## CHAPTER 8
DIATOMIC MOLECULES
OUTLINE

Homework Questions Attached

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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(H$_2^+$) and subtracts this energy from a reference energy; i.e. $D_e = E_{\text{ref}} - E(H_2^+)$. 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 $\sigma_g2p$ (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 $\pi_u2p$ (bonding) orbitals and one of the $\pi_g^*2p$ (antibonding) orbitals. What do the subscripts “u” and “g” stand for?

(f) One of the $\sigma$ 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 $\pi$ molecular orbitals in the diatomic molecule, C$_2$, is given approximately by: $\phi = (0.82 \cdot 2p_{ya}) + (-0.82p_{yb})$

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 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:

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

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 ($\phi_a$) and an orbital on atom b ($\phi_b$). 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, $\psi_B$, and $\psi_A$.

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. \((\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2\))

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

(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:

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

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

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

\[
\psi_{IV} = N \psi_{\text{Spatial}} \psi_{\text{Spin}} = N \left[ \sigma_g 1s(1) \sigma_u^* 1s(2) - \sigma_u^* 1s(1) \sigma_g 1s(2) \right] \beta_1 \beta_2
\]

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 °C.

**Note:** As discussed in class, you can ignore the non-thermal contribution to the internal energy; i.e. we are assuming that \(\varepsilon_0\) and \(E_0\) (=\(N\alpha_0\)) are zero.

**Data**

**Order of Orbital Energies: Homonuclear Diatomic Molecules**

\[ \sigma_1s < \sigma^*1s < \sigma_2s < \sigma^*_2s < \pi_2p < \sigma_g^*2p < \sigma_g2p < \sigma^*_g2p \]

**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.
Chapter 8

Diatomic Molecules

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
Hydrogen Molecular Ion:
Born-Oppenheimer Approximation

The simplest molecule is not \( \text{H}_2 \). Rather, it is \( \text{H}_2^+ \), which has two hydrogen nuclei and one electron.

\[
\begin{align*}
\text{The } \text{H}_2^+ \text{ Hamiltonian (in au)} \\
H &= -\frac{1}{2M_a} \frac{\partial^2}{\partial \mathbf{r}_a^2} - \frac{1}{2M_b} \frac{\partial^2}{\partial \mathbf{r}_b^2} - \frac{1}{2} \frac{1}{r_a} \frac{\partial}{\partial r_a} - \frac{1}{2} \frac{1}{r_b} \frac{\partial}{\partial r_b} + \frac{1}{R_{ab}} \\
\text{KE} &\quad \text{KE} \\
\text{Nuc a} &\quad \text{Nuc b} \\
\text{KE} &\quad \text{KE} \\
\text{Elect} &\quad \text{PE} \\
\text{PE} &\quad \text{PE} \\
\text{e-N} &\quad \text{e-N} \\
\text{N-N} &\quad \text{N-N} \\
\text{Attr} &\quad \text{Attr} \\
\text{Repuls} &\quad \text{Repuls}
\end{align*}
\]

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

\[
\left( -\frac{1}{2M_a} \frac{\partial^2}{\partial \mathbf{r}_a^2} - \frac{1}{2M_b} \frac{\partial^2}{\partial \mathbf{r}_b^2} + \frac{1}{R_{ab}} + E_{\text{el}} \right) \cdot \chi(R_{ab}) = E_{\text{rad}} \cdot \chi(R_{ab})
\]

\( E_{\text{el}} \) 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

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

Because \( \text{H}_2^+ \) 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

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- **Math Prelim.: Systems of Linear Equations – Cramer’s Rule**
  - LCAO Treatment of \( \text{H}_2^+ \)
  - \( \text{H}_2^+ \) Energies
  - \( \text{H}_2^+ \) Wavefunctions
- MO Treatment of the \( \text{H}_2 \) Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules
Systems of Linear Equations: Cramer’s Rule

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

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

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

A Numerical Example

$$a_{11}x_1 + a_{12}x_2 = c_1 \quad 2x_1 + 5x_2 = 1$$
$$a_{21}x_1 + a_{22}x_2 = c_2 \quad 3x_1 - 2x_2 = 11$$

$$x_1 = \frac{\begin{vmatrix} 1 & 5 \\ 11 & -2 \end{vmatrix}}{\begin{vmatrix} 2 & 5 \\ 3 & -2 \end{vmatrix}} = \frac{1(-2) - 5(11)}{2(-2) - 5(3)} = \frac{-57}{-19} = 3$$

$$x_2 = \frac{\begin{vmatrix} 2 & 1 \\ 3 & 11 \end{vmatrix}}{\begin{vmatrix} 2 & 5 \\ 3 & -2 \end{vmatrix}} = \frac{2(11) - 1(3)}{2(-2) - 5(3)} = \frac{19}{-19} = -1$$
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!!
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".

\[
\begin{align*}
  a_{11}x_1 + a_{12}x_2 &= 0 \\
  a_{21}x_1 + a_{22}x_2 &= 0 \\
  x_1 &= x_2 = 0 \text{ unless } \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 0
\end{align*}
\]

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LCAO Treatment of $\text{H}_2^+$

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 $\alpha$ and the second with spin $\beta$.

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

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

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

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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 $\text{H}_2^+$ 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:

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

shorthand

Assume that 1$s_a$ and 1$s_b$ are each normalized.
Expectation Value of the Energy

\[ \psi = c_a |s_a\rangle + c_b |s_b\rangle \]

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.

\[
\langle E \rangle = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\text{Num}}{\text{Denom}}
\]

Remember that because \( |s_a\rangle \) and \( |s_b\rangle \) are normalized.

