# Lecture 9 Molecular Structure 

## Diatomic Molecules

## Born-Oppenheimer approximation

we are forced to make an approximation at the outset.
Even the simplest molecule, $\mathrm{H}_{2}{ }^{+}$, consists of three particles, and its Schrödinger equation cannot be solved analytically.
To overcome this difficulty, we adopt the BornOppenheimer approximation, which takes note of the great difference in masses of electrons and nuclei.

## Born-Oppenheimer Approximation

Electrons can respond almost instantaneously to displacement of the nuclei. Therefore, instead of trying to solve the Schrödinger equation for all the particles simultaneously, we regard the nuclei as fixed in position and solve the Schrödinger equation for the electrons in the static electric potential arising from the nuclei in that particular arrangement. Different arrangements of nuclei may then be adopted and the calculation repeated.

Electrons are thousands of times lighter than nuclei. Therefore, they move many times faster

The set of solutions so obtained allows us to construct the molecular potential energy curve of a diatomic molecule (Fig. 8.1), and in general a potential energy surface of a polyatomic species, and to identify the equilibrium conformation of the molecule with the lowest point on this curve (or surface).
The Born-Oppenheimer approximation is very reliable for ground electronic states, but it is less reliable for excited


Fig. 8.1 A typical molecular potential energy curve for a diatomic species. states.

The Born-Oppenheimer Approximation states that since nuclei move so slowly, as the nuclei move, the electrons rearrange almost instantaneously.

## Hydrogen Molecular Ion: Born-Oppenheimer Approximation

The simplest molecule is not $\mathrm{H}_{2}$. Rather, it is $\mathrm{H}_{2}{ }^{+}$, which has two hydrogen nuclei and one electron.


The $\mathrm{H}_{2}{ }^{+}$Hamiltonian (in au)

$$
\begin{array}{cccccc}
H=-\frac{1}{2 M_{a}} \nabla_{a}^{2}-\frac{1}{2 M_{b}} \nabla_{b}^{2} & -\frac{1}{2} \nabla_{e}^{2} & -\frac{1}{r_{a}} & -\frac{1}{r_{b}} & +\frac{1}{R_{a b}} \\
\text { KE } & \text { KE } & \text { KE } & \text { PE } & \text { PE } & \text { PE } \\
\text { Nuc a } & \text { Nuc b } & \text { Elect } & \text { e-N } & \text { e-N } & \text { N-N } \\
& & & \text { Attr } & \text { Attr } & \text { Repuls }
\end{array}
$$

## Born-Oppenheimer Approximation

Electrons are thousands of times lighter than nuclei.
Therefore, they move many times faster
The Born-Oppenheimer Approximation states that since nuclei move so slowly, as the nuclei move, the electrons rearrange almost instantaneously.

With this approximation, it can be shown that one can separate nuclear coordinates (R) and electronic coordinates (r), and get separate Schrödinger Equations for each type of motion.

## Nuclear Equation

$$
\left(-\frac{1}{2 M_{a}} \nabla_{a}^{2}-\frac{1}{2 M_{b}} \nabla_{b}^{2}+\frac{1}{R_{a b}}+E_{e l}\right) \cdot \chi\left(R_{a b}\right)=E_{n u c} \cdot \chi\left(R_{a b}\right)
$$

$\mathrm{E}_{\mathrm{el}}$ is the effective potential energy exerted by the electron(s) on the nuclei as they whirl around (virtually instantaneously on the time scale of nuclear motion)

## Electronic Equation

$$
\left(-\frac{1}{2} \nabla^{2}-\frac{1}{r_{a}}-\frac{1}{r_{b}}\right) \psi=E_{e l e c t} \psi=E_{\psi}
$$

Because $\mathrm{H}_{2}{ }^{+}$has only one electron, there are no electron-electron repulsion terms.

In a multielectron molecule, one would have the following terms:

1. Kinetic energy of each electron.
2. Attractive Potential energy terms of each electron to each nucleus.
3. Repulsive Potential energy terms between each pair of electrons

# An application: the hydrogen molecule-ion Treatment of $\mathbf{H}_{2}{ }^{+}$ <br> Molecular Orbitals 

When we dealt with multielectron atoms, we assumed that the total wavefunction is the product of 1 electron wavefunctions ( 1 for each electron), and that one could put two electrons into each orbital, one with spin $\alpha$ and the second with spin $\beta$.

In analogy with this, when we have a molecule with multiple electrons, we assume that the total electron wavefunction is product of 1 electron wavefunctions ("Molecular Orbitals"), and that we can put two electrons into each orbital.

$$
\psi(1,2,3, \ldots N)=\left(\psi_{1}^{M O}(1) \alpha_{1}\right) \cdot\left(\psi_{1}^{M O}(2) \beta_{2}\right) \cdot\left(\psi_{2}^{M O}(3) \alpha_{3}\right) \cdot\left(\psi_{2}^{M O}(4) \alpha_{4}\right) \ldots
$$

Actually, that's not completely correct. We really use a Slater Determinant of product functions to get an Antisymmetrized total wavefunctions (just like with atoms).

## Linear Combination of Atomic Orbitals (LCAO)

Usually, we take each Molecular Orbital (MO) to be a Linear Combination of Atomic Orbitals (LCAO), where each atomic orbital is centered on one of the nuclei of the molecule.

For the $\mathrm{H}_{2}{ }^{+}$ion, there is only 1 electron, and therefore we need only 1 Molecular Orbital.

The simplest LCAO is one where the MO is a combination of hydrogen atom 1 s orbitals on each atom:

$$
\begin{aligned}
\psi=c_{a} \phi_{1 s a}+c_{b} \phi_{1 s b}= & c_{a} 1 s_{a}+c_{b} 1 s_{b} \\
& \text { shorthand }
\end{aligned}
$$

b

Assume that $1 \mathrm{~s}_{\mathrm{a}}$ and $1 \mathrm{~s}_{\mathrm{b}}$ are each normalized.

## Expectation Value of the Energy

$$
\psi=c_{a} 1 s_{a}+c_{b} 1 s_{b}
$$

Our goal is to first develop an expression relating the expectation value of the energy to $c_{a}$ and $c_{b}$.

Then we will use the Variational Principle to find the best set of coefficients; i.e. the values of $c_{a}$ and $c_{b}$ that minimize the energy.

$$
\langle E\rangle=\frac{\int \psi^{*} H \psi d \tau}{\int \psi^{*} \psi d \tau}=\frac{\langle\psi| H|\psi\rangle}{\langle\psi \mid \psi\rangle}=\frac{\text { Num }}{\text { Denom }}
$$

$$
\psi=c_{a} 1 s_{a}+c_{b} 1 s_{b}
$$

$$
\begin{aligned}
& \text { Denom }=\langle\psi \mid \psi\rangle=\left\langle c_{a} 1 s_{a}+c_{b} 1 s_{b} \mid c_{a} 1 s_{a}+c_{b} 1 s_{b}\right\rangle \\
& \text { Denom }=c_{a}^{2}\left\langle 1 s_{a} \mid 1 s_{a}\right\rangle+c_{a} c_{b}\left\langle 1 s_{a} \mid 1 s_{b}\right\rangle+c_{b} c_{a}\left\langle 1 s_{b} \mid 1 s_{a}\right\rangle+c_{b}^{2}\left\langle 1 s_{b} \mid 1 s_{b}\right\rangle
\end{aligned}
$$

Remember that $\left\langle 1 s_{a} \mid 1 s_{a}\right\rangle=\left\langle 1 s_{b} \mid 1 s_{b}\right\rangle=1$ because $1 \mathrm{~s}_{\mathrm{a}}$ and $1 \mathrm{~s}_{\mathrm{b}}$ are normalized.
Define: $S_{a b}=\left\langle 1 s_{a} \mid 1 s_{b}\right\rangle=\left\langle 1 s_{b} \mid 1 s_{a}\right\rangle$, where $S_{a b}$ is the overlap integral.

