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Simple Electronic Spectroscopy, Crystal Field Theory, Molecular Orbital Theory and Ligand Field Splitting

Mutasem Z. Bani-Fwaz

Review

Electronic Spectroscopy

Crystal Field Theory

Molecular Orbital Theory and Character Tables

1. MO Theory Background
2. Polyatomic Molecules
3. Transition-Metal Complexes and Ligand Field Splitting

Review

QUANTUM NUMBERS

We define each quantum number and describe the range of values it may take.

1. The **principal quantum number**, n , describes the *main energy level*, or shell, an electron occupies. It may be any positive integer:

$$n = 1, 2, 3, 4, \dots$$

2. The **angular momentum quantum number**, ℓ , designates the *shape of the region* in space that an electron occupies. Within a shell (defined by the value of n , the principal quantum number) different sublevels or subshells are possible, each with a characteristic shape. The angular momentum quantum number designates a *sublevel*, or specific *shape* of atomic orbital that an electron may occupy. This number, ℓ , may take integral values from 0 up to and including $(n - 1)$:

$$\ell = 0, 1, 2, \dots, (n - 1)$$

Thus, the maximum value of ℓ is $(n - 1)$. We give a letter notation to each value of ℓ . Each letter corresponds to a different sublevel (subshell).

$$\ell = 0, 1, 2, 3, \dots, (n - 1)$$

$s \quad p \quad d \quad f$

In the first shell, the maximum value of ℓ is zero, which tells us that there is only an s subshell and no p subshell. In the second shell, the permissible values of ℓ are 0 and 1, which tells us that there are only s and p subshells.

3. The **magnetic quantum number**, m_ℓ , designates the specific orbital within a subshell. Orbitals within a given subshell differ in their orientations in space, but not in their energies. Within each subshell, m_ℓ may take any integral values from $-\ell$ through zero up to and including $+\ell$:

$$m_\ell = (-\ell), \dots, 0, \dots, (+\ell)$$

The maximum value of m_ℓ depends on the value of ℓ . For example, when $\ell = 1$, which designates the p subshell, there are three permissible values of m_ℓ -1 , 0 , and $+1$. Thus, three distinct regions of space, called atomic orbitals, are associated with a p subshell. We refer to these orbitals as the p_x , p_y , and p_z orbitals

Permissible Values of the Quantum Numbers Through $n = 4$

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0 (1s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0 (2s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1 (2p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
3	0 (3s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1 (3p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (3d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
4	0 (4s)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1 (4p)	-1, 0, +1	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (4d)	-2, -1, 0, +1, +2	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
	3 (4f)	-3, -2, -1, 0, +1, +2, +3	$\pm\frac{1}{2}$ for each value of m_ℓ	14	

4. The **spin quantum number**, m_s , refers to the spin of an electron and the orientation of the magnetic field produced by this spin. For every set of n , ℓ , and m_ℓ values, m_s can take the value $+\frac{1}{2}$ or $-\frac{1}{2}$:

$$m_s = \pm\frac{1}{2}$$

Shell n	Number of Subshells per Shell n	Number of Atomic Orbitals n^2	Maximum Number of Electrons $2n^2$
1	1	1 (1s)	2
2	2	4 (2s, 2p _x , 2p _y , 2p _z)	8
3	3	9 (3s, three 3p's, five 3d's)	18
4	4	16	32
5	5	25	50

ELECTRON CONFIGURATIONS

Two general rules help us to predict electron configurations.

1. Electrons are assigned to orbitals in order of increasing value of $(n + \ell)$.
2. For subshells with the same value of $(n + \ell)$, electrons are assigned first to the subshell with lower n .

Three rules define how the orbitals fill:

The Pauli Exclusion Principle

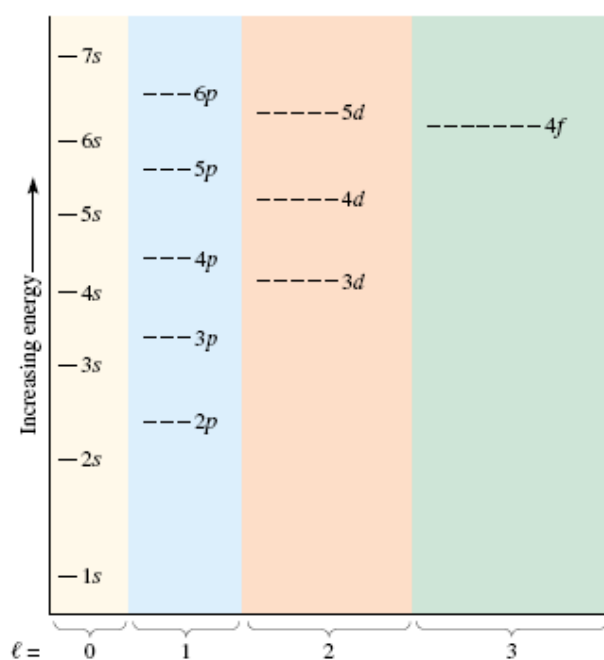
Each orbital can be occupied by **no more than two** electrons.

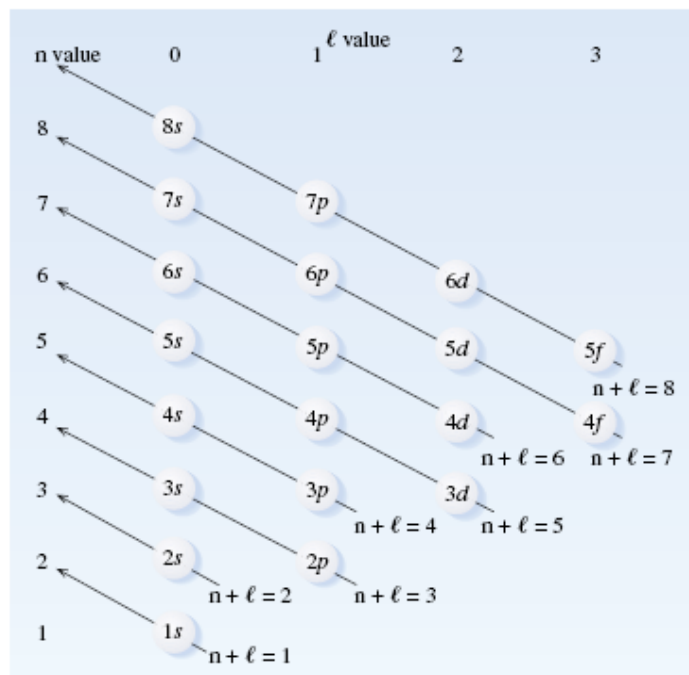
The Aufbau Principle

The electrons occupy the **lowest energy orbitals** available. The “**Ground State**” for an atom is when every electron is in its **lowest energy orbital**.

Hund’s Rule

When more than one orbital exists of the same energy (p, d, and f orbitals), place **one electron in each orbital**





Orbital Notation

	1s	Simplified Notation
${}_1\text{H}$	\uparrow	$1s^1$
${}_2\text{He}$	$\uparrow\downarrow$	$1s^2$

Orbital Notation

	1s	2s	2p	Simplified Notation	
${}_3\text{Li}$	$\uparrow\downarrow$	\uparrow		$1s^2 2s^1$	or $[\text{He}] 2s^1$
${}_4\text{Be}$	$\uparrow\downarrow$	$\uparrow\downarrow$		$1s^2 2s^2$	$[\text{He}] 2s^2$
${}_5\text{B}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow — —	$1s^2 2s^2 2p^1$	$[\text{He}] 2s^2 2p^1$
${}_6\text{C}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow —	$1s^2 2s^2 2p^2$	$[\text{He}] 2s^2 2p^2$
${}_7\text{N}$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	$1s^2 2s^2 2p^3$	$[\text{He}] 2s^2 2p^3$
${}_8\text{O}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	$1s^2 2s^2 2p^4$	$[\text{He}] 2s^2 2p^4$
${}_9\text{F}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	$1s^2 2s^2 2p^5$	$[\text{He}] 2s^2 2p^5$
${}_{10}\text{Ne}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$1s^2 2s^2 2p^6$	$[\text{He}] 2s^2 2p^6$

	Orbital Notation		Simplified Notation
	3s	3p	
^{11}Na	[Ne] \uparrow		[Ne] $3s^1$
^{12}Mg	[Ne] $\uparrow\downarrow$		[Ne] $3s^2$
^{13}Al	[Ne] $\uparrow\downarrow$	\uparrow — —	[Ne] $3s^2 3p^1$
^{14}Si	[Ne] $\uparrow\downarrow$	\uparrow \uparrow —	[Ne] $3s^2 3p^2$
^{15}P	[Ne] $\uparrow\downarrow$	\uparrow \uparrow \uparrow	[Ne] $3s^2 3p^3$
^{16}S	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	[Ne] $3s^2 3p^4$
^{17}Cl	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	[Ne] $3s^2 3p^5$
^{18}Ar	[Ne] $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	[Ne] $3s^2 3p^6$

	Orbital Notation			Simplified Notation
	3d	4s	4p	
^{19}K	[Ar]	\uparrow		[Ar] $4s^1$
^{20}Ca	[Ar]	$\uparrow\downarrow$		[Ar] $4s^2$
^{21}Sc	[Ar] \uparrow — — — —	$\uparrow\downarrow$		[Ar] $3d^1 4s^2$
^{22}Ti	[Ar] \uparrow \uparrow — — —	$\uparrow\downarrow$		[Ar] $3d^2 4s^2$
^{23}V	[Ar] \uparrow \uparrow \uparrow — —	$\uparrow\downarrow$		[Ar] $3d^3 4s^2$
^{24}Cr	[Ar] \uparrow \uparrow \uparrow \uparrow \uparrow	\uparrow		[Ar] $3d^5 4s^1$
^{25}Mn	[Ar] \uparrow \uparrow \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] $3d^5 4s^2$
^{26}Fe	[Ar] $\uparrow\downarrow$ \uparrow \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] $3d^6 4s^2$
^{27}Co	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow \uparrow	$\uparrow\downarrow$		[Ar] $3d^7 4s^2$
^{28}Ni	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow \uparrow	$\uparrow\downarrow$		[Ar] $3d^8 4s^2$
^{29}Cu	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	\uparrow		[Ar] $3d^{10} 4s^1$
^{30}Zn	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$		[Ar] $3d^{10} 4s^2$
^{31}Ga	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow — —	[Ar] $3d^{10} 4s^2 4p^1$
^{32}Ge	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow —	[Ar] $3d^{10} 4s^2 4p^2$
^{33}As	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow \uparrow \uparrow	[Ar] $3d^{10} 4s^2 4p^3$
^{34}Se	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ \uparrow \uparrow	[Ar] $3d^{10} 4s^2 4p^4$
^{35}Br	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ \uparrow	[Ar] $3d^{10} 4s^2 4p^5$
^{36}Kr	[Ar] $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$	[Ar] $3d^{10} 4s^2 4p^6$