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

\[
\text{Denom} = c_a^2 + 2c_a c_b S_{ab} + c_b^2
\]
\[ \psi = c_a 1_{s_a} + c_b 1_{s_b} \]

\[ \text{Num} = \langle \psi | H | \psi \rangle = \langle c_a 1_{s_a} + c_b 1_{s_b} | H | c_a 1_{s_a} + c_b 1_{s_b} \rangle \]

\[ \text{Num} = c_a^2 \langle 1_{s_a} | H | 1_{s_a} \rangle + c_a c_b \langle 1_{s_a} | H | 1_{s_b} \rangle + c_a c_b \langle 1_{s_b} | H | 1_{s_a} \rangle + c_b^2 \langle 1_{s_b} | H | 1_{s_b} \rangle \]

\[ H_{aa} = \langle 1_{s_a} | H | 1_{s_a} \rangle \]
\[ H_{bb} = \langle 1_{s_b} | H | 1_{s_b} \rangle \]
\[ H_{ab} = \langle 1_{s_b} | H | 1_{s_a} \rangle \]
\[ H_{ba} = \langle 1_{s_a} | H | 1_{s_b} \rangle = H_{ab} \quad \text{because } H \text{ is Hermitian} \]

\[ \text{Num} = c_a^2 H_{aa} + 2 c_a c_b H_{ab} + c_b^2 H_{bb} \quad \text{Note: For this particular problem,} \]
\[ H_{bb} = H_{aa} \text{ by symmetry.} \]
\[ \text{However, this is not true in general.} \]

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

**Minimizing \( \langle E \rangle \): The Secular Determinant**

In order to find the values of \( c_a \) and \( c_b \) which minimize \( \langle E \rangle \), we 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 \( \langle E \rangle \) 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 responsibly only for the concept of how we get to the "Secular Determinant"
\[ \langle E \rangle = \frac{c_a^2 H_{aa} + 2c_a c_b H_{ab} + c_b^2 H_{bb}}{c_a^2 + 2c_a c_b + c_b^2} \]

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

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

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

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

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

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

\[ \langle E \rangle c_a + \langle E \rangle c_b S_{ab} = c_a H_{aa} + c_b H_{bb} \]

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

or

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

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:

\[ (H_{bb} - \langle E \rangle S_{ab}) c_a + (H_{ab} - \langle E \rangle) c_b = 0 \]
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 \textit{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.

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

\textbf{The Secular Determinant}

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**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:

\[
\left| H_{ij} - \langle E \rangle S_{ij} \right| = 0
\]

After you have made the Secular Determinant, set the diagonal overlaps, \( S_{ii} = 1 \).
\[ |H_f - \langle E \rangle S| = 0 \]

For example, if \( \psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 \)

Then the Secular Determinant is:
\[
\begin{vmatrix}
H_{aa} - \langle E \rangle S_{aa} & H_{ab} - \langle E \rangle S_{ab} & H_{ac} - \langle E \rangle S_{ac} \\
H_{ba} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle S_{bb} & H_{bc} - \langle E \rangle S_{bc} \\
H_{ca} - \langle E \rangle S_{ac} & H_{cb} - \langle E \rangle S_{bc} & H_{cc} - \langle E \rangle S_{cc}
\end{vmatrix} = 0
\]

Setting diagonal \( S_{ii} = 1 \)
\[
\begin{vmatrix}
H_{aa} - \langle E \rangle & H_{ab} - \langle E \rangle S_{ab} & H_{ac} - \langle E \rangle S_{ac} \\
H_{ba} - \langle E \rangle S_{ab} & H_{bb} - \langle E \rangle & H_{bc} - \langle E \rangle S_{bc} \\
H_{ca} - \langle E \rangle S_{ac} & H_{cb} - \langle E \rangle S_{bc} & H_{cc} - \langle E \rangle
\end{vmatrix} = 0
\]

Outline

- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
- Math Prelim.: Systems of Linear Equations – Cramer’s Rule
- LCAO Treatment of \( H_2^+ \(141,296),(884,403)
- \( H_2^+ \) Energies
- \( H_2^+ \) Wavefunctions
- MO Treatment of the \( H_2 \) Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules
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 \( c_b \).
Solving for the Energies

\[
\left( \langle E \rangle - H_{aa} \right)^2 = \left( H_{ab} - \langle E \rangle S_{ab} \right)^2
\]

\[
\langle E \rangle - H_{aa} = \pm \left( H_{ab} - \langle E \rangle S_{ab} \right) = \pm H_{ab} \mp \langle E \rangle S_{ab}
\]

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

Therefore:

\[
\langle E \rangle = \frac{H_{aa} \pm H_{ab}}{1 \pm S_{ab}}
\]

or

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

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, \( R \).

\[
H_{aa} = -\frac{1}{2} - \frac{1}{R} + \left(1 + \frac{1}{R}\right) e^{-2R}
\]

\[
S_{ab} = e^{-R} \left( \frac{R^3}{3} + R + 1 \right)
\]

\[
H_{ab} = -\frac{1}{2} S_{ab} - (R + 1) e^{-R}
\]
$\langle E \rangle_+ = \frac{H_{aa} + H_{ab}}{1 + S_{ab}}$  \hspace{1cm} $\langle V \rangle_+ = \frac{1}{R} = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} + \frac{1}{R}$

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

$\langle E \rangle_+$ 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, $1/R$

---

Asymptotic limit of $E_H$ as $R \to \infty$

$V(\infty) = -0.50 \text{ au}$

Calculated Minimum Energy

$E_{\text{min}}(\text{cal}) = -0.565 \text{ au}$ at $R_{\text{min}}(\text{cal}) = 2.49 \text{ a}_0 = 1.32 \text{ Å}$
**Comparison with Experiment**

- Calculated Minimum Energy:
  - $E_{\text{min}}(\text{cal}) = -0.565 \text{ au}$
  - $R_{\text{min}}(\text{cal}) = 1.32 \text{ Å}$

- Dissociation Energy:
  - $D_{e}(\text{cal}) = E_H - E_{\text{min}}(\text{cal})$
    - $= -0.5 \text{ au} - (-0.565 \text{ au})$
    - $= +0.065 \text{ au}$
    - $= 27.21 \text{ eV/au}$
    - $= 1.77 \text{ eV}$

