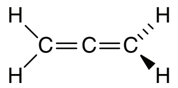
Symmetry and Bonding: Exercises
对称性与成键：习题

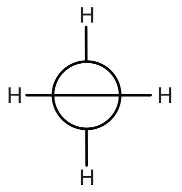
It is **not necessary** to complete all of the exercises. You supervisor will select an appropriate subset, and you may find the remainder useful for revision.

Ex. 1

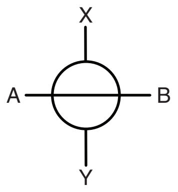
Allene, C_3H_4, has a structure in which the two terminal CH_2 groups lie in planes at 90° to one another. The molecule has a four-fold axis of improper rotation (S_4) along its long axis. The effect of the resulting symmetry operations is best seen by viewing the molecule down its long axis and the indicating the positions of the CH_2 groups using a Newman-like projection. To follow the effect of the symmetry operations it is useful to label the equivalent hydrogen atoms A, B, X and Y, as shown on the right.



allene



view down long axis



labelling

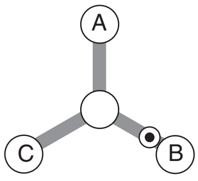
(a) Draw diagrams, similar to those in Fig. 2.1 on page 11, to show the effect of all the operations generated by this four-fold improper axis i.e. S_4, $(S_4)^2$ ….

(b) Shown that $(S_4)^2 \equiv C_2$ (where the two-fold axis is also along the long axis) and that $(S_4)^2 \equiv E$.

(c) Hence identify the *distinct* symmetry operations generated by this four-fold axis of improper rotation.

Ex. 2

BF_3 is planar; it has a three-fold axis of improper rotation (S_3) coming out of the plane of the molecule and passing through the central boron atom. To follow the effect of the symmetry operations it is useful to label the equivalent fluorine atoms A, B, and C, and to include an arrow, attached to one of the bonds and initially pointing out of the plane of the molecule.



(a) Draw diagrams, similar to those in Fig. 2.1 on page 11, to show the effect of all the operations generated by this three-fold improper axis i.e. S_3, $(S_3)^2$ ….

(b) How many times must S_3 be applied in order to return the molecule to its starting position? (This is a hint about the answer to part (a).)

(c) By considering the other symmetry elements possessed by this molecule (e.g. C_3 and σ_h), identify which of the operations $(S_3)^n$ results in an orientation of the molecule which cannot be achieved by any of the other symmetry operations i.e. which $(S_3)^n$ are unique.

Ex. 3

(a) With the aid of diagrams, explain why the three σ_v mirror planes in BF_3 are in the same class.

(b) Are the three mirror planes in C_2H_4 in the same class? Give reasons for your answer.

(c) XeF_4 has a planar structure in which the fluorine atoms are at the corners of a square and the xenon atom is in the middle. It has a four-fold axis of symmetry, two mirror planes which pass through fluorine atoms at opposite corners of the square, two mirror planes which pass through the mid points on opposite sides of the square, and a mirror plane in the plane of the molecule. Group the mirror planes into classes, giving your reasons.

Ex. 4
For each of the following molecules identify the key elements of symmetry and hence determine the point group. Having identified the point group verify that all of the symmetry elements whose presence is indicated in the relevant character table are indeed present. Make *clear, labelled* sketches showing the positions of all of the symmetry elements present. If you are uncertain about the structures of any of the molecules mentioned, look them up in a reliable source.

(a) formaldehyde (methanal)

(b) all of the isomers of dichlorobenzene

(c) cis and trans FN=NF

(d) allene (see Ex. 1; hint there are *three* two-fold axes)

(e) biphenyl, Ph–Ph, where the angle between the plane of the two benzene rings is: (i) 0°; (ii) 90°; (iii) some angle greater than 0° but less that 90°. Hint: the answer to (d) may be helpful.

(f) the chair and boat conformations of cyclohexane

(g) SF_5Cl; H_2O_2; O_3; N_2O; SF_6; $POCl_3$

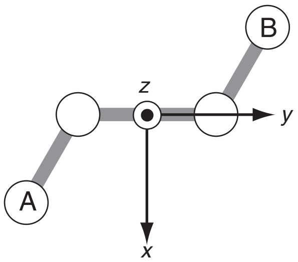
(h) the eclipsed and staggered conformations of ethane

(i) ferrocene with the two five-membered rings (i) eclipsed, (ii) staggered.

Ex. 5
For H_2O, determine the effect of each symmetry operation on each of the five oxygen $3d$ orbitals by using a similar approach to that shown in Fig. 3.1 on page 20. Hence determine the representation generated by each orbital, and then by inspection of the character table determine to which irreducible representation this corresponds. (Of course you can read the answers straight off the table, but this is not what you are being asked to do.)

Ex. 6

(a) Determine the point group of trans FN=NF.