Electron Configurations and Quantum Numbers

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration	
1,2	1	0	0	$+\frac{1}{2}$	$1s^2$	
	1	0	0	$-\frac{1}{2}$		
3,4	2	0	0	$+\frac{1}{2}$	$2s^2$	
	2	0	0	$-\frac{1}{2}$		
5, 6, 7	2	1	-1	$+\frac{1}{2}$ or $-\frac{1}{2}$	$2p_x^1$	
	2	1	0	$+\frac{1}{2}$ or $-\frac{1}{2}$		$2p_y^1$
	2	1	+1	$+\frac{1}{2}$ or $-\frac{1}{2}$		

Electron	n	ℓ	m_ℓ	m_s	e^- Configuration
1, 2	1	0	0	$\pm\frac{1}{2}$	$1s^2$
3, 4	2	0	0	$\pm\frac{1}{2}$	$2s^2$
5-10	2	1	-1	$\pm\frac{1}{2}$	$2p^6$
		1	0	$\pm\frac{1}{2}$	
		1	+1	$\pm\frac{1}{2}$	
11, 12	3	0	0	$\pm\frac{1}{2}$	$3s^2$
13-17	3	1	-1	$\pm\frac{1}{2}$	$3p^5$
		1	0	$\pm\frac{1}{2}$	
		1	+1	$\pm\frac{1}{2}$ or $-\frac{1}{2}^*$	

Group IA IIA IIIB IVB VB VIB VIIB VIIIB VIIIIB IB IIB IIIA IVA VA VIA VIIA VIIIA
 (1) (2) (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14) (15) (16) (17) (18)

Period	1																	1	2
1	H																	H	He
	1s																	1s	
2	3	4											5	6	7	8	9	10	
	Li	Be											B	C	N	O	F	Ne	
	2s												2p						
3	11	12											13	14	15	16	17	18	
	Na	Mg											Al	Si	P	S	Cl	Ar	
	3s												3p						
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
	4s		3d										4p						
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
	5s		4d										5p						
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
	6s		5d										6p						
7	87	88	89	104	105	106	107	108	109	110	111	112							
	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										
	7s		6d																

6	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	4f													
7	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	5f													

Metal ion	d^n configuration	S	$\mu_{\text{eff}}(\text{spin-only}) / \mu_B$	Observed values of μ_{eff} / μ_B
Sc ³⁺ , Ti ⁴⁺	d^0	0	0	0
Ti ³⁺	d^1	$\frac{1}{2}$	1.73	1.7–1.8
V ³⁺	d^2	1	2.83	2.8–3.1
V ²⁺ , Cr ³⁺	d^3	$\frac{3}{2}$	3.87	3.7–3.9
Cr ²⁺ , Mn ³⁺	d^4	2	4.90	4.8–4.9
Mn ²⁺ , Fe ³⁺	d^5	$\frac{5}{2}$	5.92	5.7–6.0
Fe ²⁺ , Co ³⁺	d^6	2	4.90	5.0–5.6
Co ²⁺	d^7	$\frac{3}{2}$	3.87	4.3–5.2
Ni ²⁺	d^8	1	2.83	2.9–3.9
Cu ²⁺	d^9	$\frac{1}{2}$	1.73	1.9–2.1
Zn ²⁺	d^{10}	0	0	0

d^4

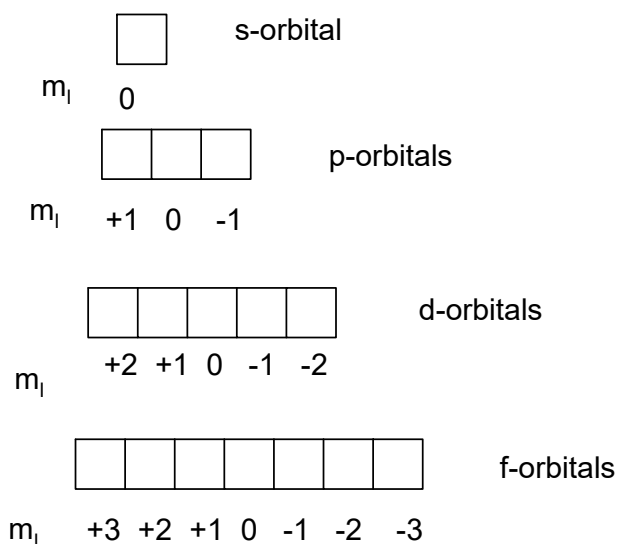
Low-spin will have two unpaired

electrons ($n = 2$), and high-spin will have four ($n = 4$).

$$\mu(\text{spin-only}) = \sqrt{n(n+2)}$$

For low-spin: $\mu(\text{spin-only}) = \sqrt{8} = 2.83$

For high-spin: $\mu(\text{spin-only}) = \sqrt{24} = 4.90$



Atomic Spectra, Term Symbols and Hund's Rules

Atomic Term Symbols

From a spectroscopic perspective, we need to know the values for the various types of angular momenta. Term symbols provide three pieces of information

1. Total orbital angular momentum, L
2. Multiplicity of the term, $2S+1$
3. Total angular momentum, J

$$^{2S+1}L_J$$

The total orbital angular momentum is given by

$$\vec{L} = \sum_j \vec{l}_j$$

a vector addition. The total spin angular momentum is given by

$$\vec{S} = \sum_j \vec{s}_j$$

another vector addition. The z components of \vec{L} and \vec{S} are given by the scalar sums

$$L_z = \sum_i l_{z,i} = \sum_i m_i = M_L$$

and

$$S_z = \sum_i s_{z,i} = \sum_i m_{s,i} = M_S$$

Thus there are $2L + 1$ values of M_L spanning $-L, -L+1, -L+2, \dots, L-1, L$ and $2S + 1$ values of M_S for S spanning $-S, -S+1, -S+2, \dots, S-1, S$.

The leading $2S+1$ superscript in the term symbol is called the spin multiplicity.

Names for the leading superscripts of atomic term symbols.

2S+1	Name
1	singlet
2	doublet
3	triplet

Letter conversions for atomic term symbols.

Value of L	Letter
0	S
1	P
2	D
3	F
4	G
5	H

Total Angular Momentum

Permitted values of J again, given by a Clebsch-Gordon series

$$J = L + S, L + S - 1, L + S - 2 \dots |L - S|$$

Multiplicity

Can also determine the multiplicity for the term using a Clebsch-Gordon series

$$S = \frac{1}{2} + \frac{1}{2}, \frac{1}{2} - \frac{1}{2} \quad \text{for two electron system} \\ = 1, 0$$

Multiplicity given by $2S + 1$

$$\text{For } S = 1: 2S + 1 = 3 \quad \text{Called a triplet state} \\ \text{For } S = 0: 2S + 1 = 1 \quad \text{Called a singlet state}$$

As a first example,

$$\text{For case with } L = 1, S = \frac{1}{2} \quad J = 1 + \frac{1}{2} \text{ and } 1 - \frac{1}{2}$$

term symbols are ${}^2P_{3/2}$ and ${}^2P_{1/2}$

For boron, there are two terms to consider ${}^2P_{3/2}$ or ${}^2P_{1/2}$.

These are both doublet terms, and both have $L = 1$. For

The p^1 configuration, the p level is less than half-filled, and

Therefore, the ground state level is the one with the lower

Value of J , i.e. ${}^2P_{1/2}$..(see the rules in next pages)

What about Ne?

For $2p^6$ configuration, only one set of possible values.

$$\begin{aligned} M_L &= m_1 + m_2 + m_3 + m_4 + m_5 + m_6 \\ &= 1 + 1 + 0 + 0 + (-1) + (-1) = 0 \end{aligned}$$

And in this case we also have

$$\begin{aligned} S &= |M_s| = m_{s1} + m_{s2} + m_{s3} + m_{s4} + m_{s5} + m_{s6} \\ &= \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} + \frac{1}{2} - \frac{1}{2} = 0 \end{aligned}$$

Thus, term is 1S_0 . We will find this to be true for ANY filled subshell. More interesting then to consider unfilled shells.

Summary Examples

H (1s¹)

ground state term symbol is $^2S_{1/2}$

He (1s²)

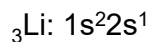
Ground state term symbol is 1S_0

For the relative energies of terms for a given electronic Configuration:

1. The term with the highest spin multiplicity has the lowest Energy.
2. If two or more terms have the same multiplicity (e.g. 3F And 3P), the term having the highest value of L has the Lowest energy (e.g. 3F is lower than 3P).
3. For terms having the same multiplicity and the same Values of L (e.g. 3P_0 and 3P_1), the level with the lowest Value of J is the lowest in energy if the sub-level is less than Half-filled (e.g. p^2), and the level with the highest value of J Is the more stable if the sub-level is more than half-filled (e.g. p^4). If the level is half-filled with maximum spin Multiplicity (e.g. p^3 with $S=3/2$), L must be zero, and $J=S$.

What is the ground state term symbol for the following atoms ${}_3\text{Li}$, ${}_{14}\text{Si}$ and ${}_{21}\text{Sc}$?

Note: ground state term symbol for lowest energy configuration.



$\sum ml = 0$

$\sum ms = +1/2$

$2S + 1 = 2(1/2) + 1 = 2$

symbol $L = 0$ S

$J = L + S \dots \dots$

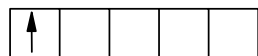
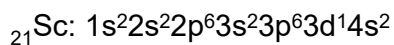
until absolute value of

term symbol ${}^2S_{1/2}$

$L - S$

$J = 1/2$

${}^2S_{1/2}$ most stable



ml $+2$ $+1$ 0 -1 -2

$\sum ml = 2$

$\sum ms = +1/2$

$2S + 1 = 2(1/2) + 1 = 2$

$L = 2$ D

${}^2D_{5/2}$

$J = 5/2$ and $3/2$

${}^2D_{3/2}$ most stable

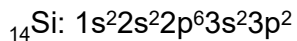
$\sum ml = +1 + 0 = 1$

$\sum ms = +1/2 + 1/2 = +1$

$2S + 1 = 2(1) + 1 = 3$

$L = 1$ P

$J = 2, 1, 0$



ml $+1$ 0 -1

${}^3P_2, {}^3P_1, {}^3P_0$

3P_0 most stable

if we have j spinorbitals and need to place k electrons we have

$$\binom{j}{k} = \frac{j!}{k!(j-k)!}$$

microstates.

