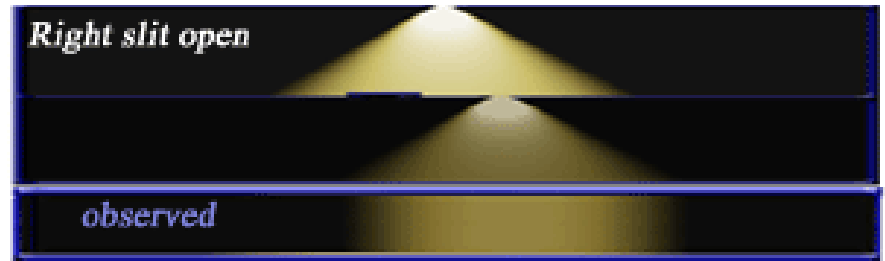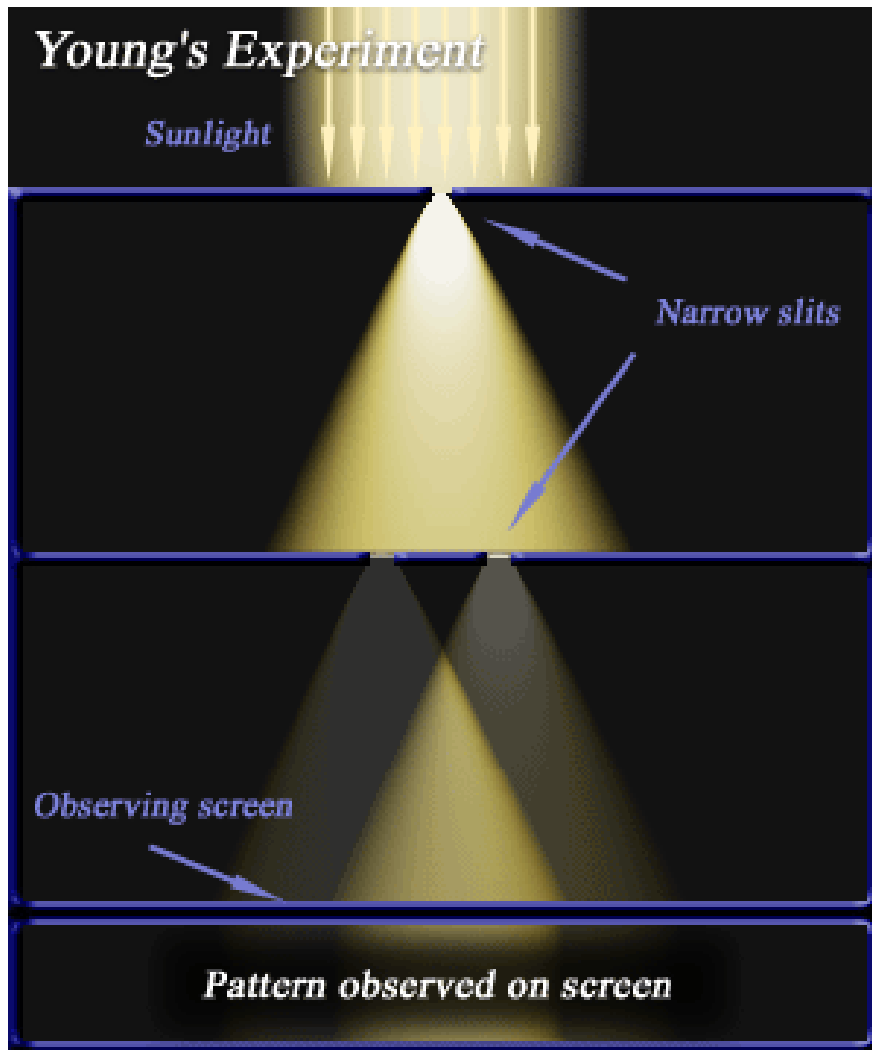
The Two-Slit Experiment: Electrons

8 electrons

270 electrons

2000 electrons

6000 electrons

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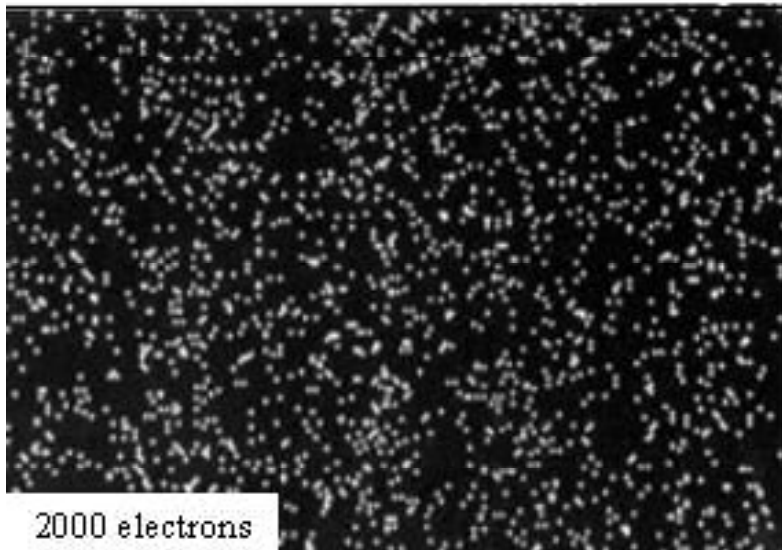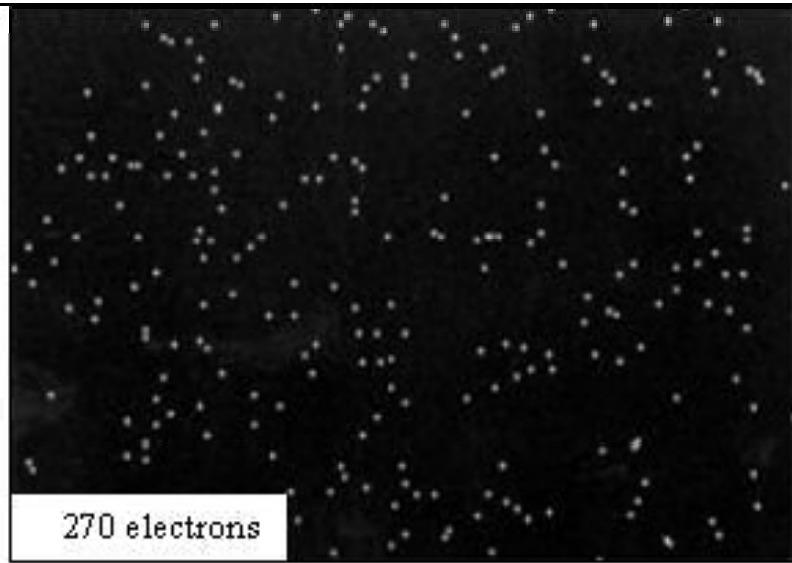
Atomic Structure and Bonding

The Structure of an Atom

- An atom consists of a dense nucleus that contains positively charged protons and neutral neutrons.

http://www.aboutnuclear.org
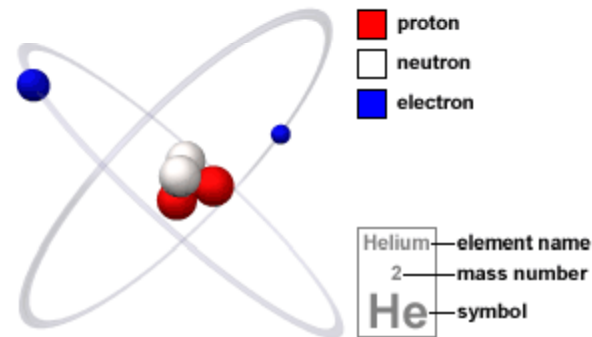
- The nucleus is positively charged

- The space around the nucleus contains negatively charge electrons

- The amount of positive charge in protons and negative charge in electrons is the same, so a neutral atom has an equal number of protons and electrons.

- Protons and neutrons have approximately the same mass and are 1833 times as massive as electrons.

- Atoms can become charged as a result of gaining or losing electrons.

- The numbers of protons in an atom does not change.

Distribution of Electrons in an Atom

- Electrons are continuously "moving" within an atom or molecule

- Quantum Mechanics (QM) uses the same mathematical equations that describe the wave motion of a guitar string to characterize the motion of an electron around a nucleus

- The most useful version of QM to chemist was proposed by Erwin Schrödinger

- The behavior of each electron in an atom or a molecule can be described by a wave equation. A wave equation has a series of solutions → wave functions.

- Solving the wave equation for a given electron tells us the volume of space around the nucleus where the electron is most likely to be found → This volume of space is called an orbital

- The orbitals can be described by its wave function ψ, which is the mathematical description of the shape of the wave.

Atom Orbitals

- According to QM, the electrons in an atom can be thought of as occupying a set of concentric shells that surround the nucleus.

- The 1st shell is the one closest to the nucleus. The 2nd shell lies farther from the nucleus, and even farther out lie the third and higher-numbered shells.

- Each shell contains subshells → atomic orbitals.