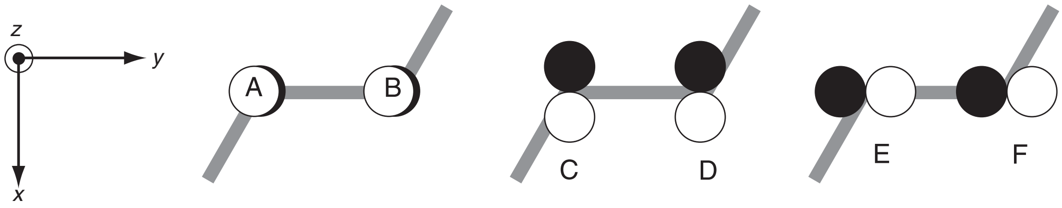
(b) Using a similar approach to that in section 3.1.2 on page 21, determine the two-by-two representative matrix for each operation of the group using the two fluorine $2s$ AOs A and B as the basis.

(c) Hence find the corresponding characters of the representation and, by inspection of the character table, to which irreducible representations this can be reduced.

(d) For the same basis determine the characters using the 'counting method'.

Ex. 7

This exercise also refers to trans FN=NF.



(a) Using the 'counting method' determine the characters of the representations generated by: (i) the two nitrogen $2p_z$ AOs A and B; (ii) the two nitrogen $2p_x$ AOs C and D; (iii) the two nitrogen $2p_y$ AOs E and F. In each case determine, by inspection of the relevant character table, the corresponding irreducible representations.

(b) In each case (i)–(iii) sketch the form of the two symmetry orbitals arising from each pair of orbitals and identify to which irreducible representation each belongs.

Ex. 8

(a) In formaldehyde (methanal) determine the irreducible representation which each of the following AOs on the carbon transforms as: the $2s$, the three $2p$ AOs and the five $3d$. Repeat the process for the corresponding AOs on the oxygen.

(b) The species $[PtCl_2Br_2]^{2-}$ has square planar coordination about the platinum atom with the two chlorine ligands being placed at opposite corners of the square. Determine the point group and hence the irreducible representation for each of the five $5d$ AOs on the platinum.

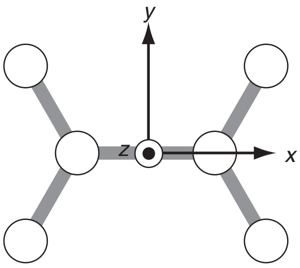
Ex. 9

This question refers to the point group D_{3h}.

(a) Using a similar approach to that in section 3.2.1 on page 27, form the two-by-two representative matrices in a basis consisting of a unit vector along x and one along y for (i) one of the C_2 operations; (ii) the σ_h operation; (iii) one of the S_3 operations; (iv) one of the σ_v operations. (Hint: you can simplify the calculations by choosing the C_2 and σ_v to lie along x or y.)

(b) Hence determine the characters for each operation and verify that in this point group (x, y) transforms in the expected way.

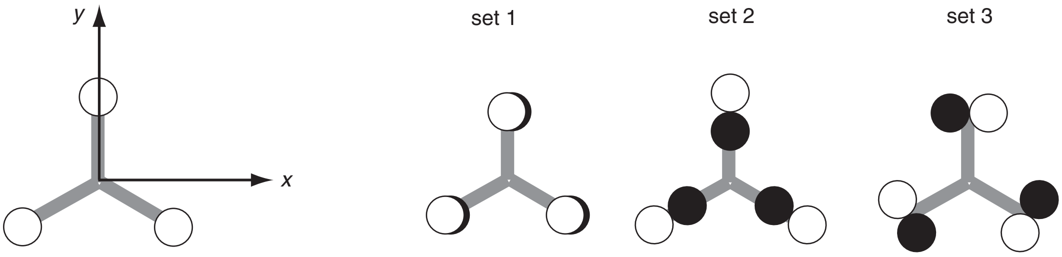
Ex. 10
This exercise refers to tetrafluoroethene; use the axis system indicated below.



(a) State the point group.

(b) Using the 'counting method' determine the characters of the representation generated by the following sets of orbitals and in each case use the reduction formula to determine the corresponding irreducible representations: (i) the four fluorine $2s$ AOs; (ii) the four fluorine $2p_z$ AOs; (iii) the four fluorine $2p_x$ AOs; (iv) the four fluorine $2p_y$ AOs; (v) the two carbon $2s$ AOs; (vi) the two carbon $2p_z$ AOs; (vii) the two carbon $2p_x$ AOs; (viii) the two carbon $2p_y$ AOs.

Ex. 11
This exercise refers to BF_3; use the axis system indicated below.



(a) State the point group.

(b) Using the 'counting method' determine the characters of the representation generated by the three fluorine $2p_z$ AOs, set 1. *Using the reduction formula* determine the corresponding irreducible representations.

(c) Do the same for the three fluorine $2p$ AOs forming set 2.

