

CHAPTER 8
DIATOMIC MOLECULES
OUTLINE

Homework Questions Attached

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

- | | |
|----|---|
| 1. | Hydrogen Molecular Ion: Born-Oppenheimer Approximation |
| 2. | Math Preliminary: Systems of Linear Equations - Cramer's Rule |
| 3. | LCAO Treatment of H_2^+ |
| 4. | H_2^+ Energies |
| 5. | H_2^+ Wavefunctions |
| 6. | MO Treatment of the H_2 Molecule |
| 7. | Homonuclear Diatomic Molecules |
| 8. | Heteronuclear Diatomic Molecules |

Chapter 8 Homework

1. Qualitative Questions (see PowerPoint slides and class notes for answers)
 - (a) As discussed in class, the Secular Determinant is the determinant of the coefficients of the homogeneous linear equations which result from use of the Variational Theorem to minimize the energy. Why must the Secular Determinant equal zero?
 - (b) To compute the dissociation energy of H_2^+ , one calculates $E(\text{H}_2^+)$ and subtracts this energy from a reference energy; i.e. $D_e = E_{\text{ref}} - E(\text{H}_2^+)$. What is the reference state for this calculation?
 - (c) It was shown in class that when the dissociation energy of H_2^+ was computed using a linear combination of 6 atomic orbitals on each H atom, the calculated value of D_e actually **increased** rather than decreased. Is this a violation of the Variational Principle? Why or why not?
 - (d) Sketch the $\sigma_g 2p$ (bonding) orbital and $\sigma_u^* 2p$ (antibonding) orbital in homonuclear diatomic molecules. What do the subscripts “g” and “u” stand for?
 - (e) Sketch one of the $\pi_u 2p$ (bonding) orbitals and one of the $\pi_g^* 2p$ (antibonding) orbitals. What do the subscripts “u” and “g” stand for?
 - (f) One of the σ molecular orbitals in the diatomic molecule, C_2 , is given approximately by: $\phi = (-0.17 \cdot 1s_a + 0.50 \cdot 2s_a) + (-0.17 \cdot 1s_b + 0.50 \cdot 2s_b)$
Is this a bonding or antibonding orbital? Why?
 - (g) One of the π molecular orbitals in the diatomic molecule, C_2 , is given approximately by: $\phi = (0.82 \cdot 2p_{ya}) + (-0.82 p_{yb})$
Is this a bonding or antibonding orbital? Why?
2. Write the complete Hamiltonian (include Nuclear-Nuclear repulsion as well as electronic terms) for the HeH molecule (in au). The nuclei are stationary and separated by a distance, R.

3. In class, we showed that the antibonding energy level of the H_2^+ molecular ion is:

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

Starting with $\psi = c_a 1s_a + c_b 1s_b$ and the linear equations from the Secular Determinant (see PP slides), show that the antibonding wavefunction is given by:

$$\psi_- = \frac{1}{\sqrt{2 - 2S_{ab}}} (1s_a - 1s_b)$$

Note: First show that $c_b = -c_a$ and then calculate the normalization constant.

4. Consider the two orbital interaction between an orbital on atom a (ϕ_a) and an orbital on atom b (ϕ_b). The two resulting wavefunctions are of the form:

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

For this interaction, the Hamiltonian matrix elements and overlap are:

$$H_{aa} = -20 \text{ eV}, H_{bb} = -12 \text{ eV}, H_{ab} = -3 \text{ eV}, S_{ab} = 0$$

- (a) Before you solve this problem numerically, answer the following questions:

- (i) What is the “upper bound” for the energy of the bonding orbital.
- (ii) Which is larger in the antibonding orbital, $|c_a|$ or $|c_b|$.

- (b) Calculate the bonding and antibonding energy levels, E_B and E_A .

- (c) Calculate the **normalized** bonding and antibonding wavefunctions, ψ_B , and ψ_A .

Note: Assume that $1s_a$ and $1s_b$ are normalized.

- (d) What fraction of the electron density is on atom a and what fraction on atom b in the bonding orbital (wavefunction).

5. If the electronegativities of the two atoms are not too different, the a heteronuclear diatomic molecule has the same ordering of energy levels as homonuclear diatomic molecules.

The only difference is that heteronuclear diatomic molecules have no inversion center, and therefore there is no “g” or “u” in the orbital description.

(a) What is the electron configuration in the diatomic molecule CO?
(e.g. $(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2 \dots$)

(b) What is the spin multiplicity in CO^{2-} ? (i.e. Singlet , Doublet, etc.)

(c) Which has the shortest bond length: CO, CO^+ , CO^{2+} ?

(d) Which has the lowest vibrational frequency: CO, CO^- , CO^{2-} ?

6. Consider the lowest excited state of the diatomic molecule, N_2 .

(a) Write the electron configuration of the first excited electronic state of N_2
(e.g. $(\sigma_g 1s)^2(\sigma_u^* 1s)^2 \dots$)

(b) What is the bond order in this excited state.

(c) Would you expect the N-N bond length in the excited state to be greater or less than in the ground state of N_2 . Explain your answer.

7. Consider an excited state of the H_2 molecule with the electron configuration, $(\sigma_g 1s)^1(\sigma_u^* 1s)^1$. Several possible wavefunctions to describe this configuration are:

$$\psi_I = N \psi_{Spat} \psi_{Spin} = N [\sigma_g 1s(1) \sigma_u^* 1s(2) + \sigma_u^* 1s(1) \sigma_g 1s(2)] [\alpha_1 \beta_2 - \beta_1 \alpha_2]$$

$$\psi_{II} = N \psi_{Spat} \psi_{Spin} = N [\sigma_g 1s(1) \sigma_u^* 1s(2)] [\alpha_1 \beta_2 - \beta_1 \alpha_2]$$

$$\psi_{III} = N \psi_{Spat} \psi_{Spin} = N [\sigma_g 1s(1) \sigma_u^* 1s(2) - \sigma_u^* 1s(1) \sigma_g 1s(2)] [\alpha_1 \beta_2 - \beta_1 \alpha_2]$$

$$\psi_{IV} = N \psi_{Spat} \psi_{Spin} = N [\sigma_g 1s(1) \sigma_u^* 1s(2) - \sigma_u^* 1s(1) \sigma_g 1s(2)] \beta_1 \beta_2$$

Determine whether each of the above functions is a valid wavefunction **and** explain why or why not.

8. The ground electronic state of NO is a doublet. The lowest lying excited state is also a doublet with an energy 174 cm^{-1} above the ground state.

Calculate the electronic contributions to the internal energy, enthalpy, entropy and Gibbs energy for two (2) moles of NO at $200\text{ }^{\circ}\text{C}$.

Note: As discussed in class, you can ignore the non-thermal contribution to the internal energy; i.e. we are assuming that ϵ_0 and $E_0 (=N_A\epsilon_0)$ are zero.

Data

Order of Orbital Energies: Homonuclear Diatomic Molecules

$$\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p < \sigma_g 2p < \pi_g^* 2p < \sigma_u^* 2p$$

Order of Orbital Energies: Heteronuclear Diatomic Molecules

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p < \sigma 2p < \pi^* 2p < \sigma^* 2p$$

Some “Concept Question” Topics

Refer to the PowerPoint presentation for explanations on these topics.

- Hamiltonians of multi-electron atoms
- Application of Cramer’s rule to systems of homogeneous equations, and how it requires that the Determinant of coefficients being zero.
- Relative signs (i.e. overlap) of atomic orbitals in bonding and antibonding molecular orbitals
- Definition and calculation of bond order in diatomic molecules
- Slater Determinants of diatomic molecules
- Effect of relative atomic orbital energies (of two combining orbitals) on the amount of stabilization of the molecular orbital
- Effect of relative atomic orbital energies on the atomic orbital coefficients of bonding and antibonding molecular orbitals
- Effect of atomic orbital coefficients on electron densities in molecular orbitals.

- Effect of electronic ground-state multiplicity on Stat. Mech. Internal Energies, Enthalpies, Entropies and Gibbs Energies (for molecules with no accessible excited electronic states).

Chapter 8

Diatomic Molecules

Slide 1

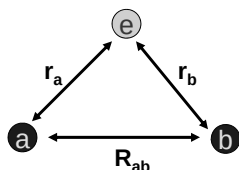
Outline

- **Hydrogen Molecular Ion: Born-Oppenheimer Approximation**
- Math Prelim.: Systems of Linear Equations – Cramer's Rule
- LCAO Treatment of H_2^+
- H_2^+ Energies
- H_2^+ Wavefunctions
- MO Treatment of the H_2 Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 2

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 H_2^+ Hamiltonian (in au)

$$H = \underbrace{-\frac{1}{2M_a} \nabla_a^2}_{\text{KE Nuc a}} - \underbrace{\frac{1}{2M_b} \nabla_b^2}_{\text{KE Nuc b}} - \underbrace{\frac{1}{2} \nabla_e^2}_{\text{KE Elect}} - \underbrace{\frac{1}{r_a}}_{\substack{\text{PE} \\ \text{e-N} \\ \text{Attr}}} - \underbrace{\frac{1}{r_b}}_{\substack{\text{PE} \\ \text{e-N} \\ \text{Attr}}} + \underbrace{\frac{1}{R_{ab}}}_{\substack{\text{PE} \\ \text{N-N} \\ \text{Repuls}}}$$

Slide 3

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)

Slide 4

Electronic Equation

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

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

Slide 5

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- **Math Prelim.: Systems of Linear Equations – Cramer's Rule**
- LCAO Treatment of H_2^+
- H_2^+ Energies
- H_2^+ Wavefunctions
- MO Treatment of the H_2 Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 6

Systems of Linear Equations: Cramer's Rule

$$a_{11}x_1 + a_{12}x_2 = c_1$$

$$a_{21}x_1 + a_{22}x_2 = c_2$$

In these equations, the a_{ij} and c_i are constants.

