

#1.

Consider a calculation on H_2O in which the basis consists of $2p_x, 2p_y$ and $2p_z$ on oxygen as well as $1s$ on each of the hydrogens. Assume that the interaction $\langle 1s_{\text{H}} | H | 2p_{\text{O}} \rangle$ numerically is much smaller than the difference between the $1s$ orbital energy $E(1s_{\text{H}})$ and the $2p$ orbital energy $E(2p_{\text{O}})$. In this case the orbital energies and molecular orbitals can be found by perturbation theory. Assume further that $2p_{\text{O}}$ is of lower energy than $1s_{\text{H}}$.

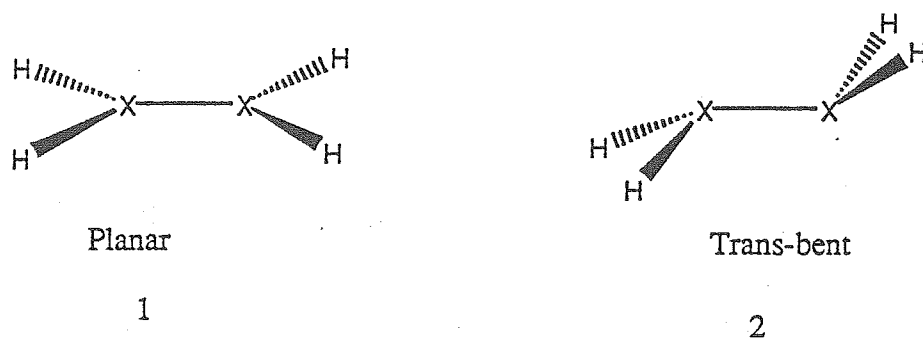
(a) Give an expression for the molecular orbital energies in H_2O using *second* perturbation theory in terms of $E(1s_{\text{H}})$ and $E(2p_{\text{O}})$, the H-O-H bond angle Φ , as well as the $S_{\alpha}(1s_{\text{H}}, 2p_{\text{O}})$ overlap. Make use of the approximation

$$\langle 1s_{\text{H}} | H | 2p_{\text{O}} \rangle = \langle 1s_{\text{H}} | 2p_{\text{O}} \rangle [E(1s_{\text{H}}) + E(2p_{\text{O}})]$$

(b) Assuming that the total energy is the sum of the orbital energies find the optimal bond angle Φ for H_2O according to perturbation *theory* theory. Discuss qualitatively how this prediction might be modified by including $2s_{\text{O}}$ into the basis.

#2

The molecules X_2H_4 , where $X = C, Si, Ge, Sn,$ and Pb , might be considered as dimers of the carbene type fragments. The X_2H_4 systems can have either the planar configuration 1 or the trans-bent conformation 2 in the ground-state depending on X .



(a) Construct a molecular orbital level diagram for XH_2 according to the simple theory of the notes. Indicate the ground state and the first excited state

(b) What are the point group symmetries of 1 and 2

(c) Construct the molecular orbital diagram and molecular orbitals of

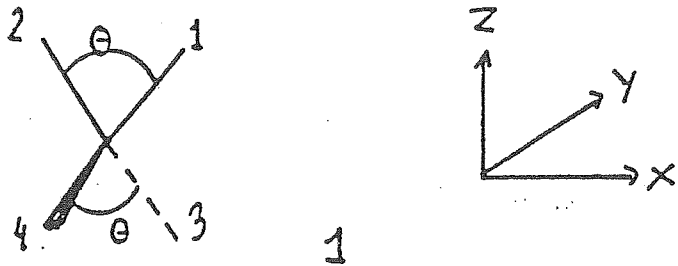
1 and 2. Construct the orbitals of 1 and 2 as linear combinations of the XH_2 fragment orbitals. Indicate the symmetry and occupations of the orbitals.

