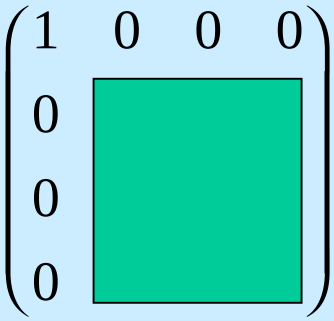
Reduction of representations

Our 4-dimensional matrix representation is block-diagonal; all the representatives have the form shown.



Implication: the symmetry operations of $\mathbf{C_{3v}}$ never mix s_N with the other functions. Hence, we can split the representation into two, one part for s_N, the other for (s_A,s_B,s_C).

This splitting into bases of lower dimension is called **reduction** of the representation. We write

$$\Gamma^{(4)} = \Gamma^{(3)} \oplus \Gamma^{(1)}$$

Direct sum - constructing a space (matrix) of higher dimension from matrices of lower dimension.

The representation then takes the form:

$$\begin{array}{ccc}
E & C_3^+ & C_3^- \\
1 & 1 & 1 \\
\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \\
\sigma_v & \sigma_v' & \sigma_v'' \\
1 & 1 & 1 \\
\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}
\end{array}$$

The 1-d representation of numbers, 1 in each case, is called the **unfaithful representation**. (In it, **all** classes have the same character.)

NB Characters of representatives of the same class are still the same.

Question: Is $\Gamma^{(3)}$ still reducible?

Answer: Yes. The transformation $\left(s_N, s_A, s_B, s_C\right) \rightarrow \left(s_N, s_1, s_2, s_3\right)$

leads to the representatives

$$\left.\begin{array}{lll}
\mathbf{D}(E)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix} &
\mathbf{D}\left(C_3^+\right)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-\frac{1}{2}&-\frac{1}{2}\\0&0&\frac{3}{2}&-\frac{1}{2}\end{pmatrix} &
\mathbf{D}\left(C_3^-\right)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-\frac{1}{2}&\frac{1}{2}\\0&0&-\frac{3}{2}&-\frac{1}{2}\end{pmatrix} \\
\mathbf{D}\left(\sigma_v\right)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&-1\end{pmatrix} &
\mathbf{D}\left(\sigma_v^{'}\right)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-\frac{1}{2}&\frac{1}{2}\\0&0&\frac{3}{2}&\frac{1}{2}\end{pmatrix} &
\mathbf{D}\left(\sigma_v^{''}\right)=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&-\frac{1}{2}&-\frac{1}{2}\\0&0&-\frac{3}{2}&\frac{1}{2}\end{pmatrix}
\end{array}\right\}$$

Corr. to

$$\Gamma^{(4)} = \Gamma^{(2)} \oplus \Gamma^{(1)} \oplus \Gamma^{(1)}$$

We can now give an exact meaning to the vague notion that s_1 "has the same symmetry as" s_N - <u>both can act as a basis of the same matrix representation</u>.

It turns out that our $\Gamma^{(2)}$ cannot be reduced further - the representations we have found are ***irreducible representations****, or* ***irreps****.*

Irreps are given labels (symmetry species) based on the list of characters in the representation.

One-dimensional irreps are either A or B. (+1 under rotation --> A; -1 --> B)

Two-dimensional irreps are E. Three-dimensional irreps are T.

Subscripts indicate further aspects of variation in behavior (e.g. under reflection).

Here we have a representation with characters:

1	1	1	1	1	1	A_1
2	-1	-1	0	0	0	E

We say that the basis (s_N, s_A, s_B, s_C) **spans** the irreps $A_1 \oplus E$

The character table is the list of all possible irreps of a group.

The use of such tables is based on reducing a particular representation (determined by choice of basis) into irrep form (i.e. finding out which irreps the basis **spans**).

This can sometimes be done “by inspection”: for more complicated cases, mathematical tools are needed.

Tools of group theory: GOT and LOT

(For proofs see e.g. Atkins and Friedman, *Molecular Quantum Mechanics*)

Great Orthogonality Theorem:

$$\sum_R D_{ij}^{(l)}(R)^* D_{i'j'}^{(l')}(R) = \frac{h}{d_l}\delta_{ii'}\delta_{jj'}\delta_{ll'}$$

Group of order h; $\mathbf{D}^{(l)}(R)$ is the representative of operation R in a d_l-dimensional irrep of symmetry species $\Gamma^{(l)}$.

Usually the $D^{(l)}_{ij}(R)$ are not complex, but they can be.

Implication: Select any location in the matrix of one irrep and any location in the matrix of another irrep (which may be the same irrep); multiply the numbers in those two locations and sum over all the operations of the group - the answer is zero unless the same locations in the matrices of the same irrep are chosen, in which case the answer is h/d_l.