We want to solve these two equations for the values of the variables, x_1 and x_2

Cramer's Rule

$$x_1 = \frac{\begin{vmatrix} c_1 & a_{12} \\ c_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{\text{Det of "Augmented" matrix}}{\text{Det of original matrix of coefficients}}$$

$$x_2 = \frac{\begin{vmatrix} a_{11} & c_1 \\ a_{12} & c_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{\text{Det of "Augmented" matrix}}{\text{Det of original matrix of coefficients}}$$

Slide 7

A Numerical Example

$$a_{11}x_1 + a_{12}x_2 = c_1$$

$$a_{21}x_1 + a_{22}x_2 = c_2$$



$$2x_1 + 5x_2 = 1$$

$$3x_1 - 2x_2 = 11$$

$$x_1 = \frac{\begin{vmatrix} c_1 & a_{12} \\ c_2 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{\begin{vmatrix} 1 & 5 \\ 11 & -2 \end{vmatrix}}{\begin{vmatrix} 2 & 5 \\ 3 & -2 \end{vmatrix}} = \frac{1(-2) - 5(11)}{2(-2) - 5(3)} = \frac{-57}{-19} = 3$$

$$x_2 = \frac{\begin{vmatrix} a_{11} & c_1 \\ a_{12} & c_2 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{\begin{vmatrix} 2 & 1 \\ 3 & 11 \end{vmatrix}}{\begin{vmatrix} 2 & 5 \\ 3 & -2 \end{vmatrix}} = \frac{2(11) - 1(3)}{2(-2) - 5(3)} = \frac{+19}{-19} = -1$$

Slide 8

Homogeneous Linear Equations

$$a_{11}x_1 + a_{12}x_2 = 0$$

$$a_{21}x_1 + a_{22}x_2 = 0$$

Question: What are the solutions, x_1 and x_2 ?

Answer: I got it!! I got it!! $x_1=0$ and $x_2=0$.

Question: That's brilliant, Corky!!
But that's the "trivial" solution.
Ya got any other solutions for me?

Answer: Lunch Time!! Gotta go!!

Slide 9

$$a_{11}x_1 + a_{12}x_2 = 0$$

$$a_{21}x_1 + a_{22}x_2 = 0$$

Let's try Cramer's rule.

$$x_1 = \frac{\begin{vmatrix} 0 & a_{12} \\ 0 & a_{22} \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{0}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = 0 \quad \text{unless} \quad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 0$$

$$x_2 = \frac{\begin{vmatrix} a_{11} & 0 \\ a_{12} & 0 \end{vmatrix}}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = \frac{0}{\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}} = 0 \quad \text{unless} \quad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 0$$

$$a_{11}x_1 + a_{12}x_2 = 0$$

$$a_{21}x_1 + a_{22}x_2 = 0$$

$$x_1 = x_2 = 0 \quad \text{unless} \quad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 0$$

If one has a set of N linear **homogeneous** equations with N unknowns, there is a non-trivial solution only if the determinant of coefficients is zero.

This occurs often in Quantum Chemistry.

The determinant of coefficients is called the “Secular Determinant”.

Slide 11

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer’s Rule
- **LCAO Treatment of H_2^+**
 - H_2^+ Energies
 - H_2^+ Wavefunctions
- MO Treatment of the H_2 Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 12

LCAO 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.

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

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).

Slide 13

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.

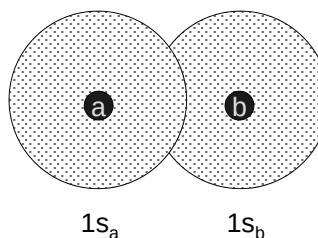
For the H_2^+ ion, there is only 1 electron, and therefore we need only 1 Molecular Orbital.

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

$$\psi = c_a \phi_{1sa} + c_b \phi_{1sb} = c_a 1s_a + c_b 1s_b$$

shorthand

Assume that $1s_a$ and $1s_b$ are each normalized.



Slide 14

Expectation Value of the Energy

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

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.

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

Slide 15

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

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

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

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.

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

Slide 16

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

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

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

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

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

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

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

$$Num = c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}$$

Note: For this particular problem, $H_{bb} = H_{aa}$ by symmetry.
However, this is not true in general.

Slide 17

$$Num = c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb} \quad Denom = c_a^2 + 2c_a c_b S_{ab} + c_b^2$$

$$\langle E \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{Num}{Denom} = \frac{c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + 2c_a c_b S_{ab} + c_b^2}$$

Minimizing <E>: The Secular Determinant

In order to find the values of c_a and c_b which minimize <E>, we

$$\text{want: } \frac{\partial \langle E \rangle}{\partial c_a} = 0 \quad \text{and} \quad \frac{\partial \langle E \rangle}{\partial c_b} = 0$$

It would seem relatively straightforward to take the derivatives of the above expression for <E> and set them equal to 0.

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

If, instead, one uses "implicit differentiation", the algebra is only **relatively** messy.

I'll show it to you, but you are **not** responsible for the details.
You are responsible only for the concept of how we get to the "Secular Determinant"

Slide 18

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

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

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

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

$$\cancel{(c_a^2 + 2c_a c_b S_{ab} + c_b^2)} \frac{\partial \langle E \rangle}{\partial c_a} + \langle E \rangle (2c_a + 2c_b S_{ab} + 0) = (2c_a H_{aa} + 2c_b H_{ab} + 0)$$

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

Slide 19

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

$$\langle E \rangle c_a + \langle E \rangle c_b S_{ab} = c_a H_{aa} + c_b H_{ab} \quad \text{After dividing both sides by 2}$$

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

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

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:

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

Slide 20

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

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

Hey!!! 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.

Not so fast, Corky!! 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

Slide 21

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:

$$|H_{ij} - \langle E \rangle S_{ij}| = 0$$

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

Slide 22

$$|H_{ij} - \langle E \rangle S_{ij}| = 0$$

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

Then the Secular Determinant is:

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



Setting diagonal $S_{ii} = 1$

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

Slide 23

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer's Rule
- LCAO Treatment of H_2^+
- **H_2^+ Energies**
- H_2^+ Wavefunctions
- MO Treatment of the H_2 Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 24

H₂⁺ Energies

Linear Equations

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

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

Secular Determinant

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

- Outline:**
1. We will expand the Secular Determinant.
This will give us a quadratic equation in $\langle E \rangle$.
 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 $\langle E \rangle$, we will calculate the MO;
i.e. the coefficients, c_a and c_b .

Slide 25

Expansion of the Secular Determinant

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

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

This expression can be expanded, yielding a quadratic equation in $\langle E \rangle$. This equation can be solved easily using the quadratic formula.

However, let's remember that for this problem: $H_{aa} = \langle 1s_a | H | 1s_a \rangle$

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

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

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

Slide 26

Solving for the Energies

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

↓

$$\langle E \rangle - H_{aa} = \pm (H_{ab} - \langle E \rangle S_{ab}) = \pm H_{ab} \mp \langle E \rangle S_{ab}$$

↓

$$\langle E \rangle \pm \langle E \rangle S_{ab} = H_{aa} \pm H_{ab} \rightarrow \langle E \rangle (1 \pm S_{ab}) = H_{aa} \pm H_{ab}$$

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

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

Slide 27

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

Evaluating the Matrix Elements and Determining $\langle E \rangle_+$ and $\langle E \rangle_-$

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 .

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

$$H_{ab} = -\frac{1}{2} S_{ab} - (R + 1)e^{-R}$$

Slide 28

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

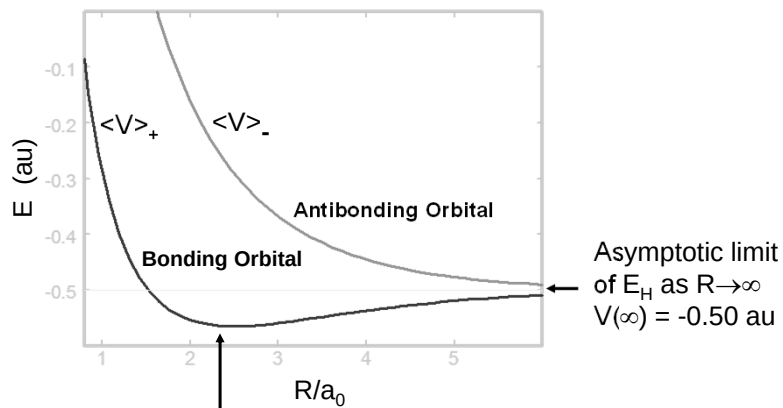
$$\langle E \rangle_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \quad \langle V \rangle_- = \langle E \rangle_- + \frac{1}{R} = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} + \frac{1}{R}$$

$\langle E \rangle_+$ and $\langle E \rangle_-$ represent the **electronic** energy of the H_2^+ ion.

