LECTURE 1.
THE REDUCTION FORMULA AND PROJECTION OPERATORS

1.1 Revision of character tables for C_{2v}, C_{3v} and T_d

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	–1	–1	R_z	xy
B_1	1	–1	1	–1	x, R_y	xz
B_2	1	–1	–1	1	y, R_z	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	–1	R_z	
E	2	–1	0	(x, y) (R_x, R_y)	$(x^2–y^2, xy)$ (xz, yz)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2–x^2–y^2, x^2–y^2)$
T_1	3	0	–1	1	–1	(R_x, R_y, R_z)	
T_2	3	0	–1	–1	1	(x, y, z)	(xy, xz, yz)

Terminology:
Irreducible representations
Character ($\chi(R)$)
Symmetry elements (classes) *vs.* operations
Group order
Schoflies symbols
Mulliken symbols
Dimensionality
Linear functions, quadratic functions, cubic functions, *etc.*

1.2 The reduction formula

The reduction formula gives us a "handle turning" procedure for reducing the representation spanned by a set of basis functions. The formula looks abstract and somewhat impenetrable when first encountered, but is actually quite simple to use in practice.

EQUATION 1:

$$n(i) = \frac{1}{h}\sum_{R} \chi_r(R)\,\chi_i(R)$$

where:

$n(i)$	=	Number of times the i^{th} irreducible representation occurs in the representation r that we are aiming to reduce.
h	=	Order of group, *i.e.* the number of operations in the group (this is not always the same as the number of classes of operations).
$\sum_R$	=	This denotes a summation over all the operations R in the group. If there is more than one operation in a given class we must remember to include each operation in the summation.
$\chi_r(R)$	=	Character of the reducible representation r under the symmetry operation R.
$\chi_i(R)$	=	Character of the irreducible representation i under the symmetry operation R.

Consider for example the problem of finding the irreducible representations spanned by the set of 4 H 1s basis functions in the methane molecule. Each operation is represented by a (4×4) matrix, but we are only interested in the diagonal sum of the transformation matrix.

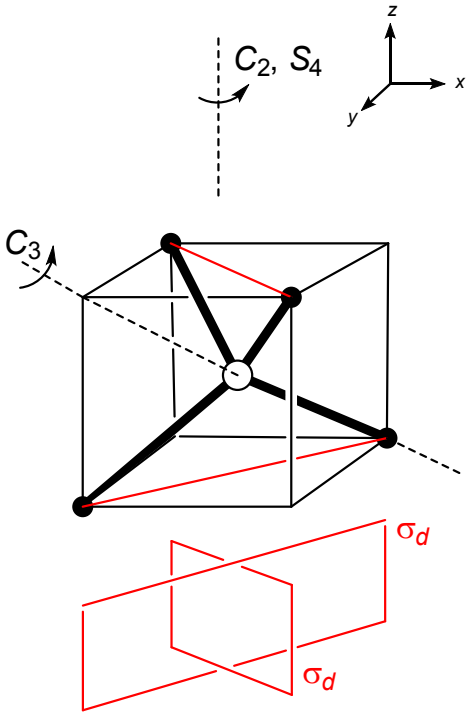


Figure 1. Symmetry operations for the tetrahedron.

Remembering that it is only when an atom is unshifted that it can contribute to this sum it is easily seen that the characters $\chi_r(R)$ are given simply by the number of H atoms that are unshifted under each symmetry operation. Moreover, it is always the case that the character is the same for each symmetry operation of a given class so we need inspect the effects of only one operation within each class.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	–1	–1		
E	2	–1	2	0	0		$(2z^2–x^2–y^2, x^2–y^2)$
T_1	3	0	–1	1	–1	(R_x,R_y,R_z)	
T_2	3	0	–1	–1	1	(x,y,z)	(xy, xz, yz)
Γ(H1s)	**4**	**1**	**0**	**0**	**2**		

$n(A_1)$ = 1/24{(4×1×1) + (1×1×8) + (0×1×3) + (0×1×6) + (2×1×6)} = 1
$n(A_2)$ = 1/24{(4×1×1) + (1×1×8) + (0×1×3) + [0×(–1)×6] + [2×(–1)×6)] = 0
$n(E)$ = 1/24{(4×2×1) + [1×(–1)×8] + (0×2×3) + (0×0×6) + (2×0×6)} = 0
$n(T_1)$ = 1/24{(4×3×1) + (1×0×8) + [0×(–1)×3] + (0×1×6) + [2×(–1)×6]} = 0
$n(T_2)$ = 1/24{(4×3×1) + (1×0×8) + [0×(–1)×3] + [0×(–1)×6] + (2×1×6)} = 1