One important consequence of GOT: the number of symmetry species is equal to the number of classes.

Little Orthogonality Theorem:

$$\sum_R \chi^{(l)}(R)^* \chi^{(l')}(R) = h\delta_{ll'}$$

Consequently also, $\sum_c g(c)\left|\chi^{(l')}(c)^2\right| = h$

Number of members of class c

i.e. The sum of squares of characters of any irrep is equal to the order of the group.

Character Tables and Orbitals

The character under the identity operation E reveals the degeneracy of orbitals spanning a particular irrep:

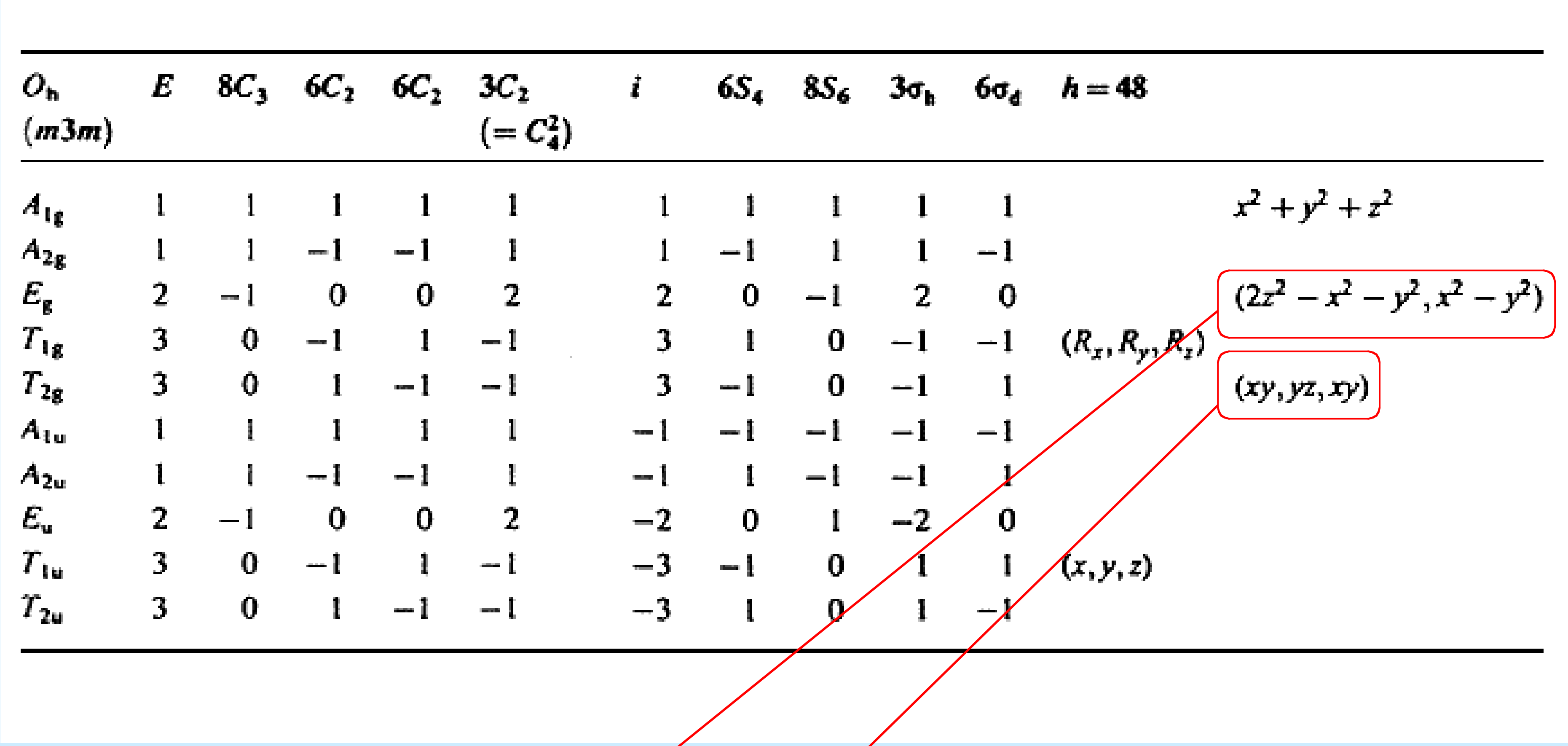
Ex.: In $\mathbf{C}_{3v}$ any orbital with symmetry label a_1 or a_2 is non-degenerate, any with label e is doubly degenerate. No orbital in this group may be more than doubly degenerate.

(look at self-test 15.2 on p440)

Individual orbitals: Sign under symmetry operation +1 indicates orbital unchanges, -1 indicates orbital changes sign. (0 indicates orbital maps onto somewhere else entirely.)

