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Physical Methods in Inorganic Chemistry:

Electronic structure of inorganic and coordination compounds

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Copertina:
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www.graphiceye.it

Redazione e impaginazione:
Luigi Diego Di Donna

Finito di stampare nel dicembre 2018
Prima edizione dicembre 2018

ISBN 978-88-3369-034-6

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Preface

The collected lectures summarize the contents of the course "Physical methods in Inorganic Chemistry". I first time gave this course in 1981 at the University of Milano, then from 2000 to 2017 at the University of Milano-Bicocca.
The reader is here conducted, by using the symmetry properties of the molecules, to understand the chemical bond models of inorganic and coordination compounds.
Special emphasis was given to the crystal field theory and to the possibility of designing the energy level trends by electronic spectra and magnetic measurements. In 1981 this was a research topic, which then became routine investigation to be regularly teached.
When I am preparing the course the first time, my daughter Diletta was 3 years and she asked me each evening to repeat the lecture of the day after, sat on her small bad. In two years she was able and want to directly write on the transparency I reported here as cover, at that time used during the lecture. I dedicate this lecture collection her, who is now a young women, is an economist and fortunately she did not decide to follow the mother traces.

Introduction

The knowledge of the molecular nature of matter and of its changes constitutes at the present the necessary pathway to understand the chemical properties and the reactivity. The goal is, basing on molecular properties, also inclusive of the electronic properties, to reach more valuable and extensive laws in chemistry. The complexity of studying even a simple molecule suggests that approximate methods have to be used in the quantum mechanical treatment, taking also into account the macroscopic peculiarities of the chemicals, e.g. the shape.

In the case of inorganic molecules a convenient approximation comes from the symmetry, which constrains the electronic energies and the chemical bonds. Thus the present text will give special emphasis to the symmetry rules and will compare the use of symmetry operators with that of Hamiltonian operators. If possible, also the reactivity of the molecules will be rationalized in terms of symmetry properties. Electronic spectroscopy and magnetism will be used to provide experimental confirmation of the electronic energy levels.

The book is a collection of lectures, thus it cannot be considered exhaustive for the exam preparation; however it constitutes a useful guideline to understand the essential role of symmetry in approaching the chemical properties of inorganic and coordination compounds.

1. The electronic structure determination

This is a peculiar physical problem, and only later in the time, with respect to the atomic structure determination by physical scientists, the chemists investigated the molecular case of study. Expectedly the preferential object for chemists lies in the rationalization of the reactivity, where also a number of experimental data are considered. With this in mind the problem solving pathway is in the following:

I) The Schrodinger equation $H\Psi_n = E\Psi_n$ is very difficult to be resolved for a molecular system, being the E_n values

$$E_n = \langle \Psi_n^* | H | \Psi_n \rangle / \langle \Psi_n^* | \Psi_n \rangle$$

impossible to be calculated in the absence of H and Ψ_n expressions.

II) Hypotheses on Ψ_n and/or H have to be made in order to optimize Ψ_n, by ***variation*** or ***perturbation*** methods.

III) The eigenvalues of the Schrodinger equation are calculated by assuming approximated values of $\langle \Psi_n^* | H | \Psi_n \rangle$ **in agreement with the peculiar properties of the compound.**

IV) The calculated eigenvalues are compared with the experimental ones, derived from electronic spectra, in order to obtain structure-chemical property relations.

1.1 Variation method (molecular orbital linear combination of atomic orbitals, MO LCAO)

The hypothesis on Ψ_n is that it consists in a linear combinations of atomic orbitals

$$\Psi_j = \sum_r c_{jr} \phi_r$$

The hypothesis on *H* is absent

For a biatomic bielectronic system

$\Psi = C_1\varphi_1 + C_2\varphi_2$ $E = E(C_1 C_2)$

$E = \int \Psi^* H \Psi \, d\tau / \Psi^* \Psi \, d\tau =$

$\int (C_1\varphi_1 + C_2\varphi_2)^* H (C_1\varphi_1 + C_2\varphi_2) \, d\tau / (C_1\varphi_1 + C_2\varphi_2)^* (C_1\varphi_1 + C_2\varphi_2) \, d\tau =$

$\int [C_1\varphi_1^* H C_1\varphi_1 + C_1\varphi_1^* H C_2\varphi_2 + C_2\varphi_2^* H C_1\varphi_1 + C_2\varphi_2^* H C_2\varphi_2] / [C_1\varphi^*_1 C_1\varphi_1 + C_1^*\varphi_1 C_2\varphi_2 + C_2^*\varphi_2 C_1\varphi_1 + C_1^*\varphi_2 C_1\varphi_2] \, d\tau$

if $\int \varphi_i^* H \varphi_j \, d\tau = H_{ij}$ and $\int \varphi_i^* \varphi_j \, d\tau = S_{ij}$ $H_{21} = H_{12}$ $S_{21} = S_{12}$

H_{ii}= Coulomb integral

H_{ij}= resonance integral

S_{ij}= overlap integral

$E = C_1^2 H_{11} + 2 C_1 C_2 H_{12} + C_2^2 H_{22} / C_1^2 S_{11} + 2C_1 C_2 S_{12} + C_2^2 S_{22}$

The energies have to be minimum varying C_1 and C_2 (variation condition)

$dE/dc_1 = 0$ **(A)**

$dE/dc_2 = 0$

(A) is a two equation linear system, to derive $E_{1,2}$ and $C_{1,2}$ values.

$E_{1,2}$ are depending on the Coulomb, and on the Resonance and Overlap integrals, which are difficult to be calculated.

The system (A) becomes

$C_1 (H_{21} - E S_{21}) + C_2 (H_{12} - E S_{12}) = 0$

$C_1 (H_{21} - E S_{21}) + C_2 (H_{22} - E S_{22}) = 0$

One solution is $C_1 = C_2 = 0$ $\Psi = 0$

The other ones may be obtained from the following determinant:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

If the two atoms are the same

$(H_{11} - E)^2 - (H_{12} - S_{12}E)^2 = 0$

Given $S_{11} = S_{22} = 1$ $S_{12} = S_{21}$ $H_{11} = H_{22}$ $H_{12} = H_{21}$

$E_1 = H_{11} + H_{12}/1 + S_{12}$ $\quad E_1 = H_{11} - H_{12}/1 - S_{12}$

The determinant dimension is equal to the number of atomic orbitals used in the linear combination. The *E* energy values, substituted in (A) and combined with the additional equation $\mathbf{C_1^2 + C_2^2 = 1}$ **allow to calculate C coefficients**

$\underline{\mathbf{S}}_{\mathbf{ij}}$ **is obtained from the molecular structure**

$\mathbf{H_{ij}}$ **cannot be precisely determined for complex molecules and all methods denominated MO LCAO differ in the different approximations to calculate the** $\mathbf{H_{ij}}$ **integrals.**

The calculations of both energies and the atomic orbital coefficients can be done by solving an eigenvalues eigenvector equation.

The most simple approximation is the **Hückel approximation** essentially based on symmetry properties and frequently used for organic molecules

1.2 Hückel requirements

1) Resonance integrals = 0 for unconnected atoms,
   = **β** (scalar value) for connected ones
2) Coulomb integrals = **α** (scalar value)
3) Overlap integrals = 1 for connected atoms,
   = 0 for unconnected ones

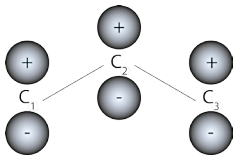
The results of calculation, obtained by solving the linear system (secular determinant), allow to express the energies as a function of α and β, then determined on the basis of the experimental absorption

1.2.1 The case of the allyl anion (MO-LCAO of π orbitals)

The H**ü**ckel method allows to obtain the energy of MO **π** orbitals, constituted by three p atomic orbitals of the three carbon atoms (Scheme 1), as eigenvalues of the secular determinant . At the same time the coefficients of the atomic orbitals within the molecular orbitals are obtained as eigenvectors. Being $\boldsymbol{\varphi}_1\,\boldsymbol{\varphi}_2\,\boldsymbol{\varphi}_3$ the three **π** atomic orbitals corresponding to the three carbon atoms, the three MO take the following increasing energies (eigenvalues):

$\boldsymbol{\alpha + \beta\,(2)^{1/2}} \qquad \boldsymbol{\alpha} \qquad \boldsymbol{\alpha - \beta\,(2)^{1/2}}$

The corresponding eigenvectors are:



Scheme 1 - The π system of the allyl radical anion

$1/2\varphi_1 + 1/(2)^{1/2}\varphi_2 + 1/2\varphi_3$ Bonding 2 electrons

$1/(2)^{1/2}\varphi_1 - 1/(2)^{1/2}\varphi_3$ Non Bonding 2 electrons

$1/2\varphi_1 - 1/(2)^{1/2}\varphi_2 + 1/2\varphi_3$ Antibonding empty

having increasing energy with the given order.

Basing on these results, the electron density on the allyl ion is concentrated on the terminal carbons, in fact:

If we define the electron density on the r atom as

$\mathbf{q_r = -\sum_j n_j c_{jr}^2}$ n_j is the electron number in the jth MO

c_{jr} is the coefficient of the rth atomic orbital (AO) in the jth MO

for the filled orbitals we obtain

$q_1 = -3/2$ $q_2 = -1$ $q_3 = -3/2$

The electronic charge located on the terminal C atoms is higher than on the intermediate one, thus we can expect that the reactions involving a dipolar interaction are oriented in a way as the terminal atoms interact with the positive pole of the reactant **e.g**

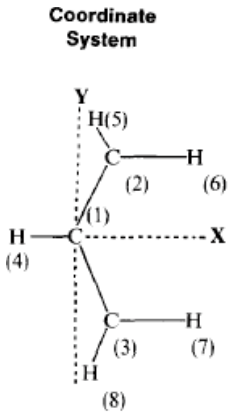
$CH_3\text{-}CH{=}CH_2 + R^-MgX^+ \rightarrow CH_2{=}CH\text{-}CH_2^{-\bullet} + RH + MgX^+$

$^{-\bullet}CH_2\text{-}CH{=}CH_2 + MgX^+ \rightarrow CH_2MgX\text{-}CH{=}CH_2$

1.3 Extended Hückel procedure

In this approximation for H_{ii} is taken the valence state ionization potential. H_{ij} is approximated by 1/2k Sij (Hii + Hjj) still obtained from the ionization data.

Tables 1 and 2 reports the atomic orbitals (AO) coefficient calculated by the extended Hückel approximation, for a single molecular orbital (MO), in the allyl ion (Scheme 2)



Scheme 2 - Allyl anion

Table 1- Extended Hückel coefficients for allyl anion

(*The vertical numbers correspond to A.O.'s and the horizontal ones to M.O.'s*)

A.O.'s ↓	M.O.'s → 1	2	3	4	5	6	7	8_π	9_π
1	−1.80	−0.00	0.24	−0.00	0.27	−0.00	0.25	−0.00	0.00
2	0.00	0.00	0.00	−0.00	0.00	−0.00	0.00	−0.97	−0.00
3	−0.51	−0.00	−0.35	0.00	−1.31	0.00	−0.24	0.00	−0.00
4	0.00	−1.28	−0.00	−0.68	−0.00	−0.29	−0.00	−0.00	−0.00
5	0.76	1.12	0.87	−0.38	−0.01	0.22	0.01	−0.00	0.00
6	−0.00	−0.00	−0.00	0.00	0.00	−0.00	0.00	0.65	−0.74
7	−0.43	−0.53	0.31	−0.58	0.30	0.62	−0.65	0.00	−0.00
8	−0.68	−0.13	0.58	−0.89	−0.53	−0.54	0.15	−0.00	0.00
9	0.76	−1.12	0.87	0.33	−0.01	−0.22	0.01	−0.00	−0.00
10	−0.00	−0.00	−0.00	0.00	−0.00	0.00	−0.00	0.65	0.74
11	−0.43	0.53	0.31	0.58	0.30	−0.62	−0.65	−0.00	−0.00
12	0.68	−0.13	−0.58	−0.89	0.53	−0.54	−0.15	0.00	0.00
13	0.28	0.00	−0.30	0.00	−1.17	0.00	−0.61	−0.00	0.00
14	−0.07	−0.48	−0.61	0.49	0.46	0.68	−0.59	0.00	0.00
15	0.15	−0.09	−0.75	0.82	−0.03	−0.55	0.61	−0.00	−0.00
16	0.15	0.09	−0.75	−0.82	−0.03	0.55	0.161	0.00	0.00

		10	11	12_π	13	14	15	16	17
C	1	−0.00	0.01	−0.00	0.00	−0.09	0.33	−0.00	0.48
C	2	−0.00	−0.00	−0.56	0.00	−0.00	−0.00	−0.00	0.00
	3	−0.00	0.33	−0.00	−0.00	−0.36	−0.17	−0.00	0.01
C	4	−0.49	−0.00	−0.00	−0.30	0.00	−0.00	0.16	−0.00
	5	−0.14	0.05	0.00	−0.03	−0.03	−0.20	0.44	0.36
C	6	−0.00	0.00	−0.40	−0.00	0.00	−0.00	0.00	0.00
	7	−0.12	−0.35	−0.00	0.37	−0.12	−0.12	0.01	−0.00
C	8	0.41	0.00	−0.00	0.07	0.29	−0.14	0.02	−0.01
	9	0.14	0.05	−0.00	0.03	−0.03	−0.20	−0.44	0.36
C	10	0.00	0.00	−0.40	0.00	−0.00	−0.00	0.00	0.00
	11	0.12	−0.35	−0.00	−0.37	−0.12	−0.12	−0.01	−0.00
	12	0.41	−0.00	−0.00	0.07	−0.29	0.14	0.02	0.01
	13	0.00	−0.40	−0.00	0.00	0.27	0.32	0.00	0.08
H	14	0.37	0.26	0.00	−0.15	0.27	−0.15	0.17	0.04
H	15	−0.07	−0.33	0.00	0.36	0.02	−0.23	0.19	0.05
H	16	0.07	−0.33	0.00	−0.36	0.02	−0.23	−0.19	0.05
H	17	−0.37	0.26	−0.00	0.15	0.27	−0.15	−0.17	0.04

M.O.'s 10 to 17 have $2e^-$
" 9 has $1e^-$
" 1 to 8 empty

Atomic Orbitals 1–4, 5–8, and 9–12 are carbon orbitals in the order 2*s*, $2p_z$, $2p_x$, $2p_y$ for each atom.
A.O.'s 13 to 17 are hydrogen 1*s*.

Table 2 - Energy of MO in allyl anion. M.O. 12

Is the lowest energy occupied molecular orbital with π symmetry. It is composed by - 0.40 $2p_z(C_2)$ - 0.56 $2p_z(C_1)$ - 0.40 $2p_z(C_3)$ E = -14.03 eV. This is in agreement with the results of the simple Hückel approach.

M.O.	Energy (eV)	Occ.
1	53.22	0
2	36.55	0
3	28.31	0
4	22.97	0
5	18.76	0
6	7.30	0
7	5.19	0
8	−4.63	0
9	−10.16	1
10	−12.67	2
11	−13.83	2
12	−14.03	2
13	−15.01	2
14	−15.96	2
15	−19.40	2
16	−22.83	2

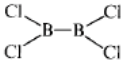
In all cases until now considered it is mandatory to select the atomic orbitals which have to be used in the linear combination and give the MO. At the maximum limit all AO can be employed. However it is not convenient to consider all the orbitals, because some of them give no relevant contribution to MO (see allyl anion Table of M.O and A.O.)

How to select those which give the maximum contribution? Let we consider that the MO shape should reflect the symmetry of the molecule and the AO have to be combined in agreement to this symmetry. In order to control the symmetry of MO we have to use the *Group Theory*.

WHY ?

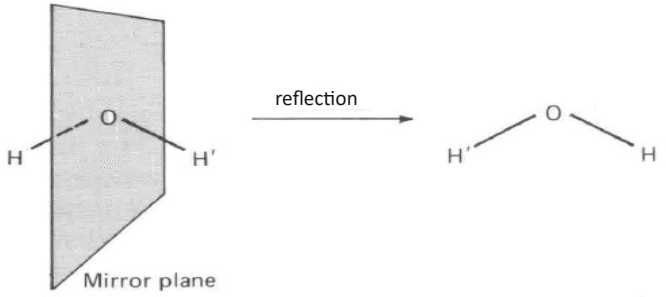
Let we consider firstly the symmetry operations of a molecule, which are the motions of the molecule reproducing it unchanged.

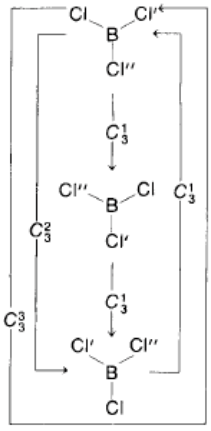
Table 3 - Symmetry elements and associated operations

Symmetry Operation	Symmetry Element	Symbol	Examples
identity		E	all molecules
reflection	plane	σ	H_2O, BF_3 (planar
inversion	point (center of symmetry)	i	
proper rotation	axis	C_n (n-order)	NH_3, H_2O
improper[a] rotation (rotation by $2\pi/n$ followed by reflection in plane perpendicular to axis)	axis *and* plane	S_n (n-order)	ethane, ferrocene (staggered structur

[a]Ferrocene is staggered and possesses an S_{10} improper rotation axis.

As example the clockwise rotation on the BCl_3 molecule and the reflection by a mirror plane for the H_2O molecule





Since the molecular energy is time invariant and independent of the position of the molecule, the Hamiltonian must be invariant under a symmetry operation. Thus any symmetry operation is associated to a symmetry operator which commutes with the Hamiltonian i.e $\boldsymbol{HR = RH}$ ($\boldsymbol{R}$ is the symmetry operator associated to the symmetry operation). If we take the wave equation $\boldsymbol{H\Psi_n = E\Psi_n}$ and multiply each side by the symmetry operator $\boldsymbol{R}$, we get

$\boldsymbol{HR\Psi_n = ER\Psi_n}$ thus $\boldsymbol{R\Psi_n}$ is a eigenfunction

Being $\boldsymbol{\Psi_n}$ normalized, it is normalized also $\boldsymbol{R\Psi_n}$, that is $\int \boldsymbol{R\Psi_n}$ $\boldsymbol{R\Psi_n d\tau = 1}$ $\boldsymbol{d\tau}$ is the coordinate space

$\boldsymbol{R\Psi_n = \pm 1\Psi_n}$

The molecular eigenfunction do not vary under the symmetry operators of the molecular point symmetry group, in analogy to the irreducible representation base function (see further details in the group theory chapter).

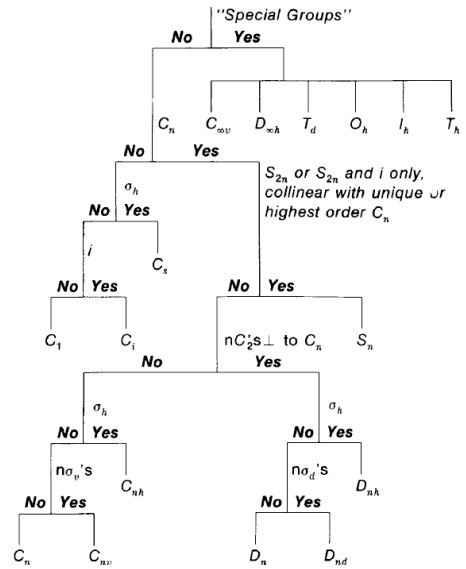
1.4 Group Theory

The point groups collect the possible symmetry operations for a given molecule.

Table 4 - Symmetry elements in some common point groups

Point Group	Symmetry Elements[a]	Examples
C_1	no symmetry	SiBrClFI
C_2	one C_2 axis	H_2O_2
C_{nh}	one *n*-fold axis and a horizontal plane σ_h which must be perpendicular to the *n*-fold axis	*trans*-$C_2H_2Cl_2$ (C_2h)
C_{2v}	one C_2 axis and two σ_v planes	H_2O, SO_2Cl_2, $SiCl_2Br_2$
C_{3v}	one C_3 axis and three σ_v planes	NH_3, CH_3Cl, $POCl_3$
D_{2h}	three C_2 axes all $\perp$, two σ_v planes, one σ_h plane, and a center of symmetry	N_2O_4 (planar)
D_{3h}	one C_3, three C_2 axes $\perp$ to C_3, three σ_v planes and one σ_h	BCl_3
D_{2d}	three C_2 axes, two σ_d planes and one S_4 (coincident with one C_2)	$H_2C{=}C{=}CH_2$
T_d	three C_2 axes $\perp$ to each other, four C_3, six σ and three S_4 containing C_2	CH_4, $SiCl_4$
[a] All point group possess the identity element, *E*.		

