Lecture 9 Molecular Structure

Diatomic Molecules

Born–Oppenheimer approximation

we are forced to make an approximation at the outset. Even the simplest molecule, H_2^+ , consists of three particles, and its Schrödinger equation cannot be solved analytically.

To overcome this difficulty, we adopt the **Born**– **Oppenheimer approximation**, which takes note of <u>the</u> <u>great difference</u> 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 states.



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

The Born-Oppenheimer Approximation <u>states that</u> 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* H_2 . Rather, it is H_2^+ , which has two hydrogen nuclei and one electron.



The H₂⁺ Hamiltonian (in au)



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

$$\left(-\frac{1}{2M_{a}}\nabla_{a}^{2}-\frac{1}{2M_{b}}\nabla_{b}^{2}+\frac{1}{R_{ab}}+E_{el}\right)\cdot\chi(R_{ab})=E_{nuc}\cdot\chi(R_{ab})$$

 E_{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

$$\left(-\frac{1}{2}\nabla^2 - \frac{1}{r_a} - \frac{1}{r_b}\right)\psi = E_{elect}\psi = E\psi$$

Because 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 H**₂+ **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 α and the second with spin β .

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.

 $\psi(1,2,3,...N) = (\psi_1^{MO}(1)\alpha_1) \cdot (\psi_1^{MO}(2)\beta_2) \cdot (\psi_2^{MO}(3)\alpha_3) \cdot (\psi_2^{MO}(4)\alpha_4)...$

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 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 1s orbitals on each atom:

$$\psi = C_a \phi_{1sa} + C_b \phi_{1sb} = C_a \mathbf{1}S_a + C_b \mathbf{1}S_b$$

shorthand

Assume that $1s_a$ and $1s_b$ 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.

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

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

$$Denom = \langle \psi | \psi \rangle = \langle c_a \mathbf{1} \mathbf{s}_a + c_b \mathbf{1} \mathbf{s}_b | c_a \mathbf{1} \mathbf{s}_a + c_b \mathbf{1} \mathbf{s}_b \rangle$$
$$Denom = c_a^2 \langle \mathbf{1} \mathbf{s}_a | \mathbf{1} \mathbf{s}_a \rangle + c_a c_b \langle \mathbf{1} \mathbf{s}_a | \mathbf{1} \mathbf{s}_b \rangle + c_b c_a \langle \mathbf{1} \mathbf{s}_b | \mathbf{1} \mathbf{s}_a \rangle + c_b^2 \langle \mathbf{1} \mathbf{s}_b | \mathbf{1} \mathbf{s}_b \rangle$$

Remember that $\langle 1s_a | 1s_a \rangle = \langle 1s_b | 1s_b \rangle = 1$ because $1s_a$ and $1s_b$ are normalized.

Define: $S_{ab} = \langle 1s_a | 1s_b \rangle = \langle 1s_b | 1s_a \rangle$, where S_{ab} is the overlap integral.

 $Denom = c_a^2 + 2c_a c_b S_{ab} + c_b^2$

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

 $Num = \langle \psi | H | \psi \rangle = \langle c_a 1 s_a + c_b 1 s_b | H | c_a 1 s_a + c_b 1 s_b \rangle$

 $Num = c_a^2 \langle 1s_a | H | 1s_a \rangle + c_a c_b \langle 1s_a | H | 1s_b \rangle + c_b c_a \langle 1s_b | H | 1s_a \rangle + c_b^2 \langle 1s_b | H | 1s_b \rangle$

$$H_{aa} = \langle 1s_a | H | 1s_a \rangle$$

$$H_{bb} = \langle 1s_b | H | 1s_b \rangle$$

$$H_{ab} = \langle 1s_a | H | 1s_b \rangle$$

$$H_{ba} = \langle 1s_b | H | 1s_a \rangle = H_{ab}$$
 because H is Hermitian

 $Num = c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}$ Note: For this particular problem, $H_{bb} = H_{aa}$ by symmetry. However, this is not true in general. $Num = c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb} \qquad Denom = c_a^2 + 2c_a c_b S_{ab} + c_b^2$ $\left\langle E \right\rangle = \frac{\left\langle \psi \left| H \right| \psi \right\rangle}{\left\langle \psi \left| \psi \right\rangle} = \frac{Num}{Denom} = \frac{c_a^2 H_{aa}^2 + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + 2c_a c_b S_{ab} + c_b^2}$

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 $\langle E \rangle$ and set them equal to 0.