For degenerate orbitals (E or T) the characters are the sums of the characters for individual orbitals in a basis. E.g. If one is unchanged but the other reverses sign the character is zero.

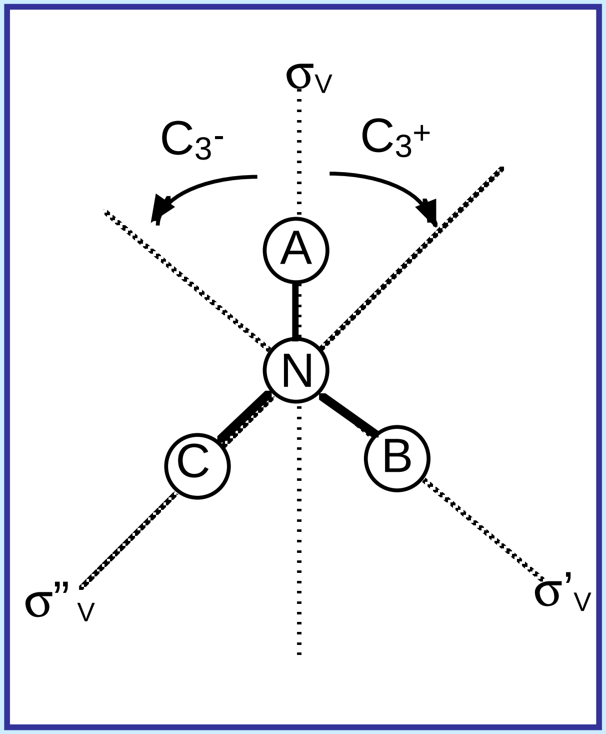
Orbitals on a central atom: An s orbital is always A_1 (totally symmetric); p_x, p_y, p_z transform as x, y, z; d_{xy}, d_{xz}, d_{yz}, d_{z^2}, $d_{x^2-y^2}$ transform as xy, xz, yz, $3z^2-r^2$, x^2-y^2.



O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_2$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$\boxed{(2z^2-x^2-y^2, x^2-y^2)}$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		$\boxed{(xy, yz, xy)}$
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

E_g

T_{2g}

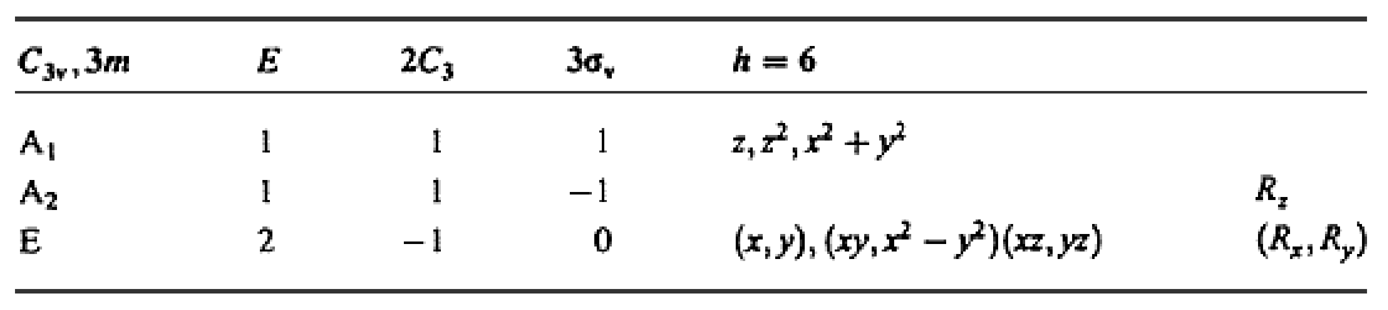


Linear combinations of orbitals:

$$\psi_1 = \psi_A + \psi_B + \psi_C$$

$$\left.\begin{array}{l}\chi(E)=1\\ \chi(C_3)=1\\ \chi(\sigma_v)=1\end{array}\right\} \Rightarrow A_1$$

Wavefunction ψ_1 is unchanged under all operations of **C_{3v}** *- we label it A_1, and say it belongs to the totally symmetric representation.*



$C_{3v}, 3m$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	-1		R_z
E	2	-1	0	$(x,y), (xy, x^2-y^2)(xz, yz)$	(R_x, R_y)

Irreps spanned by a given basis

With NH_3 we had an overall (reducible) representation for the basis (s_N,s_A,s_B,s_C) given by the traces of $\Gamma^{(4)}$.

$$\left.\begin{array}{ccc} E & 2C_3 & 3\sigma_v \\ 4 & 1 & 2 \end{array}\right\} \xrightarrow{\qquad\qquad} 2A_1+E$$

We can often tell "by inspection" how a representation can be broken down into irreps.