The ***followIng flow chart*** (Scheme 3) provides a systematic way to approach the classifications of molecules in their proper point groups, through identification of the symmetry operations.



Scheme 3 - Flow chart for assigning the group symmetry

1.4.1 Rules for the elements which constitute a group

1. the product of groups elements must still produce a group element.
For product is intended the combination of two operations, performed in a given order.

e.g. $C_2 \times \sigma_v$ or $\sigma_v \times C_2$

2. It is mandatory the existence of one operation commuting with the others and leaving them unchanged. This is the identity element

$E \times \sigma_2 = \sigma_2 \times E = \sigma_2$

3. The associative property must be applicable

AB(C) = A(BC)

4. Each element must have a reciprocal among the group elements. For each symmetry operation there will be another one which anneals the first. C_3 has C_3^2 as reciprocal element, thus $C_3 \times C_3^2 = E$

1.4.2 Group multiplication tables

Let we consider the ammonia molecule NH_3 and its symmetry operations E, $2C_3$, $3\sigma_v$ in C_{3v} group.
If we examine the combination of two symmetry operations the following matrix has been obtained.

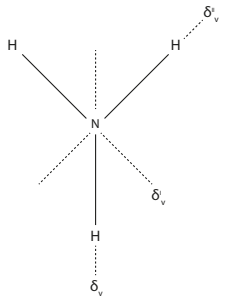
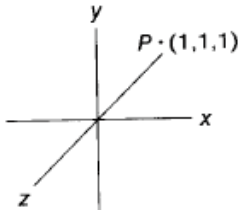


Table 5 - Combination of symmetry operations in NH_3

	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v'	C_3	C_3^2	E

The matrix elements (Table 5) indicate that the group can be decomposed in subgroups which are smaller groups of elements satisfying all the requirements of group theory, e.g E C_3 C_3^2, σ_v σ_v' σ_v''

1.4.3 Representation of symmetry operations by matrices



For the point P with cartesian *x y z* coordinates, when undergone the **identity operation**, the following matrix notation can be assumed

where the ternary matrix corresponds to the identity operation, ***X´ Y´ Z'*** represents the vector undergone the identity symmetry operation; that leads

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

X= X´ Y=Y´ Z=Z´

the result of the **operation σ_{yz}** is

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

That of **σ_{xz}** is

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

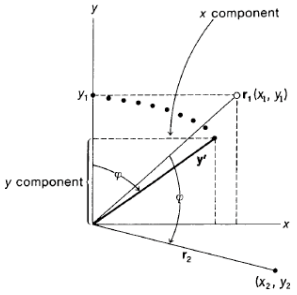
For the **inversion operation** the equation is

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

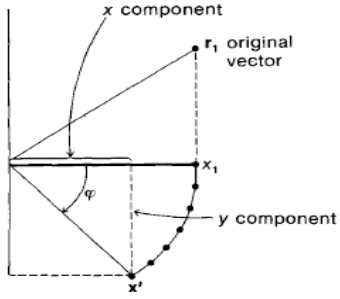
For the **clockwise rotation** of the point *x,y* (vector P) by a φ angle the rotation around the *z* axis does not change the *z* component

$$\begin{bmatrix} & & 0 \\ & & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

As for the *x* and *y* components each of them become a linear combination of both *x* and *y* components.

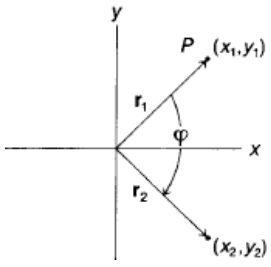


Rotation of the y coordinate



Rotation of the x coordinate

Rotation of the z coordinate



In total for both coordinates

$$x_2 = x_1 \cos \varphi + y_1 \sin \varphi$$
$$y_2 = -x_1 \sin \varphi + y_1 \cos \varphi$$

Writing in a matrix form these equations for a clockwise proper rotation of two coordinates

$$\begin{bmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$

For all three coordinates

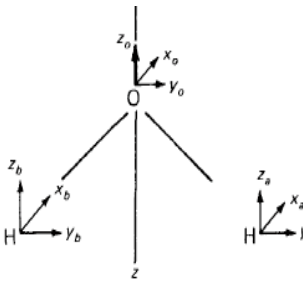
$$\begin{bmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

In the particular case of C_2 rotation

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The multiplication of two symmetry operations can be associated to the multiplication of the corresponding matrices

$$\sigma_{xz} \times \sigma_{xz} = E$$
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$



1.5 Irreducible representations

Let we consider a molecule belonging to C_{2v} symmetry group (e.g. the H_2O molecule) and the matrices representing the group operations based on the three cartesian coordinates

E **C_2** **σ_{xz}** **σ_{yz}**

$$E = \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix} \quad C_2 = \begin{bmatrix} -1 & & \\ & -1 & \\ & & 1 \end{bmatrix} \quad \sigma_{xz} = \begin{bmatrix} 1 & & \\ & -1 & \\ & & 1 \end{bmatrix} \quad \sigma_{yz} = \begin{bmatrix} -1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$$

Each matrix is composed by three one dimension matrices, which lie on the diagonal. If we are concerned with a one dimensional vector like {x, 0, 0}, only the first row of the total set of the four matrices is necessary to represent the behaviour of vector (1, -1, 1, -1). The row is called irreducible representation and takes the denomination of B_1. The irreducible representation for {0, y, 0} is (1, -1,-1, 1), labeled B_2, that for {0, 0, z} is (1, 1, 1, 1) labeled A_1.
If a different object (function or operation) is selected to be base of the C_{2v} symmetry operations, e.g. the C_2 rotation, also the behaviour of this object can be associated to an irreducible representation, in this case (1, 1, -1, -1), labeled A_2.

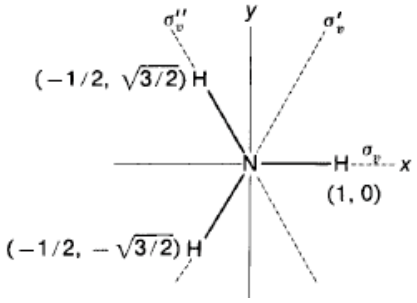
1.5.1 Character Table of groups

The table of Characters associated to the C_{2v} group is

	E	**C_2**	**σ_{xz}**	**σ'_{yz}**	
A_1	+1	+1	+1	+1	z
A_2	+1	+1	−1	−1	R_z
B_1	+1	−1	+1	−1	x, R_y
B_2	+1	−1	−1	+1	y, R_x

where the first column reports the name of the irreducible representation of the corresponding row and the last column indicates the base objects undergoing the symmetry transformations. As for the label of the irreducible representations:
A and B refer to representations which have one single function as base of the symmetry operations, A in particular has +1 character and B has -1 for the C_n operation; 1 and 2 refer to the symmetric and antisymmetric role of the the σ_{xz} operation.

Let we consider the NH_3 molecule and its symmetry operations



$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

For σ_v

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

For σ'_v and σ''_v

$$\sigma_v' = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_v'' = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

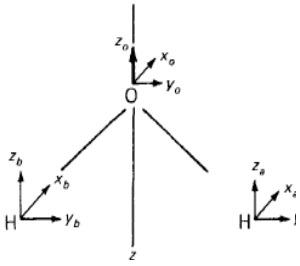
The table of characters for the C_{3v} group is

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	$(x, y)\ R_x R_y$	$(x^2 - y^2, xy)(xz, yz)$
I		II		III	IV

In the first column is the representation label, where E is a bidimensional representation, that means has a double base function.
In the second there are the trace of matrices, in the third and forth the base functions

1.5.2 Factoring the total representation into irreducible representation

Let we consider the H_2O molecule, having C_{2v} symmetry, and attribute 3 cartesian coordinates to each atom. Looking at the symmetry representations, for the **E** operation



$$\begin{bmatrix} 1 & & & & & & & & \\ & 1 & & & & & & & \\ & & 1 & & & & & & \\ & & & 1 & & & & & \\ & & & & 1 & & & & \\ & & & & & 1 & & & \\ & & & & & & 1 & & \\ & & & & & & & 1 & \\ & & & & & & & & 1 \end{bmatrix} \begin{bmatrix} x_o \\ y_o \\ z_o \\ x_a \\ y_a \\ z_a \\ x_b \\ y_b \\ z_b \end{bmatrix} = \begin{bmatrix} x_o' \\ y_o' \\ z_o' \\ x_a' \\ y_a' \\ z_a' \\ x_b' \\ y_b' \\ z_b' \end{bmatrix}$$

For the C_2 operation

$$\begin{bmatrix} -1 & & & & & & & & \\ & -1 & & & & & & & \\ & & 1 & & & & & & \\ & & & 0 & 0 & 0 & -1 & 0 & 0 \\ & & & 0 & 0 & 0 & 0 & -1 & 0 \\ & & & 0 & 0 & 0 & 0 & 0 & 1 \\ & & & -1 & 0 & 0 & 0 & 0 & 0 \\ & & & 0 & -1 & 0 & 0 & 0 & 0 \\ & & & 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_o \\ y_o \\ z_o \\ x_a \\ y_a \\ z_a \\ x_b \\ y_b \\ z_b \end{bmatrix} = \begin{bmatrix} x_o' \\ y_o' \\ z_o' \\ x_a' \\ y_a' \\ z_a' \\ x_b' \\ y_b' \\ z_b' \end{bmatrix}$$

similarly complicated matrices can be constructed for σ_{xz} and σ_{yz} operations.
The traces of the matrices result

$$\begin{array}{cccccc} & E & C_2 & \sigma_{v_{xz}} & \sigma'_{v_{yz}} \\ \chi_T = & 9 & -1 & +1 & 3 \end{array}$$

They can be more easily obtained with the following rules, as alternative to construct the complete representation matrices:
I) Any vector which is unchanged by the symmetry operations contributes +1
II) Any vector which changes into its opposite by the symmetry operations contributes -1
III) Any vector which changes in another one under the symmetry operations contributes 0.
By these rules it can be constructed the character of the total (reducible) representation. The character is used to decompose the reducible representation into irreducible ones by the following theorem.

$$a_i = \frac{1}{h} \sum_R g\chi_i(R)\chi_T(R)$$

Where a_i is the number of irreducible representations of type *i* contained in the total one *t*, χ_i and χ_t are the characters under the different symmetry operations ***R*** added each other for all the operations, *h* is the number of the group operations, *g* the number of operations having the same character (class).
For the water molecule, having C_{2v} symmetry group

$$a_{A_1} = \frac{1}{4}\left[g\chi_{A_i}(E)\chi_T(E) + g\chi_{A_i}(C_2)\chi_T(C_2) + g\chi_{A_i}(\sigma_v)\chi_T(\sigma_v) + g\chi_{A_i}(\sigma_v')\chi_T(\sigma_v'\right.$$

$$= \frac{1}{4}\left[1 \times 1 \times 9 + 1 \times 1 \times (-1) + 1 \times 1 \times 1 + 1 \times 1 \times 3\right] = 3$$

$$a_{A_2} = \frac{1}{4}\left[1 \times 1 \times 9 + 1 \times 1 \times (-1) + 1 \times (-1) \times 1 + 1 \times (-1) \times 3\right] =$$

$$a_{B_1} = \frac{1}{4}\left[1 \times 1 \times 9 + 1 \times (-1) \times (-1) + 1 \times 1 \times 1 + 1 \times (-1) \times 3\right] =$$

$$a_{B_2} = \frac{1}{4}\left[1 \times 1 \times 9 + 1 \times (-1) \times (-1) + 1 \times (-1) \times 1 + 1 \times 1 \times 3\right] =$$

The total representation consists of the sum of $3A_1$ $1A_2$ $2B_1$ $3B_2$ irreducible representations, for a total number of 9 representations.

1.5.3 Relation between molecular wave functions and irreducible representations

Let we still consider that the energy of a molecule is unchanged by carrying out a symmetry operation, as well as the Hamiltonian too. Thus a symmetry operator *R* commutes with the Hamiltonian operator.

$$\boldsymbol{HR = RH}$$

If we take the wave equation

$\boldsymbol{H\Psi_i = E\Psi_i}$ and multiply each side by the symmetry operation *R*, we obtain

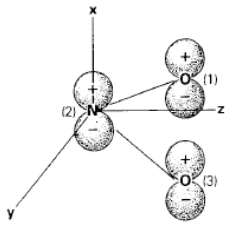
$\boldsymbol{HR\Psi_i = ER\Psi_i}$ due to the commutation of operators

$\boldsymbol{R\Psi_i}$ is the eigenfunction

$\boldsymbol{R\Psi_i = \pm 1\Psi_i}$ and Ψ_i results basis of irriproducible representation

1.5.4 Obtaining molecular orbitals with a given symmetry

Given the symmetry properties of the molecular orbitals, it appears not mandatory but very convenient that the molecular eigenfunctions were choosen as symmetry adapted linear combination of atomic orbitals. They supply the operative bases to perform the MO calculation, avoiding the long and unuseful calculations necessary in the case the eigenfunctions are not bases of irreducible representation. Let we consider the nitrite anion (Scheme 4).



Scheme 4 - π orbitals in nitrite anion

Taking as operative basis the three p orbitals, in a C_{2v} symmetry group, the following values are obtained

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
	3	−1	+1	−3

to describe the behaviour of the reducible representation. This later can be decomposed into $A_2 + 2B_1$ irreducible representations We can now use the projection operators,

working on the basis set of the three p orbitals, and annihilate any element in the basis set that does not contribute to a given irreducible representation. We generally work on an atomic orbital φ_i (i = 1, 2, 3) , e.g. the p orbital of the an atom i, with the operator

$$\hat{P} = \frac{l}{h} \sum_R \chi_R \hat{R}$$

$\hat{R}$ is the symmetry operation, χ_R is the character of the symmetry operator, l is the dimension of the irreducible representation, h is the group order (number of group operations). The sum is extended over all the symmetry operations. If we operate on φ_1 with the A_2 symmetry operator

$$\psi \text{ (for } A_2) = \hat{P}(A_2)\varphi_1 = \frac{1}{4}\left[(1)E\varphi_1 + (1)C_2\varphi_1 + (-1)\sigma_v\varphi_1 + (-1)\sigma_v'\varphi_1\right]$$

The numbers in parethesis are the elements of the A_2 irreducible representation, and φ_1 is the atomic orbital to be modified under the symmetry operation

$$\begin{aligned}\hat{P}(A_2)\varphi_1 &= \frac{1}{4}\left[(1)(1)\varphi_1 + (1)(-1)\varphi_3 + (-1)(1)\varphi_3 + (-1)(-1)\varphi_1\right] \\ &= N[\varphi_1 - \varphi_3]\end{aligned}$$

If we operate on the φ_2 orbital

$$\hat{P}(A_2)\varphi_2 = \frac{1}{4}\left[(1)(1)\varphi_2 + (1)(-1)\varphi_2 + (-1)(1)\varphi_2 + (-1)(-1)\varphi_2\right] = 0$$

That means to remove (annihilate) the φ_2 orbital from the linear combination having A_2 symmetry.
The coefficient determination results

$$\int (C_1\varphi_1 - C_1\varphi_3)^2\, d\tau = C_1^2 \int \varphi_1^2\, d\tau - 2C_1^2 \int \varphi_1\varphi_3\, d\tau + C_1^2 \int \varphi_3^2\, d\tau = 1$$

$$\int \varphi_1^2\, d\tau = 1; \int \varphi_1\varphi_3\, d\tau = 0; \quad \text{and} \quad \int \varphi_3^2\, d\tau = 1.$$

$2C_1^2 = 1$ and the normalized function $(1/2)^{1/2}$ $(\varphi_1 - \varphi_3)$
No eigenfunctions with A_1 symmetry are expected from the decomposition of the reducible representation

$$\hat{P}(A_1)\varphi_1 = \frac{1}{4}[(1)(1)\varphi_1 + (1)(-1)\varphi_3 + (1)(1)\varphi_3 + (1)(-1)\varphi_1] = 0$$

Nor with B_2

$$\hat{P}(B_2)\varphi_1 = \frac{1}{4}[(1)\varphi_1 + (+1)\varphi_3 + (-1)\varphi_3 + (-1)\varphi_1] = 0$$

Instead two eigenfunctions with B_1 symmetry are expected

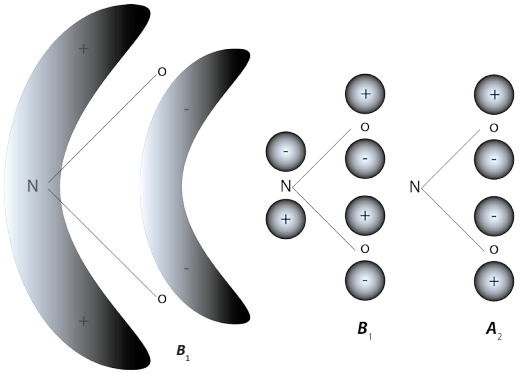
$$\hat{P}(B_1)\varphi_1 = \frac{1}{4}[(1)(1)\varphi_1 + (-1)(-1)\varphi_3 + (1)(1)\varphi_3 + (-1)(-1)\varphi_1]$$
$$= N[\varphi_1 + \varphi_3]$$

$$\hat{P}(B_1)\varphi_2 = \frac{1}{4}[(1)(1)\varphi_2 + (-1)(-1)\varphi_2 + (1)(1)\varphi_2 + (-1)(-1)\varphi_2] = \varphi_2$$

These two eigenfunctions with identical symmetry can mix as

$$\psi_1 = a\varphi_1 + b\varphi_2 + a\varphi_3$$
$$\psi_2 = a'\varphi_1 - b'\varphi_2 + a'\varphi_3$$

Significantly the magnitude of *a* and *b* cannot be determined by only symmetry considerations; we can picture however the three symmetry adapted molecular orbitals



Scheme 5 - Symmetry adapted orbitals of nitrite anion

in terms of B_1 *ligand* orbital involving the in phase linear combination of three atomic p orbitals, B_1 *antiligand* orbital involving the out of phase linear combination, A_2 *non ligand* orbital involving the combination of only two p atomic orbitals located on non adiacent atoms. This can give a precise idea of the electronic distribution among the symmetry eigenfunctions built by π atomic orbitals.

2. Symmetry orbitals for different bis and polyatomic molecules

The description will involve the examples of **H_2** and the **linear diatomic omonuclear molecules of the periodic table first row,** of **H_2O , NH_3, CO, CH_4** molecules.

H_2 The molecule belongs to the $D_{\infty h}$ symmetry group, as well as all the diatomic omonuclear molecules of the periodic table first row, reported below. Assuming as atomic base function that constituted by two s orbitals, φ_1 and φ_2, the character tables for this base becomes:

$D_{\infty h}$	E	C_∞^{φ}	σ_v	i	S_∞^{φ}	C_{2v}
χ_t	2	2	2	0	0	0

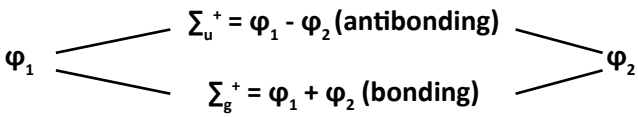
χ_t indicates the total representation of the base of the two s orbitals.

If the characters of the two irreducible representations $\sum_g^+$ and $\sum_u^+$ are considered, the total representation results the sum of both $\chi_t = \sum_g^+ + \sum_u^+$

By using the projection operator, new symmetry eigenfunctions can be obtained

$D_{\infty h}$	E	C_∞^{φ}	σ_v	i	S_∞^{φ}	C_{2v}
$\sum_g^+$	1	1	1	1	1	1
$\sum_u^+$	1	1	1	-1	-1	-1
Φ_1	φ_1	φ_1	φ_1	φ_2	φ_2	φ_2
Φ_2	φ_2	φ_2	φ_2	φ_1	φ_1	φ_1

$\sum_g^+ = \varphi_1 + \varphi_2$ (bonding) and $\sum_u^+ = \varphi_1 - \varphi_2$ (antibonding), in the following energy scheme



2.1 Omonuclear diatomic molecules A-A of the periodic table first row

We assume the following base of atomic orbitals

For the **2s** orbitals

$\varphi_1 = 2s_A$ $\varphi_2 = 2s_B$ leads to

$\sum_g^+ = \varphi_1 + \varphi_2$ (bonding) $\sum_u^+ = \varphi_1 - \varphi_2$ (antibonding)

For the **2p** orbitals $\varphi_1^A = 2p_x$ $\varphi_2^A = 2p_y$ $\varphi_3^A = 2p_z$; $\varphi_4^B = 2p_x$ $\varphi_5^B = 2p_y$ $\varphi_6^B = 2p_z$

$D_{\infty h}$	E	C_∞^φ	σ_v	i	S_∞^φ	C_{2v}
χ_t	6	$2+4\cos\varphi$	2	0	0	0

χ_t indicates the total representation of the base containing the six **p** orbitals.

