Symmetry and Group Theory – Exercise Set 5, Solutions

5.1) Show that the nitrogen p_x and p_y orbitals in NH_3 form the basis for an irreducible representation of C_{3v}.

We write the two p orbitals as a vector $\begin{pmatrix}\Psi_r \cdot x\\ \Psi_r \cdot y\end{pmatrix}$, where Ψ_r respresents the radial part of the wavefunction. We find that the following matrices for the symmetry operations.

$$E = \begin{pmatrix}1 & 0\\ 0 & 1\end{pmatrix},\ \sigma_v = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},\ C_3 = \begin{pmatrix}\cos\frac{2\pi}{3} & \sin\frac{2\pi}{3}\\ -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3}\end{pmatrix} = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{pmatrix}$$

The corresponding characters are $\chi(E) = 2$, $\chi(\sigma_v) = 0$, $\chi(C_3) = -1$. The p_x and p_y orbitals therefore form a basis for the irreducible representation E.
Alternative easy solution, which is possible if we have access to a character table and if the character table shows transformation of Cartesian coordinates: Clearly, p_x transforms as x and p_y transforms as y. Inspecting the character table, we see that (x, y) transforms as the two-dimensional irrep E.

5.2) The characters $\chi(R)$ of the representation of a direct product are the products of the characters $\chi_1(R)$ and $\chi_2(R)$ of the representations for which the individual functions are the basis, *i.e.* $\chi(R) = \chi_1(R)\chi_2(R)$. Demonstrate this for one-dimensional (irreducible) representations, where the proof is particularly simple.

$$\chi(R)XY = R(XY) = R(X)R(Y) = \chi_1(R)X \cdot \chi_2(R)Y = \chi_1(R)\chi_2(R)XY$$

hence $\chi(R) = \chi_1(R) \cdot \chi_2(R)$, where $\chi_1(R)$ is the character of Γ_1, $\chi_2(R)$ is the character of Γ_2, and $\chi(R)$ is the character of $\Gamma = \Gamma_1 \otimes \Gamma_2$.

5.3) In the C_{3v} point group, what are the characters of the representation belonging to the direct products $A_1 \otimes A_1$, $A_1 \otimes A_2$, $A_2 \otimes E$, $E \otimes E$, and $E \otimes E \otimes E$? Which irreducible representations are contained?

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
$A_1 \otimes A_1$	1	1	1	$= A_1$
$A_1 \otimes A_2$	1	1	-1	$= A_2$
$A_2 \otimes E$	2	-1	0	$= E$
$E \otimes E$	4	1	0	$= A_1 \oplus A_2 \oplus E$
$E \otimes E \otimes E$	8	-1	0	$= A_1 \oplus A_2 \oplus 3E$

5.4) Determine the symmetry species (the irreducible representation(s)) of the carbon p orbitals in CH_4.

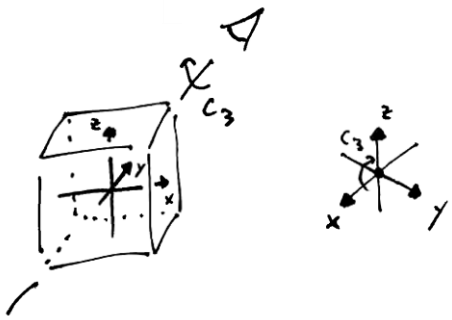
	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{Cp} = T_2$	3	0	-1	-1	1

Easy solution: Clearly, p_x transforms as x, p_y transforms as y, and p_z transforms as z. Inspecting the character table, we see that (x, y, z) (which is also the vector representation Γ_{vec}) transforms as the three-dimensional irrep T_2. Hence the carbon p orbitals transform as T_2.

Alternative solution: If the character table did not show transformation of Cartesian coordinates, effectively we would have to determine the characters of the vector representation.

(Below, the characters are found using a specific orientation of the molecule along x, y, z axes and the clockwise convention from Ulrich Lorenz's lecture notes for C_3 rotation. While the matrices depend on the choice, the characters do not depend on the choice of basis, which means that they do not depend on the orientation of the molecule with respect to x, y, z axes or on the sense of rotation for C_3.)

$\chi(E) = 3$ is trivial. To find the character of the C_3 rotation, consider a Cartesian coordinate system inscribed into a cube (with the CH_4 hydrogens occupying four of the eight corners). We consider a Cartesian coordinate system, because we know that the p_x, p_y, and p_z orbitals are proportional to x, y, and z, respectively. When viewed along the C_3 axis, we recognize that the C_3 rotation interchanges the three Cartesian axes.



We therefore obtain $C_3 = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$, with $\chi(C_3) = 0$.