(d) Do the same for the three fluorine $2p$ AOs forming set 3.

Ex. 12
For each part of this exercise you will need to determine or state the point group of the molecule in question.

(a) Determine the characters of the representation generated by the six out-of-plane carbon $2p$ AOs in benzene. Reduce the representation.

(b) Determine the characters of the representation generated by the four hydrogen $1s$ AOs in methane. Reduce the representation.

(c) Determine the characters of the representation generated by the four chlorine $3s$ AOs in the square planar species $[PtCl_4]^{2-}$. Reduce the representation.

(d) The cyclopentadienyl anion, $[C_5H_5]^-$, is planar and the five carbons form a regular pentagon. Determine the characters of the representation generated by the five out-of-plane carbon $2p$ AOs. Reduce the representation.

Ex. 13

(a) Using direct products determine the irreducible representations spanned by the following cartesian functions in the point group C_{2v}: x^2, xz, xy and xyz. (Of course most of these you can read off the table, but you are asked here to find the IRs by computing the direct product yourself.)

(b) In the point group D_{3h} compute the following direct products and, if necessary, reduce the resulting representation: $A_1' \otimes E'$, $A_2' \otimes E'$, $A_1'' \otimes A_2''$, $E'' \otimes E''$, $E' \otimes E'$.

(c) In the point group C_{2v} the result of which of the following triple direct products contains the totally symmetric irreducible representation:

$$A_1 \otimes A_2 \otimes A_1 \quad A_2 \otimes A_1 \otimes A_2 \quad B_1 \otimes A_1 \otimes B_2 \quad B_2 \otimes B_2 \otimes A_2 \quad A_2 \otimes B_1 \otimes B_2 \text{ ?}$$

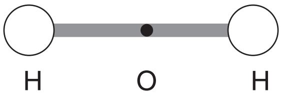
(d) In the point group D_{3h} the result of which of the following triple direct products contains the totally symmetric irreducible representation:

$$A_1' \otimes A_2'' \otimes A_2'' \quad A_1' \otimes E' \otimes A_2'' \quad A_1' \otimes A_2'' \otimes E' \quad A_1' \otimes E' \otimes E' \text{ ?}$$

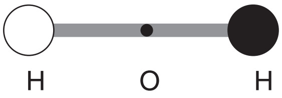
Ex. 14
This exercise is concerned with a hypothetical linear geometry of the water molecule H–O–H. Such a molecule belongs to the point group $D_{\infty h}$; note that the z-axis coincides with the long axis of the molecule.

In this group the oxygen $2s$ transforms as the irreducible representation Σ_g^+, the $2p_z$ transforms as Σ_u^+, and the $2p_x$ and $2p_y$ AOs transform together as the two-dimensional IR Π_u. The two hydrogen $1s$ AOs form two symmetry orbitals shown below, along with their symmetry labels.

Σ_g^+



Σ_u^+



(a) Using the same approach as in Fig. 6.1 on page 50 construct an approximate MO diagram for water in this geometry.

(b) Label each MO with its appropriate symmetry label (remember that lower case letters are used for MOs, so an MO transforming as Σ_g^+ is labelled σ_g^+).

(c) Determine which MOs are occupied and sketch their forms.

(d) Compare your MO diagram to that for water in its bent geometry. Which do you think has the greater degree of bonding overall?

Ex. 15
This exercise is concerned with constructing an MO diagram for ammonia, NH_3, which has a trigonal pyramidal geometry.

(a) Determine the point group of this molecule.

(b) Classify the valence orbitals (i.e. the $2s$ and $2p$) on nitrogen according to symmetry.

(c) Determine the characters of the representation generated by the three hydrogen $1s$ AOs, reduce the representation and sketch the form of the resulting symmetry orbitals. (These are easiest to draw if you take a view looking down on the molecule.)

(d) Writing the three hydrogen AO wavefunctions as s_{A}, s_{B} an s_{C}, write down the form of the SOs and normalize them.

(e) Construct an MO diagram, labelling each MO with an appropriate symmetry label.

(f) Sketch the form of the occupied MOs and comment on the extent of bonding shown by each.

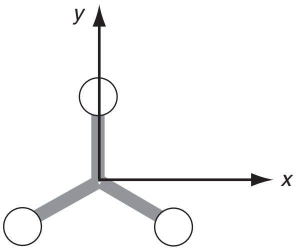
Ex. 16

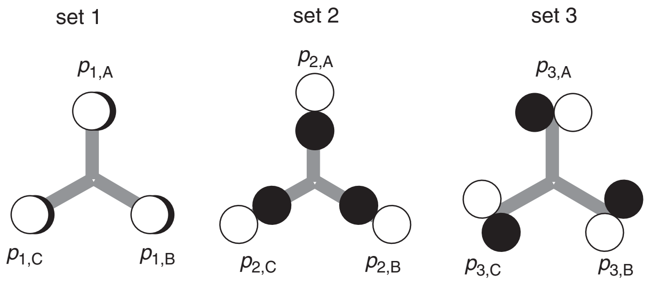
Consider an alternative geometry for NH_3 in which the molecule is flat i.e. point group D_{3h}. The MO diagram for BH_3, shown in Fig. 6.4 on page 56, can be used to describe the bonding in trigonal planar NH_3. Determine which MOs are occupied, compare the overall degree of bonding between the trigonal planar and trigonal pyramidal geometries, and hence rationalize the known geometry of NH_3.