Looking at the Character Tables of the linear groups

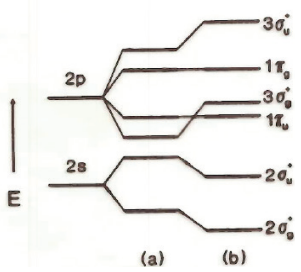
$C_{\infty v}$	E	$2C_\infty^\Phi$	...	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	...	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	...	−1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\Phi$	...	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\Phi$	...	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	$2\cos 3\Phi$	...	0		
...	...	...	...	...		

$D_{\infty h}$	E	$2C_\infty^\Phi$	...	$\infty\sigma_v$	i	$2S_\infty^\Phi$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2+y^2, z^2
Σ_g^-	1	1	...	−1	1	1	...	−1	R_z	
Π_g	2	$2\cos\Phi$	...	0	2	$-2\cos\Phi$	...	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\Phi$	...	0	2	$2\cos 2\Phi$	...	0		(x^2-y^2, xy)
...	...	...	...	...	...	...	...	...		
Σ_u^+	1	1	...	1	−1	−1	...	−1	z	
Σ_u^-	1	1	...	−1	−1	−1	...	1		
Π_u	2	$2\cos\Phi$	...	0	−2	$2\cos\Phi$	...	0	(x, y)	
Δ_u	2	$2\cos 2\Phi$	...	0	−2	$-2\cos 2\Phi$	...	0		
...	...	...	...	...	...	...	...	...		

and considering the character table of the irreducible representations of the $D_{\infty h}$ group

$D_{\infty h}$	E	C_∞^φ	σ_v	i	S_∞^φ	C_{2v}
$\sum_g^+$	1	1	1	1	1	1
$\sum_u^+$	1	1	1	-1	-1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0

the base of six p atomic orbitals allows to built the following symmetry orbitals reported in a general scheme 6 with the s based atomic orbitals where the number before the symmetry orbital indicates the progression of orbitals of analogous symmetry.



Scheme 6 – General energy trend for the first raw biatomic molecules

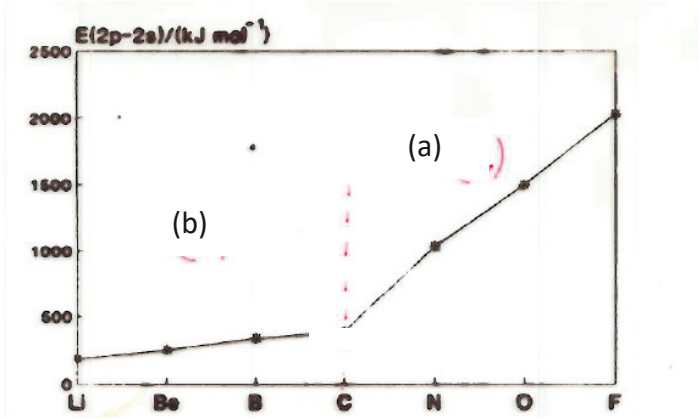
$$\phi_{3\sigma_g^+} = (2p_{zA} + 2p_{zB})$$

$$\phi_{3\sigma_u^+} = (2p_{zA} - 2p_{zB})$$

$$\phi_{1\pi_u} = (2p_{xA} + 2p_{xB}); (2p_{yA} + 2p_{yB})$$

$$\phi_{1\pi_z} = (2p_{xA} - 2p_{xB}); (2p_{yA} - 2p_{yB})$$

The scheme 7 shows the different energy trends for the first row biatomic molecules labeled **(a)** and for those labeled **(b),** and indicates that for the molecules **(b)** an energy inversion of σ^+_g and π_u is active. This is connected to the small energy difference between s and p orbitals of the interacting atoms.



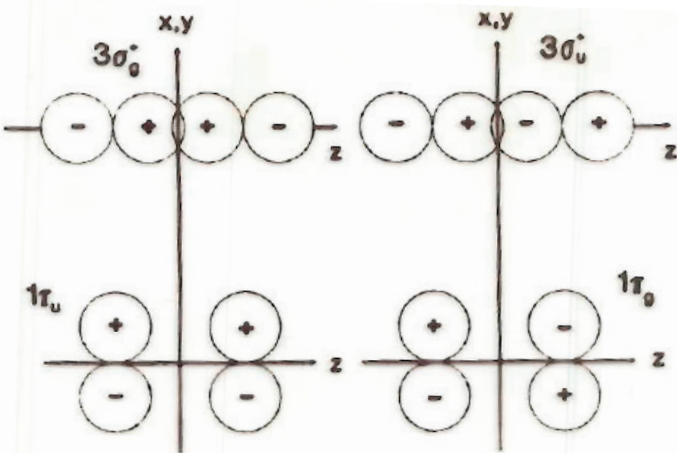
Scheme 7 – Energy trend for the first row biatomic molecules as a function of the atomic species

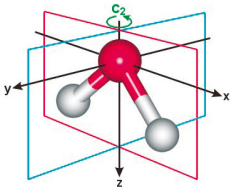
On proceeding along the first raw of the periodic table, increasing the atomic number, the electronic population in Table 6 is expected, where the bond stregth of the molecules is associated to the number and the type of populated symmetry orbitals.

Table 6 - Orbital population for the first row biatomic molecules

Molecule/ion	$2\sigma_g^+$	$2\sigma_u^+$	$3\sigma_g^+$	$1\pi_u$	$1\pi_g$	$3\sigma_u^+$
Li_2	2					
Be_2	2	2				
B_2	2	2		2		
C_2	2	2		4		
N_2	2	2	2	4		
N_2^+	2	2	1	4		
N_2^-	2	2	2	4	1	
O_2	2	2	2	4	2	
O_2^+	2	2	2	4	1	
O_2^-	2	2	2	4	3	
O_2^{2-}	2	2	2	4	4	
F_2	2	2	2	4	4	
Ne_2	2	2	2	4	4	2

The overlap detail for the different orbitals is represented as





Scheme 8 – Water molecule representation

2.2 Water molecule, as example of triatomic molecule

We assume the following base of atomic orbitals $\boldsymbol{\varphi}_1 = 1s_{H1}$ $\boldsymbol{\varphi}_2 = 1s_{H2}$ $\boldsymbol{\varphi}_3 = 1s_O$ $\boldsymbol{\varphi}_5 = 2p_{Ox}$ $\boldsymbol{\varphi}_6 = 2p_{Oy}$ $\boldsymbol{\varphi}_7 = 2p_{Oz}$ (Scheme 8)

In C_{2v} symmetry	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz$
χ_T	6	0	2	4
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

$\chi_T = 3\,A_1 + 2\,B_2 + B_1$

the φ_3 orbital has energy too different from the other ones to be conveniently combined by symmetry rules. The remaining ones give rise, by the use of the projection operator, to symmetry adapted conbinations associated to the C_{2v} symmetry of H_2O.

Considering the representation table for the six base orbitals

C_{2v}				
φ_1	φ_1	φ_2	φ_2	φ_1
φ_2	φ_2	φ_1	φ_1	φ_2
φ_4	φ_4	φ_4	φ_4	φ_4
φ_5	φ_5	$-\varphi_5$	φ_5	$-\varphi_5$
φ_6	φ_6	$-\varphi_6$	$-\varphi_6$	φ_6
φ_7	φ_7	φ_4	φ_7	φ_7

and having as objective the construction of the six symmetry adapted linear combinations of atomic orbitals (SALC)

$2A_1$ $\varphi_1 + \varphi_2$; φ_4 ; φ_7 $\rightarrow$ $\varphi_1 + \varphi_2 + \varphi_4$

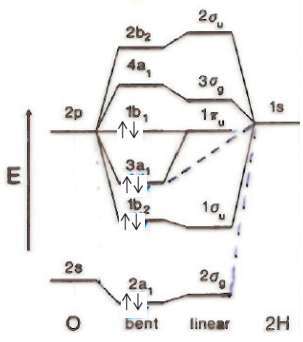
$1B_2$ $-\varphi_1 + \varphi_2 + \varphi_6$

$3A_1$ $\boldsymbol{\varphi}_1 + \varphi_2 - \boldsymbol{\varphi}_7 - \boldsymbol{\varphi}_4$

$1B_1$ $\boldsymbol{\varphi}_5$

$4A_1$ $\boldsymbol{\varphi}_1 + \varphi_2 + \boldsymbol{\varphi}_7 - \boldsymbol{\varphi}_4$

$2B_2$ $\boldsymbol{\varphi}_1 - \varphi_2 + \boldsymbol{\varphi}_6$

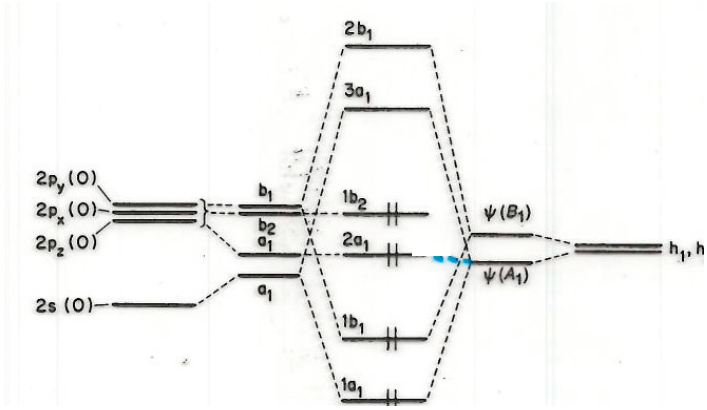


Scheme 9 – H_2O linear symmetry versus the bent one (the real one)

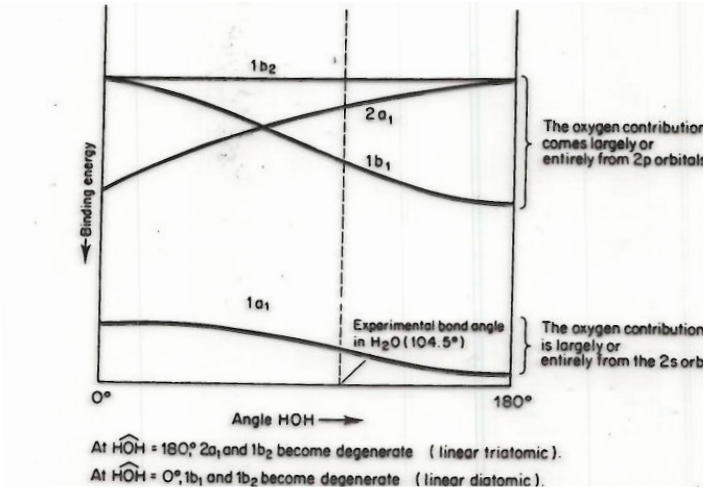
The numbers before the symmetry indicate the progression of orbitals of a given symmetry. The grey color indicates the negative sign of the function.

In the case we tentatively adopt a linear $\mathbf{D_{\infty h}}$ symmetry (Scheme 9), the irreducible representation will be $2\sigma_g$, $1\ \sigma_u$, π_u, $3\ \sigma_g$, $2\ \sigma_u$, a lower number than C_{2v}, due to degeneracy of $\boldsymbol{\pi}_u$. The lack of π_u induces stabilization of $3a_1$.

(A)



(B)



Scheme 10 – (A) energy level trend of the water symmetry orbitals (B) the same against HOH angle amplitude. b_1 and b_2 are exchanged from (A to (B)

The HOH angle of 105.5 °amplitude is the best convenient to minimize the energy of the water molecule. In Scheme 10 is reported the energy trend (A) and the H-O binding energy (B) against HOH angle.

The Photoelectron spectrum of the water molecule (Figure 1) confirms the symmetry energy trend, excluding the presence of degenerate π_u states.

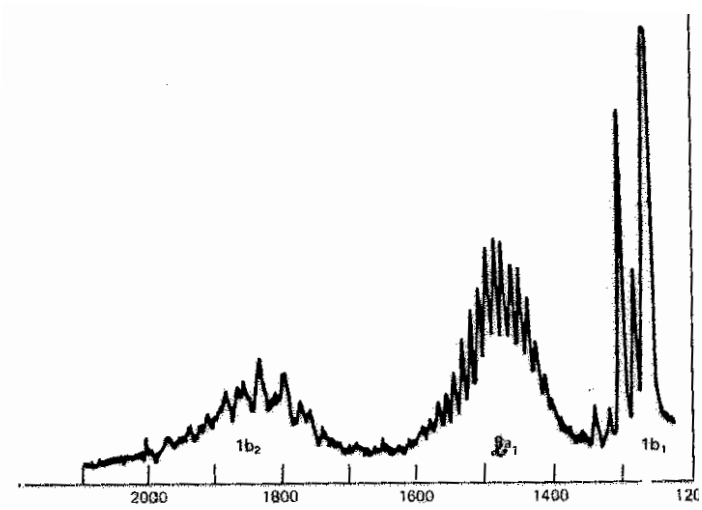
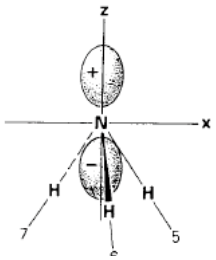


Fig. 1 - Photoelectron spectrum of water, indicating the electronic transitions

2.3 Ammonia molecule, as example of tetratomic molecule



Scheme 11 – NH_3 molecule

We assume the following base of atomic orbitals $\varphi_1 = 2s_N$ $\boldsymbol{\varphi}_2 = 2p_x$ $\boldsymbol{\varphi}_3 = 2p_y$ $\boldsymbol{\varphi}_4 = 2p_z$ $\boldsymbol{\varphi}_5 = 1s\ (H_5)$ $\boldsymbol{\varphi}_6 = 1s\ (H_6)$ $\boldsymbol{\varphi}_7 = 1s\ (H_7)$ (Scheme 11)

Referring to C_{3v} symmetry, the characters of the reducible representation under the related symmetry operations are

E	**$2C_3$**	**$3\sigma_v$**
7	**1**	**3**

Decomposed into the irreducible ones:

$$\mathbf{3A_1 + 2\ E}$$

In order to apply the projection operator the following transformation table is compiled

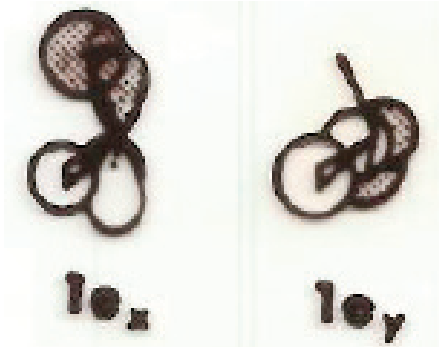
Transformation table of the base function

C_{3v}	E	C_3	C_3^2	$\sigma_v(H_5)$	$\sigma_v(H_6)$	$\sigma_v(H_7)$
φ_1	φ_1	φ_1	φ_1	φ_1	φ_1	φ_1
φ_2	φ_2	$(-1/2\ \varphi_2 - \sqrt{3}/2\ \varphi_3)$	$(-1/2\ \varphi_2 + \sqrt{3}/2\ \varphi_3)$	φ_2	$(-1/2\ \varphi_2 + \sqrt{3}/2\ \varphi_3)$	$(-1/2\ \varphi_2 - \sqrt{3}/2\ \varphi_3)$
φ_3	φ_3	$(\sqrt{3}/2\ \varphi_2 - 1/2\ \varphi_3)$	$(-\sqrt{3}/2\ \varphi_2 - 1/2\ \varphi_3)$	$-\varphi_3$	$(\sqrt{3}/2\ \varphi_2 + 1/2\ \varphi_3)$	$(-\sqrt{3}/2\ \varphi_2 + 1/2\ \varphi_3)$
φ_4	φ_4	φ_4	φ_4	φ_4	φ_4	φ_4
φ_5	φ_5	φ_6	φ_7	φ_5	φ_7	φ_6
φ_6	φ_6	φ_7	φ_5	φ_7	φ_6	φ_5
φ_7	φ_7	φ_5	φ_6	φ_6	φ_5	φ_7

By using the projection operator, applied to either not degenerate or degenerate representations (A_1 and E) the following symmetry orbitals are obtained.

$$\mathbf{2A_1} = \boldsymbol{\varphi}_2 + \boldsymbol{\varphi}_5 + \boldsymbol{\varphi}_6 + \boldsymbol{\varphi}_7$$

$$\mathbf{1E_x} = -\boldsymbol{\varphi}_2 - 2\boldsymbol{\varphi}_5 + \boldsymbol{\varphi}_6 + \boldsymbol{\varphi}_7$$
$$\mathbf{1E_y} = \boldsymbol{\varphi}_3 + \boldsymbol{\varphi}_6 - \boldsymbol{\varphi}_7$$

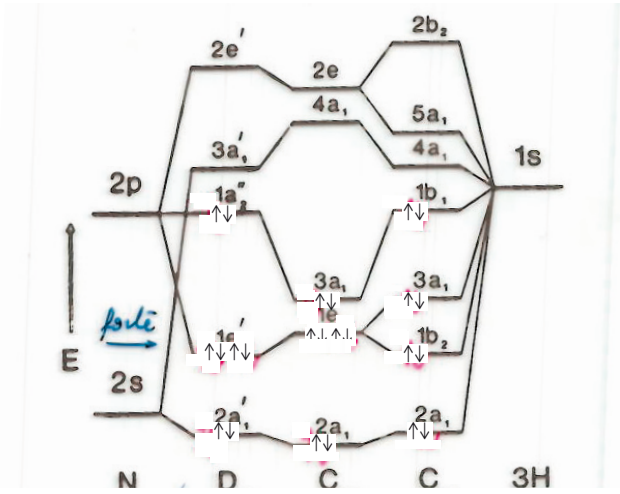


$3A_1 = -\varphi_1 + \varphi_5 + \varphi_6 + \varphi_7 - \varphi_4$

$4A_1 = -\varphi_1 + \varphi_5 + \varphi_6 + \varphi_7 + \varphi_4$

$2E_x = 2\varphi_5 + \varphi_6 + \varphi_7 - \varphi_2$

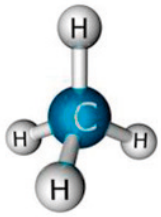
$2E_y = \varphi_3 - \varphi_6 + \varphi_7$



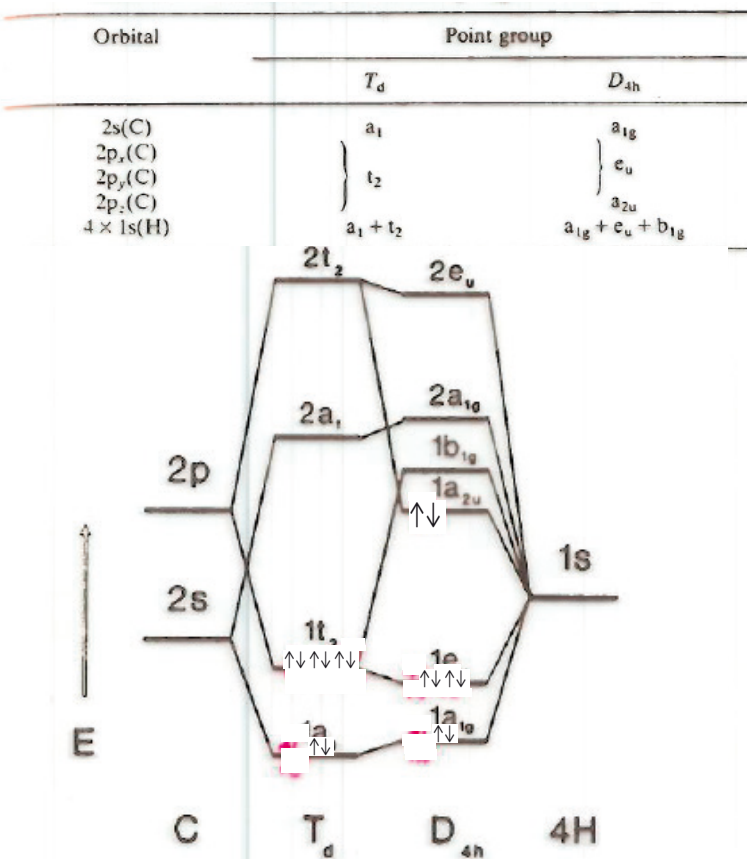
Scheme 12 - Energy levwel trend of NH_3 symmetry orbitals

The scheme 12 reports the energy level trends of ammonia for different possible symmetries. The stablilization of $3a_1$ energy level in C_{3v} symmetry, due to interaction with the ground state, is responsible for the stability of the pyramidal C_{3v} structure.