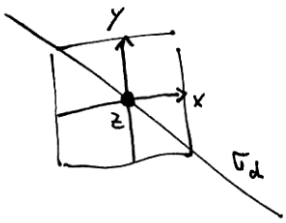
Furthermore, it is easy to see that

$C_{2z} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, with $\chi(C_{2z}) = -1$;

$S_{4z} = \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$, with $\chi(S_{4z}) = -1$; and

$\sigma_d = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, with $\chi(\sigma_d) = 1$.

The transformation matrix for σ_d becomes apparent when viewing a cube along the –z direction, as shown below.

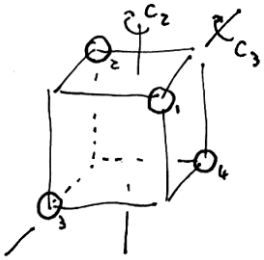


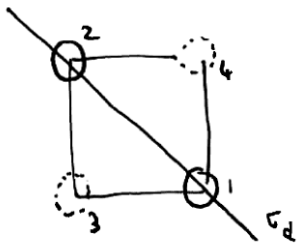
5.5) Determine the symmetry species (the irreducible presentation(s)) of the four hydrogen 1s orbitals in CH_4.

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{H1s} = A_1+T_2	4	1	0	0	2

Easy solution: The four hydrogen 1s orbitals form a basis for a four-dimensional permutation representation. The character of symmetry operation R is the number of hydrogens that remain in their original position. Therefore, e.g., $\chi(C_3) = 1$ because only one hydrogen remains at its original place. Likewise, we can fill in the rest of the characters in the table. Because there is no 4-dimensional irrep of the point group of CH_4, the representation must be reducible. Using the procedure for reduction, we find that $\Gamma = 1 \cdot A_1 \oplus 1 \cdot T_2$

Alternative solution: We can find the characters in a more tedious way by evaluating the representation matrices explicitly. (Below, we use again the convention from Ulrich Lorenz's lecture notes.)
With the help of the sketches below, we find





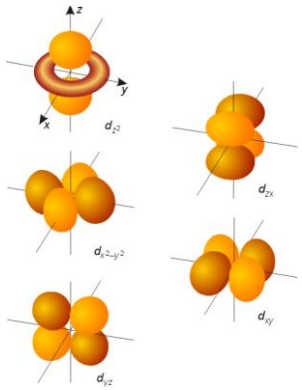
$$C_3 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \text{ with } \chi(C_3) = 1$$

$$C_{2z} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \text{ with } \chi(C_{2z}) = 0$$

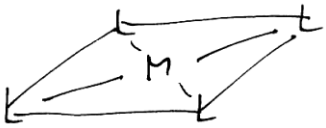
$$S_{4z} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \text{ with } \chi(S_{4z}) = 0$$

$$\sigma_d = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \text{ with } \chi(\sigma_d) = 2$$

5.6) In the context of crystal or ligand field theory, we frequently deal with the symmetry of the metal orbitals. For a square planar complex ML_4, determine the irreducible representations of the metal s, p, and d orbitals. In this case, this can still be easily done by visual inspection. The shape of the d orbitals is sketched to the right.



A square planar complex belongs to the point group D_{4h}, which is the direct product of the groups D_4 and C_i, $D_4 \otimes C_i$, *i.e.* all the symmetry operations in D_4 and C_i commute with the ones of the other group. We can therefore solve the problem for the point group D_4 and then simply add the labels 'g' or 'u' to the irreducible representations that we obtain.



In the following, we first find the characters of the reducible representations in D_4 and determine the irreducible representations. The characters for the additional symmetry operations in D_{4h} are also listed for completeness. However, they are simply derived by considering that upon inversion, an s orbital remains unchanged ('g'), a p orbital changes sign ('u'), and a d orbital remains again unchanged ('g').

We could determine the matrix representation as above by writing down the orbitals as a vector (the p orbitals are proportional to x, y, or z; the d orbitals to xy, zy, yz, …). However, the problem is simple enough so that we can deduce the behavior just by visual inspection.

For the s orbital, we find,

$D_4 \mid D_{4h}$	E	$2C_4$	C_2 $(=C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_s = A_1 \mid A_{1g}$	1	1	1	1	1	1	1	1	1	1

We conclude that the s orbital belongs to the representation A_{1g} in D_{4h}.

For the p orbitals,

$D_4 \mid D_{4h}$	E	$2C_4$	C_2 $(=C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_p = A_2+E \mid A_{2u}+E_u$	3	1	-1	-1	-1	-3	-1	1	1	1

We conclude that the p orbitals belong to the representations A_{2u} and E_u in D_{4h}.