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

Slide 29

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

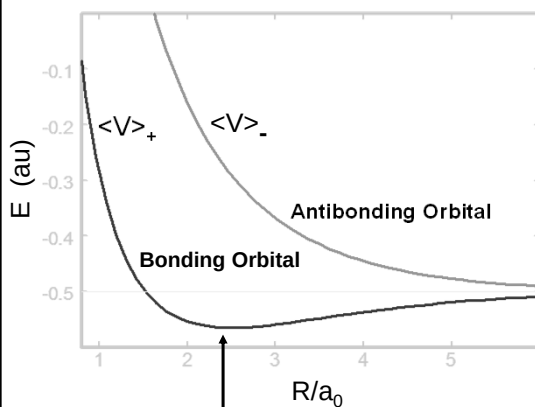


(R Optimum Value)
 Calculated Minimum Energy

$$E_{\min}(\text{cal}) = -0.565 \text{ au} \quad \text{at} \quad R_{\min}(\text{cal}) = 2.49 a_0 = 1.32 \text{ \AA}$$

Slide 30

Comparison with Experiment



$$E_{\min}(\text{cal}) = -0.565 \text{ au}$$

$$R_{\min}(\text{cal}) = 1.32 \text{ \AA}$$

Dissociation Energy

$$\begin{aligned} D_e(\text{cal}) &= E_H - E_{\min}(\text{cal}) \\ &= -0.5 \text{ au} - (-0.565 \text{ au}) \\ &= +0.065 \text{ au} \cdot 27.21 \text{ eV/au} \\ &= 1.77 \text{ eV} \end{aligned}$$

$R_{\min}$ D_e

Cal. 1.32 Å 1.77 eV

Expt. 1.06 2.79

(R) Calculated Minimum Energy

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

Slide 31

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer's Rule
- LCAO Treatment of H_2^+
- H_2^+ Energies
- **H_2^+ Wavefunctions**
- MO Treatment of the H_2 Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 32

H₂⁺ Wavefunctions (aka Molecular Orbitals)

The LCAO Wavefunction: $\psi = c_a 1s_a + c_b 1s_b$

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 $\langle E \rangle$

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

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.

Slide 33

Bonding Wavefunction

$$(H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b = 0 \quad \xleftarrow{\text{Plug in}} \quad \langle E \rangle_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$$

$$\left(H_{aa} - \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \right) c_a + \left(H_{ab} - \frac{H_{aa} + H_{ab}}{1 + S_{ab}} S_{ab} \right) c_b = 0$$

$$(H_{aa}(1 + S_{ab}) - H_{aa} - H_{ab}) c_a + (H_{ab}(1 + S_{ab}) - H_{aa} S_{ab} - H_{ab} S_{ab}) c_b = 0$$

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

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

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

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

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

Slide 34

$$c_b = c_a \quad + \quad \psi = c_a 1s_a + c_b 1s_b \quad \longrightarrow \quad \psi_+ = c_a (1s_a + 1s_b)$$

$$\text{or} \quad \psi_+ = N_+ (1s_a + 1s_b)$$

$N_+ (=c_a)$ is determined by normalizing ψ_+

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

$$1 = \langle N_+ (1s_a + 1s_b) | N_+ (1s_a + 1s_b) \rangle = N_+^2 (\langle 1s_a | 1s_a \rangle + \langle 1s_a | 1s_b \rangle + \langle 1s_b | 1s_a \rangle + \langle 1s_b | 1s_b \rangle)$$

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

$$N_+ = \frac{1}{\sqrt{2 + 2S_{ab}}} \quad \longrightarrow \quad \psi_+ = N_+ (1s_a + 1s_b) = \frac{1}{\sqrt{2 + 2S_{ab}}} (1s_a + 1s_b)$$

Slide 35

Antibonding Wavefunction

$$(H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b = 0 \quad \xleftarrow{\text{Plug in}} \quad \langle E \rangle_- = \frac{H_{aa} - H_{ab}}{1 - S_{ab}}$$

$$\left(H_{aa} - \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \right) c_a + \left(H_{ab} - \frac{H_{aa} - H_{ab}}{1 - S_{ab}} S_{ab} \right) c_b = 0$$

↓ HW

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

$$\psi_- = c_a (1s_a - 1s_b) = N_- (1s_a - 1s_b) = \frac{1}{\sqrt{2 - 2S_{ab}}} (1s_a - 1s_b)$$

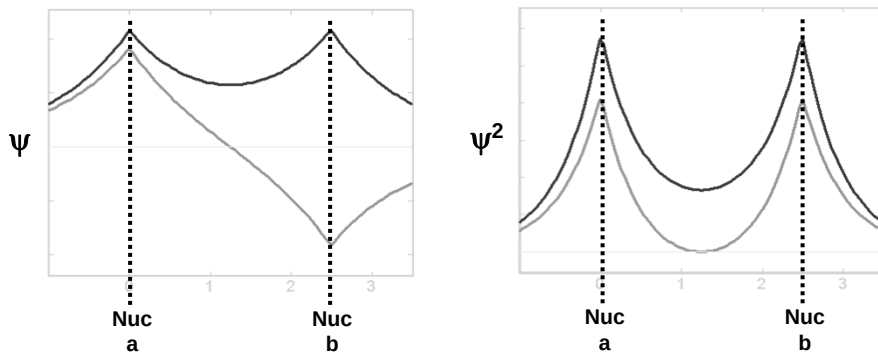
↑ HW

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

Slide 36

Plotting the Wavefunctions

$$\psi_+ = N_+(1s_a + 1s_b) \quad \psi_- = N_-(1s_a - 1s_b)$$



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 37

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:

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

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

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

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

Slide 38

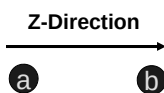
$$\psi = c_a \phi_a + c_b \phi_b = c_a \sqrt{\frac{Z'^3}{\pi}} e^{-Z' r_a} + c_b \sqrt{\frac{Z'^3}{\pi}} e^{-Z' r_b}$$

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

Slide 39

An Even Better Improvement: More Atomic Orbitals

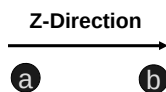


Instead of expanding the wavefunction as a linear combination of just one orbital on each atom, put in more atomic orbitals. e.g.

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

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 $N \times N$ Secular Determinant and N Molecular Orbitals.

Slide 40



We ran a calculation using: 4 s orbitals, 2 p_z orbitals and 1 d_{z^2} 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

Slide 41

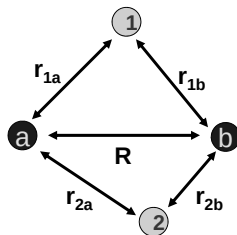
Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer's Rule
- LCAO Treatment of H_2^+
- H_2^+ Energies
- H_2^+ Wavefunctions
- **MO Treatment of the H_2 Molecule**
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules

Slide 42

MO Treatment of the H₂ Molecule

The H₂ Electronic Hamiltonian

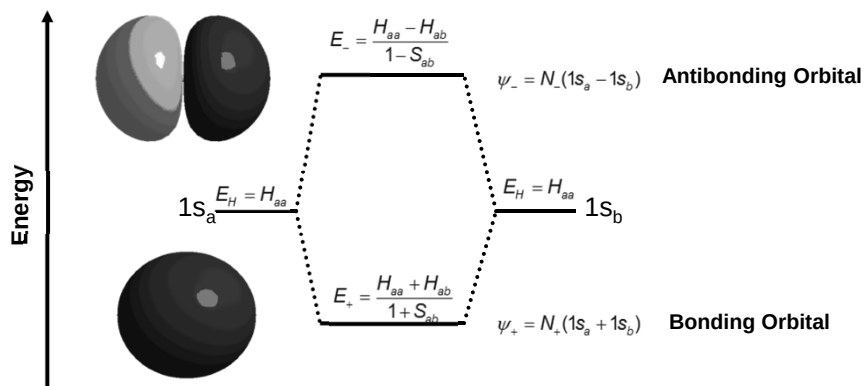


$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}$$

KE	KE	PE	PE	PE	PE	PE
e ₁	e ₂	e-N	e-N	e-N	e-N	e-e
		Attr	Attr	Attr	Attr	Repuls

Slide 43

The LCAO Molecular Orbitals

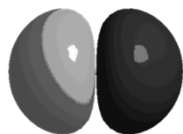


$H_{aa} = \langle 1s_a | H | 1s_a \rangle$ is the energy of an electron in a hydrogen 1s orbital.