Speculate about how the molecular geometry might change along the series NH_3, NH_3^+, NH_3^{2+}.

Ex. 17

This exercise is concerned with constructing the symmetry orbitals arising from each of the sets of $2p$ orbitals in BF_3 (point group D_{3h}) shown below. *Do not use the projection formula.*





(a) For each set find the characters of the representation and then reduce the representation.

(b) By drawing an analogy between the orbital coefficients and relevant cartesian functions, sketch the form of the SOs clearly labelling each with the appropriate IR.

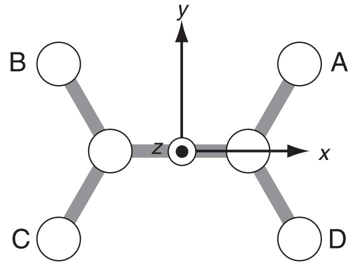
(c) Give the normalized form of each SO.

Ex. 18

Construct an MO diagram for BF_3 which has a trigonal planar geometry. Consider the boron $2s$ and $2p$ AOs, and *only* the fluorine $2p$ AOs (you will need the results of the previous exercise). Determine which MOs are occupied and comment on the result. (You are *not* asked to sketch the MOs.)

Ex. 19

This exercise refers to tetrafluoroethene; use the axis system and labelling indicated below.



(a) State the point group.

(b) Determine the characters of the representation generated by the four fluorine $2p_z$ AOs; reduce the representation.

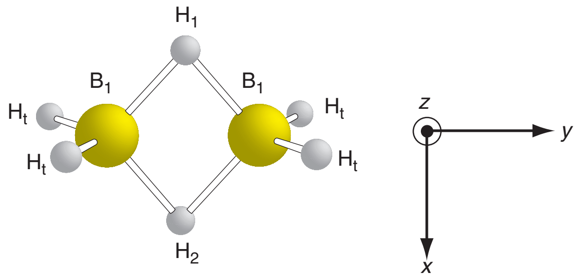
(c) *Using the projection formula* find the SO corresponding to each irreducible representation found in (b) (apply the projection operator to the orbital at position A).

(d) Sketch the SOs you have found in (c) and check that they match up with the form you would expect simply by drawing an analogy between the orbital coefficients are relevant cartesian functions.

(e) Repeat the process for: (i) the four fluorine $2p_y$ AOs; (ii) the four fluorine $2p_x$ AOs. In each case apply the projection operator to the orbital at position A.

(f) Returning to the four fluorine $2p_z$ AOs repeat the process, but this time apply the projection operator to the orbital at position B.

Ex. 20
This exercise is concerned with the molecule diborane B_2H_6, shown below. The boron atoms together with H_1 and H_2 lie in a plane (here the xy plane). The so-called terminal hydrogens H_t lie in a perpendicular plane (here yz), and the coordination around each boron is approximately tetrahedral.



A simple view of the bonding in this molecule is to imagine that the boron atoms are sp^3 hybridized. The hybrid atomic orbital (HAO) pointing towards each terminal hydrogen is involved in forming a simple two-centre two-electron B–H_t bond; these account for a total of eight electrons. We will construct MOs from the remaining four HAOs which lies in the xy plane and point towards H_1 and H_2, and the two hydrogen $1s$ AOs.

(a) Determine the point group of this molecule.

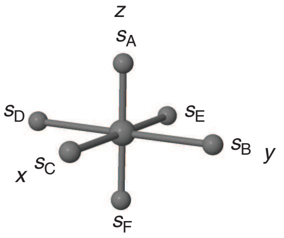
(b) Construct symmetry orbitals from the boron HAOs which lie in the xy plane, and do the same for the two hydrogen $1s$ AOs. Use the axis system indicated above. (Do not use the projection formula).

(c) Hence draw up an MO diagram, giving each MO an appropriate symmetry label.

(d) State which MOs are occupied and sketch their form.

(e) B_2H_6 is sometimes described as 'electron deficient'. Does your MO description support such a description?

Ex. 21
Consider a molecule in which there are six ligands surrounding a central atom in an octahedral arrangement (point group O_h). Each ligand provides a single s orbital. Use the axis system and the labelling shown below.



(a) Make sketches showing where you have chosen to place the different types of mirror plane.

(b) Find the representation generated by the six ligand s orbitals; reduce this representation.

(c) By using the additional information in the character table construct the six symmetry orbitals. (Do not use the projection formula). Sketch each SO and give it the appropriate symmetry label.