<table>
<thead>
<tr>
<th>$R_{\text{min}}$</th>
<th>$D_{e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal. 1.32 Å</td>
<td>1.77 eV</td>
</tr>
<tr>
<td>Expt. 1.06</td>
<td>2.79</td>
</tr>
</tbody>
</table>

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

---

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- Hydrogen Molecular Ion: Born-Oppenheimer Approximation.
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- LCAO Treatment of $H_2^+$
- $H_2^+$ Energies
- $H_2^+$ Wavefunctions
- MO Treatment of the $H_2$ Molecule
- Homonuclear Diatomic Molecules
- Heteronuclear Diatomic Molecules
H₂⁺ Wavefunctions (aka Molecular Orbitals)

The LCAO Wavefunction: \( \psi = c_a \Phi_1 + c_b \Phi_2 \)

Remember that by using the Variational Principle on the expression for \( \langle E \rangle \), we developed two homogeneous linear equations relating \( c_a \) and \( c_b \):

\[
\begin{align*}
(H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b &= 0 \\
(H_{ab} - \langle E \rangle S_{ab}) c_a + (H_{bb} - \langle E \rangle) c_b &= 0
\end{align*}
\]

We then solved the Secular Determinant of the matrix coefficients to get two values for \( \langle E \rangle \):

\[
\langle E \rangle_+ = \frac{H_{aa} + H_{bb}}{1 + S_{ab}} \\
\langle E \rangle_- = \frac{H_{aa} - H_{bb}}{1 - S_{ab}}
\]

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

\[
\begin{align*}
(H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b &= 0 & \text{Plug in} & \langle E \rangle_+ = \frac{H_{aa} + H_{bb}}{1 + S_{ab}} \\
(H_{aa} - \langle E \rangle) c_a + (H_{ab} - \langle E \rangle S_{ab}) c_b &= 0 \\
(H_{aa} (1 + S_{ab}) - H_{aa} - H_{ab}) c_a + (H_{ab} (1 + S_{ab}) - H_{aa} S_{ab} - H_{ab} S_{ab}) c_b &= 0 \\
(H_{aa} S_{ab} - H_{ab}) c_a + (H_{ab} S_{ab} - H_{aa} S_{ab}) c_b &= 0 \\
(H_{aa} S_{ab} - H_{ab}) c_a + (H_{ab} S_{ab} - H_{aa} S_{ab}) c_b &= 0
\end{align*}
\]

\[
\begin{align*}
(H_{aa} S_{ab} - H_{ab}) c_a + (H_{ab} S_{ab} - H_{aa} S_{ab}) c_b &= 0 \\
(H_{aa} S_{ab} - H_{ab}) c_a + (H_{ab} S_{ab} - H_{aa} S_{ab}) c_b &= 0 \\
H_{aa} S_{ab} - H_{ab} &= 0 \\
H_{ab} S_{ab} - H_{aa} S_{ab} &= 0
\end{align*}
\]

\( c_a - c_b = 0 \quad \quad c_b = c_a \)

Note: Plugging into the second of the two linear equations gets you the same result.
\[ c_b = c_a + \psi = c_a \psi_{a} + c_b \psi_{b} \rightarrow \psi_{\pm} = c_a (1s_a + 1s_b) \]

or \[ \psi_{\pm} = N_{\pm} (1s_a + 1s_b) \]

\( N_{\pm} = c_{\pm} \) is determined by normalizing \( \psi_{\pm} \).

**Normalization:**

\[ 1 = \int \psi_{\pm} \psi_{\pm}^* d\tau = \langle \psi_{\pm} | \psi_{\pm} \rangle \]

\[ 1 = \langle N_{\pm} (1s_a + 1s_b) | N_{\pm} (1s_a + 1s_b) \rangle = N_{\pm}^2 (\langle 1s_a | 1s_a \rangle + \langle 1s_b | 1s_b \rangle + \langle 1s_a | 1s_b \rangle + \langle 1s_b | 1s_a \rangle) \]

\[ 1 = N_{\pm}^2 (1 + 2S_{ab} + 1) = N_{\pm}^2 (2 + 2S_{ab}) \]

\[ N_{\pm} = \frac{1}{\sqrt{2 + 2S_{ab}}} \rightarrow \psi_{\pm} = N_{\pm} (1s_a + 1s_b) = \frac{1}{\sqrt{2 + 2S_{ab}}} (1s_a + 1s_b) \]

---

**Antibonding Wavefunction**

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

Plug in \( \langle E \rangle = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \)

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

\( c_a + c_b = 0 \rightarrow c_a = -c_b \)

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

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

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

Note that the bonding MO, \( \psi_+ \), has significant electron density in the region between the two nuclei.

Note that the antibonding MO, \( \psi_- \), has a node (zero electron density in the region between the two nuclei.

---

Improving the Results

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

We used hydrogen atom 1s orbitals:

\[ \phi_{1s_a} = 1s_a = \frac{1}{\sqrt{\pi}} e^{-r_{a}} \quad \text{and} \quad \phi_{1s_b} = 1s_b = \frac{1}{\sqrt{\pi}} e^{-r_{b}} \quad \text{(in atomic units)} \]

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

\[ \phi_a = \frac{Z^{1/2}}{\sqrt{\pi}} e^{-Z'r_a} \quad \text{and} \quad \phi_b = \frac{Z^{1/2}}{\sqrt{\pi}} e^{-Z'r_b} \]

The expectation value for the energy, \( <E> \), is now a function of both \( Z' \) and \( R \).
\[ \psi = c_a \phi_a + c_b \phi_b = c_a \sqrt{\frac{Z'^{3}}{\pi}} e^{-Z'^{1/2}} + c_b \sqrt{\frac{Z'^{3}}{\pi}} e^{-Z'^{1/2}} \]

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.