For example $3d^2$ has

$$\binom{10}{2} = \frac{10!}{2!8!} = 45$$

microstates. How about $3d^8$?

$$\binom{10}{8} = \frac{10!}{8!2!} = 45 \quad \text{microstates.}$$

N ($1s^2 2s^2 2p^3$) {lowest energy configuration}

This configuration has
 $6!/3!3! = 20$ microstates

Draw all the possibilities

	+1	0	-1	M_L	M_S
	↑	↑	↑	0	3/2
	↓	↓	↓	0	-3/2
	↑↓	↑	—	2	1/2
	↑	↑↓	—	1	1/2
	↑	↑	↓	0	1/2
	↑↓	—	↑	1	1/2
	↑	↓	↑	0	1/2
	↑	—	↑↓	-1	1/2
	↓	↑	↑	0	1/2
	—	↑↓	↑	-1	1/2
	—	↑	↑↓	-2	1/2
	↑↓	↓	—	2	-1/2
	↓	↑↓	—	1	-1/2
	↓	↓	↑	0	-1/2
	↑↓	—	↓	1	-1/2
	↓	↑	↓	0	-1/2
	↓	—	↑↓	-1	-1/2
	↑	↓	↓	0	-1/2
	—	↑↓	↓	-1	-1/2
	—	↓	↑↓	-2	-1/2

Tabulate the totals

	+2	1	1		
	+1	2	2		
M_l	0	1	3	3	1
	-1	2	2		
	-2	1	1		
		+3/2	+1/2	-1/2	-3/2
		M_s			

Assign Terms

M_l	+2	1	1		
	+1	1	1		
	0	1	1		
	-1	1	1		
	-2	1	1		
		1/2	-1/2		
		M_s			
		2D			

M_l	+1	1	1	
	0	1	1	
	-1	1	1	
		1/2	-1/2	
		M_s		
		2P		

M_l	0	1	1	1	1
		3/2	1/2	-1/2	-3/2
		M_s			
		4S			

The ground configuration of the nitrogen is $1s^2 2s^2 2p^3$, which leads to atomic term symbols 4S , 2P , and 2D .

Total Angular Momentum

Permitted values of J again, given by a Clebsch-Gordon series

$$J = L + S, L + S - 1, L + S - 2 \dots |L - S|$$

4S

$$S = 3/2$$

$$L = 0$$

$$(2S+1)(2L+1) = (2(3/2) + 1) ((2(0) + 1)) = 4 \text{ microstates}$$

$$J = 3/2$$

$$J = 3/2$$

$^4S_{3/2}$

2P $S = 1/2$

$$(2S+1)(2L+1) = (2(1/2) + 1) ((2(1) + 1)) = 6 \text{ microstates}$$

$$L = 1$$

$$J = 3/2, 1/2$$

2D

$$(2S+1)(2L+1) = (2(1/2) + 1) ((2(2) + 1)) = 10 \text{ microstates}$$

$$S = 1/2$$

$$L = 2$$

$$J = 5/2, 3/2$$

This is meaning range from $L + S$ to absolute value of $L - S$

Total $4 + 6 + 10 = 20$ microstates

See the discussion and rules next page

$^4S_{3/2}$ most stable $(2J+1) = 2(3/2) + 1 = 4$ microstates

$^2P_{3/2}$ $(2J+1) = 2(3/2) + 1 = 4$ microstates

$^2P_{1/2}$ $(2J+1) = 2(1/2) + 1 = 2$ microstates

Total = 20 microstates

$^2D_{5/2}$ $(2J+1) = 2(5/2) + 1 = 6$ microstates

$^2D_{3/2}$ $(2J+1) = 2(3/2) + 1 = 4$ microstates

For a given electron configuration

The combination of an S value and an L value is called a **term**, and has a statistical weight

(i.e., number of possible microstates) of $(2S+1)(2L+1)$; a combination of S , L and J is called a **level**. A given level has a statistical weight of $(2J+1)$, which is the number of possible microstates associated with this level in the corresponding term; A combination of L , S , J and MJ determines a single **state**.

As an example, for $S = 1$, $L = 2$, there are $(2 \times 1 + 1)(2 \times 2 + 1) = 15$ different microstates corresponding to the 3D term, of which $(2 \times 3 + 1) = 7$ belong to the 3D_3 ($J=3$) level. The sum of $(2J+1)$ for all levels in the same term equals $(2S+1)(2L+1)$. In this case, J can be 1, 2, or 3, so $3 + 5 + 7 = 15$.

****Optical spectroscopy of atomic nitrogen has revealed atomic levels arising from the $1s^2 2s^2 2p^3$ configuration at the energies listed below. The number of states observed when the atoms are placed in a magnetic field is also noted for each atomic level below.

Identify the levels listed above with the atomic terms and levels, which you derived in previous page of this lecture.

Energy	Number of States	Term symbols
28842 cm^{-1}	splits into 2 states	${}^2P_{1/2}$
28838 cm^{-1}	splits into 4 states	${}^2P_{3/2}$
19231 cm^{-1}	splits into 4 states	${}^2D_{3/2}$
19223 cm^{-1}	splits into 6 states	${}^2D_{5/2}$
0 cm^{-1}	splits into 4 states	${}^4S_{3/2}$

*****Answer written by hand at the last column in this table

Some results of this procedure for your amusement:

Configuration	Terms
p^1, p^5	2P
p^2, p^4	$^3P, ^1D, ^1S$
p^3	$^4S, ^2P, ^2D$
d^1, d^9	2D
d^2, d^8	$^3P, ^3F, ^1S, ^1D, ^1G$
d^3, d^7	$^2P, ^2D, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$
d^4, d^6	$^1S, ^1S, ^1D, ^1D, ^1F, ^1G, ^1G, ^1I, ^3P, ^3P, ^3D, ^3F, ^3F, ^3G, ^3H, ^5D$
d^5	$^2S, ^2P, ^2D, ^2D, ^2D, ^2F, ^2F, ^2G, ^2G, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

Why Molecular term symbols are important?

As soon as ligands are coordinated to a transition-metal centre, a molecular symmetry is imposed and the d orbital split according to the ligand field. In these cases, **molecular term symbols** have to be used.

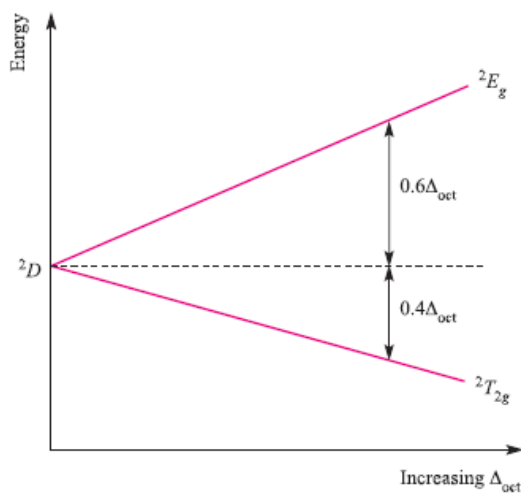
Term	Components in an octahedral field
S	A_{1g}
P	T_{1g}
D	$T_{2g} + E_g$
F	$A_{2g} + T_{2g} + T_{1g}$
G	$A_{1g} + E_g + T_{2g} + T_{1g}$
H	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Similar splitting occur in a tetrahedral field, but the g labels are no longer applicable.

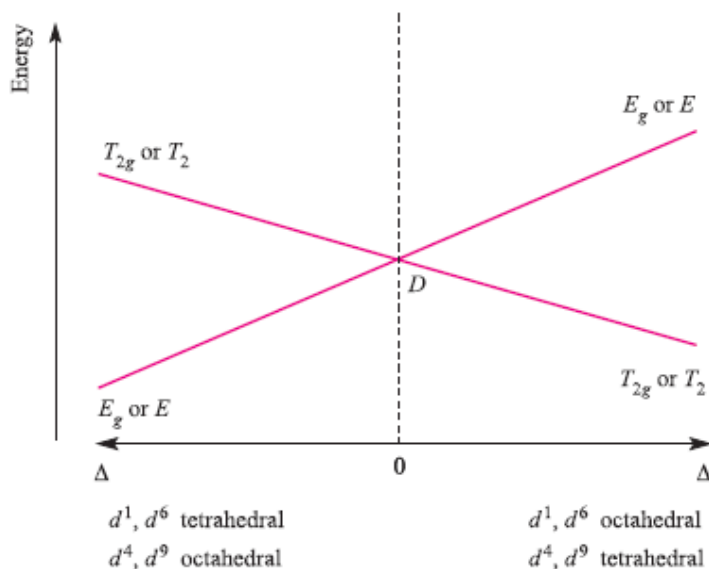
Correlation diagrams

Electronic spectra of octahedral and tetrahedral complexes:

We can draw a correlation diagram between atomic terms and molecular terms. For the d^1 electron configuration, we split the 2D term into ${}^2T_{2g}$ and 2E_g . The degree of splitting depends on the strength of the ligand field and has a value of Δ_o as shown below.

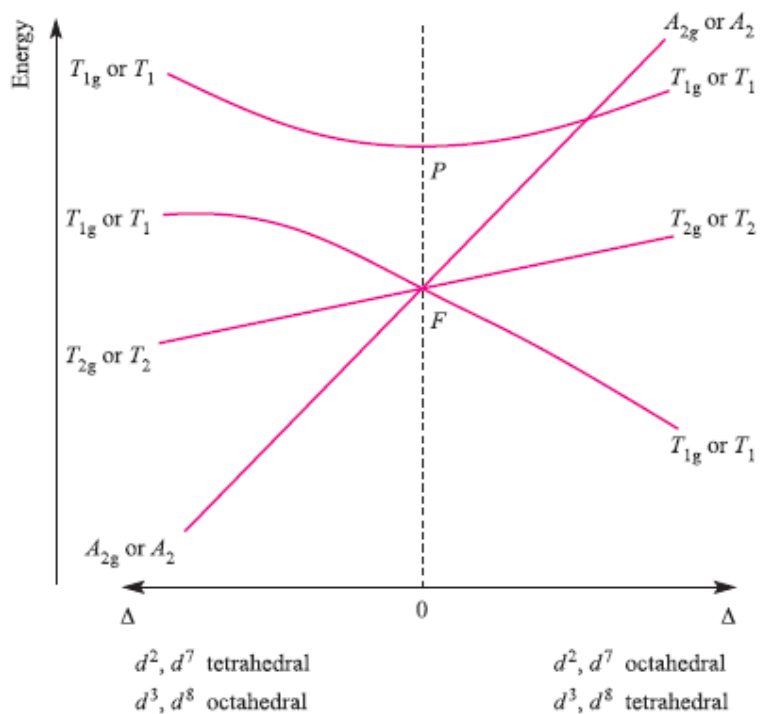


Energy level diagram for a d^1 ion in an octahedral field.



Orgel diagram for d^1 , d^4 (high-spin), d^6 (high spin) and d^9 ions in octahedral (for which T_{2g} and E_g labels are relevant) and tetrahedral (E and T_2 labels) fields. In contrast to Previous Figure, multiplicities are not stated because

They depend on the d^n configuration.



