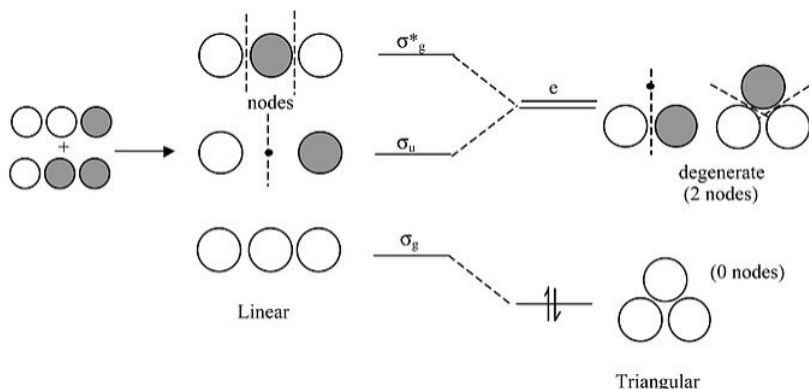


2.8: Three-center Bonding

Many (but not all) of the problems we will solve with MO theory derive from the MO diagram of the H_2 molecule (Fig. 2.1.5), which is a case of two-center bonding. The rest we will solve by analogy to the H_3^+ ion, which introduces the concept of three-center bonding.

We can draw the H_3^+ ion (and also H_3 and H_3^-) in either a **linear** or **triangular** geometry.

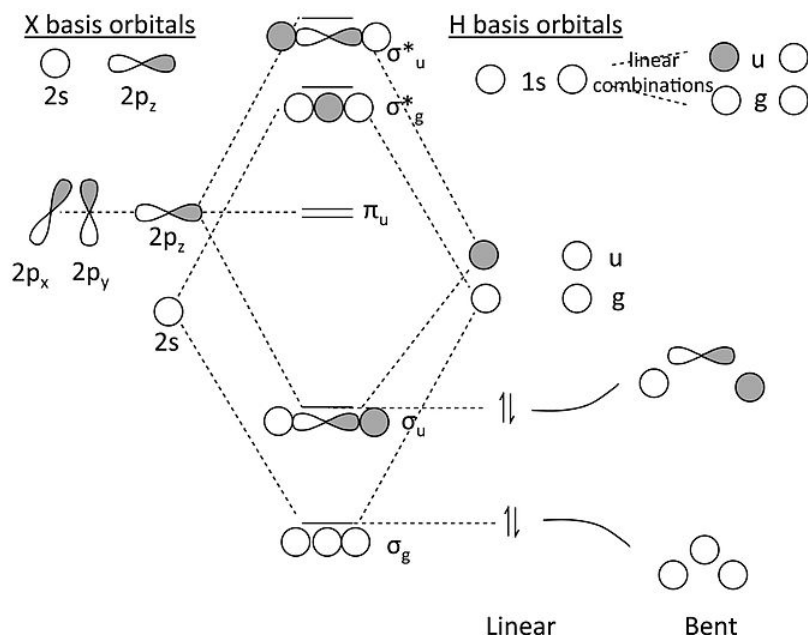
Walsh correlation diagram for H_3^+ :



A few important points about this diagram:

- For the linear form of the ion, the highest and lowest MO's are symmetric with respect to the inversion center in the molecule. Note that the central 1s orbital has **g symmetry**, so by symmetry it has **zero overlap** with the **u combination** of the two 1s orbitals on the ends. This makes the σ_u orbital a **nonbonding** orbital.
- In the triangular form of the molecule, the orbitals that derive from σ_u and σ_g^* become degenerate (i.e., they have identically the same energy by symmetry). The term symbol “e” means **doubly degenerate**. We will see later that “t” means triply degenerate. Note that we drop the “g” and “u” for the triangular orbitals because a triangle does not have an inversion center.
- The **triangular form is most stable** because the two electrons in H_3^+ have lower energy in the lowest orbital. Bending the molecule creates a third bonding interaction between the 1s orbitals on the ends.

MO diagram for XH_2 ($X = Be, B, C...$):



Some key points about this MO diagram:

- In the linear form of the molecule, which has inversion symmetry, the 2s and 2p orbitals of the X atom factor into three symmetry classes:

$$2s = \sigma_g$$

$$2p_z = \sigma_u$$

$$2p_x, 2p_y = \pi_u$$
- Similarly, we can see that the two H 1s orbitals make two linear combinations, one with σ_g symmetry and one with σ_u symmetry. They look like the bonding and antibonding MO's of the **H₂ molecule** (which is why we say we use that problem to solve this one).
- The π_u orbitals must be **non-bonding** because there is no combination of the H 1s orbitals that has π_u symmetry.
- In the MO diagram, we make bonding and antibonding combinations of the σ_g 's and the σ_u 's. For BeH₂, we then populate the lowest two orbitals with the four valence electrons and discover (not surprisingly) that the molecule has **two bonds** and can be written **H-Be-H**. The correlation diagram shows that a bent form of the molecule should be **less stable**.

An interesting story about this MO diagram is that it is difficult to predict a priori whether CH₂ should be linear or bent. In 1970, Charles Bender and Henry Schaefer, using quantum chemical calculations, predicted that the ground state should be a bent triplet with an H-C-H angle of 135°.^[4] The best experiments at the time suggested that methylene was a linear singlet, and the theorists argued that the experimental result was wrong. *Later experiments proved them right!*

"A theory is something nobody believes, except the person who made it. An experiment is something everybody believes, except the person who made it." – Einstein

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