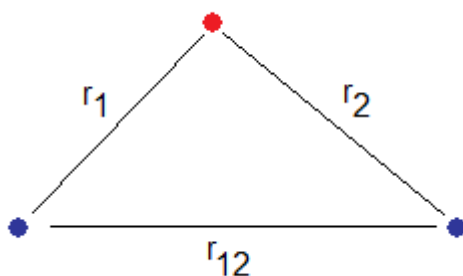


Chapter 9: Molecules

Quantum mechanics can be used to predict a large number of properties, especially those related to electronic spectroscopy, for diatomic molecules. A number of the concepts discussed in this chapter can be expanded to explain a great deal of the behavior of polyatomic molecules as well.

Potential Energy and the Hamiltonian

The first task of applying quantum mechanics to a problem is writing the Hamiltonian. This requires deriving an expression for potential energy. Consider as an example, the simplest diatomic molecule, H_2^+ .



In the above diagram, the blue dots indicate protons and the red dot, an electron. There will be attractive forces between the electron and protons 1 and 2 (separated by r_1 and r_2 respectively) and a repulsive force between the two protons, separated by a distance r_{12} . In atomic units, the Hamiltonian can be written

$$\hat{H} = \hat{T}_1 + \hat{T}_2 + \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

where T_1 , T_2 and T_e indicate the kinetic energies of protons 1 and 2 and the electron, respectively. As was the case in the helium atom, the H_2^+ molecule involves a three body problem which cannot be solved analytically. As such, an approximation must be made in order to proceed.

The Born-Oppenheimer Approximation

The **Born-Oppenheimer approximation** (Born & Oppenheimer, 1927) is made in order to simplify the problem in the case of a molecule. This approximation is based on the relative masses (and therefore the relative speeds) of the heavy nuclei compared to the light electron. It says that if the nuclei move (such as due to molecular vibration) that the electron(s) will react to

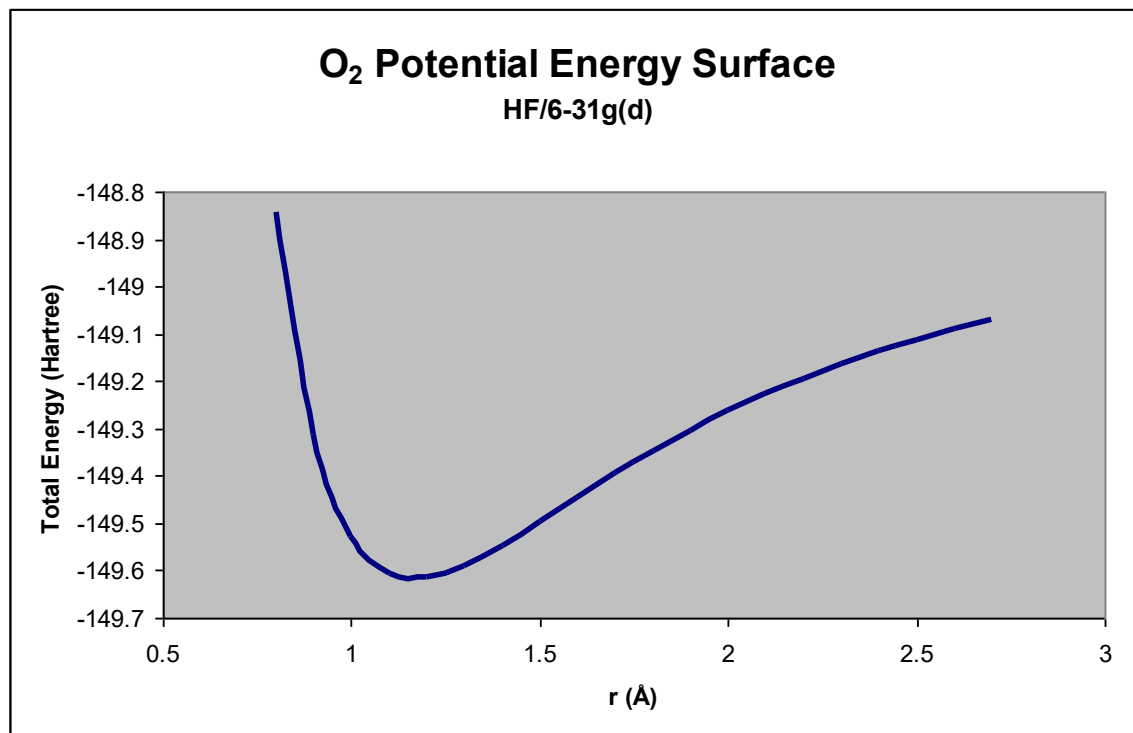
a change in the potential energy field instantaneously. As such, the internuclear distance (r_{12}) can be fixed, and the wave function for the electron optimized. If the nuclear coordinates are fixed, the Hamiltonian becomes

$$\hat{H} = \hat{T}_e - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{r_{12}}$$

and the value of $1/r_{12}$ becomes a constant.

There are many cases where the Born-Oppenheimer approximation breaks down, such as Renner-Teller interactions and Jahn-Teller interactions which involve strong coupling between vibrational motion of a molecule and the electronic state. For the purposes of this text, we will stick to examples where the Born-Oppenheimer approximation is reasonable.

The Born-Oppenheimer approximation makes it possible to calculate a number of properties for molecules. Below is an example of a potential energy surface of O_2 calculated using molecular modeling software at the HF/6-31G(d) level of theory. Basically, the program optimizes the wavefunctions describing the molecular orbitals based on a fixed internuclear separation. After populating the resultant orbitals with electrons, a total molecular energy is generated. After repeating this process at several different internuclear separation values, the curve can be constructed.



Such calculations are based entirely on the electronic structure of the molecule. As such, some insight into the nature of molecular orbitals and their wavefunctions is needed to proceed.

Molecular Orbital Theory

There are a number of ways to describe the electronic structure in diatomic molecules and the wavefunctions that are needed for the descriptions. **Molecular Orbital theory** provides one such example. There are many ways to describe molecular orbitals. One of the most commonly used is the method of using **linear combinations of atomic orbitals** (lcao).

Linear Combinations of Atomic Orbitals (LCAO)

Consider a wavefunctions derived from the Schrodinger equation that can be expressed as linear combinations of the 1s orbitals centered on each atom. The wavefunction can then be written

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = c_1(1s_1) + c_2(1s_2)$$

In this expression, r_1 and r_2 are the coordinates (position vectors) for nuclei 1 and 2. $1s_1$ and $1s_2$ refer to the 1s orbitals centered on nuclei 1 and 2 respectively. Due to the symmetry of the molecule, the magnitudes of c_1 and c_2 must be the same.

$$c_1 = c_2 = c$$

In order to be normalized, the wave function must satisfy

$$\begin{aligned} 1 &= c^2 \int (1s_1 + 1s_2)(1s_1 + 1s_2) d\tau \\ &= c^2 \int 1s_1 1s_1 d\tau + 2c^2 \int 1s_1 1s_2 d\tau + c^2 \int 1s_2 1s_2 d\tau \end{aligned}$$

The first and the third integrals in this expression are unity due to the fact that the 1s orbitals are themselves normalized. This the expression becomes

$$\begin{aligned} 1 &= 2c^2 + 2c^2 \int 1s_1 1s_2 d\tau \\ &= 2c^2 \left(1 + \int 1s_1 1s_2 d\tau \right) \end{aligned}$$

The integral in this expression $\int 1s_1 1s_2 d\tau$ does not vanish due to orthogonality as we have seen in other examples, since the wavefunctions are centered in different locations. The magnitude of the integral, therefore, depends on the degree to which the two orbitals overlap one another. The **overlap integral** is commonly given the symbol S . The magnitude of the normalization constant for the molecular wavefunction will depend intimately on the magnitude of this overlap.

$$1 = 2c^2(1 + S)$$

Solving for c , the following results

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$$c = [2(1+S)]^{1/2}$$

And the wavefunction can be written as

$$\psi(\mathbf{r}_1, \mathbf{r}_1) = \frac{1}{[2(1+S)]^{1/2}} (1s_1 + 1s_2)$$

The value of the overlap integral S will depend on the size of the orbitals and also the internuclear separation. The above wavefunction is an example of a **bonding orbital** as the value of the overlap S will be positive. Positive overlap is a stabilizing condition and acts to hold a molecule together. But just as a linear combination can be constructed from the sum of the $1s$ orbitals on the two H atoms, one can also be constructed from the difference.

$$\psi(\mathbf{r}_1, \mathbf{r}_1) = c(1s_1 - 1s_2)$$

This wavefunction will have **negative overlap** and thus produce an **antibonding orbital** which, if populated, has the effect of destabilizing the molecule.