$$
\text { Denom }=c_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}
$$

$$
\psi=c_{a} 1 s_{a}+c_{b} 1 s_{b}
$$

$$
\begin{aligned}
& \text { Num }=\langle\psi| H|\psi\rangle=\left\langle c_{a} 1 s_{a}+c_{b} 1 s_{b}\right| H\left|c_{a} 1 s_{a}+c_{b} 1 s_{b}\right\rangle \\
& \begin{aligned}
& \text { Num }=c_{a}^{2}\left\langle 1 s_{a}\right| H\left|1 s_{a}\right\rangle+c_{a} c_{b}\left\langle 1 s_{a}\right| H\left|1 s_{b}\right\rangle+c_{b} c_{a}\left\langle 1 s_{b}\right| H\left|1 s_{a}\right\rangle+c_{b}^{2}\left\langle 1 s_{b}\right| H\left|1 s_{b}\right\rangle \\
& H_{a a}=\left\langle 1 s_{a}\right| H\left|1 s_{a}\right\rangle \\
& H_{b b}=\left\langle 1 s_{b}\right| H\left|1 s_{b}\right\rangle \\
& H_{a b}=\left\langle 1 s_{a}\right| H\left|1 s_{b}\right\rangle \\
& H_{b a}=\left\langle 1 s_{b}\right| H\left|1 s_{a}\right\rangle=H_{a b} \quad \text { because H is Hermitian }
\end{aligned}
\end{aligned}
$$

Num $=c_{a}^{2} H_{a a}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b} \quad$ Note: For this particular problem, $H_{b b}=H_{a a}$ by symmetry.

However, this is not true in general.

$$
\text { Num }=c_{a}^{2} H_{a a}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b} \quad \text { Denom }=c_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}
$$

$$
\langle E\rangle=\frac{\langle\psi| H|\psi\rangle}{\langle\psi \mid \psi\rangle}=\frac{N u m}{D e n o m}=\frac{C_{a}^{2} H_{a a}^{2}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b}}{C_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}}
$$

## Minimizing <E>: The Secular Determinant

In order to find the values of $c_{a}$ and $c_{b}$ which minimize $<E>$, we want: $\frac{\partial\langle E\rangle}{\partial c_{a}}=0$ and $\frac{\partial\langle E\rangle}{\partial c_{b}}=0$
It would seem relatively straightforward to take the derivatives of the above expression for $<\mathrm{E}>$ and set them equal to 0 .

However, the algebra to get where we want is extremely messy.

$$
\begin{gathered}
\langle E\rangle=\frac{c_{a}^{2} H_{a a}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b}}{c_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}} \\
\left(c_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}\right)\langle E\rangle=c_{a}^{2} H_{a a}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b}
\end{gathered}
$$

Differentiate both sides w.r.t. $\mathrm{c}_{\mathrm{a}}$ : Use product rule on left side

$$
\begin{aligned}
& \frac{\partial\left[\left(c_{a}^{2}+2 c_{a} c_{b} S_{a b}+c_{b}^{2}\right)\langle E\rangle\right]}{\partial c_{a}}=\frac{\partial\left[c_{a}^{2} H_{a a}+2 c_{a} c_{b} H_{a b}+c_{b}^{2} H_{b b}\right]}{\partial c_{a}} \\
& \frac{\left(c_{a}^{2}+2 c_{a} c_{b a}+c_{b}^{2}\right) \frac{\partial\langle E\rangle}{\partial c_{a}}+\langle E\rangle\left(2 c_{a}+2 c_{b} S_{a b}+0\right)=\left(2 c_{a} H_{a a}+2 c_{b} H_{a b}+0\right)}{}
\end{aligned}
$$

Set $\frac{\partial\langle E\rangle}{\partial c_{a}}=0$ and group coefficients of $c_{a}$ and $c_{b}$

$$
\begin{gathered}
\langle E\rangle\left(2 c_{a}+2 c_{b} S_{a b}\right)=\left(2 c_{a} H_{a a}+2 c_{b} H_{a b}\right) \\
\langle E\rangle c_{a}+\langle E\rangle c_{b} S_{a b}=c_{a} H_{a a}+c_{b} H_{a b}
\end{gathered}
$$

After dividing both sides by 2

$$
0=\left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}
$$

or

$$
\left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0
$$

This is one equation relating the two coefficients, $\mathrm{c}_{\mathrm{a}}$ and $\mathrm{c}_{\mathrm{b}}$.
We get a second equation if we repeat the procedure, except differentiate w.r.t. $\mathrm{c}_{\mathrm{b}}$ and set the derivative $=0$.

The second equation is:

$$
\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{a}+\left(H_{b b}-\langle E\rangle\right) c_{b}=0
$$

$$
\begin{aligned}
& \left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0 \\
& \left(H_{a b}-\langle E\rangle S_{a b}\right) c_{a}+\left(H_{b b}-\langle E\rangle\right) c_{b}=0
\end{aligned}
$$

Now we have two equations with two unknowns, $\mathrm{c}_{\mathrm{a}}$ and $\mathrm{c}_{\mathrm{b}}$. All we have to do is use Cramer's Rule to solve for them.

Those are homogeneous equations. The only way we can get a solution other than the trivial one, $\mathrm{c}_{\mathrm{a}}=\mathrm{C}_{\mathrm{b}}=0$, is if the determinant of coefficients of $c_{a}$ and $c_{b}$ is zero.

$$
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

## The Secular Determinant

## Extension to Larger Systems

The $2 \times 2$ Secular Determinant resulted from using a wavefunction consisting of a linear combination of atomic orbitals.

If, instead, you use a linear combination of N orbitals, then you get an NxN Secular Determinant

A simple way to remember how to build a Secular Determinant is to use the "generic" formula:

$$
\left|H_{i j}-\langle E\rangle S_{i j}\right|=0
$$

After you have made the Secular Determinant, set the diagonal overlaps, $\mathrm{S}_{\mathrm{ii}}=1$.

$$
\left|H_{i j}-\langle E\rangle S_{i j}\right|=0
$$

For example, if $\quad \psi=c_{a} \phi_{a}+c_{b} \phi_{b}+c_{c} \phi_{c}$
Then the Secular Determinant is:

$$
\begin{gathered}
\left|\begin{array}{ccc}
H_{a a}-\langle E\rangle S_{a a} & H_{a B}-\langle E\rangle S_{a b} & H_{a c}-\langle E\rangle S_{a c} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle S_{b b} & H_{b c}-\langle E\rangle S_{b c} \\
H_{a c}-\langle E\rangle S_{a c} & H_{b c}-\langle E\rangle S_{b c} & H_{c c}-\langle E\rangle S_{c c}
\end{array}\right|=0 \\
\text { Setting diagonal } S_{\mathrm{ii}}=1
\end{gathered}\left|\begin{array}{ccc}
H_{a a}-\langle E\rangle & H_{a B}-\langle E\rangle S_{a b} & H_{a c}-\langle E\rangle S_{a c} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle & H_{b c}-\langle E\rangle S_{b c} \\
H_{a c}-\langle E\rangle S_{a c} & H_{b c}-\langle E\rangle S_{b c} & H_{c c}-\langle E\rangle
\end{array}\right|=0 .
$$

## $\mathrm{H}_{2}{ }^{+}$Energies

## Linear Equations

$$
\begin{aligned}
& \left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0 \\
& \left(H_{a b}-\langle E\rangle S_{a b}\right) c_{a}+\left(H_{b b}-\langle E\rangle\right) c_{b}=0
\end{aligned}
$$

Secular Determinant

$$
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

Outline: 1. We will expand the Secular Determinant. This will give us a quadratic equation in $<E>$.
2. We will solve for the two values of $<\mathrm{E}>$ as a function of $\mathrm{H}_{\mathrm{a}}, \mathrm{H}_{\mathrm{ab}}, \mathrm{S}_{\mathrm{ab}}$.
3. We will explain how the matrix elements are evaluated and show the energies as a function of $R$
4. For each value of $\langle E\rangle$, we will calculate the MO ; i.e. the coefficients, $\mathrm{c}_{\mathrm{a}}$ and $\mathrm{c}_{\mathrm{b}}$.