- 1st shell: an *s* atomic orbital

- 2nd shell: *s* and *p* atomic orbitals

- 3rd shell: s, p, and d atomic orbitals

- 4th shell: s, p, d and f atomic robitals

Atomic Orbitals
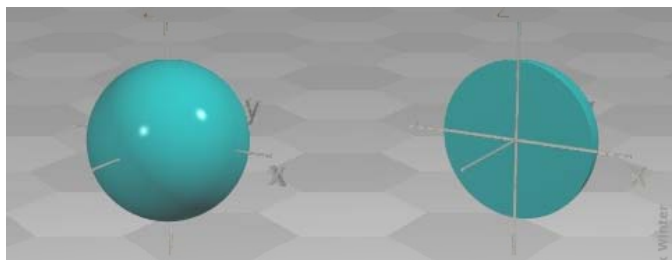
The shape of the 1s orbital.
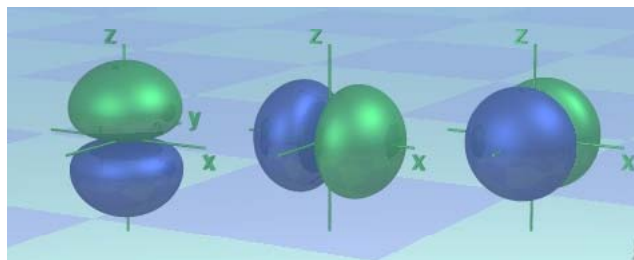
The shape of the three 2p orbitals. From left to right: 2p_z, 2p_x, and 2p_y. For each, the blue zones are where the <u>wave functions</u> have negative values and the green zones denote positive values.
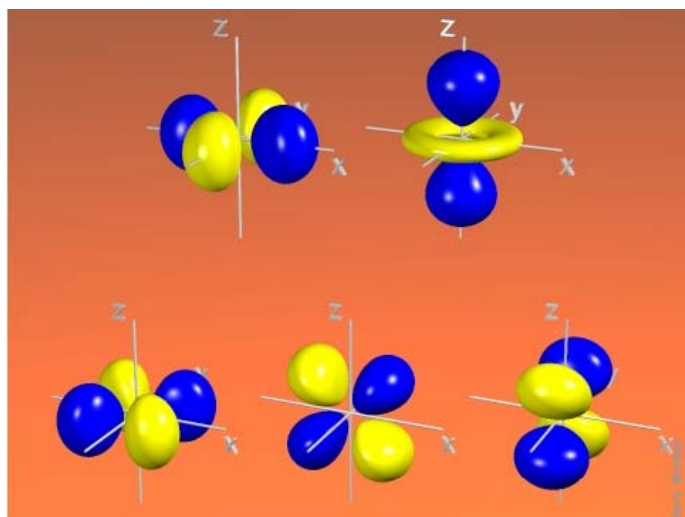
The shape of the five 3d orbitals. From left to right: (top row) 3$d_{x^2-y^2}$ and 3d_{z^2} (bottom row) 3d_{xy}, 3d_{xz}, and 3d_{yz}. For each, the yellow zones are where the wave functions have negative values and the blue zones denote positive values.
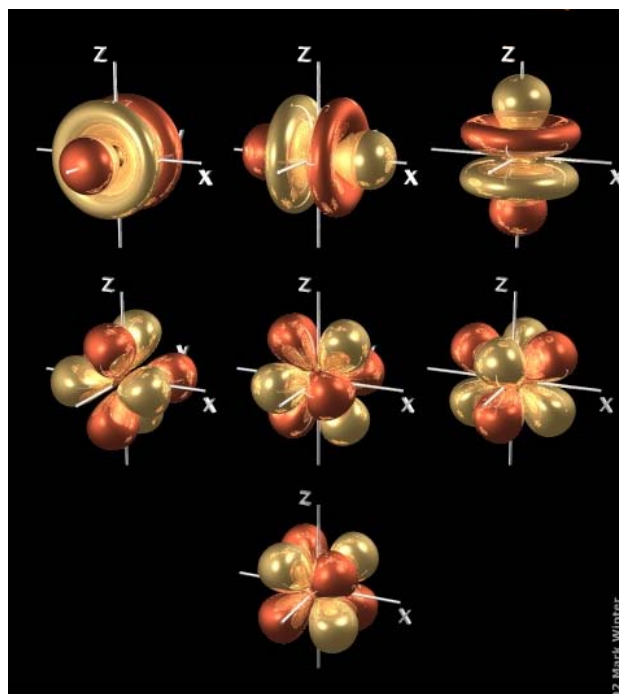
Degenerate orbitals

The shape of the seven 4f orbitals (cubic set). From left to right: (top row) 4f_y^3, 4f_x^3, 4f_z^3, (middle row) 4$f_{x(z^2-y^2)}$, 4$f_{y(z^2-x^2)}$, 4$f_{z(x^2-y^2)}$, and (bottom row) 4f_{xyz}. For each, the copper zones are where the wave functions have negative values and the gold zones denote positive values.

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Which Orbitals are Occupied?

- Aufbau principle: an electron always goes into the available orbital with the lowest energy

1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f

- Pauli exclusion principle: (a) no more than two electrons can occupy each orbital and (b) the two electrons must be of opposite spin ($+\frac{1}{2}\ or\ -\frac{1}{2}$)

- Hund's rule: when there are degenerate orbitals, an electron will occupy an empty orbital before it will pair up with another electron.

Hybridization and Molecular Shapes

• Bond angles in organic compounds are usually close to 109⁰ (tetrahedral), 120⁰ (trigonal), or 180⁰ (linear).

• The shapes of these organic molecules cannot result from bonding between simple s and p atomic orbitals.

• We assume that the s and p orbitals combine to form hybrid atomic orbitals that separate the electron pairs more widely in space and place more electron density in the bonding region between the nuclei.

Hybrid Orbitals

	Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs sp		Linear	$180°$ $BeCl_2$
Three electron pairs sp^2		Trigonal-planar	$120°$ BF_3
Four electron pairs sp^3		Tetrahedral	$109.5°$ CH_4

σ Bond Formation by Orbital Overlap

H   **H**
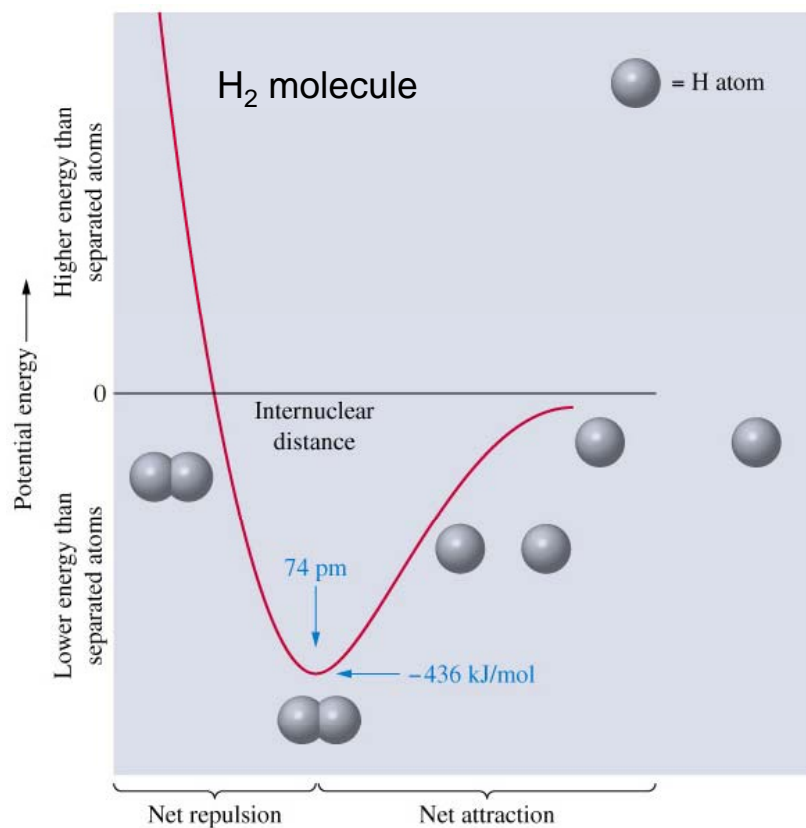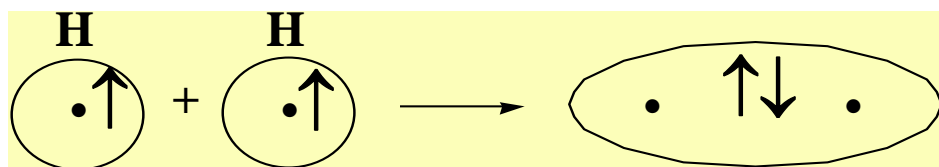
σ bond: The bonding MO has most of its electron density centered along the line connecting the nuclei

- All single bonds in organic compounds are σ bonds;

- Every double or triple bond contains one σ bond

H₂ molecule   = H atom

Potential energy

Higher energy than separated atoms

Lower energy than separated atoms

0

Internuclear distance

74 pm

−436 kJ/mol

Net repulsion   Net attraction

Example: two p orbitals overlap
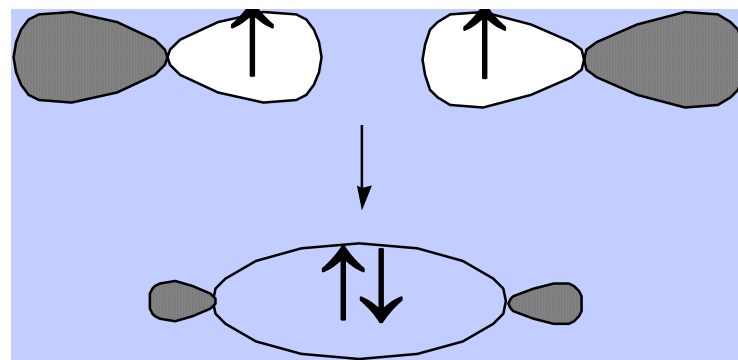
π Bond Formation by Orbital Overlap

A π bond results from overlap between two p orbitals oriented perpendicular to the line connecting the nuclei. All of the electron density is centered above and below the line connecting the nuclei.
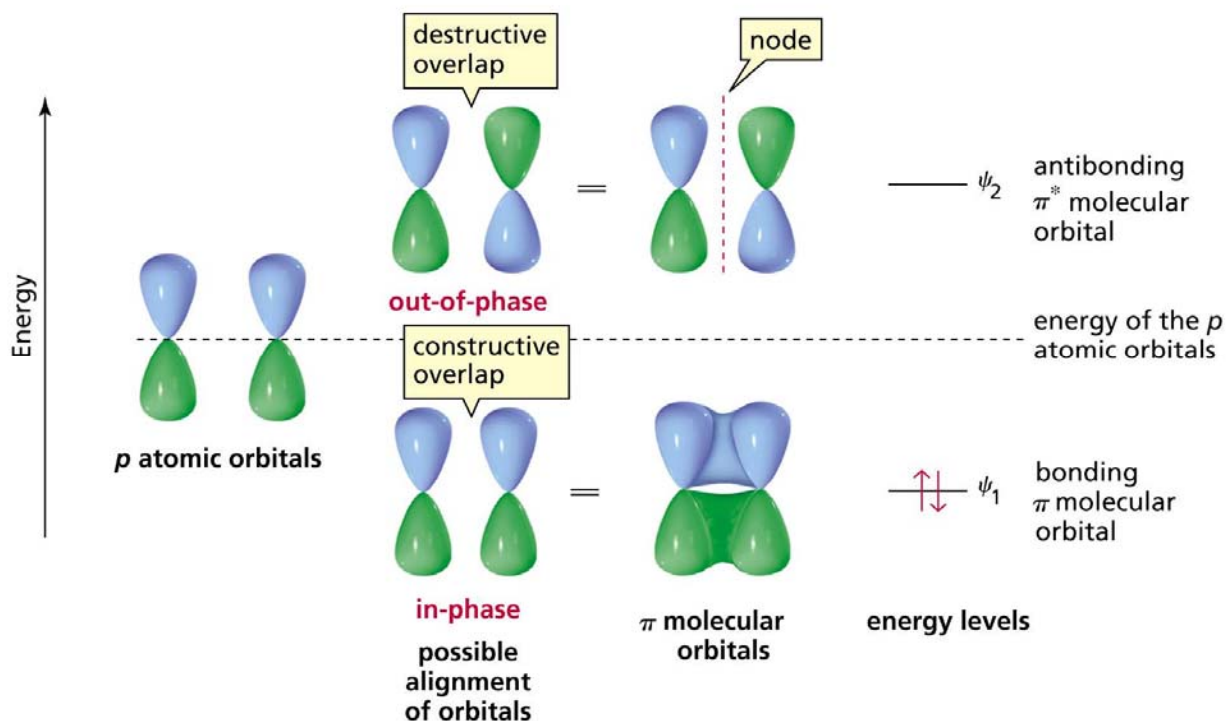
The sideways overlap of two p orbitals leads to a π bonding MO and a π antibonding MO. A π bond is not as strong as most σ bonds.

