

Quiz 7

Chemistry 3BB3; Winter 2004

1. For BeH_2 write the form of the bonding and antibonding molecular orbitals formed from the Be $2s$ and $2p_z$ orbitals and the H $1s$ orbitals? Assume the H atoms are located on the z -axis, and the Beryllium atom is at the origin. Assume that the H atom $1s$ orbital located on the positive real axis, ψ_{1s}^+ , and the H atom $1s$ orbital located on the negative real axis, ψ_{1s}^- , are both positive. Assume the Beryllium $2s$ orbital is negative at the Beryllium nucleus. Assume that the Beryllium $2p_z$ is positive on the positive z -axis.
2. Write the form of the Beryllium sp hybrid orbitals used to describe BeH_2 .
3. In transition metal compounds, the d orbitals are often treated using ligand field theory, wherein they are “split” by the field of the ligands but are not heavily involved in chemical bonding. This may be explained by the fact that:
 - (a) The metal d orbitals tend to have only a weak overlap with the molecular orbitals of the ligand, which inhibits bonding.
 - (b) The metal d orbitals tend to have a strong overlap with the molecular orbitals of the ligand, which inhibits bonding.
4. In HeH^+ , a simple molecular-orbital description predicts that the at the bond midpoint is very close to that of the Helium atom. In H_2 , the electron density at the bond midpoint is substantially larger than the sum of the densities of the Hydrogen atoms. Explain.

5-6. For each of the following molecules, use Hund's localization criteria to determine whether the molecular orbitals can be written in terms of localized orthogonal orbitals.

Molecule	Can Localized Orbitals be constructed (Yes/No)
BeH_2^+	
The transition state of the S_N2 reaction (examine the central Carbon), $\text{N}^{\delta-} \cdots \text{CH}_3 \cdots \text{L}^{\delta-}$. Here $\text{N}^{\delta-}$ is the nucleophile, $\text{L}^{\delta-}$ is the leaving group, and δ^- denotes the partial negative charge on these species.	

7-10. For each of the following, indicate whether the statement pertains to molecular orbital (MO) or valence bond (VB) theory.

_____ In the simplest form, this theory gives a poor description of molecular dissociation.

_____ This theory is associated with orbital hybridization.

_____ This theory is associated with the theory of resonance.

_____ Using this theory, it is difficult to predict the results of electronic spectroscopy.

_____ In this theory, the pairing of electrons to form lone pairs and chemical bonds is of primary importance.

_____ Using this method, it is easy to predict the multiplicity and bond order of diatomic molecules.

_____ This method is easier computationally.

_____ In order to turn this theory into an exact description of molecular phenomena, we must add contributions from ionic electron configurations.

_____ In order to turn this theory into an exact description of molecular phenomena, we must mix excited-state Slater determinants into the ground state.

_____ In this theory, a simple wave function can usually be written as a single Slater determinant.

_____ In this approach, it is rare that the simplest wave functions are single Slater determinants.

_____ The Heitler-London wave function is associated with this theory.

Quiz 7 Key

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- For BeH_2 write the form of the bonding and antibonding molecular orbitals formed from the Be $2s$ and $2p_z$ orbitals and the H $1s$ orbitals? Assume the H atoms are located on the z -axis, and the Beryllium atom is at the origin. Assume that the H atom $1s$ orbital located on the positive real axis, ψ_{1s}^+ , and the H atom $1s$ orbital located on the negative real axis, ψ_{1s}^- , are both positive. Assume the Beryllium $2s$ orbital is positive at the Beryllium nucleus. Assume that the Beryllium $2p_z$ is positive on the positive z -axis.

bonding: $\psi_{2s}(\mathbf{r}) - \psi_{1s}^-(\mathbf{r}) - \psi_{1s}^+(\mathbf{r}); \psi_{2p_z}(\mathbf{r}) - \psi_{1s}^-(\mathbf{r}) + \psi_{1s}^+(\mathbf{r})$

antibonding: $\psi_{2s}(\mathbf{r}) + \psi_{1s}^-(\mathbf{r}) + \psi_{1s}^+(\mathbf{r}); \psi_{2p_z}(\mathbf{r}) + \psi_{1s}^-(\mathbf{r}) - \psi_{1s}^+(\mathbf{r})$