## Expansion of the Secular Determinant

$$
\begin{aligned}
& \left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0 \longrightarrow\left(H_{a a}-\langle E\rangle\right)\left(H_{b b}-\langle E\rangle\right)-\left(H_{a b}-\langle E\rangle S_{a b}\right)^{2}=0 \\
& \quad \text { or } \quad\left(\langle E\rangle-H_{a a}\right)\left(\langle E\rangle-H_{b b}\right)-\left(H_{a b}-\langle E\rangle S_{a b}\right)^{2}=0
\end{aligned}
$$

This expression can be expanded, yielding a quadratic equation in <E>. This equation can be solved easily using the quadratic formula.

However, let's remember that for this problem: $H_{a a}=\left\langle 1 s_{a}\right| H\left|1 s_{a}\right\rangle$

$$
H_{b b}=\left\langle 1 s_{b}\right| H\left|1 s_{b}\right\rangle
$$

Therefore, $\mathrm{H}_{\mathrm{bb}}=\mathrm{H}_{\mathrm{aa}}$ (by symmetry)
The equation then simplifies to:

$$
\left(\langle E\rangle-H_{a a}\right)^{2}=\left(H_{a b}-\langle E\rangle S_{a b}\right)^{2}
$$

## Solving for the Energies

$$
\begin{gathered}
\left(\langle E\rangle-H_{a a}\right)^{2}=\left(H_{a b}-\langle E\rangle S_{a b}\right)^{2} \\
\downarrow \\
\langle E\rangle-H_{a a}= \pm\left(H_{a b}-\langle E\rangle S_{a b}\right)= \pm H_{a b} \mp\langle E\rangle S_{a b} \\
\downarrow \\
\langle E\rangle \pm\langle E\rangle S_{a b}=H_{a a} \pm H_{a b} \rightarrow\langle E\rangle\left(1 \pm S_{a b}\right)=H_{a a} \pm H_{a b}
\end{gathered}
$$

Therefore: $\langle E\rangle=\frac{H_{a a} \pm H_{a b}}{1 \pm S_{a b}}$

$$
\langle E\rangle_{+}=\frac{H_{a a}+H_{a b}}{1+S_{a b}} \quad \text { and } \quad\langle E\rangle_{-}=\frac{H_{a a}-H_{a b}}{1-S_{a b}}
$$

$$
\langle E\rangle_{+}=\frac{H_{a a}+H_{a b}}{1+S_{a b}} \quad \text { and } \quad\langle E\rangle_{-}=\frac{H_{a a}-H_{a b}}{1-S_{a b}}
$$

## Evaluating the Matrix Elements and Determining <E> ${ }_{+}$and <E>.

This is the easiest part because we won't do it.
These are very specialized integrals. For $\mathrm{H}_{\mathrm{ab}}$ and $\mathrm{S}_{\mathrm{ab}}$, they involve two-center integrals. That's because $1 \mathrm{~s}_{\mathrm{a}}$ is centered on nucleus a, whereas $1 \mathrm{~s}_{\mathrm{b}}$ is centered on nucleus b .

They can either be evaluated numerically, or analytically using a special "confocal elliptic" coordinate system. We will just present the results. They are functions of the internuclear distance, R.

$$
\begin{aligned}
& H_{a a}=-\frac{1}{2}-\frac{1}{R}+\left(1+\frac{1}{R}\right) e^{-2 R} \quad S_{a b}=e^{-R}\left(\frac{R^{3}}{3}+R+1\right) \\
& H_{a b}=-\frac{1}{2} S_{a b}-(R+1) e^{-R}
\end{aligned}
$$

$$
\begin{array}{ll}
\langle E\rangle_{+}=\frac{H_{a a}+H_{a b}}{1+S_{a b}} & \langle V\rangle_{+}=\langle E\rangle_{+}+\frac{1}{R}=\frac{H_{a a}+H_{a b}}{1+S_{a b}}+\frac{1}{R} \\
\langle E\rangle_{-}=\frac{H_{a a}-H_{a b}}{1-S_{a b}} & \langle V\rangle_{-}=\langle E\rangle_{-}+\frac{1}{R}=\frac{H_{a a}-H_{a b}}{1-S_{a b}}+\frac{1}{R}
\end{array}
$$

$<E>_{+}$and $\left.<E\right\rangle_{-}$represent the electronic energy of the $\mathrm{H}_{2}+$ ion.
The total energy, $\left\langle\mathrm{V}_{+}\right\rangle_{+}$and $\langle\mathrm{V}\rangle_{\text {. }}$, also includes the internuclear repulsion, 1/R

$$
\langle V\rangle_{+}=\langle E\rangle_{+}+\frac{1}{R}=\frac{H_{a a}+H_{a b}}{1+S_{a b}}+\frac{1}{R} \quad\langle V\rangle_{-}=\langle E\rangle_{-}+\frac{1}{R}=\frac{H_{a a}-H_{a b}}{1-S_{a b}}+\frac{1}{R}
$$



Asymptotic limit of $E_{H}$ as $R \rightarrow \infty$ $V(\infty)=-0.50 \mathrm{au}$
(R QqausulatandsMininimum Energy
$\mathrm{E}_{\text {min }}(\mathrm{cal})=-0.565 \mathrm{au}$ at $\mathrm{R}_{\text {min }}(\mathrm{cal})=2.49 \mathrm{a}_{0}=1.32 \AA$

## Comparison with Experiment



The calculated results aren't great, but it's a start. We'll discuss improvements after looking at the wavefunctions.

## $\mathrm{H}_{2}{ }^{+}$Wavefunctions

The LCAO Wavefunction: $\psi=c_{a} 1 s_{a}+c_{b} 1 s_{b}$

Remember that by using the Variational Principle on the expression for <E>, we developed two homogeneous linear equations relating $\mathrm{c}_{\mathrm{a}}$ and $\mathrm{c}_{\mathrm{b}}$.

$$
\begin{aligned}
& \left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0 \\
& \left(H_{a b}-\langle E\rangle S_{a b}\right) c_{a}+\left(H_{b b}-\langle E\rangle\right) c_{b}=0
\end{aligned}
$$

We then solved the Secular Determinant of the matrix coefficients to get two values for <E>

$$
\langle E\rangle_{+}=\frac{H_{a a}+H_{a b}}{1+S_{a b}} \quad\langle E\rangle_{-}=\frac{H_{a a}-H_{a b}}{1-S_{a b}}
$$

We can now plug one of the energies (either $<\mathrm{E}>_{+}$or $<\mathrm{E}>$. $_{\text {) }}$ into either of the linear equations to get a relationship between $c_{a}$ and $c_{b}$ for that value of the energy.