For the d orbitals,

D_4 | D_{4h}	E	$2C_4$	C_2 (=C_4^2)	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_d = $A_1+B_1+B_2+E$ | $A_{1g}+B_{1g}+B_{2g}+E_g$	5	-1	1	1	1	5	1	1	1	1

We conclude that the d orbitals belong to the representations A_{1g}, B_{1g}, B_{2g}, and E_g in D_{4h}.

5.7) Construct the qualitative MO diagram of CH_3^+ (trigonal planar).

0) Point group? – D_{3h}

D_{3h} $(\bar{6})m2$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

1) Which AOs will contribute to the MOs of CH_3^+?
Carbon 2s and $2p_{x,y,z}$ orbitals as well the hydrogen 1s orbitals.

2) Use groups of symmetry equivalent orbitals as bases to form reducible representations. Then use the reduction formula to determine which irreducible representations contribute.

The carbon 2s orbital is invariant under all symmetry operations and therefore belongs to the symmetry species A_1'. Using the character table, we can also conclude that the $2p_z$ orbital (proportional to z) transforms according to A_2'', while the $2p_x$ and $2p_y$ orbitals transform according to E'.

Finally, the three hydrogen 1s orbitals form the basis for a reducible representation with the following characters.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma_{H1s} = A_1' + E'$	3	0	1	3	0	1

We find that the hydrogen 1s orbitals belong to the symmetry species A_1' and E'.

3) Determine Symmetry Adapted Linear Combinations for groups of orbitals.

We can easily see that the hydrogen 1s orbitals with A_1' symmetry, the correct Symmetry Adapted Linear Combination is

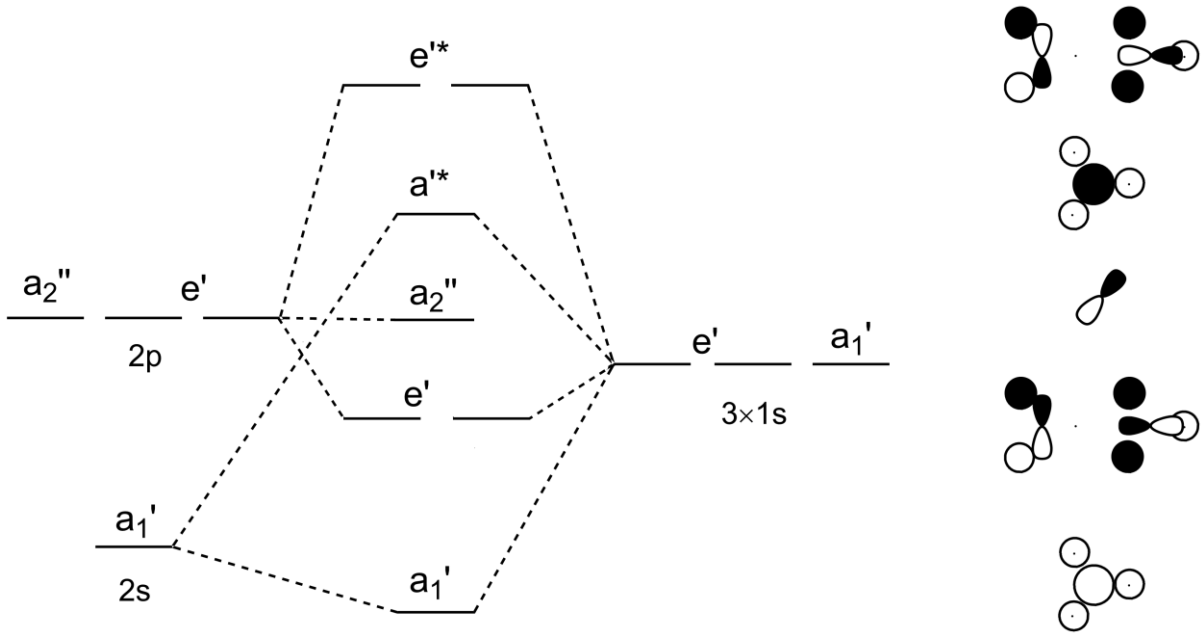
$$\Phi_{H1s}(A_1') = s_1 + s_2 + s_3$$

The two E' orbitals must match the p_x and p_y orbitals (compare the character table).

$$\Phi_{H1s}(E')_1 = 2s_1 - s_2 - s_3$$
$$\Phi_{H1s}(E')_2 = s_2 - s_3$$

In order to get the correct coefficients for the individual orbitals, we have also used the fact that the orbitals have to be orthogonal to each other and to the $\Phi_{H1s}(A_1')$ orbital.