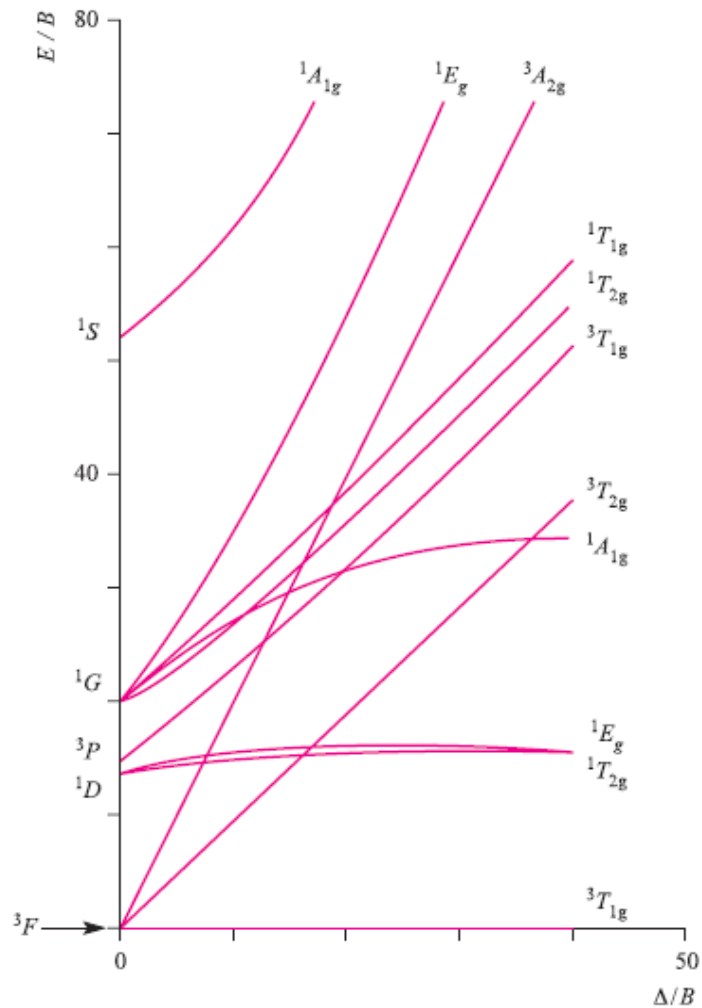
Orgel diagram for d^2 , d^3 , d^7 and d^8 ions (high spin)

In octahedral (for which T_{1g} , T_{2g} and A_{2g} labels are Relevant) and tetrahedral (T_1 , T_2 and A_2 labels) fields.

Multiplicities are not stated because they depend on the d^n Configuration, e.g. for the octahedral d^2 ion, ${}^3T_{1g}$, ${}^3T_{2g}$ and ${}^3A_{2g}$ labels are appropriate.

Interpretation of electronic spectra:

Tanabe--Sugano diagrams



Tanabe–Sugano diagram for the d^2 configuration in an octahedral field.

Note:

The simple correlation diagram had multiples of B
On the energy axis to denote the
Relative energies of the atomic terms.

Selection rules

Electronic energy levels are labelled with term symbols. For the most part, we shall use the simplified form of these labels, omitting the J states.

Thus, the term symbol is written in the general form:

$$\text{Multiplicity of the term} \rightarrow (2S+1)L \leftarrow \begin{cases} L=0 & S \text{ term} \\ L=1 & P \text{ term} \\ L=2 & D \text{ term} \\ L=3 & F \text{ term} \\ L=4 & G \text{ term} \end{cases}$$

Electronic transitions between energy levels obey the following selection rules:

Spin selection rule: $\Delta S = 0$

Transitions may occur from singlet to singlet, or from triplet to triplet states, and so on, but a change in spin multiplicity is *forbidden*.

Laporte selection rule: There must be a change in parity:

allowed transitions: $g \leftrightarrow u$

forbidden transitions: $g \leftrightarrow g$ $u \leftrightarrow u$

This leads to the selection rule:

$$\Delta l = \pm 1$$

and, thus, *allowed* transitions are $s \rightarrow p, p \rightarrow d, d \rightarrow f$;
forbidden transitions are $s \rightarrow s, p \rightarrow p, d \rightarrow d, f \rightarrow f$,
 $s \rightarrow d, p \rightarrow f$ etc.

We have seen some transitions are not allowed, for example, transitions where the spin of the electron is changed are spin-forbidden. This does not mean that such a transition will never occur, but that it is less likely and that the intensity (molar absorption coefficient) of such an absorption band is very low. Whether transitions are allowed or forbidden, and to what degree they may be forbidden depends on selection rules:

(i) spin selection rule

Electromagnetic radiation usually cannot change the relative orientation of an electron spin. The selection rule states that the overall spin S of a complex must not change during an electronic transition, hence, $\Delta S = 0$.

This selection rule can be relaxed by spin-orbit coupling, i.e., coupling between spin angular momentum and orbital angular momentum. However, spin-forbidden transitions remain generally much weaker than spin-allowed transitions. Spin-orbit coupling is particularly strong for heavy d-metals. In the 3d series, spin-forbidden transitions have $\epsilon_{\max} = 1 \text{ L mol}^{-1} \text{ cm}^{-1}$.

In an octahedral d^3 transition-metal complex, the ${}^2E_g \leftarrow {}^4A_{2g}$ transition is spin-forbidden. It is still visible as a very weak absorption band in the UV-visible spectrum (see above).

(ii) Laporte selection rule

The Laporte selection rule is particularly applicable for centrosymmetric molecules, i.e., molecules with an inversion centre. Orbitals and states in such molecules can be described with the symmetry labels g (gerade) and u (ungerade). Laporte-allowed transitions are accompanied with a change of parity (g to u); this means, transitions from a g -state to a u -state and vice versa are Laporte-allowed and transitions from a g - to a g -state and from a u - to a u -state are Laporte-forbidden. All d orbitals are gerade (have g symmetry). Therefore, d-d transitions, e.g., ${}^4T_{2g} \leftarrow {}^4A_{2g}$ in an octahedral d^3 complex, are Laporte-forbidden.

The Laporte selection rule is relaxed by (a) deviation of perfect centrosymmetric symmetry due to ligands of less symmetry or chelate ligands and (b) asymmetric vibrations. While d orbitals are always centrosymmetric by themselves, for a non-centrosymmetric ligand field the Laporte selection rule is strictly not applicable anymore. As a consequence, Laporte-forbidden d-d transitions have $\epsilon_{\max} = 20$ to $100 \text{ L mol}^{-1} \text{ cm}^{-1}$, while Laporte-allowed d-d transitions have $\epsilon_{\max} = \text{ca. } 500 \text{ L mol}^{-1} \text{ cm}^{-1}$.

Intensities of spectroscopic bands in 3d complexes	
Band type	$\epsilon_{\max} / \text{L mol}^{-1} \text{ cm}^{-1}$
Spin-forbidden	<1
Laporte-forbidden d-d	20-100
Laporte-allowed d-d	ca. 500
Symmetry-allowed (e.g. CT)	1000 – 50 000

(iii) Symmetry-allowed transitions

Transitions which are not governed by symmetry restrictions (e.g. Laporte rule) have much larger intensities in the electronic absorption spectra. Such transitions are usually charge transfer bands that give rise to intense colorations.

Charge transfer absorptions

We introduced charge transfer bands in the

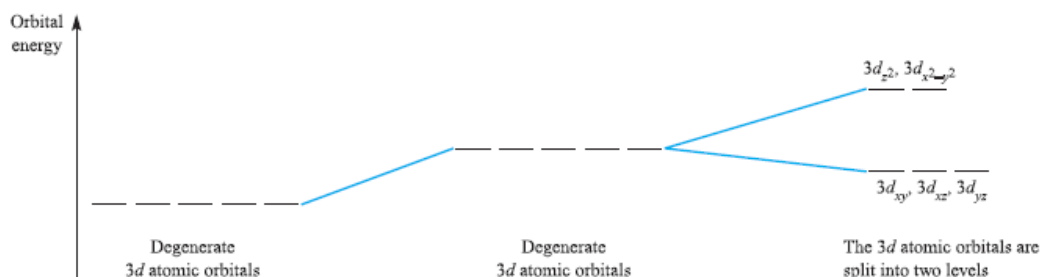
context of their appearance in the UV region of the spectra of halogen-containing charge transfer complexes. In metal complexes, intense absorptions (typically in the UV or visible part of the electronic spectrum) may arise from ligand-centred $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions, or from the transfer of electronic charge between ligand and metal orbitals. The latter fall into two categories:

- transfer of an electron from an orbital with primarily ligand character to one with primarily metal character (ligand-to-metal charge transfer, LMCT).
- transfer of an electron from an orbital with primarily metal character to one with primarily ligand character (metal-to-ligand charge transfer, MLCT).

Charge transfer transitions are not restricted by the selection Rules that govern 'd-d' transitions. The probability Of these electronic transitions is therefore high, and the Absorption bands are therefore intense.

- $[\text{MnO}_4]^-$ (528 nm), $[\text{TcO}_4]^-$ (286 nm), $[\text{ReO}_4]^-$ (227 nm);
- $[\text{CrO}_4]^{2-}$ (373 nm), $[\text{MoO}_4]^{2-}$ (225 nm), $[\text{WO}_4]^{2-}$ (199 nm);
- $[\text{FeCl}_4]^{2-}$ (220 nm), $[\text{FeBr}_4]^{2-}$ (244 nm);
- $[\text{OsCl}_6]^{3-}$ (282 nm), $[\text{OsCl}_6]^{2-}$ (370 nm).

Crystal field theory



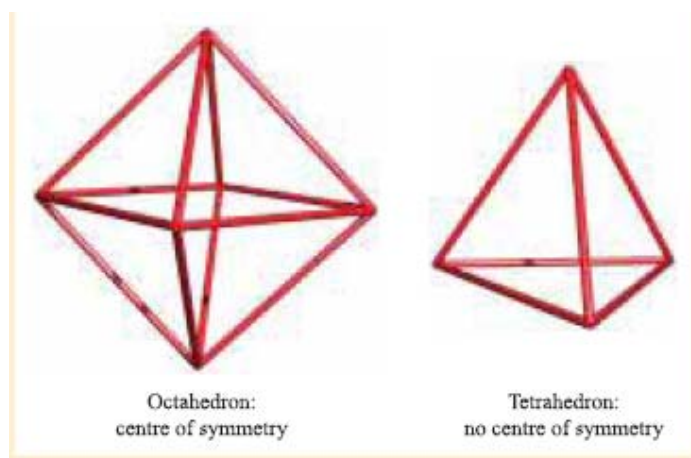
Metal ion M^{n+} and six ligands L at an infinite distance away



If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the 3d orbitals are raised uniformly



If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the 3d orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands is lowered with respect to the spherical field

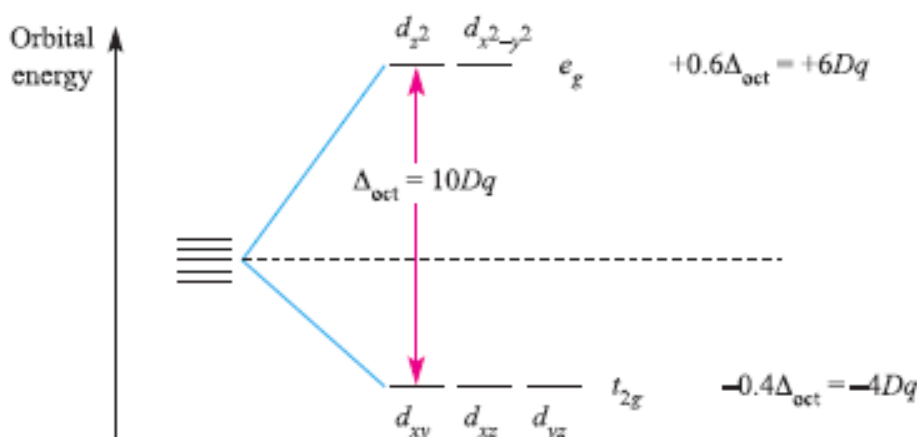


A subscript letter "g" or "u", standing for *gerade* (German for 'even') or *ungerade* ('odd').