<table>
<thead>
<tr>
<th>( R_{\text{min}} )</th>
<th>( D_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal. (( Z=1 ))</td>
<td>1.32 Å</td>
</tr>
<tr>
<td>Cal. (( Z'=1.24 ))</td>
<td>1.06</td>
</tr>
<tr>
<td>Expt.</td>
<td>1.06</td>
</tr>
</tbody>
</table>

**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.

\[ \psi = c_1 1s_a + c_2 2s_a + c_3 2p_{xa} + c_4 1s_b + c_5 2s_b + c_6 2p_{xa} \]

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_{z^2} orbital on each atom. The calculation took 12 seconds. We'll call it Cal.(Big)

<table>
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<tbody>
<tr>
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</tr>
<tr>
<td>Cal.(Z'=1.24)</td>
<td>1.06</td>
<td>2.35</td>
</tr>
<tr>
<td>Cal.(Big)</td>
<td>1.06</td>
<td>2.78</td>
</tr>
<tr>
<td>Expt.</td>
<td>1.06</td>
<td>2.79</td>
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MO Treatment of the H₂ Molecule

The H₂ Electronic Hamiltonian

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

<table>
<thead>
<tr>
<th>KE</th>
<th>KE</th>
<th>PE</th>
<th>PE</th>
<th>PE</th>
<th>PE</th>
<th>PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>e₁</td>
<td>e₂</td>
<td>e-N</td>
<td>e-N</td>
<td>e-N</td>
<td>e-N</td>
<td>e-e</td>
</tr>
<tr>
<td>Attr</td>
<td>Attr</td>
<td>Attr</td>
<td>Attr</td>
<td>Repuls</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The LCAO Molecular Orbitals

\[ \psi_+ = N_s (1s_a - 1s_b) \]  [Antibonding Orbital]
\[ \psi_- = N_s (1s_a + 1s_b) \]  [Bonding Orbital]

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

We can put both electrons in H₂ into the bonding orbital, \( \psi_+ \), one with \( \alpha \) spin and one with \( \beta \) spin.
Notation

Antibonding Orbital

\[ \psi_- = N_z \left( 1s_y - 1s_x \right) = \sigma_g^* 1s \]

Bonding Orbital

\[ \psi_+ = N_z \left( 1s_y + 1s_x \right) = \sigma_g 1s \]

\[ \sigma_g 1s \quad \text{Combin. of} \quad 1s \text{ orbitals} \]

\[ \sigma_u^* 1s \quad \text{antisymmetric w.r.t.} \quad \text{inversion} \]

\[ \text{e}^{-} \text{ density max. on internuclear axis} \]

\[ \text{symmetric w.r.t. inversion} \]

The Molecular Wavefunction

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

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

Form the antisymmetrized product using a Slater Determinant.

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

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

\[
\psi_{\text{MO}} = \begin{bmatrix} \sigma_g 1s(1) \sigma_g 1s(2) \end{bmatrix} \frac{1}{\sqrt{2}} \left[ \alpha_1 \beta_2 - \beta_1 \alpha_2 \right] = \psi_{\text{spat}} \cdot \psi_{\text{spin}}
\]
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.

\[
\psi_{\text{spin}} = \frac{1}{\sqrt{2}} [\alpha \beta_2 - \beta \alpha_2] \quad \text{The spin wavefunction is already normalized (see Chap. 8 PowerPoint for He).}
\]

The MO Energy of H₂

\[
\psi_{\text{spal}} = \sigma_g \uparrow s(1) \sigma_g \uparrow s(2) = \left[ N_i \left( 1s_a + 1s_b \right) \right] \left[ N_i \left( 1s_a + 1s_b \right) \right]
\]

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

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

\[
E = \langle \psi_{\text{spal}} | H | \psi_{\text{spal}} \rangle
\]

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:

\[
V(R) = E(R) + \frac{1}{R}
\]
De: Dissociation Energy

\[ 2E_H - E_{\text{min}}(\text{cal}) \]

\[ D_e = +0.099 \text{ au} = 2.69 \text{ eV} \]

\[ R_{\text{min}} = 0.85 \text{ Å} \]

\[ E_{\text{min}}(\text{cal}) = -1.099 \text{ au} \]

Improving the Results

As for \( \text{H}_2^+ \), one can add a variational parameter to the atomic orbitals used in \( \sigma_g 1s \).

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

The energy is now a function of both \( Z' \) and \( R \).

One can find the values of both that minimize the energy.

\[ R_{\text{min}} \quad D_e \]

\begin{align*}
\text{Cal.}(Z=1) & : 0.85 \text{ Å} & 2.70 \text{ eV} \\
\text{Cal.}(\text{Var. } Z') & : 0.73 & 3.49 \\
\text{Expt.} & : 0.74 & 4.73
\end{align*}
An Even Better Improvement: More Atomic Orbitals

As for $\text{H}_2^+$, one can make the bonding orbital a Linear Combination of more than two atomic orbitals; e.g.

$$\sigma_g 1s = c_1 1s_a + c_2 2s_a + c_3 2\rho_{z_a} + c_4 1s_b + c_5 2s_b + c_6 2\rho_{z_b}$$

We performed a Hartree-Fock calculation on $\text{H}_2$ using an LCAO that included 4 $s$ orbitals, 2 $p_z$ orbitals and 1 $d_{z^2}$ orbitals on each hydrogen.

<table>
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<td>Cal.(Z=1)</td>
<td>0.85 Å</td>
<td>2.70 eV</td>
</tr>
<tr>
<td>Cal.(Var. $Z'$)</td>
<td>0.73</td>
<td>3.49</td>
</tr>
<tr>
<td>Cal.(HF-Big)</td>
<td>0.74</td>
<td>3.62</td>
</tr>
<tr>
<td>Expt.</td>
<td>0.74</td>
<td>4.73</td>
</tr>
</tbody>
</table>

**Question:** Hey!! What went wrong??

When we performed this level calculation on $\text{H}_2^+$, we nailed the Dissociation Energy almost exactly.