(d) Write down the mathematical form of each SO in terms of the AO wavefunctions $s_A, s_B \ldots$. Normalize the SOs.

Ex. 22

Consider an octahedral transition metal complex and concentrate on the metal-based non-bonding $1t_{2g}$ and antibonding $2e_g$ sets of MOs. The d electrons originating on the metal are accommodated within these sets of MOs.

(a) For between 0 and 10 d electrons make a table showing how the $1t_{2g}$ and $2e_g$ MOs are occupied, indicating in the usual way (i.e. ↑ and ↓) how the electron spins are arranged. When both are possible, illustrate separately the low- and high-spin arrangements.

(b) Take the energy of the $1t_{2g}$ MOs to be zero and that of the $2e_g$ MOs to be Δ_o; also assume that each pair of parallel spins *lowers* the energy by an amount K. Add to your table the energy of each configuration computed using these parameters.

(c) Assume that $K = 1$ and $\Delta_o = \frac{1}{2}$ (in arbitrary units). On a graph, plot the energy of the configurations you have determined as a function of the number of d electrons; where relevant, plot the data for both the high- and low-spin arrangements.

(d) Now assume that $K = 1$ and $\Delta_o = 4$. Recalculate the energies and hence draw a further graph.

(e) Comment on what the two graphs imply about the preference for of high- or low-spin configurations.

Ex. 23

(a) Using the spin-only formula, draw up a table giving the value of μ_{eff} for an octahedral complex with 4, 5, 6 and 7 d electrons in both the low- and high-spin configurations. Express your results as decimals.

(b) Use the following experimentally measured values of μ_{eff} to determine whether the given octahedral complex is high or low spin. (Be aware that the spin-only formula is not expected to give precise agreement with experimental data; in the complex $[Co(NO_2)_6]^{4-}$ the ligands are $[NO_2]^-$).

complex	μ_{eff} / B.M.	complex	μ_{eff} / B.M.
$[Co(NO_2)_6]^{4-}$	1.9	$[Cr(H_2O)_6]^{3+}$	3.8
$[Cr(H_2O)_6]^{2+}$	4.8	$[Mn(H_2O)_6]^{2+}$	5.9
$[Fe(CN)_6]^{3-}$	2.3	$[Fe(H_2O)_6]^{2+}$	5.3

Ex. 24

(a) Consider an octahedral transition metal complex in which each ligand is a simple anion, such as Cl^-. Each ligand has a two p orbitals oriented perpendicular to the M–L bond. Find the representation generated by these twelve orbitals and show that it reduces to $T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$. (Use the axis system and choice of location for the mirror planes shown on page 70.)

(b) With the aid of a suitable diagram explain why the presence of low-lying (in energy terms) filled π-type orbitals on the ligands generally results in a decrease in Δ_o.

(c) Similarly explain why the presence of higher-lying empty π-type orbitals generally results in an increase in Δ_o. What kind of ligand has such orbitals?

Ex. 25

This exercise is concerned with a transition metal complex ML_4 where M is a first-row metal and L is a structureless ligand. The coordination around the metal is tetrahedral.

(a) State the point group of the molecule.

(b) Classify the $3d$, $4s$ and $4p$ AOs on the metal atom according to symmetry (i.e. determine the IR of each).

(c) Suppose that each ligand contributes a σ-type orbital directed towards the metal. Determine and reduce the representation generated by these four orbitals.

(d) Hence construct an MO diagram assuming that the ligand orbitals lie lower in energy that the metal $3d$ AOs. Give each MO an appropriate symmetry label.

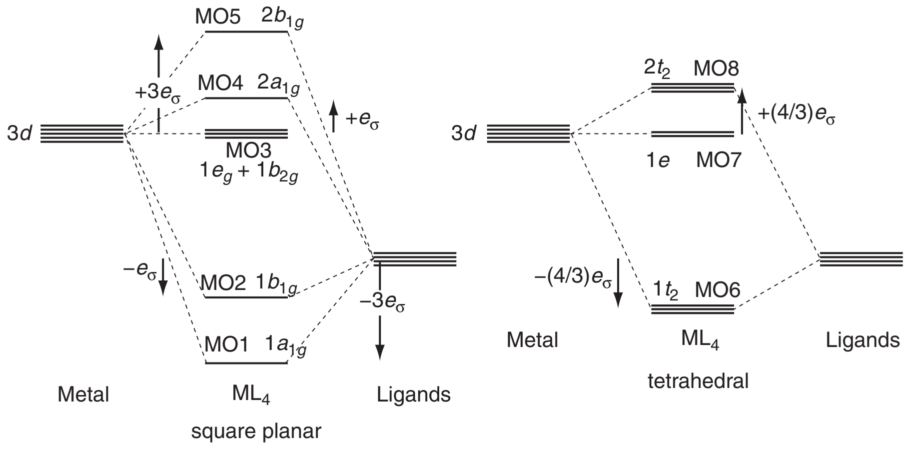
(e) Identify the metal-based MOs which accommodate the d electrons and mark the splitting Δ_t on your diagram.