## Bonding Wavefunction

$$
\begin{gathered}
\left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0 \stackrel{\text { Plug in }}{\longleftarrow} \quad\langle E\rangle_{+}=\frac{H_{a a}+H_{a b}}{1+S_{a b}} \\
\left(H_{a a}-\frac{H_{a a}+H_{a b}}{1+S_{a b}}\right) c_{a}+\left(H_{a b}-\frac{H_{a a}+H_{a b}}{1+S_{a b}} S_{a b}\right) c_{b}=0 \\
\left(H_{a a}\left(1+S_{a b}\right)-H_{a a}-H_{a b}\right) c_{a}+\left(H_{a b}\left(1+S_{a b}\right)-H_{a a} S_{a b}-H_{a b} S_{a b}\right) c_{b}=0 \\
\left(H_{a a}+H_{a a} S_{a b}-H_{a b}\right) c_{a}+\left(H_{a b}+H_{a b} S_{a b}-H_{a a} S_{a b}-H_{a b} S_{a b}\right) c_{b}=0 \\
\left(H_{a a} S_{a b}-H_{a b}\right) c_{a}+\left(H_{a b}-H_{a a} S_{a b}\right) c_{b}=0 \\
\left(\frac{H_{a a} S_{a b}-H_{a b}}{H_{a a} S_{a b}-H_{a b}}\right) c_{a}+\left(\frac{H_{a b}-H_{a a} S_{a b}}{H_{a a} S_{a b}-H_{a b}}\right) c_{b}=0 \\
c_{a}-c_{b}=0
\end{gathered}
$$

Note: Plugging into the second of the two linear equations gets you the same result.

$$
\begin{array}{r}
\left.c_{b}=c_{a}+\psi=c_{a} 1 s_{a}+c_{b} 1 s_{b} \longrightarrow \begin{array}{l}
\psi_{+}=c_{a}\left(1 s_{a}+1 s_{b}\right) \\
\text { or } \quad \psi_{+}=N_{+}\left(1 s_{a}+1 s_{b}\right)
\end{array} . \begin{array}{r} 
\\
\hline
\end{array}\right)
\end{array}
$$

## $\mathrm{N}_{+}\left(=\mathrm{C}_{\mathrm{a}}\right)$ is determined by normalizing $\psi_{+}$

Normalization: $\quad 1=\int \psi_{+}^{*} \psi_{+} d \tau=\left\langle\psi_{+} \mid \psi_{+}\right\rangle$

$$
\begin{aligned}
& 1=\left\langle N_{+}\left(1 s_{a}+1 s_{b}\right) \mid N_{+}\left(1 s_{a}+1 s_{b}\right)\right\rangle=N_{+}^{2}\left(\left\langle 1 s_{a} \mid 1 s_{a}\right\rangle+\left\langle 1 s_{a} \mid 1 s_{b}\right\rangle+\left\langle 1 s_{b} \mid 1 s_{a}\right\rangle+\left\langle 1 s_{b} \mid 1 s_{b}\right\rangle\right) \\
& 1=N_{+}^{2}\left(1+S_{a b}+S_{a b}+1\right)=N_{+}^{2}\left(2+2 S_{a b}\right) \\
& N_{+}=\frac{1}{\sqrt{2+2 S_{a b}}} \longrightarrow \quad \psi_{+}=N_{+}\left(1 s_{a}+1 s_{b}\right) \\
&=\frac{1}{\sqrt{2+2 S_{a b}}}\left(1 s_{a}+1 s_{b}\right)
\end{aligned}
$$

## Antibonding Wavefunction

$$
\begin{gathered}
\left(H_{a a}-\langle E\rangle\right) c_{a}+\left(H_{a b}-\langle E\rangle S_{a b}\right) c_{b}=0 \underset{\text { Plug in }}{\rightleftarrows} \quad\langle E\rangle_{-}=\frac{H_{a a}-H_{a b}}{1-S_{a b}} \\
\left(H_{a a}-\frac{H_{a a}-H_{a b}}{1-S_{a b}}\right) c_{a}+\left(H_{a b}-\frac{H_{a a}-H_{a b}}{1-S_{a b}} S_{a b}\right) c_{b}=0 \\
\|_{\text {HW }} \\
c_{a}+c_{b}=0 \underset{H_{b}=-c_{a}}{\longrightarrow} c_{\text {HW }}
\end{gathered}
$$

Note: Plugging into the second of the two linear equations gets you the same result.

## Plotting the Wavefunctions

$$
\psi_{+}=N_{+}\left(1 s_{a}+1 s_{b}\right)
$$

$$
\psi_{-}=N_{-}\left(1 s_{a}-1 s_{b}\right)
$$




Note that the bonding MO, $\psi_{+}$, has significant electron density in the region between the two nuclei.

Note that the antibonding $\mathrm{MO}, \psi_{\_}$, has a node (zero electron density in the region between the two nuclei.

## Improving the Results

One way to improve the results is to add more versatility to the atomic orbitals used to define the wavefunction.

We used hydrogen atom 1s orbitals:

$$
\begin{equation*}
\phi_{1 s a}=1 s_{a}=\sqrt{\frac{1}{\pi}} e^{-r_{a}} \quad \text { and } \quad \phi_{1 s b}=1 s_{b}=\sqrt{\frac{1}{\pi}} e^{-r_{b}} \tag{inatomicunits}
\end{equation*}
$$

Instead of assuming that each nucleus has a charge, $Z=1$, we can use an effective nuclear charge, $Z^{\prime}$, as a variational parameter.

$$
\phi_{a}=\sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{a}} \text { and } \phi_{b}=\sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{b}}
$$

The expectation value for the energy, <E>, is now a function of both $Z$ ' and $R$.

$$
\psi=c_{a} \phi_{a}+c_{b} \phi_{b}=c_{a} \sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{a}}+c_{b} \sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{b}}
$$

This expression for the wavefunction can be plugged into the equation for $<E>$. The values of $Z$ ' and $R$ which minimize $<E>$ can then be calculated. The best $Z^{\prime}$ is 1.24 .

|  | $R_{\text {min }}$ | $D_{e}$ |
| :--- | :--- | :--- |
| Cal. $(Z=1)$ | $1.32 \AA$ | 1.77 eV |
| Cal.(Z'=1.24) | 1.06 | 2.35 |
| Expt. | 1.06 | 2.79 |

## An Even Better Improvement: More Atomic Orbitals

## Z-Direction



Instead of expanding the wavefunction as a linear combination of just one orbital on each atom, put in more atomic orbitals. e.g.

$$
\psi=c_{1} 1 s_{a}+c_{2} 2 s_{a}+c_{3} 2 p_{z a}+c_{4} 1 s_{b}+c_{5} 2 s_{b}+c_{6} 2 p_{z a}
$$

Note: A completely general rule is that if you assume that a Molecular Orbital is an LCAO of $N$ Atomic Orbitals, then you will get an NxN Secular Determinant and N Molecular Orbitals.

## Z-Direction



We ran a calculation using: 4 s orbitals, $2 \mathrm{p}_{\mathrm{z}}$ orbitals and $1 \mathrm{~d}_{\mathrm{z} 2}$ orbital on each atom.

The calculation took 12 seconds. We'll call it Cal.(Big)

|  | $R_{\text {min }}$ | $D_{e}$ |
| :--- | :---: | :--- |
| Cal.(Z=1) | $1.32 \AA$ | 1.77 eV |
| Cal.(Z'=1.24) | 1.06 | 2.35 |
| Cal.(Big) | 1.06 | 2.78 |
| Expt. | 1.06 | 2.79 |

## Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations - Cramer's Rule
- LCAO Treatment of $\mathrm{H}_{2}{ }^{+}$
- $\mathrm{H}_{2}{ }^{+}$Energies
- $\mathrm{H}_{2}{ }^{+}$Wavefunctions
- MO Treatment of the $\mathrm{H}_{2}$ Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules


## MO Treatment of the $\mathrm{H}_{2}$ Molecule

## The $\mathrm{H}_{2}$ Electronic Hamiltonian



$$
\begin{array}{ccccccc}
H=-\frac{1}{2} \nabla_{1}^{2}-\frac{1}{2} \nabla_{2}^{2} & -\frac{1}{r_{1 a}} & -\frac{1}{r_{1 b}} & -\frac{1}{r_{2 a}} & -\frac{1}{r_{2 b}} & +\frac{1}{r_{12}} \\
\text { KE } & \text { KE } & \text { PE } & \text { PE } & \text { PE } & \text { PE } & \text { PE } \\
\mathrm{e}_{1} & \mathrm{e}_{2} & \mathrm{e}-\mathrm{N} & \mathrm{e}-\mathrm{N} & \mathrm{e}-\mathrm{N} & \text { e-N } & \text { e-e } \\
& & \text { Attr } & \text { Attr } & \text { Attr } & \text { Attr } & \text { Repuls }
\end{array}
$$

## The LCAO Molecular Orbitals


$H_{a a}=\left\langle 1 s_{a}\right| H\left|1 s_{a}\right\rangle$ is the energy of an electron in a hydrogen 1s orbital.