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

Slide 44

Notation



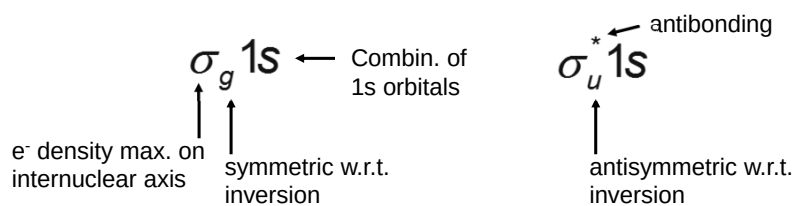
Antibonding Orbital

$$\psi_- = N_- (1s_a - 1s_b) = \sigma_u^* 1s$$



Bonding Orbital

$$\psi_+ = N_+ (1s_a + 1s_b) = \sigma_g 1s$$



Slide 45

The Molecular Wavefunction

Put 1 electron in $\sigma_g 1s$ with α spin: $\sigma_g 1s(1) \alpha_1$

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

Form the antisymmetrized product using a Slater Determinant.

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

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

$$\psi_{MO} = \underbrace{[\sigma_g 1s(1) \sigma_g 1s(2)]}_{\Psi_{\text{spat}}} \underbrace{\left[\frac{1}{\sqrt{2}} [\alpha_1 \beta_2 - \beta_1 \alpha_2] \right]}_{\Psi_{\text{spin}}} = \psi_{\text{spat}} \cdot \psi_{\text{spin}}$$

Slide 46

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

$$\psi_{spin} = \frac{1}{\sqrt{2}} [\alpha_1\beta_2 - \beta_1\alpha_2]$$

The spin wavefunction is already normalized (see Chap. 8 PowerPoint for He).

Because the Hamiltonian doesn't operate on the spin, the spin wavefunction has no effect on the energy of H₂.

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.

$$\psi_{spat} = \sigma_g 1s(1)\sigma_g 1s(2) = [N_+(1s_a + 1s_b)][N_+(1s_a + 1s_b)]$$

Slide 47

The MO Energy of H₂

$$\psi_{spat} = \sigma_g 1s(1)\sigma_g 1s(2) = [N_+(1s_a + 1s_b)][N_+(1s_a + 1s_b)]$$

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}}$$

The expectation value for the ground state H₂ electronic energy is given by:

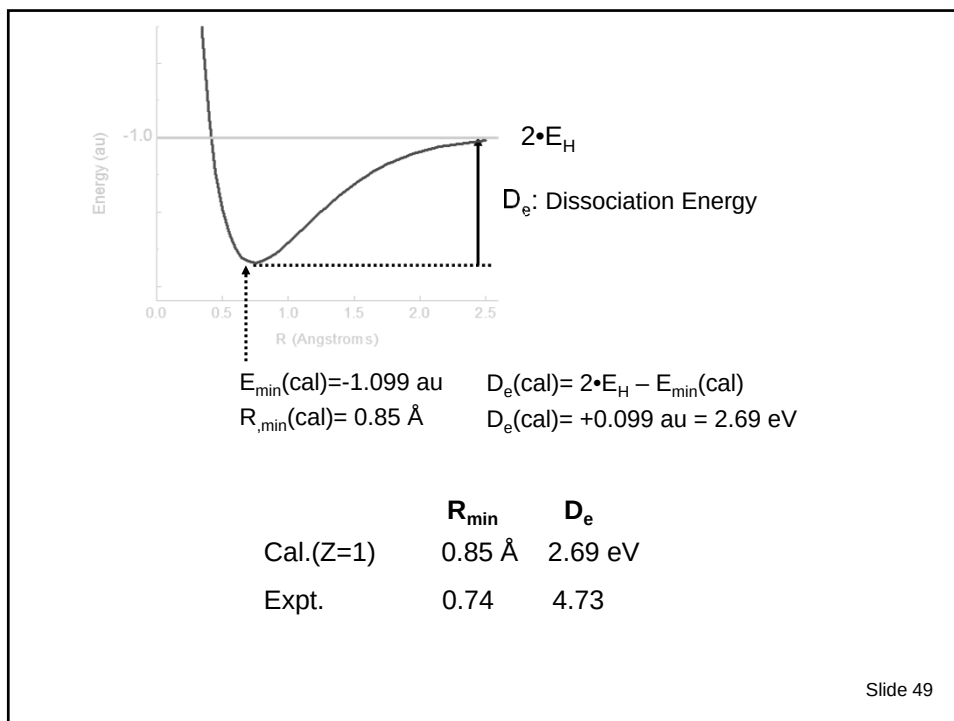
$$E = \langle \psi_{spat} | H | \psi_{spat} \rangle$$

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

Slide 48



Improving the Results

As for H₂⁺, one can add a variational parameter to the atomic orbitals used in σ_g1s.

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

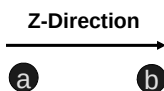
$$\psi_{\text{spat}} = \sigma_g 1s(1) \sigma_g 1s(2) = [N(\phi_a + \phi_b)] [N(\phi_a + \phi_b)]$$

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

Slide 50

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.

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

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

Slide 51

Question: Hey!! 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, Corky, is that unlike H_2^+ , H_2 has 2 (two, dos, zwei) electrons, whose motions are correlated. Hartree-Fock calculations don't account for the electron correlation energy.

Don't you remember **anything** from Chapter 7??

Question: Does your watch also say 3:00 ?
Tee Time – Gotta go!!!

Slide 52

Inclusion of the Correlation Energy

There are methods to calculate the Correlation Energy correction to the Hartree-Fock results. We'll discuss these methods in Chapter 9.

We used a form of "Configuration Interaction", called QCISD(T), to calculate the Correlation Energy and, thus, a new value for D_e

	$R_{\min}$	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
Cal.(QCISD(T))	0.74	4.69 ← That's Better!!
Expt.	0.74	4.73

Slide 53

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer's Rule
- LCAO Treatment of H_2^+
- H_2^+ Energies
- H_2^+ Wavefunctions
- MO Treatment of the H_2 Molecule
- **Homonuclear Diatomic Molecules**
- Heteronuclear Diatomic Molecules

Slide 54

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).

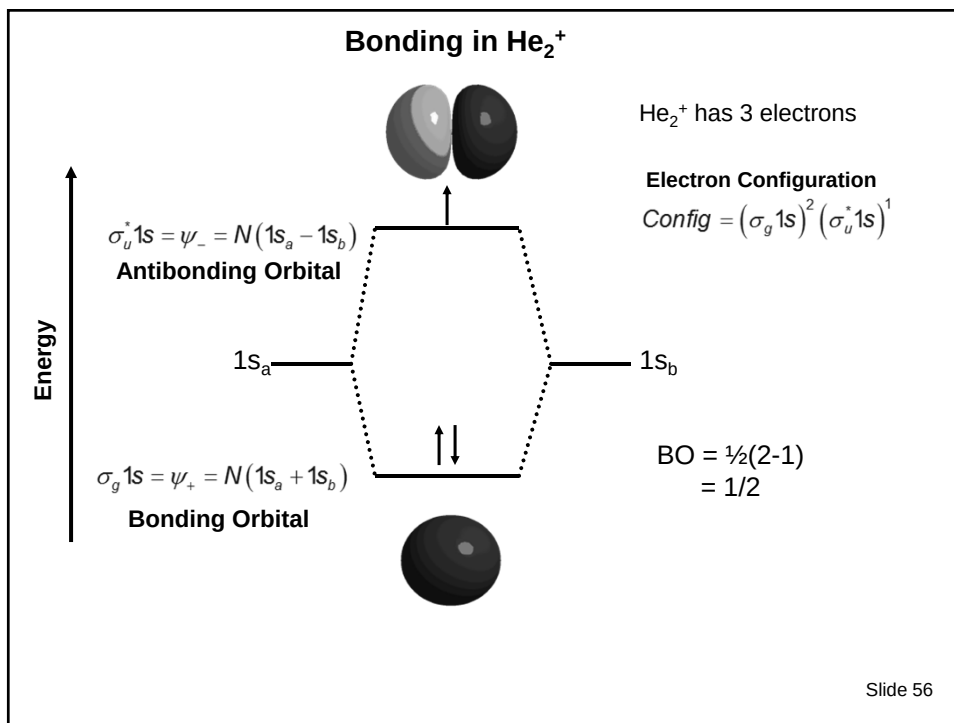
We can place two electrons into each Molecular Orbital.