σ Bonds in C₂H₄

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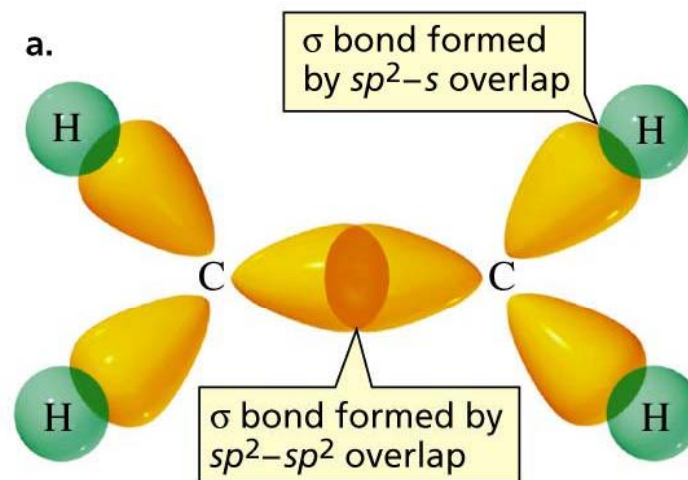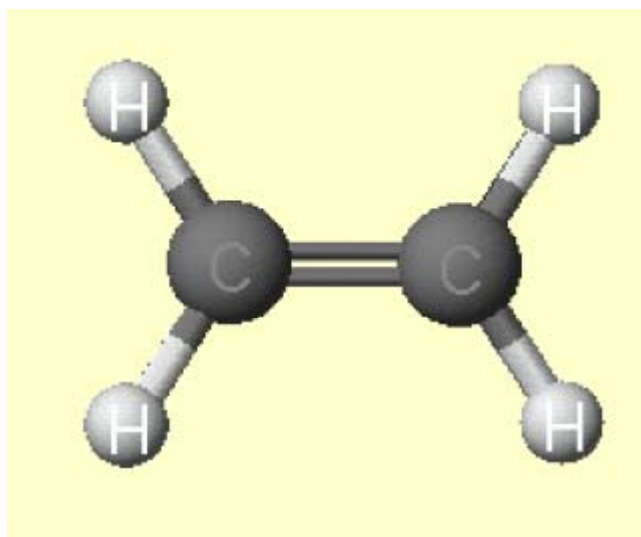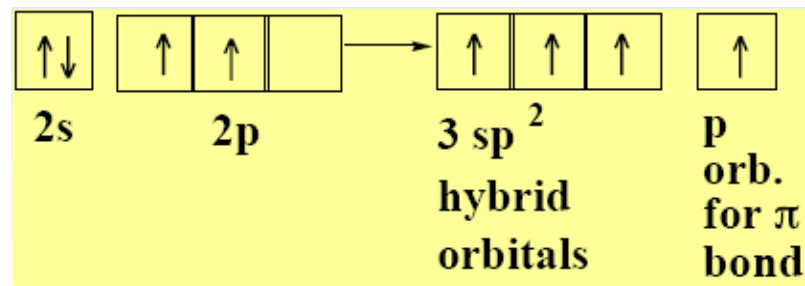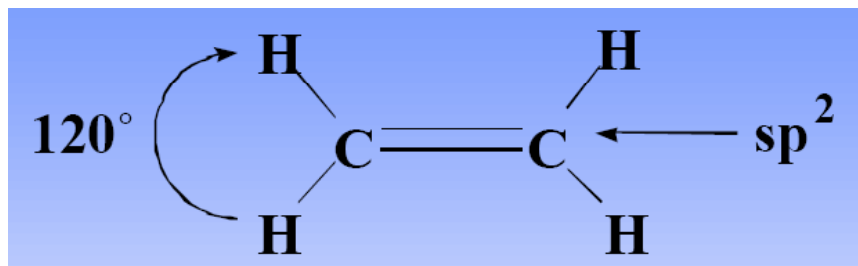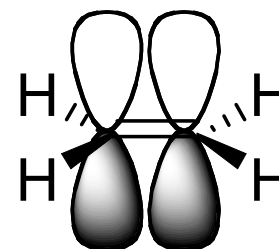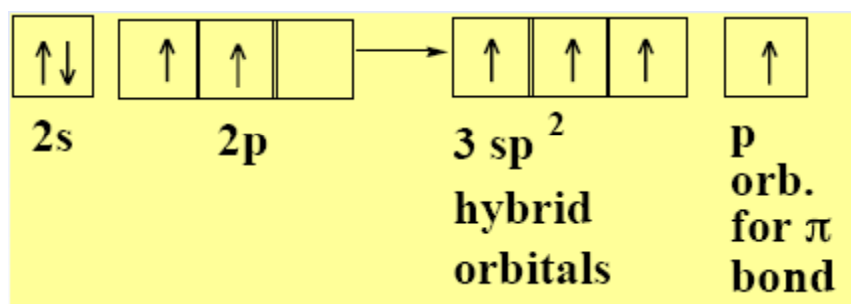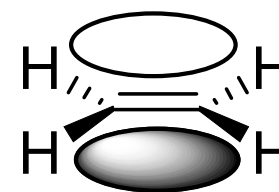
π Bonds in C₂H₄

The unused p orbital on each C atom contains an electron and this p orbital overlaps the p on the neighboring atom to form the π bond.
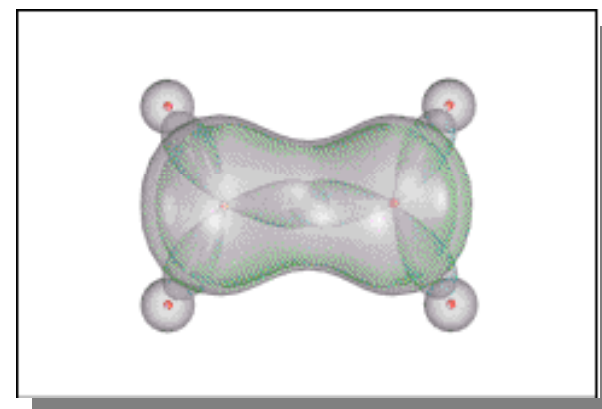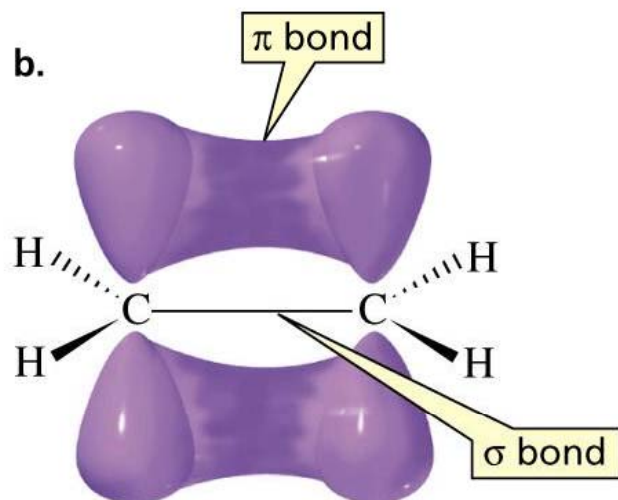
σ and π Bonds in C$_2$H$_4$
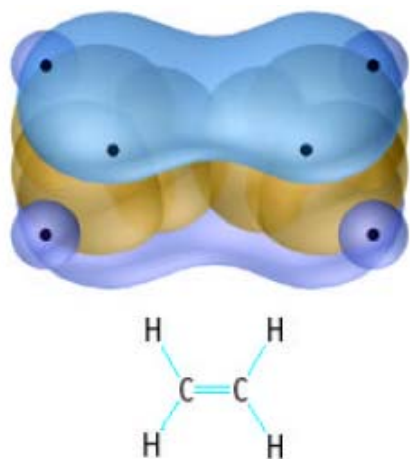
(a) Lewis structure and bonding of ethylene, C$_2$H$_4$.
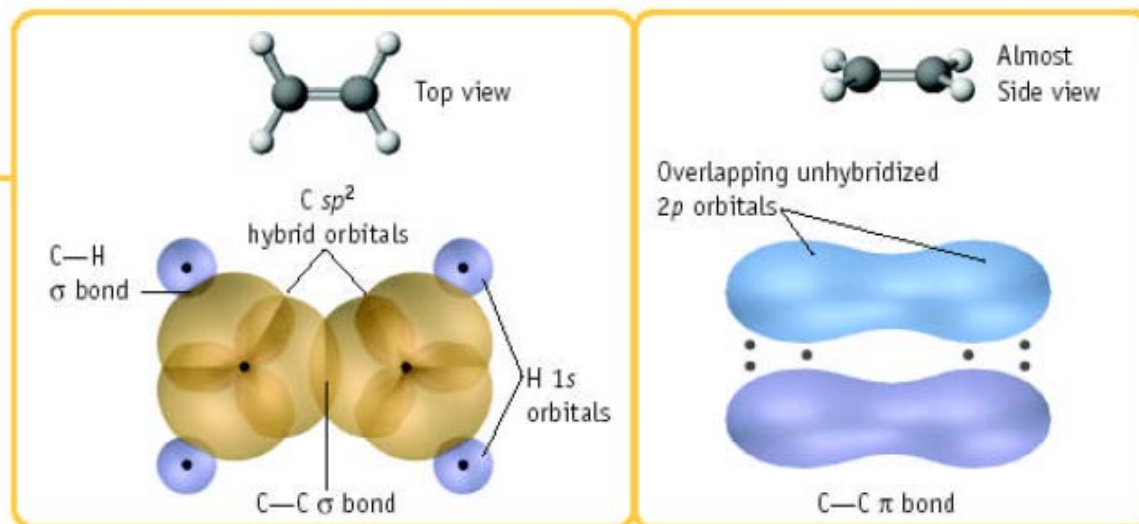
(b) The C—H σ bonds are formed by overlap of C atom sp^2 hybrid orbitals with H atom $1s$ orbitals. The σ bond between C atoms arises from overlap of sp^2 orbitals.

(c) The carbon-carbon π bond is formed by overlap of an unhybridized $2p$ orbital on each atom. Note the lack of electron density along the C—C bond axis.

We will return to Bonding later… (H_2^+)

Questions: Atom Structure and Bonding?

Next: Computational Quantum Mechanics

MM vs. QM

$$-\frac{dV}{dr} = m\frac{d^2r}{dt^2}$$

- In classical mechanics, Newton's second law is used to describe the dynamics of the system, i.e. how the system evolves in time.