Alternatively (and necessarily for complex cases) this can be done by formula.

If $\Gamma = \sum_l a_l \Gamma^{(l)}$, then it can be shown using the LOT that $a_l = \frac{1}{h}\sum_c g(c)\chi^{(l)}(c)\chi(c)$

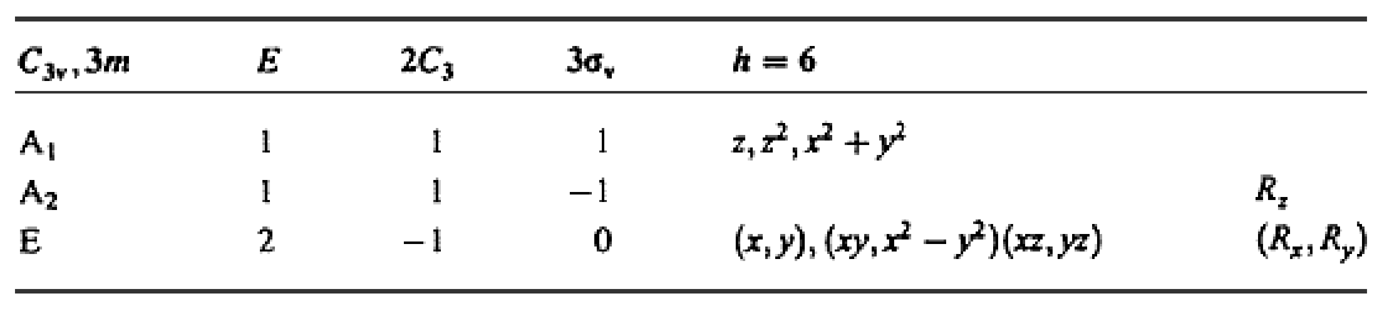
irrep l

number of times $\Gamma^{(l)}$ appears

reducible representation

irrep l

reducible representation



C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z, z^2, x^2+y^2	
A_2	1	1	-1		R_z
E	2	-1	0	$(x,y), (xy, x^2-y^2)(xz, yz)$	(R_x, R_y)

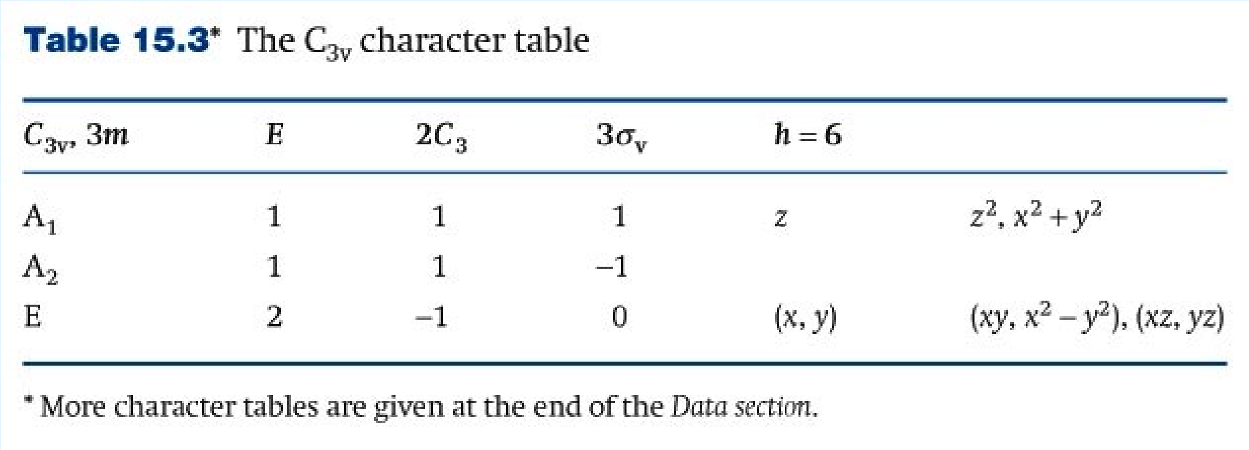


Table 15.3* The C_{3v} character table

C_{3v}, $3m$	E	$2C_3$	$3\sigma_v$	$h = 6$	
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	−1		
E	2	−1	0	(x, y)	$(xy, x^2-y^2), (xz, yz)$

* More character tables are given at the end of the *Data section*.

$$a_l = \frac{1}{h}\sum_c g(c)\chi^{(l)}(c)\chi(c)$$

E $2C_3$ $3\sigma_v$

Here

$$a_{A_1} = \frac{1}{6}(1\times1\times4+2\times1\times1+3\times1\times2)$$

$$= \frac{12}{6} = 2$$

whereas

$$a_{A_2} = \frac{1}{6}(1\times1\times4+2\times1\times1+3\times-1\times2)$$

$$= 0$$

Exercise: Calculate what a_E is.