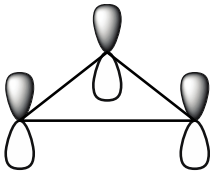
4) Construct a qualitative MO diagram.



Homework

5.8) In the cyclopropenyl cation ($C_3H_3^+$), the three carbon atoms form an equilateral triangle. One can use the three carbon $2p_z$ orbitals to construct the molecular π orbitals of the cyclopropenyl cation.

a) Determine the symmetry species of these molecular π orbitals.
b) Draw a qualitative MO diagram for these π orbitals. In other words, draw an energy diagram showing how the three p orbitals split up to form the molecular orbitals.
c) Write down the Symmetry Adapted Linear Combinations (SALCs) of these π orbitals (neglect normalization). Hint: You can figure the coefficients of the SALCs out by considering the shape of atomic orbitals of the same symmetry species.



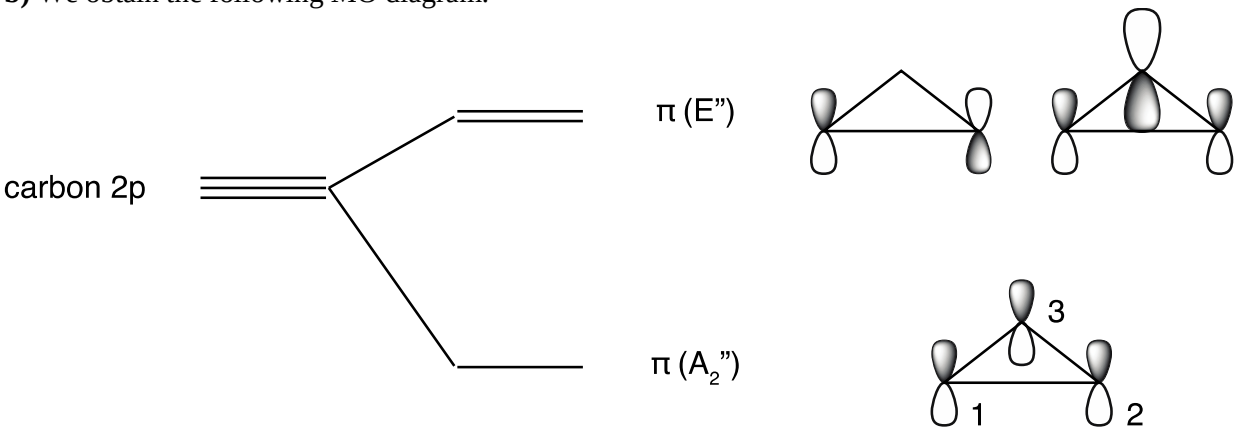
a) Point group D_{3h}.

Using the three carbon $2p_z$ orbitals as a basis we obtain the following reducible representation.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma = A_2'' + E''$	3	0	-1	-3	0	1

With the help of the reduction formula, we find that the three p orbitals give rise to one molecular π orbital of A_2'' symmetry as well as two degenerate E'' orbitals.

b) We obtain the following MO diagram.



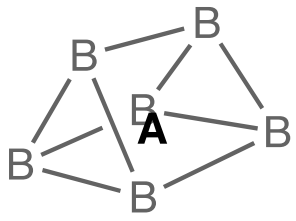
c) For the SALCs, we obtain

$$\pi(A_2'') = p_1 + p_2 + p_3$$
$$\pi(E'')_1 = p_1 - p_2$$
$$\pi(E'')_2 = p_1 + p_2 - 2p_3$$

The shape of the E'' orbitals becomes clear when one considers that the d_{xz} and d_{yz} orbitals belong to the same irreducible representation and that these two orbitals should be orthogonal to the A_2'' orbital.

5.9) A molecule AB_6 has a trigonal prismatic structure. Assume that the orbitals of atom A that are involved in bonding are the 2s orbital and the three 2p orbitals. For the atoms B, assume that each bond is with an s orbital.

a) Determine the symmetry species of all orbitals.
b) Draw a qualitative MO diagram. The exact energy ordering of the MOs is not important.



a) Point group D_{3h}.

Using the character table, we find that the 2s orbital on A has A_1' symmetry, the $2p_x$ and $2p_y$ orbitals have E' symmetry, and the $2p_z$ orbital has A_2'' symmetry.

Using the six s orbitals on the B atoms as a basis, we obtain the following reducible representation.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\Gamma = A_1' + A_2'' + E' + E''$	6	0	0	0	0	2

With the help of the reduction formula, we find that the six s orbitals give rise to one SALC of A_1' symmetry, one of A_1'' symmetry, two degenerate SALCs of E' symmetry, and two of E'' symmetry.

b) We obtain the following MO diagram.