- Molecular Mechanics (also known as force field methods) ignore the electronic motions and calculate the energy of a system as a function of the nuclear positions only.

- MM is thus invariably used to perform calculations on systems containing significant numbers of atoms.

- In some cases, MM can provide answers that are very accurate within short time compare to QM

- However, MM cannot provide properties that depend upon the electronic distribution in a molecule, such as forming or breaking bonds.

- QM is often used to determine parameters for MM simulations.

QM: Schrödinger Equation

• Electrons are very light particles

• They display both wave and particle characteristics, and must be described in terms of wavefunction, Ψ.

• The starting point for many discussion of quantum mechanics is:

Time-dependent Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V \right\} \Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}$$

• A single particle (e.g. an electron) of mass m which is moving through space and time (t) under the influence of an external field V (which might be the electrostatic potential generated by the nuclei in a molecule).

• The kinetic energy operator:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

QM vs. MM

- **Pros:**

  1. Quantum mechanics explicitly represents the electrons in the calculation, so it is possible to derive properties that depend upon the electronic distribution and, in particular, to investigate chemical reactions in which bonds are broken and formed.

  2. Well-defined hierarchy – in principle can always be systematically improved to obtain chemical accuracy

  3. Does not need to be parameterized or calibrated with respect to experiment

  4. Can describe excited electronic states, structure, properties, and energetics

- **Cons:**

  Computationally very expensive

Wavefunction and Probability

- Ψ is the wavefunction which characterizes the particle's motion
- contains all the measurable information about the particle
- The wavefunction represents the probability amplitude for finding a particle at a given point in space at a given time
- $|\Psi|^2$ is the probability distribution of the particles
- The integration of the probability of finding the particle over all space must be 1:

$$\int \Psi^* \Psi \, d\tau = 1$$

- The wavefunction of a complete system is commonly composed of a set of single-particle orbitals.

Time-Independent Schrödinger Equation

When the external potential is independent of time then the wave function can be written as the product of a spatial part and a time part:

$$\Psi(r,t) = \Psi(r)T(t)$$

This results in the time-independent Schrödinger equation:

$$\left\{ -\frac{\hbar^2}{2m}\nabla^2 + V \right\}\Psi(r) = E\Psi(r)$$

where *E* is the energy of the particle.

Hamiltonian operator: $\hat{\mathrm{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V$

Time-Independent Schrödinger Equation

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

- Find values of E and functions Ψ

- Partial differential eigenvalue equations: an operator acts on a function (the eigenfunction) and returns the function multiplied by a scalar (the eigenvalue)

- Example of an eigenvalue equation:

operator

$$\frac{d}{dx}(y) = ry$$

One eigenfunction is
$$y = e^{ax}$$
with the eigenvalue r being equal to a

- The Schrödinger equation is a second-order differential equation as it involves the second derivative of Ψ

Hamiltonian for a Molecule

$$\hat{\mathbf{H}} = \sum_{i}^{electrons} \frac{-\hbar^2}{2m_e}\nabla_i^2 + \sum_{A}^{nuclei} \frac{-\hbar^2}{2m_A}\nabla_A^2 + \sum_{i}^{electrons}\sum_{A}^{nuclei} \frac{-e^2 Z_A}{r_{iA}} + \sum_{i>j}^{electrons} \frac{e^2}{r_{ij}} + \sum_{A>B}^{nuclei} \frac{e^2 Z_A Z_B}{r_{AB}}$$

- kinetic energy of the electrons
- kinetic energy of the nuclei
- electrostatic interaction between the electrons and the nuclei
- electrostatic interaction between the electrons
- electrostatic interaction between the nuclei

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Variational Theorem

- The expectation value of the Hamiltonian is the variational energy

$$\frac{\int \Psi^* \hat{\mathbf{H}} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau} = E_{var} \geq E_{exact}$$

- An approximate wavefunction for a molecular system, when substituted into the Schrödinger equation, will always yield a higher energy than the actual energy of the system.

- The more precise the wavefunction that is chosen, the closer will the calculated energy be to the true energy.

- The computational method using this principle to obtain approximations to correct wavefunctions is called the *variational method*.

- The method is commonly restricted to the *ground state,* but can be extended to others provided they are orthogonalized to the (true) ground state.

Hartree Approximation

- Assume that a many electron wavefunction can be written as a product of one electron functions

$$\Psi(r_1, r_2, r_3, \cdots) = \phi(r_1)\phi(r_2)\phi(r_3)\cdots$$

- if we use the variational energy, solving the many electron Schrödinger equation is reduced to solving a series of one electron Schrödinger equations

- each electron interacts with the average distribution of the other electrons

Hartree-Fock Approximation

- Pauli exclusion principle: a maximum of two electrons can occupy an orbital and the spins of the electrons are paired, i.e. opposed.

- The principle demands: the wavefunction for a many-electron system must be asymmetric with respect to the permutation of the space-spin coordinates for every pair of electrons.

- For a system of N electron in N spin orbitals, can be done by writing the wavefunction as a Slater determinant

$$\Psi = \frac{1}{\sqrt{n!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \cdots & \phi_1(n) \\ \phi_2(1) & \phi_2(2) & \cdots & \phi_2(n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(1) & \phi_n(1) & \cdots & \phi_n(n) \end{vmatrix} = \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_n \end{vmatrix}$$

E

ψ_4

ψ_3

ψ_2

ψ_1
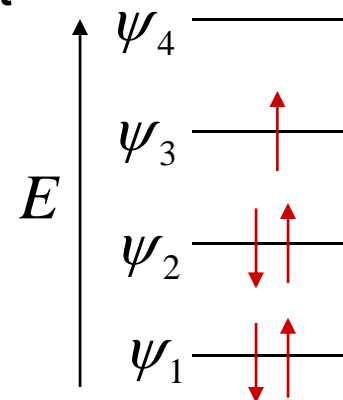
The Fock Equation

- take the Hartree-Fock wavefunction

$$\Psi = \begin{vmatrix} \phi_1 & \phi_2 & \cdots & \phi_n \end{vmatrix}$$

- put it into the variational energy expression

$$E = \frac{\int \Psi^* \hat{\mathbf{H}} \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

- minimize the energy with respect to changes in the orbitals

$$\partial E / \partial \phi_i = 0$$

- yields the Fock equation: $\quad \underline{f_i}\phi_i = \underline{\varepsilon_i}\phi_i$

Effective one electron Hamiltonian for the electron in the polyelectronic system

Molecular orbital energy

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Fock Operator

$$\hat{\mathbf{F}} = \hat{\mathbf{T}} + \hat{\mathbf{V}}_{NE} + \hat{\mathbf{J}} - \hat{\mathbf{K}}$$

- Coulomb operator (electron-electron repulsion)

$$\hat{\mathbf{J}}\phi_i = \{\sum_j^{electrons} \int \phi_j \frac{e^2}{r_{ij}} \phi_j \, d\tau\} \phi_i$$

- exchange operator (purely quantum mechanical -arises from the fact that the wavefunction must switch sign when you exchange two electrons)

$$\hat{\mathbf{K}}\phi_i = \{\sum_j^{electrons} \int \phi_j \frac{e^2}{r_{ij}} \phi_i \, d\tau\} \phi_j$$

- Both determined by molecular orbital

Solving the Fock Equations

$$\hat{\mathbf{F}}\phi_i = \varepsilon_i \phi_i$$

- A general approach: Self-consistent Field (SCF)

1. obtain an initial guess for all the orbitals ϕ_i

2. use the current ϕ_i to construct a new Fock operator

3. solve the Fock equations for a new set of ϕ_i

4. if the new ϕ_i are different from the old ϕ_i, go back to step 2.

Stop when the one electron wavefunction is converged

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Linear Combination of Atomic Orbitals

• The most important wave property of atomic orbitals

• LCAO: Wave functions are added and subtracted to give the wave functions of new orbitals.

• When orbitals on the same atom interact, they give *hybrid atomic orbitals* that define the geometry of the bonds formed.

• When orbitals on different atoms interact, they produce molecular orbitals that lead to *bonding* (or antibonding)

LCAO Approximation

- Direct solution of the Hartree-Fock equations is not a practical proposition for molecules

- The most popular strategy is to write each spin orbital as a linear combination of single electron orbitals (atomic orbital, LCAO):

molecular orbital coefficient

$$\phi_i = \sum_\mu c_{\mu,i} \chi_\mu$$

The one-electron orbitals are commonly called *basis functions* and often correspond to the atomic orbitals.

- The objective is to determine the set of coefficients that gives the lowest energy of the system

$$\frac{\partial E}{\partial c_{\mu,i}} = 0$$

Roothaan-Hall Equations

- For a closed-shell system with N electrons in N/2 orbitals, the derivation of the Hartree-Fock equations was first proposed by Roothaan and independently by Hall (1951).

- They recast the Fock equations in matrix form, which can be solved using standard techniques and can be applied to systems of any geometry.

$$\mathbf{F}\,\mathbf{C}_i = \varepsilon_i\,\mathbf{S}\,\mathbf{C}_i$$

- $\mathbf{F}$ – Fock matrix

- $\mathbf{C}_i$ – column vector of the molecular orbital coefficients

- ε_i – orbital energy

- $\mathbf{S}$ – overlap matrix

- In Fock matrix, The two-electron integrals, i.e. $(\mu\nu|\lambda\sigma)$, may involve up to four different basis functions $(\mu, \nu, \lambda, \sigma)$, which may in turn be located at four different centers.

Solving the Roothaan-Hall Equations

1. choose a basis set

2. calculate all the one and two electron integrals

3. obtain an initial guess for all the molecular orbital coefficients $\mathbf{C}_i$

4. use the current $\mathbf{C}_i$ to construct a new Fock matrix

5. solve $\mathbf{F}\,\mathbf{C}_i = \varepsilon_i\,\mathbf{S}\,\mathbf{C}_i$ for a new set of $\mathbf{C}_i$

6. if the new $\mathbf{C}_i$ are different from the old $\mathbf{C}_i$, go back to step 4.

Questions: Computational Quantum Mechanics?