(d) Correlate the orbitals of 1 with those of 2 and indicate the differences in mixing for the two conformations

(e) Comment on why some elements X might prefer 2 over 1

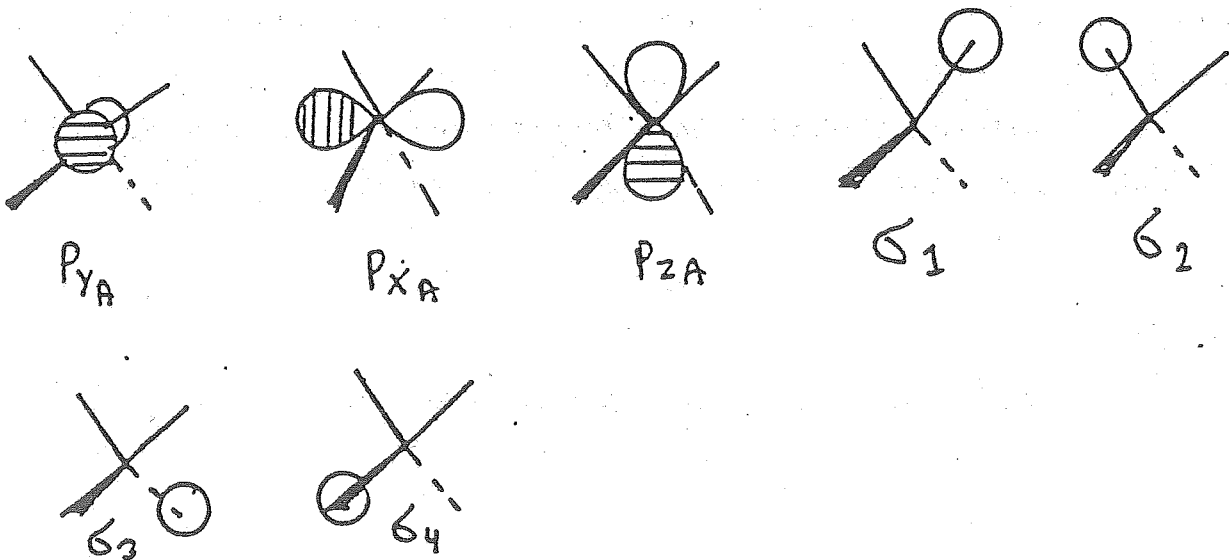
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Consider the AY_4 molecule with d_{2d} symmetry as shown in 1.



We have Y_1, A, Y_2 in the xz -plane and Y_3, A, Y_4 in the yz -plane. Our angular degree of freedom is $\theta = Y_1 A Y_2 = Y_3 A Y_4$.

The basis set for our calculation is given in 2.



a/ What is the symmetry (e.i. : a_1, a_2, b_1, b_2, e) of $p_{x_A}, p_{y_A}, p_{z_A}$ according to the character table for d_{2d} given below.

b/ From the four atomic σ -orbitals (i.e. : $\sigma_1, \sigma_2, \sigma_3, \sigma_4$) construct four symmetry orbitals $\{X_1, X_2, X_3, X_4\}$ such that X_2, X_3, X_4 only have non-zero overlaps with p_{x_A}, p_{y_A} and p_{z_A} respectively, and X_1 have zero overlap with all three p-orbitals.

indicate their

Illustrate the orbitals and ~~assign~~ symmetry according to the character table.

c/ Find the molecular orbital energies as a function of (K, a, θ) and correlate orbitals at $\theta = 109^\circ$ with orbitals at $\theta = 180^\circ$. The constants a, K are defined in

d)

What is the optimal angle θ for a molecule with 4-electrons, 5-electrons and 6-electrons respectively.