- Write the form of the Beryllium sp hybrid orbitals used to describe BeH_2 .

$$\psi_{2s}(\mathbf{r}) + \psi_{2p_z}(\mathbf{r}); \psi_{2s}(\mathbf{r}) - \psi_{2p_z}(\mathbf{r})$$

- In transition metal compounds, the d orbitals are often treated using ligand field theory, wherein they are “split” by the field of the ligands but are not heavily involved in chemical bonding. This may be explained by the fact that:

(a) The metal d orbitals tend to have only a weak overlap with the molecular orbitals of the ligand, which inhibits bonding.

(b) The metal d orbitals tend to have a strong overlap with the molecular orbitals of the ligand, which inhibits bonding.

- In HeH^+ , a simple molecular-orbital description predicts that the at the bond midpoint is very close to that of the Helium atom. In H_2 , the electron density at the bond midpoint is substantially larger than the sum of the densities of the Hydrogen atoms. Explain.

When forming a covalent bond, there is a buildup of charge in the bonding region associated with the overlap of the atomic orbitals that combine to form a molecular orbital. One has that

$\psi_{MO}(\mathbf{r}) \approx c_1\psi_1(\mathbf{r}) + \sqrt{1 - c_1^2}\psi_2(\mathbf{r})$ with an approximate buildup of charge (relative to the atomic-orbital densities) of

$$2 \frac{|c_1\psi_1(\mathbf{r}) + \sqrt{1 - c_1^2}\psi_2(\mathbf{r})|^2}{1 + c_1\sqrt{1 - c_1^2}S_{12}} - |\psi_1(\mathbf{r})|^2 - |\psi_2(\mathbf{r})|^2.$$

Here, S_{12} denotes the overlap integral. In H_2 , $c_1 = \frac{1}{\sqrt{2}}$, and one finds that there is a rather substantial buildup of charge. However, if one has an ionic bond (as in HeH^+), then $c_1 \approx 1$ for the He $1s$ -orbital, and one has that

$$2 \frac{|c_1\psi_1(\mathbf{r}) + \sqrt{1 - c_1^2}\psi_2(\mathbf{r})|^2}{1 + c_1\sqrt{1 - c_1^2}S} - 2|\psi_1(\mathbf{r})|^2 \approx 0.$$

5-6. For each of the following molecules, use Hund's localization criteria to determine whether the molecular orbitals can be written in terms of localized orthogonal orbitals.

Molecule	Can Localized Orbitals be constructed (Yes/No)
BeH_2^+	No. Be has 1 bonding electron but two neighboring atoms.
The transition state of the S_N2 reaction (examine the central Carbon), $\text{N}^{\delta-} \cdots \text{CH}_3 \cdots \text{L}^{\delta-}$. Here $\text{N}^{\delta-}$ is the nucleophile, $\text{L}^{\delta-}$ is the leaving group, and δ^- denotes the partial negative charge on these species.	No. The central Carbon atom has 4 bonding orbitals, 4 bonding electrons, but 5 neighbors.

7-10. For each of the following, indicate whether the statement pertains to molecular orbital (MO) or valence bond (VB) theory.

__MO__ In the simplest form, this theory gives a poor description of molecular dissociation.

__VB__ This theory is associated with orbital hybridization.

__VB__ This theory is associated with the theory of resonance.

__VB__ Using this theory, it is difficult to predict the results of electronic spectroscopy.

__VB__ In this theory, the pairing of electrons to form lone pairs and chemical bonds is of primary importance.

__MO__ Using this method, it is easy to predict the multiplicity and bond order of diatomic molecules.

__MO__ This method is easier computationally.

__VB__ In order to turn this theory into an exact description of molecular phenomena, we must add contributions from ionic electron configurations.

__MO__ In order to turn this theory into an exact description of molecular phenomena, we must mix excited-state Slater determinants into the ground state.

__MO__ In this theory, a simple wave function can usually be written as a single Slater determinant.

__VB__ In this approach, it is rare that the simplest wave functions are single Slater determinants.

__VB__ The Heitler-London wave function is associated with this theory.