Vanishing Integrals and Orbital Overlap

$$I = \int f_1 f_2 d\tau \neq 0 \Leftrightarrow f_1 f_2 \quad spans \quad A_1$$

(The totally symmetric irrep.)

(form of an overlap integral)

$$\langle f_1 | f_2 \rangle$$

(This implies that the integral does not change sign under any symmetry operation of the group - if it **does** change sign, the average over all space is zero.)

Method:

(1) Look up character table and write down the symmetry species of f_1 and f_2.

(2) The product of two functions spans the **direct product** of their irreps (formed by multiplying together corresponding elements).

Example: ammonia (again).

For $f_1=s_N$, $f_2=s_B-s_C$ (s_3 in prev. notation)

f_1	1	1	1	A_1
f_2	2	-1	0	E
$f_1 f_2$	2	-1	0	$A_1 \times E = E$

Does not contain A_1 - no overlap!

while for $f_1=s_N$, $f_2=s_A+s_B+s_C$ (s_1)

f_1	1	1	1	A_1
f_2	1	1	1	A_1
$f_1 f_2$	1	1	1	$A_1 \times A_1 = A_1$

This does contain A_1, and so this integral **may** be nonzero. (It may still be zero for reasons unrelated to group theory.)

Other kinds of integral: $I = \int f_1 f_2 f_3 d\tau \equiv \langle f_1 | f_2 | f_3 \rangle$

(For example a matrix element related to the probability of a spectroscopic transition.)

Example: $\left\langle d_{x^2-y^2} \middle| x \middle| d_{z^2} \right\rangle$ in O_h.

		E	$8C_3$	$6C_2$	$6C_2$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$
(A_1)	$f_1 = x^2 - y^2$	1	1	1	1	1	1	1	1	1	1	
(T_{1u})	$f_2 = x$	3	0	−1	1	−1	−3	−1	0	1	1	
(A_1)	$f_3 = 3z^2 - r^2$	1	1	1	1	1	1	1	1	1	1	
$A_1 \times T_{1u} \times A_1$	$= T_{1u}$	3	0	−1	1	−1	−3	−1	0	1	1	

Spectroscopic example: $\mu_{z,fi} = \langle f | \mu_z | i \rangle = -e \langle f | z | i \rangle$

Spectroscopic selection rules are often determined by symmetry.

See example on p447 of Atkins: Can an electron in an a_1 orbital on H_2O make an electric dipole transition to a b_1 orbital? In this case we need to consider x, y, and z components.

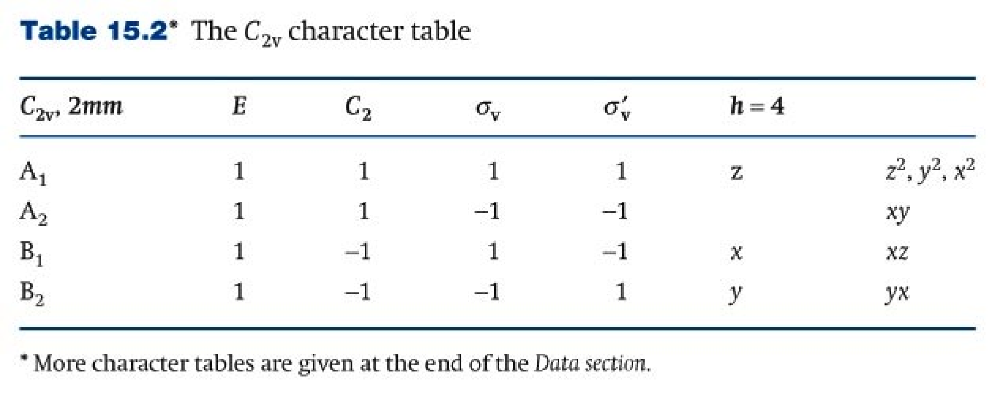


Table 15.2* The C_{2v} character table

C_{2v}, 2mm	E	C_2	σ_v	σ_v'	$h=4$	
A_1	1	1	1	1	z	z^2, y^2, x^2
A_2	1	1	−1	−1		xy
B_1	1	−1	1	−1	x	xz
B_2	1	−1	−1	1	y	yx

* More character tables are given at the end of the *Data section*.

$$\langle b_1 | x | a_1 \rangle = B_1 \times B_1 \times A_1 = A_1$$
$$\langle b_1 | y | a_1 \rangle = B_1 \times B_2 \times A_1 = A_2$$
$$\langle b_1 | z | a_1 \rangle = B_1 \times A_1 \times A_1 = B_1$$

Only the x-component is allowed; x-polarized light can induce this transition.