(f) Suppose that each ligand also contributes two p orbitals arranged at right angles to the M–L bond. Determine and reduce the representation generated by these eight orbitals.

(g) Assuming that these ligand p orbitals are similar in energy to the ligand σ-type orbitals explain, using a diagram, what effect the presence of these p orbitals will have on the value of Δ_t.

Ex. 26

This exercise is about how the energy difference between a square planar and tetrahedral ML_4 complex varies with the number of d electrons. Shown below are partial MO diagrams for the two geometries: *only* those MOs which have a contribution from the metal orbitals are shown. Each MO is given its appropriate symmetry label, but for simplicity the MOs are also numbered. Note that MO3 is in fact the $1e_g$ and $1b_{2g}$ MOs together, giving three orbitals in total.



A simplified MO treatment shows that the amount by which each MO is shifted in energy on forming the complex can be expressed in terms of a single energy parameter e_σ. For example, MO1 is shifted down in energy by $3e_\sigma$, whereas MO8 is shifted up in energy by $\frac{4}{3}\,e_\sigma$. MO3 and MO7 are nonbonding and so do not change energy.

In the square-planar geometry MO1 and MO2 are occupied by two electrons each, contributing an total energy change of $2 \times (-3e_\sigma) + 2 \times (-e_\sigma) = -8e_\sigma$. Similarly in the tetrahedral geometry the triply degenerate MO6 is occupied by six electrons, contributing an total energy change of $6 \times (-\frac{4}{3}e_\sigma) = -8e_\sigma$ i.e. exactly the same amount. In comparing the two geometries, we can therefore ignore these filled orbitals.

The electrons originating from the metal $3d$ AOs can fill MO3, MO4 and MO5 in the square-planar case, and MO7 and MO8 in the tetrahedral case. The precise details of which orbitals are occupied will determine the relative energy of the two possible geometries for ML_4.

Consider the case of four d electrons. Assuming a high-spin configuration, in the square-planar complex three electrons will occupy the three degenerate orbitals MO3, which contribute nothing to the energy change, and one will occupy MO4, which contributes $+e_\sigma$. The energy change is thus $+e_\sigma$. In the tetrahedral case, two electrons occupy MO7 and two occupy MO8, so the energy change is $2 \times 0 + 2 \times (+\frac{4}{3}e_\sigma) = 2.67\, e_\sigma$. It is clear that the square-planar geometry is preferred since the energy increase due to the d electrons is smaller than that for the tetrahedral case.

(a) Repeat this calculation for between one and ten d electrons (assuming a high-spin configuration), and hence identify those configurations for which the square-planar geometry is preferred.

(b) Now consider the case where the square-planar complex is low spin (meaning that MO5 is not occupied until *both* MO3 *and* MO4 are full) but the tetrahedral complex is still high spin. Again identify those configurations for which the square-planar geometry is preferred.

(c) In the light of your calculations, comment on the fact that square-planar complexes are most commonly found for metals with d^8 configurations in conjunction with ligands which give rise to large splitting of the d orbitals.

Ex. 27

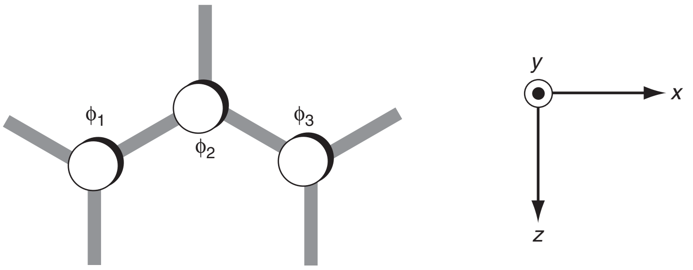
Using the Hückel approximations write down the secular equations for the π system of the allyl fragment (see section 7.1.2 on page 88). Work through the solution to these equations for yourself, finding the energies and normalized form of all three MOs.

Ex. 28

For the butadiene π system described in section 7.2.1 on page 92 set up the secular equations for the B_g SOs, solve them to find the energies and (normalized) orbital coefficients of the two resulting MOs. (Use an approach which is analogous to the calculation for the A_u SOs given in the notes; check that your results for the B_g MOs match those quoted in the notes in Eqn. 7.12 on page 97.)

Ex. 29

The π system of the allyl fragment consists of three out-of-plane p orbitals, ϕ_1, ϕ_2 and ϕ_3. These can be thought of as being arranged in the geometry below which has C_{2v} symmetry.



(a) Show that the three SOs arising from the three p orbitals are

$$\theta_a = \frac{1}{\sqrt{2}}(\phi_1 + \phi_3) \qquad \theta_b = \phi_2 \qquad \theta_c = \frac{1}{\sqrt{2}}(-\phi_1 + \phi_3),$$

where θ_a and θ_b have B_2 symmetry, and θ_c has A_2 symmetry.