But on $\text{H}_2$ the calculated $D_e$ is almost 25% too low.

**Answer:** The problem, Corky, is that unlike $\text{H}_2^+$, $\text{H}_2$ 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!!!
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 $D_e$

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</tr>
<tr>
<td>Cal.(QCISD(T))</td>
<td>0.74</td>
</tr>
<tr>
<td>Expt.</td>
<td>0.74</td>
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That's Better!!

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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 \( \text{H}_2^+ \) and \( \text{H}_2 \).

These same orbitals may be used to describe the bonding in \( \text{He}_2^+ \) and lack of bonding in \( \text{He}_2 \).

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. \( \text{Li}_2 \)).

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
Slater Determinant: $\text{He}_2^+$

$$Config = (\sigma_g \, 1s)^2 (\sigma_v^* \, 1s)^1$$

$$\psi_{MO} = \frac{1}{\sqrt{3!}} \begin{vmatrix} \sigma_g \, 1s(1)\alpha_i & \sigma_g \, 1s(1)\beta_i & \sigma_v^* \, 1s(1)\alpha_i \\ \sigma_g \, 1s(2)\alpha_i & \sigma_g \, 1s(2)\beta_i & \sigma_v^* \, 1s(2)\alpha_i \\ \sigma_g \, 1s(3)\alpha_i & \sigma_g \, 1s(3)\beta_i & \sigma_v^* \, 1s(3)\alpha_i \end{vmatrix}$$

Shorthand Notation

$\text{He}_2$ has 4 electrons

$Electron\ Configuration$

$Config = (\sigma_g \, 1s)^2 (\sigma_v^* \, 1s)^1$

$\sigma_v^* \, 1s = \psi_v' = N(1s_a - 1s_b)$

Antibonding Orbital

$\sigma_g \, 1s = \psi_s = N(1s_a + 1s_b)$

Bonding Orbital

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

$= 0$

Actually, $\text{He}_2$ forms an extremely weak “van der Waal’s complex”, with $R_{\text{min}} \approx 3 \, \text{Å}$ and $D_e \approx 0.001 \, \text{eV}$ [it can be observed at $T = 10^{-3} \, \text{K}$].
Second Row Homonuclear Diatomic Molecules

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

\[ \begin{align*}
\sigma^+ & \quad \text{and} \quad \sigma^- \\
2s_a & \quad \text{and} \quad 2s_b \\
\end{align*} \]

- \( \sigma^+ \) MO's: Max. e\(^-\) density along internuclear axis
- \( \sigma^- \) MO's: Max. e\(^-\) density along internuclear axis

\[ \begin{align*}
\pi^+ & \quad \text{and} \quad \pi^- \\
2p_{ya} & \quad \text{and} \quad 2p_{yb} \\
\end{align*} \]

- \( \pi^+ \) MO's: Max. e\(^-\) density above/below internuclear axis
- \( \pi^- \) MO's: Max. e\(^-\) density along internuclear axis

\( 2p_{xa} \) and \( 2p_{xb} \) also combine to give \( \pi \) MO's

---

Sigma-2s Orbitals

- **Antibonding Orbital**: \( \sigma_u^+ 2s = N(2s_a - 2s_b) \)
- **Bonding Orbital**: \( \sigma_g 2s = N(2s_a + 2s_b) \)
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 \( 2p_{ya} \) and \( 2p_{yb} \).
Consider Li₂

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

σ₂ 2p
π₂ 2p
σ₂ 2p
π₂ 2p

6 Electrons

σ₂ 2s
σ₂ 2s
σ₁ 1s
σ₁ 1s

(σ₂ 1s)² (σ₁ 1s)² (σ₁ 2s)²

BO = ½(4-2) = 1

S = 0 : Singlet
Consider $F_2$
(a) What is the electron configuration?
(b) What is the Bond Order?
(c) What is the spin multiplicity?
(Singlet, Doublet or Triplet)

\[
\begin{align*}
\sigma_g^{2p} & \quad \uparrow \quad \uparrow \\
\pi_u^{2p} & \quad \uparrow \quad \downarrow \\
\sigma_g^{2p} & \quad \uparrow \quad \downarrow \\
\pi_u^{2p} & \quad \uparrow \quad \downarrow \\
\sigma_g^{1s} & \quad \uparrow \\
\sigma_u^{1s} & \quad \uparrow \\
\end{align*}
\]

18 Electrons
\[
\begin{align*}
(\sigma_g^{1s})^2 (\pi_u^{1s})^2 (\sigma_g^{2s})^2 (\sigma_u^{2s})^2 (\pi_u^{2p})^4 (\sigma_g^{2p})^2 (\pi_u^{2p})^4
\end{align*}
\]

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

S = 0 : Singlet

Consider $O_2$
(a) What is the electron configuration?
(b) What is the Bond Order?
(c) What is the spin multiplicity?
(Singlet, Doublet or Triplet)

\[
\begin{align*}
\sigma_g^{2p} & \quad \uparrow \quad \uparrow \\
\pi_u^{2p} & \quad \uparrow \quad \downarrow \\
\sigma_g^{2p} & \quad \uparrow \quad \downarrow \\
\pi_u^{2p} & \quad \uparrow \quad \downarrow \\
\sigma_g^{1s} & \quad \uparrow \\
\sigma_u^{1s} & \quad \uparrow \\
\end{align*}
\]

16 Electrons
\[
\begin{align*}
(\sigma_g^{1s})^2 (\sigma_u^{1s})^2 (\sigma_g^{2s})^2 (\sigma_u^{2s})^2 (\pi_u^{2p})^4 (\sigma_g^{2p})^2 (\pi_u^{2p})^2
\end{align*}
\]

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

S = 1 : Triplet
Consider \( \text{O}_2 \), \( \text{O}_2^+ \), \( \text{O}_2^- \):

(a) Which has the longest bond?
(b) Which has the highest vibrational frequency?
(c) Which has the highest Dissociation Energy?