The Expectation Value for Energy

The energies of these bonding and antibonding orbitals can be calculated from the following expressions

$$\begin{aligned} \langle E \rangle &= \frac{\int \psi^* \hat{H} \psi \, d\tau}{\int \psi^* \psi \, d\tau} \\ &= \frac{\int (c_1 1s_1 + c_2 1s_2) \hat{H} (c_1 1s_1 + c_2 1s_2) \, d\tau}{\int (c_1 1s_1 + c_2 1s_2) (c_1 1s_1 + c_2 1s_2) \, d\tau} \\ &= \frac{c_1^2 H_{11} + 2c_1 c_2 H_{12} + c_2^2 H_{22}}{c_1^2 + 2c_1 c_2 S + c_2^2} \end{aligned}$$

In this expression, H_{11} and H_{22} are the **Coulomb integrals** defined by

$$H_{ii} = \int 1s_i \hat{H} 1s_i \, d\tau$$

It can be easily shown that $H_{11} = H_{22}$ by symmetry. The other type of integral (besides S , the overlap integral which has already been discussed) is H_{12} , called the **exchange integral**.

$$H_{ij} = \int 1s_i \hat{H} 1s_j \, d\tau$$

The energy of the wavefunction is minimized by use of the variational principle. Specifically, the coefficients c_1 and c_2 must be chosen so as to minimize the energy of the wavefunction. This is done by differentiating the energy expression and setting it equal to zero (since the derivative will be zero at the minimum.) For simplicity, the expression is rearranged so that implicit differentiation is easier to see.

$$E(c_1^2 + 2c_1c_2S + c_2^2) = c_1^2H_{11} + 2c_1c_2H_{12} + c_2^2H_{22}$$

Differentiation of this expression with respect to c_1 and c_2 yields two expressions which can be used to find the two unknowns, c_1 and c_2 .

$$E(2c_1 + 2c_2S) + \frac{\partial E}{\partial c_1}(c_1^2 + 2c_1c_2S + c_2^2) = 2c_1H_{11} + 2c_2H_{12}$$

$$E(2c_2 + 2c_1S) + \frac{\partial E}{\partial c_2}(c_1^2 + 2c_1c_2S + c_2^2) = 2c_2H_{22} + 2c_1H_{12}$$

Since $\frac{\partial E}{\partial c_1} = 0$ at the minimum, the second terms on the left sides of the above equations vanish.

(How nice of them!)

$$E(2c_1 + 2c_2S) = 2c_1H_{11} + 2c_2H_{12}$$

$$E(2c_2 + 2c_1S) = 2c_2H_{22} + 2c_1H_{12}$$

These expressions can be rearranged.

$$c_1(E - H_{11}) + c_2(SE - H_{12}) = 0$$

$$c_1(H_{12} - SE) + c_2(E - H_{22}) = 0$$

So long as the Coulomb, Exchange and Overlap integrals can be determined, the coefficients can be as well. The non-trivial solution for c_1 and c_2 can be found from the determinant of the matrix shown below being set to zero.

$$\begin{vmatrix} H_{11} - E & SE - H_{12} \\ H_{12} - SE & E - H_{22} \end{vmatrix} = 0$$

It can be shown (although it will not be shown here) that

$$H_{ii} = E(1s) + J$$

where $E(1s)$ is the energy of a 1s orbital in hydrogen and J is an expression that depends on internuclear distance (r), given by

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

Similarly, H_{ij} can be determined from

$$H_{ij} = E(1s)S + K$$

where K is given by

$$K = \frac{S}{r} - e^{-r} (1 + r)$$

Notice that the expressions for both J and K vanish as r approaches ∞ . Given these substitutions, the determinant equation becomes

$$\begin{vmatrix} E_{1s} + J + E & E_{1s} + K - SE \\ E_{1s}S + K - SE & E_{1s} + J + E \end{vmatrix} = 0$$

Or

$$(E_{1s} + J + E)^2 - (E_{1s} + K - SE)^2 = 0$$

Being quadratic in E , this expression yields two solutions for the energy. One will give the energy of the bonding orbital and the other will be the energy of the antibonding orbital. (Now how much would you pay?) These energies are given by the expressions

$$E_{\text{bonding}} = E_{1s} + \frac{J + K}{1 + S}$$

and

$$E_{\text{antibonding}} = E_{1s} + \frac{J - K}{1 - S}$$

The following diagrams show the radial wavefunctions (across the z -axis of the molecule) for both the bonding and antibonding combinations of 1s orbitals. The graph on the left shows the value of the wavefunction, while the one on the right shows the square of the wavefunction. Note the node in the middle of the molecule in the antibonding orbital!

The following figures show the axial wavefunction for the

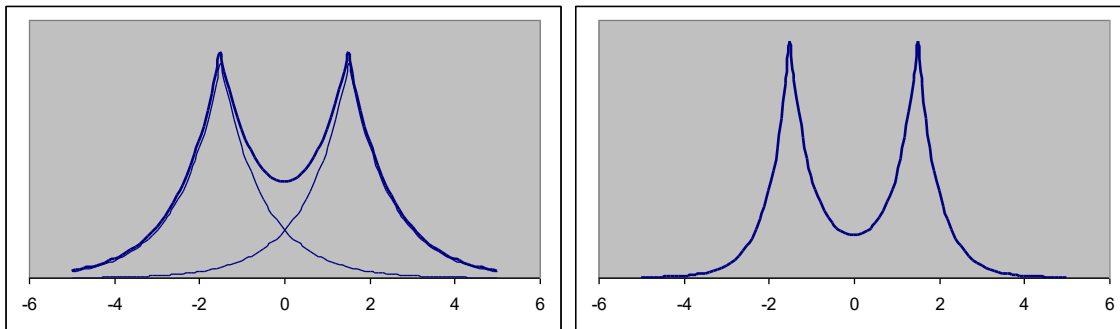
$$\psi = 1s_A + 1s_B$$

bonding and the

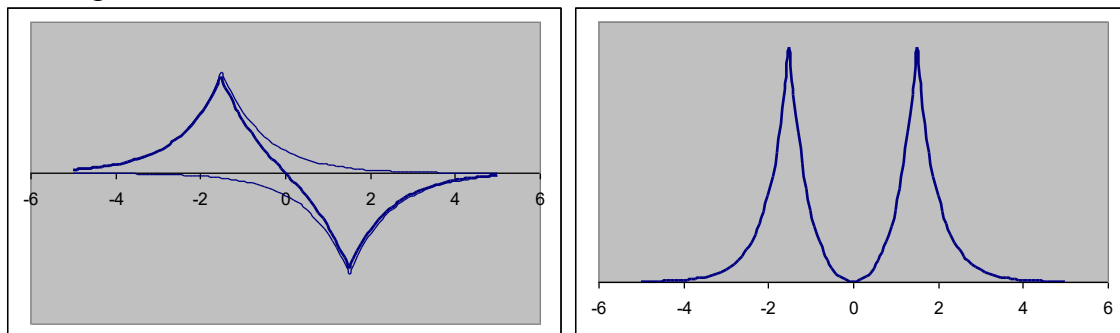
$$\psi = 1s_A - 1s_B$$

antibonding orbitals (on the left) and the corresponding squared axial wavefunctions on the right.

Bonding:



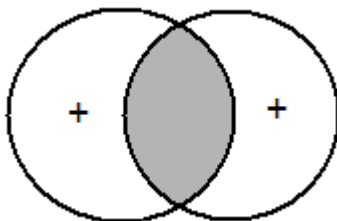
Antibonding:



These orbitals are easy to visualize and understand based on a pictorial approach of linear combinations of orbitals as well. In the pictorial approach, the emphasis is on the sign of the function in the overlap region.

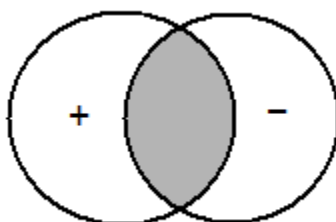
Bonding and Antibonding Orbitals Constructed from s Orbitals

The combination of 1s orbitals can be visualized in the following diagram



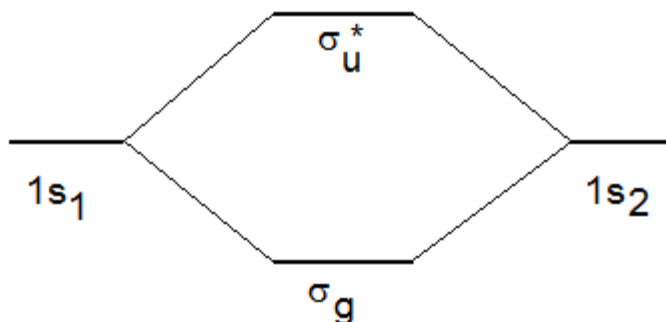
In this diagram, depicting the symmetric overlap to two 1s orbitals, it can be seen that the region of overlap will have a positive value (as it is given by the product of two positive numbers). This is an example of a s orbital since it is cylindrically symmetric about the internuclear axis.