Next: H_2^+

H$_2^+$: A Model System For Chemical Bonding
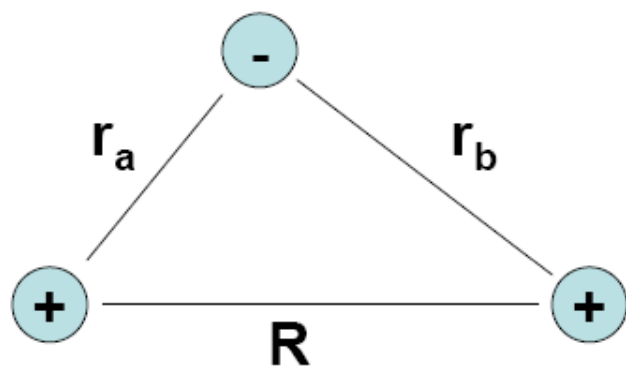
The first issue we have to deal with is the multiple nuclei; now we can have nuclear vibrations and rotations for the first time. **Important digression: Born-Oppenheimer approximation.**
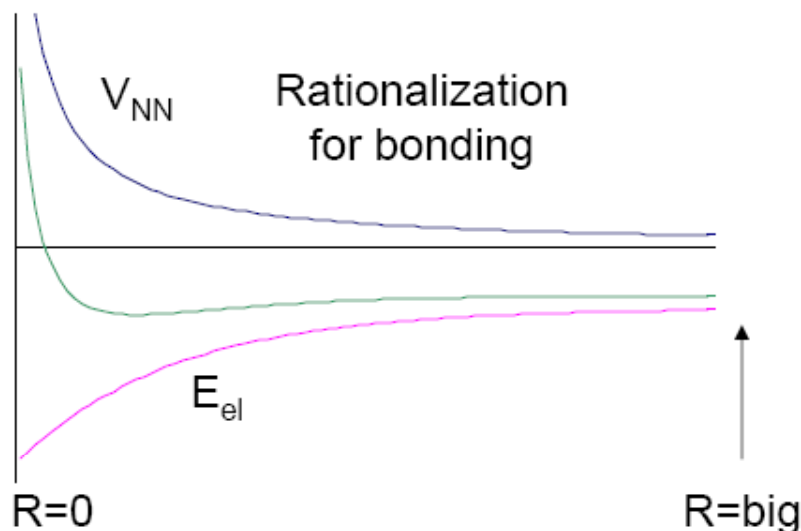
Overall potential can be rationalized in terms of competition between 1) internuclear repulsion, which blows up as R decreases, and 2) the purely electronic energy, which is more favorable as R decreases.

H_2^+: Hamiltonian

$$\hat{H} = \hat{T}_N + \hat{T}_e + V_{NN} + V_{Ne} + V_{ee}$$

Kinetic

$$\hat{T}_N = -\frac{\hbar^2}{2}\sum_\alpha \frac{1}{m_\alpha}\nabla_\alpha^2$$

$$\hat{T}_e = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2$$

N = "nuclear"; e = "electronic"
i,j = indices over electrons
α,β = indices over nuclei
Z = nuclear charges

Potential

$$V_{NN} = e^2 \sum_\alpha \sum_{\beta>\alpha} \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

$$V_{Ne} = -e^2 \sum_\alpha \sum_i \frac{Z_\alpha}{r_{i\alpha}}$$

$$V_{ee} = e^2 \sum_i \sum_{j>i} \frac{1}{r_{ij}}$$

Born-Oppenheimer Approximation

- Representation of the complete wavefunction as a product of an electronic and a nuclear part:

$$\Psi\,(r,R) = \Psi_e\,(r;\,R)\,\Psi_N(R)$$

- where the two wavefunctions may be determined separately by solving two different Schrödinger equations.

- the ratio of electronic to nuclear mass ($m/M \cong 5 \times 10^{-4}$) is sufficiently small and the nuclei, as compared to the rapidly moving electrons, appear to be fixed

- the nuclei are much heavier than the electrons and move more slowly than the electrons

- in the Born-Oppenheimer approximation, we freeze the nuclear positions, R, and calculate the electronic wavefunction, Ψ_e(r;R) and energy E(R)

H$_2^+$: Born-Oppenheimer Approximation

$$\hat{H} = \hat{T}_N + \hat{T}_e + V_{NN} + \boxed{V_{Ne}} + V_{ee}$$

This term is troublesome because it couples electron motion to nuclear motion. Without it, we could solve for nuclear eigenfunctions and electronic eigenfuctions independently.

- The Born-Oppenheimer approximation invokes an *adiabatic* separation of the nuclear and electronic motions, on the basis of the large difference in mass between nuclei and electrons.
- Classically you can envision that the nuclei move much slower than the electrons, such that the electronic degrees of freedom "instantaneously" adjust to the nuclear positions.
- Operationally, we make the electronic Hamiltonian *parametrically* dependent on nuclear positions.

H$_2^+$: Born-Oppenheimer Approximation

$$\hat{H} = \hat{T}_N^{\;\;0} + \hat{T}_e + V_{NN} + \boxed{V_{Ne}} + V_{ee}$$

$$\hat{H}_e^{eff}(\vec{r}_\alpha) = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - e^2\sum_\alpha \sum_i \frac{Z_\alpha}{r_{i\alpha}} + e^2\sum_i\sum_j \frac{1}{r_{ij}} + V_{NN}$$

Back to H$_2^+$
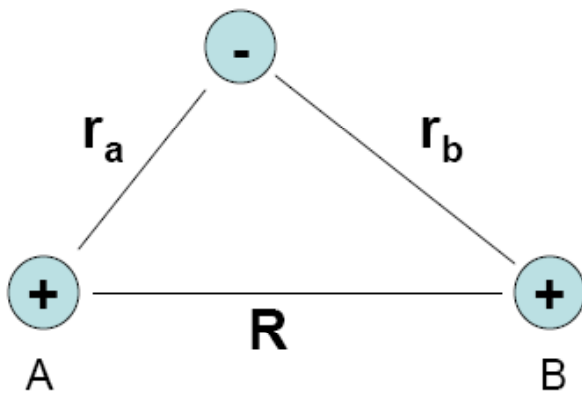
This can be added in because it's a constant for fixed nuclear positions.

$$\hat{H}_e = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b}$$

H_2^+: Trial Wavefunction with 2 Basis Functions

$$\varphi = c_1 f_1 + c_2 f_2$$

$$
\begin{aligned}
E_\phi &= \frac{\int \phi \hat{H} \phi}{\int \phi \phi} \\[2ex]
&= \frac{\int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2)}{\int (c_1 f_1 + c_2 f_2)(c_1 f_1 + c_2 f_2)} \\[2ex]
&= \frac{c_1^2 \int f_1 \hat{H} f_1 + c_1 c_2 \int f_1 \hat{H} f_2 + c_1 c_2 \int f_2 \hat{H} f_1 + c_2^2 \int f_2 \hat{H} f_2}{c_1^2 \int f_1 f_1 + c_1 c_2 \int f_1 f_2 + c_1 c_2 \int f_2 f_1 + c_2^2 \int f_2 f_2} \\[2ex]
&= \frac{c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}}
\end{aligned}
$$

H$_2^+$: Trial Wavefunction with 2 Basis Functions

$$E_\phi = \frac{c_1^2 H_{11} + c_1 c_2 H_{12} + c_1 c_2 H_{21} + c_2^2 H_{22}}{c_1^2 S_{11} + c_1 c_2 S_{12} + c_1 c_2 S_{21} + c_2^2 S_{22}}$$

Taking advantage of the variational principle, we aim to minimize this expression with respect to the "variational parameters" c_1 and c_2, i.e.,

$$\frac{\partial E_\phi}{\partial c_1} = 0$$

$$\frac{\partial E_\phi}{\partial c_2} = 0$$

These two expressions lead to the following linear equations:

$$c_1(H_{11} - ES_{11}) + c_2(H_{21} - ES_{21}) = 0$$
$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

This now becomes a standard problem in linear algebra, which can be expressed as a matrix problem.

H$_2^+$: Matrix Formulation of Eigenvalue Problem

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

$$H_{ij} = \int f_i \hat{H} f_j$$

$$S_{ij} = \int f_i f_j$$

If basis set is chosen to be "orthonormal", i.e., $S_{ij} = \delta_{ij}$

$$\begin{vmatrix} H_{11} - E & H_{12} & \cdots \\ H_{21} & H_{22} - E & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} = 0$$

Except for very simple problems, solving these equations (essentially root finding of polynomial equation) is handled numerically (e.g., Householder diagonalization).

H₂⁺: Variational Treatment

As a trial wavefunction, let's use something very simple, specifically a sum of 1s orbitals centered around each nucleus (this fits with our intuition about bonding arising from orbital overlap):

$$\psi = c_A \psi_A + c_B \psi_B$$

$\psi_A = 1s$ orbital centered on nucleus A

$\psi_B = 1s$ orbital centered on nucleus B

c = coefficients to be determined

The secular determinant is

$$\begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} =$$

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{AA} - E \end{vmatrix} = 0$$

$$H_{AA} = \int \psi_A \hat{H} \psi_A = \int \psi_B \hat{H} \psi_B = H_{BB}$$

$$H_{AB} = \int \psi_A \hat{H} \psi_B = \int \psi_B \hat{H} \psi_A = H_{BA}$$

$$S = S_{AB} = S_{BA} = \int \psi_A \psi_B$$

$$S_{AA} = S_{BB} = 1$$

H$_2^+$: A Closer Look at the Integrals

$$H_{AA} = \int \psi_A \hat{H} \psi_A$$

$$= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} \right) \psi_A$$

This is just the Hamiltonian for a H atom centered on A, and thus ψ_A is an eigenfunction of it.

$$= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} \right) \psi_A - e^2 \int \psi_A \frac{1}{r_b} \psi_A$$

$$= \int \psi_A \hat{H}_A^0 \psi_A - e^2 \int \psi_A \frac{1}{r_b} \psi_A$$

$$= E_0 - e^2 \int \psi_A \frac{1}{r_b} \psi_A$$

$$= E_0 - J$$

These types of integrals are referred to as "Coulomb" integrals, and together with "exchange" integrals (next slide), play a very important role in electronic structure calculations.