\( \text{O}_2 \): 16 Electrons – BO = 2
\( \text{O}_2^+ \): 15 Electrons – BO = 2.5
\( \text{O}_2^- \): 17 Electrons – BO = 1.5

\( \text{O}_2^- \) has the longest bond.
\( \text{O}_2^+ \) has the highest vibrational frequency.
\( \text{O}_2^+ \) has the highest Dissociation Energy.

A More General Picture of Sigma Orbital Combinations

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

In actuality, each of the 6 \( \sigma \) MO’s is really a combination of all 6 AO’s.

\[
\psi_{\text{MO}} = c_1s_a + c_2s_a + c_32p_{za} + c_4s_b + c_52s_a + c_62p_{zb}
\]
Approximate vs. Accurate MO's in C₂

\[ \psi_{\text{MO}} = c_1s_1 + c_2s_2 + c_3p_{2a} + c_4s_1 + c_5s_2 + c_6p_{2b} \]

\[ \sigma_{2p} \text{ MO (E \approx -15 eV)} \]

\[ \psi_{\text{Approx}} \approx 0.70 \cdot 2p_{2a} + 0.70 \cdot 2p_{2b} \]

\[ \psi_{\text{Accur}} = [-0.07 \cdot 1s + 0.40 \cdot 2s + 0.60 \cdot 2p_{2a}] + [-0.07 \cdot 1s + 0.40 \cdot 2s - 0.60 \cdot 2p_{2b}] \]

\[ \sigma_{2s} \text{ MO (E \approx -40 eV)} \]

\[ \psi_{\text{Approx}} \approx 0.70 \cdot 2s + 0.70 \cdot 2s_b \]

\[ \psi_{\text{Accur}} = [-0.17 \cdot 1s + 0.50 \cdot 2s + 0.23 \cdot 2p_{2a}] + [-0.17 \cdot 1s + 0.50 \cdot 2s + 0.23 \cdot 2p_{2b}] \]

\[ \sigma_{1s} \text{ MO (E \approx -420 eV)} \]

\[ \psi_{\text{Approx}} \approx 0.70 \cdot 1s + 0.70 \cdot 1s_b \]

\[ \psi_{\text{Accur}} = [0.70 \cdot 1s + 0.01 \cdot 2s] + [0.70 \cdot 1s_b + 0.01 \cdot 2s_b] \]

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
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.

\[|c_b| \neq |c_a|\]

**Antibonding (A)**

\[\psi_a = c_a \phi_a + c_b \phi_b\]

**Bonding (B)**

\[\psi_b = c_b \phi_a + c_a \phi_b\]

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**

\[\text{Large } S_{ab}\]

\[\text{Small } S_{ab}\]

Generally, \(S_{ab} \approx 0.1 - 0.2\)

Commonly, to simplify the calculations, it is approximated that \(S_{ab} \approx 0\)
Haa, Hbb < 0

Commonly, Haa is estimated as –IE, where IE is the Ionization Energy of an electron in the atomic orbital, \( \phi_a \).

Hab is approximately proportional to:
1. The orbital overlap
2. The average of Haa and Hab

Traditionally, Hab is called the “Resonance Integral”.

Hab is calculated as

\[
H_{ab} = \langle \phi_a | H | \phi_b \rangle = \int \phi_a^* H \phi_b \, d\tau
\]

Energy of an electron in atomic orbital, \( \phi_a \), in an unbonded atom.

Energy of an electron in atomic orbital, \( \phi_b \), in an unbonded atom.

Traditionally, Haa and Hbb are called “Coulomb Integrals”.

Wolfsberg-Helmholtz Formula
(used in Extended Hückel Model)

Hab < 0
Interpretation of Orbital Coefficients

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

\[ \psi_{\text{MO}} = N (c_a \phi_a + c_b \phi_b) \]

Normalization:

\[ 1 = \int \psi_{\text{MO}}^2 d\tau = \langle \psi_{\text{MO}} \rangle \psi_{\text{MO}} \]

\[ 1 = \langle N(c_a \phi_a + c_b \phi_b) \rangle \langle N(c_a \phi_a + c_b \phi_b) \rangle \]

\[ 1 = N^2 \left( c_a^2 \langle \phi_a | \phi_a \rangle + c_b^2 \langle \phi_b | \phi_b \rangle + 2c_a c_b \langle \phi_a | \phi_b \rangle \right) \]

\[ 1 = N^2 \left( c_a^2 + c_b^2 + 2c_a c_b S_{ab} \right) \]

where \( S_{ab} = \langle \phi_a | \phi_b \rangle \)

\[ N = \frac{1}{\sqrt{c_a^2 + c_b^2 + 2c_a c_b S_{ab}}} \]

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If \( S_{ab} \approx 0 \):

\[ \psi_{\text{MO}} = \frac{c_a}{\sqrt{c_a^2 + c_b^2}} \phi_a + \frac{c_b}{\sqrt{c_a^2 + c_b^2}} \phi_b \]

\[ f_a = \frac{c_a^2}{c_a^2 + c_b^2} \]

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:

\[ \psi_{\text{MO}} = N \sum c_i \phi_i \]

\[ f_i = \frac{c_i^2}{\sum c_i^2} \]

Fraction of electron density in orbital i

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Homonuclear Diatomic Molecules:

\[ f_a = \frac{c_a^2}{c_a^2 + c_b^2} \quad f_b = \frac{c_b^2}{c_a^2 + c_b^2} \]

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

\[ H_{ab} = H_{aa} \]

\[ |c_b| = |c_a| \]

\[ f_a = f_b = 0.50 \]

Heteronuclear Diatomic Molecules:

\[ H_{ab} \neq H_{aa} \]

\[ |c_b| \neq |c_a| \]

\[ f_b \neq f_a \]