Just as the symmetric combination can be depicted, the antisymmetric combination is also easy to generate.



In this depiction, it should be clear that the region of overlap has a negative value. Another way to think about this is that the wavefunction must change sign as it crosses from left to right. This implies a node between the nuclei!

As stated before, the positive overlap depicted in the first orbital is a stabilizing condition, and the negative overlap in the second is destabilizing. This can be depicted in an orbital diagram.



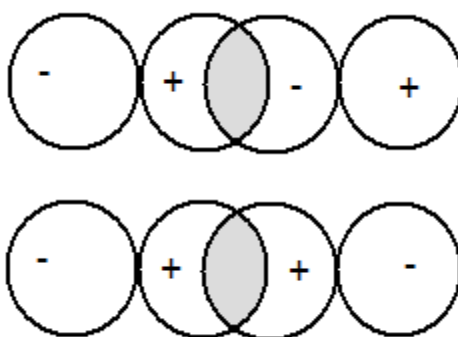
In this diagram, the atomic orbitals on the separated atoms are shown on the far right and left, and the orbitals in the middle column are the molecular orbitals that arise from the linear combination of the atomic orbitals. σ_g indicates the bonding orbital and σ_u^* indicates the antibonding orbital resulting from the symmetric and antisymmetric combinations of the 1s orbitals. The subscripts g and u state for **gerade** and **ungerade** respectively. Gerade is a German word meaning even, which ungerade means odd. Specifically, these terms (and subscripts) are used to indicate the symmetry of a function with respect to inversion. The g/u

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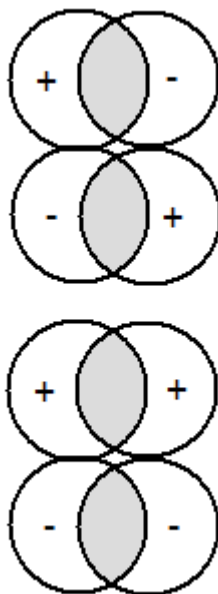
symmetry can be determined by drawing an arrow through the middle of a picture of a molecular orbital. If the arrow ends in a point with the opposite sign, the wavefunction is ungerade. However, it must be noted that this symmetry applies only to homonuclear diatomic molecules (and other molecules that possess an inversion center symmetry elements.) More will be discussed about molecular symmetry in later chapters.

Bonding and Antibonding Orbitals constructed from p Orbitals

Bonding and antibonding σ orbitals can be constructed from p-orbitals that are aligned on axis. In the diagram below, the upper picture indicates an antibonding orbital while the lower image is a bonding orbital.

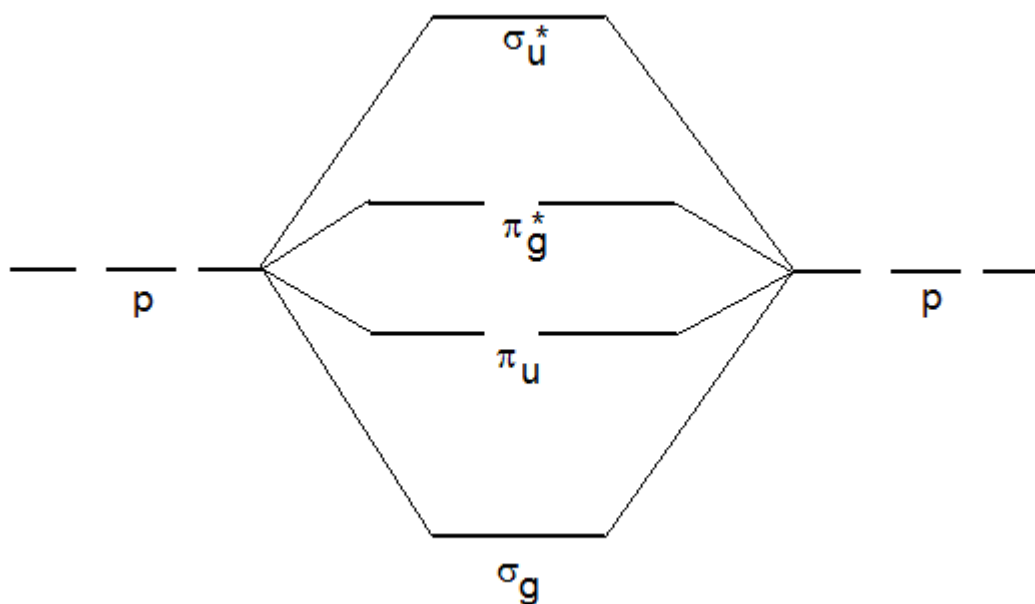


In addition to σ orbitals, π orbitals can also be constructed.



Clearly the π -bonding orbital is ungerade, while the π -antibonding orbital is gerade (if an inversion center exists within the molecule). It is also important to note that π -type overlap is smaller than σ -overlap, due to the need to get two nuclei so close together for strong overlap of

the p orbitals in a π orientation. As such, the π orbitals are less stabilizing or destabilizing relative to the atomic orbital energies.



The σ bonding and antibonding orbitals will be formed by the symmetric and antisymmetric combinations of the p_z orbitals on the separated atoms, whereas the π orbitals will be formed from the p_x and p_y orbitals from the separated atoms.

Electronic Configurations

Electronic configurations can be written for molecules just as they can be for atoms. Instead of being numbered by the principle quantum number, however, molecular orbitals are numbered sequentially from the lowest energy orbital of a certain symmetry. Consider the following list of electronic configurations for homonuclear diatomic molecules formed using the first ten elements.

| Molecule | Electronic Configuration | Bond Order | Electronic State |
|-----------------|--|------------|------------------|
| H ₂ | $(1\sigma_g)^2$ | 1 | $^1\Sigma_g^+$ |
| He ₂ | $(1\sigma_g)^2 (1\sigma_u^*)^2$ | 0 | unbound |
| Li ₂ | KK $(2\sigma_g)^2$ | 1 | $^1\Sigma_g^+$ |
| Be ₂ | KK $(2\sigma_g)^2 (2\sigma_u^*)^2$ | 0 | unbound |
| B ₂ | KK $(2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2$ | 1 | $^1\Sigma_g^+$ |
| C ₂ | KK $(2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2$ | 2 | $^3\Sigma_g^-$ |
| N ₂ | KK $(2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^4$ | 3 | $^1\Sigma_g^+$ |
| O ₂ | KK $(2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g^*)^2$ | 2 | $^3\Sigma_g^-$ |

| | | | |
|-----------------|---|---|--|
| F ₂ | KK (2σ _g) ² (2σ _u [*]) ² (3σ _g) ² (1π _u) ⁴ (1π _g [*]) ⁴ | 1 | ¹ Σ _g ⁺ |
| Ne ₂ | KK (2σ _g) ² (2σ _u [*]) ² (3σ _g) ² (1π _u) ⁴ (1π _g [*]) ⁴ (3σ _u [*]) ² | 0 | unbound |

In this table, the older shell notation is used to indicate a filling of the inner shell electrons, (1σ_g)² (1σ_u^{*})². These are given the symbol KK.

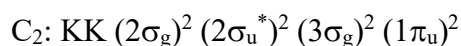
Bond Order

The bond order of a molecule is determined by adding the number of electrons in bonding orbitals, subtracting the number of electrons in antibonding orbitals and dividing the result by 2 (since there are two electrons per orbital.)

$$\text{Bond Order} = \frac{\# \text{bonding} - \# \text{antibonding}}{2}$$

The larger the bond order, the stronger a chemical bond is predicted to be. Also, since strong bonds are short bonds, the larger the bond order, the shorter a bond is predicted to be.

Ionization of a molecule may have a profound affect on the bond order, and therefore the bond length. Consider the molecule C₂ that has an electronic configuration given by



The addition of an electron to form C₂⁻ will require the electron to go into the 1π_g^{*} antibonding subshell. This will have the effect of strengthening the bond (since it increases the bond order.) Removal of an electron to form C₂⁺ would weaken the bond since it involves the removal of a bonding electron.