We can put both electrons in $\mathrm{H}_{2}$ into the bonding orbital, $\psi_{+}$, one with $\alpha$ spin and one with $\beta$ spin.

## Notation

## Antibonding Orbital

$$
\psi_{-}=N_{-}\left(1 s_{a}-1 s_{b}\right)=\sigma_{u}^{*} 1 s
$$

## Bonding Orbital

$$
\psi_{+}=N_{+}\left(1 s_{a}+1 s_{b}\right)=\sigma_{g} 1 s
$$

e- density max. on internuclear axis
symmetric w.r.t.
inversion
$\sigma_{u}^{*} \overleftarrow{1 S}^{\text {antibonding }}$ antisymmetric w.r.t. inversion

## The Molecular Wavefunction

Put 1 electron in $\sigma_{g} 1 \mathrm{~s}$ with $\alpha$ spin: $\sigma_{g} 1 \mathrm{~s}(1) \alpha_{1}$
Put 1 electron in $\sigma_{g} 1 \mathrm{~s}$ with $\beta$ spin: $\sigma_{g} 1 \mathrm{~s}(2) \beta_{2}$
Form the antisymmetrized product using a Slater Determinant.

$$
\begin{gathered}
\psi_{M O}=\frac{1}{\sqrt{2!}}\left|\begin{array}{cc}
\sigma_{g} 1 s(1) \alpha_{1} & \sigma_{g} 1 s(1) \beta_{1} \\
\sigma_{g} 1 s(2) \alpha_{2} & \sigma_{g} 1 s(2) \beta_{2}
\end{array}\right| \\
\psi_{M O}=\frac{1}{\sqrt{2}}\left[\sigma_{g} 1 s(1) \alpha_{1} \cdot \sigma_{g} 1 s(2) \beta_{2}-\sigma_{g} 1 s(1) \beta_{1} \cdot \sigma_{g} 1 s(2) \alpha_{2}\right] \\
\psi_{M O}=\frac{\left[\sigma_{g} 1 s(1) \sigma_{g} 1 s(2)\right]}{\psi_{\text {spat }}} \frac{\frac{1}{\sqrt{2}}\left[\alpha_{1} \beta_{2}-\beta_{1} \alpha_{2}\right]}{\psi_{\text {spin }}}=\psi_{\text {spat }} \cdot \psi_{\text {spin }}
\end{gathered}
$$

$$
\begin{gathered}
\psi_{M O}=\left[\sigma_{g} 1 s(1) \sigma_{g} 1 s(2)\right] \cdot \frac{1}{\sqrt{2}}\left[\alpha_{1} \beta_{2}-\beta_{1} \alpha_{2}\right] \\
\psi_{\text {spin }}=\frac{1}{\sqrt{2}}\left[\alpha_{1} \beta_{2}-\beta_{1} \alpha_{2}\right] \quad \text { The spin wavefunction is already normalizeD }
\end{gathered}
$$

Because the Hamiltonian doesn't operate on the spin, the spin wavefunction has no effect on the energy of $\mathrm{H}_{2}$.

This independence is only because we were able to write the total wavefunction as a product of spatial and spin functions. This cannot be done for most molecules.

$$
\psi_{\text {spat }}=\sigma_{g} 1 s(1) \sigma_{g} 1 s(2)=\left[N_{+}\left(1 s_{a}+1 s_{b}\right)\right]\left[N_{+}\left(1 s_{a}+1 s_{b}\right)\right]
$$

## The MO Energy of $\mathrm{H}_{2}$

$$
\begin{gathered}
\psi_{\text {spat }}=\sigma_{g} 1 s(1) \sigma_{g} 1 s(2)=\left[N_{+}\left(1 s_{a}+1 s_{b}\right)\right]\left[N_{+}\left(1 s_{a}+1 s_{b}\right)\right] \\
H=-\frac{1}{2} \nabla_{1}^{2}-\frac{1}{2} \nabla_{2}^{2}-\frac{1}{r_{1 a}}-\frac{1}{r_{1 b}}-\frac{1}{r_{2 a}}-\frac{1}{r_{2 b}}+\frac{1}{r_{12}}
\end{gathered}
$$

The expectation value for the ground state $\mathrm{H}_{2}$ electronic energy is given by:

$$
E=\left\langle\psi_{\text {spat }}\right| H\left|\psi_{\text {spat }}\right\rangle
$$

using the wavefunction and Hamiltonian above.
The (multicenter) integrals are very messy to integrate, but can be integrated analytically using confocal elliptic coordinates, to get $E$ as a function of $R$ (the internuclear distance)

The total energy is then: $V(R)=E(R)+\frac{1}{R}$


## Improving the Results

As for $\mathrm{H}_{2}{ }^{+}$, one can add a variational parameter to the atomic orbitals used in $\sigma_{g} 1 \mathrm{~s}$.

$$
\begin{aligned}
\phi_{a} & =\sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{a}} \text { and } \phi_{b}=\sqrt{\frac{Z^{\prime 3}}{\pi}} e^{-Z^{\prime} r_{b}} \quad \text { (in at } \\
\psi_{\text {spat }} & =\sigma_{g} 1 s(1) \sigma_{g} 1 s(2)=\left[N\left(\phi_{a}+\phi_{b}\right)\right]\left[N\left(\phi_{a}+\phi_{b}\right)\right]
\end{aligned}
$$

The energy is now a function of both $Z$ ' and $R$.
One can find the values of both that minimize the energy.

|  | $R_{\text {min }}$ | $D_{e}$ |
| :--- | :--- | :--- |
| Cal.(Z=1) | $0.85 \AA$ | 2.70 eV |
| Cal.(Var. Z') | 0.73 | 3.49 |
| Expt. | 0.74 | 4.73 |

## An Even Better Improvement: More Atomic Orbitals



As for $\mathrm{H}_{2}{ }^{+}$, one can make the bonding orbital a Linear Combination of more than two atomic orbitals; e.g.

$$
\sigma_{g} 1 s=c_{1} 1 s_{a}+c_{2} 2 s_{a}+c_{3} 2 p_{z a}+c_{4} 1 s_{b}+c_{5} 2 s_{b}+c_{6} 2 p_{z a}
$$

We performed a Hartree-Fock calculation on $\mathrm{H}_{2}$ using an LCAO that included 4 s orbitals, $2 \mathrm{p}_{\mathrm{z}}$ orbitals and $1 \mathrm{~d}_{\mathrm{z} 2}$ orbitals on each hydrogen.

|  | $R_{\text {min }}$ | $D_{e}$ |  |
| :--- | :---: | :--- | :--- |
| Cal.(Z=1) | $0.85 \AA$ | 2.70 eV |  |
| Cal.(Var. Z') | 0.73 | 3.49 |  |
| Cal.(HF-Big) | 0.74 | 3.62 | Question: Hey!! What went wrong?? |
| Expt. | 0.74 | 4.73 |  |

## Question: What went wrong??

When we performed this level calculation on $\mathrm{H}_{2}{ }^{+}$, we nailed the Dissociation Energy almost exactly.

But on $\mathrm{H}_{2}$ the calculated $\mathrm{D}_{\mathrm{e}}$ is almost $25 \%$ too low.
Answer: The problem, is that unlike $\mathrm{H}_{2}{ }^{+}, \mathrm{H}_{2}$ has
2 (two) electrons, whose motions are correlated.

## Homonuclear Diatomic Molecules

We showed that the Linear Combination of 1s orbitals on two hydrogen atoms form 2 Molecular Orbitals, which we used to describe the bonding in $\mathrm{H}_{2}{ }^{+}$and $\mathrm{H}_{2}$.

These same orbitals may be used to describe the bonding in $\mathrm{He}_{2}{ }^{+}$and lack of bonding in $\mathrm{He}_{2}$.