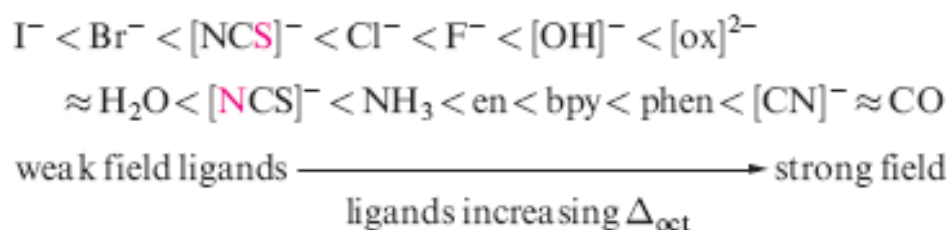
- a triply degenerate level is labelled t ;
- a doubly degenerate level is labelled e .

The subscript *g* means *gerade* and the subscript *u* means *ungerade*. *Gerade* and *ungerade* designate the behaviour of the wavefunction under the operation of *inversion*, and denote the *parity* (even or odd) of an orbital.

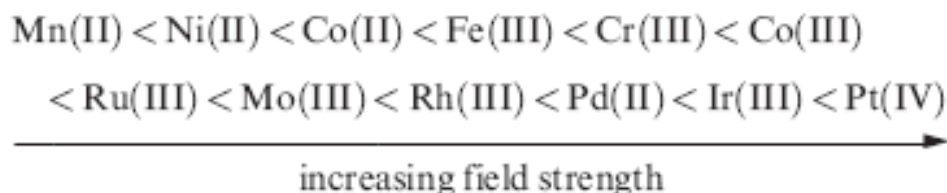
$$\Delta_{\text{oct}}(\text{weak field}) < \Delta_{\text{oct}}(\text{strong field})$$



Splitting of the d orbitals in an octahedral crystal field, with the energy changes measured with respect to the barycentre, the energy level shown by the hashed line.



Trends in values of Δ_{oct} lead to the conclusion that metal ions can be placed in a spectrochemical series which is independent of the ligands:



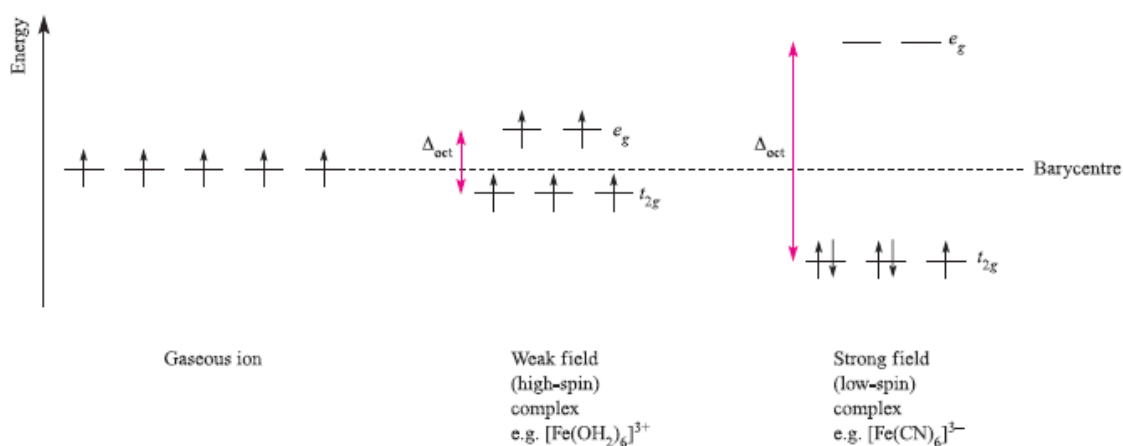
For high-spin: $\Delta_{\text{oct}} < P$

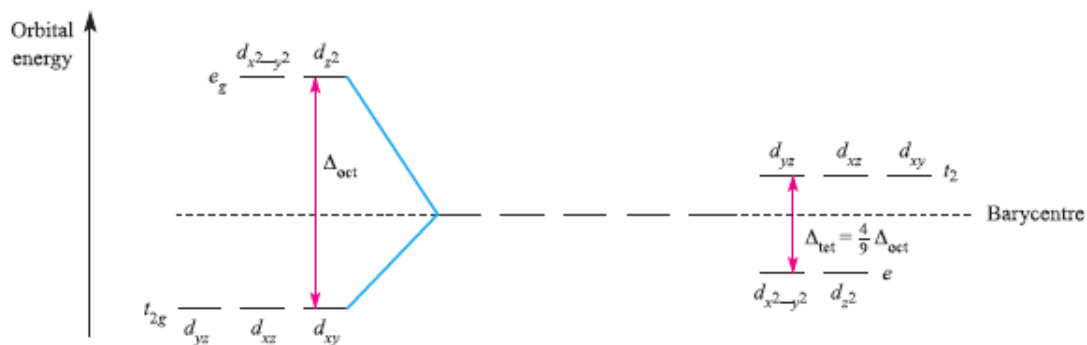
For low-spin: $\Delta_{\text{oct}} > P$

$$\Delta_0 \text{ } 3d < 4d < 5d.$$

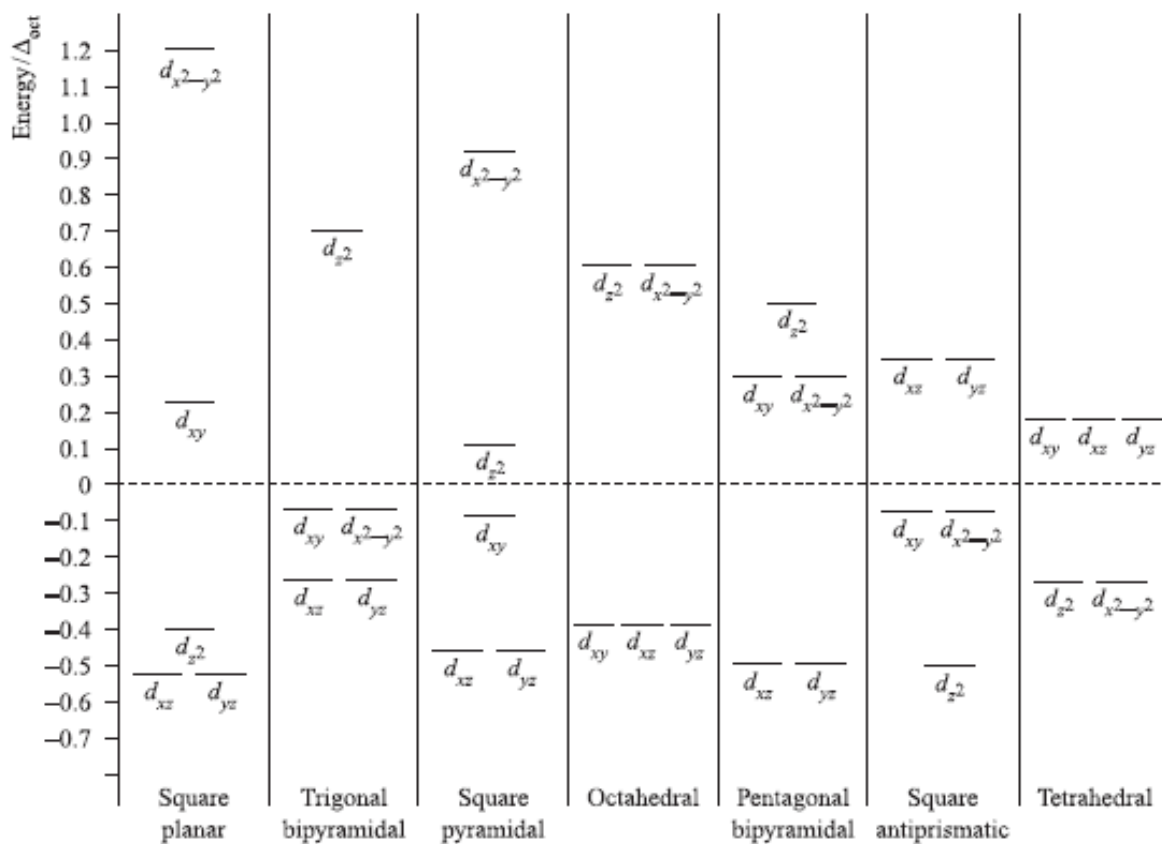
Octahedral crystal field stabilization energies (CFSE) for d^n configurations; pairing energy, P , terms are included where appropriate. High- and low-spin octahedral complexes are shown only where the distinction is appropriate.

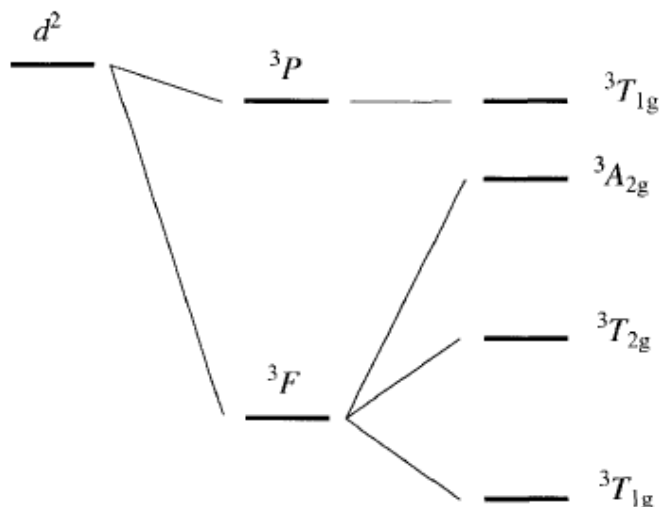
d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_{\text{oct}}$		
d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_{\text{oct}}$		
d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_{\text{oct}}$		
d^4	$t_{2g}^3 e_g^1$	$-0.6\Delta_{\text{oct}}$	$t_{2g}^4 e_g^0$	$-1.6\Delta_{\text{oct}} + P$
d^5	$t_{2g}^3 e_g^2$	0	$t_{2g}^5 e_g^0$	$-2.0\Delta_{\text{oct}} + 2P$
d^6	$t_{2g}^4 e_g^2$	$-0.4\Delta_{\text{oct}}$	$t_{2g}^6 e_g^0$	$-2.4\Delta_{\text{oct}} + 2P$
d^7	$t_{2g}^5 e_g^2$	$-0.8\Delta_{\text{oct}}$	$t_{2g}^6 e_g^1$	$-1.8\Delta_{\text{oct}} + P$
d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_{\text{oct}}$		
d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_{\text{oct}}$		
d^{10}	$t_{2g}^6 e_g^4$	0		