Paramagnetism

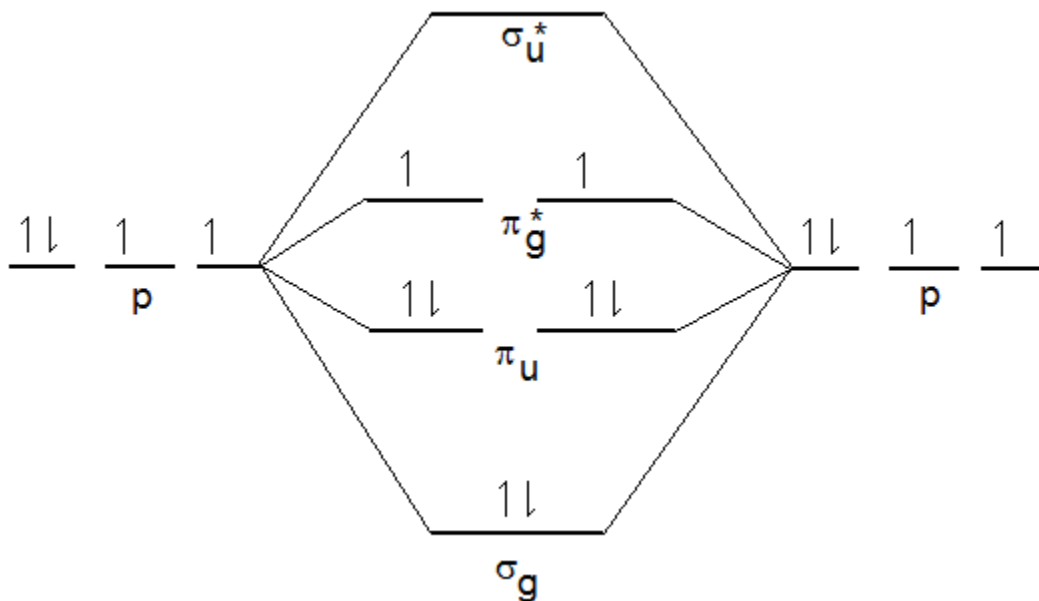
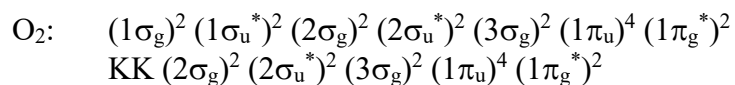
While the bond order of oxygen (O₂) is correctly predicted by a Lewis Structure, the Lewis structure fails to predict that the molecule will be **paramagnetic**.

Paramagnetism is a property of a molecule or atom that occurs when the system has unpaired electrons. These electrons each have a small magnetic moment which can align with an external magnetic field, lowering the energy of the atom or molecule. As such, the atom or molecule will be attracted to a magnetic field.

Oxygen, which has an electronic configuration given by



Photograph showing liquid oxygen being trapped in a magnetic field due to its paramagnetic nature.



It is clear that there are two unpaired electrons. This is a property that cannot be predicted based on the Lewis Structure!

Hund's coupling cases (a) and (b)

There are clearly sources of angular momentum in a molecule due to orbital and spin considerations. But unlike atoms, molecules can also have angular momentum contributions from molecular rotation. There are many ways to describe the coupling of these different types of angular momentum. This text will focus on two specific cases, Hund's coupling cases a and b.

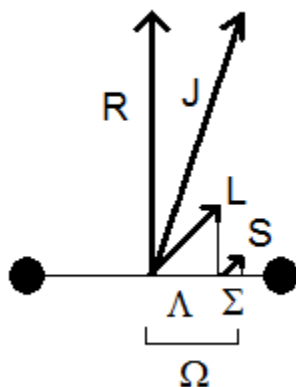
Hund's case (a)

In **Hund's case (a)** coupling, the orbital and spin angular momenta are strongly coupled to the internuclear axis of the molecule. This defines the quantum number Λ and Σ , which are the internuclear axis projections of L and S . The sum of Λ and Σ give the total electronic angular momentum along the internuclear axis, Ω .

$$\Lambda + \Sigma = \Omega$$

Ω is then coupled to the end-over-end rotational angular momentum of the molecule (R) to give J , the total angular momentum.

$$J = \Omega + R$$



For a molecule that is well described by Hund's case (a) coupling, that is in a $^1\Pi$ electronic state, the lowest value of J possible is $J = 1$. The one unit of angular momentum comes from the orbital part of the wave function, so $J = 1$ actually describes a non-rotating molecule ($R = 0$)!

Hund's case (a) does a good job of describing molecules which exhibit moderate spin-orbit coupling. If the coupling is extremely strong, another case (case (c), for example) is needed to describe the molecule's properties.

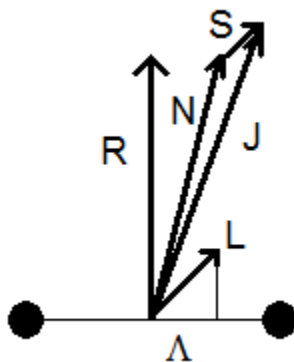
Hund's case (b)

Hund's case (b) is slightly different from case (a) in that the spin angular momentum is uncoupled from the internuclear axis. As such, in Hund's case (b) coupling, the quantum numbers Σ and Ω are undefined. In this case, the end-over-end rotation (R) of the molecule couples with Λ to produce N , which describes the sum of rotation plus orbital angular momentum.

$$N = \Lambda + R$$

N can then couple with S to give J , the total angular momentum.

$$J = N + S$$



Singlet states, with $S = 0$, are always well described by Hund's case (b) coupling. Hund's case (b) is a good description for molecules where spin-orbit coupling is weak (or immeasurably small.)

In the section describing the rotation of molecules as rigid rotators, the quantum number J was used to describe the total angular momentum due to rotation. This is consistent with both Hund's cases (a) and (b) for molecules in $^1\Sigma$ states, where $\Lambda = 0$ and $S = 0$ (implying where appropriate that $\Sigma = 0$ as well.)

Diatomic Term Symbols

A term symbol for a diatomic molecule contains a great deal of information about symmetry properties of the wavefunction which describes the electronic state. The symmetry properties are closely related to the values of the quantum numbers which specify the wavefunction. The pattern used to assign a symbol to a value for a quantum number is very similar to the pattern used for atomic systems. The major difference is that the quantum numbers must reflect the cylindrical symmetry of diatomic molecules rather than the spherical symmetry of atoms.

| Quantum Number | One Electron | | Many Electrons | |
|----------------|--------------|------------------------|----------------|------------------------|
| | Atom (l) | Molecule (λ) | Atom (L) | Molecule (Λ) |
| 0 | s | σ | S | Σ |
| 1 | p | π | P | Π |
| 2 | d | δ | D | Δ |
| 3 | f | ϕ | F | Φ |

Just as there is a $(2l+1)$ degeneracy in the spherical wavefunctions, there is also an important degeneracy pattern in the wavefunctions of diatomic molecules. Σ and σ states are singly degenerate whereas all other are doubly degenerate. Why this should become apparent as we develop the united atom method for decomposing spherical symmetry to cylindrical symmetry.

| λ or Λ | Wavefunction Symmetry | degeneracy |
|------------------------|-----------------------|------------|
|------------------------|-----------------------|------------|

| | | | |
|---|----------|----------|---|
| 0 | σ | Σ | 1 |
| 1 | π | Π | 2 |
| 2 | δ | Δ | 2 |
| 3 | ϕ | Φ | 2 |

There are three methods commonly used to derive terms symbols for diatomic molecules. All of the methods are based on determining the quantum number Λ and the total spin quantum number. In the case of homonuclear diatomic molecules, the inversion symmetry is also important.

Σ states have another important symmetry designation. Σ states can have either + or - symmetry depending on whether or not the state is symmetric with respect to reflection through a plane containing the internuclear axis. Symmetric states are designated as Σ^+ state and antisymmetric ones are Σ^- . Π , Δ and all other states with $L \neq 0$ are doubly degenerate as they have both + and - components.

There is always an odd number of S states generated for the United Atom method or the Separated Atom method. They will come in pairs of Σ^+ , Σ^- and the odd remaining state will have +/- symmetry as determined by the **Wigner-Witmer rule**. For this, one must consider the associated atomic state (using either the United Atom or the Separated Atom method). The +/- symmetry is determined by whether the indicated sum is even or odd according to the following table.

| Method | Sum | Value | Parity |
|----------------|-----------------------------------|-------|--------|
| United Atom | $L + \sum l_i$ | even | + |
| | | odd | - |
| Separated Atom | $L_A + \sum l_A + L_B + \sum l_B$ | even | + |
| | | odd | - |

United Atom Method

Think of the molecule as an atom with the same number of electrons. The atom will have spherical symmetry. The task is to reduce the spherical symmetry of the atomic wavefunction to the cylindrical symmetry of the diatomic molecule. In this case, the z-axis of the unified atom becomes the internuclear axis of the molecule. Thus, the quantum numbers will transform as

$$\begin{aligned} M_L &\rightarrow \Lambda \\ S &\rightarrow S \end{aligned}$$

Example: What molecular terms are predicted for the OH radical?