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

$$\left\langle E\right\rangle = \frac{c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + 2c_a c_b S_{ab} + c_b^2}$$

$$\left(\boldsymbol{c}_{a}^{2}+2\boldsymbol{c}_{a}\boldsymbol{c}_{b}\boldsymbol{S}_{ab}+\boldsymbol{c}_{b}^{2}\right)\left\langle \boldsymbol{E}\right\rangle =\boldsymbol{c}_{a}^{2}\boldsymbol{H}_{aa}+2\boldsymbol{c}_{a}\boldsymbol{c}_{b}\boldsymbol{H}_{ab}+\boldsymbol{c}_{b}^{2}\boldsymbol{H}_{bb}$$

Differentiate both sides w.r.t. c_a: Use product rule on left side

$$\frac{\partial \left[\left(c_a^2 + 2c_a c_b S_{ab} + c_b^2 \right) \langle E \rangle \right]}{\partial c_a} = \frac{\partial \left[c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb} \right]}{\partial c_a}$$
$$\left(\frac{c_a^2 + 2c_a c_b S_{ab} + c_b^2}{\partial c_a} + \frac{\partial \langle E \rangle}{\partial c_a} + \langle E \rangle \left(2c_a + 2c_b S_{ab} + 0 \right) = \left(2c_a H_{aa} + 2c_b H_{ab} + 0 \right) \right)$$

Set $\frac{\partial \langle E \rangle}{\partial c_a} = 0$ and group coefficients of c_a and c_b

$$\langle E \rangle (2c_a + 2c_b S_{ab}) = (2c_a H_{aa} + 2c_b H_{ab})$$

$$\langle E \rangle c_a + \langle E \rangle c_b S_{ab} = c_a H_{aa} + c_b H_{ab}$$

$$0 = (H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b$$
After dividing both sides by 2

or
$$(H_{aa} - \langle E \rangle)c_a + (H_{ab} - \langle E \rangle S_{ab})c_b = 0$$

This is one equation relating the two coefficients, c_a and c_b .

We get a second equation if we repeat the procedure, except differentiate w.r.t. c_b and set the derivative =0.

The second equation is:

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

$$(H_{aa} - \langle E \rangle)c_{a} + (H_{ab} - \langle E \rangle S_{ab})c_{b} = 0$$
$$(H_{ab} - \langle E \rangle S_{ab})c_{a} + (H_{bb} - \langle E \rangle)c_{b} = 0$$

Now we have two equations with two unknowns, c_a and c_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, $c_a=c_b=0$, is if the determinant of coefficients of c_a and c_b is zero.

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

The Secular Determinant

Extension to Larger Systems

The 2x2 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:

$$\left|\boldsymbol{H}_{ij}-\left\langle\boldsymbol{E}\right\rangle\boldsymbol{S}_{ij}\right|=0$$

After you have made the Secular Determinant, set the diagonal overlaps, $S_{ii} = 1$.

$$\left|\boldsymbol{H}_{ij}-\left\langle\boldsymbol{E}\right\rangle\boldsymbol{S}_{ij}\right|=0$$

For example, if $\psi = c_a \phi_a + c_b \phi_b + c_c \phi_c$

Then the Secular Determinant is:

$$\begin{vmatrix} H_{aa} - \langle E \rangle S_{aa} & H_{aB} - \langle E \rangle S_{ab} & H_{ac} - \langle E \rangle S_{ac} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle S_{bb} & H_{bc} - \langle E \rangle S_{bc} \\ H_{ac} - \langle E \rangle S_{ac} & H_{bc} - \langle E \rangle S_{bc} & H_{cc} - \langle E \rangle S_{cc} \end{vmatrix} = 0$$

$$\begin{vmatrix} Setting diagonal S_{ii} = 1 \\ H_{aa} - \langle E \rangle & H_{aB} - \langle E \rangle S_{ab} & H_{ac} - \langle E \rangle S_{ac} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle & H_{bc} - \langle E \rangle S_{bc} \end{vmatrix} = 0$$

H₂⁺ Energies

Linear EquationsSecular Determinant $(H_{aa} - \langle E \rangle)c_a + (H_{ab} - \langle E \rangle S_{ab})c_b = 0$ $H_{aa} - \langle E \rangle H_{ab} - \langle E \rangle S_{ab}$ $H_{ab} - \langle E \rangle S_{ab} = 0$ $(H_{ab} - \langle E \rangle S_{ab})c_a + (H_{bb} - \langle E \rangle)c_b = 0$ $H_{ab} - \langle E \rangle S_{ab} H_{bb} - \langle E \rangle$ $H_{ab} - \langle E \rangle S_{ab}$ $H_{bb} - \langle E \rangle$

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 $\langle E \rangle$ as a function of H_{aa} , H_{ab} , S_{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 <E>, we will calculate the MO; i.e. the coefficients, c_a and c_b .