Symmetry-adapted linear combinations and their uses

Symmetry-adapted linear combination - combination of orbitals which is adapted to transform according to a particular irrep. (Example: orbitals (s_N, s_1, s_2, s_3) for NH_3.) Derivation uses the GOT and *projection operators* (a tool for generating all the members of a basis, given a single member) - see e.g. Atkins and Friedman, *Molecular Quantum Mechanics.*

Generation method:

$$p^{(l)} f_j = \underbrace{\frac{d_l}{h} \sum_R \chi^{(l)}(R)^* R f_j}_{\text{this is easier to understand by example}} = \ldots = \sum_i f_i^{(l)}$$

projection operator

basis function

linear combination of f_i corresponding to irrep l

Example: NH_3. The s-orbital basis spans $2A_1 + E$. We want to construct symmetry-adapted linear combinations. (Here all characters are real.)

(1) Draw up table headed by basis set and showing in columns the effect of the operations. (Headings are f_j and entries are Rf_j.)

(2) Multiply each member of the column by the character of the corresponding operation. (This gives $\chi(R)Rf_j$ at each location.)

(3) Add the entries within each column. (Giving $\Sigma_R\, \chi(R)Rf_j$.)

(4) Multiply by the dimension of the irrep and divide by the order of the group.

Step 1: (h=6)

R	s_N	s_A	s_B	s_C
E	s_N	s_A	s_B	s_C
C_3^+	s_N	s_C	s_A	s_B
C_3^-	s_N	s_B	s_C	s_A
σ_v	s_N	s_A	s_C	s_B
σ_v'	s_N	s_B	s_A	s_C
σ_v''	s_N	s_C	s_B	s_A

Then

For A_1, d=1 and $\chi(R)$=1 for all operations R.

1st column gives

$$\frac{1}{6}\left(1\times s_N+1\times s_N+1\times s_N+1\times s_N+1\times s_N+1\times s_N\right)=s_N$$

2nd column gives

$$\frac{1}{6}\left(1\times s_A+1\times s_B+1\times s_C+1\times s_A+1\times s_B+1\times s_C\right)$$

$$=\frac{1}{3}\left(s_A+s_B+s_C\right)$$

(and the last 2 cols also give this result)

For E, d=2 and $\chi(R)$=(2,-1,-1,0,0,0)

1st col $$\frac{2}{6}\left(2\times s_N-1\times s_N-1\times s_N+0+0+0\right)=0$$

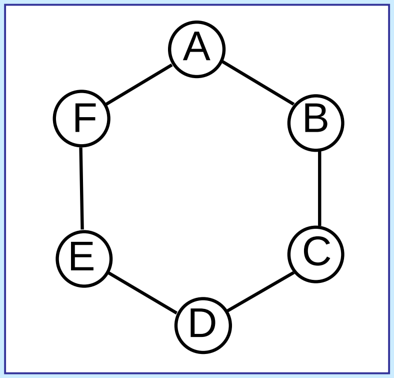
2nd col $$\frac{2}{6}\left(2\times s_A-1\times s_B-1\times s_C+2\times s_A-1\times s_B-1\times s_C\right)=\frac{1}{3}\left(2s_A-s_B-s_C\right)$$

3rd and 4th $$\frac{1}{3}\left(2s_B-s_C-s_A\right) \qquad \frac{1}{3}\left(2s_C-s_A-s_B\right)$$

not all linearly independent

We form a linear combination of the second two which is orthogonal to the first: $s_B - s_C$

Uses of symmetry-adaptation



Ex. 1: (1) Hűckel MOs of benzene

Use the p orbitals on the C atoms as a basis set for the π-system. Construct symmetry-adapted orbitals in D_{6h}.

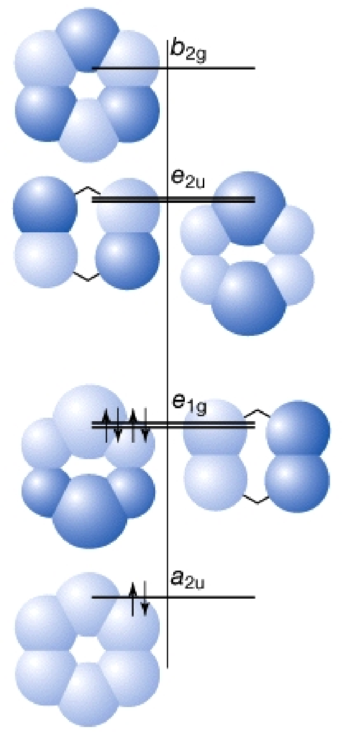
The Hűckel determinant factorizes (block-diagonalizes) because there are no nonzero matrix elements between MOs spanning different irreps.