Solution: The unified atom with the same number of electrons as OH is fluorine. The ground state designation for atomic fluorine is 2P . For this state, $L = 1$ and so M_L can be -1, 0 or +1. The only values of $|M_L|$ are 0 and 1. Therefore, the predicted terms will be Σ and Π . The multiplicity will be the same as the unified atom ($S = 1/2$). The Σ state will be symmetric with respect to

reflection through a plane containing the z-axis since

$$L + \sum l_i$$

is even for fluorine. So the expected terms are

$$^2\Sigma^+ \text{ and } ^2\Pi$$

As it turns out, the ground state of OH is $^2\Pi$. The only way to confirm the ground state, however, is to use the molecular orbital method.

Separated Atom Method

A second method for determining molecular term symmetries is the separated atom method. This method is similar to the atomic term symbol method of writing out an exhaustive list of microstates and then accounting for each one. The quantum numbers which are important are determined from the sums of the z-component quantum numbers of the atomic wavefunctions. Thus, the values of Λ which are possible will be given by all possible combinations of M_L . Values of the same magnitude are then paired to make the two degenerate components for any values of $|\Lambda| > 0$.

Example: What molecular terms arise for HLi, formed from a ground state hydrogen atom and a ground state lithium atoms?

Solution: The ground state of lithium is 2S . For this set of atoms, we can construct the following table to combine values of M_L to form values of Λ and values of S as well.

| | H (2S) | Li (2S) | Λ and S |
|-------|---------------|---------------|-------------------|
| M_L | 0 | 0 | 0 |
| S | $\frac{1}{2}$ | $\frac{1}{2}$ | 1, 0 |

It is clear that the only value of Λ that can be generated from these separated atom states is $\Lambda = 0$, or a Σ state. The sum of $L_A + L_B + \Sigma l_A + \Sigma l_B$ is given by $0 + 0 + 0 + 0 = 0$, which is even. Hence, the Σ state has Σ^+ symmetry. So the resulting states are $^1\Sigma_g^+$ and $^3\Sigma_g^+$. The ground state of Li_2 is $^1\Sigma_g^+$, but this can only be confirmed by the use of the molecular orbital method.

Example: What molecular terms are predicted for the OH radical?

Solution: The ground state atomic term for O is 3P and that for H is 2S . The following table shows the possible combinations of M_L to form Λ and the combinations of S which form the familiar Clebsch series of resultant S values.

| | H (² S) | O (³ P) | Λ and S |
|----------------|---------------------|---------------------|-----------------|
| M _L | 0 | +1, 0, -1 | +1, 0, -1 |
| S | 1/2 | 1 | 3/2, 1/2 |

The combination of a P term and an S term gives one Π ($\Lambda = \pm 1$) and one Σ ($\Lambda = 0$) term. The sum $L_A + L_B + \Sigma l_A + \Sigma l_B$ is given by $1 + 0 + 4 + 0$ and is clearly odd. Therefore, the Σ state will be of Σ^- symmetry. The spin quantum numbers which are possible are 3/2 and 1/2. Therefore, the possible term symbols are $^4\Pi$, $^4\Sigma^-$, $^2\Pi$ and $^2\Sigma^-$. (The ground state of the OH radical happens to be of $^2\Pi$ symmetry, but again, this can only be confirmed using a molecular orbital approach.) Notice that there is no g/u symmetry indicated in this case because the molecule does not include an inversion center being a heteronuclear diatomic molecule!

Example: What molecular terms arise for CO formed from a ground state carbon atom and a ground state oxygen atom?

Solution: The ground state of both C and O is 3P . the following table summarizes the decomposition of the two atomic states from spherical to cylindrical symmetry.

| | C (³ P) | O (³ P) | Λ and S |
|----------------|---------------------|---------------------|--------------------------------|
| M _L | +1, 0, -1 | +1, 0, -1 | $\pm 2, \pm 1, \pm 1, 0, 0, 0$ |
| S | 1 | 1 | 2, 1, 0 |

The resultant state are Δ , 2 Π and 3 Σ . Of the three Σ states, two will form a pair of Σ^+/Σ^- . The last S state must have its +/- symmetry determined by the Wigner-Witmer rule.

$$L_C + L_O + \Sigma l_C + \Sigma l_O = 1 + 1 + 2 + 4 = 8 \text{ (even)}$$

So the final Σ state is Σ^+ . The spin states generated are quintet, triplet and singlet. So the set of molecular states generated are

$$^5\Delta, ^5\Pi, ^5\Pi, ^5\Sigma^+, ^5\Sigma^-, ^5\Sigma^+ \\ ^3\Delta, ^3\Pi, ^3\Pi, ^3\Sigma^+, ^3\Sigma^-, ^3\Sigma^+ \\ ^1\Delta, ^1\Pi, ^1\Pi, ^1\Sigma^+, ^1\Sigma^-, ^1\Sigma^+$$

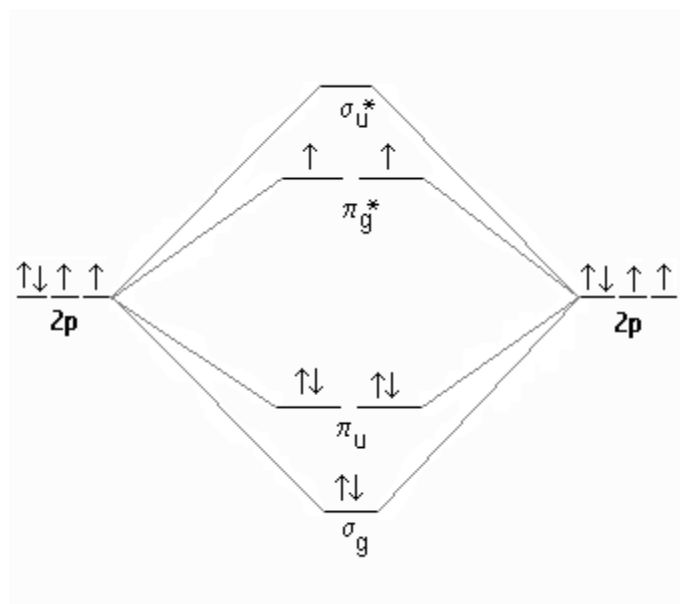
The ground state of CO is in fact $^1\Sigma^+$, but as always, this can only be reliably predicted using the molecular orbital method.

The number of states generated from separated atoms increases rapidly as the angular momentum in the separated atoms increases.

Molecular Orbital Method

The molecular orbital method requires the construction of a molecular orbital diagram. As was the case in the atomic term symbol problem, the molecular terms can be constructed considering only partially filled subshells.

The quantum numbers will then be given by the vectorial sums of the one-electron quantum numbers. Consider the orbital diagram for the oxygen molecule.



The only important electrons in this case are the two π_g^* electrons. (Ignore all of the ones in completely filled subshells - just as was done in the case of atoms as these always contribute $\Lambda = 0$ and $S = 0$.) The orbital angular momentum λ of one of the π_g^* electrons will cancel that of the other as one will have a value of $\lambda = -1$ and the other has $\lambda = +1$. (This is similar to the atomic case where one electron was in an orbital with $m_l = -1$ and the other in an orbital with $m_l = +1$. The sum of the two is zero.) Thus, Λ will be 0. Hence the predicted term will be a Σ state.

Since one of the π_g^* orbitals is symmetric with respect to reflection through a plane containing the nuclei and the other is antisymmetric, the predicted term will be antisymmetric with respect to this symmetry operation.

$$(\text{sym}) \times (\text{antisym}) = \text{antisym}$$

Thus, the state will be of Σ^- symmetry. In a similar manner, the gerade/ungerade symmetry can be determined by the product of the one-electron orbital symmetries.

$$(g) \times (g) = g$$

Finally, the spin multiplicity can be determined in the usual way.

$$S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2|$$

$$S = 1 \text{ and } 0$$

The predicted terms for this electronic configuration are $^3\Sigma_g^-$ and $^1\Sigma_g^-$. The ground state of O_2 is $^3\Sigma_g^-$. And since this result was generated using the molecular orbital method, the result is reliable that this is indeed the ground state of the O_2 molecule!

Herzberg Diagrams

One of the important reasons for describing the electronic structures and angular momentum coupling in diatomic molecules is to apply these descriptions to the prediction of the rotational branch structure in molecular spectra. As always, the first concern when predicting patterns in molecular spectra is the determination of selection rules. The selection rules for which the transition moment does not vanish are summarized below.

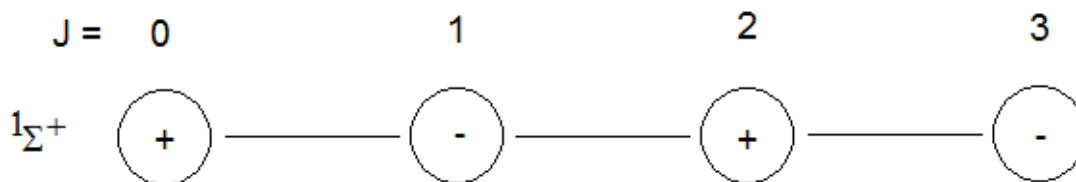
$$\begin{aligned}\Delta S &= 0 \\ \Delta \Lambda &= 0, \pm 1 \\ + \leftrightarrow -, - \leftrightarrow +\end{aligned}$$

Based on these selection rules, Herzberg diagrams can be used to predict the rotational branch structure and “first lines” in each branch based on the symmetries of upper and lower states in a given transition.