2.4 Methane molecule, as example of pentatomic molecule



T_d symmetry (Scheme 13) guaranties the highest stability for the CH_4 unit due to the decrease of b_{1g} eigenfunction



Scheme 13 – Energy level trend of methane symmetry orbitals

2.5 Considerations about the models of chemical bond in use before the adoption of the symmetry molecular orbital model

In the time before the introduction of the molecular orbital model, two different models were proposed to rational-

ize the molecular shape, the reactivity and the electronic configuration. 1) the primitive Lewis model that does not consider any molecular shape and takes into account only the filling of the valence shell (8 electrons model); 2) the valence electron pair repulsion (VSEPR) theory which rationalizes the molecular shape in terms of the minimum pair repulsion, keeping the couples of bound atoms each ones separated in their interaction (also using hybrid orbitals).
The symmetry adapted molecular orbitals takes as molecular orbitals those which are base of the symmery group of the molecule.
Step by step the model implementation goes from the only consideration of the electron number, to the total consideration of electrons and orbitals of the molecules, assessing that the bonding is in charge to all the atomic orbitals, not only to those bonding two atoms. By this way (see water molecule) both the shape and some reactivity can be rationalized. The spectroscopic experimental data (XPS) are in agreement with this symmetry approach.
It can be suggested that the symmetry constitutes a unifying approach to treat the chemical bond, as well as the molecular symmetry has the function of including all the constituents of the chemical bonds in the entire molecule. No energy is implied in the symmetry operations, thus the symmetry is only a way to describe in easy way the electronic properties, and to suggest that the symmetry is a condition to whom the electrons must obey.
On the purpose of the unique value of the symmetry, it has been invoqued also in the music composition; it was suggested that several composers, mainly Ludwing Van Beethoven, assembled the musical text by using measures related by symmetry operations. This guaranties the correlation among the various sections of the text.

3. Perturbation theory

The hypothesis on $\boldsymbol{\Psi}_n$ is that they consist of known solutions $\boldsymbol{\Psi}_n^0$ of the equation

$$\mathbf{H^0}\,\Psi_n^0 = E_n^0\,\Psi_n^0$$

The hypothesis on H is that
$\mathbf{H} = \mathbf{H^0} + \mathbf{H'}$ where $\mathbf{H'}$ is the operator associated to the perturbation energy with respect to pristine $\mathbf{H^0}$
The following equation has to be solved

$$\mathbf{H}\,\Psi_n = E_n\,\Psi_n$$

$$E_n = E_n^0 + \langle \Psi^0_n \,|\, \mathbf{H'} \,|\, \Psi^0_n \rangle$$

$$\boldsymbol{\Psi}_n = \boldsymbol{\Psi}^0_n + \sum_{k\neq n} \langle \Psi^0_k \,|\, \mathbf{H'} \,|\, \Psi^0_n \rangle \times \boldsymbol{\Psi}^0_k \,/\, E_n^0 - E_k^0$$

Evidently the perturbed energy is the addition of the unperturbed one and of the perturbation energy obtained by the $\mathbf{H'}$ operator.
The perturbed eigenfunctions are the unperturbed ones modified by the perturbation energy, weighted on the energy differences between the ground state and the excited interacting states.
Assuming as example a system whose unperturbed eigenfunctions are $\boldsymbol{\Psi}^0_1$ and $\boldsymbol{\Psi}^0_2$, corresponding to energies E^0_1 and E^0_2
the determinant

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix}$$

where $H_{11} = \langle \boldsymbol{\Psi}^0_1 \,|\, \mathbf{H} \,|\, \boldsymbol{\Psi}^0_1 \rangle$ $\qquad$ $H_{22} = \langle \boldsymbol{\Psi}^0_2 \,|\, \mathbf{H} \,|\, \boldsymbol{\Psi}^0_2 \rangle$

has H_{11} and H_{22} as solutions, when $H_{21} = H_{12}$, thus

$E_1 = H_{11} = \langle \Psi^0_1 | \mathbf{H}^0 + \mathbf{H}' | \Psi^0_1 \rangle = \langle \Psi^0_1 | \mathbf{H}^0 | \Psi^0_1 \rangle + \langle \Psi^0_1 | \mathbf{H}' | \Psi^0_1 \rangle = E^0_1 + \langle \Psi^0_1 | \mathbf{H}' | \Psi^0_1 \rangle$

$E_2 = H_{22} = E^0_2 + \langle \Psi^0_2 | \mathbf{H}' | \Psi^0_2 \rangle$

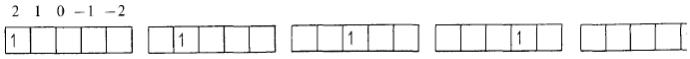
In a similar way as LCAO method, it is still a great difficulty to calculate the H_{ij} integrals. We will evaluate them by a semiempirical method, using the experimental parameters from spectroscopic measurements.

The perturbation method can be positively applied when the perturbation energy is well lower than the energies of the unperturbed system and it never describes the covalent bond.

Basing on this assumption, in the following we will describe the perturbations that modellize the atomic electronic structure.

3.1 Interelectronic repulsion perturbation

If an atomic system has one electron there is no energy difference whatever is the occupied orbital by the electron. See for example one electron in the five d orbitals named by its m_l value

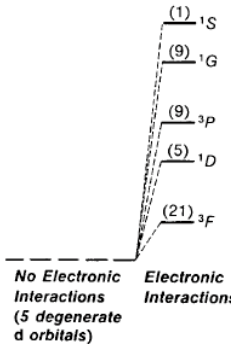


When the system contains two electrons, the energy level is depending on the relative occupation of the orbitals. It is necessary to combine all the possible electronic distributions by using the so called atomic vector model. The following table reports all possible combinations of two electrons into d orbitals (microstates), with their associated m_l value. In the columns there is the sum of m_l values ($\mathbf{M_L}$) relatable to the sum of l values (**L**). Also $\mathbf{m_s}$ values of the individual electrons are reported as well as in the line there is the sum of the individual m_s ($\mathbf{M_S}$).

Table 7 - Electronic microstates for the d^2 configuration

M_L \ M_S	(++) +1 (↑↑)	(+ −) 0 (↑↓)	(− −) −1 (↓↓)
4		$\boxed{2^+2^-}$	
3	(2^+1^+)	$\boxed{2^+1^-}$ (2^-1^+)	(2^-1^-)
2	(2^+0^+)	$\boxed{2^+0^-}$ (2^-0^+) (1^+1^-)	(2^-0^-)
1	(2^+-1^+) $[1^+0^+]$	$\boxed{2^+-1^-}$ (2^--1^+) (1^+0^-) $[1^-0^+]$	$(2^--1^-)[1^-0^-]$
0	$(2^+-2^+)[1^+-1^+]$	$\boxed{2^+-2^-}$ (2^--2^+) (1^+-1^-) $[1^--1^+]$ 0^-0^+	$(2^--2^-)[1^--1^-]$

In table 7, the same brackets include the terms of a given L. The letters S, P, D, F, G, H, I corresponding to L = 0, 1, 2, 3, 4, 5, 6 indicate the effects of the electron-electron repulsion. Also the spin multiplicity **2S+1** is reported at the left top of the letter and it results from the table.



Scheme 14 - Energy levels obtained for a d^2 configuration

In the case of d^1 electronic system

$m_L = M_L = 2, 1, 0, -1, -2$ **D** term

$m_S = M_S = -1/2 , +1/2$ **S = ½** doublet term **^{2}D**

In the case of d^2 electronic system

$M_L = 4, 3, 2, 1, 0$ L = 4, 3, 2, 1, 0

L = 4 M_L = -4, -3, -2, -1, 0, 1, 2, 3, 4 **G** term

L = 3 M_L = -3, -2, -1, 0, 1, 2, 3 **F** term

L = 2 M_L = -2, -1, 0, 1, 2 **D** term

L = 1 M_L = -1, 0, 1 **P** term

L = 0 M_L = 0 **S** term

S = 1 M_S = -1, 0, +1 **^{3}F and ^{3}P** terms

S = 0 M_S = 0 **^{1}G ^{1}S ^{1}D** terms

Although the vector atomic model allows to predict the type of energy states (Scheme 14), that is the orbital and spin multiplicity, the scheme does not give the relative energies of the states. In order to calculate them it is needed to apply the electronic repulsion operator. How does it work?
The perturbation operator is

$H' = \sum_{i<j} e^2/r_{ij}$ r_{ij} is the distance between the two electrons

The energies for all of the terms associated to the electronic configuration can be calculated and expressed by the Condon-Shortley parameters $\mathbf{F_0}$ $\mathbf{F_2}$ and $\mathbf{F_4}$. These parameters are abbreviations for the various repulsion integrals in the perturbation determinant and allow the values can be determined by detecting the experimental atomic transitions. The energy expression as a function of these parameters are independent of the atom but the parameter values there are. The entire atomic spectrum is fitted by the same parameter values.
For the V(III) ion d^2

$$E(^3P - {}^3F) = 15B$$
$$E(^1D - {}^3F) = 5B + 2C$$

$$B = 866 \text{ cm}^{-1} \text{ and } C/B = 3.6.$$

Racah redefined the Condon-Shortley parameters to simplify the energy separation between the states

$$B = F_2 - 5F_4 \qquad C = 35F_4$$

Still for the V(III) ion

$$E(^3P - {}^3F) = 15F_2 - 75F_4 = 13{,}000 \text{ cm}^{-1}$$
$$E(^1D - {}^3F) = 5F_2 + 45F_4 = 10{,}600 \text{ cm}^{-1}$$

$$F_2 = 1310 \text{ cm}^{-1} \text{ and } F_4 = 90 \text{ cm}^{-1}.$$

The free ion terms for the different electronic configurations are in Table 8.

Table 8 - Free ion terms for various electronic configurations

n		Terms																
d^1	d^9	^2D																
d^2	d^8	^3F	^3P	^1G	^1D	^1S												
d^3	d^7	^4F	^4P	^2H	^2G	^2F	^2D	^2D	^2P									
d^4	d^6	^5D	^3H	^3G	^3F	^3F	^3D	^3P	^3P	^1I	^1G	^1G	^1F	^1D	^1D	^1S	^1S	
d^5		^6S	^4G	^4F	^4D	^4P	^2I	^2H	^2G	^2G	^2F	^2F	^2D	^2D	^2D	^2P	^2S	

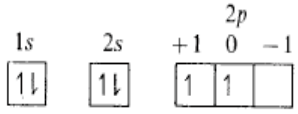
Look at the analogy between the configurations complementary in 10. This originates from the analogy of the repulsion energy between two electrons and two holes. The magnitude of the electro-electron perturbation energy is few thousand cm^{-1}.

3.2 Spin orbit coupling perturbation

This perturbation describes the energy modification in an atom due to interaction of the angular spin magnetic moment with the angular orbital magnetic moment. Two schemes are used to treat the effect: the **L.S** scheme (Russel –Saunders) and the **j-j** scheme; the first one is the most common and it is used when the spin-orbit perturbation is lower than the electronic repulsion (the major part of atoms); the second one is suitable to treat rare earth elements and the third raw transition elements.

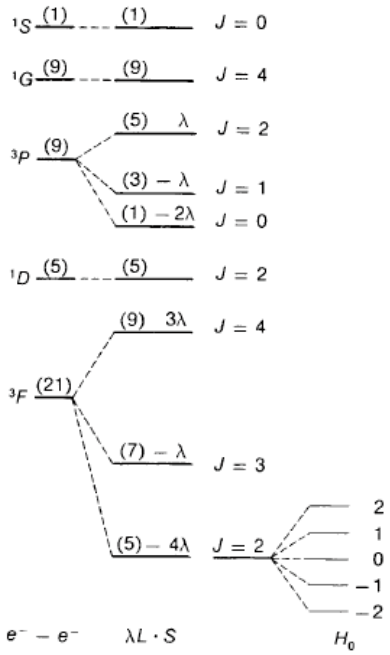
The first case will be described in detail as it is the most common. The individual $\mathbf{m_L}$ values of the single electrons undergo coupling and produce the angular momentum **L** ; the spin $\mathbf{m_s}$ values give the **S** value. The resultant momentum is called **J**, and it takes all consecutive integer values spanning from **L-S** to **L+S**.

By still using the vectorial atomic model, it is easy to predict the type of spin orbit coupled states. In fact for the carbon atom



L = 1 **S** = 1 **L-S** = 0 **L+S** = 2 **J** = 0, 1, 2 the term is $^3\mathbf{P_0}$, being the shell less than half filled

The scheme 15 describes the spin orbit coupling effects for d^2 configuration



Scheme 15 - Spin orbit coupling effect in d^2 configuration

As for the spin orbit coupling energy perturbation, two parameters, ***λ*** and ***ξ***, are used to describe the energy magnitude.

$$\xi = \frac{Z_{\text{eff}} e^2}{2m^2c^2} \langle r^{-3} \rangle$$

where $\mathbf{r^{-3}}$ is the average value of the atomic radius, $\mathbf{Z_{eff}}$ is the nuclear charge, m is the electron mass. The operator is

$$\boldsymbol{\xi L \bullet S}$$

Using the parameter λ where

$$\lambda = \pm \xi / 2S$$

and if the shell is less than half filled $\boldsymbol{\lambda}$ is positive the operator becomes λ L●S
The spin orbit effects, as in the Scheme 15, are given by

$$\tfrac{1}{2}\lambda[\,J(J+1) - L(L+1) - S(S+1)]$$

The magnitude of the spin orbit effect is generally few handred cm^{-1}.

3.3 Crystal field perturbation

The perturbation described in this paragraph is able to model the bonding interaction between a central metal ion, with a given electronic confguration, and the surrounding groups (either ions or polar molecules). Thus we shift from the atomic to a molecular context. Interestingly the information on the bond is not related to the energy decrease of the metal electrons, but it involves the electronic repulsion between the electrons of the metal ion and the negative charge of the surrounding groups.
The base for the electronic perturbation in the case of transition metal ions are the following eigenfunctions

$$Y_2^{\,0} = (5/8)^{1/2}(3\cos^2\theta - 1)\cdot(2\pi)^{-1/2}$$
$$Y_2^{\,\pm 1} = (15/4)^{1/2}\sin\theta\cos\theta\cdot(2\pi)^{-1/2}e^{\pm i\varphi}$$
$$Y_2^{\,\pm 2} = (15/16)^{1/2}\sin^2\theta\cdot(2\pi)^{-1/2}e^{\pm 2i\varphi}$$

Alternatively in a real form, the more common called d orbitals are

$$d_{z^2} = |0\rangle \qquad (d_{z^2} \text{ is really } d_{(z^2 - r^2/3)}$$
$$d_{yz} = (i/\sqrt{2})[|-1\rangle + |1\rangle]$$
$$d_{xz} = (1/\sqrt{2})[|-1\rangle - |1\rangle]$$
$$d_{xy} = -(i/\sqrt{2})[|2\rangle - |-2\rangle]$$
$$d_{(x^2 - y^2)} = (1/\sqrt{2})[|2\rangle + |-2\rangle]$$

The complete hamiltonian for the perturbed systems is

$$\boldsymbol{H = H_0 + V}$$

where $\boldsymbol{H_0}$ is the free-ion hamiltonian and $\boldsymbol{V}$ the perturbation operator which describes the electronic repulsion between the ion electrons and the ligands, these simplified as point charges. For an octahedral interaction the perturbation is

$$\hat{V} = \sum_{i=1}^{6} eZ_i/r_{ij}$$

where e is the electron charge, Z_i the effective ligand charge, r_{ij} the distance between elecron and ligand. The form of the integrals in the perturbation determinant is $\langle M_L | \boldsymbol{V} | M_L' \rangle$. When the integration is done, many quantities related to the radial part of the matrix elements appear in the determinant and have the form **1/6 ($\boldsymbol{Ze^2r^4a^{-5}}$)** where *r* is the average radius of the d elecrons of the central ion and *a* the metal-ligand distance.
This quantity is referred to as *10 Dq* and is an energy. With this considerations the determinant for an octahedral complex having a d^1 central ion is

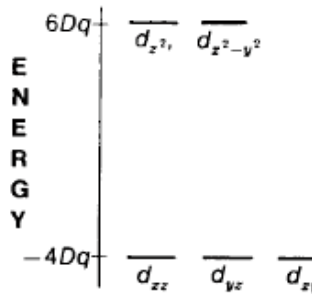
$$\begin{array}{c|ccccc|} & |2\rangle & |1\rangle & |0\rangle & |-1\rangle & |-2\rangle \\ |2\rangle & Dq-E & & & & 5Dq \\ |1\rangle & & -4Dq-E & & & \\ |0\rangle & & & 6Dq-E & & \\ |-1\rangle & & & & -4Dq-E & \\ |-2\rangle & 5Dq & & & & Dq-E \end{array} = 0$$

This gives roots

$$E(|1\rangle) = -4Dq$$
$$E(|-1\rangle) = -4Dq$$
$$E(|0\rangle) = 6Dq$$

$$\begin{array}{c|cc} & |2\rangle & |-2\rangle \\ |2\rangle & Dq-E & 5Dq \\ |-2\rangle & 5Dq & Dq-E \end{array} = 0$$

Still having the roots *-4Dq +6Dq*
Thus the crystal field effect separates the d orbitals in two sets, *10 Dq* distant, as in the Scheme 16.
For the correlation between terms and d orbitals, see the beginning of the paragraph.



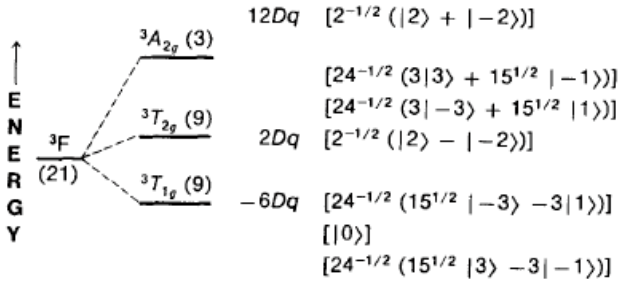
Scheme 16 - Energy diagram of d^1 configuration in octahedral crystal field

If we consider the d^2 configuration, several times discussed in the previous chapters, more free ion terms can be considered for the interaction with the octahedral crystal field. Let we start with the perturbation of the ^3F ground state. The secular determinant results

$$
\begin{array}{c|cccccc|}
 & |3\rangle & |2\rangle & |1\rangle & |0\rangle & |-1\rangle & |-2\rangle & |-3\rangle \\
\langle 3| & -3Dq-E & & & & 15^{1/2}Dq & & \\
\langle 2| & & 7Dq-E & & & & 5Dq & \\
\langle 1| & & & -Dq-E & & & & 15^{1/2}Dq \\
\langle 0| & & & & -6Dq-E & & & \\
\langle -1| & 15^{1/2}Dq & & & & -Dq-E & & \\
\langle -2| & & 5Dq & & & & 7Dq-E & \\
\langle -3| & & & 15^{1/2}Dq & & & & -3Dq-E
\end{array}
$$

The solutions are

$$
\begin{aligned}
E_1 &= -6Dq & E_5 &= 2Dq \\
E_2 &= -6Dq & E_6 &= 2Dq \\
E_3 &= -6Dq & E_7 &= 12Dq \\
E_4 &= 2Dq
\end{aligned}
$$



The denomination of the terms uses the group theory, in the way described in the next paragraph.