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

n_B = number of electrons in Bonding Orbitals

n_A = number of electrons in Antibonding Orbitals

Slide 55



Slater Determinant: He_2^+

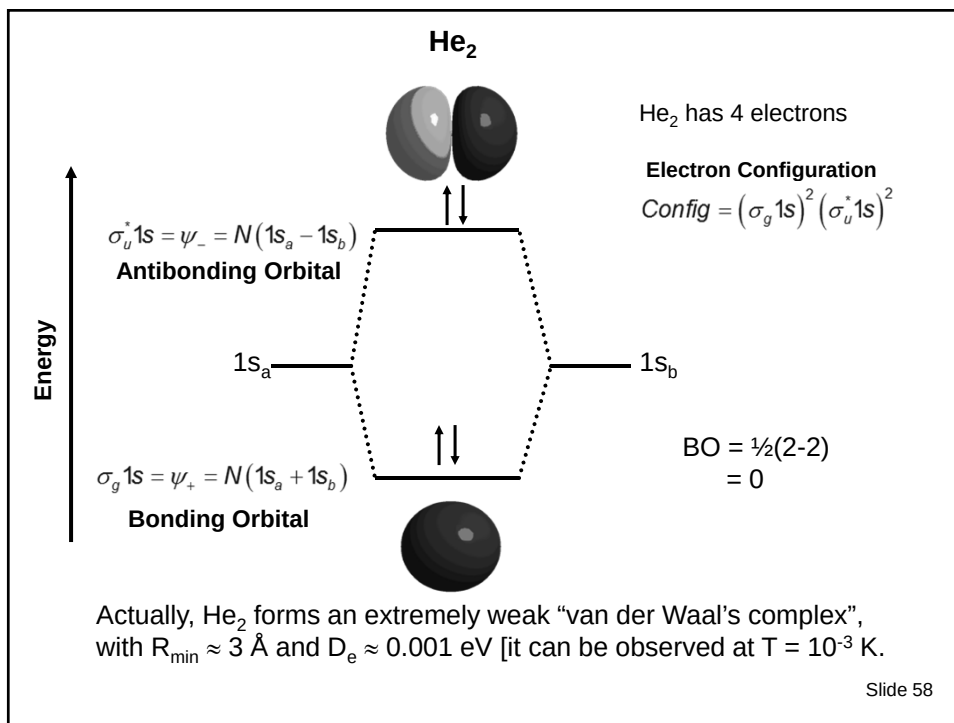
$$\text{Config} = (\sigma_g 1s)^2 (\sigma_u^* 1s)^1$$

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

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

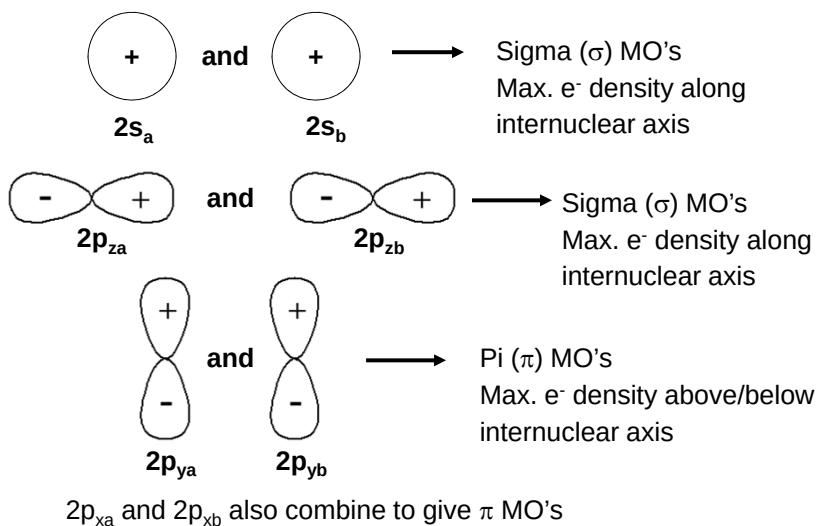
Shorthand Notation

Slide 57



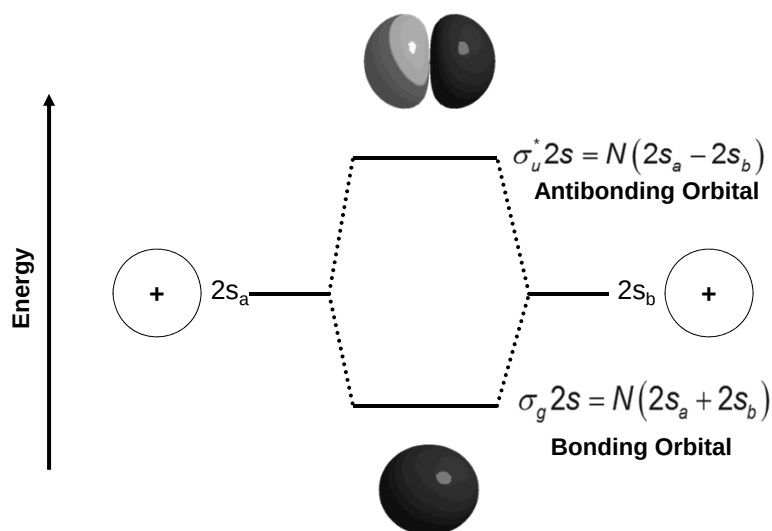
Second Row Homonuclear Diatomic Molecules

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

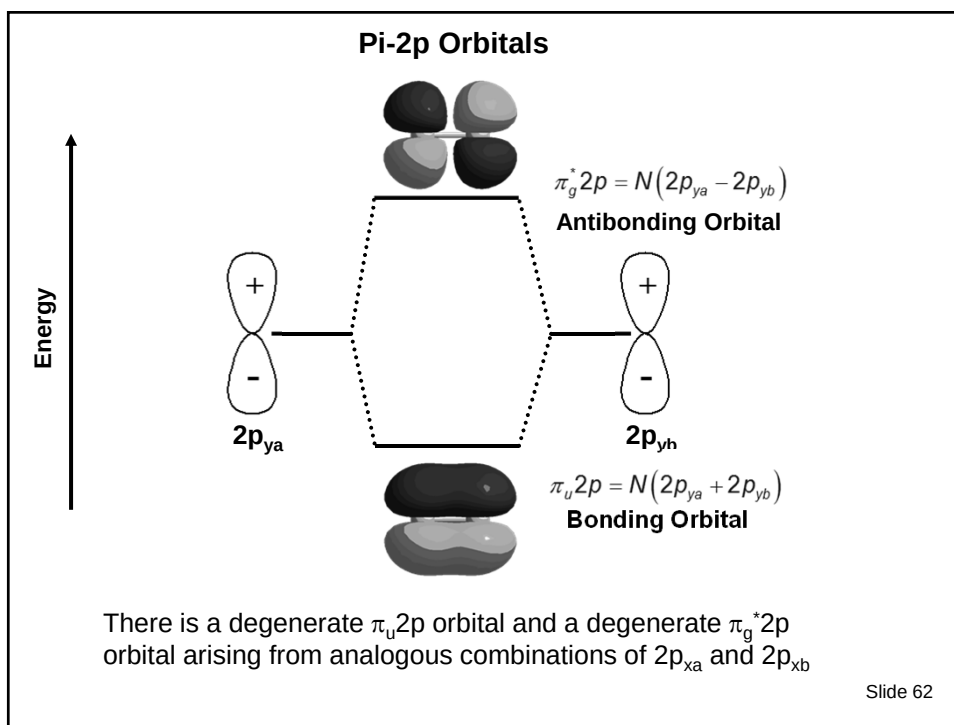
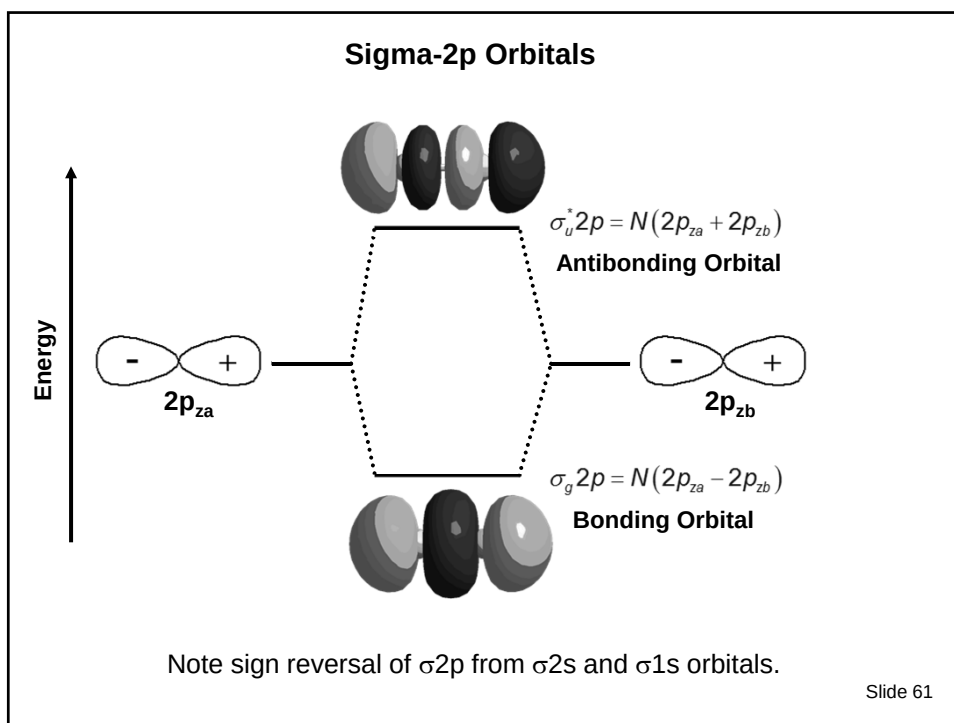