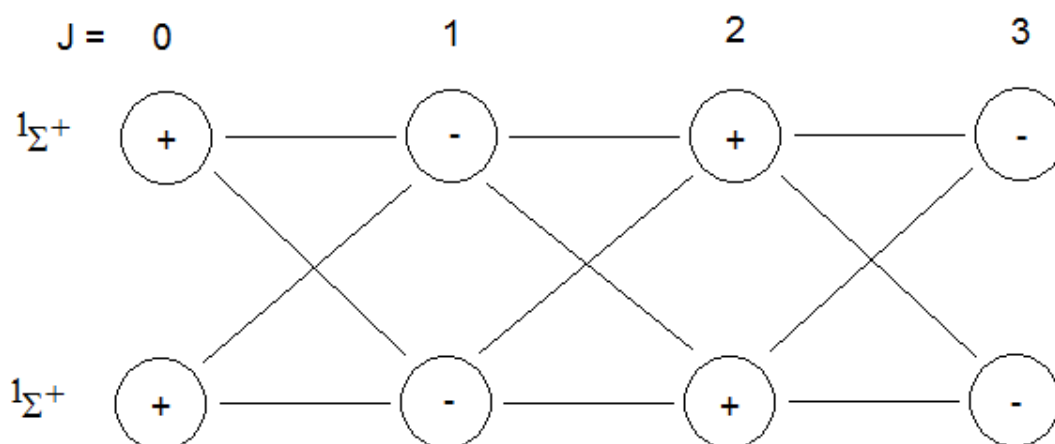
In order to discuss this very useful tool, we shall begin by discussing the description of a single state, starting with simple symmetry ($^1\Sigma^+$). In order to proceed, it is important to note the +/- symmetry of rotational wavefunctions. Basically, the rotational wavefunction is symmetric with respect to reflection through a plane containing the internuclear axis if R is even, and antisymmetric if R is odd. Thus the symmetry of the total wavefunction, given by

$$\Psi_{\text{tot}} = \psi_{\text{elec}}\psi_{\text{vib}}\psi_{\text{rot}}$$

is given by the product of the symmetries of ψ_{elec} , ψ_{vib} and ψ_{rot} . In the case of a $^1\Sigma^+$ state, ψ_{elec} is +. ψ_{vib} is always + for vibration of a diatomic molecule. The rotational contribution (ψ_{rot}) will alternate for increasing R or J . (In the case of a $^1\Sigma^+$ state, R and J have the same value, since $\Lambda = 0$ and $S = 0$.)

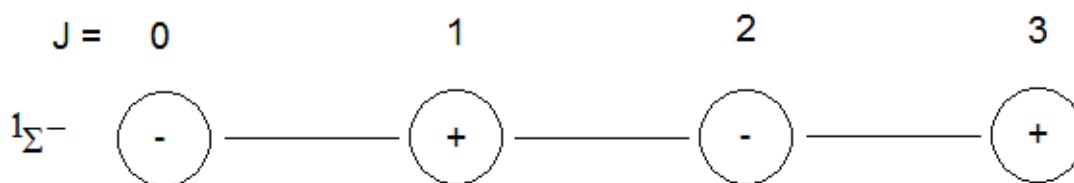


The above Herzberg diagram summarizes the +/- symmetry for the first few rotational levels.

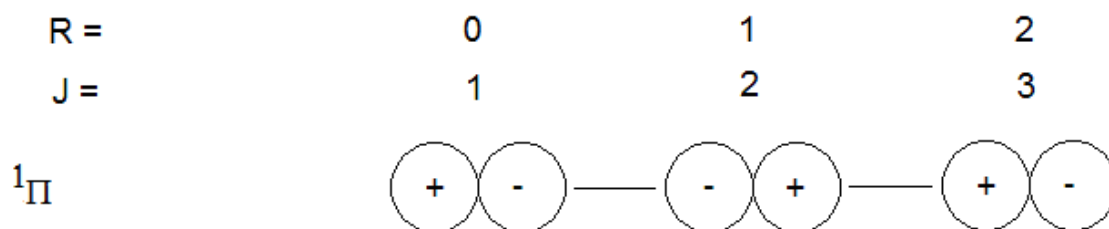


Based on this diagram, and the selection rule that $+\leftrightarrow-$ and $-\leftrightarrow+$, the branch structure for a ${}^1\Sigma^+ \leftrightarrow {}^1\Sigma^+$ transition can be predicted. Clearly, R- and P-branches are predicted in the rotational structure. This is the proper Herzberg diagram for the description of the 1-0 rotation-vibration spectrum of HCl (or other closed shell heteronuclear diatomic molecules.) Notice that $\Delta J = 0$ (Q-branch) transitions are impossible since the parity (+/- symmetry) does not change in such transitions, and hence they are forbidden.

The Herzberg diagram description of a ${}^1\Sigma^-$ state is not too different than that for a ${}^1\Sigma^+$ state. The only difference is that the +/- symmetry changes such that levels with odd J are now + and those with even J are now -.

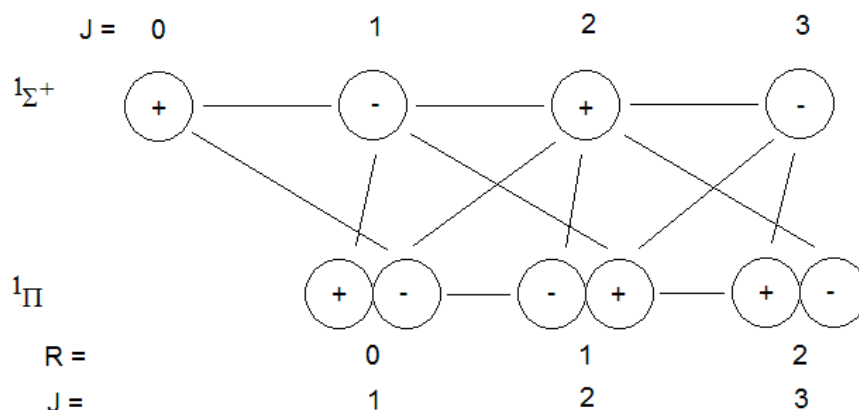
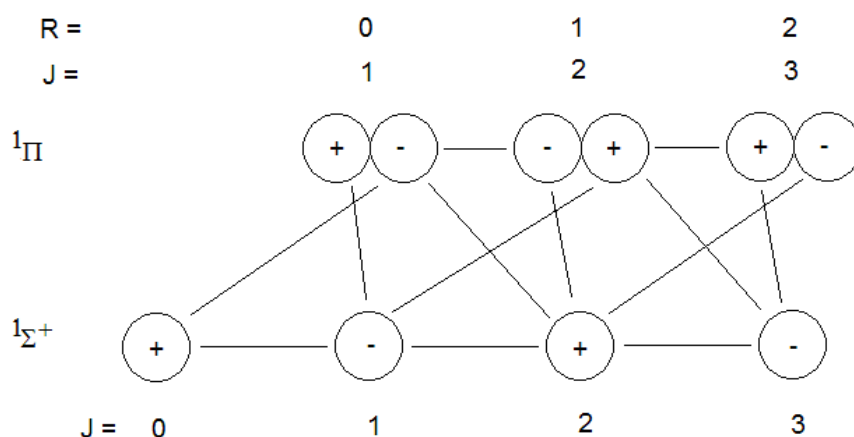


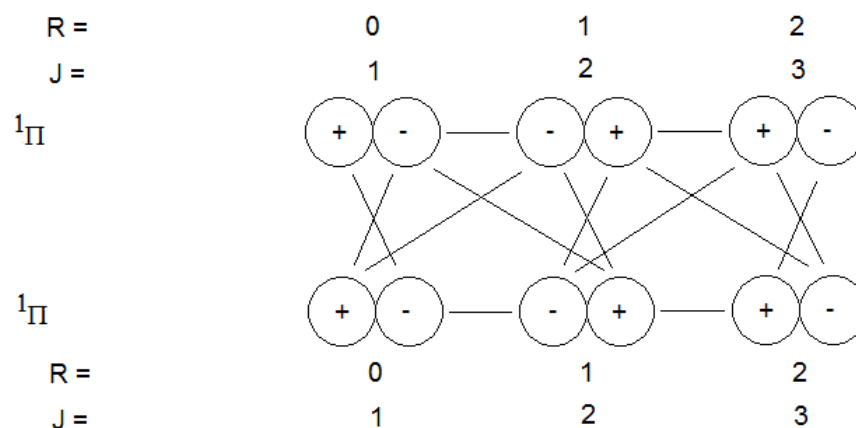
The description of a ${}^1\Pi$ state can be based on modifications to the descriptions of ${}^1\Sigma^+$ and ${}^1\Sigma^-$ states. Two important differences must be taken into account. First, since J is given by the sum of Λ and R (or Ω and R in Hund's case (a), but this will only be important if $S \neq 0$, which is not the case for a singlet state.) Second, since Π states (like Δ , Φ , etc.) have two components, both must be included in the diagram.