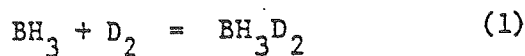
Character Table for D_{2d}

	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	1	-1
B_2	1	-1	1	-1	1
E	2	0	-2	0	0

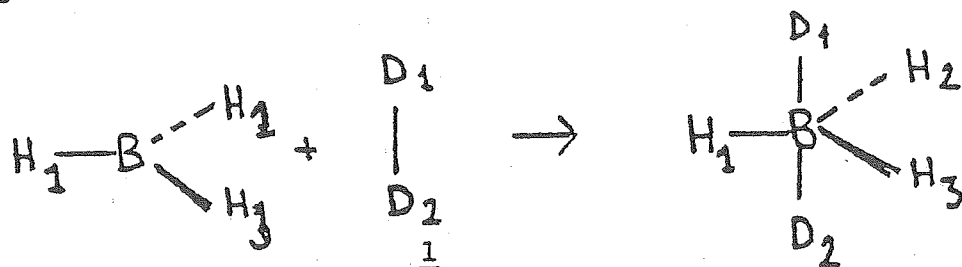
NB: You might like to read Purcell and Kotz p.82-96

a/ 4.

The molecule BH_3D_2 , where D is deuterium, would have a bipyramidal geometry of D_{3h} -sym. Consider the oxidative concerted addition of D_2 to BH_3 :

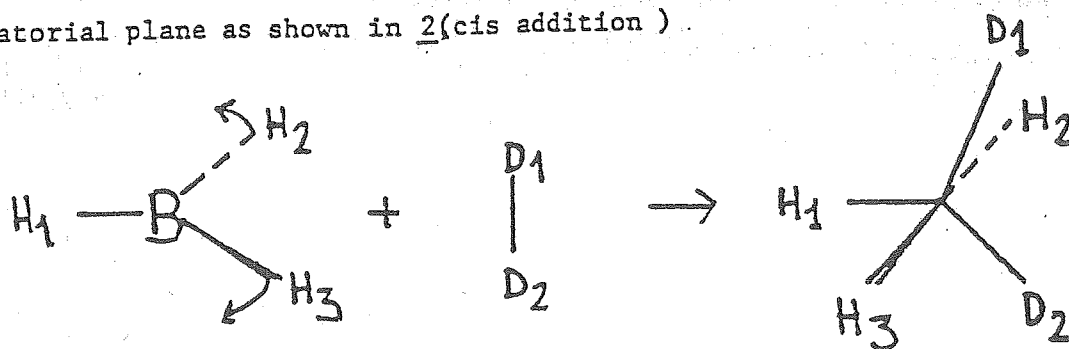


in which the D-D bond during the reaction is perpendicular to the molecular plane of BH_3 and the product have the two D-atoms in the axial positions, 1, (trans addition)



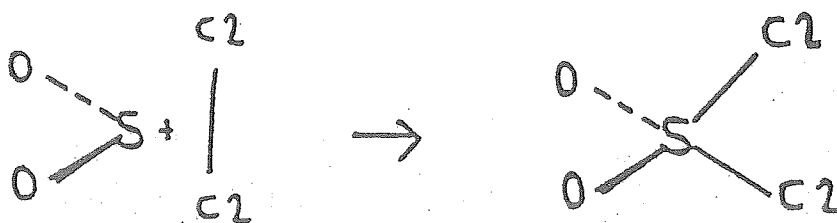
Draw a full correlation diagram for the process and discuss whether the process is symmetry forbidden or symmetry allowed.

Consider the same approach as in 1 but now with the two D-atoms adding in the equatorial plane as shown in 2 (cis addition)



Draw a full correlation diagram and discuss whether the process in 2 is symmetry forbidden or symmetry allowed

b/ Consider next the process 3



in which Cl_2 adds in a concerted process perpendicular to the molecular plane of SO_2 . The SO_2 molecule has four electrons and only one sigma orbital from each oxygen takes part in the bonding.

The Cl_2 molecule has two electrons and only one sigma orbital from each Cl-atom takes part in the bonding.

The SO_2Cl_2 molecule has six electrons and you might represent the molecular orbitals of SO_2Cl_2 by those of a AX_4 molecule but classified according to C_{2v} symmetry.

Draw a full correlation diagram for the process 3 and discuss whether it is symmetry allowed or symmetry forbidden.