Γ(H1s) = $A_1 + T_2$

1.3 Some notes about application of the reduction formula

- In evaluating the summation given in Equation 1 we deal with each class of symmetry operation in turn. We multiply the character for Γ(H1s) (appearing underneath the character table) by the character for the relevant irreducible representation and then multiply by the number of operations in a given class. Thus each term is a product of three numbers, and will be zero if any of the three is zero.
- We can check that we have obtained the correct answer by verifying that the characters for the irreducible representations we have derived add up to the set of characters for the representation we are trying to reduce.
- The $n(i)$ must always be zero or integral. If they are not something has gone wrong somewhere!
- The number of symmetry adapted function must always be the same as the number of basis functions. In the present case we start with 4 basis functions and end up with A_1 + T_2 irreducible representations. The latter is 3-fold degenerate so there are 4 symmetry adapted combinations.

1.4 The form of the SALCS for a tetrahedral system and the MO diagram for CH_4

Inspection of the character table for the T_d point group reveals that the *p* orbitals on the central atom of a molecule such as CH_4 transform like t_2. It is therefore possible to deduce the form of the t_2 SALCS simply by matching the phases of the H1s orbitals to the phases (signs) of the three orthogonal *p* orbitals. Likewise it is trivially obvious that the a_1 SALC must be simply a completely in-phase combination of H 1*s* orbitals. In constructing the MO diagram for CH_4 we then allow the C 2*s* orbital to interact with the a_1 H 1*s* SALC and each C 2*p* orbital to interact with its matching t_2 SALC. We thus arrive at the familiar MO diagram for methane, with two occupied MOs of different energy. This description of the molecule is confirmed by the observation of two bands in the photoelectron spectrum.