The description of a ${}^1\Pi - {}^1\Sigma^+$ transition can now be constructed. Note that P- Q- and R- branches are predicted. Also notice the “first line” in each branch. If the Π state is the upper state, the first lines in each branch are P(2), Q(1) and R(0). (There can be no P(1) line as the $J = 0$ level is missing in the upper state.) This is a pattern is a one way to recognize a ${}^1\Pi - {}^1\Sigma^+$ transition.

A reversal of state, such that the ${}^1\Sigma^+$ state is the upper state, causes the pattern to change. In the case of a ${}^1\Sigma^+ - {}^1\Pi$ transition, the first lines in each branch are predicted to be P(1), Q(1) and R(1).





A ${}^1\Pi - {}^1\Pi$ transition becomes a little more complex as well. In this case, it can be seen that there are two Q-branches predicted! These will be resolved only if the two Λ components of at least one of the Π state are significantly different in energy. The first lines are predicted to be P(2), Q₁(1), Q₂(1) and R(1).

While the description here has been limited to singlet states of Σ and Π symmetry, these tools can be extended to describe and predict a great deal of rotational fine structure patterns in spectroscopic transitions (Herzberg, 1950). The patterns can get extremely complex for systems with high spin or orbital angular momenta. The picture can become even more complex when nuclear spin exists in the molecule which can couple to orbital, spin and/or rotational angular momenta. Entire books are dedicated to sorting out these patterns and interpreting the spectra of molecules which require these considerations (Brink, 1994) (Bunker, 2009).

Vibronic Transitions

Just as rotational motion is important in understanding vibrational spectra, vibrational (as well as rotational) motion(s) are important in understanding electronic transition in molecules. Electronic transitions in which vibrational structure is resolved are sometimes referred to a **vibronic transition**. When rotation is thrown in to the mix, the term “**rovibronic transitions**” is sometimes used.

Vibronic transitions can be discussed in terms of the transition moment. Keeping in mind that the wavefunction for a vibronic state can be expressed as a product

$$\Psi_{\text{tot}} = \psi_{\text{elec}}\psi_{\text{vib}}$$

and that the transition moment is given by

$$\int \Psi_{\text{tot}}^* \vec{\mu} \Psi_{\text{tot}} d\tau$$

Substitution yields

$$\int (\psi_{elec} \psi_{vib})^* \tilde{\mu} (\psi_{elec} \psi_{vib}) d\tau$$

Since the dipole moment operator is a derivative operator, the chair rule must be employed, which yields

$$\int \psi_{elec}^* \psi_{elec} d\tau \int \psi_{vib}^* \tilde{\mu} \psi_{vib} d\tau + \int \psi_{elec}^* \tilde{\mu} \psi_{elec} d\tau \int \psi_{vib}^* \psi_{vib} d\tau$$

Since the electronic wavefunction must be orthogonal, the first term will vanish for transitions between two different electronic states. The second term however, does not vanish. In fact, the magnitude of the $\int \psi_{vib}^* \psi_{vib} d\tau$ will be determined by the overlap of the two vibrational levels.

(Note that since these represent vibrational wavefunctions in different electronic state, there is no reason for the wavefunctions to be orthogonal.)

Franck-Condon Factors

The intensity of a band in a vibronic transition will be governed by the magnitude of the Frank-Condon Factor for the band. The **Franck-Condon factor** (FCF) is defined by

$$\text{FCF} = \left[\int \psi_{vib}'^* \psi_{vib}'' d\tau \right]^2$$

which is governed purely by the degree of overlap between the upper state vibrational wavefunction and that in the lower state. The overlap will be large for $\Delta v = 0$ if the potential energy functions of the upper and lower states are similar (similar ω_e , $\omega_e x_e$, r_e , etc.) and strong sequences will be observed in the spectrum. If, however, the equilibrium bond length changes significantly, the maximum Franck-Condon overlap will occur for combinations of v' and v'' for which $\Delta v \neq 0$. In these cases, strong progressions will be observed.

The Franck-Condon principle is closely associated with the Born-Oppenheimer approximation. In cases where the Born-Oppenheimer breaks down, the Franck-Condon principle is compromised as well.

Term Symbols for Polyatomic Molecules

Term symbols are used to designate electronic states of polyatomic molecules, much the same as they are used to designate electronic states for both atomic systems and diatomic molecules. These can be derived in much the same manner as we have developed for diatomic molecules, by taking combinations of atomic orbitals, whose symmetries have been decomposed from the spherical symmetry of the atoms to the lowered symmetry of the molecule.

An example would be H_3^+ , which is the most common triatomic ion in the universe. (It is also an excellent example of a three-center two-electron bond in so far as it is the simplest example of a molecule possessing such a bond!) The combination of three 1s orbitals on the

three atoms will yield three molecular orbitals. The decomposition of symmetry is described in the following section.

Group Theoretical Approach to Molecular Orbitals

One of the more powerfully predictive things we can do with Group Theory is predict the symmetries of molecular orbitals. Molecular orbital symmetries can have huge ramifications on chemical bonding and chemical reactions.

The first thing we would like to be able to do is to predict the symmetries of the molecular orbitals that arise from the linear combinations of atomic orbitals. This is not too difficult. In fact, the process has many aspects in common with determining molecular vibration symmetries. The process can be summarized as follows:

1. Separate the molecule into groups of equivalent atoms.
2. For each set of equivalent atoms, determine the reducible representation that describes the atomic orbitals to be used in the construction of molecular orbitals. This is determined by assuming that the point group is centered on an atom containing the orbitals. Call this Γ_{ao} .
3. Determine $\Gamma_{unmoved}$ for the set of equivalent atoms.
4. Multiply $\Gamma_{ao} \otimes \Gamma_{unmoved}$ to determine $\Gamma_{reducible}$ for each set of equivalent atoms.
5. Add all of the $\Gamma_{reducible}$ that you have determined for each individual set of equivalent atoms. Call the result Γ_{MO} .
6. Γ_{MO} can then be resolved into components. These components give the symmetries of the molecular orbitals that result from the linear combinations of the atomic orbitals you have selected.

Example: The Molecular Orbitals for a Water Molecule

Solution: For this example, we shall consider the 1s orbitals on the H atoms, and the 2s and 2p orbitals on O. As it turns out, s orbitals are always totally symmetric in any point group, since they possess spherical symmetry. The p orbitals will transform as the x, y and z axes. So the following set of tables is used to generate Γ_{MO} for water.

First, determine Γ_H describing the H atoms.

| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
|------------------|---|-------|---------------|---------------|
| $\Gamma_{H(1s)}$ | 1 | 1 | 1 | 1 |
| Γ_{unm} | 2 | 0 | 0 | 2 |
| Γ_H | 2 | 0 | 0 | 2 |

Next, determine Γ_O describing the four orbitals on the O atom.

| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
|----------|---|-------|---------------|---------------|
|----------|---|-------|---------------|---------------|

| | | | | |
|------------------|---|----|---|---|
| $\Gamma_{O(2s)}$ | 1 | 1 | 1 | 1 |
| $\Gamma_{O(2p)}$ | 3 | -1 | 1 | 1 |
| Γ_{red} | 4 | 0 | 2 | 2 |
| Γ_{unm} | 1 | 1 | 1 | 1 |
| Γ_O | 4 | 0 | 2 | 2 |

Next, determine Γ_{MO} as the sum of $\Gamma_H + \Gamma_O$

| | | | | |
|---------------|---|-------|---------------|---------------|
| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
| Γ_H | 2 | 0 | 0 | 2 |
| Γ_O | 4 | 0 | 2 | 2 |
| Γ_{MO} | 6 | 0 | 2 | 4 |