$$\Delta_{\text{tet}} = \frac{4}{9} \Delta_{\text{oct}}$$





Octahedral field spin-triplet terms arising for d^2

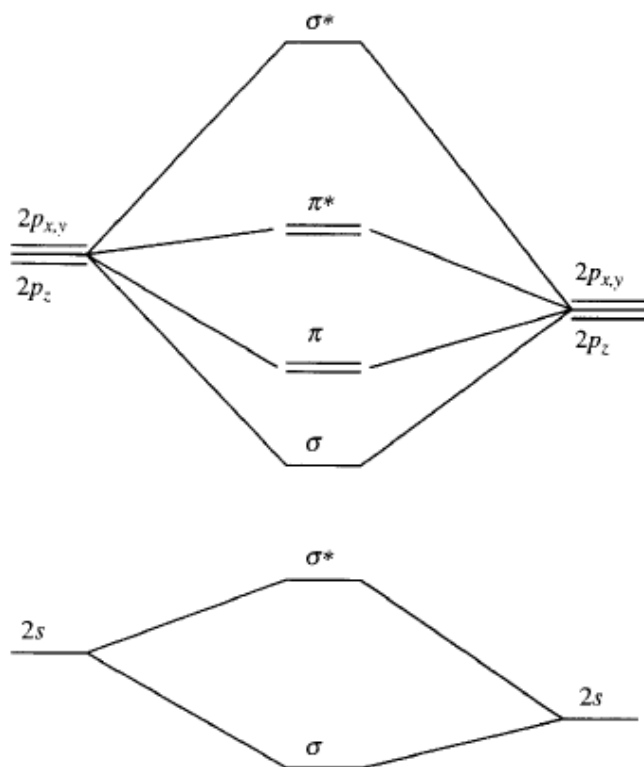
The Jahn–Teller effect, sometimes also known as Jahn–Teller distortion

The Jahn–Teller effect is most often encountered in octahedral complexes of the transition metals, and is very common in six-coordinate copper (II) complexes.^[21] The d^9 electronic configuration of this ion gives three electrons in the two degenerate e_g orbitals, leading to a doubly degenerate electronic ground state. Such complexes distort along one of the molecular fourfold axes (always labelled the z -axis), which has the effect of removing the orbital and electronic degeneracies and lowering the overall energy. The distortion normally takes the form of elongating the bonds to the ligands lying along the z axis, but occasionally occurs as a shortening of these bonds instead (the Jahn–Teller theorem does not predict the direction of the distortion, only the presence of an unstable geometry). When such an elongation occurs, the effect is to lower the electrostatic repulsion between the electron pair on the Lewis basic ligand and any electrons in orbitals with a z component, thus lowering the energy of the complex. If the undistorted complex would be expected to have an inversion centre, this is preserved after the distortion.

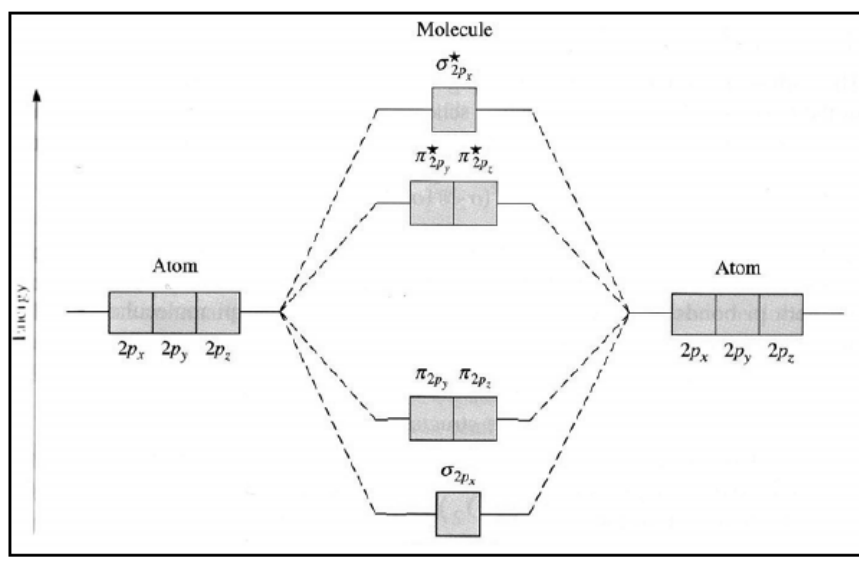
d^1 d^2 d^4 d^6 d^7 d^9

Molecular Orbitals.

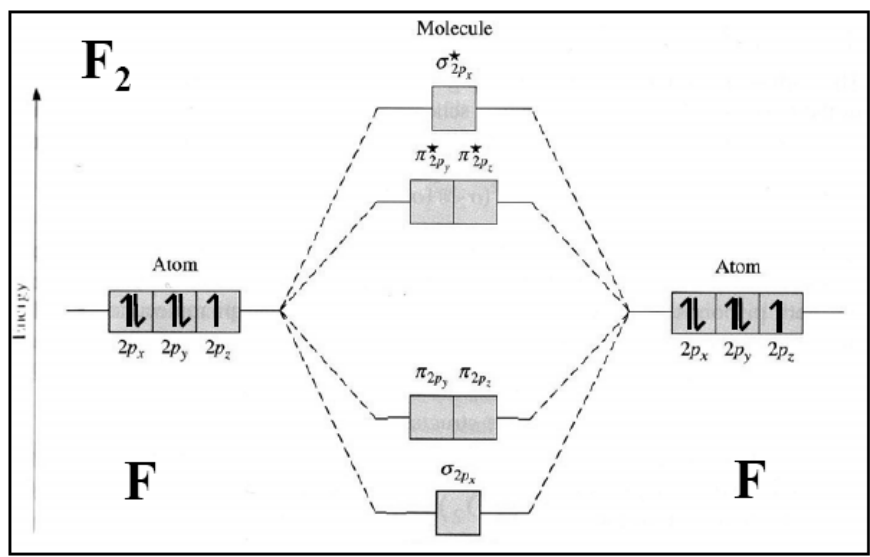
Molecular Orbitals in Diatomic Molecules (Like F_2 , O_2 , F_2etc.)



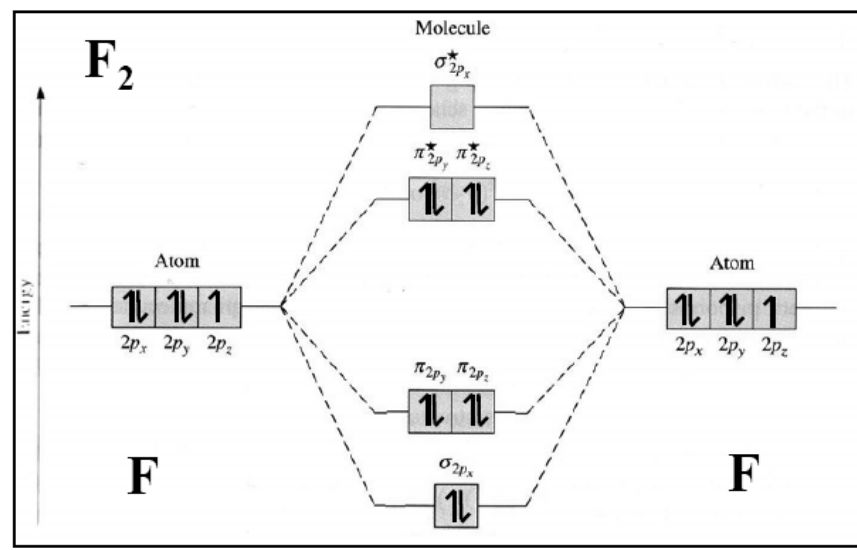
simple MO diagram for p block homonuclear diatomics
(1s and 2s MOs lower in energy - not shown):



e.g. for F_2 - each atom is $2s^2 2p^5$ - 18 valence electrons
orbitals filled from lowest to highest.....

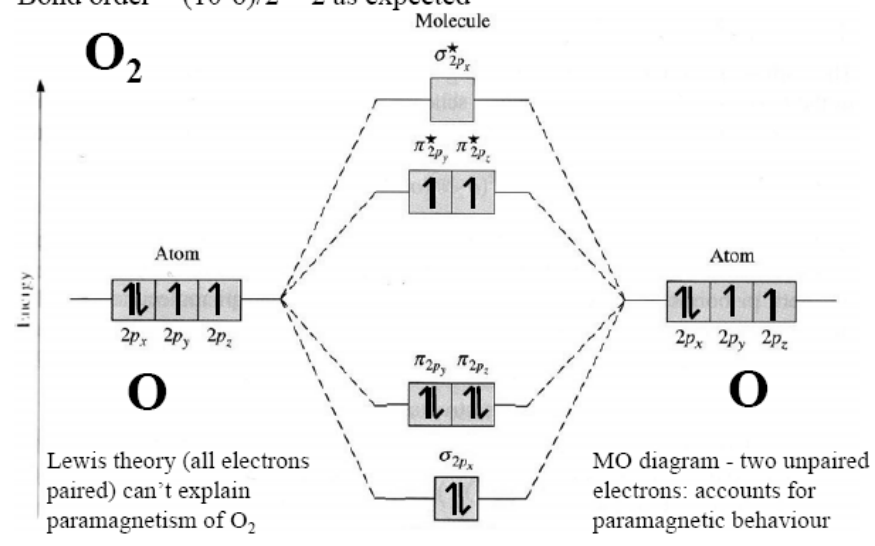


e.g. for F_2 both π_p^* orbitals full but σ_p^* empty.
Bond order = $(10-8)/2 = 1$ (as expected)

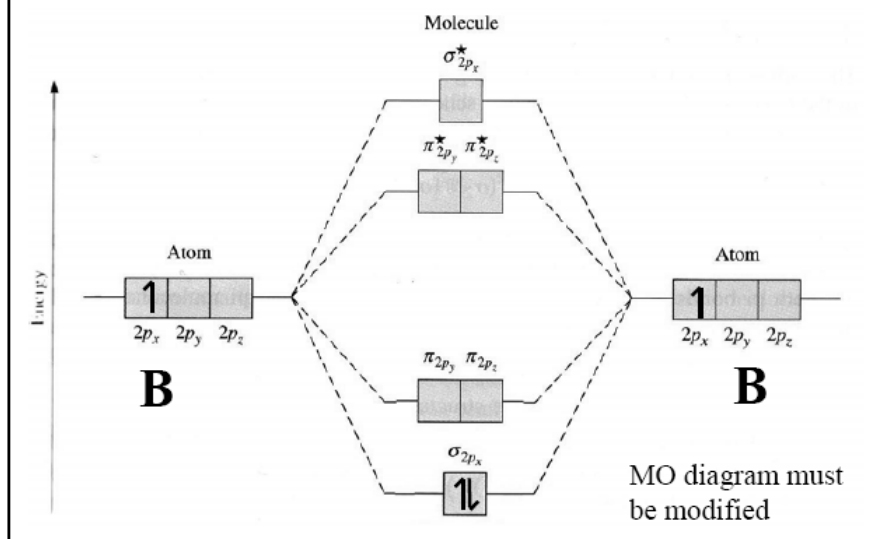


e.g. for O_2 – both π_p^* orbitals half full (Hund's Law of maximum multiplicity).

