# Molecular Orbital Theory for polyatomics--constructing MO diagrams

Divide into your groups and create a -only MO diagram for your assigned molecule. You may want to consider the following points for construction of the MO diagram:

1) What is the central atom and how many valence e- does it have?

2) What is the correct set of LGO’s for the ligand atoms?

3) How many e- does each ligand atom contribute to -bonding?

4) What are the energies of , \* and n.b. levels?

5) Draw each MO (, \*, and non-bonding)?

I will ask some groups to put their MO diagram up on the board and describe it.

**Group Molecule**

1. Square Planar CH4 (*JACS*, 1970, *92*, 4992)
2. SnCl2
3. TeF6
4. XeF2 (hint, descend in symmetry)
5. PF4+
6. PhICl2 (model the Ph group as a Cl!)
7. SnCl42- (with hypothetical C3v structure)
8. XeF4
9. IF7

Reminder of the technique for constructing LGO’s:

I Draw a Lewis structure and assign VSEPR geometry

II Assign a point group to the *molecular geometry*

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

IV use the VB hybrid orbitals as generator orbitals

V Generate the LGO’s by taking linear combinations of the ligand -orbitals (lobes) to get an orbital with the same symmetry as the generator orbital

VI Assign proper symmetry labels from the character table

Reminder of the technique for constructing MO diagrams:

I name the MO diagram and its constituents

II place AO's and LGO’s with relative energies on one sides

III place the correct number of electrons on each side

IV form MO's (bonding, antibonding and non-bonding) and give them symmetry labels

V place electrons in the MO's working from the bottom up

VI be able to draw each MO

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| ***Oh*** | ***E*** | **8*C*3** | **6*C*2** | **6*C*4** | **3*C*42** | ***i*** | **6*S*4** | **8 *S*6** | **3*h*** | **6*d*** |  |
| ***A*1*g*** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | x2+y2, z2 |
| ***A*2*g*** | 1 | 1 | -1 | -1 | 1 | 1 | -1 | 1 | 1 | -1 |  |
| ***Eg*** | 2 | -1 | 0 | 0 | 2 | 2 | 0 | -1 | 2 | 0 | (2z2-x2-y2,x2-y2) |
| ***T*1*g*** | 3 | 0 | -1 | 1 | -1 | 3 | 1 | 0 | -1 | -1 | (Rx,Ry,Rz) |
| ***T2g*** | 3 | 0 | 1 | -1 | -1 | 3 | -1 | 0 | -1 | 1 | (xz, yz, xy) |
| ***A*1*u­*** | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 |  |
| ***A*2*u*** | 1 | 1 | -1 | -1 | 1 | -1 | 1 | -1 | -1 | 1 |  |
| ***Eu*** | 2 | -1 | 0 | 0 | 2 | -2 | 0 | 1 | -2 | 0 |  |
| ***T1u*** | 3 | 0 | -1 | 1 | -1 | -3 | -1 | 0 | 1 | 1 | (x,y,z) |
| ***T2u*** | 3 | 0 | 1 | -1 | -1 | -3 | 1 | 0 | 1 | -1 |  |

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| ***D*4*h*** | ***E*** | **2*C*4** | ***C*2** | **2*C*2'** | **2*C*2"** | ***i*** | **2*S*4** | ***h*** | **2*v*** | **2*d*** |  |
| ***A*1*g*** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | x2+y2, z2 |
| ***A*2*g*** | 1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | Rz |
| ***B*1*g*** | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | 1 | -1 | x2-y2 |
| ***B*2*g*** | 1 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | xy |
| ***Eg*** | 2 | 0 | -2 | 0 | 0 | 2 | 0 | -2 | 0 | 0 | (Rx,Ry), (xz, yz) |
| ***A*1*u­*** | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 |  |
| ***A*2*u*** | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | z |
| ***B*1*u*** | 1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 |  |
| ***B*2*u*** | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 |  |
| ***Eu*** | 2 | 0 | -2 | 0 | 0 | -2 | 0 | 2 | 0 | 0 | (x, y) |

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| ***D­5h*** | ***E*** | **2C5** | ***2C52*** | ***5C2*** | **h** | **2S5** | **2S52** | **5v** |  |
| ***A*1’** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | x2+y2, z2 |
| ***A*2’** | 1 | 1 | 1 | -1 | 1 | 1 | 1 | -1 | Rz |
| ***E1*’** | 2 | 2cos72° | 2cos144° | 0 | 2 | 2cos72° | 2cos144° | 0 | (x,y) |
| ***E2*’** | 2 | 2cos144° | 2cos72° | 0 | 2 | 2cos144° | 2cos72° | 0 | (x2-y2, xy) |
| ***A1”*** | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 |  |
| ***A2”*** | 1 | 1 | 1 | -1 | -1 | -1 | -1 | 1 | Z |
| ***E1”*** | 2 | 2cos72° | 2cos144° | 0 | 2 | -2cos72° | -2cos144° | 0 | (Rx, Ry), (xz,yz) |
| ***E2*”** | 2 | 2cos144° | 2cos72° | 0 | -2 | -2cos144° | -2cos72° | 0 |  |

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| ***D*3*h*** | ***E*** | **2*C*3** | ***3C*2** | ***h*** | **2S3** | **3*v*** |  |
| ***A*1’** | 1 | 1 | 1 | 1 | 1 | 1 | x2+y2, z2 |
| ***A*2’** | 1 | 1 | -1 | 1 | 1 | -1 | Rz |
| ***E*’** | 2 | -1 | 0 | 2 | -1 | 0 | (x,y), (x2-y2, xy) |
| ***A1”*** | 1 | 1 | 1 | -1 | -1 | -1 | xy |
| ***A2”*** | 1 | 1 | -1 | -1 | -1 | 1 | z |
| ***E”*** | 2 | -1 | 0 | -2 | 1 | 0 | (Rx, Ry), (xz,yz) |

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| **Td** | ***E*** | **8*C*3** | ***3C*2** | **6S4** | **6*d*** |  |
| ***A1*** | 1 | 1 | 1 | 1 | 1 | x2+y2 +z2 |
| ***A2*** | 1 | 1 | 1 | -1 | -1 |  |
| ***E*** | 2 | -1 | 2 | 0 | 0 | (2z2-x2-y2, x2-y2) |
| ***T1*** | 3 | 0 | -1 | 1 | -1 | (Rx,Ry,Rz) |
| ***T2*** | 3 | 0 | -1 | -1 | 1 | (x,y,z)(xy,xz,yz) |

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| **C2v** | ***E*** | **C2** | ***v(xz)*** | ***v’(yz)*** |  |
| ***A1*** | 1 | 1 | 1 | 1 | Z, x2,y2 ,z2 |
| ***A2*** | 1 | 1 | -1 | -1 | Rz, xy |
| ***B1*** | 1 | -1 | 1 | -1 | x,Ry, xz |
| ***B2*** | 1 | -1 | -1 | 1 | y,Rx, yz |

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| **C3v** | ***E*** | **2C2** | ***v*** |  |
| ***A1*** | 1 | 1 | 1 | z, x2+y2 ,z2 |
| ***A2*** | 1 | 1 | -1 | Rz |
| **E** | 2 | -1 | 0 | (x,y)(Rx,Ry)(x2-y2,xy)(xz,yz) |