Expansion of the Secular Determinant

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0 \longrightarrow (H_{aa} - \langle E \rangle)(H_{bb} - \langle E \rangle) - (H_{ab} - \langle E \rangle S_{ab})^2 = 0$$

or
$$(\langle E \rangle - H_{aa})(\langle E \rangle - H_{bb}) - (H_{ab} - \langle E \rangle S_{ab})^2 = 0$$

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: $H_{aa} = \langle 1s_a | H | 1s_a \rangle$

$$\boldsymbol{H}_{bb} = \left< \mathbf{1}\boldsymbol{S}_{b} \right| \boldsymbol{H} \right| \mathbf{1}\boldsymbol{S}_{b} \right>$$

Therefore, $H_{bb} = H_{aa}$ (by symmetry)

The equation then simplifies to: $(\langle E \rangle - H_{aa})^2 = (H_{ab} - \langle E \rangle S_{ab})^2$

Solving for the Energies

Therefore:
$$\langle E \rangle = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}}$$

or
$$\langle E \rangle_{+} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$
 and $\langle E \rangle_{-} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$

$$\langle E \rangle_{+} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$
 and $\langle E \rangle_{-} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$

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 H_{ab} and S_{ab} , they involve two-center integrals. That's because $1s_a$ is centered on nucleus a, whereas $1s_b$ 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.

$$H_{aa} = -\frac{1}{2} - \frac{1}{R} + \left(1 + \frac{1}{R}\right) e^{-2R} \qquad S_{ab} = e^{-R} \left(\frac{R^3}{3} + R + 1\right)$$
$$H_{ab} = -\frac{1}{2} S_{ab} - (R+1) e^{-R}$$

$$\langle E \rangle_{+} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$\langle V \rangle_{+} = \langle E \rangle_{+} + \frac{1}{R} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} + \frac{1}{R}$$

$$\langle E \rangle_{-} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

$$\langle V \rangle_{-} = \langle E \rangle_{-} + \frac{1}{R} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} + \frac{1}{R}$$

 $\langle E \rangle_{+}$ and $\langle E \rangle_{-}$ represent the *electronic* energy of the H₂⁺ ion.

The total energy, $\langle V \rangle_{+}$ and $\langle V \rangle_{-}$, also includes the internuclear repulsion, 1/R



(R Galculateds Minimum Energy

 $E_{min}(cal) = -0.565 au$ at $R_{min}(cal) = 2.49 a_0 = 1.32 Å$

Comparison with Experiment



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

H₂⁺ 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 $\langle E \rangle$, we developed two homogeneous linear equations relating c_a and c_b .

$$(H_{aa} - \langle E \rangle)c_{a} + (H_{ab} - \langle E \rangle S_{ab})c_{b} = 0$$
$$(H_{ab} - \langle E \rangle S_{ab})c_{a} + (H_{bb} - \langle E \rangle)c_{b} = 0$$

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

$$\langle E \rangle_{+} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$
 $\langle E \rangle_{-} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$

We can now plug one of the energies (either $\langle E \rangle_+$ or $\langle E \rangle_-$) into either of the linear equations to get a relationship between c_a and c_b for that value of the energy.

Bonding Wavefunction

$$\left(H_{aa}\left(1+S_{ab}\right)-H_{aa}-H_{ab}\right)C_{a}+\left(H_{ab}\left(1+S_{ab}\right)-H_{aa}S_{ab}-H_{ab}S_{ab}\right)C_{b}=0$$

$$(H_{aa}S_{ab} - H_{ab})c_a + (H_{ab} + H_{ab}S_{ab} - H_{aa}S_{ab} - H_{ab}S_{ab})c_b = 0$$

$$(H_{aa}S_{ab} - H_{ab})c_a + (H_{ab} - H_{aa}S_{ab})c_b = 0$$

$$\left(\frac{H_{aa}S_{ab} - H_{ab}}{H_{aa}S_{ab} - H_{ab}}\right)c_a + \left(\frac{H_{ab} - H_{aa}S_{ab}}{H_{aa}S_{ab} - H_{ab}}\right)c_b = 0$$

$$c_a - c_b = 0 \longrightarrow c_b = c_a$$

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

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$$C_{b} = C_{a} + \psi = C_{a} \mathbf{1} \mathbf{s}_{a} + C_{b} \mathbf{1} \mathbf{s}_{b} \longrightarrow \psi_{+} = C_{a} \left(\mathbf{1} \mathbf{s}_{a} + \mathbf{1} \mathbf{s}_{b} \right)$$

or $\psi_{+} = N_{+} \left(\mathbf{1} \mathbf{s}_{a} + \mathbf{1} \mathbf{s}_{b} \right)$

 N_{+} (=c_a) is determined by normalizing ψ_{+}

Normalization: $1 = \int \psi_{+}^{*} \psi_{+} d\tau = \langle \psi_{+} | \psi_{+} \rangle$