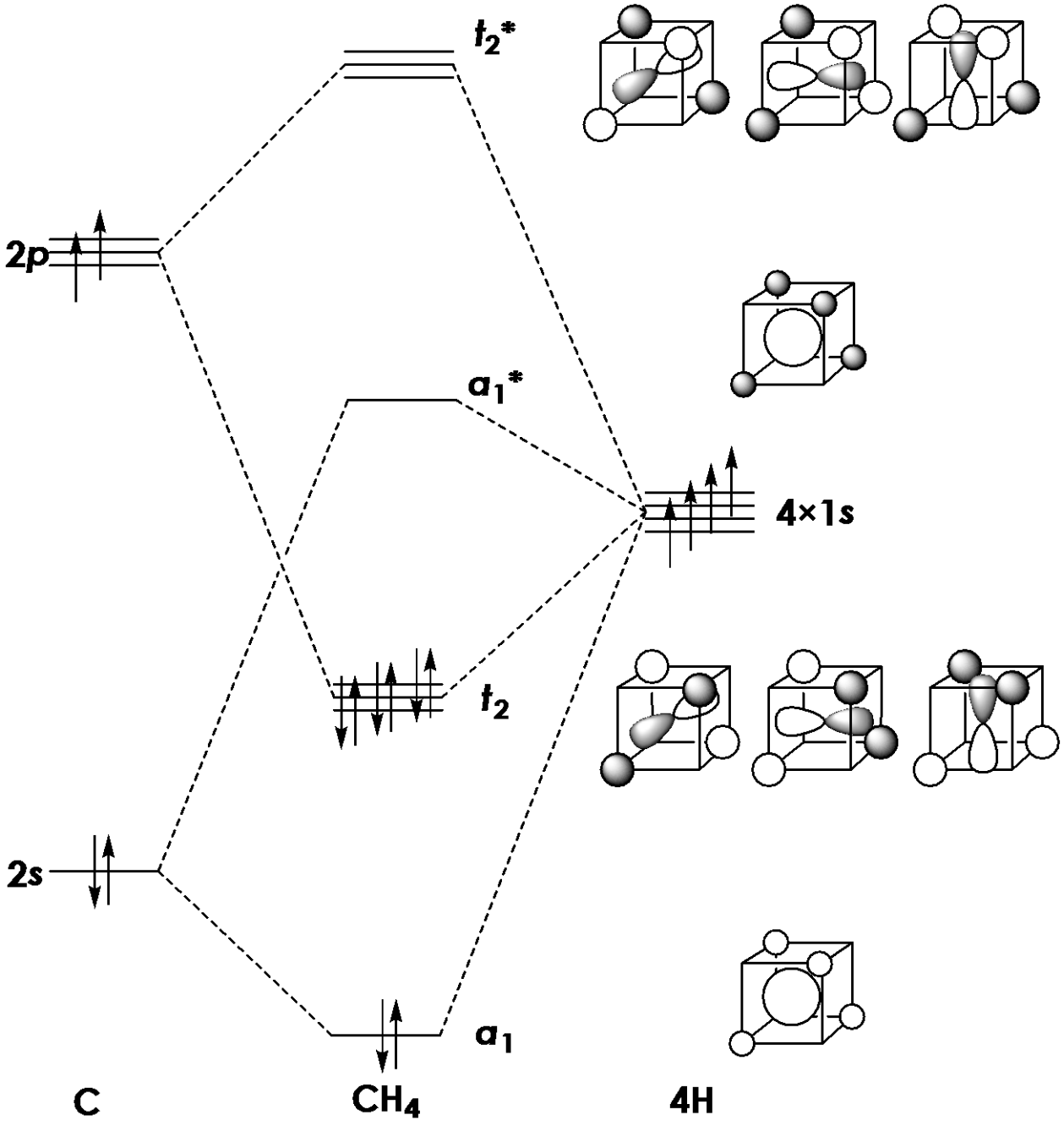


Figure 2. The molecular orbital diagram for CH_4, showing the form of the SALCS.

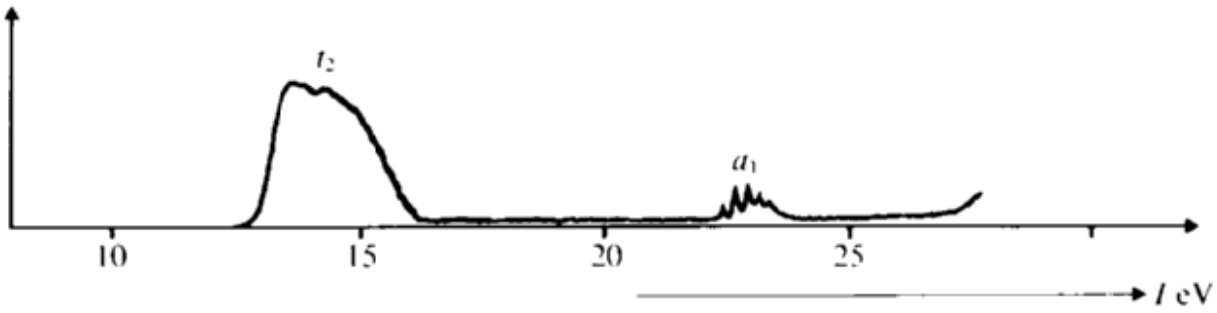


Figure 3. The photoelectron spectrum of CH_4.

1.5 Use of projection operators to deduce the form of SALCS

It is not always possible to deduce the form of a SALC by "matching" to a central atom orbital of appropriate symmetry. There exists however a handle turning group theoretical procedure to deduce the form of the SALCS. This uses so-called projection operators.

EQUATION 2:

$$\psi_i^{SALC} = P_i\phi_a = \sum_R R\phi_a \chi_i(R)$$

where:

ψ_i^{SALC}	=	the wavefunction for the SALC belonging to the i^{th} irreducible representation.
P_i	=	the projection operator for the i^{th} irreducible representation.
ϕ_a	=	one of the basis functions.
$\sum_R$	=	a summation over all operations in the group.
$R\phi_a$	=	the atomic basis function generated by the operation of R on ϕ_a
$\chi_i(R)$	=	the character of the i^{th} irreducible representation under R.

The projection operator technique is often tedious to apply because the summation extends over each operation and it is necessary to inspect the effects of each operation in turn. Thus for the T_d point group we would have to inspect the effects of all 24 operations in turn!