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.
A Numerical Example: Hydrogen Fluoride (HF)

\[ \sum_{i=1}^{n} c_i \phi_i = N(c_1 \phi_1 + c_2 \phi_2) = N(c_1 1s(H) + c_2 2p(F)) \]

Matrix Elements

\[ H_{aa} = \langle \phi_a | H | \phi_a \rangle = \langle 1s(H) | H | 1s(H) \rangle = -13.6 \text{ eV} \]
\[ H_{ab} = \langle \phi_a | H | \phi_b \rangle = \langle 2p(F) | H | 2p(F) \rangle = -17.4 \text{ eV} \]
\[ H_{bb} = \langle \phi_b | H | \phi_b \rangle = \langle 1s(F) | H | 2p(F) \rangle = -2.0 \text{ eV} \]
\[ S_{ab} = \langle \phi_a | \phi_b \rangle = \langle 1s(H) | 2p(F) \rangle \approx 0 \]

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

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

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

\[ \langle E \rangle^2 + 31.0 \langle E \rangle + 232.64 = 0 \]

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

\[ \langle E \rangle_B = \frac{-31.0 - \sqrt{30.44}}{2} = -18.26 \text{ eV} \]
\[ \langle E \rangle_A = \frac{-31.0 + \sqrt{30.44}}{2} = -12.74 \text{ eV} \]
\[
\begin{vmatrix}
-13.6 - \langle E \rangle & -2 \\
-2 & -17.4 - \langle E \rangle \\
\end{vmatrix} = 0 \\
\Rightarrow (-13.6 - \langle E \rangle)c_a - 2c_b = 0 \\
\quad -2c_a + (-17.4 - \langle E \rangle)c_b = 0
\]

**Bonding MO**

\[
\begin{align*}
\frac{c_b}{c_a} &= 2.33 \quad \Rightarrow c_b = 2.33c_a \\
\psi_B &= (c_a \phi_a^1 + c_b \phi_b^1) \\
&= c_a (\phi_a + 2.33\phi_b) \\
&= N(\phi_a + 2.33\phi_b) \\
\psi_B &= \frac{1}{\sqrt{1 + (2.33)^2}} (\phi_a + 2.33\phi_b) \\
\psi_B &= 0.394\phi_a + 0.919\phi_b \\
&= 0.394 \cdot 1s_a(H) + 0.919 \cdot 2p_b(F)
\end{align*}
\]

**Antibonding MO**

\[
\begin{align*}
\frac{c_b}{c_a} &= -0.430 \quad \Rightarrow c_b = -0.430c_a \\
\psi_A &= (c_a \phi_a^1 + c_b \phi_b^1) \\
&= c_a (\phi_a - 0.430\phi_b) \\
&= N(\phi_a - 0.430\phi_b) \\
\psi_A &= \frac{1}{\sqrt{1 + (-0.430)^2}} (\phi_a - 0.430\phi_b) \\
\psi_A &= 0.919\phi_a - 0.394\phi_b \\
&= 0.919 \cdot 1s_a(H) - 0.394 \cdot 2p_b(F)
\end{align*}
\]

**Electron Densities in Hydrogen Fluoride**

**Bonding Orbital**

\[
\begin{align*}
\psi_B &= 0.394\phi_a + 0.919\phi_b = 0.394 \cdot 1s_a(H) + 0.919 \cdot 2p_b(F) \\
&= \frac{c_b^2}{c_a^2 + c_b^2} (0.394)^2 = 0.16 \\
&= \frac{c_a^2}{c_a^2 + c_b^2} (0.919)^2 = 0.84
\end{align*}
\]

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

**Antibonding Orbital**

\[
\begin{align*}
\psi_A &= 0.919\phi_a - 0.394\phi_b = 0.919 \cdot 1s_a(H) - 0.394 \cdot 2p_b(F) \\
&= \frac{c_b^2}{c_a^2 + c_b^2} (0.919)^2 = 0.84 \\
&= \frac{c_a^2}{c_a^2 + c_b^2} (0.394)^2 = 0.16
\end{align*}
\]

The situation is reversed in the Antibonding MO. However, remember that there are no electrons in this orbital.
Statistical Thermodynamics: Electronic Contributions to Thermodynamic Properties of Gases

Here they are again.

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

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

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_{V,N} \]

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_{P,N} \]

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

\[ A = U - TS = -kT \ln Q \]

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

The Electronic Partition Function

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

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

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

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

\[ \Theta_\nu = \frac{\Delta \epsilon_i}{k} = \frac{h \nu \gamma_{\text{at}}}{k} \quad \Delta \epsilon_i \text{ is the energy of the } i{\text{th}} \text{ electronic level above the ground state, } \epsilon_0 \]

\[ \nu \text{ is the absorption frequency (in cm}^{-1} \text{) to this state.} \]
The ground state energy, $\epsilon_0$, is arbitrary (depending upon the point of reference. It is sometimes taken to be zero.

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

$$\tilde{\nu} = 20,000 \text{cm}^{-1}$$
$$\frac{T}{3,000 K}$$

$$\Theta_g = \frac{h \tilde{\nu}_g}{k} = \frac{(6.63 \times 10^{-34}) (3.00 \times 10^{10}) (20,000)}{1.38 \times 10^{-23}} = 2.88 \times 10^4 K$$

$$e^{-\frac{\Theta_g}{T}} = e^{-\frac{2.88 \times 10^4}{3000}} = e^{-9.6} = 7 \times 10^{-5}$$

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

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

For convenience, we will consider only systems with a maximum of one “accessible” excited state: $q^{\text{elect}} = e^{\frac{\Theta_g}{kT}} [g_0 + g e^{\frac{\Theta_g}{T}}]$
For any numerical examples in this section, we'll assume that $\varepsilon_0 = 0$ which leads to $E_0 = N_A \varepsilon_0 = 0$.

i.e. we're setting the arbitrary reference energy to zero in the electronic ground state.