 $1 = \left\langle N_{+} \left(1s_{a} + 1s_{b} \right) \right| N_{+} \left(1s_{a} + 1s_{b} \right) \right\rangle = N_{+}^{2} \left(\left\langle 1s_{a} \right| 1s_{a} \right\rangle + \left\langle 1s_{a} \right| 1s_{b} \right\rangle + \left\langle 1s_{b} \right| 1s_{a} \right\rangle + \left\langle 1s_{b} \right| 1s_{b} \right\rangle$

$$1 = N_{+}^{2} \left(1 + S_{ab} + S_{ab} + 1 \right) = N_{+}^{2} \left(2 + 2S_{ab} \right)$$

$$N_{+} = \frac{1}{\sqrt{2 + 2S_{ab}}} \longrightarrow \psi_{+} = N_{+} \left(1s_{a} + 1s_{b}\right)$$
$$= \frac{1}{\sqrt{2 + 2S_{ab}}} \left(1s_{a} + 1s_{b}\right)$$

Antibonding Wavefunction



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

Plotting the Wavefunctions $\psi_{+} = N_{+} (1 s_{a} + 1 s_{b}) \qquad \psi_{-} = N_{-} (1 s_{a} - 1 s_{b})$ Ψ² V 2 3 3 2 Nuc Nuc Nuc Nuc b b a

Note that the bonding MO, ψ_+ , has significant electron density in the region between the two nuclei.

Note that the antibonding MO, ψ_{-} , has a node (zero electron density in the region between the two nuclei. Slide 30

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:

$$\phi_{1sa} = \mathbf{1}s_a = \sqrt{\frac{1}{\pi}}\mathbf{e}^{-r_a}$$
 and $\phi_{1sb} = \mathbf{1}s_b = \sqrt{\frac{1}{\pi}}\mathbf{e}^{-r_b}$ (in atomic units)

Instead of assuming that each nucleus has a charge, Z=1, we can use an effective nuclear charge, Z', as a variational parameter.

$$\phi_a = \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_a}$$
 and $\phi_b = \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_b}$

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

$$\psi = c_a \phi_a + c_b \phi_b = c_a \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_a} + c_b \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_b}$$

This expression for the wavefunction can be plugged into the equation for $\langle E \rangle$. The values of Z' and R which minimize $\langle E \rangle$ can then be calculated. The best Z' is 1.24.

	R_{min}	D _e
Cal.(Z=1)	1.32 Å	1.77 eV
Cal.(Z'=1.24)	1.06	2.35
Expt.	1.06	2.79

An Even Better Improvement: More Atomic Orbitals



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

$$\psi = c_1 1 s_a + c_2 2 s_a + c_3 2 p_{za} + c_4 1 s_b + c_5 2 s_b + c_6 2 p_{za}$$

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.



We ran a calculation using: 4 s orbitals, 2 p_z orbitals and 1 d_{z2} orbital on each atom.

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

	R _{min}	D _e
Cal.(Z=1)	1.32 Å	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 H₂⁺
- H₂⁺ Energies
- H₂⁺ Wavefunctions
- MO Treatment of the H₂ Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

MO Treatment of the H₂ Molecule

The H₂ Electronic Hamiltonian




The LCAO Molecular Orbitals



Energy

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

We can put both electrons in H₂ into the bonding orbital, ψ_+ , one with α spin and one with β spin.





Antibonding Orbital

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



Bonding Orbital

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



The Molecular Wavefunction

Put 1 electron in σ_g 1s with α spin: σ_g 1s(1) α_1

Put 1 electron in $\sigma_g 1s$ with β spin: $\sigma_g 1s(2)\beta_2$

Form the antisymmetrized product using a Slater Determinant.

$$\psi_{MO} = \frac{1}{\sqrt{2!}} \begin{vmatrix} \sigma_g \mathbf{1} \mathbf{s}(1) \alpha_1 & \sigma_g \mathbf{1} \mathbf{s}(1) \beta_1 \\ \sigma_g \mathbf{1} \mathbf{s}(2) \alpha_2 & \sigma_g \mathbf{1} \mathbf{s}(2) \beta_2 \end{vmatrix}$$

$$\psi_{MO} = \frac{1}{\sqrt{2}} \left[\sigma_g \mathbf{1} \mathbf{s}(1) \alpha_1 \cdot \sigma_g \mathbf{1} \mathbf{s}(2) \beta_2 - \sigma_g \mathbf{1} \mathbf{s}(1) \beta_1 \cdot \sigma_g \mathbf{1} \mathbf{s}(2) \alpha_2 \right]$$

$$\psi_{MO} = \left[\sigma_g \mathbf{1} \mathbf{S}(\mathbf{1}) \sigma_g \mathbf{1} \mathbf{S}(\mathbf{2})\right] \cdot \frac{1}{\sqrt{2}} \left[\alpha_1 \beta_2 - \beta_1 \alpha_2\right]$$