A simple application of the technique is to derivation of the SALCs formed by the H 1*s* orbitals in NH_3. It is simple to show by application of the reduction formula that the SALCs in this case span irreducible representations $a_1 + e$. The effects of the symmetry operations on the basis functions h_1, h_2 and h_3 which can be seen in Figure 4 are summarised in the table below, which also gives the characters $\chi_i(R)$.

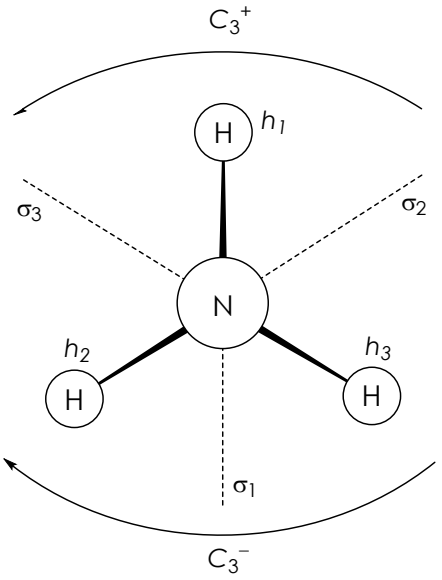


Figure 4. Symmetry operations for NH_3 viewed down the C_3 axis.

C_{3v}	E	C_3^+	C_3^-	σ_1	σ_2	σ_3
A_1	1	1	1	1	1	1
A_2	1	1	1	−1	−1	−1
E	2	−1	−1	0	0	0
Rh_1	h_1	h_2	h_3	h_1	h_3	h_2
Rh_2	h_2	h_3	h_1	h_3	h_2	h_1
Rh_3	h_3	h_1	h_2	h_2	h_1	h_3

Thus we have the following SALCS:

$\psi_{A_1} = h_1 + h_2 + h_3 + h_1 + h_2 + h_3$ (from h_1 basis function)
$\psi_{A_1} = h_2 + h_3 + h_1 + h_3 + h_2 + h_1$ (from h_2 basis function)
$\psi_{A_1} = h_3 + h_1 + h_2 + h_2 + h_1 + h_3$ (from h_3 basis function)

These can all be expressed in the same normalised form:

$$\psi_{A_1} = (1/\sqrt{3})\,(h_1+h_2+h_3)$$

Next consider the A_2 irreducible representation:

$\psi_{A_2} = h_1 + h_2 + h_3 - h_1 - h_2 - h_3 = 0$ (from h_1 basis function)
$\psi_{A_2} = h_2 + h_3 + h_1 - h_2 - h_3 - h_1 = 0$ (from h_2 basis function)
$\psi_{A_2} = h_3 + h_1 + h_2 - h_2 - h_1 - h_3 = 0$ (from h_3 basis function)

The projected function is zero in each case, as expected because the A_2 irreducible representation is not covered by the basis of 3 H1s functions.

Finally for the E irreducible representation:

$\psi_{E(1)} = (2h_1 - h_2 - h_3)$ (from h_1 basis function)
$\psi_{E(2)} = (2h_2 - h_3 - h_1)$ (from h_2 basis function)
$\psi_{E(3)} = (2h_3 - h_1 - h_2)$ (from h_3 basis function)

It will be seen that 3 different *E* SALCS have been generated but these are not orthogonal to each other. This is a problem with projection operators. However if we subtract the 3rd SALC from the 2nd we obtain the function:

$$\psi_{E(4)} = \psi_{E(2)} - \psi_{E(3)} = (2h_2 - h_3 - h_1) - (2h_3 - h_1 - h_2) = 3h_2 - 3h_3$$

$\psi_{E(4)}$ is orthogonal to $\psi_{E(1)}$ and we can finally write out the wavefunctions for *E* SALCS in the normalised forms:

$$\psi_E = (1/\sqrt{6})\ (2h_1 - h_2 - h_3)$$
$$= (1/\sqrt{2})\ (h_2 - h_3)$$

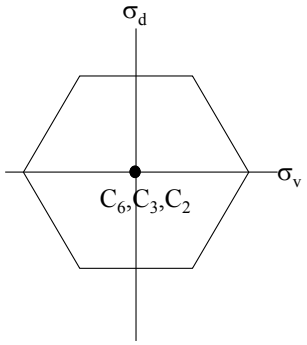
These functions match up with two orthogonal *p* orbitals.