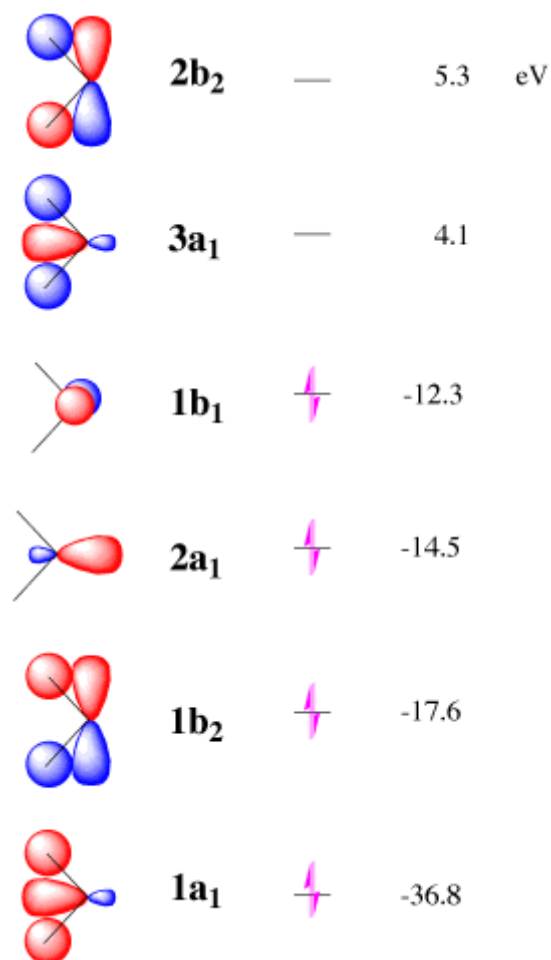
Now, decompose Γ_{MO} under C_{2v} symmetry!

| | | | | |
|---------------|---|-------|---------------|---------------|
| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
| Γ_{MO} | 6 | 0 | 2 | 4 |
| $-3 A_1$ | 3 | 3 | 3 | 3 |
| | 3 | -3 | -1 | 1 |
| $-B_1$ | 1 | -1 | 1 | -1 |
| | 2 | -2 | -2 | 2 |
| $-2 B_2$ | 2 | -2 | -2 | 2 |
| | 0 | 0 | 0 | 0 |

So

$$\Gamma_{MO} = 3 A_1 + B_1 + 2 B_2$$

The molecular orbitals of water are shown below.



(The above orbitals are generated based on a PM3 (semiempirical) orbital calculation of water. The numbering does not match the actual orbitals, but the symmetries are correct.)

The 1a₁ orbital was not generated in this example because it is essentially the 1s orbital on oxygen, which was not included in the basis set of functions we originally used. Also missing from our set are the 2b₂ and 3b₂ orbitals, which require the addition of 3p_x and 3d_{xz} orbitals on oxygen, which were not included. These orbitals are “virtual orbitals” as they are unoccupied.

The electronic configuration of H₂O is given by

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$$

The overall symmetry of the electronic state is given by the product of the se symmetries, counting each one twice since each orbital contains two electrons. In fact, all closed shell molecules (all subshells filled) will have an electronic symmetry that is totally symmetric. In this case, the electronic state is ¹A₁.

If the lowest unoccupied molecular orbital is of B₂ symmetry, then the first excited state of the molecule will be

$$\dots (1b_1)^1 (4a_1)^1$$

The total electronic symmetry is given by $B_1 \otimes A_1 = B_1$. The electronic configuration would give rise to both singlet and triplet states.

To test whether or not the transition to this state is allowed, the transition moment integral must not vanish.

$$\int \psi' \bar{\mu} \psi'' d\tau = \int B_1 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

This integral clearly will not vanish by symmetry for the component along the x-axis. Hence, the transition to this excited state of water will be a perpendicular transition.

Example: Formaldehyde

To generate the molecular orbitals in formaldehyde, consider the 1s orbitals on H, the 2s and 2p orbitals on C and O.

First, determine Γ_H describing the H atoms.

| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
|------------------|---|-------|---------------|---------------|
| $\Gamma_{H(1s)}$ | 1 | 1 | 1 | 1 |
| Γ_{unm} | 2 | 0 | 0 | 2 |
| Γ_H | 2 | 0 | 0 | 2 |

Next, determine Γ_C and Γ_O describing the four orbitals on the C atom and the O atom.

| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
|------------------|---|-------|---------------|---------------|
| $\Gamma_{C(2s)}$ | 1 | 1 | 1 | 1 |
| $\Gamma_{C(2p)}$ | 3 | -1 | 1 | 1 |
| Γ_{red} | 4 | 0 | 2 | 2 |
| Γ_{unm} | 1 | 1 | 1 | 1 |
| Γ_C | 4 | 0 | 2 | 2 |

| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
|------------------|---|-------|---------------|---------------|
| $\Gamma_{O(2s)}$ | 1 | 1 | 1 | 1 |
| $\Gamma_{O(2p)}$ | 3 | -1 | 1 | 1 |
| Γ_{red} | 4 | 0 | 2 | 2 |
| Γ_{unm} | 1 | 1 | 1 | 1 |

| | | | | |
|------------|---|---|---|---|
| Γ_O | 4 | 0 | 2 | 2 |
|------------|---|---|---|---|

The total reducible representation to be reduced is given by $\Gamma_H + \Gamma_C + \Gamma_O$.

| | | | | |
|---------------|----|-------|---------------|---------------|
| C_{2v} | E | C_2 | σ_{xz} | σ_{yz} |
| Γ_H | 2 | 0 | 0 | 2 |
| Γ_C | 4 | 0 | 2 | 2 |
| Γ_O | 4 | 0 | 2 | 2 |
| Γ_{MO} | 10 | 0 | 4 | 6 |

Decomposition of this reducible representation shows

$$\Gamma_{MO} = 5A_1 + 2B_1 + 3B_2$$

The electronic configuration for formaldehyde is given by

$$(1a_1)^2 (2a_1)^2 (3a_1)^2 (4a_1)^2 (1b_2)^2 (5a_1)^2 (1b_1)^2 (2b_2)^2$$

The $(1a_1)$ and $(2a_1)$ orbitals did not come from the above analysis as they are essentially the s orbitals on O and C that were not included in the basis set. The lowest energy unoccupied orbital is $(2b_1)$, so the first excited electronic state will have an electronic configuration given by

$$\dots (5a_1)^2 (1b_1)^2 (2b_2)^1 (2b_1)^1$$

This yields both triplet and singlet spin functions and an orbital function with symmetry given by $b_2 \otimes b_1 = a_2$. And as it turns out, the first electronic transition in formaldehyde is **orbitally forbidden** since no choice of a component of the dipole moment operator can be used to create a totally symmetric integrand for the electric dipole transition moment integral.

$$\int A_2 \cdot \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} \cdot A_1 d\tau$$

In order to see this transition in formaldehyde, there must be some involvement from vibrational motion that changes the symmetry of the overall wavefunction. Recall that

$$\Psi_{\text{tot}} = \Psi_{\text{elec}} \Psi_{\text{vib}}$$

if the Born-Oppenheimer approximation holds. The symmetries for the vibrational wavefunctions (which can be derived using the method previously discussed) are given by

$$\Gamma_{\text{vib}} = 3 A_1 + B_1 + 2 B_2$$

So excitation of a B_1 or B_2 vibrational mode (yielding an overall symmetry for the total wavefunction of either B_2 or B_1 respectively) will cause the transition to “turn on”. This type of **vibronically allowed transition** is not uncommon (similar behavior is observed in benzene) and is characterized by a missing 0-0 band in the electronic spectrum of the molecule.

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Vocabulary and Concepts

| | | | |
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| antibonding orbital | 192 | Molecular Orbital theory | 191 |
| bonding orbital | 192 | negative overlap | 192 |
| Born-Oppenheimer approximation | 189 | orbitally forbidden | 215 |
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Learning Objectives

After mastering the material covered in this chapter, one will be able to:

1. Describe the Born-Oppenheimer Approximation and how it is used to construct potential energy surfaces describing the vibration of a diatomic molecule.
2. Construct a molecular orbital diagram for a diatomic molecule depicting both bonding and antibonding orbitals of σ and π symmetries including inversion symmetry (g/u) as appropriate for homonuclear diatomic molecules. Utilize the diagram to
 - a. Predict the ground state electronic configuration of a diatomic molecule, including

- i. Magnetic properties
 - ii. Bond order
- 3. Describe the differences between Hund's Angular Momentum Cases (a) and (b) and how these cases manifest in the resulting energy levels in real molecules.
- 4. Determine molecular term symbols for diatomic molecules using the
 - a. United Atom Method
 - b. Separated Atom Method
 - c. Molecular Orbital Method
- 5. Construct Herzberg Diagrams and use them to
 - a. Determine the band structure of a spectroscopic transition, including the "first line" in each branch.
- 6. Derive the formulation for the Franck-Condon factor and explain how it determines relative intensity of vibrational bands in an electron transition.
- 7. Utilize the tools of Group Theory to predict the symmetries of the molecular orbitals that arise from linear combinations of atomic orbitals for a polyatomic molecule.

Problems