(b) Show that the secular equations arising from the B_2 symmetry SOs are

$$\begin{pmatrix} \alpha - E & \sqrt{2}\beta \\ \sqrt{2}\beta & \alpha - E \end{pmatrix}\begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0.$$

(c) Solve these equations to find the energies and (normalized) orbital coefficients of the two resulting MOs, expressing the MOs in terms of the ϕ_i.

(d) Find the energy and orbital coefficients of the A_2 MO.

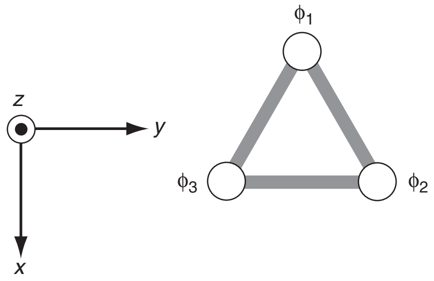
(e) Draw up an energy level diagram for the MOs and make a sketch of each. Compare your results with the MOs given on page 91.

Ex. 30

For the π system of the carboxylate anion, analysed in section 7.2.2 on page 98, solve the secular equations given in Eqn. 7.13 on page 100 for the B_2 SOs and confirm that you obtain the quoted results for both the energies and the (normalized) orbital coefficients.

Ex. 31

A possible geometry for H_3^+ is an equilateral triangle, shown below.



(a) State the point group of this molecule.

(b) Construct symmetry orbitals from the three hydrogen 1*s* AOs ϕ_1, ϕ_2 and ϕ_3; clearly state of IR to which each SO belongs and give the SO in its normalized form.

(c) Using the usual Hückel approximations, set up and solve (if necessary) the secular equations for each symmetry present: find the energies and the (normalized) coefficients of the MOs when expressed in terms of the ϕ_i. Sketch an energy level diagram and the form of the MOs.

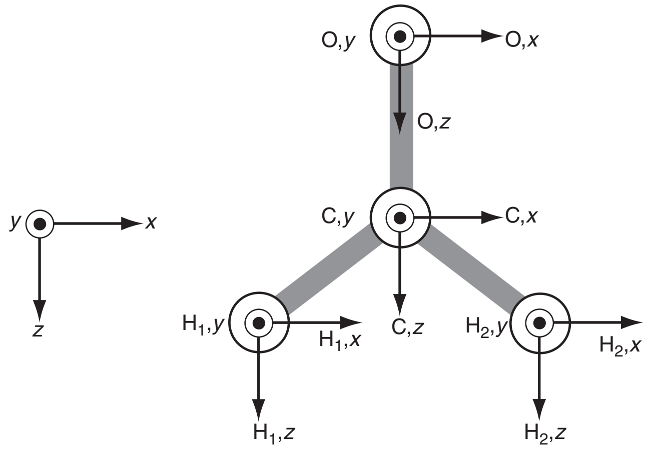
(d) Determine how many electrons there are in H_3^+, assign the electrons to an appropriate MO, and hence work out the total electron energy in terms of the Hückel α and β parameters.

(e) An alternative geometry for H_3^+ is that it is ‘bent’, like H_2O. Explain why, within the Hückel framework, the MOs for this system are exactly analogous to those of the π system of the allyl fragment. Using the values given in the notes for the energies of the MOs for this system determine the total electron energy of ‘bent’ H_3^+.

(f) According to your calculation, which geometry is favoured? Rationalize your result.

Ex. 32

This exercise is concerned with the normal modes of methanal (formaldehyde).



(a) State the point group of this molecule.

(b) Explain why, in a normal mode analysis of this molecule, it is possible to consider the pairs of displacement vectors ($H_{1,x}$, $H_{2,x}$), ($H_{1,y}$, $H_{2,y}$), and ($H_{1,z}$, $H_{2,z}$) separately. Also explain why the displacement vectors on the carbon and oxygen atoms can be classified according to symmetry simply by inspection of the character table.

(c) Determine the characters of the representation generated by ($H_{1,x}$, $H_{2,x}$); reduce the representation. Do the same for ($H_{1,y}$, $H_{2,y}$) and ($H_{1,z}$, $H_{2,z}$).

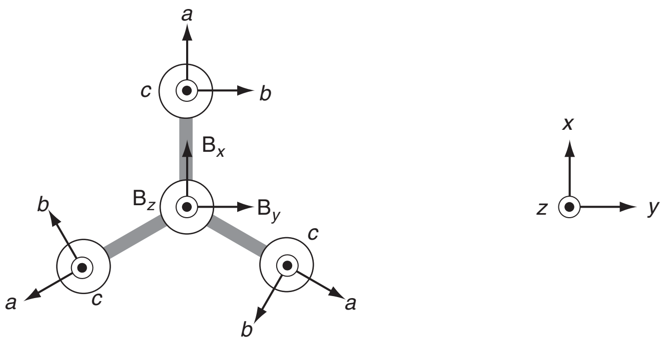
(d) Determine the irreducible representations spanned by the displacement vectors on carbon and oxygen, and hence show that together all of the displacements transform as $4A_1 \oplus A_2 \oplus 4B_1 \oplus 3B_2$.