Slide 59

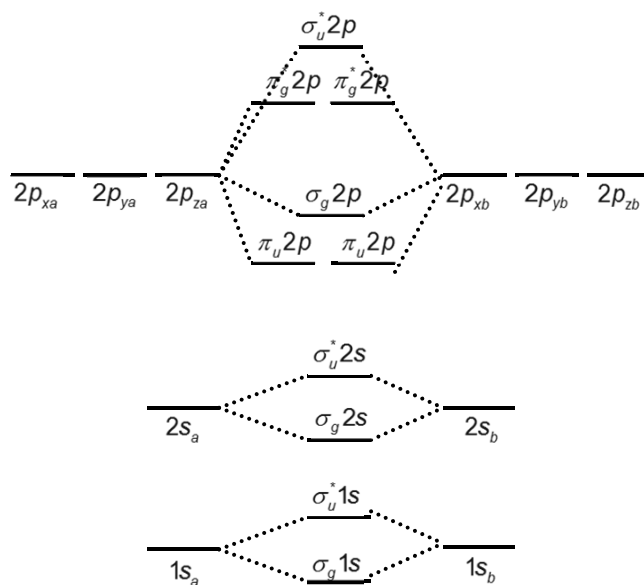
Sigma-2s Orbitals



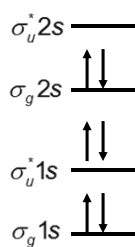
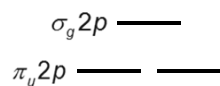
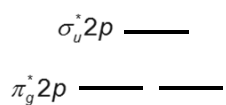
Slide 60



Homonuclear Diatomic Orbital Energy Diagram



Slide 63



Consider Li_2

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

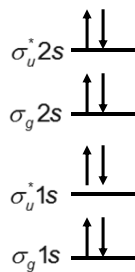
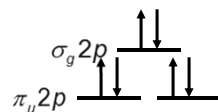
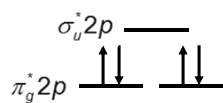
6 Electrons

$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2$$

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

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

Slide 64



Consider F_2

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

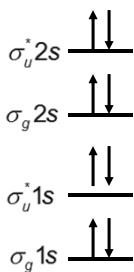
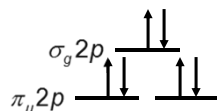
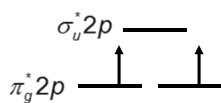
18 Electrons

$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^4$$

$$BO = \frac{1}{2}(10-8) = 1$$

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

Slide 65



Consider O_2

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

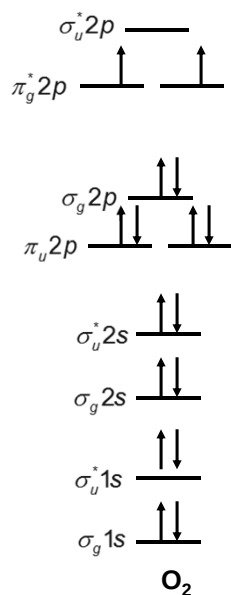
16 Electrons

$$(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4 (\sigma_g 2p)^2 (\pi_g^* 2p)^2$$

$$BO = \frac{1}{2}(10-6) = 2$$

$$S = 1 : \text{Triplet}$$

Slide 66



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^- : 17 Electrons – BO = 1.5

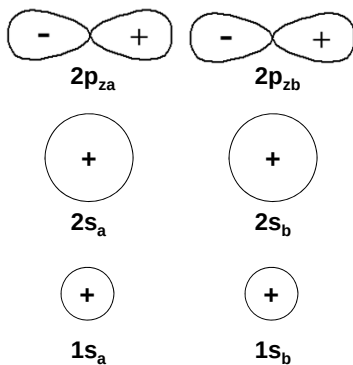
O_2^- has the longest bond.

O_2^+ has the highest vibrational frequency.

O_2^+ has the highest Dissociation Energy.

Slide 67

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.

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

Slide 68

Approximate vs. Accurate MO's in C₂

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

$\sigma 2p$ MO (E $\approx$ -15 eV)

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

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

$\sigma 2s$ MO (E $\approx$ -40 eV)

$$\psi_{Approx} \approx 0.70 \cdot 2s_a + 0.70 \cdot 2s_b$$

$$\psi_{Accur} = [-0.17 \cdot 1s_a + 0.50 \cdot 2s_a + 0.23 \cdot 2p_{za}] + [-0.17 \cdot 1s_b + 0.50 \cdot 2s_b + 0.23 \cdot 2p_{zb}]$$

$\sigma 1s$ MO (E $\approx$ -420 eV)

$$\psi_{Approx} \approx 0.70 \cdot 1s_a + 0.70 \cdot 1s_b$$

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

Slide 69

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**

Slide 70

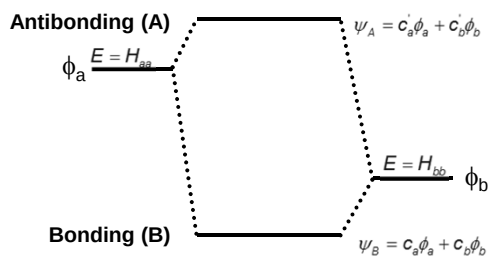
Heteronuclear Diatomic Molecules

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

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

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

$$|c_b| \neq |c_a|$$



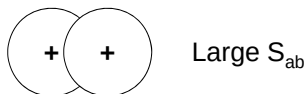
Slide 71

Interpretation of Secular Determinant Parameters

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

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

Overlap Integral



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

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

Slide 72

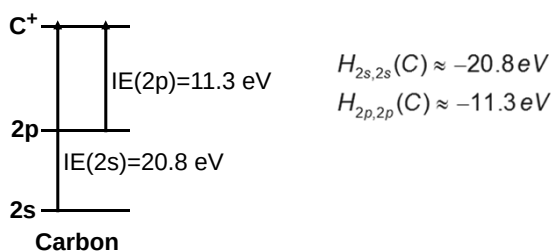
$$\begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

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

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

$H_{aa}, H_{bb} < 0$ 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 .



Slide 73

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

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

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_{bb}

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

Wolfsberg-Helmholtz Formula
(used in Extended Hückel Model)

$$H_{ab} < 0$$

Slide 74

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: $1 = \int \psi_{MO}^2 d\tau = \langle \psi_{MO} | \psi_{MO} \rangle$

$$1 = \langle N(c_a\phi_a + c_b\phi_b) | N(c_a\phi_a + c_b\phi_b) \rangle$$

$$1 = N^2 [c_a^2 \langle \phi_a | \phi_a \rangle + c_b^2 \langle \phi_b | \phi_b \rangle + 2c_a c_b \langle \phi_a | \phi_b \rangle]$$

$$1 = N^2 [c_a^2 + c_b^2 + 2c_a c_b S_{ab}] \quad \text{where} \quad S_{ab} = \langle \phi_a | \phi_b \rangle$$

$$N = \frac{1}{\sqrt{c_a^2 + c_b^2 + 2c_a c_b S_{ab}}} \quad \text{Orbital Overlap}$$

Slide 75

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

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

Slide 76

$$f_a = \frac{c_a^2}{c_a^2 + c_b^2} \quad f_b = \frac{c_b^2}{c_a^2 + c_b^2} \quad \begin{vmatrix} H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} \\ H_{ab} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle \end{vmatrix} = 0$$

Homonuclear Diatomic Molecules: $H_{bb} = H_{aa}$

$$|c_b| = |c_a|$$

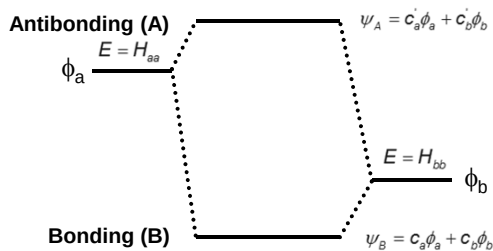
$$f_a = f_b = 0.50$$

Heteronuclear Diatomic Molecules: $H_{bb} \neq H_{aa}$

$$|c_b| \neq |c_a|$$

$$f_b \neq f_a$$

Slide 77



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

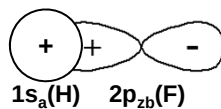
$$(H_{aa} - \langle E \rangle)(H_{bb} - \langle E \rangle) - (H_{ab} - \langle E \rangle S_{ab})(H_{ab} - \langle E \rangle S_{ab}) = 0$$

One has a quadratic equation, which can be solved to yield two values for the energy, $\langle E \rangle$.

