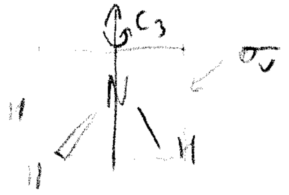
Homework solutions
Molecular Symmetry: Chapter 4.

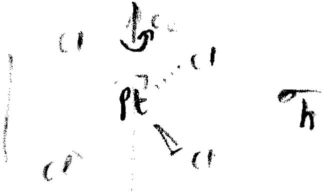
Exercises: 1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12
Problems: 2, 3, 5, 7

4.1

a) C_3 axis and σ_v plane in NH_3



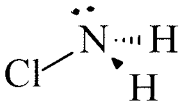
b) C_4 axis and σ_h plane in $[PtCl_4]^{2-}$



4.2

a) CO_2 has a center of inversion, but no S_4 axis
b) Acetylene, C_2H_2, has a center of inversion, but no S_4 axis
c) BF_3 does not have a center of symmetry or an S_4 axis
d) SO_4^{2-} does not have a center of symmetry but it does has an S_4 axis

4.3



a) NH_2Cl
Has only a mirror plan. Point group Cs

b) CO_3^{2-} Trigonal planar. Symmetry elements C_3, $3\sigma_v$, σ_h, $3C_2$, S_3. Point group D_{3h}

c) SiF_4 Tetrahedral. Symmetry elements $4C_3$, $3C_2$, $3S_4$, $6\sigma_d$. Point group T_d

d) HCN Symmetry elements: C_ϕ (implies you can rotate through any angle at all and it is a symmetry operation), $\infty\sigma_v$. Point group $C_{\infty v}$. Note that this point group is appropriate for all non-centrosymmetric linear molecules. Centrosymmetric linear molecules like N_2 belong to point group $D_{\infty h}$.

e) SiFClBrI. No symmetry. Point group C_1.

f) BF_4^-. Tetrahedral as for SiF_4. Point group T_d

4.4

a) An s-orbital has all symmetry elements. It is fully symmetrical.

b) A p-orbital has the same symmetry as a molecule like HCl. It has a C_ϕ rotation axis and an infinite number of σ_v planes

c) A d_{xy} orbital has the same symmetry as a molecule like the square planar complex trans-$[PtCl_2Br_2]^{2-}$. There are three perpendicular C_2 axis, three perpendicular mirror planes and a center of symmetry.

d) A d_{z2} orbital has the same symmetry as a molecule like N_2. A C_ϕ axis and infinite number of σ_v planes, a σ_h plane and a center of symmetry.

4.5

a) A molecule can not be polar if it is centrosymmetric. It can not be polar if it has more than two perpendicular mirror planes or two non-colinear rotation axes. It can not be polar if it has a rotation axis perpendicular to a mirror plane.

b) NH_2Cl
Has only a mirror plane so it is polar

b) CO_3^{2-} Symmetry elements C_3, $3\sigma_v$, σ_h, $3C_2$, S_3. Combination of C_3 and σ_h excludes polarity

c) SiF_4 Tetrahedral. Symmetry elements $4C_3$, $3C_2$, $3S_4$, $6\sigma_d$. Multiple rotation axes and mirror planes excludes polarity

d) HCN Symmetry elements: C_ϕ, $\infty\sigma_v$. Polar as there is no mirror plane perpendicular to the rotation axis.

e) SiFClBrI. No symmetry. Can be polar

f) BF_4^-. None polar as for SiF_4

4.6

a) Species with S_n axis can not be chiral.

b) NH_2Cl Has a mirror plane (S_1 axis) so it is not chiral.

CO_3^{2-} Has a mirror plane (S_1 axis) so it is not chiral

SiF_4 Has a mirror plane (S_1 axis) and S_4 axes so it is not chiral

HCN Has a mirror plane (S_1 axis) so it is not chiral

SiFClBrI. Has not symmetry so it is chiral.

BF_4^- Has a mirror plane (S_1 axis) and S_4 axes so it is not chiral.

4.7

a) The SO_3^{2-} (sulfite) ion is pyramidal like NH_3 (the sulfur has a lone pair). It belongs to the point group C_{3V}.

b) The maximum degeneracy of any irreducible representation for the point group C_{3v} is two (irreducible representation E). So the maximum degeneracy for nay possible molecular orbital must also be two.

c) By referring to the character tables for the point group C_{3v} it can be seen that the p_x and p_y orbitals transform as E and hence could be use in constructing an E symmetry pair of molecular orbitals.

4.8

a) The molecule PF_5 has a trigonal bipyramidal shape. It belongs to the point group D_{3h}.

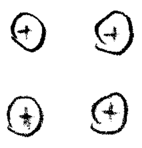
b) The maximum degeneracy of any irreducible representation for the point group D_{3h} is two (irreducible representations E' or E"). So the maximum degeneracy for nay possible molecular orbital must also be two.

c) By referring to the character tables for the point group D_{3h} it can be seen that the p_x and p_y orbitals transform as E' and hence could be use in constructing an E' symmetry doubly degenerate pair of molecular orbitals.