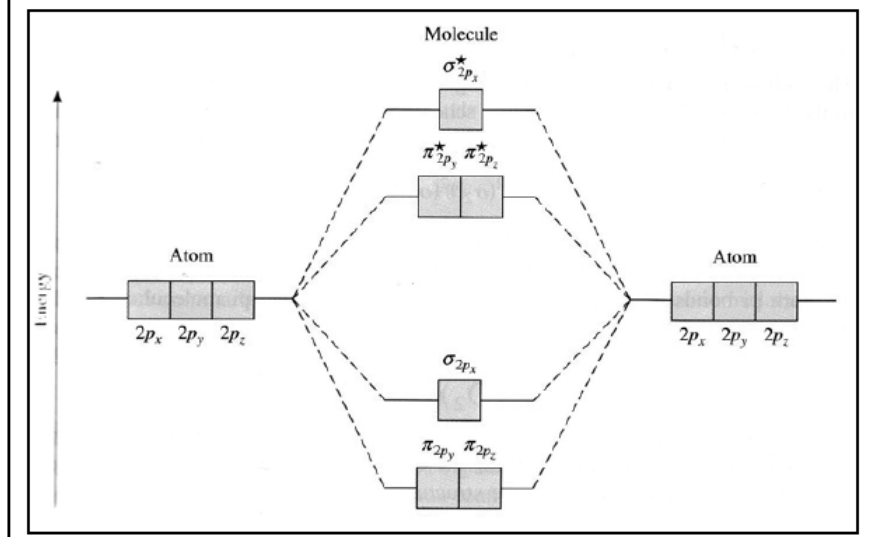
Bond order = $(10-6)/2 = 2$ as expected



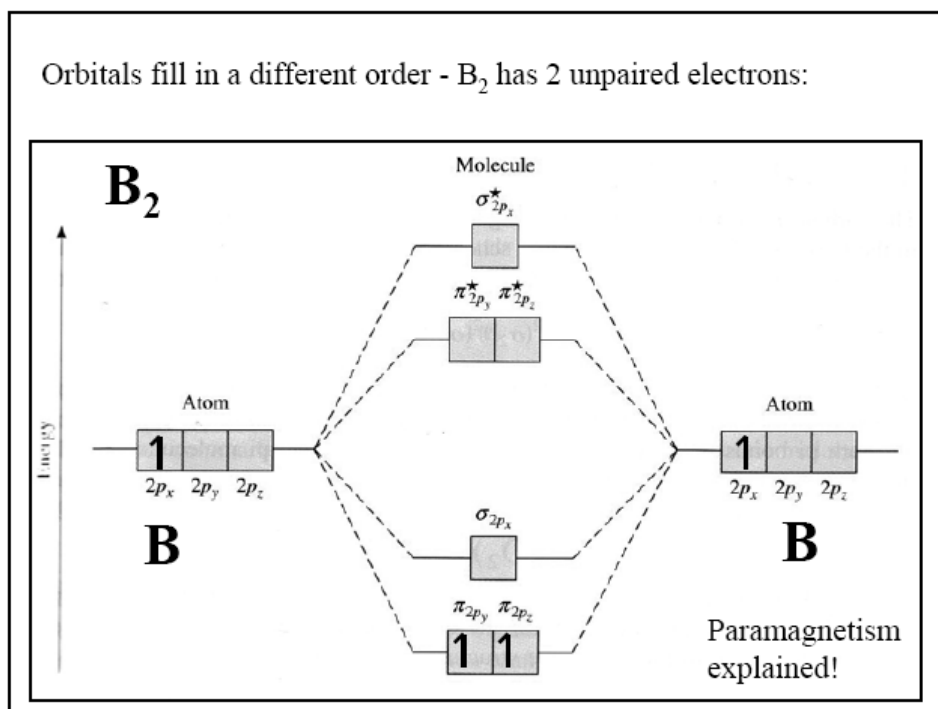
using same MO diagram B_2 – expected to have e configuration σ_p^2 (all electrons paired). Problem - B_2 is paramagnetic!



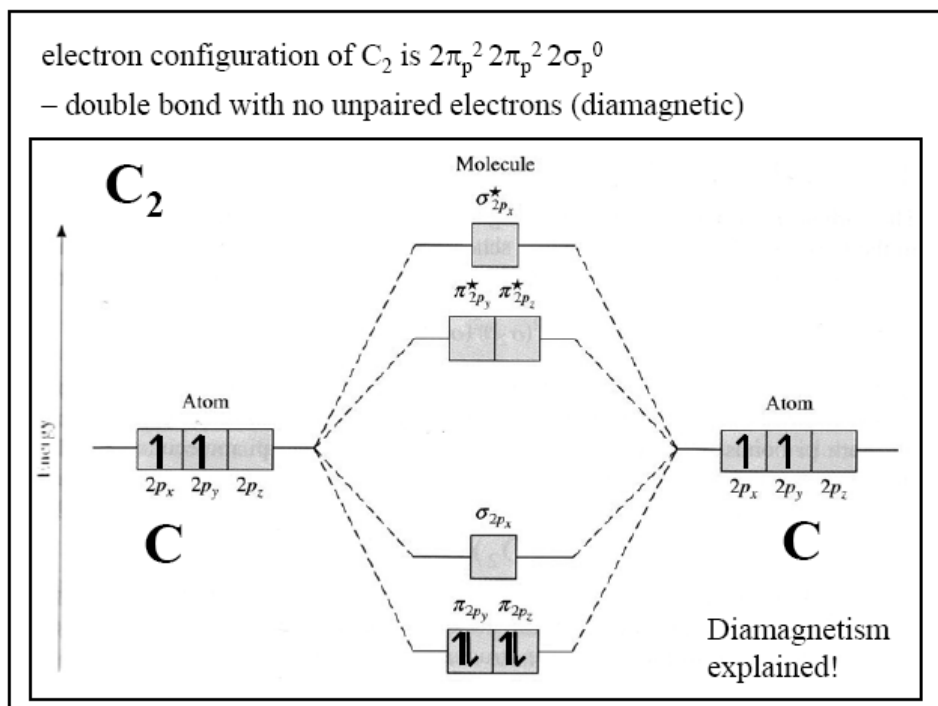
For elements B to N different MO diagram applies due to mixing of 2s and 2p orbitals σ_{2p} becomes higher in energy than π_{2p} orbitals:



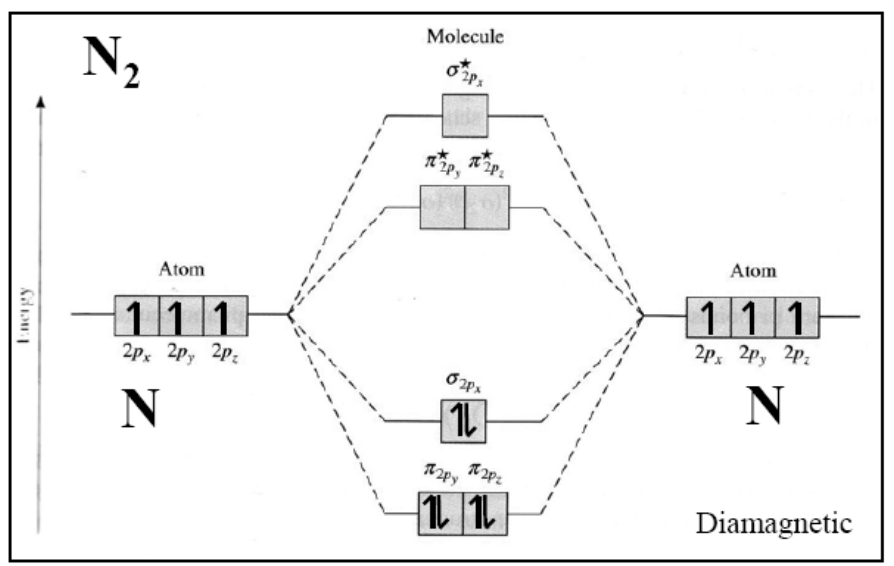
Orbitals fill in a different order - B_2 has 2 unpaired electrons:



electron configuration of C_2 is $2\pi_p^2 2\pi_p^2 2\sigma_p^0$
 – double bond with no unpaired electrons (diamagnetic)



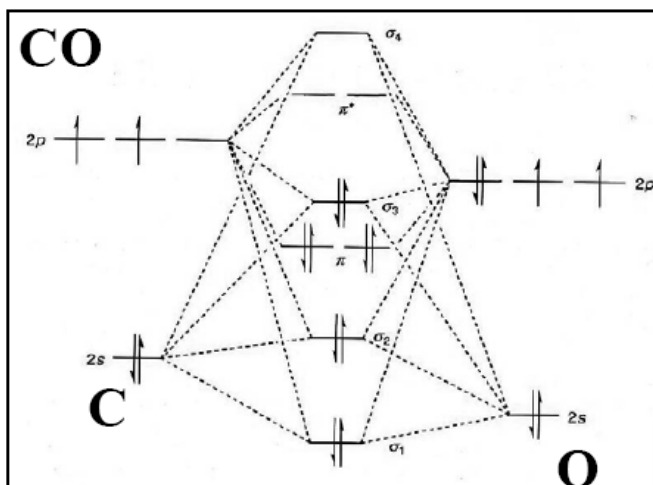
electron configuration of N_2 is $2\pi_p^2 2\pi_p^2 2\sigma_p^2$ – triple bond with no unpaired electrons (diamagnetic)



e.g. for carbon monoxide (CO) (14 electrons including 10 valence electrons) s-p mixing occurs

oxygen orbitals lower in energy than carbon's (greater electronegativity, nuclear charge)

bond order = 3
(strength = 950 kJmol^{-1})



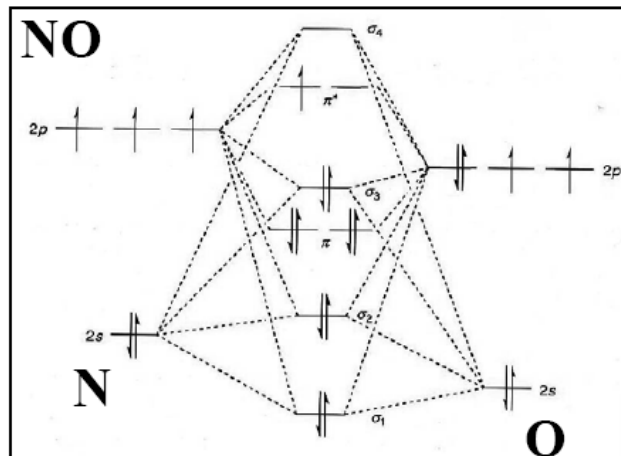
Q: Predict the bond order and magnetic properties of nitric oxide (NO)