 $\psi_{spin} = \frac{1}{\sqrt{2}} [\alpha_1 \beta_2 - \beta_1 \alpha_2]$ The spin wavefunction is already normalizeD

Because the Hamiltonian doesn't operate on the spin, the spin wavefunction has no effect on the energy of 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.

$$\psi_{spat} = \sigma_g \mathbf{1} \mathbf{S}(\mathbf{1}) \sigma_g \mathbf{1} \mathbf{S}(\mathbf{2}) = \left[N_+ \left(\mathbf{1} \mathbf{s}_a + \mathbf{1} \mathbf{s}_b \right) \right] \left[N_+ \left(\mathbf{1} \mathbf{s}_a + \mathbf{1} \mathbf{s}_b \right) \right]$$

The MO Energy of H₂

$$\psi_{spat} = \sigma_g \mathbf{1} \mathbf{S}(\mathbf{1}) \sigma_g \mathbf{1} \mathbf{S}(\mathbf{2}) = \left[N_+ \left(\mathbf{1} \mathbf{s}_a + \mathbf{1} \mathbf{s}_b \right) \right] \left[N_+ \left(\mathbf{1} \mathbf{s}_a + \mathbf{1} \mathbf{s}_b \right) \right]$$
$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}$$

The expectation value for the ground state H_2 electronic energy is given by:

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

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: $V(R) = E(R) + \frac{1}{R}$



 R_{min}
 D_e

 Cal.(Z=1)
 0.85 Å
 2.69 eV

 Expt.
 0.74
 4.73

Improving the Results

As for H_2^+ , one can add a variational parameter to the atomic orbitals used in σ_a 1s.

$$\phi_a = \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_a}$$
 and $\phi_b = \sqrt{\frac{Z'^3}{\pi}} e^{-Z'r_b}$ (in atomic units)

$$\psi_{spat} = \sigma_g \mathbf{1} \mathbf{S}(\mathbf{1}) \sigma_g \mathbf{1} \mathbf{S}(\mathbf{2}) = \left[N \left(\phi_a + \phi_b \right) \right] \left[N \left(\phi_a + \phi_b \right) \right]$$

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

	R _{min}	D _e
Cal.(Z=1)	0.85 Å	2.70 eV
Cal.(Var. Z')	0.73	3.49
Expt.	0.74	4.73

An Even Better Improvement: More Atomic Orbitals



As for H_2^+ , one can make the bonding orbital a Linear Combination of more than two atomic orbitals; e.g.

 $\sigma_{g} \mathbf{1} \mathbf{S} = c_{1} \mathbf{1} \mathbf{S}_{a} + c_{2} \mathbf{2} \mathbf{S}_{a} + c_{3} \mathbf{2} p_{za} + c_{4} \mathbf{1} \mathbf{S}_{b} + c_{5} \mathbf{2} \mathbf{S}_{b} + c_{6} \mathbf{2} p_{za}$

We performed a Hartree-Fock calculation on H_2 using an LCAO that included 4 s orbitals, 2 p_z orbitals and 1 d_{z2} orbitals on each hydrogen.

	R _{min}	D _e		
Cal.(Z=1)	0.85 Å	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 H_2^+ , we nailed the Dissociation Energy almost exactly.

But on H_2 the calculated D_e is almost 25% too low.

Answer: The problem, is that unlike H_2^+ , 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 H_2^+ and H_2 .

These same orbitals may be used to describe the bonding in He_2^+ and lack of bonding in He_2 .

Linear Combinations of 2s and 2p orbitals can be used to create Molecular Orbitals, which can be used to describe the bonding of second row diatomic molecules (e.g. Li_2).

We can place two electrons into each Molecular Orbital.

Definition: Bond Order $-BO = \frac{1}{2}(n_B - n_A)$

 n_B = number of electrons in Bonding Orbitals n_A = number of electrons in Antibonding Orbitals

Bonding in He₂+



Slater Determinant: He₂⁺

 $Config = \left(\sigma_g \mathbf{1s}\right)^2 \left(\sigma_u^* \mathbf{1s}\right)^1$

$$\psi_{MO} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \sigma_g \mathbf{1} \mathbf{s}(1)\alpha_1 & \sigma_g \mathbf{1} \mathbf{s}(1)\beta_1 & \sigma_u^* \mathbf{1} \mathbf{s}(1)\alpha_1 \\ \sigma_g \mathbf{1} \mathbf{s}(2)\alpha_2 & \sigma_g \mathbf{1} \mathbf{s}(2)\beta_2 & \sigma_u^* \mathbf{1} \mathbf{s}(2)\alpha_2 \\ \sigma_g \mathbf{1} \mathbf{s}(3)\alpha_3 & \sigma_g \mathbf{1} \mathbf{s}(3)\beta_3 & \sigma_u^* \mathbf{1} \mathbf{s}(3)\alpha_3 \end{vmatrix}$$

$$\psi_{MO} = \frac{1}{\sqrt{3!}} \left| \sigma_g 1s(1)\alpha_1 \quad \sigma_g 1s(2)\beta_2 \quad \sigma_u^* 1s(3)\alpha_3 \right|$$

