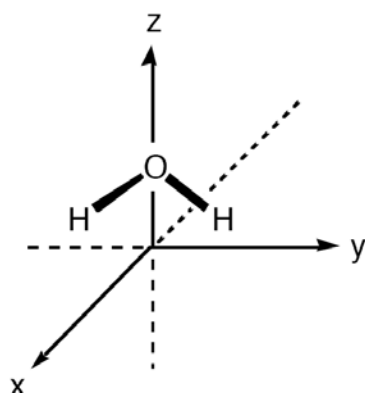


This problem set is meant to be a learning exercise and can be done readily without any references beyond class notes. Extensive research would lead to solutions to these problems, but this is highly discouraged. Do not use character tables for problem 1.

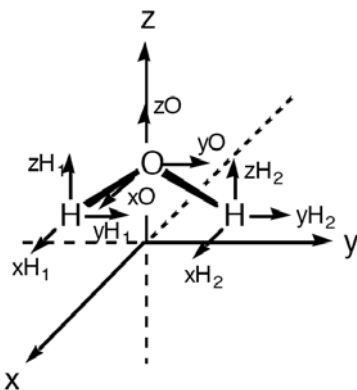
I. Determine the irreducible representations that belong to H_2O .

- a) Given the H_2O molecule of C_{2v} symmetry in the coordinate system shown below, determine the characters for the reducible representation $\Gamma_{x,y,z}$ and the irreducible representations Γ_x , Γ_y , and Γ_z for C_{2v} . (Note that x , y , and z here refer to the Cartesian axes – ignore the molecule for the moment. A handy way to check your answers is to remember that $\Gamma_{x,y,z}$ should equal the sum of Γ_x , Γ_y , and Γ_z .)



C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Γ_x				
Γ_y				
Γ_z				
$\Gamma_{x,y,z}$				

- b) Find the fourth irreducible representation of C_{2v} from orthogonality conditions.
 c) Give Mulliken symbols for the four irreducible representations. Note that the σ_v which contains the molecule has higher priority than the σ_v which does not.
 d) Consider H_2O again with the larger basis, consisting of x , y , and z vectors on each of the atoms. Give the (9×9) matrix for each of the symmetry operations of C_{2v} as applied to the column vector $[xH_1, yH_1, zH_1, xO, yO, zO, xH_2, yH_2, zH_2]$. (See page 4)



- e) From the matrices, determine the characters for the reducible representation, Γ_{tot} , for the basis set.

C_{2v}	E	C₂	σ_{xz}	σ_{yz}
Γ_{tot}				

- f) For molecules with many atoms, using large matrices to generate Γ_{tot} would be cumbersome. However, we can streamline this procedure by noticing that when an atom moves on applying a symmetry operation to the molecule, the nonzero elements in the matrix representation move off the main diagonal and therefore, do not contribute to the trace of the matrix. (Stated another way, the only way any vector can contribute to the trace of the matrix is if the atom on which this vector is fixed and does not change its location during the symmetry operation.) Therefore, we need to consider only the atoms which do not move during a symmetry operation.

(1) Determine the number of atoms which do not change location during each symmetry operation.

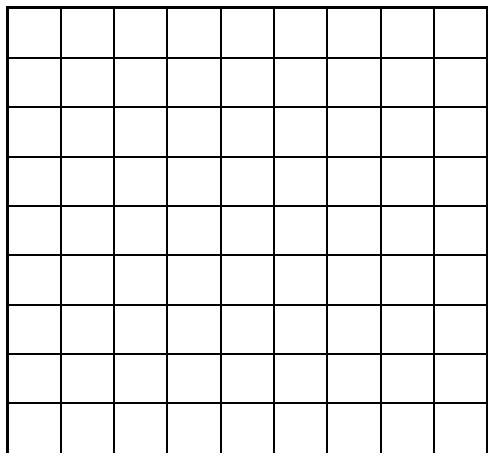
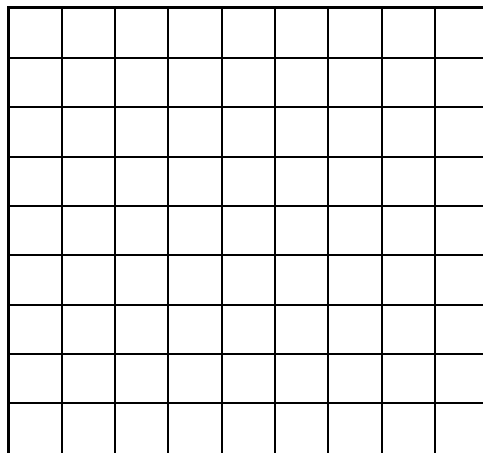
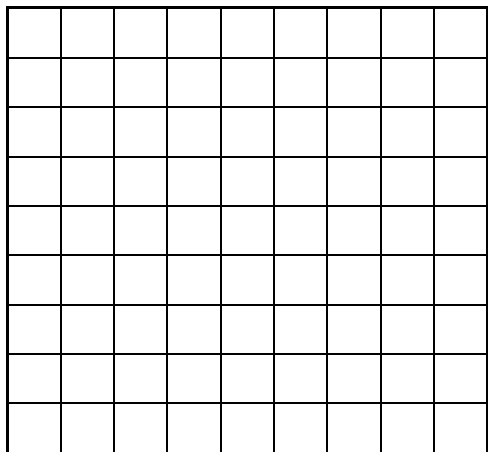
(2) For each operation, multiply the number of unmoved atoms by the character of $\Gamma_{x,y,z}$.