3.3.1 Use of the group theory to predict the orbital spitting in a given symmetry

The target is how to be able assigning the terms obtained by the octahdral perturbation to the irreducible representations of the octahedral group itself. Given that the symmetry of the crystal field perturbation decides the form of the perturbation operator, it can be expected that the eigenfunctions of both singly or multi electronic ions belong to the symmetry group of the complex . We begin by examin-

ing the effect of an octahedral field on the total representation whose the d orbitals form the basis. Since all d orbitals have symmetry center, no new information arises from the symmetry inversion operation. Thus it is easier to use the simple rotational group, the O group, which contains only the rotations present in the O_h group.

$$\begin{bmatrix} e^{2i\varphi} \\ e^{i\varphi} \\ e^{0} \\ e^{-i\varphi} \\ e^{-2i\varphi} \end{bmatrix} \xrightarrow[\text{by } \alpha]{\text{rotate}} \begin{bmatrix} e^{2i(\varphi+\alpha)} \\ e^{i(\varphi+\alpha)} \\ e^{0} \\ e^{-i(\varphi+\alpha)} \\ e^{-2i(\varphi+\alpha)} \end{bmatrix}$$

The vector contains as terms the five d orbitals, wich undergo the rotation; notably only the φ angle varies, as the remaining polar coordinates, θ and ρ are not changed by the symmetry operation.
The symmetry rotation is represented by the following matrix

$$\begin{bmatrix} e^{2i\alpha} & 0 & 0 & 0 & 0 \\ 0 & e^{i\alpha} & 0 & 0 & 0 \\ 0 & 0 & e^{0} & 0 & 0 \\ 0 & 0 & 0 & e^{-i\alpha} & 0 \\ 0 & 0 & 0 & 0 & e^{-2i\alpha} \end{bmatrix}$$

$$\begin{bmatrix} e^{li\alpha} & 0 & \cdots & 0 & 0 \\ 0 & e^{(l-1)i\alpha} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & e^{(1-\ell)i\alpha} & 0 \\ 0 & 0 & \cdots & 0 & e^{-\ell i\alpha} \end{bmatrix}$$

more in general, whatever the base orbitals
The sum of the diagonal elements is

$$\chi(\alpha) = \frac{\sin\left(\ell + \frac{1}{2}\right)\alpha}{\sin\left(\frac{\alpha}{2}\right)}$$

In the case of a 120° rotation (C_3)

$$\chi(C_3) = \frac{\sin\left[\left(2+\frac{1}{2}\right)\left(\frac{2\pi}{3}\right)\right]}{\sin\left(\frac{2\pi}{3\times 2}\right)} = \frac{\sin\frac{5\pi}{3}}{\sin\frac{\pi}{3}} = \frac{-\sin\frac{\pi}{3}}{\sin\frac{\pi}{3}} = -1$$

Using the above formula we will represent the various operations in the O rotational group

	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$
χ_T	5	−1	1	−1	1

$\boldsymbol{\chi}_T$ is decomposed in T_2 + E, in the case of O_h, T_{2g} + E_g.
The results obtained by the only symmetry considerations are the same as those deriving from the application of the perturbation operator, that is the d orbitals split in two sets of orbitals, one three times degenerate (T_{2g}) and the other two times (E_g). The symmetry considerations allow to predict the number and type of energy levels, but do not give any quantitative energy measure. See in the following table the prevision

Table 9 - Association between orbitals and their symmetry properties in O_h

Type of Orbital	l Value	Irreducible Representation[a]
s	0	a_{1g}
p	1	t_{1u}
d	2	$e_g + t_{2g}$
f	3	$a_{2u} + t_{1u} + t_{2u}$
g	4	$a_{1g} + e_g + t_{1g} + t_{2g}$
h	5	$e_u + 2t_{1u} + t_{2u}$
i	6	$a_{1g} + a_{2g} + e_g + t_{1g} + 2t_{2g}$

Let consider that the correlation among the type of orbital (l value) and the irreducible representations are valid also for the states (L values) and the irreducible representations of the states.
The prevision of the states both in the case of monoelectronic and multielectronic states can be transferred from the octahedral symmetry to the different ones. In fact the same wave functions, in different point groups, are base of different irreducible representation.

Table 10 - Correlation between the spectroscopic states in different symmetries

O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	C_{2v}	D_{3d}	D_3	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g} + B_{1g}$	$A_1 + B_1$	$A_1 + B_1$	$A_1 + A_2$	E_g	E	$A_g +$ E
T_{1g}	T_1	T_1	$A_{2g} + E_g$	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$	$A_{2g} + E_g$	$A_2 + E$	$A_g + 2$
T_{2g}	T_2	T_2	$B_{2g} + E_g$	$B_2 + E$	$B_2 + E$	$A_1 + B_1 + B_2$	$A_{1g} + E_g$	$A_1 + E$	$2A_g +$
A_{1u}	A_1	A_2	A_{1u}	B_1	A_2	A_2	A_{1u}	A_1	A_u
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_1	A_{2u}	A_2	B_u
E_u	E	E	$A_{1u} + B_{1u}$	$A_1 + B_1$	$A_2 + B_2$	$A_1 + A_2$	E_u	E	$A_u +$ E
T_{1u}	T_1	T_2	$A_{2u} + E_u$	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$	$A_{2u} + E_u$	$A_2 + E$	$A_u + 2$
T_{2u}	T_2	T_1	$B_{2u} + E_u$	$A_2 + E$	$B_1 + E$	$A_2 + B_1 + B_2$	$A_{1u} + E_u$	$A_1 + E$	$2A_u +$

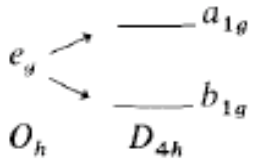
The crystal field perturbation can have different weight on the perturbed energy, that is it can be stronger (strong field) or weaker (weak field) than the inter-electronic perturbation. If we suppose the d^n electronic configurations in a strong crystal field perturbation, for the d^1 configuration the two perturbed terms are $^2T_{2g}$ and ^2E_g. In the case of d^2, we have $t_{2g}^{\ 2}$, $t_{2g}^{\ 1}e_g^{\ 1}$, $e_g^{\ 2}$ orbital arrangements and the terms are given by the direct product of the single arrangements (direct product of the irreducible representations).

$t_{2g} \times t_{2g} = T_{1g} + T_{2g} + E_g + A_{1g}$

$t^{\ 1}_{2g} \times e^{\ 1}_{\ g} = T_{1g} + T_{2g}$

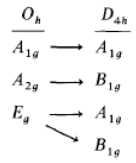
$e_g \times e_g = E_g + A_{1g} + A_{2g}$

However, while the terms are easy to be obtained by the group theory, the related spin states are not. In fact the d^2 configuration allows two spin states, the singlet and the triplet, and their attribution to the terms is not immediate. We will use the method of descending symmetry. If the $e_g^{\ 2}$ configuration is considered, when we lower the symmetry from O_h to D_{4h}, the determination of the spin state becomes straightforward, and the following configurations are expected

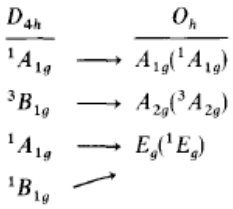


$b_{1g}^{\ 2}$ (S=0) , $a_{1g}b_{1g}$ (S=0 and S=1), $a_{1g}^{\ 2}$ (S=0) which give the terms A_{1g} (S=0) B_{1g} (S=0 and S=1) A_{1g} (S=0)

Given the following correlations:



The spin state and the orbital degeneracy can be assigned

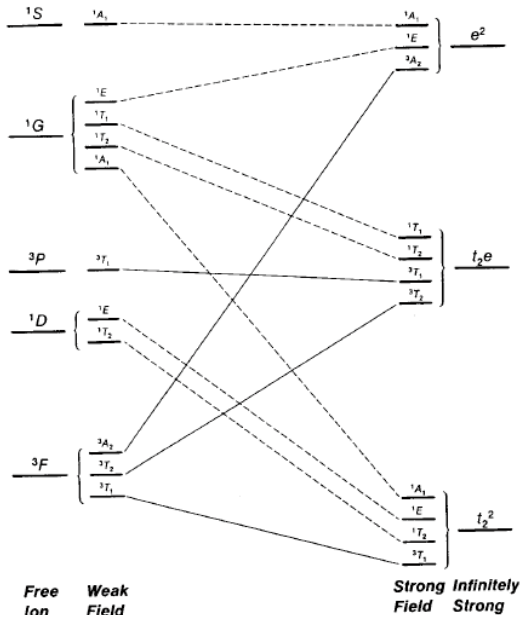


The method of descending symmetry thus consists in re-writing the electronic configuration in a symmetry where all the orbital degeneracies disappear. By this way the spin state can be definitely associated to the orbital. It results a complete correlation diagram between the one electron configurations, that correspond to very strong crystal field perturbation, and terms, where the electronic repulsion is stronger than the crystal field one (weak field).

The Scheme 17 proposes the correlation between energies of weak and strong field, and shows that these energies vary very much with the field strength, until to fully change the energy trend of the free ions states. However there is a full correspondence among high field and low spin terms.

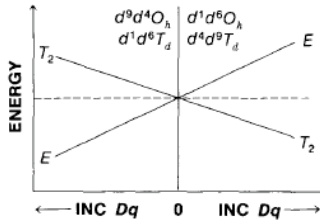
It is important to observe that no crossover is possible, along the field variation, between the states which have the same symmetry and spin state, as the same energy of two states which derive from different configurations is non sense.

Looking at the d^2 diagram the configurations are associated to a number of electronic transitions which, under excitation energy, can change the electronic state of the ion and also assign to the ion a given electronic configuration and field symmetry.

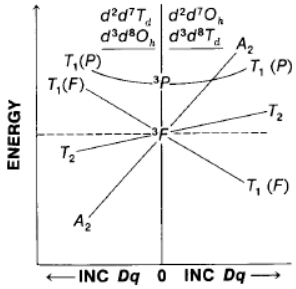


Scheme 17 - Energy diagram for d^2 configuration in different field strengths

(A)



(B)



Scheme 18 – Orgel diagrams

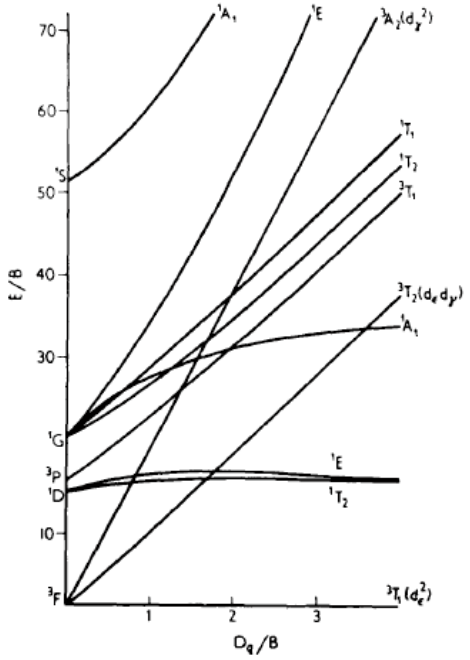
Based on the possibility of experimentally detecting the electronic transitions and consequently assigning the crystal field symmetry and the ion electronic configuration, taking also into consideration that the most probable (strong) transitions are those spin allowed, Orgel proposed the schemes on the left (Schema 18, A and B)

The transition energies reported by these schemes, plotted for increasing *Dq* values, are between states with the same spin multiplicity and refer to octahedral and tetrahedral symmetries. They allow to assign the crystal field of the spectra from d^1 to d^9 configurations and to recognize both symmetry and electronic configuration of the ion.

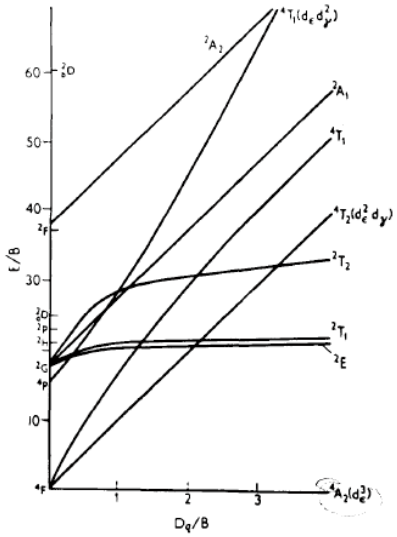
Tanabe and Sugano alternatively described the cubic (octahedral and tetrahedral) configurations by diagrams which report all the states for a single electronic configuration, independently of the similarity of their spin multiplicity. The diagrams plot the electronic energies of the ions states against the *Dq* energy values. All energy values are measured in B (Racah) units in order to make the values inde-

pendent of the different ions. On the left hand of the diagrams we read the free ion energies, on the right hand the energy for an infinitely strong field. When the strong field configuration is not indicated it is intended that it remains the same as the lower energy state.

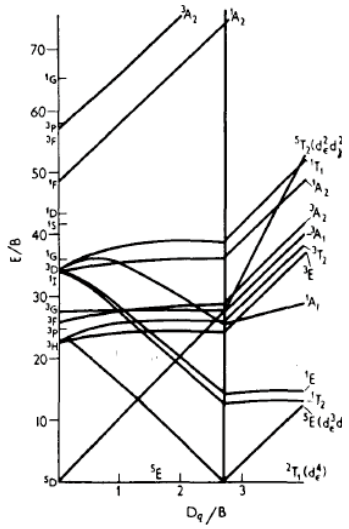
Scheme 19 – Tanabe-Sugano Diagrams for different electronic configurations



Energy diagram for the configuration d^2.



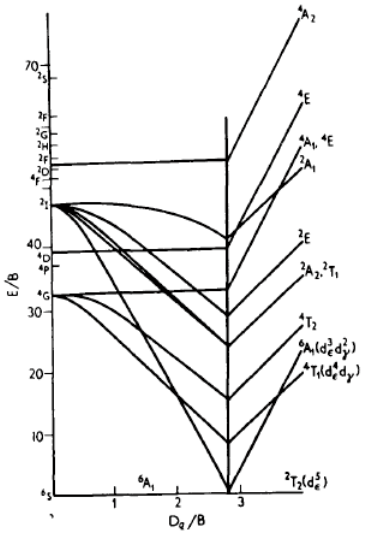
Energy diagram for the configuration d^3.



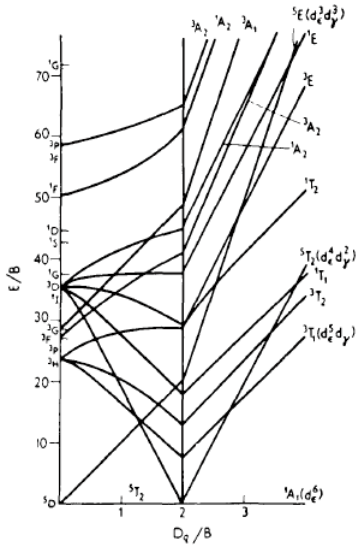
Energy diagram for the configuration d^4

From the d^4 to d^7 configuration, the diagrams contain a vertical line which separates the high spin from the low spin region for the same ion. The two regions are different in the ground and the other states.

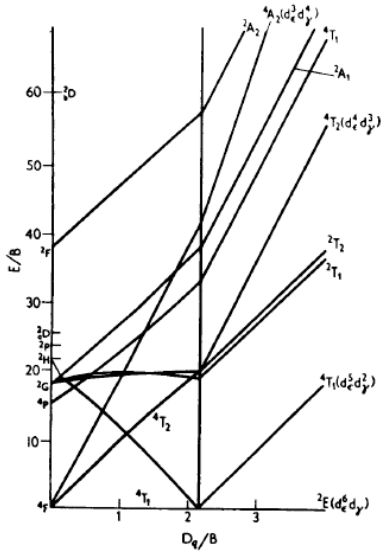
The transitions in Tanabe Sugano diagrams can be read by the same way as for the Orgel diagrams and show the complete spectrum of the absorption bands.



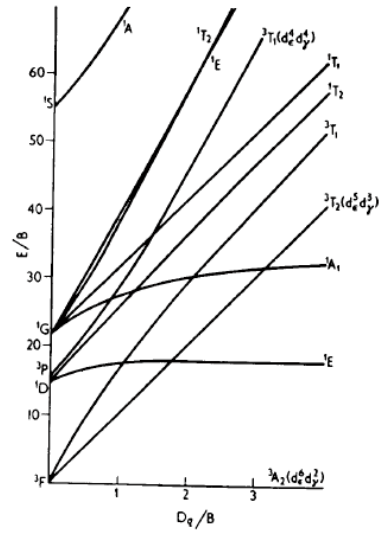
Energy diagram for the configuration d^5.



Energy diagram for the configuration d^6.



Energy diagram for the configuration d^7.



Energy diagram for the configuration d^8.

3.4 Examples of attribution of the absorption bands

Let we consider the absorption maxima of some Ni(II) octahedral complexes (Fig.2 Table 11)

Table 11 – Crystal field transitions of Ni(II)octahedral complexes

Ligand	$^3A_{2g} \rightarrow {}^3T_{2g}$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
H_2O	8500	15,400	26,000
NH_3	10,750	17,500	28,200
$(CH_3)_2SO$	7730	12,970	24,040
$HC(O)N(CH_3)_2$	8500	13,605 (14,900)	25,000
$CH_3C(O)N(CH_3)_2$	7575	12,740 (14,285)	23,810

Three bands are evident, whose assignment is obtained by the Orgel diagram for the d^8 electronic configuration. The shapes of all the spectra are similar and indicate that the electronic configuration and the symmetry are similar. Only the energy of the transitions is different (see table) and can be associated to the different crystal field strength.

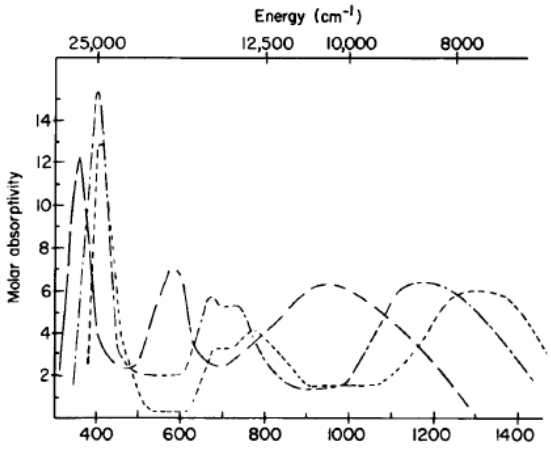
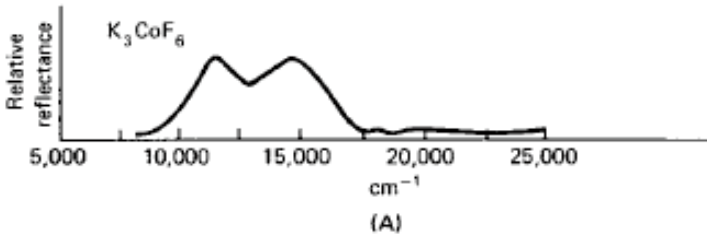
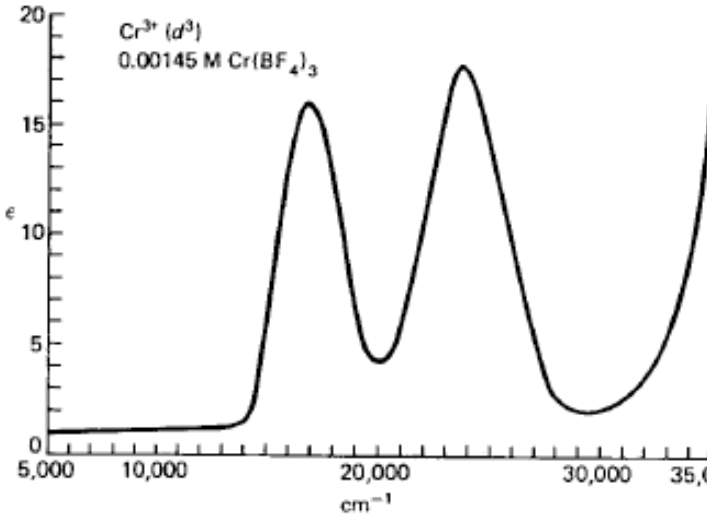


Figure 2 – Electronic absorption spectra of Ni(II) complexes

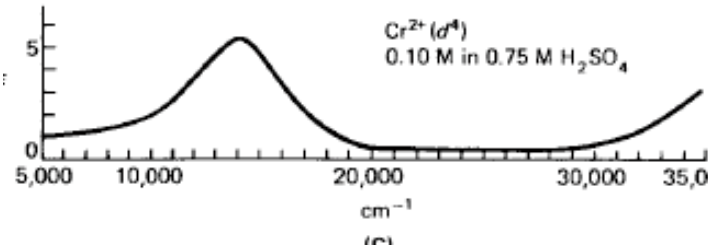
As expected the presence of N in the first coordination Ni(II) sphere induces higher field strength, due to the stronger basicity of the ligand.
In the following (Fig 3) we report and assign the electronic transitions of a number of octahedral coordination compounds, by using the Tanabe Sugano diagrams.