Linear Combinations of $2 s$ and $2 p$ orbitals can be used to create Molecular Orbitals, which can be used to describe the bonding of second row diatomic molecules (e.g. $\mathrm{Li}_{2}$ ).

We can place two electrons into each Molecular Orbital.

Definition: Bond Order - $B O=1 / 2\left(n_{B}-n_{A}\right)$
$n_{B}=$ number of electrons in Bonding Orbitals
$\mathrm{n}_{\mathrm{A}}=$ number of electrons in Antibonding Orbitals

## Bonding in $\mathrm{He}_{2}{ }^{+}$



## Slater Determinant: $\mathrm{He}_{2}{ }^{+}$

$$
\begin{gathered}
\text { Config }=\left(\sigma_{g} 1 s\right)^{2}\left(\sigma_{u}^{*} 1 s\right)^{1} \\
\psi_{M O}=\frac{1}{\sqrt{3!}}\left|\begin{array}{lll}
\sigma_{g} 1 s(1) \alpha_{1} & \sigma_{g} 1 s(1) \beta_{1} & \sigma_{u}^{*} 1 s(1) \alpha_{1} \\
\sigma_{g} 1 s(2) \alpha_{2} & \sigma_{g} 1 s(2) \beta_{2} & \sigma_{u}^{*} 1 s(2) \alpha_{2} \\
\sigma_{g} 1 s(3) \alpha_{3} & \sigma_{g} 1 s(3) \beta_{3} & \sigma_{u}^{*} 1 s(3) \alpha_{3}
\end{array}\right| \\
\psi_{M O}=\frac{1}{\sqrt{3!}}\left|\begin{array}{lll}
\sigma_{g} 1 s(1) \alpha_{1} & \sigma_{g} 1 s(2) \beta_{2} & \sigma_{u}^{*} 1 s(3) \alpha_{3}
\end{array}\right| \\
\text { Shorthand Notation }
\end{gathered}
$$


$\mathrm{He}_{2}$ has 4 electrons

## Electron Configuration

Config $=\left(\sigma_{g} 1 s\right)^{2}\left(\sigma_{u}^{*} 1 s\right)^{2}$

$$
\begin{aligned}
\mathrm{BO} & =1 / 2(2-2) \\
& =0
\end{aligned}
$$

Actually, $\mathrm{He}_{2}$ forms an extremely weak "van der Waal's complex", with $R_{\text {min }} \approx 3 \AA$ and $D_{e} \approx 0.001 \mathrm{eV}$ [it can be observed at $T=10^{-3} \mathrm{~K}$.

## Second Row Homonuclear Diatomic Molecules

We need more Molecular Orbitals to describe diatomic molecules with more than 4 electrons.


## Sigma-2s Orbitals



## Sigma-2p Orbitals



Note sign reversal of $\sigma 2 p$ from $\sigma 2$ s and $\sigma 1$ s orbitals.

## Pi-2p Orbitals



There is a degenerate $\pi_{u} 2 p$ orbital and a degenerate $\pi_{g}{ }^{*} 2 p$ orbital arising from analogous combinations of $2 p_{x a}$ and $2 p_{x b}$

## Homonuclear Diatomic Orbital Energy Diagram



## Consider $\mathrm{Li}_{2}$

$$
\sigma_{u}^{*} 2 p
$$

$$
\pi_{g}^{*} 2 p
$$

$\qquad$

$$
\begin{gathered}
\sigma_{g} 2 p \\
\pi_{u} 2 p
\end{gathered}
$$

$$
\begin{gathered}
\sigma_{u}^{*} 2 s \\
\sigma_{g} 2 s
\end{gathered}
$$

$$
\sigma_{u}^{*} 1 s \xlongequal{\uparrow \downarrow}
$$

$$
\sigma_{g} 1 s \xlongequal{\uparrow}
$$

(a) What is the electron configuration?
(b) What is the Bond Order?
(c) What is the spin multiplicity?
(Singlet, Doublet or Triplet)

## 6 Electrons

$$
\begin{aligned}
& \left(\sigma_{g} 1 s\right)^{2}\left(\sigma_{u}^{*} 1 s\right)^{2}\left(\sigma_{g} 2 s\right)^{2} \\
& B O=1 / 2(4-2)=1
\end{aligned}
$$

$$
\text { S = } 0 \text { : Singlet }
$$

## Consider $\mathrm{F}_{2}$


(a) What is the electron configuration?
(b) What is the Bond Order?
(c) What is the spin multiplicity?
(Singlet, Doublet or Triplet)


$$
\begin{aligned}
& \sigma_{u}^{*} 2 s \xlongequal{\uparrow} \xlongequal{\uparrow \downarrow} \\
& \sigma_{g} 2 s
\end{aligned}
$$

$$
\sigma_{u}^{*} 1 s \xlongequal{\uparrow \downarrow}
$$

$$
\sigma_{g} 1 s \uparrow
$$

## 18 Electrons

$$
\begin{gathered}
\left(\sigma_{g} 1 s\right)^{2}\left(\sigma_{u}^{*} 1 s\right)^{2}\left(\sigma_{g} 2 s\right)^{2}\left(\sigma_{u}^{*} 2 s\right)^{2}\left(\pi_{u} 2 p\right)^{4}\left(\sigma_{g} 2 p\right)^{2}\left(\pi_{g}^{*} 2 p\right)^{4} \\
\mathrm{BO}=1 / 2(10-8)=1 \\
S=0: \text { Singlet }
\end{gathered}
$$

## Consider $\mathrm{O}_{2}$


(a) What is the electron configuration?
(b) What is the Bond Order?
(c) What is the spin multiplicity?
(Singlet, Doublet or Triplet)

$\sigma_{u}^{*} 2 s \stackrel{\uparrow \downarrow}{ }$
$\sigma_{g} 2 s \uparrow$
$\sigma_{u}^{*} 1 s \stackrel{\uparrow \downarrow}{ }$
$\sigma_{g} 1 s \xlongequal{\uparrow}$

16 Electrons

$$
\begin{gathered}
\left(\sigma_{g} 1 s\right)^{2}\left(\sigma_{u}^{*} 1 s\right)^{2}\left(\sigma_{g} 2 s\right)^{2}\left(\sigma_{u}^{*} 2 s\right)^{2}\left(\pi_{u} 2 p\right)^{4}\left(\sigma_{g} 2 p\right)^{2}\left(\pi_{g}^{*} 2 p\right)^{2} \\
\mathrm{BO}=1 / 2(10-6)=2 \\
S=1: \text { Triplet }
\end{gathered}
$$


$\sigma_{u}^{*} 2 s \stackrel{\uparrow \downarrow}{ }$

$$
\sigma_{g} 2 s \stackrel{\uparrow \downarrow}{ }
$$

$$
\sigma_{u}^{*} 1 s \stackrel{\uparrow \downarrow}{ }
$$

$$
\sigma_{g} 1 s
$$

$$
\mathrm{O}_{2}
$$

Consider $\mathrm{O}_{2}, \mathrm{O}_{2}{ }^{+}, \mathrm{O}_{2}{ }^{-}$
(a) Which has the longest bond?
(b) Which has the highest vibrational frequency?
(c) Which has the highest Dissociation Energy?
$\mathrm{O}_{2}: 16$ Electrons $-\mathrm{BO}=2$
$\mathrm{O}_{2}^{+}: 15$ Electrons $-\mathrm{BO}=2.5$
$\mathrm{O}_{2}{ }^{-}: 17$ Electrons $-\mathrm{BO}=1.5$
$\mathrm{O}_{2}{ }^{-}$has the longest bond.
$\mathrm{O}_{2}{ }^{+}$has the highest vibrational frequency.
$\mathrm{O}_{2}{ }^{+}$has the highest Dissociation Energy.

## A More General Picture of Sigma Orbital Combinations



The assumption in the past section that only identical orbitals on the two atoms combine to form MO's is actually a bit simplistic.

