Homonuclear Diatomics; Unified Atom Limit

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Study Guide Outline

1. Homonuclear Diatomics
2. The Unified Atom Limit

1 Homonuclear Diatomics

We have already seen how symmetry plays an extremely important role in understanding how bonds are formed. Due to their molecular symmetry, diatomic molecules of one element (homonuclear diatomics) are a simple, but general test case to analyze bonding between two atoms.

When scientists tried to predict the ground state configuration for O$_2$, VB theory falsely predicted it to be a $^1\Delta$ state instead of a $^3\Sigma_g^-$ state. Although MO theory correctly predicted O$_2$, it failed (along with VB theory as well) to predict the correct state for N$_2^+$ (both predicted $^2\Pi$ instead of $^2\Sigma_g^+$). Scientists were curious what could be failing in explaining the correct ground states for some diatomics. Mullikan proposed that though atomic orbitals for individual atoms were well characterized by quantum mechanics, one could not assume that molecular orbital energy levels correlated directly the understood ordering of atomic orbitals. Instead, he proposed a different scheme where MOs were formed by atomic orbitals matched by symmetry. In order for us to visualize this and understand the consequences of this, this guide will outline the process for creating the unified atom limit diagram for homonuclear molecules.

2 The Unified Atom Limit

The unified atom limit diagram depicts how atomic orbital symmetries match into molecular orbitals of homonuclear diatomic molecules. According to our lecture, the right side of the diagram corresponds to two separated atoms, each with nuclear charge $Z$, while the left side corresponds to the two atoms completely super-imposed on top of each other, a species with nuclear charge $2Z$. Somewhere between these two limits lie the actual molecular orbital energy spacing for a particular homonuclear diatomic.

Starting with the energy levels of the unified atom limit, we consider only the bonding orbital combinations of similar atomic orbitals ($\sigma_g$ and $\pi_u$, and NOT $\sigma_u$ and $\pi_g$). In doing this, the $s$-orbitals would bond
with each other to form $\sigma_g$ orbitals. Likewise, the $\sigma$-bonding $p$-orbital, $p_z$ orbitals would bond other $p_z$ orbitals to form $\sigma_u$ orbitals. The $\pi$-bonding $p$-orbitals, $p_z$ and $p_y$ would bind with like $p$-orbitals to form $\sigma_u$ molecular orbitals. $d$-orbitals also need to be considered, and due to the symmetries of the different $d$-orbitals we get $d_{2z} \rightarrow \sigma_g$, $d_{yz}$ and $d_{xz} \rightarrow \pi_g$, and $d_{xy}$ and $d_{x^2-y^2} \rightarrow \delta_g$ orbitals.

As we start to pull the unified atoms apart, the energies of each unified orbital state changes. From a first-order approximation (i.e., neglecting orbital relaxation), energy of the $s$-orbitals from the unified atom will increase since we are moving nuclei away from the point of maximum electron density, and thus making for less favorable potential energy. However, the energy of the $p_z$ orbitals (which have $\sigma_u$ symmetry) will decrease since we are moving nuclei from the region of node into the region rich with electronic density. The $p_x$ and $p_y$ orbitals will have their energies slightly increase since we are pulling the nuclei from the $p$-orbital node across a constant node region.

The fact that there was splitting of the $p$-orbital energies means the degeneracy of the $p$-orbital was broken. Now that the unified atom has split, the resulting bonding orbital is the molecular orbital for the homonuclear diatomic. These molecular orbitals are labeled by the atomic symmetries their component atomic orbitals have, (i.e. $1s \rightarrow 1\sigma$, $2s \rightarrow 2\sigma$, $2p_z \rightarrow 3\sigma$, $2p_x$ and $2p_y \rightarrow$ a doubly degenerate $1\pi$, etc).

Now consider how these orbitals are when the atoms are at infinite separation. Each atom that comprised the homonuclear diatomic is considered a lone atom with relative atomic orbital energies that follow the Aufbau Principle. When these atoms start to approach, their atomic orbitals split to form bonding and antibonding molecular orbitals. Taking the symmetric combination of two $1s$ wavefunctions results in a $1\sigma_g$ bonding orbital, just like in the case for $H_2$. Likewise, the antisymmetric combination of the $1s$ orbitals lead to the $1\sigma_u$ antibonding orbital. The same can be done for $2s$ orbitals to obtain the $2\sigma_g$ bonding and $2\sigma_u$ antibonding orbitals.

Again, the same process of taking linear combinations of wavefunctions causes the $2p_z$ orbitals to form $3\sigma_g$ and $3\sigma_u$ molecular orbital states. The antisymmetric and symmetric combinations $2p_x$ and $2p_y$ orbitals result in the bonding and antibonding states, $1\pi_u$ and $1\pi_g$ respectively, both of which are doubly degenerate. Since the $2p_z$ orbitals form $\sigma$ bonds, they inherently have better overlap, and as a result the effects of their bonding and antibonding in the $3\sigma_g$ and $3\sigma_u$ states are greater than the corresponding bonding and antibonding of the $1\pi_u$ and $1\pi_g$ orbitals.

Now that the two sides of the diagram have been expressed, we use the non-crossing rule to connect the lowest energy state on the left side of the diagram with the lowest energy state on the right that has the same symmetry. The non-crossing rule simply states that energy levels of one symmetry will not cross a state with the same symmetry. Matching the lowest like-symmetry states will ensure that the non-crossing rule holds. The resulting map of energy levels is called a correlation diagram. It is possible to use a correlation diagram built between reactants and products to analyze the intermediate steps of a chemical reaction, and to see whether individual steps of a reaction are energetically allowed or forbidden. Experimental results allow us to determine where different symmetry states cross and thus which molecular orbitals are occupied before others, which in turn allows us to determine electronic configurations of the diatomics. With this correlation diagram, we can see how the ordering of molecular orbitals varied for $N_2^+$, and we can see that it correctly predicts the $^2\Sigma_g^+$ as its ground state.
Suggested reading:

- Molecular Orbitals and Correlation Diagrams - 8.11