H$_2^+$: A Closer Look at the Integrals

$$H_{AB} = \int \psi_A \hat{H} \psi_B$$

$$= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b} \right) \psi_B$$

This is just the Hamiltonian for a H atom centered on B, and thus ψ_B is an eigenfunction of it.

$$= \int \psi_A \left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{r_b} \right) \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B$$

$$= \int \psi_A \hat{H}_B^0 \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B$$

$$= E_0 \int \psi_A \psi_B - e^2 \int \psi_A \frac{1}{r_a} \psi_B$$

This is an "exchange" integral.

$$= S E_0 - K$$

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H$_2^+$: Solving the Secular Determinant

$$E_\pm = \frac{H_{AA} \pm H_{AB}}{1 \pm S} = E_0 + \frac{J \pm K}{1 \pm S}$$

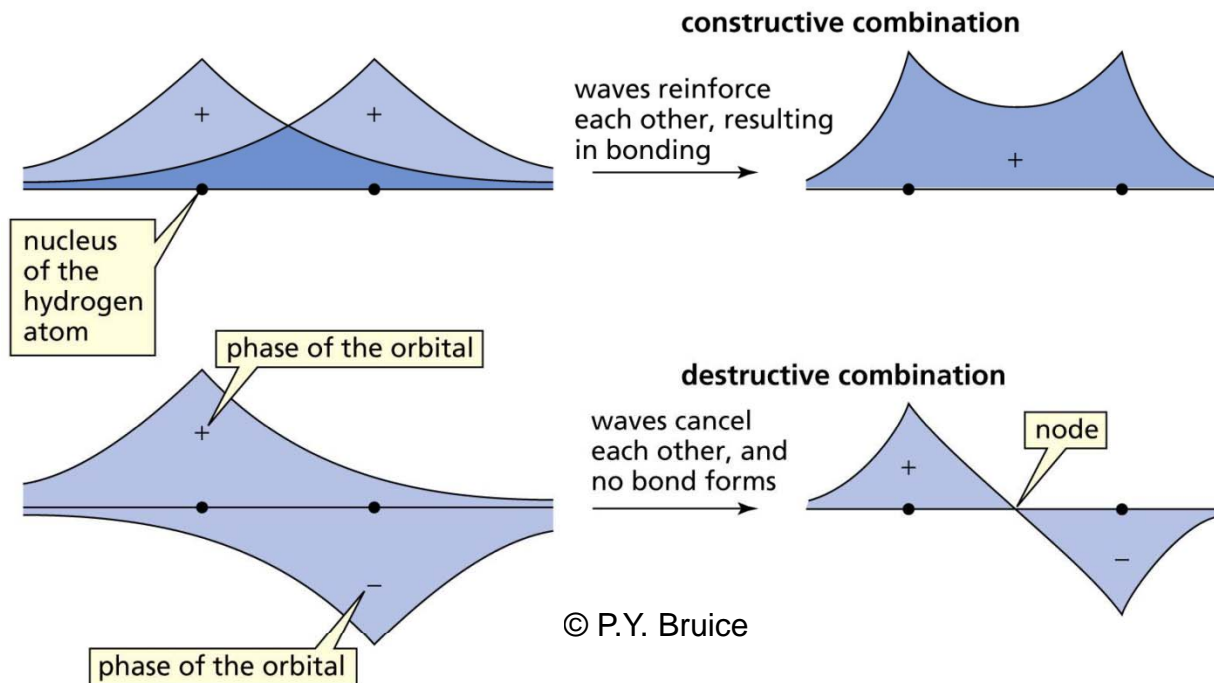$$\psi_\pm = \frac{1}{\sqrt{2(1 \pm S)}}\left(\psi_A \pm \psi_B\right)$$

We've expressed the eigenstates in terms of three types of integrals: overlap, Coulomb, and exchange. These implicitly depend on R, the internuclear distance. For H$_2^+$, these turn out to be analytical:

$$J = e^{-2R}\left(1 + \frac{1}{R}\right)$$

$$K = e^{-R}\left(1 + R\right)$$

$$S = e^{-R}\left(1 + R + \frac{R^2}{3}\right)$$

H$_2^+$: Eigenfunctions

constructive combination

waves reinforce
each other, resulting
in bonding

nucleus
of the
hydrogen
atom

phase of the orbital

destructive combination

waves cancel
each other, and
no bond forms

node

phase of the orbital

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Bonding results when
two orbitals with the
same phase interact.
When two out-of-phase
atomic orbitals overlap,
they cancel each other
and produce a node
between the nuclei.

$$\psi_+ = \frac{1}{\sqrt{2(1+S)}}\left(\psi_A + \psi_B\right)$$

$$\psi_- = \frac{1}{\sqrt{2(1-S)}}\left(\psi_A - \psi_B\right)$$

"Bonding" molecular orbital
Enhanced electron density in
internuclear area, helping to
screen protons from each other.

"Anti-Bonding" molecular orbital
Depleted electron density in
internuclear area, deshielding
the protons from each other.

© Matt Jacobson

H_2^+: Eigenenergies
(Potential Energy Curves)
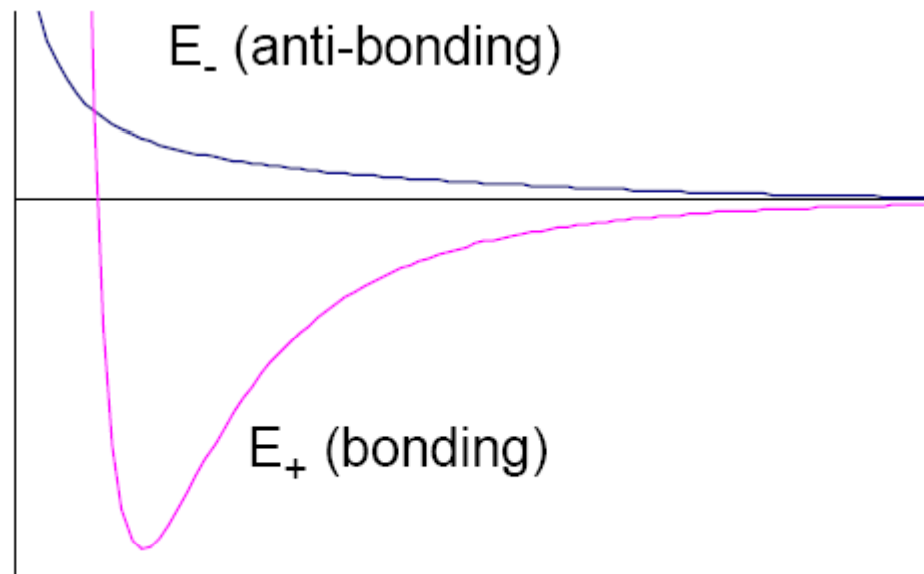
However, the expressions we got for the eigenenergies are non-trivial, and give a feeling for how electronic structure problems are solved in general

Questions: H_2^+?

Next: Basis Sets

Slater-Type Orbitals (STOs)

- The basis sets most commonly used in QM calculations are composed of atomic functions. An obvious choice would be the Slater type orbitals.

$$\chi_{1s}(\vec{r}) = \left(\zeta_{1s}^3 / \pi\right)^{1/2} \exp(-\zeta_{1s}\, r)$$

$$\chi_{2s}(\vec{r}) = \left(\zeta_{2s}^5 / 96\pi\right)^{1/2} r \exp(-\zeta_{2s}\, r/2)$$

$$\chi_{2px}(\vec{r}) = \left(\zeta_{2p}^5 / 32\pi\right)^{1/2} x \exp(-\zeta_{2p}\, r/2)$$

- Exact for hydrogen atom
- Right asymptotic form
- Correct nuclear cusp condition
- 3 and 4 center two electron integrals cannot be done analytically
- It is common in *ab initio* calculations to replace the Slater orbitals by functions based upon Gaussian

Gaussian-Type Orbitals

$$g_s(\vec{r}) = \left(2\alpha^3 / \pi\right)^{1/4} \exp(-\alpha\, r^2)$$

$$g_x(\vec{r}) = \left(128\alpha^5 / \pi^3\right)^{1/4} x \exp(-\alpha\, r^2)$$

$$g_{xx}(\vec{r}) = \left(2048\alpha^7 / 9\pi^3\right)^{1/4} x^2 \exp(-\alpha\, r^2)$$

$$g_{xy}(\vec{r}) = \left(2048\alpha^7 / \pi^3\right)^{1/4} xy \exp(-\alpha\, r^2)$$

Blue = STO
Pink = Gaussian
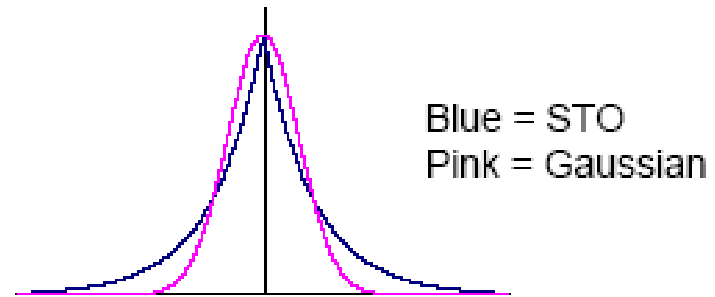
Radial Dependence of Slater and
Gaussian Basis Functions

- These completely dominate modern electronic structure calculations.

- They are convenient for computations. All two electron integrals can be done analytically

- They are actually LESS physically reasonable than the STOs

- Die off too quickly for large r

- No cusp at the origin

Using Multiple Gaussian Orbitals

Blue = STO
Pink = Gaussian
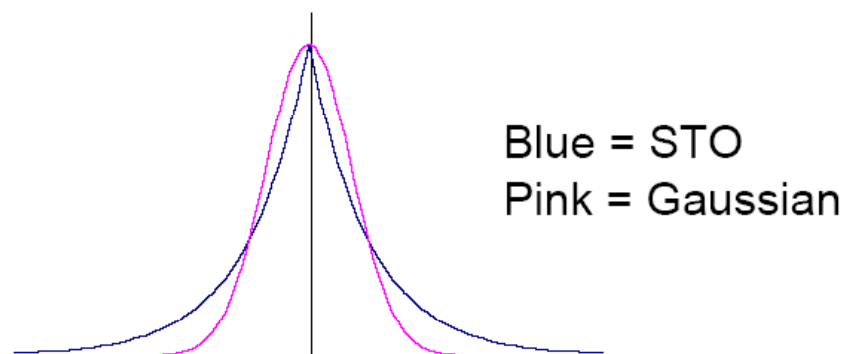
Solution: Create "contracted Gaussian functions" expressed in terms of "primitives". Typically use 3 or 6 Gaussians to approximate STO.