1.6 The π type MOs of C_6H_6

The character table for the D_{6h} point group of C_6H_6 is very unfriendly and any problem involving its use would appear to be daunting! However we can derive the irreducible representations of the π type MOs of C_6H_6 using the character table for the much friendlier group C_{6v}, which is a sub-group of D_{6h} lacking the σ_h mirror plane. C_{6v} has half the numbers of classes of operation of D_{6h} and half the number of irreducible representations. Thus each irreducible representation of C_{6v} may be derived from two different irreducible representations of D_{6h}, as detailed in tables of descent in symmetry (whose use will be further explored next week). To decide on which of the two alternatives to adopt, we need merely inspect the character table for D_{6h} and choose the alternative which has a negative character under the σ_h mirror plane operation: since the $p(\pi)$ functions all change sign under this operation any SALCs derived from them must do also.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	1	–1	–1	1	1	1	1	–1	–1
B_{1g}	1	–1	1	–1	1	–1	1	–1	1	–1	1	–1
B_{2g}	1	–1	1	–1	–1	1	1	–1	1	–1	–1	1
E_{1g}	2	1	–1	–2	0	0	2	1	–1	–2	0	0
E_{2g}	2	–1	–1	2	0	0	2	–1	–1	2	0	0
A_{1u}	1	1	1	1	1	1	–1	–1	–1	–1	–1	–1
A_{2u}	1	1	1	1	–1	–1	–1	–1	–1	–1	1	1
B_{1u}	1	–1	1	–1	1	–1	–1	1	–1	1	–1	1
B_{2u}	1	–1	1	–1	–1	1	–1	1	–1	1	1	–1
E_{1u}	2	1	–1	–2	0	0	–2	–1	1	2	0	0
E_{2u}	2	–1	–1	2	0	0	–2	1	1	–2	0	0

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$
A_1	1	1	1	1	1	1
A_2	1	1	1	1	–1	–1
B_1	1	–1	1	–1	1	–1
B_2	1	–1	1	–1	–1	1
E_1	2	1	–1	–2	0	0
E_2	2	–1	–1	2	0	0
$\Gamma(\pi)$	6	0	0	0	2	0



Application of the reduction formula only involves consideration of the E and σ_v operations:

$$n(A_1) = 1/12\,\{(6\times1\times1) + (2\times1\times3)\} = 1$$
$$n(A_2) = 1/12\,\{(6\times1\times1) + [2\times(-1)\times3]\} = 0$$
$$n(B_1) = 1/12\,\{(6\times1\times1) + (2\times1\times3)\} = 1$$
$$n(B_2) = 1/12\,\{(6\times1\times1) + [2\times(-1)\times3]\} = 0$$
$$n(E_1) = 1/12\,\{(6\times2\times1) + (2\times0\times3)\} = 1$$
$$n(E_2) = 1/12\,\{(6\times2\times1) + (2\times0\times3)\} = 1$$

We next consider the table of descent in symmetry:

D_{6h}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
C_{6v}	A_1	A_2	B_2	B_1	E_1	E_2	A_2	A_1	B_1	B_2	E_1	E_2

Consideration of the requirement that the character under σ_h is negative leads to the following correlations for the $p(\pi)$ orbitals:

$$A_1 \rightarrow A_{2u}$$
$$B_1 \rightarrow B_{2g}$$
$$E_1 \rightarrow E_{1g}$$
$$E_2 \rightarrow E_{2u}$$

Thus the **$p(\pi)$ SALCS for C_6H_6 are A_{2u} + B_{2g} + E_{1g} + E_{2u}**. Note that this analysis tells nothing at this stage about the form of the SALCs or about their relative energy ordering. It is left as an exercise to derive the form of the SALCS and to deduce their relative energies.

PROBLEMS

1. Apply the reduction formula to derive the irreducible representations of the SALCS formed by the 3 H1*s* orbitals in NH_3. Hence construct an MO diagram for this molecule.

2. Use projection operators in C_{6v} to deduce the form of the SALCs for the π-type C 2*p* orbitals in C_6H_6. Ingenuity will be needed to find the form of the pairs of orthogonal doubly degenerate SALCs.

3. Use the reduction formula to derive the irreducible representations spanned by the π-type C 2*p* orbitals in C_4H_4. You can use either the character table for D_{4h} or C_{4v}.