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

Slide 78

A Numerical Example: Hydrogen Fluoride (HF)



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

$$\psi_{MO} = N(c_a \phi_a + c_b \phi_b) = N(c_a 1s_a(H) + c_b 2p_{zb}(F))$$

Matrix Elements

$$H_{aa} = \langle \phi_a | H | \phi_a \rangle = \langle 1s_a(H) | H | 1s_a(H) \rangle = -13.6 \text{ eV}$$

$$H_{bb} = \langle \phi_b | H | \phi_b \rangle = \langle 2p_{zb}(F) | H | 2p_{zb}(F) \rangle = -17.4 \text{ eV}$$

$$H_{ab} = \langle \phi_a | H | \phi_b \rangle = \langle 1s_a(H) | H | 2p_{zb}(F) \rangle = -2.0 \text{ eV}$$

$$S_{ab} = \langle \phi_a | \phi_b \rangle = \langle 1s_a(H) | 2p_{zb}(F) \rangle \approx 0$$

Slide 79

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



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

$$(-13.6 - \langle E \rangle)(-17.4 - \langle E \rangle) - (-2)(-2) = 0$$

$$\langle E \rangle^2 + 31.0 \langle E \rangle + 232.64 = 0$$

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

$$\langle E \rangle_B = \frac{-31.0 - \sqrt{30.44}}{2} = -18.26 \text{ eV}$$

$$\langle E \rangle_A = \frac{-31.0 + \sqrt{30.44}}{2} = -12.74 \text{ eV}$$

Slide 80

$$\begin{vmatrix} -13.6 - \langle E \rangle & -2 \\ -2 & -17.4 - \langle E \rangle \end{vmatrix} = 0 \longrightarrow \begin{aligned} (-13.6 - \langle E \rangle) c_a - 2c_b &= 0 \\ -2c_a + (-17.4 - \langle E \rangle) c_b &= 0 \end{aligned}$$

Bonding MO

$$[-13.6 - (-18.25)] c_a - 2c_b = 0$$

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

$$\begin{aligned} \psi_B &= (c_a \phi_a + c_b \phi_b) \\ &= c_a (\phi_a + 2.33 \phi_b) \\ &= N (\phi_a + 2.33 \phi_b) \end{aligned}$$

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

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

Antibonding MO

$$[-13.6 - (-12.74)] c_a - 2c_b = 0$$

$$\frac{c_b}{c_a} = -0.430 \rightarrow c_b = -0.430c_a$$

$$\begin{aligned} \psi_A &= (c_a \phi_a + c_b \phi_b) \\ &= c_a (\phi_a - 0.430 \phi_b) \\ &= N (\phi_a - 0.430 \phi_b) \end{aligned}$$

$$\psi_A = \frac{1}{\sqrt{1 + (-0.430)^2}} (\phi_a - 0.430 \phi_b)$$

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

Slide 81

Electron Densities in Hydrogen Fluoride

Bonding Orbital

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

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

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

Antibonding Orbital

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

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

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

Slide 82

Statistical Thermodynamics: Electronic Contributions to Thermodynamic Properties of Gases

Here they are again.

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

$$H = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} + kT \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$$

$$C_P = \left(\frac{\partial H}{\partial T} \right)_{P,N}$$

$$S = k \ln Q + \frac{U}{T}$$

$$A = U - TS = -kT \ln Q$$

$$G = H - TS = -kT \ln Q + kT \left(\frac{\partial \ln Q}{\partial \ln V} \right)_{T,N}$$

Slide 83

The Electronic Partition Function

$$q^{elect} = \sum_{i=0}^{\infty} g_i e^{-\frac{\epsilon_i}{kT}} = g_0 e^{-\frac{\epsilon_0}{kT}} + g_1 e^{-\frac{\epsilon_1}{kT}} + g_2 e^{-\frac{\epsilon_2}{kT}} + \dots$$

$$\text{or } q^{elect} = e^{-\frac{\epsilon_0}{kT}} \cdot \sum_{i=0}^{\infty} g_i e^{-\frac{\epsilon_i - \epsilon_0}{kT}} = e^{-\frac{\epsilon_0}{kT}} \cdot \left[g_0 + g_1 e^{-\frac{\epsilon_1 - \epsilon_0}{kT}} + g_2 e^{-\frac{\epsilon_2 - \epsilon_0}{kT}} + \dots \right]$$

$$q^{elect} = e^{-\frac{\epsilon_0}{kT}} \cdot \sum_{i=0}^{\infty} g_i e^{-\frac{\Delta \epsilon_i}{kT}} = e^{-\frac{\epsilon_0}{kT}} \cdot \left[g_0 + g_1 e^{-\frac{\Delta \epsilon_1}{kT}} + g_2 e^{-\frac{\Delta \epsilon_2}{kT}} + \dots \right]$$

$$q^{elect} = e^{-\frac{\epsilon_0}{kT}} \cdot \sum_{i=0}^{\infty} g_i e^{-\frac{\Theta_{ei}}{T}} = e^{-\frac{\epsilon_0}{kT}} \cdot \left[g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} + g_2 e^{-\frac{\Theta_{e2}}{T}} + \dots \right]$$

$$\Theta_{ei} = \frac{\Delta \epsilon_i}{k} = \frac{hc \tilde{\nu}_{ei}}{k}$$

$\Delta \epsilon_i$ is the energy of the i'th electronic level above the ground state, ϵ_0

$\tilde{\nu}$ is the absorption frequency (in cm^{-1}) to this state.

Slide 84

$$q^{elect} = e^{-\frac{\epsilon_0}{kT}} \cdot \sum_{i=0}^{\infty} g_i e^{-\frac{\Theta_{ei}}{T}} = e^{-\frac{\epsilon_0}{kT}} \cdot \left[g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} + g_2 e^{-\frac{\Theta_{e2}}{T}} + \dots \right] \quad \Theta_{ei} = \frac{\Delta \epsilon_i}{k} = \frac{hc\tilde{\nu}_{ei}}{k}$$

The ground state energy, ϵ_0 , is arbitrary (depending upon the point of reference). It is sometimes taken to be zero.

Excited state energies above $\sim 5,000$ - $10,000 \text{ cm}^{-1}$ don't contribute significantly to q^{elect} (or to thermodynamic properties). For example,

$$\begin{aligned} \tilde{\nu}_{ei} &= 20,000 \text{ cm}^{-1} \\ T &= 3,000 \text{ K} \end{aligned} \quad \Theta_{ei} = \frac{hc\tilde{\nu}_{ei}}{k} = \frac{(6.63 \times 10^{-34})(3.00 \times 10^{10})(20,000)}{1.38 \times 10^{-23}} = 2.88 \times 10^4 \text{ K}$$

$$e^{-\frac{\Theta_{ei}}{T}} = e^{-\frac{2.88 \times 10^4}{3,000}} = e^{-9.60} \approx 7 \times 10^{-5}$$

At room temperature (298 K): $e^{-\frac{\Theta_{ei}}{T}} \approx 1 \times 10^{-42}$

Thus, one can ignore all but very low-lying electronic states, except at elevated temperatures.

Slide 85

For convenience, we will consider only systems with a maximum of one "accessible" excited state: $q^{elect} = e^{-\frac{\epsilon_0}{kT}} \left[g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \right]$

Internal Energy and Enthalpy

$$U^{elect} = kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N}$$

Q^{elect} independent of V

$$H^{elect} = kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N} + \cancel{kT \left(\frac{\partial \ln Q^{elect}}{\partial \ln V} \right)_{T,N}} = U^{elect}$$

$$H^{elect} = U^{elect} = kT^2 \left(\frac{\partial \ln Q^{elect}}{\partial T} \right)_{V,N} = kT^2 \left(\frac{\partial \ln [q^{elect}]^N}{\partial T} \right)_{V,N} = nRT^2 \left(\frac{\partial \ln q^{elect}}{\partial T} \right)_{V,N}$$

Slide 86

$$H^{elect} = U^{elect} = \frac{nRg_1\Theta_{e1}e^{-\frac{\Theta_{e1}}{T}}}{g_0 + g_1e^{-\frac{\Theta_{e1}}{T}}} \quad \Theta_{e1} = \frac{\Delta\epsilon_1}{k} = \frac{hc\tilde{\nu}_{e1}}{k}$$

Numerical Example #1

The electronic ground state of CO is a singlet, with no accessible excited electronic levels. Calculate H^{elect} at 298 K and 3000 K

If there are no "accessible" excited states, that means that $\Theta_{e1}/T \gg 1$. This leads to:

$$H^{elect} = \frac{nRg_1\Theta_{e1}e^{-\frac{\Theta_{e1}}{T}}}{g_0 + g_1e^{-\frac{\Theta_{e1}}{T}}} = \frac{nRg_1\Theta_{e1}e^{-\infty}}{g_0 + g_1e^{-\infty}} = 0$$

By the same reasoning, $H^{elect} = U^{elect} = 0$ for molecules with ground states of any multiplicity if the excited states are inaccessible.

Slide 89

$$H^{elect} = U^{elect} = \frac{nRg_1\Theta_{e1}e^{-\frac{\Theta_{e1}}{T}}}{g_0 + g_1e^{-\frac{\Theta_{e1}}{T}}} \quad \Theta_{e1} = \frac{\Delta\epsilon_1}{k} = \frac{hc\tilde{\nu}_{e1}}{k}$$

Numerical Example #2

The electronic ground state of O_2 is a triplet (refer back to orbital diagram for O_2 earlier in the chapter).

There is an excited electronic state doublet 7882 cm^{-1} above the GS .