STO-3G

STO-6G

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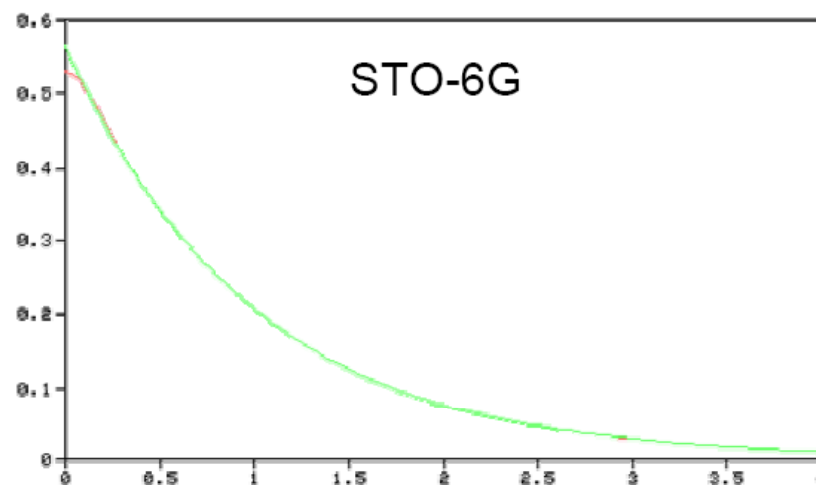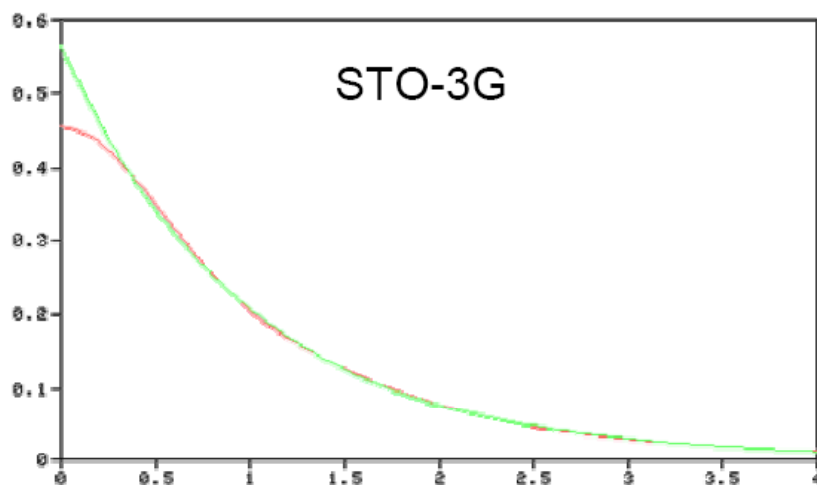
Basis Sets

Minimal Basis

1 basis function for each atomic orbital

H: 1 (1s)   Example:
C: 5 (1s, 2s, 2p$_x$, 2p$_y$, 2p$_z$)   STO-3G

Split Valence

Problem: Size of orbitals held fixed for all systems.
Solution: Double (or even triple) the number of basis functions for each orbital, with different orbital exponents (widths, sometimes called "**zeta**").

inner p function
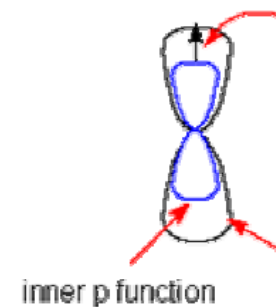
Double Zeta: 2 basis functions for each orbital   H: 2
                                                  C: 10

Triple Zeta: 3 basis functions for each orbital   H: 3   Example:
                                                  C: 15   6-311G

Split Valence: 1 basis function for each core orbital,   H: 2   Example:
but 2 for valence.   C: 9   3-21G

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Basis Sets

Diffuse Functions

Problem: When dealing with systems with lone pairs, anions, and excited states, electrons can move far from the nucleus.

Example: 6-31G+

Solution: Introduce "diffuse functions", really large basis functions.

Large size versions of s- and p-type atomic orbitals

Polarization Functions

Problem: Basis functions are isotropic around the nucleus, but bonding (or hydrogen bonding) introduces anisotropy.

Solution: Introduce "polarization functions" to permit anisotropy. **Change shape**

For p orbitals, add in d functions (6 of them)

Example: 6-31G* = 6-31G(d)

For s orbitals, add in p functions (3 of them)

Example: 6-31G = 6-31G(d,p)**
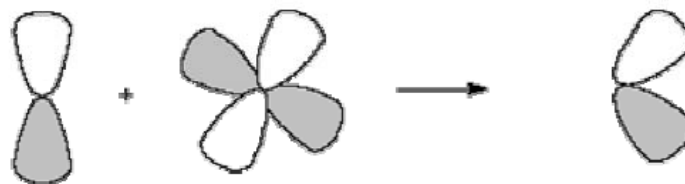
Polarization of a p orbital by mixing with a d function

What the Basis Set Names Mean

6-311+G**

Each inner shell (core) basis function composed of 6 primitives

Triple-zeta split valence basis: One is contracted function of 3 primitives, and the other two are single Gaussians

Add diffuse functions

Polarization of p-orbitals with d functions

Polarization of s-orbitals with p functions

Correlation Energy

Hartree-Fock, at least with a sufficiently large basis set, can predict lots of properties with reasonable accuracy, e.g., equilibrium structures and relative energies. But there are some notable failures ...

Example: Dissociation energies

Molecule	Experiment	HF
N_2	9.9 eV	5.3 eV
F_2	1.6 eV	-1.4 eV

- Remember, HF only treats electron correlation in an average, not instantaneous sense.
- In fact, the motions of electrons are correlated and they tend to avoid each other, giving rise to a lower energy. Their motion must be "correlated"
- For a given basis set, the correlation energy is:

$$E_{correlation} = E_{exact} - E_{HF}$$

Hartree-Fock+CI

- There are many ways in which correlation effects can be incorporated into an ab initio molecular orbital calculation.

- A popular approach is configuration interaction (CI), in which excited states are included in the description of an electronic state.

- The overall wavefunction is a linear combination of the ground and excited-state wavefunctions.

Configuration Interaction

- determine CI coefficients using the variational principle

$$\Psi = \Psi_0 + \sum_{ia} t_i^a \Psi_i^a + \sum_{ijab} t_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijkabc} t_{ijk}^{abc} \Psi_{ijk}^{abc} + \cdots$$

$$\text{minimize } E = \frac{\int \Psi^* \hat{\mathbf{H}} \Psi d\tau}{\int \Psi^* \Psi d\tau} \text{ with respect to } t$$

- CIS – include all single excitations
  - useful for excited states, but not for correlation of the ground state
- CISD – include all single and double excitations
  - most useful for correlating the ground state
  - O^2V^2 determinants (O=number of occ. orb., V=number of unocc. orb.)
- CISDT – singles, doubles and triples
  - limited to small molecules, ca O^3V^3 determinants
- Full CI – all possible excitations
  - $((O+V)!/O!V!)^2$ determinants
  - exact for a given basis set
  - limited to ca. 14 electrons in 14 orbitals

Perturbation Theory Methods

Perturbation theory works on the idea that if we know the answer to one problem we can work out an answer to a closely related problem. Let us suppose that we know the solution of the Schrödinger equation for one problem, i.e. for one Hamiltonian operator. If we have a problem with a Hamiltonian operator which is fairly close to the first one, we treat the difference between the Hamiltonian operators as a small perturbation to the first solution. We can expand the solution to the second problem in terms of the first solution and terms in various powers of the perturbation.

A particularly successful application to molecules and the correlation problem goes back to Møller and Plesset in 1933. This is now the MPn method. The Hartree-Fock solution is an approximate solution to the exact Hamiltonian operator. It is however an exact solution to an approximate Hamiltonian operator which is the sum of Fock operators for each electron. We treat the perturbation as the difference between the exact Hamiltonian operator and this sum of Fock operators. We then treat the Hartree-Fock solution as the zero order term and evaluate terms in powers of the perturbation. The zero-order energy is the sum of orbital energies. The first order correction to the energy is just the two-electron integrals that correct the sum of orbital energies to give the normal Hartree-Fock energy. The first important correction is the second order term and this leads to MP2. MP2 is relatively economic to evaluate and gives a reasonable proportion of the correlation energy. Higher order terms become more and more expensive. MP3 is commonly used but does not seem to give much improvement over MP2. MP4, with some terms removed to speed things up, is often used. MP4 gives reasonable results but it is much more expensive than MP2. Higher order terms than 4'th order are rarely evaluated.

Code exists in various programs to calculate optimized geometries with analytic first derivatives of the energy with respect to atomic coordinates at MP2 level. MP2 is thus often the highest level of theory where optimized geometries are obtained. Similarly analytic second derivatives are available and harmonic frequencies are also evaluated at the MP2 level.

Møller-Plesset Perturbation Theory

- choose $\mathbf{H}_0$ such that its eigenfunctions are determinants of molecular orbitals

$$\hat{\mathbf{H}}_0 = \sum \hat{\mathbf{F}}_i$$

- expand perturbed wavefunctions in terms of the Hartree-Fock determinant and singly, doubly and higher excited determinants

$$\Psi_1 = \sum_{ia} a_i^a \Psi_i^a + \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab} + \sum_{ijkabc} a_{ijk}^{abc} \Psi_{ijk}^{abc} + \cdots$$

- perturbational corrections to the energy

$$E_{HF} = E_0 + E_1 = \int \Psi_0 \hat{\mathbf{H}}_0 \Psi_0 d\tau + \int \Psi_0 \hat{\mathbf{V}} \Psi_0 d\tau$$

$$E_{MP2} = E_{HF} + E_2 = E_{HF} + \int \Psi_0 \hat{\mathbf{V}} \Psi_1 d\tau = E_{HF} - \sum_{i>j,a>b} \frac{[\int \Psi_0 \hat{\mathbf{V}} \Psi_{ij}^{ab} d\tau]^2}{\varepsilon_a + \varepsilon_a - \varepsilon_i - \varepsilon_j}$$

Møller-Plesset Basis Sets

- Basic idea: Treat instantaneous electron correlation as a perturbation to the HF-SCF solutions. In other words, the perturbation is the difference between the exact $1/r_{12}$ coupling and the SCF solution. Much more efficient than full CI!
- The HF-SCF, with a large basis set, is in fact the correct 1st-order perturbation theory result for electron correlation. So the first new term is the 2nd order perturbation theory result. This is "MP2".
- There are also higher order theories, i.e., MP3, MP4. As with all perturbation theory, higher order does not guarantee higher accuracy. [And in fact, going to higher and higher order is not at all guaranteed to converge on the right answer.]
- Need a good basis set! Frequently used basis sets include the Dunning sets:

cc-pVDZ

diffuse functions (aug)-cc-pVTZ **"polarization Valence Triple Zeta"**

"correlation consistent"

- These have a little different philosophy: develop contractions by SCF calculations on atoms, thus building some electron correlation into basis set.
- Frozen core approximation often invoked for MP calculations as well.

Questions: Basis Sets?

Next: Semi-Empirical Methods

Semi-Empirical MO Methods

- the high cost of ab initio MO calculations is largely due to the many integrals that need to be calculated (esp. two electron integrals)
- semi-empirical MO methods start with the general form of ab initio Hartree-Fock calculations, but make numerous approximations for the various integrals
- many of the integrals are approximated by functions with empirical parameters
- these parameters are adjusted to improve the agreement with experiment
- Intermediate between real (ab initio) QM and MD force field approaches in terms of speed and accuracy

Eliminating HF Integrals

The rate-limiting step in HF is evaluating the N^4 different integrals of the form:

$$\iint f_r(1)f_t(2)\frac{1}{r_{12}}f_s(1)f_u(2) = (rs|tu)$$

Commonly used shorthand notation

- This is a two electron integral (representing the electron repulsion), but it involves up to four basis functions: *r, s, t, u*.
- If all four basis functions are on the same atom, it is a 1-center integral.
- If the basis functions are on 2 different atoms, it is a 2-center integral, etc.
- The 3- and 4-center integrals are the most difficult to evaluate, and are also the most copious. Semi-empirical methods eliminate these entirely.