Shorthand Notation



Energy

with $R_{min} \approx 3$ Å and $D_e \approx 0.001$ eV [it can be observed at T = 10⁻³ 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 $\sigma 2p$ from $\sigma 2s$ and $\sigma 1s$ orbitals.

Pi-2p Orbitals



There is a degenerate $\pi_u 2p$ orbital and a degenerate $\pi_g^* 2p$ orbital arising from analogous combinations of $2p_{xa}$ and $2p_{xb}$

Homonuclear Diatomic Orbital Energy Diagram





Consider Li₂

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

6 Electrons

$$\left(\sigma_{g}\mathbf{1s}
ight)^{2}\left(\sigma_{u}^{*}\mathbf{1s}
ight)^{2}\left(\sigma_{g}\mathbf{2s}
ight)^{2}$$

 $BO = \frac{1}{2}(4-2) = 1$

S = 0: Singlet



 $\sigma_g 2p$

Consider F₂

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

18 Electrons



 $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^4$ BO = ½(10-8) = 1 S = 0 : Singlet



 $\sigma_g 2p$



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

16 Electrons



 $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2$ $BO = \frac{1}{2}(10-6) = 2$

S = 1: Triplet







Consider O_2 , O_2^+ , O_2^-

- (a) Which has the longest bond?
- (b) Which has the highest vibrational frequency?
- (c) Which has the highest Dissociation Energy?
 - O_2 : 16 Electrons BO = 2
 - O_2^+ : 15 Electrons BO = 2.5
 - O_2^{-1} : 17 Electrons BO = 1.5
 - O_2^- has the longest bond.

 O_2^+ has the highest vibrational frequency.

O₂⁺ 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 σ MO's is really a combination of all 6 AO's.

 $\psi_{MO} = c_1 1 s_a + c_2 2 s_a + c_3 2 p_{za} + c_4 1 s_b + c_5 2 s_b + c_6 2 p_{zb}$

Approximate vs. Accurate MO's in C_2 $\psi_{MO} = c_1 1s_a + c_2 2s_a + c_3 2p_{za} + c_4 1s_b + c_5 2s_b + c_6 2p_{zb}$

σ2p MO (E ≈ -15 eV)

 $\psi_{Approx} \approx 0.70 \cdot 2\rho_{za} + 0.70 \cdot 2\rho_{zb}$

 $\psi_{Accur} = \left[-0.07 \cdot 1s_a + 0.40 \cdot 2s_a + 0.60 \cdot 2p_{za}\right] + \left[-0.07 \cdot 1s_b + 0.40 \cdot 2s_b - 0.60 \cdot 2p_{zb}\right]$

σ 2s MO (E \approx -40 eV)

 $\psi_{Approx} \approx 0.70 \cdot 2s_a + 0.70 \cdot 2s_b$ $\psi_{Accur} = \left[-0.17 \cdot 1s_a + 0.50 \cdot 2s_a + 0.23 \cdot 2p_{za}\right] + \left[-0.17 \cdot 1s_b + 0.50 \cdot 2s_b + 0.23 \cdot 2p_{zb}\right]$ $\sigma 1s \text{ MO (E} \approx -420 \text{ eV)}$

 $\psi_{Approx} \approx 0.70 \cdot 1s_a + 0.70 \cdot 1s_b$ $\psi_{Accur} = [0.70 \cdot 1s_a + 0.01 \cdot 2s_a] + [0.70 \cdot 1s_b + 0.01 \cdot 2s_b]$

Heteronuclear Diatomic Molecules

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$
$$H_{bb} \neq H_{aa}$$

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



Interpretation of Secular Determinant Parameters

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

$$S_{ab} = \left\langle \phi_a \, \middle| \, \phi_b \right\rangle = \int \phi_a^* \phi_b d\tau$$

Overlap Integral



Generally, $S_{ab} \approx 0.1 - 0.2$

Commonly, to simplify the calculations, it is approximated that $S_{ab}\approx 0$

$$\boldsymbol{H}_{aa} = \left\langle \phi_{a} \left| \boldsymbol{H} \right| \phi_{a} \right\rangle = \int \phi_{a}^{*} \boldsymbol{H} \phi_{a} \boldsymbol{d} \tau$$

Energy of an electron in atomic orbital, ϕ_a , in an unbonded atom.