$$b_{2g} = \frac{1}{\sqrt{6}}\left(p_A - p_B + p_C - p_D + p_E - p_F\right)$$

$$e_{2u} = \begin{cases} (a) & \dfrac{1}{\sqrt{12}}\left(2p_A - p_B - p_C + 2p_D - p_E - p_F\right) \\ (b) & \dfrac{1}{2}\left(p_B - p_C + p_E - p_F\right) \end{cases}$$

$$e_{1g} = \begin{cases} (a) & \dfrac{1}{\sqrt{12}}\left(2p_A + p_B - p_C - 2p_D - p_E + p_F\right) \\ (b) & \dfrac{1}{2}\left(p_B + p_C - p_E - p_F\right) \end{cases}$$

$$a_{2u} = \frac{1}{\sqrt{6}}\left(p_A + p_B + p_C + p_D + p_E + p_F\right)$$



Energy

$$\alpha - 2\beta$$

$$\left.\right\}\alpha - \beta$$

$$\left.\right\}\alpha + \beta$$

$$\alpha + 2\beta$$

Notes on solving symmetry-adapted secular determinants:

1-dimensional irreps lead to “1x1 determinants” and are straightforward - i.e. you don’t actually need to solve a determinant.

2-dimensional irreps lead to 2x2 determinants, i.e. quadratic equations. However, these turn out to be diagonal here because of reflection symmetry differences.

Example: $\left\langle a_{2u} \middle| \hat{\mathcal{H}} \middle| a_{2u} \right\rangle = \frac{1}{6}\left\langle p_A + p_B + \ldots + p_F \middle| \hat{\mathcal{H}} \middle| p_A + p_B + \ldots + p_F \right\rangle = \ldots = \alpha + 2\beta$

Homework questions:

(1) What is the total ground state energy and ground state symmetry of benzene? (Remember that the symmetry of a **state** is the product of the symmetries of the occupied orbitals, but written with an initial capital letter rather than lowercase.)

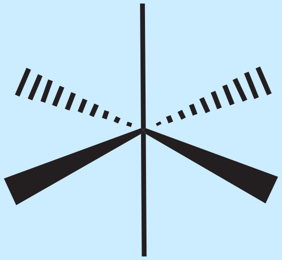
(2) By multiplying out the integrals and using the usual assumptions of Hückel theory, verify that: (1) $\left\langle b_{2g} \middle| \hat{\mathcal{H}} \middle| b_{2g} \right\rangle = \alpha - 2\beta$

(2) $\left\langle a_{2u} \middle| \hat{\mathcal{H}} \middle| b_{2g} \right\rangle = 0$

Ex.2: Transition metal complexes

Another important application of symmetry-adapted functions is in ligand field theory.

(Cf. Advanced Inorganic Chemistry.) Consider a set of transition metal d-orbitals interacting with σ-orbitals on (Lewis base) ligands disposed octahedrally around the metal center.



d orbitals: 5d --->

$$\begin{cases} 2E_g & d_{z^2}, d_{x^2-y^2} \\ 3T_{2g} & d_{xy}, d_{xz}, d_{yz} \end{cases}$$

while the σ-orbitals can be shown by the foregoing methods to span $A_{1g}+E_g+T_{1u}$ in the point group $\mathbf{O}_h$.

SALCs of ligand orbitals (which we'll call λ) only:

$$\psi(A_{1g}) = \frac{1}{\sqrt{6}}(\lambda_1+\lambda_2+\lambda_3+\lambda_4+\lambda_5+\lambda_6)$$

$$\psi(E_g) = \begin{cases} (a) & \dfrac{1}{\sqrt{12}}(2\lambda_5+2\lambda_6-\lambda_1-\lambda_2-\lambda_3-\lambda_4) \\ (b) & \dfrac{1}{2}(\lambda_1+\lambda_2-\lambda_3-\lambda_4) \end{cases}$$

$$\psi(T_{1u}) = \begin{cases} (a) & \dfrac{1}{\sqrt{2}}(\lambda_1-\lambda_2) \\ (b) & \dfrac{1}{\sqrt{2}}(\lambda_3-\lambda_4) \\ (c) & \dfrac{1}{\sqrt{2}}(\lambda_5-\lambda_6) \end{cases}$$

Now consider linear combinations of the SALCs and the d-orbitals of the same symmetry type:

Considering linear combinations of the SALCs and the d-orbitals of the same symmetry type:

$$a_{1g} = \psi\left(A_{1g}\right)$$

$$e_g = \begin{cases} (a) & c_1\phi\left(d_{z^2}\right) + c_2\psi\left(E_{g,a}\right) \\ (b) & c_1'\phi\left(d_{x^2-y^2}\right) + c_2'\psi\left(E_{g,b}\right) \end{cases}$$

$$t_{1u} = \psi\left(T_{1u}\right)$$

$$t_{2g} = \begin{cases} (a) & d_{xy} \\ (b) & d_{xz} \\ (c) & d_{yz} \end{cases}$$