(A)



(B)



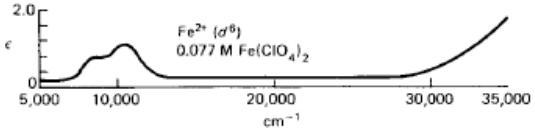
(C)

→

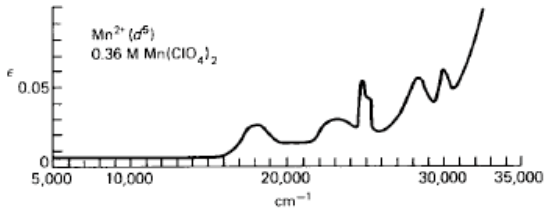
(A) Co^{3+} d^6 $^5T_{2g} \rightarrow {}^5E_g$

(B) Cr^{3+} d^3 $^4A_{2g} \rightarrow {}^4T_{2g}$ $\quad {}^4A_{2g} \rightarrow {}^4T_{1g}$ (F)

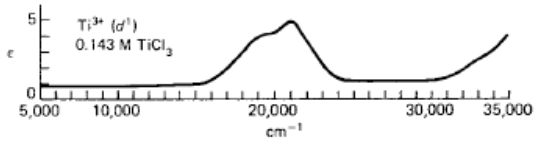
(C) Cr^{2+} d^4 $^5E_g \rightarrow {}^5T_{2g}$


2.0
ε
0
Fe^{2+} (d^6)
0.077 M $Fe(ClO_4)_2$
5,000
10,000
20,000
30,000
35,000
cm^{-1}

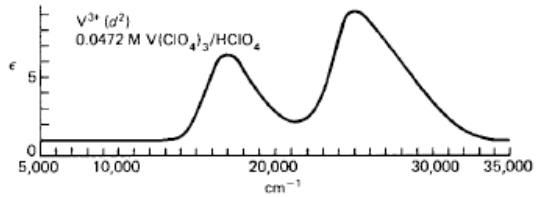
(D)


ε
0.05
0
Mn^{2+} (d^5)
0.36 M $Mn(ClO_4)_2$
5,000
10,000
20,000
30,000
35,000
cm^{-1}

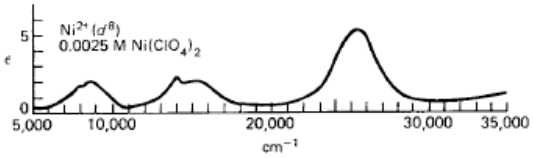
(E)


5
ε
0
Ti^{3+} (d^1)
0.143 M $TiCl_3$
5,000
10,000
20,000
30,000
35,000
cm^{-1}

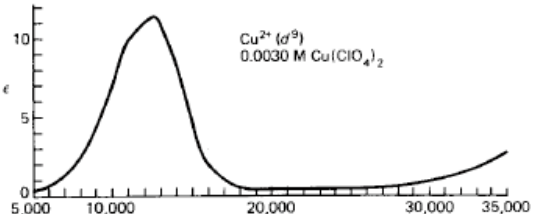
(F)


ε
5
0
V^{3+} (d^2)
0.0472 M $V(ClO_4)_3/HClO_4$
5,000
10,000
20,000
30,000
35,000
cm^{-1}

(G)


5
ε
0
Ni^{2+} (d^8)
0.0025 M $Ni(ClO_4)_2$
5,000
10,000
20,000
30,000
35,000
cm^{-1}

(H)


10
ε
5
0
Cu^{2+} (d^9)
0.0030 M $Cu(ClO_4)_2$
5,000
10,000
20,000
30,000
35,000

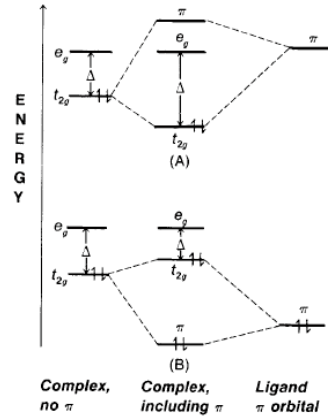
(D) Fe^{2+} d^6 $^5T_{2g} \rightarrow {}^5E_g$
(E) Mn^{2+} d^5 no spin allowed electronic transitions
(F) Ti^{3+} d^1 $^2T_{2g} \rightarrow {}^2E_g$

(G) V^{3+} d^2 $^3T_{1g}(F) \rightarrow {}^3T_{2g}$ $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$
(H) Ni^{2+} d^8 $^3A_{2g} \rightarrow {}^3T_{2g}$ $^3A_{2g} \rightarrow {}^3T_{1g\rightarrow}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$
(I) Cu^{2+} d^9 $^2E_g \rightarrow {}^2T_{2g}$

Fig. 3 - Electronic spectra of different d^n configurations. The transitions are assigned basing on Tanabe Sugano diagrams.

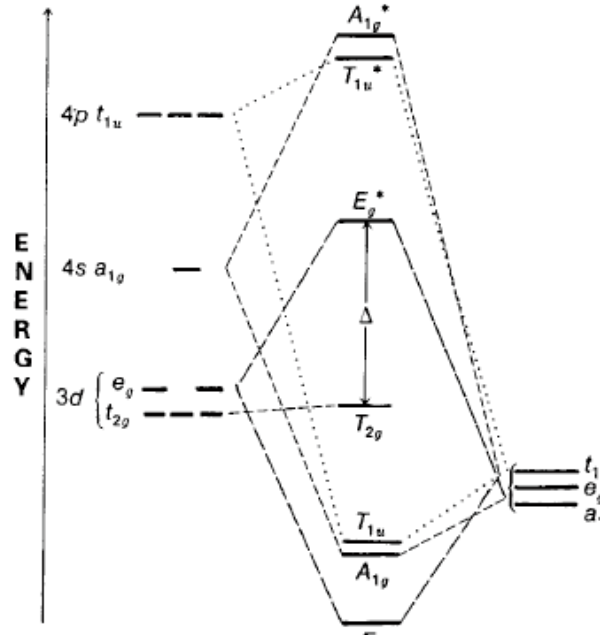
3.5 Crystal field limits

Several limitations affect the crystal field theory, due to the simplified model which considers the ligands as negative spheres and the interaction between valence electrons and the negative ligand charge a mere Coulomb repulsion. No covalent interaction is admitted.
For this reason the experimental *Dq* value results different from that expected from the simple crystal field approximation. The following diagrams show the variations of *Dq* when the overlap between ***σ*** or ***π*** ligand orbitals and d orbitals is taken into account.
In Scheme 19 (A) indicates the overlap of d orbitals with empty π orbitals (B) with the filled ones and cause respectively an increase of *Dq* ***(Δ)*** and a decrease with respect to the crystal field value.



Scheme 19 - Ligand field effect by π orbitals

Scheme 20 indicates the overlap of d orbitals with the σ ligand orbitals



Scheme 20 - Ligand field effect by σ orbitals

The covalent interaction leads to an increase of *Dq* value. Thus it is possible to order the effects of the different ligand molecules basing on the π and σ interactions they display. The trend is called spectrochemical series and the comparison among the ligand effect have to be made only for the same crystal field effect of the metal ion

$I^- < Br^- < —SCN^- < F^- <$ urea $< OH^- < CH_3CO_2^- < C_2O_4^{2-} <$
$H_2O <$ —$NCS^- <$ glycine $< C_5H_5N \sim NH_3 <$ ethylenediamine $<$
$SO_3^{2-} <$ *o*-phenanthroline $< NO_2^- < CN^-$

Crystal field trend (magnitude of 10 ***Dq***) for different metal ions By this way we change the crystal field theory in ligand field theory.

Mn(II) < Ni(II) < Co(II) < Fe(II) < V(II) < Fe(III) < Cr(III) < V(III) < Co(III) < Mn(IV) < Mo(III) < Rh(III) < Pd(IV) < Ir(III) < Re(IV) < Pt(IV)

3.6 Effect of distortion from cubic symmetry

The group theory allows an easy indication of the crystal field effects on the atomic states and we reported the examples in the previous chapters. However the extensive treatment was for cubic symmetry. It is expected that in the case of lower symmetry, or distortion from the cubic one, the perturbation field effects on the ion states are different. In fact for a d^1 ion in distorted octahedral symmetry (elongated tetragonal), the pristine O_h states split as shown on the left.
For a low spin Co(III) d^6 the ground state splits into.
Fig 4 reports as example the electronic spectra of three Co(III) complexes with different symmetries (Fig 4) (A) octahedral (B) cis-difluoro bis ethylenediamine (C) trans-difluoro bis ethylenediamine. On passing from (A) to (B) and (C) the two bands gradually broaden and at the end split in (C) where the distortion from the octahedral symmetry is highest. More in general looking at the change of energy in the absorption spectra, as a function of the percent (Scheme21) of distortion in Ni(II) complexes.

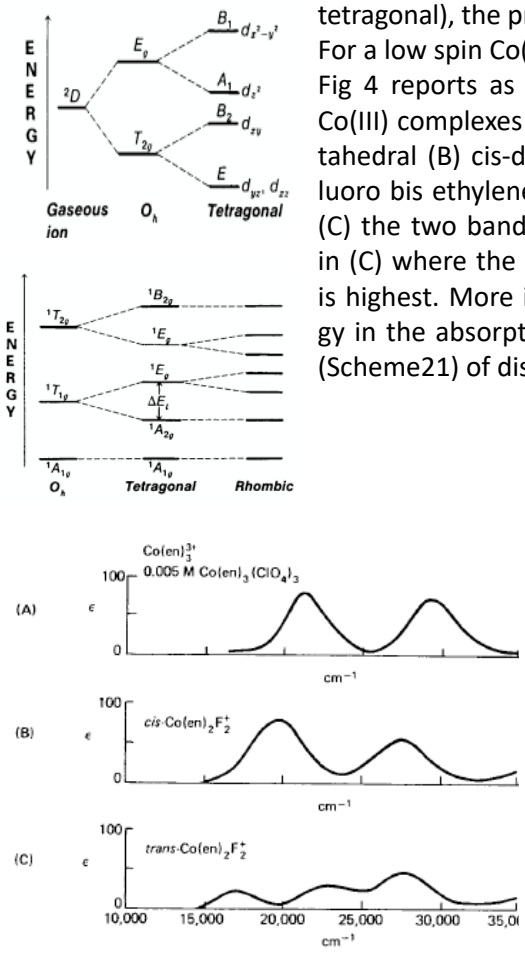
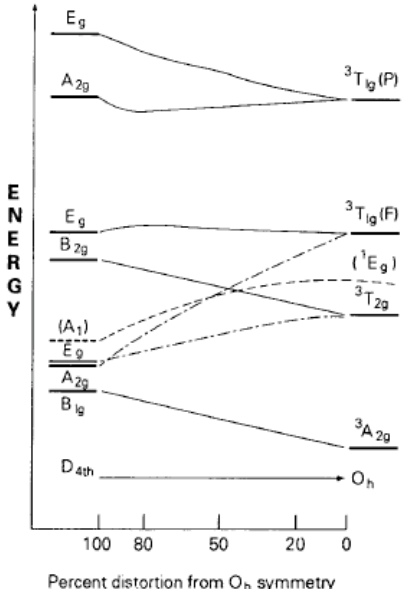


Figure 4 - Electronic spectra of Co(III) complexes



Scheme 21 - Electronic spectra of Ni(II) complexes, as a function of the distortion from O_h

Large variations both in the number and in the energy of the states are observed by lowering the symmetry. Thus it is not so easy to assign the symmetry and the electronic configuration in the presence of large distortion from the cubic symmetry. Instead it is sometimes simple to distinguish the tetrahedral from the octahedral symmetry of a given ion (Co(II) in Fig 5), basing on the intensity of transitions. These are much more intense in tetrahedral symmetry, due to the mixing between d and p orbitals allowed in T_d symmetry. By this mixing the d-d transition is no more pure and no more forbidden.

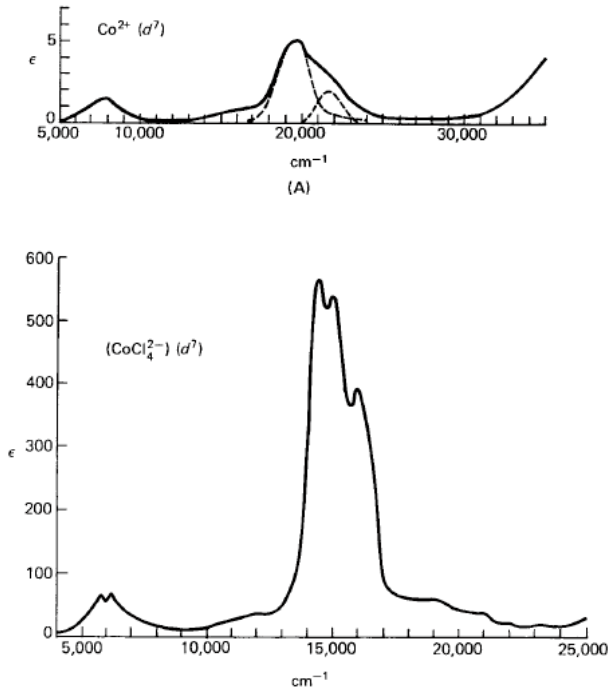


Figure 5 - Electronic spectra of octahedral and tetrahedral Co(III) complexes

In conclusion the group theory allows the prevision of the type of the electronic states due to the crystal field perturbation and of the expected transitions. By this approach both the coordination geometry and the electronic configuration of the ion can be hypothesized.

3.7 Table of Characters to be used in the reported molecules

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)

O	E	$6C_4$	$3C_2(=C_4^2)$	$8C_3$	$6C_2$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	−1	1	1	−1		
E	2	0	2	−1	0		$(2z^2 - x^2 - y^2,$ $x^2 - y^2)$
T_1	3	1	−1	0	−1	(R_x, R_y, R_z); (x, y, z)	
T_2	3	−1	−1	0	1		(xy, xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 +$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2$ $x^2 -$
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		$(xz,$
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		

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}[a]	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2,
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

[a] σ_v passes through the atoms and σ_d bisects the bond angles.

$C_{\infty v}$	E	$2C_\infty^{\Phi}$	...	$\infty\sigma_v$		
$A_1 \equiv \Sigma^+$	1	1	...	1	z	x^2+y^2, z^2
$A_2 \equiv \Sigma^-$	1	1	...	−1	R_z	
$E_1 \equiv \Pi$	2	$2\cos\Phi$	...	0	$(x, y); (R_x, R_y)$	(xz, yz)
$E_2 \equiv \Delta$	2	$2\cos 2\Phi$	...	0		(x^2-y^2, xy)
$E_3 \equiv \Phi$	2	$2\cos 3\Phi$	...	0		
...	...	...	...	...		

$D_{\infty h}$	E	$2C_\infty^{\Phi}$	...	$\infty\sigma_v$	i	$2S_\infty^{\Phi}$	...	∞C_2		
Σ_g^+	1	1	...	1	1	1	...	1		x^2+y^2,
Σ_g^-	1	1	...	−1	1	1	...	−1	R_z	
Π_g	2	$2\cos\Phi$	...	0	2	$-2\cos\Phi$	...	0	(R_x, R_y)	(xz, yz)
Δ_g	2	$2\cos 2\Phi$	...	0	2	$2\cos 2\Phi$	...	0		$(x^2-y^2,$
...	...	...	...	...	...	...	...	...		
Σ_u^+	1	1	...	1	−1	−1	...	−1	z	
Σ_u^-	1	1	...	−1	−1	−1	...	1		
Π_u	2	$2\cos\Phi$	...	0	−2	$2\cos\Phi$	...	0	(x, y)	
Δ_u	2	$2\cos 2\Phi$	...	0	−2	$-2\cos 2\Phi$	...	0		
...	...	...	...	...	...	...	...	...		

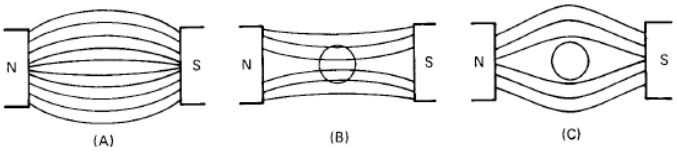
C_{2v}[a]	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

[a] For a planar molecule the x-axis is taken perpendicular to the plane.

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	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz$

4. Magnetism

The magnetic properties play a fundamental role in the understanding of the electronic structure of ions and molecules. In fact starting from the energy of interaction between the electrons and the magnetic field it becomes possible to locate the unpaired electrons of the ground state and to hypothesize the energy trend of the remaining electronic states. The magnetic data come from measurements of magnetic susceptibility and from electron spin resonance spectra. When a material is immersed between the polarities of a magnetic field, different modifications affect the magnetic flux lines, depending on the vacuum presence (A), the presence of a paramagnetic solid (B), the presence of a diamagnetic solid (C).



In order to quantify this effect it is convenient to define a quantity called magnetic induction expressed as vector $\vec{\mathbf{B}}$

$$\vec{\mathbf{B}} = \vec{\mathbf{H}}_0 + 4\pi\vec{\mathbf{M}}$$

$\vec{\mathbf{H}}_0$ is the external field and $\vec{\mathbf{M}}$ the intensity of magnetization per unit volume. Dividing by $\vec{\mathbf{H}}_0$

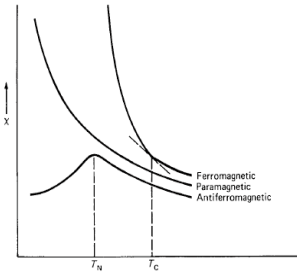
$$\frac{B}{H_0} = 1 + 4\pi\frac{M'}{H_0} = 1 + 4\pi\chi_v$$

$\boldsymbol{X}_v$ is the magnetic susceptibility for unit volume, dimensionless

$\boldsymbol{X}_v/d = X_g$ gram susceptibility (cm^3/gr) $X_g \bullet MW$ ($cm^3/mole$) molar susceptibility

Table 12 - Different types of magnetic behavior

Type	Sign	Magnitude	Field Dependence of χ	Origin
Diamagnetism	–	10^{-6} emu units	Independent	Field induced, paired electron circulations
Paramagnetism	+	0 to 10^{-4} emu units	Independent	Angular momentum of the electr
Ferromagnetism	+	10^{-4} to 10^{-2} emu units	Dependent	Spin alignment from dipole-dipo interaction of moments on adjace atoms, ↑↑
Antiferromagnetism	+	0 to 10^{-4} emu units	Dependent	Spin pairing, ↑↓, from dipole-dipo interactions



Scheme 22 - Variation of the magnetic properties with temperature

For our purposes is specially important the origin of the magnetic behavior, as it is this aspect that can be relatable to the electronic properties. The variation of the magnetic properties with the temperature is also indicative of the different behavior. Consider that the diamagnetic behavior is independent of the temperature.

Diamagnetism arises from field induced electron circulation of paired electrons, which generates a field opposed to the applied field. Thus all the molecules have contributions from diamagnetic effects. The diamagnetic susceptibility of an atom is proportional to the number of electrons n and to the sum of the square value of the average orbital radius of the i th electron

$$\chi_A = -\frac{Ne^2}{6mc^2}\sum_i^n \bar{r}_i^{\,2} = -2.83 \times 10^{10}\sum_i^n \bar{r}_i^{\,2}$$

The molar diamagnetic susceptibility can be obtained by the sum of the diamagnetic contributions of all the atoms $\boldsymbol{\chi_A}$ and of the functional groups $\boldsymbol{\chi_B}$, as indicated in the table 13. When a magnetic measurements is performed the magnetic susceptibility is the difference between the measured value and the value of the diamagnetic susceptibility.

$$\chi_{PARA} = \chi_{MEAS} - \chi_{DIA}$$

Table 13 - Diamagnetic contributions

Atoms, χ_A				Bonds, χ_B	
Atom	χ_A ($\times 10^{-6}$ cm^3 mole^{-1})	Atom	χ_A ($\times 10^{-6}$ cm^3 mole^{-1})	Bond	χ_B ($\times 10^{-6}$ cm^3 mole^{-1})
H	−2.93	F	−63	C=C	+5.5
C	−6.00	Cl	−20.1	C≡C	+0.8
C (aromatic)	−6.24	Br	−30.6	C=N	+8.2
N	−5.57	I	−44.6	C≡N	+0.8
N (aromatic)	−4.61	Mg^{2+}	−5	N=N	+1.8
N (monamide)	−1.54	Zn^{2+}	−15	N=O	+1.7
N (diamide, imide)	−2.11	Pb^{2+}	−32.0	C=O	+6.3
O	−4.61	Ca^{2+}	−10.4		
O_2 (carboxylate)	−7.95	Fe^{2+}	−12.8		
S	−15.0	Cu^{2+}	−12.8		
P	−26.3	Co^{2+}	−12.8		
		Ni^{2+}	−12.8		

An example, the pyridine molecule

C_5H_5N

SUM OF CONTRIBUTIONS TO χ ($\times 10^{-6}$ CM^3 MOLE^{-1})

$$5 \times \text{C (ring)} = -31.2$$

$$5 \times \text{H} = -14.6$$

$$1 \times \text{N (ring)} = -4.6$$

$$\chi = \sum_i \chi_{A_i} + \sum_j \chi_{B_j} = -50.4 \times 10^{-6} \text{ cm}^3 \text{ mole}^{-1}$$

The functional groups are accounted for by using the ring values for carbon a nitrogen, so $\Sigma\, \chi_B$ equals zero.