 $H_{bb} = \langle \phi_b | H | \phi_b \rangle = \int \phi_b^* H \phi_b d\tau \quad \text{Energy of an electron in atomic orbital,}$ $\phi_{\rm b}$, in an unbonded atom.

 H_{aa} , H_{bb} < 0 Traditionally, H_{aa} and H_{bb} are called "Coulomb Integrals"

Commonly, H_{aa} is estimated as -IE, where IE is the Ionization Energy of an electron in the atomic orbital, ϕ_a .

$$\begin{vmatrix} H_{aa} - \left\langle E \right\rangle & H_{ab} - \left\langle E \right\rangle S_{ab} \\ H_{ab} - \left\langle E \right\rangle S_{ab} & H_{bb} - \left\langle E \right\rangle \end{vmatrix} = 0$$

 $H_{ab} = \langle \phi_a | H | \phi_b \rangle = \int \phi_a^* H \phi_b d\tau \quad \text{Interaction energy between atomic orbitals,} \\ \phi_a \text{ and } \phi_b \text{ .}$

Traditionally, H_{ab} is called the "Resonance Integral".

 H_{ab} is approximately proportional to: (1) the orbital overlap (2) the average of H_{aa} and H_{ab}

$$H_{ab} \approx K \left[\frac{H_{aa} + H_{bb}}{2} \right] S_{ab} \qquad K \approx 1.75$$

Wolfsberg-Helmholtz Formula (used in Extended Hückel Model)

$$H_{ab} < 0$$

Interpretation of Orbital Coefficients

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

 $\psi_{MO} = N(c_a\phi_a + c_b\phi_b)$

Normalization: $1 = \int \psi_{MO}^{2} d\tau = \langle \psi_{MO} | \psi_{MO} \rangle$ $1 = \langle N(c_{a}\phi_{a} + c_{b}\phi_{b}) | N(c_{a}\phi_{a} + c_{b}\phi_{b}) \rangle$ $1 = N^{2} \Big[c_{a}^{2} \langle \phi_{a} | \phi_{a} \rangle + c_{b}^{2} \langle \phi_{b} | \phi_{b} \rangle + 2c_{a}c_{b} \langle \phi_{a} | \phi_{b} \rangle \Big]$ $1 = N^{2} \Big[c_{a}^{2} + c_{b}^{2} + 2c_{a}c_{b}S_{ab} \Big] \quad \text{where} \quad S_{ab} = \langle \phi_{a} | \phi_{b} \rangle$ $N = \frac{1}{\sqrt{c_{a}^{2} + c_{b}^{2} + 2c_{a}c_{b}}S_{ab}} \quad \text{Orbital}$

$$\psi_{MO} = \frac{1}{\sqrt{c_a^2 + c_b^2 + 2c_a c_b S_{ab}}} \left(c_a \phi_a + c_b \phi_b \right)$$

If
$$S_{ab} \approx 0$$
: $\psi_{MO} = \frac{C_a}{\sqrt{C_a^2 + C_b^2}} \phi_a + \frac{C_b}{\sqrt{C_a^2 + C_b^2}} \phi_b$

$$f_a = \frac{c_a^2}{c_a^2 + c_b^2}$$

Fraction of electron density in orbital a

$$f_b = \frac{c_b^2}{c_a^2 + c_b^2}$$

Fraction of electron density in orbital b

General:
$$\psi_{MO} = N \sum c_i \phi_i$$

$$f_i = \frac{c_i^2}{\sum c_i^2}$$

Fraction of electron density in orbital i

$$f_a = rac{c_a^2}{c_a^2 + c_b^2} \qquad f_b = rac{c_b^2}{c_a^2 + c_b^2}$$

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

Homonuclear Diatomic Molecules:

$$H_{bb} = H_{aa}$$

 $|c_b| = |c_a|$
 $f_a = f_b = 0.50$

Heteronuclear Diatomic Molecules:

$$H_{bb} \neq H_{aa}$$

 $\left| \boldsymbol{C}_{b} \right| \neq \left| \boldsymbol{C}_{a} \right|$

 $f_b \neq f_a$



$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

$$(H_{aa} - \langle E \rangle) (H_{bb} - \langle E \rangle) - (H_{ab} - \langle E \rangle S_{ab}) (H_{ab} - \langle E \rangle S_{ab}) = 0$$

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

One can then determine c_b/c_a for both the bonding and antibonding orbitals.