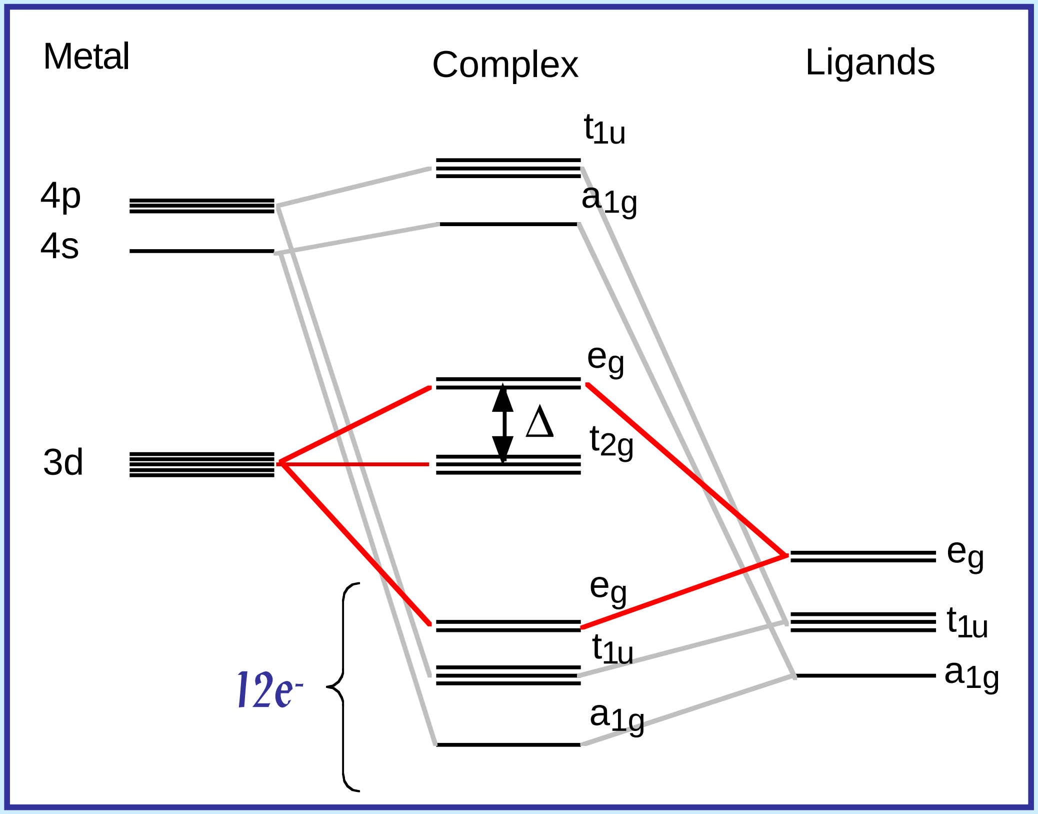
Leading to:

e_g $\left\{ \begin{array}{l} \text{bonding - mostly on ligands} \\ \text{antibonding - mostly on metal} \end{array} \right.$

a_{1g}, t_{1u} nonbonding - entirely on ligands

t_{2g} nonbonding - entirely on metal

The spin state of the complex is determined by the filling of the e_g antibonding and t_{2g} nonbonding orbitals on the metal (see next slide):



We consider an octahedral ML_6 metal-ligand complex with the (Lewis base) ligands each contributing two σ-type electrons.

With n electrons from the metal this leads to 12+n electrons overall.

12 electrons go into the low-lying a_{1g}, t_{1u}, and e_g bonding orbitals, leaving n to put in e_g and t_{2g}.

(For bookkeeping purposes we may treat these as if they were simply the metal electrons.)

Splitting between e_g and t_{2g} (the ligand field splitting Δ) can be strong or weak, leading to two cases:

(i) Strong-field case (Δ large) - t_{2g} orbitals filled completely before any electrons enter e_g.

(ii) Weak-field case (Δ small) - t_{2g} orbitals occupied singly, then e_g occupied singly, then electrons start pairing in t_{2g}.

Weak field <--> less spin-pairing <--> "high-spin" complexes.

Strong field <--> more spin-pairing <--> "low-spin" complexes.

The configurations t_{2g}^4, t_{2g}^5, t_{2g}^6, $t_{2g}^6e_g^1$ - low-spin - 2,1,0,1 unpaired spins
$t_{2g}^3e_g^1$, $t_{2g}^3e_g^2$, $t_{2g}^4e_g^2$, $t_{2g}^5e_g^2$ - high-spin - 4,5,4,3 unpaired spins
d^4 d^5 d^6 d^7 are the only ones for which the
ambiguity exists.