The calculation of the diamagnetic contribution allows, after the experimental measure of the total magnetic contribution, the determination of the paramagnetic contribution. The goal is at this point to relate the value of the paramagnetic contribution to the electronic properties.

4.1 Interaction between electrons and magnetic field

The effect of the magnetic field on the electronic spin is better explainable in terms of the quantum mechanical approach than by the magnetic field classical interaction. It is well known that each system having discrete energy levels may be associated to the equation (1)

$$\boldsymbol{\Lambda}_i \boldsymbol{\psi}_i = \boldsymbol{\lambda}_i \boldsymbol{\psi}_i \quad \textbf{(1)}$$

where $\boldsymbol{\Lambda}$ is the operator describing the potential energy of the system to which we associate the energy states **i**, eigenvalues, and the wave functions **i,** eigenfunctions. The $\boldsymbol{\Lambda}$ determination is a delicate point, to be done by attempts.

We will proceed through the following considerations:

a) By immersing a magnetic dipole $\boldsymbol{\mu}$ in a magnetic field **H** (fig.5) the energy of the system is given by the expression (2)

$$\mathbf{W = -\vec{\mu} \cdot \vec{H} = -\vec{\mu} \cdot H \cos(\vec{\mu}H)} \qquad \mathbf{(2)}$$

b) Both the orbital and the spin angular momentum undergo quantization (Fig 6,7), as well as their components in a space direction, being their values

$$\mathbf{L(L+1)^{1/2}\, h/2\pi \quad S(S+1)^{1/2}\, h/2\pi}$$

$\mathbf{M_L}$ 2L+1 values from –L to +L

$\mathbf{M_S}$ 2S+1 values from –S to +S

c) The moment of the magnetic dipole is proportional both to the orbital and the spin angular momentum.

The property associated to the rotation of the electron negative charge, and the related relations are

$\boldsymbol{\mu_z = \gamma M_L}\, h/2\pi$

$\boldsymbol{\mu_z = \gamma M_S}\, h/2\pi$ and if $\boldsymbol{\gamma = -ge/2mc}$ $\boldsymbol{\beta = eh/4\pi mc} \rightarrow$

$\boldsymbol{\mu_z = -g\beta M_S}$

From the **a** and **c** considerations the energy of one electron with $\mathbf{M_S = \pm ½}$ is

$$\mathbf{W = g\beta H M_S = \pm ½\, g\beta H} \qquad \boldsymbol{\Delta = g\beta H}$$

Based on points **a – c**, the spin properties of the system under investigation determine its behavior; thus the Hamiltonian equation for a spin only case results

$$\boldsymbol{S_z \psi_i = M_s \psi_i} \qquad \boldsymbol{S_z \psi_i (M_s \pm ½) = \pm ½\, M_s \psi_i (M_s \pm ½)}$$

As $\mathbf{S_z}$ is commutative with the Hamiltonian operator ***H,***

$$\boldsymbol{H\, \psi_i (M_s \pm ½) = W_{\pm ½}\, \psi_i (M_s \pm ½)}$$

By associating to the magnetic moment $\boldsymbol{\mu_z}$ the corresponding operator

$$\boldsymbol{\mu_z = -g\beta M_s}$$

$$\boldsymbol{\mu_z = -g\beta S_z}$$

and to the energy $\mathbf{W = -\mu_z H}$

The corresponding Hamiltonian $\boldsymbol{H = g\beta H S_z}$

$$\mathbf{W_{1/2} = ½\, g\beta H}$$

$$\mathbf{W_{-1/2} = -½\, g\beta H}$$

$$\boldsymbol{\Delta W = g\beta H} \text{ (Fig. 8)}$$

***The energy transition is ΔW and is tuned by* H, provided**

Δ M_s = ± 1 as selection rule **g** is a value peculiar of the electron behavior

See the comparison between quantum mechanical and classical approaches:

Energy of a classical magnetic dipole in a magnetic field as a function of the angle Θ between the magnetic field and the axis of the dipole

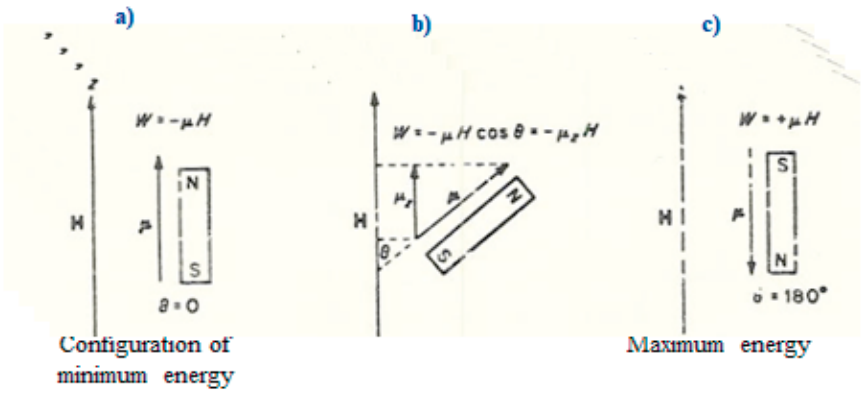


Fig.6 - Energy interaction of one electron in a magnetic field

Allowed values of the total spin angular momentum $[S(S+1)]^{1/2}$ and of the component M_s (in units ħ) in a fixed direction

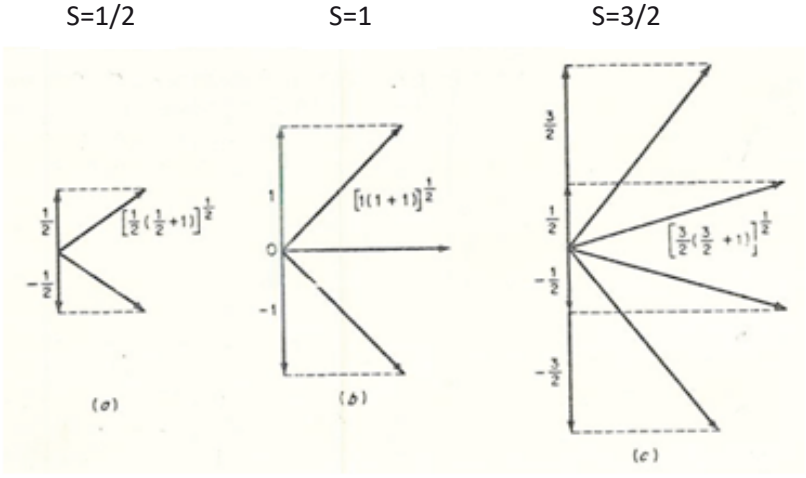


Fig 7 - Quantum mechanical effect on the spin angular momentum

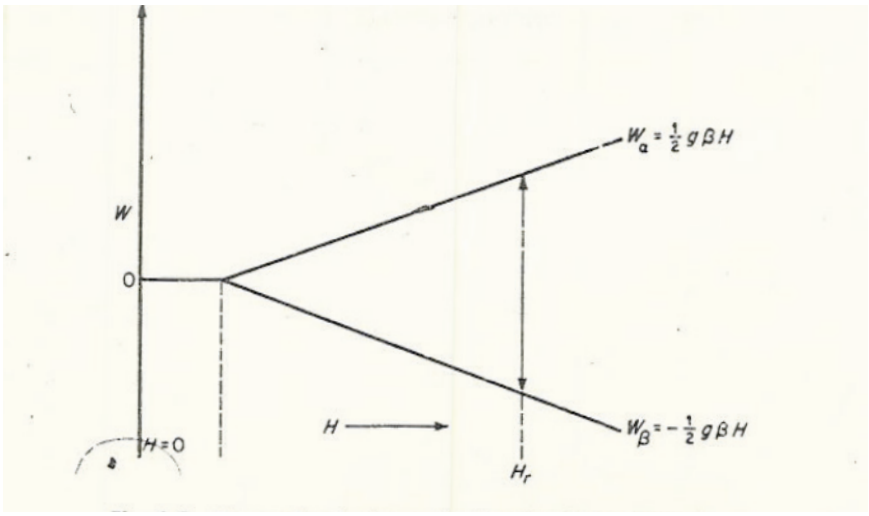


Fig 8 - Energy changes induced by the magnetic field on one electron

4.2 Magnetic susceptibility expression for S=1/2

Considering that for a given electron *n* $\mu_n = -g\beta M_s$ and $W_n = g\beta H M_s = \pm \frac{1}{2} g\beta H$ and that the energy difference between the spin states is lower than KT, both the states of S=1/2 are populated at room temperature. The probability P_n for populated states with energy E_n is given by

$$P_n = \frac{N_n}{N} = \frac{\exp\left(\frac{-E_n}{kT}\right)}{\sum_n \exp\left(\frac{-E_n}{kT}\right)}$$

N_n refers to the population of the state *n*, while N to the total population of all the existing states.The population-weighted sum of magnetic moments over the individual states gives the macroscopic magnetic moment *M.* For a mole of material

$$M = \underline{N} \sum_{m_s} \mu_n P_n$$

Where N is the number of Avogadro. Substituting P_n

$$M = \frac{\underline{N} \sum_{m_s=-1/2}^{+1/2} \mu_n \exp\left(\frac{-E_n}{kT}\right)}{\sum_{m_s=-1/2}^{+1/2} \exp\left(\frac{-E_n}{kT}\right)}$$

Substituting μ_n ed E_n

$$M = \frac{Ng\beta}{2}\left[\frac{\exp\left(\frac{g\beta H}{2kT}\right) - \exp\left(\frac{-g\beta H}{2kT}\right)}{\exp\left(\frac{g\beta H}{2kT}\right) + \exp\left(\frac{-g\beta H}{2kT}\right)}\right]$$

in general given the short distance between the magnetic levels *gβH/KT <<1*, thus

$$\exp\left(\frac{\pm g\beta H}{2kT}\right) \approx \left(1 \pm \frac{g\beta H}{2kT}\right)$$

$$M = \frac{Ng^2\beta^2 H}{4kT}$$

since $\chi_{para} = \vec{M}/\vec{H}$

$$\chi = \frac{Ng^2\beta^2}{4kT} \qquad \chi = \frac{Ng^2\beta^2}{3kT} S(S+1)$$

Which is the **Curie law**. This expression gives the para-magnetic susceptibility for spin only systems
If we define a new scalar quantity

$$\mu_{\text{eff}} = \left(\frac{3k}{N\beta^2}\right)^{1/2} (\chi T)^{1/2} = 2.828(\chi T)^{1/2} \text{ (BM)}$$

$$\mu_{\text{eff}} \text{ (spin-only)} = g[S(S+1)]^{1/2} \text{ (BM)}$$

Number of Unpaired Electrons	S	μ_{eff}(spin-only)(BM)
1	1/2	1.73
2	1	2.83
3	3/2	3.87
4	2	4.90
5	5/2	5.92
6	3	6.93
7	7/2	7.94

Thus the μ_{eff} value allows to detect the number of unpaired electrons in spin only systems. If the systems include magnetic contribution different from that of the spin one, the μ_{eff} values are different. In this case the system is associated to the Hamiltonian

$$\hat{H} = \lambda \hat{L} \cdot \hat{S} + \beta(\hat{L} + g_e \hat{S}) \cdot H$$

$$E_n = \underset{\lambda \mathbf{L} \cdot \mathbf{S}}{E_n^{(0)}} + \underset{\text{first-order Zeeman (diagonal terms)}}{HE_n^{(1)}} + \underset{\text{second-order Zeeman (off-diagonal terms)}}{H^2 E_n^{(2)}}$$

By replacing in the Curie expression $\exp(-E_n/KT)$ with

$$\exp\left(\frac{-E_n^{(0)} - HE_n^{(1)} - H^2E_n^{(2)} + \cdots}{kT}\right) \cong \left(1 - \frac{HE_n^{(1)}}{kT}\right) \exp\left(\frac{-E_n^{(0}}{kT}\right.$$

$$\mu_n = \frac{-\partial E_n}{\partial H} = -E_n^{(1)} - 2HE_n^{(2)}$$

$$M = \underline{N} \frac{\sum_n (-E_n^{(1)} - 2HE_n^{(2)}) \left(1 - \frac{HE_n^{(1)}}{kT}\right) \exp\left(\frac{-E_n^{(0)}}{kT}\right.}{\sum_n \exp\left(\frac{-E_n^{(0)}}{kT}\right)\left(1 - \frac{HE_n^{(1)}}{kT}\right)}$$

Being M=0 for H=0

$$-\sum_n E_n^{(1)} \exp\left(\frac{-E_n^{(0)}}{kT}\right) = 0$$

Neglecting the terms higher than $E^{(2)}{}_n$ and $E^{(2)}{}_n \times E^{(1)}{}_n$

$$\chi = \underline{N} \frac{\sum_n \left[\frac{(E_n^{(1)})^2}{kT} - 2E_n^{(2)}\right] \exp\left(\frac{-E_n^{(0)}}{kT}\right)}{\sum_n \exp\left(\frac{-E_n^{(0)}}{kT}\right)}$$

This is the ***Van Vleck equation***, where the magnetic susceptibility contains different contributions to the interaction with

the magnetic field, that field independent and that first order dependent. The difference of μ_{eff} with respect to the spin only value is due to the contribution of the orbital magnetic moment. It is mainly this difference to contribute the assignment of the electronic state. If an electron can occupy degenerate orbitals that permit circulation of the electron about an axis, an orbital angular momentum can result. Table 14 reports the cases where the angular momentum is active or quenched.
The behavior depends on the electronic configuration and on the crystal field symmetry, thus the quenching or not gives an indication of the coordination geometry and of the electronic configuration.

Table 14 - Relations between magnetism and crystal field properties for different d^n

		Stereochemistry					
		Octahedral			Tetrahedral		
No. of d-electrons	Free ion ground term	$t_{2g}^n e_g^m$ ground configuration	ligand field ground term	Quenching of orbital contribution*	$e^n t_2^m$ ground configuration	ligand field ground term	Quenching of orbital contribution*
1	^2D	t_{2g}^1	$^2T_{2g}$	No	e^1	^2E	Yes
2	^3F	t_{2g}^2	$^3T_{1g}$	No	e^2	$^3A_2$	Yes
	^4F	t_{2g}^3	$^4A_{2g}$	Yes	$e^2 t_2^1$	$^4T_1$	No
4	^5D	$t_{2g}^3 e_g^1$	^5E_g	Yes	$e^2 t_2^2$	$^5T_2$	No
		t_{2g}^4	$^3T_{1g}$	No	–	–	–
5	^6S	$t_{2g}^3 e_g^2$	$^6A_{1g}$	Yes	$e^2 t_2^3$	$^6A_1$	Yes
		t_{2g}^5	$^2T_{2g}$	No	–	–	–
6	^5D	$t_{2g}^4 e_g^2$	$^5T_{2g}$	No	$e^3 t_2^3$	^5E	Yes
		t_{2g}^6	$^1A_{1g}$	Yes	–	–	–
7	^4F	$t_{2g}^5 e_g^2$	$^4T_{1g}$	No	$e^4 t_2^3$	$^4A_2$	Yes
		$t_{2g}^6 e_g^1$	^2E_g	Yes	–	–	–
8	^3F	$t_{2g}^6 e_g^2$	$^3A_{2g}$	Yes	$e^4 t_2^4$	$^3T_1$	No
9	^2D	$t_{2g}^6 e_g^3$	^2E_g	Yes	$e^4 t_2^5$	$^2T_2$	No

Let you consider the d^3 electronic configuration: in octahedral field symmetry the three electrons lie in t_{2g} orbitals, with parallel spins and no orbital circulation is allowed. Thus the quenching of the orbital momentum is fully justified. Instead in tetrahedral symmetry field there is one electron in t_{2g} orbitals and the orbital circulation is active.

4.3 *Electron spin resonance*

The resonance condition (energy of the magnetic transition) for one electron is

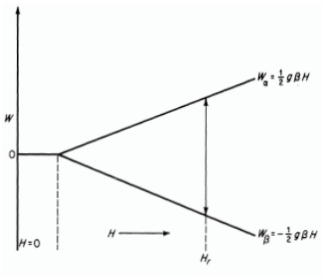


Fig 9 - Energy changes induced by the magnetic field on one electron

W = g β H M_s = ± ½ g β H Δ = g β H resonance condition

g = hν/$\beta$$H_r$ where ν is the irradiation frequency and H_r is the magnetic field where the absorption happens.

The experimental choice is to fix the frequency ν and to measure the field H_r. The **g** value depends on the electronic surrounding of the unpaired electron, thus it is typical of a given paramagnetic center. In the case of a free electron **g = 2.0023.** Different values are due to spin-orbit coupling interaction and can show a**nisotropic behavior** (g is represented by **a tensor**) in the form of **cubic, axial or rhombic symmetry.** In order to precisely measure the g value it is mandatory to precisely measure

ν and H_r

In general the measure is obtained by using a precise ν and calibrating the magnetic field by a standard sample with **known g value**

$g_s = h\nu/\beta H_s$ $g_x = h\nu/\beta H_x$ $g_s/g_x = H_x/H_s$

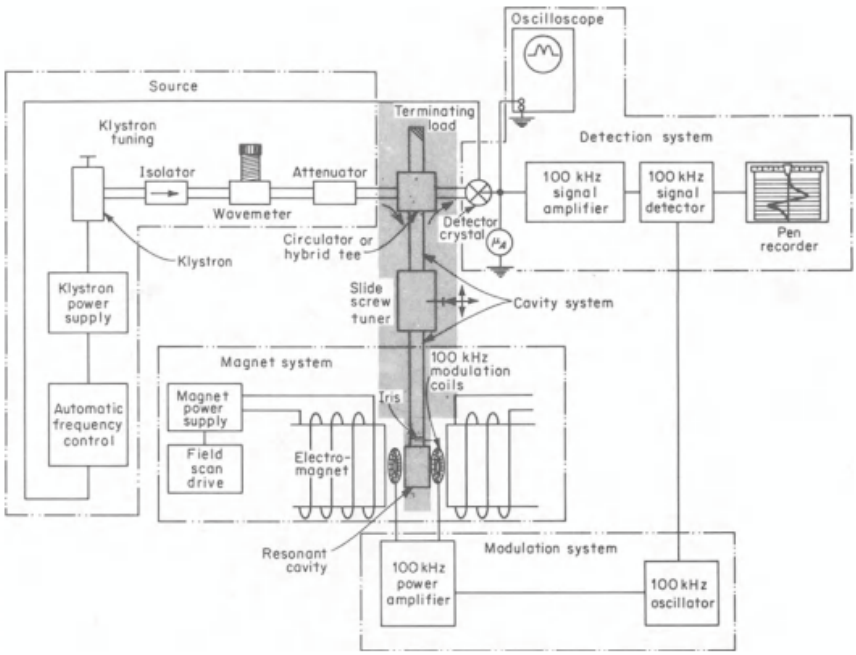
A used standard molecule used is diphenyl pycrilhydrazil **(DPPH) g = 2.0037.**

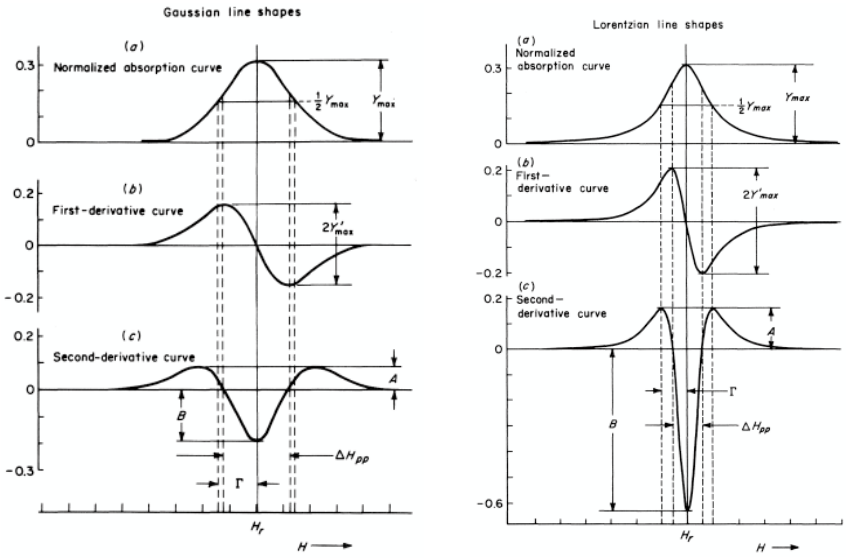
The shape of the spectrum corresponds to Gaussian or Lorenzian lines (Fig.11) and is taken mostly as a derivative curve, to identify the overlapping absorptions .The most common **used frequencies** of the microwave source are:

9.417 GHz (X band) 35 GHz (Q band)

Block diagram of a typical X-band ESR spectrometer employing 100 gHz phases-sensitive detection is as it follows

Fig.10 - Scheme of the ESR apparatus





a) Absorption spectrum
b) First-derivative spectrum
c) Second-derivative spectrum

a) Absorption spectrum
b) First-derivative spectrum
c) Second-derivative spectrum

Fig. 11 - Spectra general shape

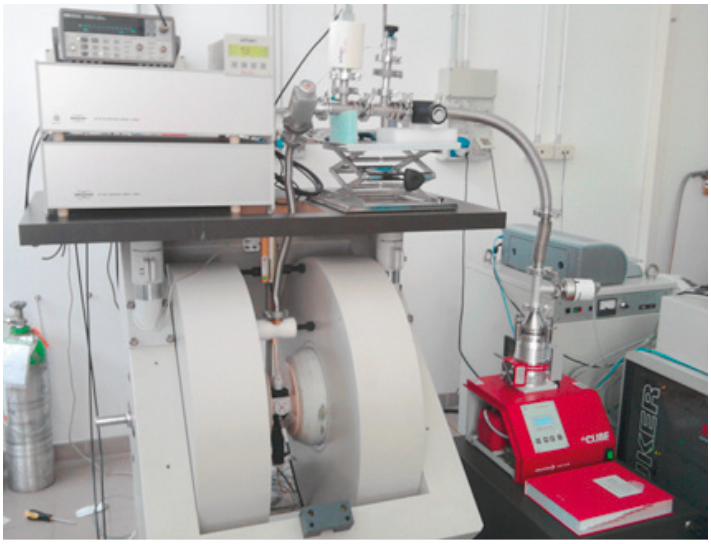


Fig.12 - Electron Spin Resonance spectrometer

4.3.1 Hyperfine Nuclear Interaction

The **electron** magnetic moment and the **nuclear** magnetic moment **interact**, modifying the microwave absorption. The number of single resonances increases, although they are centered on a unique resonance field $\mathbf{H_r}$, which corresponds

to the absorption field in the absence of electron-nucleus interaction.