(e) Take away the irreducible representations for the overall translation and rotation of the molecule, and hence find the irreducible representations of the normal modes. Check that you have the expected number of normal modes.

(f) Now consider only the C–H stretches of this molecule. Show that these stretches give rise to an A_1 and a B_1 normal mode; sketch these modes.

Ex. 33

This exercise is concerned with the normal modes of BH_3.



(a) State the point group of this molecule.

(b) Explain why the analysis of the normal modes of this molecule is made more convenient by the choice of the three sets of displacement vectors a, b and c shown above for the hydrogen atoms.

(c) Determine the irreducible representations of the normal modes of this molecule and verify that the total number of normal modes is as expected.

(d) Determine the symmetry of those normal modes involving just B–H stretches; sketch these modes.

Ex. 34

In methanal (formaldehyde) three of the normal modes are found to have the following wavenumber: 2783 cm^{-1} (mode 1, symmetry A_1), 1249 cm^{-1} (mode 2, symmetry B_1), 1167 cm^{-1} (mode 3, symmetry B_2). You may assume that for any normal modes not mentioned specifically the molecule is in the ground state.

(a) Draw a diagram, roughly to scale, showing the energy of the ground, first and second excited states for each normal mode (i.e. the states with $v = 0, 1, 2$). Label each state with the irreducible representation to which it belongs.

(b) By computing the appropriate triple direct products, determine whether or not the $v = 0 \rightarrow 1$ transition is allowed in the infra-red for each normal mode. State the frequency of any allowed transitions, and mark the transitions on your diagram.

(c) For each normal mode, determine whether or not the $v = 0 \rightarrow 2$ transition (i.e. the first overtone) is symmetry allowed in the infra-red. Compute the frequency of any allowed transitions, and mark the transitions on your diagram.

(d) Determine whether or not the following combination lines are symmetry allowed in the infra-red: (i) mode 1 $v_1 = 0 \rightarrow 1$ together with mode 2 $v_2 = 0 \rightarrow 1$; (ii) mode 1 $v_1 = 0 \rightarrow 1$ together with mode 3 $v_3 = 0 \rightarrow 1$; (iii) mode 2 $v_2 = 0 \rightarrow 1$ together with mode 3 $v_3 = 0 \rightarrow 1$. Compute the frequency of any allowed transitions.

Ex. 35

Consider again the normal modes of BH_3 found in Ex. 33. Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there i.e. how many of these features occur at the same frequency in the infra-red and Raman spectra?

Ex. 36

This exercise is concerned with the normal modes of NH_3.

(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes. (You may find it convenient to use a set of displacement vectors analogous to those uses in Ex. 33 for BH_3 in which the a set of vectors are along the line of the N–H bonds.)

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman.

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there i.e. how many of these features occur at the same frequency in the infra-red and Raman spectra?

(e) Determine the symmetry of those normal modes involving just N–H stretches, sketch these modes and state whether or not their fundamentals will be active in the infra-red or Raman.

Ex. 37

The organometallic species $Cr(CO)_6$ has octahedral coordination about the metal atom; for each ligand the Cr–C–O fragment is linear. The C–O stretches have a much higher frequency than any of the other bonds in this molecule and so, to a good approximation, can be considered separately.

(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes involving C–O stretches; sketch these modes.

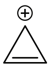
(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

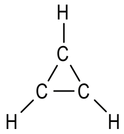
(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

(e) The experimental infra-red spectrum of this molecule shows a single strong absorbtion in the carbonyl region. Is this consistent with the assumed geometry?

Ex. 38

The cyclopropenyl cation, $[C_3H_3]^+$ has a structure in which the three carbon atoms, and the three hydrogen atoms, are arranged equilateral triangles.





(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes. (Think carefully about your choice of displacement vectors.)

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?

Ex. 39

The complex $[Ni(CN)_4]^{2-}$ has square-planar coordination about the metal atom; for each ligand the Ni–C–N fragment is linear. The C–N stretches have a much higher frequency than any of the other bonds in this molecule and so, to a good approximation, can be considered separately.

(a) State the point group of this molecule.

(b) Determine the symmetries of the normal modes involving C–N stretches; sketch these modes.

(c) Considering only the fundamental transition of each normal mode, draw up a table showing whether or not each transition is allowed in the infra-red and/or Raman. Does the rule of mutual exclusion apply?

(d) How many features would you expect to see in the infra-red spectrum, and how many in the vibrational Raman spectrum? How many coincidences are there?