Calculate H^{elect} for one mole of O_2 at 3000 K and 298 K.

$$\Theta_{e1} = \frac{hc\tilde{\nu}_{e1}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(7882 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 11,360 \text{ K}$$

$$H^{elect} = \frac{nRg_1\Theta_{e1}e^{-\frac{\Theta_{e1}}{T}}}{g_0 + g_1e^{-\frac{\Theta_{e1}}{T}}} = \frac{(1 \text{ mol}) \cdot (8.31 \text{ J/mol} \cdot \text{K})(2)(11360 \text{ K})e^{-\frac{11360}{3000}}}{3 + 2e^{-\frac{11360}{3000}}} = 1400 \text{ J} = 1.40 \text{ kJ}$$

$$\text{At 298 K: } H^{elect} = 2 \times 10^{-15} \text{ kJ} \approx 0$$

Slide 90

Entropy

$$S^{elect} = k \ln Q^{elect} + \frac{U^{elect}}{T} = k \ln (q^{elect})^N + \frac{U^{elect}}{T} = Nk \ln q^{elect} + \frac{U^{elect}}{T}$$

$$S^{elect} = nR \ln q^{elect} + \frac{U^{elect}}{T} \quad \text{because } Nk = nN_A k = nR$$

$$q^{elect} = e^{-\frac{\epsilon_0}{kT}} \left[g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \right] = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \quad \text{because we're assuming that } \epsilon_0 = 0.$$

Slide 91

$$S^{elect} = nR \ln q^{elect} + \frac{U^{elect}}{T} \quad q^{elect} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}}$$

Numerical Example: O₂ again

The electronic ground state of O₂ is a triplet.

There is an excited electronic state doublet 7882 cm⁻¹ above the GS .

$$\Theta_{e1} = \frac{hc\tilde{\nu}_{e1}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm / s})(7882 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J / K}} = 11,360 \text{ K}$$

Let's calculate S^{elect} for one mole at 3000 K.

$$U^{elect} = H^{elect} = 1400 \text{ J (from earlier calculation)}$$

$$q^{elect} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} = 3 + 2e^{-\frac{11360}{3000}} = 3 + 0.045 = 3.045$$

Slide 92

$$S^{\text{elect}} = nR \ln q^{\text{elect}} + \frac{U^{\text{elect}}}{T} \quad q^{\text{elect}} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} = 3.045$$

$$U^{\text{elect}} = 1400 \text{ J}$$

$$S^{\text{elect}} = nR \ln q^{\text{elect}} + \frac{U^{\text{elect}}}{T} = (1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K}) \ln(3.045) + \frac{1400 \text{ J}}{3000 \text{ K}}$$

$$S^{\text{elect}} = 9.25 + 0.47 = 9.72 \text{ J/K at } 3000 \text{ K}$$

At 25 °C = 298 K: $U^{\text{elect}} = 0.00 \text{ J}$

$$q^{\text{elect}} = g_0 = 3$$

$$S^{\text{elect}} = R \ln(3) + 0/298 = 9.13 \text{ J/K at } 298 \text{ K}$$

Slide 93

$$S^{\text{elect}} = nR \ln q^{\text{elect}} + \frac{U^{\text{elect}}}{T} \quad q^{\text{elect}} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}}$$

At 25 °C = 298 K: $S^{\text{elect}} = R \ln(3) + 0/298 = 9.13 \text{ J/K}$

Recall from above that, if there are no accessible excited states, then $H^{\text{elect}} = U^{\text{elect}} = 0$, independent of ground-state multiplicity.

In contrast, if the electronic ground-state of a molecule has a multiplicity, $g_0 > 1$, then $S^{\text{elect}} > 0$, even if there are no accessible excited states.

Slide 94

O₂ Entropy: Comparison with experiment

$$\text{O}_2: S_{\text{mol}}(\text{exp}) = 205.1 \text{ J/mol-K at } 298.15 \text{ K}$$

$$\bar{S}^{\text{tran}} + \bar{S}^{\text{rot}} + \bar{S}^{\text{vib}} = 151.9 + 43.8 + 0.035 = 195.7$$

Chap. 3 Chap. 4 Chap. 5

We were about 5% too low. Let's add in the electronic contribution.

$$\bar{S}^{\text{tran}} + \bar{S}^{\text{rot}} + \bar{S}^{\text{vib}} + \bar{S}^{\text{elect}} = 151.9 + 43.8 + 0.035 + 9.1 = 204.8$$

Note that the agreement with experiment is virtually perfect.

Note: If a molecule has a **singlet** electronic ground-state and **no** accessible excited electronic states, then there is no electronic contribution to S .

Slide 95

Helmholtz and Gibbs Energy

$$A^{\text{elect}} = U^{\text{elect}} - TS^{\text{elect}} = -kT \ln Q^{\text{elect}}$$

Q^{elect} independent of V

$$G^{\text{elect}} = H^{\text{elect}} - TS^{\text{elect}} = -kT \ln Q^{\text{elect}} + kT \left(\frac{\partial \ln Q^{\text{elect}}}{\partial \ln V} \right)_{T,N} = A^{\text{elect}}$$

Numerical Example: O₂ Once More

The electronic ground state of O₂ is a triplet.

There is an excited electronic state doublet 7882 cm⁻¹ above the GS .

$$\Theta_{e1} = \frac{hc\tilde{\nu}_{e1}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}) (3.00 \times 10^{10} \text{ cm / s}) (7882 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J / K}} = 11,360 \text{ K}$$

Let's calculate G^{elect} (= A^{elect}) for one mole of O₂ at 3000 K.

Slide 96

$$G^{elect} = A^{elect} = -kT \ln Q^{elect} \quad q^{elect} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \quad \begin{array}{l} \Theta_{e1} = 11,360 \text{ K} \\ g_0 = 2 \\ g_1 = 3 \end{array}$$

$$q^{elect} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} = 3 + 2e^{-\frac{11360}{3000}} = 3.045$$

$$G^{elect} = -kT \ln Q^{elect} = -kT \ln (q^{elect})^N = -NkT \ln q^{elect} = -nRT \ln q^{elect}$$

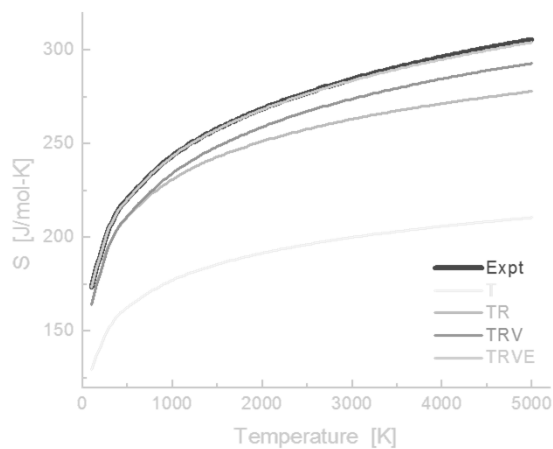
$\uparrow$
 $Nk = nN_A k = nR$

$$G^{elect} = -nRT \ln q^{elect} = -(1 \text{ mol})(8.31 \text{ J/mol} \cdot \text{K})(3000 \text{ K}) \ln(3.045)$$

$$G^{elect} = A^{elect} = -27,760 \text{ J} = -27.8 \text{ kJ}$$

Slide 97

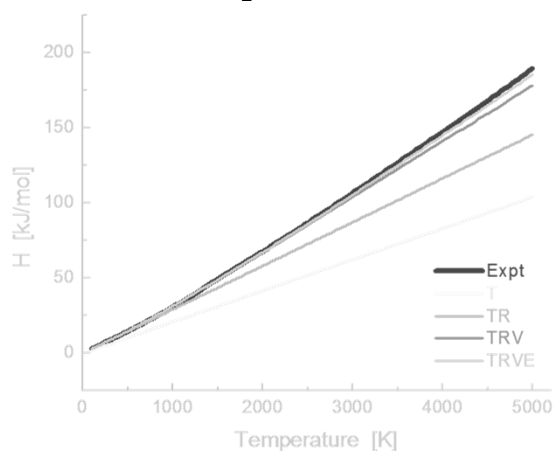
O₂: Entropy



The agreement of the calculated entropy including electronic contributions with experiment is close to perfect.

Slide 98

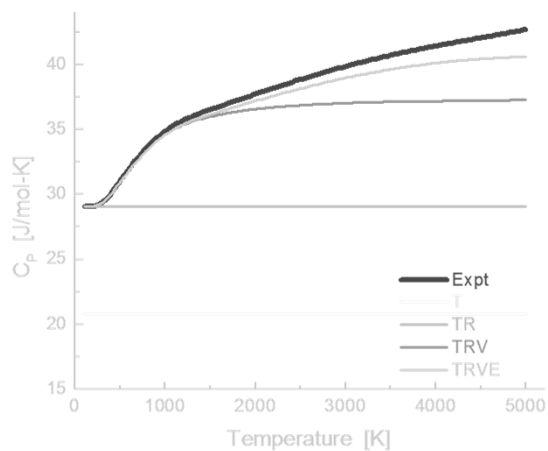
O₂: Enthalpy



The agreement of the calculated enthalpy including electronic contributions with experiment is close to perfect.

Slide 99

O₂: Heat Capacity



The calculated heat capacity is the most sensitive function of any neglect in the calculations.

We have neglected several subtle factors, including vibrational anharmonicity, centrifugal distortion and vibration-rotation coupling

Slide 100