$\mathbf{H_{eff} = H + H_{local}}$ $\mathbf{H_{local}}$ is due to nuclear interaction

From the quantum mechanical approach for the spin nuclear momentum **I , 2I+1** components are expected. In the case of hydrogen atom I = ½ M_I ***= ± ½ ; the spectrum shows two*** resonances

$$\mathbf{H_{eff} = H \pm a/2 = H \pm a M_i}$$ (where **a** is a measure of the interaction)

The energy of hyperfine interaction in the isotropic form was investigated by Fermi and is defined with the following equation

$\mathbf{W_{iso} = 8\pi/3\,(\psi_0)^2 \mu_{ez}\,\mu_{nz}}$ where $\boldsymbol{\psi_0}$ is the wave function evaluated on the nucleus

$\boldsymbol{\mu_{ez}\,\mu_{nz}}$ are the components of electronic and nuclear magnetic moments along the **H** direction.

4.3.2 Hyperfine interaction by quantum mechanical approach

By using quantum mechanical operators:

$$\boldsymbol{\mu_{ez} = -g\beta\, S_z}$$

$$\boldsymbol{\mu_{nz} = -g_n\, \beta_n\, I_z}$$

$$\boldsymbol{H_{iso} = 8\pi/3 g\beta\, g_n\, \beta_n\, (\psi_0)^2\, S_z\, I_z = hA_0\, S_z\, I_z}$$

where $\mathbf{A_0}$ is the isotropic hyperfine coupling constant (hertz)

In the case of the hydrogen atom the complete Hamiltonian operator is

$$\boldsymbol{H = g\beta\, H\, S_z + hA_0\, S_z\, I_z}$$

By associating the eigenvalues of $\boldsymbol{S_z}$ and of $\boldsymbol{I_z}$ to the four spin and nuclear states

$$\mathbf{M_s = ½ \equiv \alpha_e \quad M_s = -½ \equiv \beta_e}$$

$$\mathbf{M_I = ½ \equiv \alpha_N \quad M_I = -½ \equiv \beta_N}$$

four different states are generated

$$\boldsymbol{(\alpha_e\, \alpha_N)\ (\beta_e\, \alpha_N)\ (\alpha_e\, \beta_N)\ (\beta_e\, \beta_N)}$$

Operating by the ***H*** operator on each one of the states

$$\mathbf{W_{\alpha e\, \alpha N} = \langle \alpha_e\, \alpha_N \mid g\beta\, H\, S_z + hA_0\, S_z\, I_z \mid \alpha_e\, \alpha_N \rangle = ½\, g\beta H + 1/4h\, A_0}$$

$$W_{\alpha e\,\beta N} = \tfrac{1}{2} g\beta H - 1/4h A_0$$

$$W_{\beta e\,\beta N} = -\tfrac{1}{2} g\beta H + 1/4h A_0$$

$$W_{\beta e\,\alpha N} = -\tfrac{1}{2} g\beta H - 1/4h A_0$$

The microwave induced energy transition undergoes the following selection rules

$$\Delta M_s \pm 1 \; \Delta M_I = 0$$

The energy transition is consequently

$$H_k = h\nu_0/g\beta - a/2 \quad M_I = \tfrac{1}{2}$$

$$H_m = h\nu_0/g\beta + a/2 \quad M_I = -\tfrac{1}{2}$$

where $a = hA_0/g\beta$

The microwave induced energy transition undergoes the following selection rules

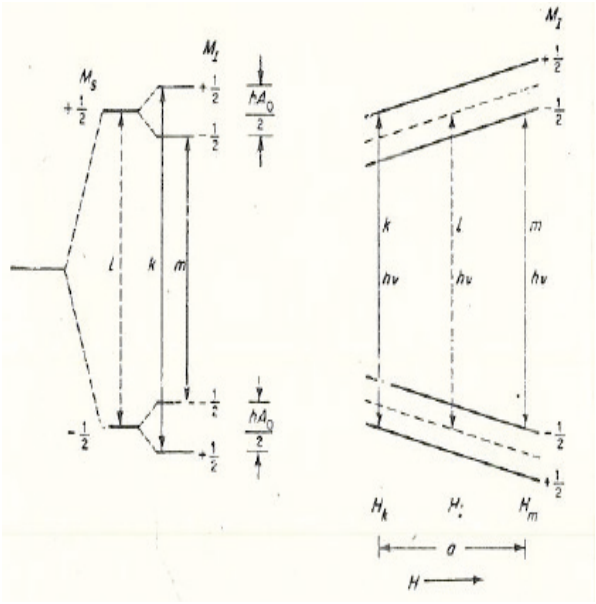
$$\Delta M_s \pm 1 \; \Delta M_I = 0$$

The energy transition is consequently

$$H_k = h\nu_0/g\beta - a/2 \quad M_I = \tfrac{1}{2}$$

$$H_m = h\nu_0/g\beta + a/2 \quad M_I = -\tfrac{1}{2}$$

where $a = hA_0/g\beta$



Scheme 23 - Effect of the hyperfine interaction for hydrogen atom

4.3.3 The electronic interaction with the magnetic field in oriented systems

In the most general case the interaction energy of an electron with the magnetic field is anisotropic , provided the physical status does not induce averaging of the magnetic interactions. g is represented by a tensor and the Hamiltonian operator is

$$\boldsymbol{H} = \boldsymbol{\beta}\, S\, g\, \boldsymbol{H} \qquad S \text{ and } \boldsymbol{H} \text{ are both vectors}$$

$$\boldsymbol{H} = \boldsymbol{\beta}\,(S_x g_{xx} \boldsymbol{H}_x + S_y g_{yy} \boldsymbol{H}_y + S_z g_{zz} \boldsymbol{H}_z)$$

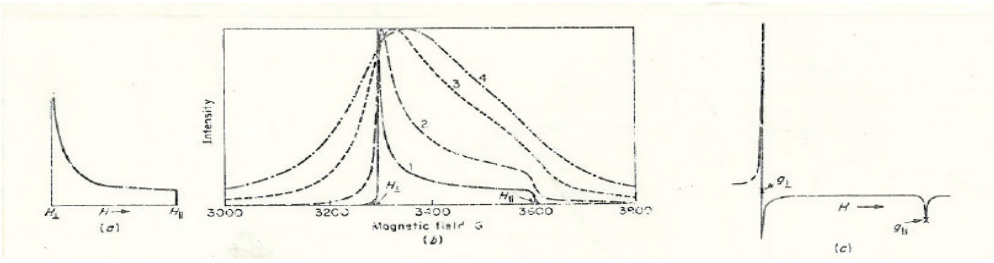


Figure 13 - Resonance spectra for axially symmetry

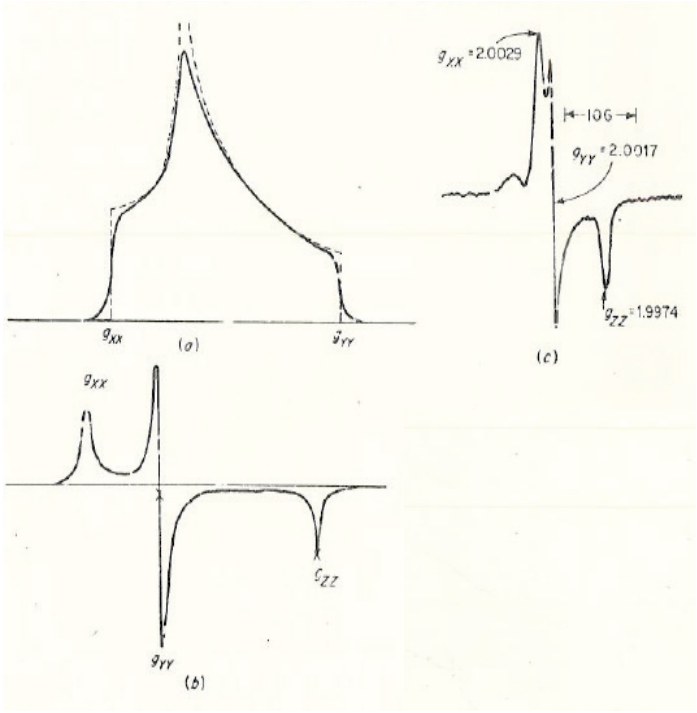


Figure 14 - Resonance spectra for rhombic symmetry

4.3.4 The electronic interaction with the magnetic field in oriented systems

g_{xx} g_{yy} g_{zz} are the g components along three directions, called principal magnetic axes, observed when the magnetic field is oriented along these directions.

For different orientations, the g value follows the expression:

$$g_{eff}^2 = g_{xx} \cos^2\vartheta_{HX} + g_{yy} \cos^2\vartheta_{HY} + g_{zz} \cos^2\vartheta_{HZ}$$

ϑ is the angle between the magnetic field component and the g tensor component.

In the following $\cos^2\vartheta_{HX} = l_z$

$$g_{eff}^2 = [\, l_x \; l_y \; l_z \,] \begin{bmatrix} g_{xx}^2 & 0 & 0 \\ 0 & g_{yy}^2 & 0 \\ 0 & 0 & g_{yy}^2 \end{bmatrix} \begin{bmatrix} l_x \\ l_y \\ l_z \end{bmatrix}$$

The g_{eff}^2 matrix is diagonal only when the H directions are coincident with the magnetic ones (principal directions).

In general the principal magnetic directions are unknown and g is measured with respect to an arbitrary system

$$g_{eff}^2 = [\, l_x \; l_y \; l_z \,] \begin{bmatrix} g_{xx}^2 & g_{xy}^2 & g_{xz}^2 \\ g_{yx}^2 & g_{yy}^2 & g_{yz}^2 \\ g_{zx}^2 & g_{zy}^2 & g_{zz}^2 \end{bmatrix} \begin{bmatrix} l_x \\ l_y \\ l_z \end{bmatrix}$$

The matrix is then diagonalized to obtain g principal values and their orientation with respect to the magnetic field

4.3.5 The origin of the g anisotropic behavior

The observation that the **g** parameter has anisotropic behavior is not simply relatable to the symmetry of the field where the electron is located and interacts with the external magnetic field. It is more suitably explained as the interaction between the external magnetic field and both the spin and the orbital electron magnetic moments. The total interaction is described by the Zeeman operator:

$$H = \beta H L + g_e \beta H S$$

If the spin and the orbital angular moments interact between them, the spin orbit coupling operator $\zeta L S$ perturbs the spin eigenfunctions

$$\psi_0 |\alpha/\beta\rangle \text{ to new states } |\pm\rangle$$

$$\pm\rangle = |\psi_0 \alpha/\beta\rangle - \Sigma_n \langle n|\zeta LS|\psi_0\alpha/\beta\rangle \bullet (1/E_n - E_0)\, |n\rangle$$

Let we consider a new operator $\underline{S}$ which operates at it follows:

$\underline{S}_z |\pm> = \pm 1/2 |\pm>$ $\quad \underline{S}_x |+> = 1/2 |->$ $\quad \underline{S}_y |+> = 1/2i |->$

where $\underline{S}$ works on the states $|\pm>$ as S on the states $|\alpha/\beta>$

Then the magnetic field is along the **z axis,** the Hamiltonian operator is

$H = \beta H (g_{xz} \underline{S}_x + g_{yz} \underline{S}_y + g_{zz} \underline{S}_z)$ and it operates on the $|\pm>$ **eigenfunctions** as it follows

<+|	½ βHg$_{zz}$	½ βH(g$_{xz}$-ig$_{yz}$)
< -|	½ βH(g$_{xz}$+ig$_{yz}$)	-½ βHg$_{zz}$
<+|		<-|

(a)

The true Zeeman Hamiltonian for **H** along **z** is $H = \beta H(L_z + g_e S_z)$ and It is associated to the energy matrix

βH <+\| L_z+ g$_e$S$_z$ \|+> $\quad \beta$H <+\| L_z+ g$_e$S$_z$ \|->

βH < -\| L_z+ g$_e$S$_z$ \|+> $\quad \beta$H < -\| L_z+ g$_e$S$_z$ \|-> ***(b)***

Considering the analogy between matrices ***(a)*** and ***(b),*** the g component expression can be expressed as it follows

$g_{zz} = 2 <+| L_z + g_e S_z |+> = g_e - 2\zeta \Sigma_n <\psi_0| L_z | \psi_n> <\psi_n| L_z | \psi_0> \bullet 1/(E_n - E_0)$

$g_{xz}+ig_{yz} = 2 <-| L_z + g_e S_z |+> = g_e - 2\zeta \Sigma_n <\psi_0| L_z | \psi_n> <\psi_n| L_x | \psi_0> \bullet 1/(E_n - E_0)$

The g values contain the free electron value, g_e, 2.0023, and a perturbation term which is a function of the spin orbit coupling and of the energy difference between the ground electronic state and the excited ones interacting by spin orbit coupling

4.3.6 g expressions for a d^1 electronic configuration in tetragonal symmetry field

$$\mathbf{d_{(x2-y2)} < d_{xz,yz} < d(z^2)}$$

If the unpaired electron lies in the **d(x^2-y^2)** orbital:

$$\mathbf{g_{zz} = 2 - 8\zeta/\Delta \quad \Delta = E(d_{x2-y2}) - E(d_{xy})}$$

$$\mathbf{g_{xx,yy} = 2 - 2\zeta/\delta \quad \delta = E(d_{xz,yz}) - E(d_{x2-y2})}$$

If the unpaired electron lies in the **d(z^2)** Energy of orbital:

$$\mathbf{g_{zz} = 2}$$

$$g_{xx,yy} = 2 - 6\zeta / E(d_{xz,yz}) - E\, d(z^2)$$

If the unpaired electron lies in the (d_{xy}) orbital

$$g_{zz} = 2 - 8\zeta/\Delta$$

$$g_{xx,yy} = 2 - 2\zeta/\delta$$

4.3.7 *g tensor dependence on the energy level trend of the paramagnetic centers*

In the case of valence electrons

$$g_{ij} = g_e - 2\zeta \sum_{n \neq \psi_0} \frac{<\psi_0 | L_i | \psi_n><\psi_n | L_j | \psi_0>}{E_n^0 - E_0^0}$$

In the case of gap electrons

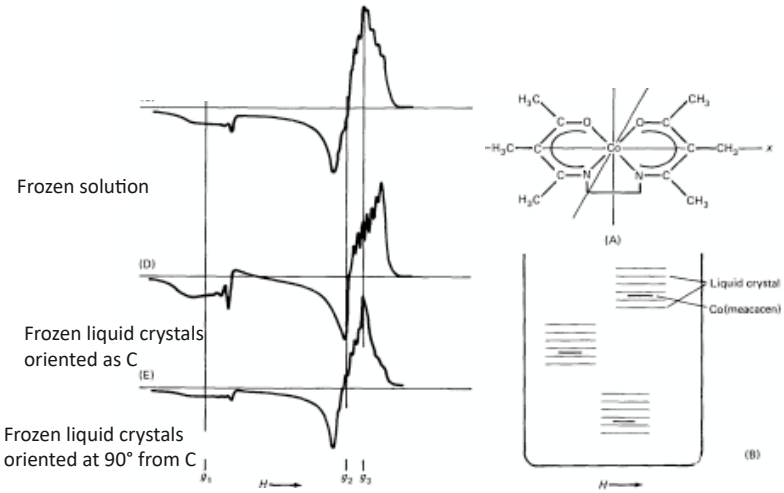
$$g_{ij} = g_e - 2\zeta \sum_{n \neq \psi_0} \frac{<\psi_0 | L_i | \psi_n><\psi_n | L_j | \psi_0>}{E_n^0 - E_0^0}$$

E_0 near C_B $g<g_e$ E_0 near V_B $g>g_e$

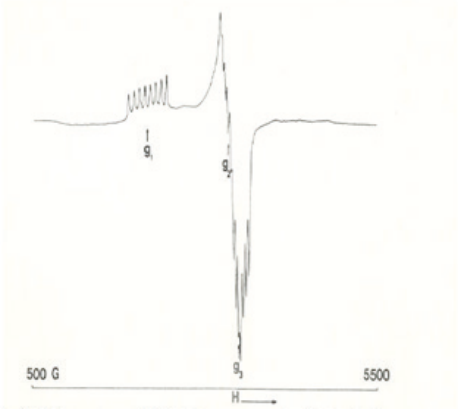
Let you observe that the expression indicate the free electron g value, perturbed by the contribution of the angular momentum, weighted on the energy differences among the interacting states.

Fig. 15 - Some examples of electron spin resonance spectra in different physical states

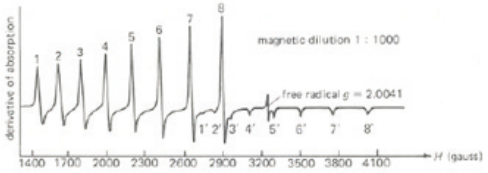
CoMe Acacen spectra in liquid crystal



CoAcacen diluted in NiAcacen as powder spectrum

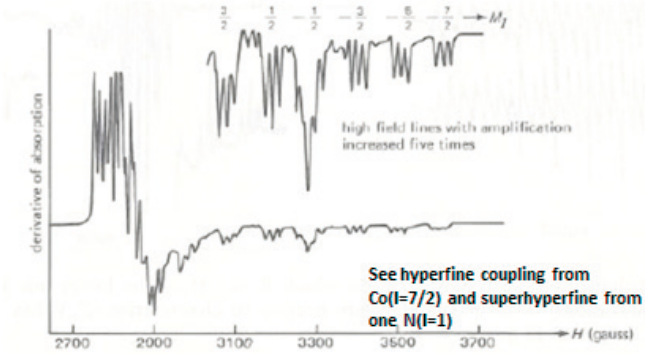


Co Phthalocyanine diluted in Ni Phthalocyanine as powder spectrum



See hyperfine coupling from Co(I=7/2)

Co Phthalocyanine dissolved in 4 methyl pyridine



See hyperfine coupling from Co(I=7/2) and superhyperfine from one N(I=1)

5. General observation

The reported lectures outline the fundamental role of the Group Theory in simplifying the modelling of the chemical bond. It shows the possibility of fast interpretation of the data of electronic spectroscopy and magnetism.
A simple quantum mechanical treatment is used as the wave equation is solved by the aid of the symmetry operators.
For a chemist it has a great value to simplify the quantum mechanical approach, as the molecules are complex systems whose electronic properties risk to be absolutely unknown.
For me there was no better satisfaction as to look to a spectrum and in a short time to approach the molecular structure.