This simpler procedure gives the characters of Γ_{tot} . Use this streamlined method to generate Γ_{tot} .

C_{2v}	E	C₂	σ_{xz}	σ_{yz}
$\Gamma_{x,y,z}$				
# unmoved atoms				
Γ_{tot}				

- g) Using the formula given in class, decompose Γ_{tot} to a sum of irreducible representations in C_{2v} , showing your work.

- II. Consider the silane molecule, SiH_4 . What is its VSEPR predicted structure? Suppose that you wondered why it wasn't flat, point group symmetry D_{4h} . In order to examine whether such a structure is reasonable, derive the molecular orbital diagram in D_{4h} to compare with the diagram derived in class for CH_4 (and by extension, for T_d silane). Follow the steps below to lead you through the process.
- Using the four hydrogen 1s sigma orbitals as a basis, generate a reducible representation $\Gamma_{4\text{H}\sigma}$ for this sigma bonding framework, and reduce this to a sum of irreducible representations in the D_{4h} point group (use the handy dandy formula if you cannot do it by inspection).
 - Use the projection operator to obtain the coefficients of each hydrogen 1s for each of the SALC's based on the irreducible representations (show all your work).
 - Show that each SALC is normalized, and show that each of your SALC's is orthogonal to the others.
 - Sketch out all the SALC's.
 - The valence orbitals on silicon are the 3s and $3p_x$, $3p_y$, $3p_z$. Using the character table, determine how these orbitals transform in the D_{4h} point group (*i.e.* to what irreducible representations do they belong?).
 - Sketch the bonding, nonbonding, and antibonding MO's.
 - Generate the molecular orbital diagram from your results in (a-f), following the examples done in class by placing the silicon valence atomic orbitals on the left and the ligand (hydrogen) orbitals on the right. Match them in the center according to their symmetries. Don't forget to fill in the correct number of electrons.
 - Comment on the predicted relative stabilities of D_{4h} and T_d silane structures using your MO diagram and the one generated in class.
- III. The molecule BF_3 has D_{3h} symmetry. It also has p orbitals which must be considered when drawing MO diagrams. Without drawing the full MO, do the preparation by completing the following:
- Using the three fluorine 2s sigma orbitals as a basis, generate a reducible representation $\Gamma_{3\text{F}\sigma}$ for this sigma bonding framework, and reduce this to a sum of irreducible representations in the D_{3h} point group (use the handy dandy formula if you cannot do it by inspection). Show your work.
 - Using the three fluorine 2p orbitals that also participate in sigma bonding as a basis, generate a reducible representation $\Gamma_{3\text{F}(2p)\sigma}$ for this sigma bonding framework, and reduce this to a sum of irreducible representations. Show your work.
 - Using the three fluorine 2p orbitals that can participate in pi bonding as a basis, generate a reducible representation $\Gamma_{3\text{F}(2p)\pi\perp}$ for this pi bonding framework, and reduce this to a sum of irreducible representations. Show your work.
 - Repeat for $\Gamma_{3\text{F}(2p)\pi\parallel}$.
 - From the character table, find $\Gamma_{x,y,z}$. Multiply this representation by Γ_σ . Take that product and subtract Γ_σ . How does this answer relate to parts c and d?

E**C₂** **$\sigma(xz)$**  **$\sigma(yz)$** 