Zero Differential Overlap (ZDO)

- two electron repulsion integrals are one of the most expensive parts of ab initio MO calculations

$$(\mu\nu \mid \lambda\sigma) = \int \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2)\,d\tau_1 d\tau_2$$

- neglect integrals if orbitals are not the same

$$(\mu\nu \mid \lambda\sigma) = (\mu\mu \mid \lambda\lambda)\ \delta_{\mu\nu}\ \delta_{\lambda\sigma}$$

$$where\ \delta_{\mu\nu} = 1\ if\ \mu = \nu,\ \delta_{\mu\nu} = 0\ if\ \mu \neq \nu$$

- CNDO, INDO and MINDO semi-empirical methods

Neglect of Diatomic Differential Overlap (NDDO)

- fewer integrals neglected

$$(\mu\nu \mid \lambda\sigma) = \int \chi_\mu(1)\chi_\nu(1)\frac{1}{r_{12}}\chi_\lambda(2)\chi_\sigma(2)d\tau_1 d\tau_2$$

- neglect integrals if μ and ν are not on the same atom or λ and σ are not on the same atom

- integral approximations are more accurate and have more adjustable parameters than in ZDO methods

- parameters are adjusted to fit experimental data and ab initio calculations

- MNDO, AM1 and PM3 semi-empirical methods

Semi-Empirical Family Tree

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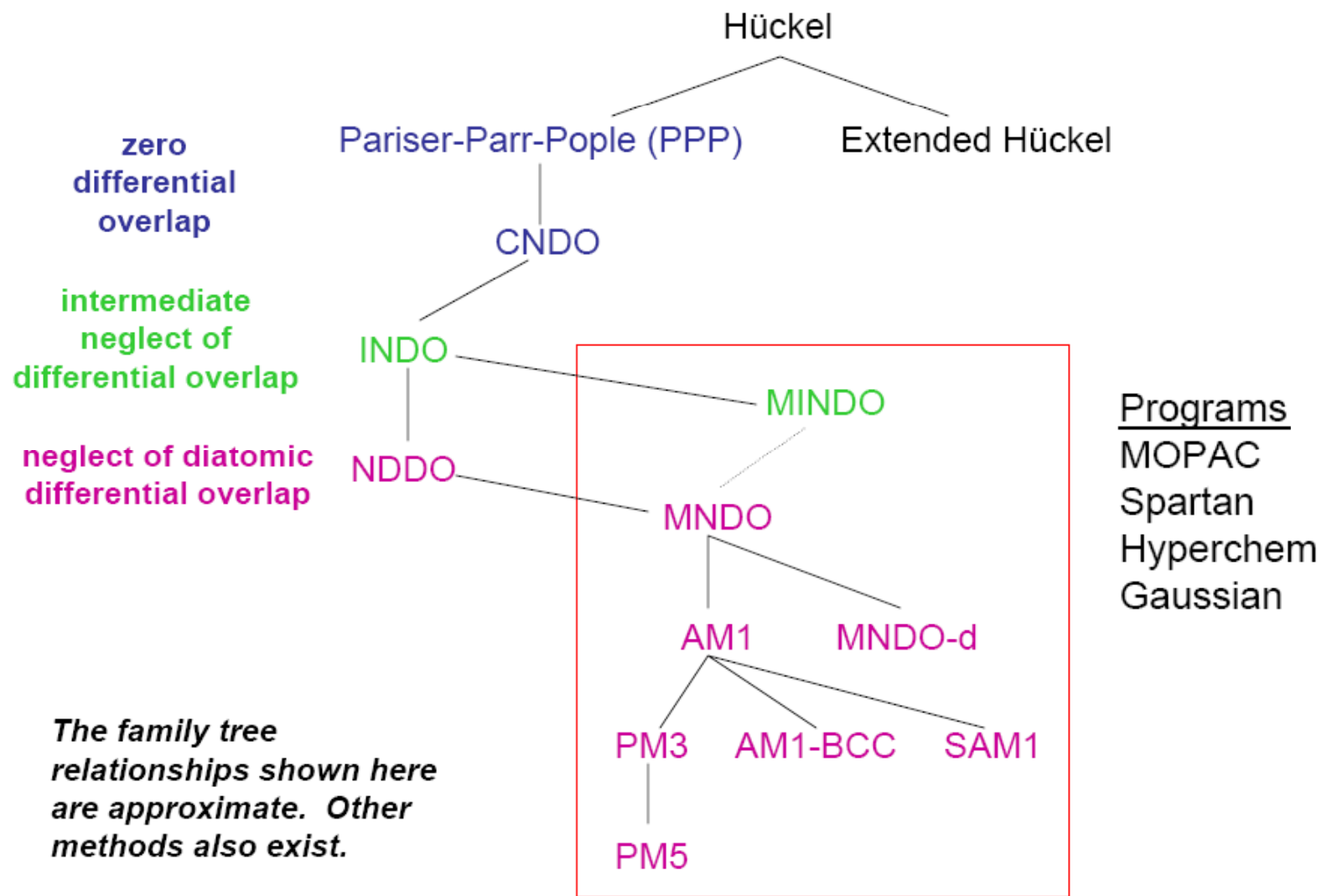
Semiempirical Methods

Advantages:

- Cheaper than ab initio and DFT
- Only truly viable QM like method for entire proteins, but even small proteins are barely within reach
- Can be reparametrized for each system / process

Disadvantages:

- H-bond strengths often incorrect (off by several kcal/mol)
- Still expensive

Questions: Semi-Empirical Methods?

Next: Density Functional Theory

Density Functional Theory

• DFT is an approach to solve the electronic structure of atoms and molecules which has enjoyed an increasing interest since the late 1980s and 1990s

• DFT replaces the wave function with the electron density as the fundamental unknown:

$$\rho(r_1) = \int dr_2 \cdots dr_n \psi^*(r_1 \cdots r_n) \psi(r_1 \cdots r_n)$$

Wavefunction – 3n coordinates

Charge Density – 3 coordinates

DFT Functionals

Hohenberg and Kohn: the ground state energy and other properties of a system were uniquely defined by the electron density.

◆ DFT expression for the energy:

$$E[\rho] = T[\rho] + \int \rho V_{nuclei} + \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + K_{XC}[\rho]$$

Kinetic energy

e- e- repulsion

e-/nuclei attraction

Exchange / Correlation

[] denotes functional – take function and return a number
For example, a definite integral is a type of functional...

$$I[f] = \int_a^b f(r) dr$$

So How Can This Work?

- K_{XC} is UNKNOWN!! (And is unlikely to ever be known in a form which is simpler than solving the electronic Schrodinger equation)

- T is also unknown, but can be approximated if the density is associated with a wavefunction.

- Kohn and Sham introduced the orbital concept into DFT

$$T[\rho] = \sum_i \int \psi_i(r)\left(-\frac{\nabla^2}{2}\right)\psi_i(r)dr$$

- they wrote the density of the system as the sum of the square moduli of a set of one-electron orthonormal orbitals.

$$\rho(r) = \sum_i |\psi_i(r)|^2$$

DFT and HF

- Need to define K_{XC} (approximated in various ways)
- Exactly the same ansatz is used as HF – the only difference is in the Fockian operator

$$\hat{F}_{HF}\left(c^{MO}\right) = \sum_i \hat{h}(i) + \left(\sum_{j \in occ} 2\hat{J}_j\left(c^{MO}\right) - \hat{K}_j\left(c^{MO}\right)\right)$$

$$\hat{F}_{KS}\left(c^{MO}\right) = \sum_i \hat{h}(i) + \left(\sum_{j \in occ} 2\hat{J}_j\left(c^{MO}\right)\right) + \boxed{\hat{K}_{xc}\left[\rho, \nabla\rho\right]}$$

Same SCF procedure as in HF since the equation is nonlinear...

In most DFT programs, the Kohn-Sham orbitals are expressed as linear combination of atomic-centered basis functions:

$$\psi_i(r) = \sum_v c_{vi}\phi_v$$

Behavior of DFT and HF

- By definition, HF has no electron correlation
  this implies more serious errors
  for stretched/distorted bonds, i.e. disfavors
  overcoordination
- Pure DFT overestimates correlation
  Preference for overcoordination
- Hence success of hybrid functionals which add exchange
  to DFT, e.g. B3LYP

- Hartree-Fock alone is *not* very useful – barriers are usually
  overestimated by more than DFT underestimates

DFT: Exchange Correlation Functions

1. LDA: Local density approximation. Basic idea is to approximate $E_{xc}[\rho]$ using the exchange and correlation energy of "jellium": a homogeneous electron gas with density ρ (but electrically neutral). Valid if electron density changes slowly with position. Not sufficiently accurate for most purposes.

2. Gradient-corrected functionals: Most modern functionals fall into this category. Basic idea: make the functional depend not only on ρ but also

$$\nabla \rho$$

The gradient part accounts for rate of change in density, which is ignored in LDA. Also called a "nonlocal" functional.
   - Most important gradient-corrected *exchange* functional due to Becke (1988): B88. Uses LDA but adds in new complicated term involving gradient and an empirical parameter, fit to HF exchange energies.
   - Most important gradient-corrected *correlation* functional due to Lee-Yang-Parr: LYP.
   - Put them together and you get "BLYP".

3. Hybrid functionals. Calculate exchange integrals explicitly as in HF, and then combine this term with functionals, e.g., "B3LYP" ("3"=3 parameters).

Problems with DFT

- Is DFT a panacea? No!
  - Even the best DFT often yield errors of 5 kcal/mol
  - No hierarchy for improvement
    - Different functionals = Different answers
  - Poor for proton transfer and bond rearrangment
    - Tendency to overcoordinate...
    - Extreme example: LDA predicts no proton transfer barrier in malonaldehyde

instead of

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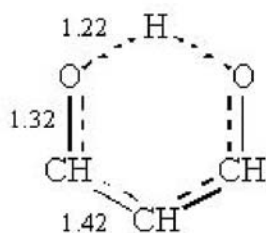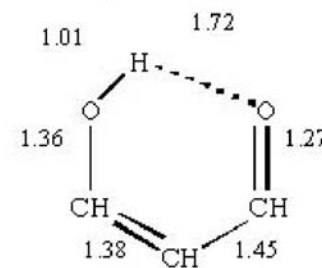
Questions: Density Functional Theory?

Resources and Further Reading

WWW:

– Glossary of terms used in theoretical organic chemistry:

http://www.iupac.org/reports/1999/7110minkin

– Online courses:

http://www.chem.wayne.edu/~hbs/chm6440

http://francisco.compbio.ucsf.edu/~jacobson/biophys206/biophys_206_links.htm

– Atomic orbitals and molecular orbitals:

http://www.cem.msu.edu/~reusch/VirtualText/intro3.htm

http://winter.group.shef.ac.uk/orbitron

Books:

"Molecular Modeling-Principle and Application", Andrew R. Leach, Chapter 2, 3
"Organic Chemistry", Paula Yurkanis Bruice, Chapter 1
"Organic Chemistry", L.G.Wade, Jr. Chapter 2