In actuality, each of the $6 \sigma$ MO's is really a combination of all 6 AO's.

$$
\psi_{M O}=c_{1} 1 s_{a}+c_{2} 2 s_{a}+c_{3} 2 p_{z a}+c_{4} 1 s_{b}+c_{5} 2 s_{b}+c_{6} 2 p_{z b}
$$

## Approximate vs. Accurate MO's in $\mathrm{C}_{2}$

$$
\begin{gathered}
\psi_{M O}=c_{1} 1 s_{a}+c_{2} 2 s_{a}+c_{3} 2 p_{z a}+c_{4} 1 s_{b}+c_{5} 2 s_{b}+c_{6} 2 p_{z b} \\
\sigma 2 \mathrm{p} \text { MO }(\mathrm{E} \approx-15 \mathrm{eV})
\end{gathered}
$$

$$
\begin{gathered}
\psi_{\text {Approx }} \approx 0.70 \cdot 2 p_{z a}+0.70 \cdot 2 p_{z b} \\
\psi_{\text {Accur }}=\left[-0.07 \cdot 1 s_{a}+0.40 \cdot 2 s_{a}+0.60 \cdot 2 p_{z a}\right]+\left[-0.07 \cdot 1 s_{b}+0.40 \cdot 2 s_{b}-0.60 \cdot 2 p_{z b}\right] \\
\sigma 2 \mathrm{~s} \mathrm{MO}(E \approx-40 \mathrm{eV})
\end{gathered}
$$

$$
\begin{aligned}
& \psi_{\text {Approx }} \approx 0.70 \cdot 2 s_{a}+0.70 \cdot 2 s_{b} \\
& \psi_{\text {Accur }}=\left[-0.17 \cdot 1 s_{a}+0.50 \cdot 2 s_{a}+0.23 \cdot 2 p_{z a}\right]+\left[-0.17 \cdot 1 s_{b}+0.50 \cdot 2 s_{b}+0.23 \cdot 2 p_{z b}\right]
\end{aligned}
$$

$$
\sigma 1 \mathrm{~s} \text { MO }(E \approx-420 \mathrm{eV})
$$

$$
\begin{aligned}
& \psi_{\text {Approx }} \approx 0.70 \cdot 1 s_{a}+0.70 \cdot 1 s_{b} \\
& \psi_{\text {Accur }}=\left[0.70 \cdot 1 s_{a}+0.01 \cdot 2 s_{a}\right]+\left[0.70 \cdot 1 s_{b}+0.01 \cdot 2 s_{b}\right]
\end{aligned}
$$

## Heteronuclear Diatomic Molecules

$$
\begin{gathered}
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0 \\
H_{b b} \neq H_{a a}
\end{gathered}
$$

Therefore, the energies are not symmetrically displaced, and the magnitudes of the coefficients are no longer equal.

$$
\left|c_{b}\right| \neq\left|c_{a}\right|
$$



## Interpretation of Secular Determinant Parameters

$$
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

$$
S_{a b}=\left\langle\phi_{a} \mid \phi_{b}\right\rangle=\int \phi_{a}^{*} \phi_{b} d \tau
$$

## Overlap Integral



Generally, $\mathrm{S}_{\mathrm{ab}} \approx 0.1-0.2$
Commonly, to simplify the calculations, it is approximated that $\mathrm{S}_{\mathrm{ab}} \approx 0$

$$
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

$H_{a a}=\left\langle\phi_{a}\right| H\left|\phi_{a}\right\rangle=\int \phi_{a} H \phi_{a} d \tau \quad$ Energy of an electron in atomic orbital, $\phi_{\mathrm{a}}$, in an unbonded atom.
$H_{b b}=\left\langle\phi_{b}\right| H\left|\phi_{b}\right\rangle=\int \phi_{b}^{*} H \phi_{b} d \tau \quad$ Energy of an electron in atomic orbital, $\phi_{b}$, in an unbonded atom.

$$
\mathrm{H}_{\mathrm{aa}}, \mathrm{H}_{\mathrm{bb}}<0 \quad \text { Traditionally, } \mathrm{H}_{\mathrm{aa}} \text { and } \mathrm{H}_{\mathrm{bb}} \text { are called "Coulomb Integrals" }
$$

Commonly, $\mathrm{H}_{\mathrm{aa}}$ is estimated as -IE, where IE is the Ionization Energy of an electron in the atomic orbital, $\phi_{a}$.


$$
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

$$
H_{a b}=\left\langle\phi_{a}\right| H\left|\phi_{b}\right\rangle=\int \phi_{a} H \phi_{b} d \tau \quad \text { Interaction energy between atomic orbitals, }
$$ $\phi_{a}$ and $\phi_{b}$.

## Traditionally, $\mathrm{H}_{\mathrm{ab}}$ is called the "Resonance Integral".

$\mathrm{H}_{\mathrm{ab}}$ is approximately proportional to:
(1) the orbital overlap
(2) the average of $\mathrm{H}_{\mathrm{aa}}$ and $\mathrm{H}_{\mathrm{ab}}$

$$
H_{a b} \approx K\left[\frac{H_{a a}+H_{b b}}{2}\right] S_{a b} \quad K \approx 1.75
$$

Wolfsberg-Helmholtz Formula (used in Extended Hückel Model)

$$
\mathrm{H}_{\mathrm{ab}}<0
$$

## Interpretation of Orbital Coefficients

Let's assume that an MO is a linear combination of 2 normalized AO's:

$$
\psi_{M O}=N\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right)
$$

Normalization: $\quad 1=\int \psi_{M O}^{2} d \tau=\left\langle\psi_{M O} \mid \psi_{M O}\right\rangle$

$$
\begin{aligned}
& 1=\left\langle N\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right) \mid N\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right)\right\rangle \\
& 1=N^{2}\left[c_{a}^{2}\left\langle\phi_{a} \mid \phi_{a}\right\rangle+c_{b}^{2}\left\langle\phi_{b} \mid \phi_{b}\right\rangle+2 c_{a} c_{b}\left\langle\phi_{a} \mid \phi_{b}\right\rangle\right] \\
& 1=N^{2}\left[c_{a}^{2}+c_{b}^{2}+2 c_{a} c_{b} S_{a b}\right] \quad \text { where } \quad \\
& \\
& N=\frac{S_{a b}=\left\langle\phi_{a} \mid \phi_{b}\right\rangle}{\sqrt{c_{a}^{2}+c_{b}^{2}+2 c_{a} c_{b} S_{a b}}} \quad \begin{array}{cc}
\text { Orbital }
\end{array}
\end{aligned}
$$

$$
\begin{gathered}
\psi_{M O}=\frac{1}{\sqrt{c_{a}^{2}+c_{b}^{2}+2 c_{a} c_{b} S_{a b}}}\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right) \\
\text { If } \mathrm{S}_{\mathrm{ab}} \approx 0: \quad \psi_{M O}=\frac{c_{a}}{\sqrt{c_{a}^{2}+c_{b}^{2}}} \phi_{a}+\frac{c_{b}}{\sqrt{c_{a}^{2}+c_{b}^{2}}} \phi_{b} \\
f_{a}=\frac{c_{a}^{2}}{c_{a}^{2}+c_{b}^{2}} \quad \text { Fraction of electron density in orbital a } \\
f_{b}=\frac{c_{b}^{2}}{c_{a}^{2}+c_{b}^{2}} \quad \text { Fraction of electron density in orbital b }
\end{gathered}
$$

General: $\psi_{M O}=N \sum c_{i} \phi_{i}$

$$
f_{i}=\frac{c_{i}^{2}}{\sum c_{i}^{2}}
$$

Fraction of electron density in orbital i

$$
f_{a}=\frac{c_{a}^{2}}{c_{a}^{2}+c_{b}^{2}} \quad f_{b}=\frac{c_{b}^{2}}{c_{a}^{2}+c_{b}^{2}} \quad\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0
$$

