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### **Deriving the MO diagram for square planar methane.**

This exercise assumes familiarity with the graphical method for forming LGOs described elsewhere.<sup>1-2</sup> The first step (determining LGOs for square planar methane) is also presented using the projection operator technique,<sup>3</sup> but the graphical method will be used here.<sup>4</sup>

Draw a Lewis structure for square planar methane. How many C-H bonds do you expect?

Let's compare this result to that found using MO theory. We will start by generating LGOs for square planar methane. With no lone pairs, the electronic and molecular geometry are the same.

#### Technique for constructing LGO's:

I Draw Lewis structure and assign VSEPR geometry (already done above)

II Assign a point group to the *molecular geometry*

III determine the central atom's VB hybrid orbitals for the *electronic geometry*

Now carry out the following three steps.

IV use the VB hybrid orbitals as generator functions (GF)

V Generate the LGOs by taking linear combinations of the ligand  $\sigma$ -orbitals (lobes) to get an orbital with the same symmetry as the generator function

VI Assign proper symmetry labels from the character table

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Now we can form the MO diagram for  $D_{4h}$   $CH_4$  using the carbon AOs and the four LGOs. The instructions are on this page; draw your MO diagram on the blank page that follows.

I name the MO diagram and its constituents

Name the central atom on one side (the left) and the LGOs on the other (right). Then in the center, place the name of the molecule. For completeness, include the point group.

II place AOs and LGOs with relative energies on one sides

Include all valence orbitals on the central atom, and the LGOs you generated. Estimate the energy levels using principal quantum number and electronegativity. Each energy level is a short horizontal line. The LGOs can be alternatively be drawn with all having the same energy (since they are further away than bonding distance). Label each AO and LGO with a symmetry label.

III place the correct number of electrons on each side

Only include valence electrons for the central atom, and only include a single electron forming the  $\sigma$ -bond from the ligand. For hydrogen, it only has one electron, but if this were  $Cl_2O$ , you would still only include the single bonding electron on each chlorine.

IV form MOs (bonding, antibonding and non-bonding) and give them symmetry labels Match symmetry labels on both sides of the MO diagram to find out which orbitals can interact. For example, an  $a_1$  MO can interact with an  $a_1$  LGO, but not with a  $b_2$  LGO. Any orbitals that are not used remain as non-bonding orbitals with the same energy as the initial AO or LGO. Label each MO with  $\sigma/\sigma^*$ ,  $\pi/\pi^*$ , or nb, and the symmetry label.

V place electrons in the MOs working from the bottom up

VI be able to sketch each MO

How many C-H bonds are there in square planar methane?

Estimate the relative stability of tetrahedral methane vs. square planar methane.

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Draw your MO diagram here

### Additional remarks

When considering the  $b_{1g}$   $a_{2u}$  non-bonding MOs, which is the LUMO and which is the HOMO? One shortfall of any “back of the envelope” MO method is the inability to determine exact MO energies, or even relative in some cases. The ionization energy of carbon is 11.3 eV, while that of a hydrogen atom is 13.6 eV, suggesting that the carbon based orbital is the LUMO.<sup>5</sup> However, the ionization energy of four hydrogen 1s orbitals in a square plane at approximately 1 Å bonding distance from a central carbon is not obvious. Hoffman places the  $p_z$  orbital below the  $b_{1g}$  LGO,<sup>6</sup> and Gaussian calculations (B3LYP, 6-311G(d,p)) support this assignment with the carbon  $p_z$  orbital at -0.183 hartree and the unoccupied LGO at -0.066 hartree when the C-H bonds are fixed at 1.09 Å. I would never expect anyone to be able to know the exact MO ordering without doing a Gaussian calculation, thus, the exact ordering of HOMO and LUMO would not be required for full credit by this technique.

### Cited References

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