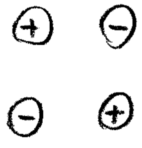
4.9

a)

A_{1g}



B_{1g}



E_u

b) The point group for a complex $[MH_4L_2]$ where the two ligands L are axial and the four H atoms are in square plane around the metal is D_{4h}.

c) By referring to the character table D_{4h} it can be seen that the d_{z^2} orbital can overlap with the A_{1g} combination, the $d_{x^2-y^2}$ orbital can interact with the B_{1g} combination and that there are no d-orbitals of appropriate symmetry to interact with the E_u combination.

4.11

For a mode to be both Raman and IR active it must belong to the same irreducible representation as either x, y or z (components of dipole moment opperator) and x^2, xy , xz etc. (components of polarizability operator).

a) By inspection of the character table for SF_6 (point group O_h) it can be seen that there are no modes that are both Raman and IR active for this molecule (this is true for all centrosymmetric molecules).

b) By inspection of the character table for BF_3 (point group D_{3h}) it can be seen that modes of E' symmetry would be both Raman and IR active.

4.12

By inspection of the character table for the point group C6v it can be seen that vibrations with symmetry A_2, B_1, and B_2 would not appear in either Raman or IR spectra.

Problems

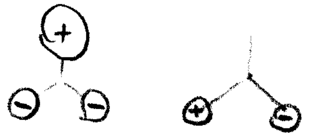
2 The tetrahedral molecular ions NH_4^+ belongs to point group T_d. It has only four stretching modes as there are only 4 N-H bonds.

a) Inspection of the T_d character table shows that the only IR active mode is triply degenerate (T_2 symmetry) so degeneracy is important. We will in fact only see at most one stretching mode in the IR.

b) The molecule $NH_2D_2^+$ belongs to the point group C_{2v}. There are no degenerate irreducible representations for this point group so there will be no degenerate IR modes.

3 The labeling of the MO energy level diagram is consistent with point group D_{3h} (CH_3^+ is trigonal planar)
An in phase sum of all 3 H1s orbitals will participate in the a_1' symmetry MO.
Only the C 2s orbital can participate in the a_1' symmetry MO (NOTE s orbitals on the central atom always transform as the highest symmetry irreducible representation).

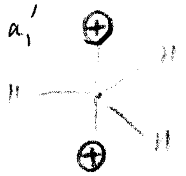
The e' combinations of H1 S orbitals are

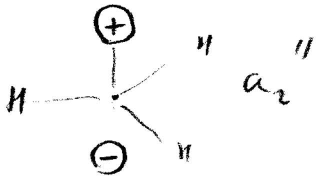


Carbon $2p_x$ and $2p_y$ transform at e' (by inspection of the character table).
Carbon $2p_z$ transforms as a_2'' (by inspection of the character table).

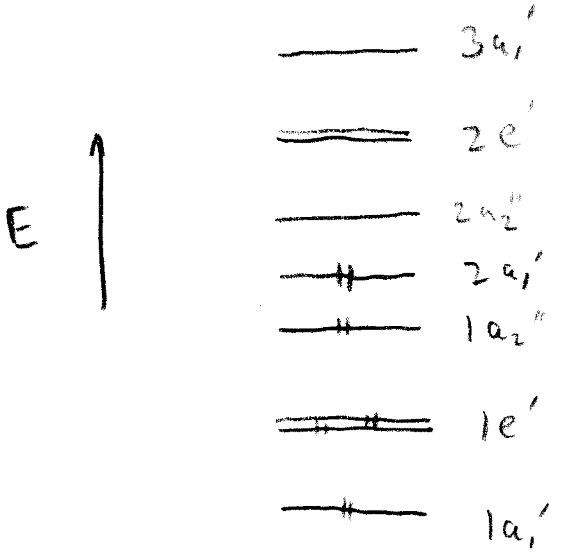
No linear combination of the three H1s orbitals has a_2'' symmetry. We have already established that the three possible combinations have a_1' and e' symmetry.

If we add H atoms above and below the plane we can generate an in phase linear combination of these two new 1S orbital and an out of phase combination. The in phase combination will have a_1' symmetry and the out of phase combination will have a_2'' symmetry.