A Numerical Example: Hydrogen Fluoride (HF)



$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

 $\psi_{MO} = N(c_a\phi_a + c_b\phi_b) = N(c_a1s_a(H) + c_b2p_{zb}(F))$

Matrix Elements

$$H_{aa} = \langle \phi_a | H | \phi_a \rangle = \langle 1s_a(H) | H | 1s_a(H) \rangle = -13.6 \text{ eV}$$
$$H_{bb} = \langle \phi_b | H | \phi_b \rangle = \langle 2p_{zb}(F) | H | 2p_{zb}(F) \rangle = -17.4 \text{ eV}$$
$$H_{ab} = \langle \phi_a | H | \phi_b \rangle = \langle 1s_a(F) | H | 2p_{zb}(F) \rangle = -2.0 \text{ eV}$$
$$S_{ab} = \langle \phi_a | \phi_b \rangle = \langle 1s_a(H) | 2p_{zb}(F) \rangle \approx 0$$

$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

$$\begin{vmatrix} -13.6 - \langle E \rangle & -2 \\ -2 & -17.4 - \langle E \rangle \end{vmatrix} = 0$$

$$3.6 - \langle E \rangle) (-17.4 - \langle E \rangle) - (-2)(-2) = 0$$

$$H_{aa} = -13.6 \,\mathrm{eV}$$

 $H_{bb} = -17.4 \,\mathrm{eV}$
 $H_{ab} = -2.0 \,\mathrm{eV}$
 $S_{ab} \approx 0$

$$(-13.6 - \langle E \rangle)(-17.4 - \langle E \rangle) - (-2)(-2) = 0$$
$$\langle E \rangle^{2} + 31.0 \langle E \rangle + 232.64 = 0$$
$$\langle E \rangle = \frac{-31.0 \pm \sqrt{(31.0)^{2} - 4(1)(232.64)}}{2}$$

$$\langle E \rangle_{B} = \frac{-31.0 - \sqrt{30.44}}{2} = -18.26 \, eV \qquad \langle E \rangle_{A} = \frac{-31.0 + \sqrt{30.44}}{2} = -12.74 \, eV$$

$$\begin{vmatrix} -13.6 - \langle E \rangle & -2 \\ -2 & -17.4 - \langle E \rangle \end{vmatrix} = 0$$

Bonding MO
$$\begin{bmatrix} -13.6 - (-18.25) \end{bmatrix} c_a - 2c_b = 0$$

$$\frac{c_b}{c_a} = 2.33 \rightarrow c_b = 2.33c_a$$

$$\psi_B = (c_a \phi_a + c_b \phi_b)$$

$$= c_a (\phi_a + 2.33\phi_b)$$

$$= N(\phi_a + 2.33\phi_b)$$

$$\psi_B = \frac{1}{\sqrt{1 + (2.33)^2}} (\phi_a + 2.33\phi_b)$$

$$\psi_B = 0.394\phi_a + 0.919\phi_b$$

= 0.394 \cdot 1s_a(H) + 0.919 \cdot 2p_{zb}(F)

 $(-13.6-\langle E \rangle)c_a-2c_b=0$ $-2c_a + (-17.4 - \langle E \rangle)c_b = 0$ **Antibonding MO** $\left[-13.6 - (-12.74)\right] c_a - 2c_b = 0$ $\frac{c_b}{c_a} = -0.430 \quad \rightarrow \quad c_b = -0.430c_a$ $\psi_{A} = (C_{a}\phi_{a} + C_{b}\phi_{b})$ $= c_{a} (\phi_{a} - 0.430\phi_{b})$ $= N(\phi_a - 0.430\phi_b)$ $\psi_{A} = \frac{1}{\sqrt{1 + (-0.430)^{2}}} (\phi_{a} - 0.430\phi_{b})$

$$\psi_{A} = 0.919\phi_{a} - 0.394\phi_{b}$$
$$= 0.919 \cdot 1s_{a}(H) - 0.394 \cdot 2p_{zb}(F)$$

Electron Densities in Hydrogen Fluoride Bonding Orbital

$$\psi_B = 0.394\phi_a + 0.919\phi_b = 0.394 \cdot 1s_a(H) + 0.919 \cdot 2p_{zb}(F)$$

$$f_a = f_H = \frac{c_a^2}{c_a^2 + c_b^2} = (0.394)^2 = 0.16$$
 $f_b = f_F = \frac{c_b^2}{c_a^2 + c_b^2} = (0.919)^2 = 0.84$

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

Antibonding Orbital

$$\psi_A = 0.919\phi_a - 0.394\phi_b = 0.919 \cdot 1s_a(H) - 0.394 \cdot 2p_{zb}(F)$$

$$f_a = f_H = \frac{c_a^2}{c_a^2 + c_b^2} = (0.919)^2 = 0.84$$
 $f_b = f_F = \frac{c_b^2}{c_a^2 + c_b^2} = (0.394)^2 = 0.16$

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