In this case, we could have started with:

$$q^{\text{elect}} = \varepsilon_0 \left[ g_0 + g_1 e^{\frac{\Theta_{el}}{T}} \right]$$

which would have led to:

$$H^{\text{elect}} = nE_0 + \frac{nRg_1 \Theta_{el} e^{\frac{\Theta_{el}}{T}}}{g_0 + g_1 e^{\frac{\Theta_{el}}{T}}}$$

For any numerical examples in this section, we'll assume that $\varepsilon_0 = 0$ which leads to $E_0 = N_A \varepsilon_0 = 0$.

i.e. we're setting the arbitrary reference energy to zero in the electronic ground state.

In this case, we could have started with:

$$q^{\text{elect}} = \varepsilon_0 \left[ g_0 + g_1 e^{\frac{\Theta_{el}}{T}} \right] = g_0 + g_1 e^{\frac{\Theta_{el}}{T}}$$

which would have led to:

$$H^{\text{elect}} = nE_0 + \frac{nRg_1 \Theta_{el} e^{\frac{\Theta_{el}}{T}}}{g_0 + g_1 e^{\frac{\Theta_{el}}{T}}}$$
Numerical Example #1

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

If there are no "accessible" excited states, that means that $\Theta_e / T >> 1$. This leads to:

$$H_{\text{elect}} = U_{\text{elect}} = \frac{nRg_0e^{-\Theta_e/T}}{g_0 + g_0e^{-\Theta_e/T}} = 0$$

By the same reasoning, $H_{\text{elect}} = U_{\text{elect}} = 0$ for molecules with ground states of any multiplicity if the excited states are inaccessible.

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 $H_{\text{elect}}$ for one mole of O$_2$ at 3000 K and 298 K.

$$\Theta_{el} = \frac{\hbar \nu_{el}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{10} \text{ cm/s})(7882 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 11360 \text{ K}$$

$$H_{\text{elect}} = \frac{nRg_0e^{-\Theta_{el}/T}}{g_0 + g_0e^{-\Theta_{el}/T}} = \frac{(1 \text{ mol}) \cdot (8.31 \text{ J/mol/K}) \cdot (11360 \text{ K}) \cdot e^{\frac{11360}{3000}}}{3 + 2e^{\frac{11360}{3000}}} = 1400 \text{ J} \approx 1.40 \text{ kJ}$$

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

\[ S^{\text{elect}} = k \ln Q^{\text{elect}} + \frac{U^{\text{elect}}}{T} = k \ln \left( q^{\text{elect}} \right)^{n} + \frac{U^{\text{elect}}}{T} = Nk \ln q^{\text{elect}} + \frac{U^{\text{elect}}}{T} \]

because \( Nk = nN_{A}k = nR \)

\[ q^{\text{elect}} = e^{-\frac{\Theta_{\text{eq}}}{T}} = g_{0} + g_{1}e^{-\frac{\Theta_{\text{eq}}}{T}} \]

because we're assuming that \( \varepsilon_{0} = 0 \).

The electronic ground state of \( \text{O}_2 \) is a triplet. There is an excited electronic state doublet 7882 cm\(^{-1}\) above the GS.

\[ \Theta_{\text{eq}} = \frac{h \nu_{\text{eq}}}{k} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^{16} \text{ cm/s})(7882 \text{ cm}^{-1})}{1.38 \times 10^{-23} \text{ J/K}} = 11,360 \text{ K} \]

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

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

\[ q^{\text{elect}} = g_{0} + g_{1}e^{-\frac{\Theta_{\text{eq}}}{T}} = 3 + 2e^{-\frac{11360}{3000}} = 3 + 0.045 = 3.045 \]
At 25 °C = 298 K: $U_{\text{elect}} = 0.00 \text{ J}$

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

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

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.
O₂ Entropy: Comparison with experiment

\[ S_{\text{mol}}(\text{exp}) = 205.1 \text{ J/mol-K at 298.15 K} \]

\[ S_{\text{S0}} + S_{\text{ent}} + S_{\text{vb}} = 151.9 + 43.8 + 0.035 = 195.7 \]

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

\[ S_{\text{S0}} + S_{\text{ent}} + S_{\text{vb}} + S_{\text{elect}} = 151.9 + 43.8 + 0.035 + 9.1 = 204.8 \]

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.

---

Helmholtz and Gibbs Energy

\[ A_{\text{elect}} = U_{\text{elect}} - TS_{\text{elect}} = -kT \ln Q_{\text{elect}} \]

\[ G_{\text{elect}} = H_{\text{elect}} - TS_{\text{elect}} = -kT \ln Q_{\text{elect}} + kT \ln \left( \frac{1}{T} \right) \]

Q_{\text{elect}} independent of V

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.

\[ \Theta_{\text{elect}} = \frac{h \nu}{k} = \left( 6.63 \times 10^{-34} \text{ J-s} \right) \left( 3.00 \times 10^{10} \text{ cm/s} \right) \left( 7882 \text{ cm}^{-1} \right) \]

\[ = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}} \]

\[ = 11,360 \text{ K} \]

Let's calculate \( G_{\text{elect}} \) (= \( A_{\text{elect}} \)) for one mole of O₂ at 3000 K.

---

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\[ G^{\text{elect}} = A^{\text{elect}} = -kT \ln Q^{\text{elect}} \]

\[ q^{\text{elect}} = g_0 + g_1 e^{-\frac{\Theta_{e1}}{T}} \]

\[ q^0 = g_0 e^{-\Theta_{e1} \cdot \frac{g_1}{g_0} + \frac{T}{T}} = 3 + 2e^{\frac{11360}{3000}} = 3.045 \]

\[ G^{\text{elect}} = -kT \ln Q^{\text{elect}} = -kT \ln q^{\text{elect}} = -NkT \ln q^{\text{elect}} = -nRT \ln q^{\text{elect}} = \frac{Nk}{nN_k} = nR \]

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

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

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

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**O₂: Enthalpy**

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

---

**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.