Homonuclear Diatomic Molecules: $\quad H_{b b}=H_{a a}$

$$
\begin{aligned}
& \left|c_{b}\right|=\left|c_{a}\right| \\
& f_{a}=f_{b}=0.50
\end{aligned}
$$

Heteronuclear Diatomic Molecules: $\quad H_{b b} \neq H_{a a}$

$$
\begin{aligned}
& \left|c_{b}\right| \neq\left|c_{a}\right| \\
& f_{b} \neq f_{a}
\end{aligned}
$$

$$
\begin{gathered}
\text { Antibonding (A) } \\
\phi_{a} \xlongequal[E=H_{a a}]{\psi_{A}=c_{a} \phi_{a}+c_{b} \phi_{b}} \\
E=H_{b b} \phi_{b} \\
\text { Bonding (B) } \\
\psi_{B}=c_{a} \phi_{a}+c_{b} \phi_{b} \\
\left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0 \\
\left(H_{a a}-\langle E\rangle\right)\left(H_{b b}-\langle E\rangle\right)-\left(H_{a b}-\langle E\rangle S_{a b}\right)\left(H_{a b}-\langle E\rangle S_{a b}\right)=0
\end{gathered}
$$

One has a quadratic equation, which can be solved to yield two values for the energy, <E>.

One can then determine $\mathrm{c}_{\mathrm{b}} / \mathrm{c}_{\mathrm{a}}$ for both the bonding and antibonding orbitals.

## A Numerical Example: Hydrogen Fluoride (HF)

$$
\left.\begin{gathered}
\text { ( } \\
\psi_{M O}=N\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right)=N\left(c_{a} 1 s_{a}(H)+c_{b} 2 p_{z b}(F)\right) \\
H_{a a}-\langle E\rangle \\
H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} \\
H_{b}-\langle E\rangle
\end{gathered} \right\rvert\,=0
$$

## Matrix Elements

$$
\begin{gathered}
H_{a a}=\left\langle\phi_{a}\right| H\left|\phi_{a}\right\rangle=\left\langle 1 s_{a}(H)\right| H\left|1 s_{a}(H)\right\rangle=-13.6 \mathrm{eV} \\
H_{b b}=\left\langle\phi_{b}\right| H\left|\phi_{b}\right\rangle=\left\langle 2 p_{z b}(F)\right| H\left|2 p_{z b}(F)\right\rangle=-17.4 \mathrm{eV} \\
H_{a b}=\left\langle\phi_{a}\right| H\left|\phi_{b}\right\rangle=\left\langle 1 s_{a}(F)\right| H\left|2 p_{z b}(F)\right\rangle=-2.0 \mathrm{eV} \\
S_{a b}=\left\langle\phi_{a} \mid \phi_{b}\right\rangle=\left\langle 1 s_{a}(H) \mid 2 p_{z b}(F)\right\rangle \approx 0
\end{gathered}
$$

$$
\begin{aligned}
& \left|\begin{array}{cc}
H_{a a}-\langle E\rangle & H_{a b}-\langle E\rangle S_{a b} \\
H_{a b}-\langle E\rangle S_{a b} & H_{b b}-\langle E\rangle
\end{array}\right|=0 \\
& H_{a \mathrm{a}}=-13.6 \mathrm{eV} \\
& H_{b b}=-17.4 \mathrm{eV} \\
& H_{a b}=-2.0 \mathrm{eV} \\
& S_{a b} \approx 0 \\
& \left|\begin{array}{cc}
-13.6-\langle E\rangle & -2 \\
-2 & -17.4-\langle E\rangle
\end{array}\right|=0 \\
& (-13.6-\langle E\rangle)(-17.4-\langle E\rangle)-(-2)(-2)=0 \\
& \langle E\rangle^{2}+31.0\langle E\rangle+232.64=0 \\
& \langle E\rangle=\frac{-31.0 \pm \sqrt{(31.0)^{2}-4(1)(232.64)}}{2} \\
& \langle E\rangle_{B}=\frac{-31.0-\sqrt{30.44}}{2}=-18.26 \mathrm{eV} \quad\langle E\rangle_{A}=\frac{-31.0+\sqrt{30.44}}{2}=-12.74 \mathrm{eV}
\end{aligned}
$$

$$
\left|\begin{array}{cc}
-13.6-\langle E\rangle & -2 \\
-2 & -17.4-\langle E\rangle
\end{array}\right|=0 \longrightarrow \begin{aligned}
& (-13.6-\langle E\rangle) c_{a}-2 c_{b}=0 \\
& -2 c_{a}+(-17.4-\langle E\rangle) c_{b}=0
\end{aligned}
$$

## Bonding MO

$$
\begin{aligned}
& {[-13.6-(-18.25)] c_{a}-2 c_{b}=0} \\
& \begin{aligned}
\frac{c_{b}}{c_{a}} & =2.33 \rightarrow c_{b}=2.33 c_{a} \\
\psi_{B} & =\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right) \\
& =c_{a}\left(\phi_{a}+2.33 \phi_{b}\right) \\
& =N\left(\phi_{a}+2.33 \phi_{b}\right)
\end{aligned}
\end{aligned}
$$

$$
\psi_{B}=\frac{1}{\sqrt{1+(2.33)^{2}}}\left(\phi_{a}+2.33 \phi_{b}\right)
$$

$$
\psi_{B}=0.394 \phi_{a}+0.919 \phi_{b}
$$

$$
=0.394 \cdot 1 s_{a}(H)+0.919 \cdot 2 p_{z b}(F)
$$

## Antibonding MO

$$
\begin{aligned}
& {[-13.6-(-12.74)] c_{a}-2 c_{b}=0} \\
& \begin{aligned}
\frac{c_{b}}{c_{a}} & =-0.430 \rightarrow c_{b}=-0.430 c_{a} \\
\psi_{A} & =\left(c_{a} \phi_{a}+c_{b} \phi_{b}\right) \\
& =c_{a}\left(\phi_{a}-0.430 \phi_{b}\right) \\
& =N\left(\phi_{a}-0.430 \phi_{b}\right)
\end{aligned}
\end{aligned}
$$

$$
\psi_{A}=\frac{1}{\sqrt{1+(-0.430)^{2}}}\left(\phi_{a}-0.430 \phi_{b}\right)
$$

$$
\psi_{A}=0.919 \phi_{a}-0.394 \phi_{b}
$$

$$
=0.919 \cdot 1 s_{a}(H)-0.394 \cdot 2 p_{z b}(F)
$$

## Electron Densities in Hydrogen Fluoride

## Bonding Orbital

$$
\begin{gathered}
\psi_{B}=0.394 \phi_{a}+0.919 \phi_{b}=0.394 \cdot 1 s_{a}(H)+0.919 \cdot 2 p_{z b}(F) \\
f_{a}=f_{H}=\frac{c_{a}^{2}}{c_{a}^{2}+c_{b}^{2}}=(0.394)^{2}=0.16 \quad f_{b}=f_{F}=\frac{c_{b}^{2}}{c_{a}^{2}+c_{b}^{2}}=(0.919)^{2}=0.84
\end{gathered}
$$

Over $80 \%$ of the electron density of the two electrons in the bonding MO resides on the Fluorine atom in HF.

## Antibonding Orbital

$$
\begin{gathered}
\psi_{A}=0.919 \phi_{a}-0.394 \phi_{b}=0.919 \cdot 1 s_{a}(H)-0.394 \cdot 2 p_{z b}(F) \\
f_{a}=f_{H}=\frac{c_{a}^{2}}{c_{a}^{2}+c_{b}^{2}}=(0.919)^{2}=0.84 \quad f_{b}=f_{F}=\frac{c_{b}^{2}}{c_{a}^{2}+c_{b}^{2}}=(0.394)^{2}=0.16
\end{gathered}
$$

The situation is reversed in the Antibonding MO. However, remember that there are no electrons in this orbital.

