

Diatomic Molecules

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1 Chemical Bonds in Diatomic Molecules: Overlaps and Delocalization of Electrons

1.1 H_2^+ Molecule

Consider the process where 2 atomic nuclei and associated electron (1 electron atom) are brought closer together from ∞ . What happens to the distribution of electronic density as a result of this process?

Essentially, we are asking what happens when we form a chemical bond.

- Many-Electron Atoms: Atomic Wavefunction derived from Atomic orbitals
- Many-Atom Molecules: Molecular Wavefunction derived from Molecular orbitals
- Many-Atom Molecules: Molecular Orbitals derived from Atomic Orbitals **LCAO-MO**

For this case, the molecular orbital can be derived from atomic orbitals on each nucleus. Since there is only one electron, we can start with the simplest molecular orbital as a linear combination of atomic orbitals (LCAO-MO):

$$\sigma = c_a \phi_{H1s_a} \pm c_b \phi_{H1s_b}$$

If we consider the spatial extent of the molecular orbital, we see that there are 2 cases:

The first case corresponds to a **bonding orbital** and the second to an **anti-bonding orbital**

We can also consider the probability density for the electron being in the volume around the nuclei:

- Electrons in a chemical bond are thus **delocalized** in the volume surrounding the nuclei
- A bonding orbital enhances electron density **in between** the nuclei
- An anti-bonding orbital depletes electron density between the nuclei, and concentrates it away from the axis between the two nuclei. Reduced probability of finding an electron in the region between nuclei.
- A bonding orbital possesses significant **overlap** of the atomic wavefunctions combining to form the molecular orbital.
- An anti-bonding orbital has little or no overlap
- A bonding orbital represents a stable state relative to the nuclei being far away
- An anti-bonding orbital is an unstable state relative to ∞ separation of nuclei. The infinitely separated nuclei form the most stable state in that case. (Figure 23.4 Engel and Reid).

In general, a molecular wavefunction can be written as an anti-symmetrized Slater determinant consisting of molecular orbitals, which in turn are represented as linear combinations of atomic orbitals as:

$$\sigma_j(1) = \sum_i c_{ij} \phi_i(1)$$

where the sum is over all atomic orbitals. In the case of H_2 , both electrons are in the same molecular orbital (Pauli principle holds for molecular orbitals as well):

$$\sigma_1(1) = \frac{1}{\sqrt{2 + 2S_{ab}}} [\phi_{H1s_a}(1) + \phi_{H1s_b}(1) \text{ right}]$$

1.2 Symmetry of molecular orbitals

Atomic orbital symmetry is important when forming molecular orbitals. **Only atomic orbitals of the same symmetry will combine with one another.** This is because of the resulting overlap that is met with different types of orbitals.

What types of symmetry do we consider?

- symmetry under **inversion through an inversion center**

$$\hat{i}\sigma x, y, z = \sigma -x, -y, -z = \pm\sigma(x, y, z)$$

- inversion symmetry: gerade or ungerade (eigenvalue 1 or -1)
- symmetry under reflection through a plane

$$\hat{r}\sigma x, y, z = \sigma x, y, -z = \pm\sigma(x, y, z)$$

- symmetry under rotation by an angle θ

$$\hat{R}_{z,\theta}\sigma(x, y, z) = \sigma(x\cos\theta + y\sin\theta, y\cos\theta - x\sin\theta, -z) = \pm\sigma(x, y, z)$$

Examples of symmetry complementarity (Figure 24.1 in Engel and Reid)

- For rotation along the axis containing the nuclei: σ symmetry if such rotation leaves things unchanged.
- If internuclear axis contains a nodal plane, then π symmetry for the MO

Some general features of molecular orbitals

- 2 interacting atomic orbitals lead to 2 molecular orbitals. Each MO has different energy than the AO energies from which they are derived. For this to happen, there **must be nonzero overlap**.
- The bonding orbital has energy that is lower than the lower AO forming the MO.
- The anti-bonding orbital has energy that is higher than the higher energy AO forming the MO.
- the energy splitting increases with overlap (the overlap integral in Engel and Reid) as one would intuitively expect.
- The relative contribution of 2 atomic orbitals is determined by their expansion coefficients.
- Little mixing or combination of atomic orbitals of similar symmetry occurs if the energies of the atomic orbitals are not close.

2 Homonuclear Diatomic Molecules: H_2 to F_2

Filling of molecular orbitals for H_2 to N_2 (energies based on Hartree-Fock calculations):

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* < 1\pi_u < 3\sigma_g < 1\pi_g^*$$

For O_2 and F_2 , there is an inversion in the $1\pi_u$ and $3\sigma_g$ orbital energies, so the molecular orbital filling order changes to:

$$1\sigma_g < 1\sigma_u^* < 2\sigma_g < 2\sigma_u^* \ll 3\sigma_g < 1\pi_u$$

This inversion arises due to the increased effective nuclear charge moving across the row of elements. The π symmetry orbitals are not affected as significantly as the σ symmetry molecular orbitals. Thus, we observe an inversion. Figure 24.10 in Engel and Reid shows this inversion.

2.1 Bond Order: Singles, Doubles, Triples

The order of a bond is determined from the occupancy of bonding and antibonding orbitals.

$$\text{Bond order} = \frac{1}{2} \left[N_{\text{bonding}}^{e^-} - N_{\text{antibonding}}^{e^-} \right]$$