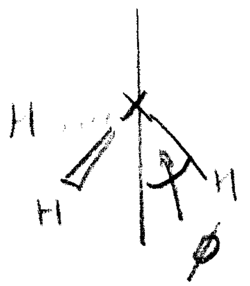


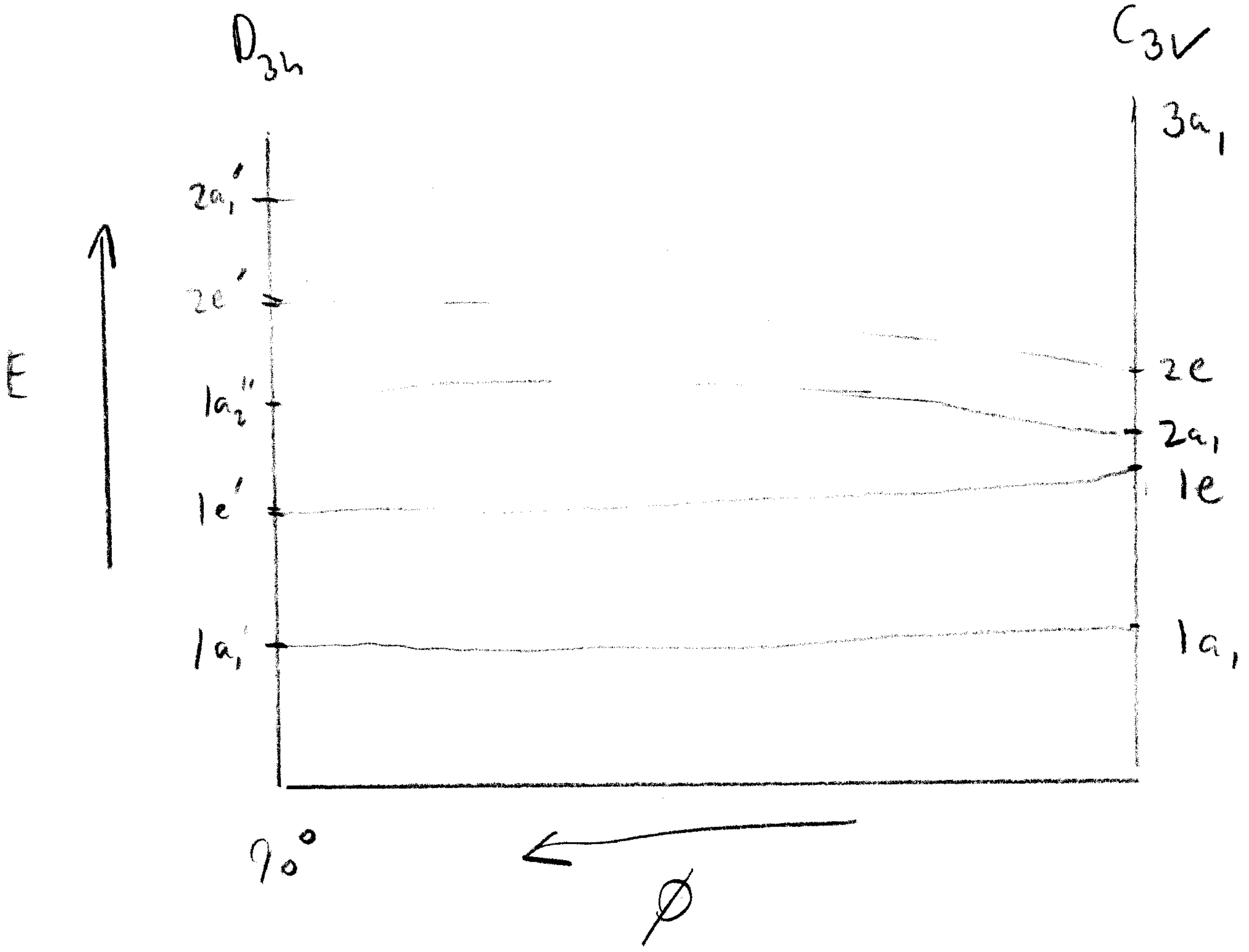


The final MO diagram for this CH_5^+ trigonal bipyramidal species will look as shown below. Note that 10 electrons can be accommodates in bonding and nonbonding orbital suggesting that CH_5^+ may have some stability (actually postulated as an intermediate in some reactions)



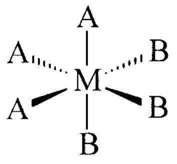
Walsh diagram for XH_3



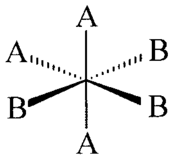


None bonding a_2'' orbital becomes a_1 in point group C_{3v}. It mixes with H_{1s} combination and is lowered in energy. This is why NH_3 is not flat !!

There are two geometrical isomers for "octahedral" MA_3B_3 complexes.



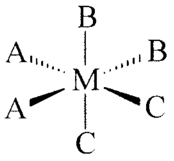
Facial or 'fac'



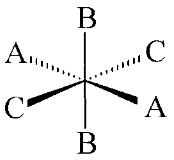
Meridional or "mer"

The facial isomer belongs to point group C_{3v}. Not chiral due to mirror planes.
The meridional isomer belongs to point group C_{2v}. Not chiral due to mirror plane.

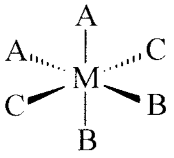
There are five geometrical isomers for "octahedral" $MA_2B_2C_2$ complexes.



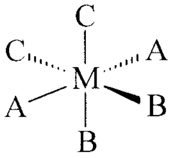
Pairs of ligands all cis. Point group C_1. This is chiral.



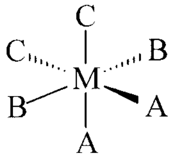
Pairs of ligands all trans. Point group D_{2h}. This is not chiral



One pair of ligands trans, the others cis. Point group C_{2v}. This is not chiral



One pair of ligands trans, the others cis. Point group C_{2v}. This is not chiral



One pair of ligands trans, the others cis. Point group C_{2v}. This is not chiral