A: Same MO diagram as above but 15 electrons including 11 valence electrons

– (electron in π^*) - paramagnetic, bond order = $(10-5)/2 = 2.5$

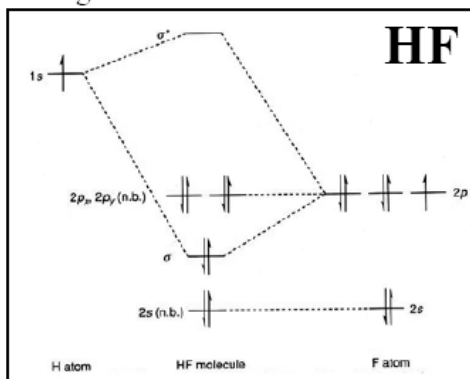
NO is a neutral,

odd-electron molecule (a radical)



simple MO diagram for hydrogen fluoride (HF):

- note different energies of orbitals due to F nuclear charge



- orbital energies so different that H 1s can only sigma bond with F $2p_x$

- remaining F orbitals don't participate in MOs – hold lone pairs

-only one F 2p orbital participates in bonding - others remain as lone pairs. Bond order = $(8-6)/2 = 1$ as expected

Polyatomic molecules

Can use MO theory to explain delocalised π bonding

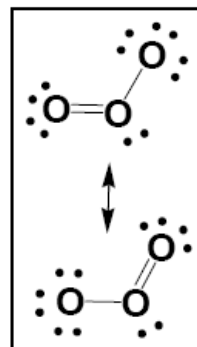
Can work out strength of π -bonding (and total bond order)

e.g. **ozone (O_3)** VSEPR – 18 valence electrons – treat all atoms as sp^2 hybridised

- Lewis structure requires two resonance forms:

though molecule known to be symmetrical

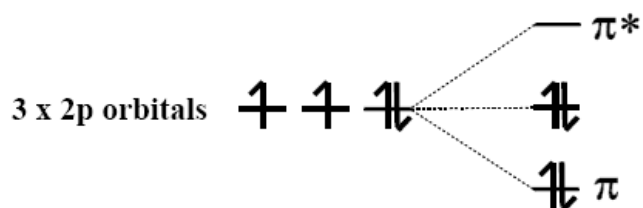
instead MO theory describes delocalised three-centre π -bonding



5 lone pairs, 2 sigma bonds = 14 electrons

4 electrons left contribute to delocalised π -bonding

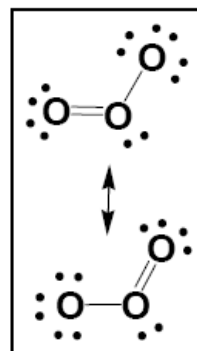
three 2p orbitals overlap to form 3 MOs – one bonding, one non-bonding, one anti-bonding



bond order = 1 or 0.5 for each O-O

total bond order (including σ bonds) = 1.5

O_3 is isoelectronic with nitrite (NO_2^-)

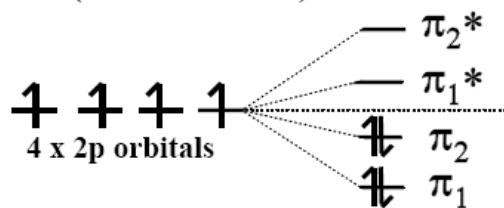


Can also calculate bond strengths in unsaturated hydrocarbons e.g.

Butadiene (C₄H₆) – four carbon skeleton = 16 valence electrons

- 6 electrons in C-C σ bonds
- 6 electrons in C-H σ bonds
- 4 delocalised electrons (in 2p orbitals)

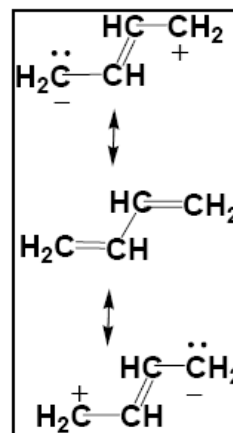
four 2p orbitals overlap to form four MOs (two π and two π^*)



- π bond order = 2 (spread across whole molecule)

π bond order = 2/3 (for each bond)

- with σ bonding C-C bond order = 1.67



Q: In the azide ion (N₃⁻) what's the bonding arrangement and N-N bond order?

A: Count the number of valence electrons:

5 for each N, 1 for -ve charge = 16 valence electrons
= 8 valence electron pairs

structural formula must be N—N—N

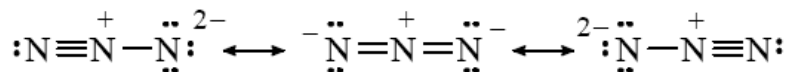
(6 valence pairs remain to complete octets)

4 lone pairs and 2 π -bonds satisfy octet for all atoms

no lone pairs on central atom - must be sp hybridised (linear)

Terminal nitrogens are sp² hybridised

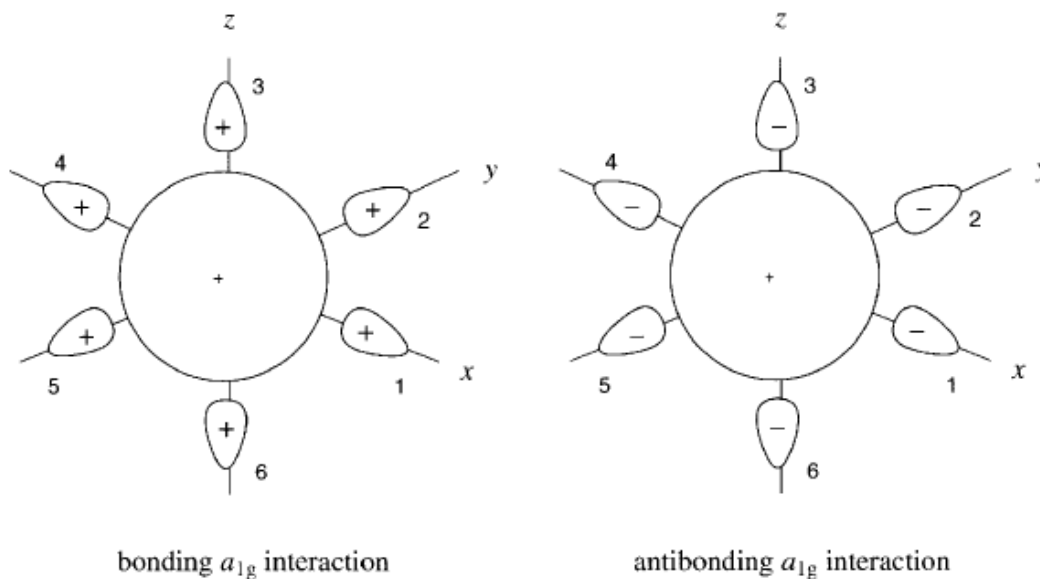
bond order = 2 (there are two N=N double bonds)



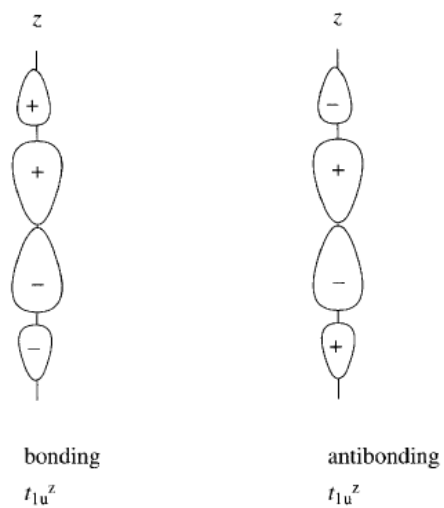
n.b. N₃⁻ is isoelectronic with CO₂

Oh

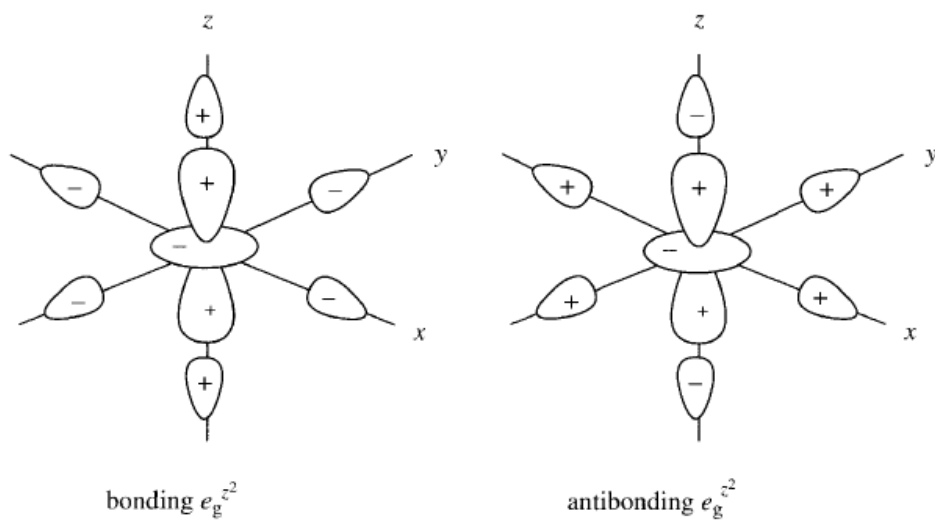
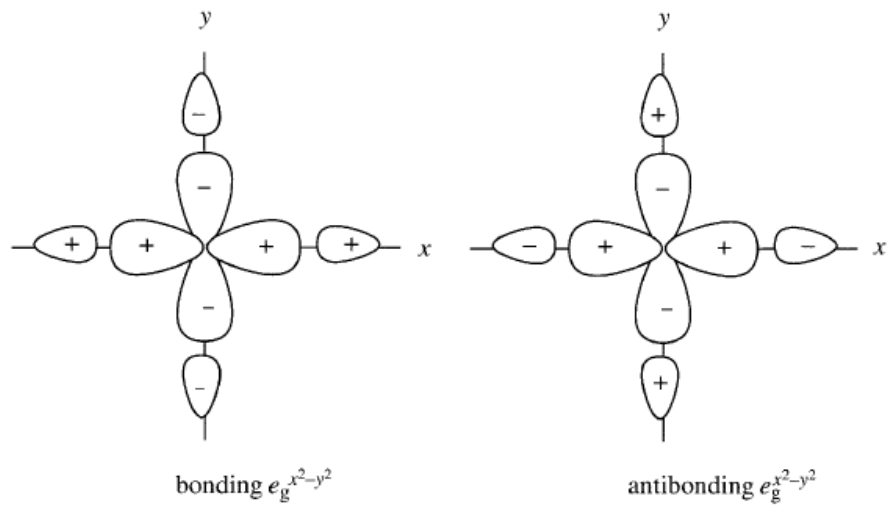
. Interaction with the metal s orbital.



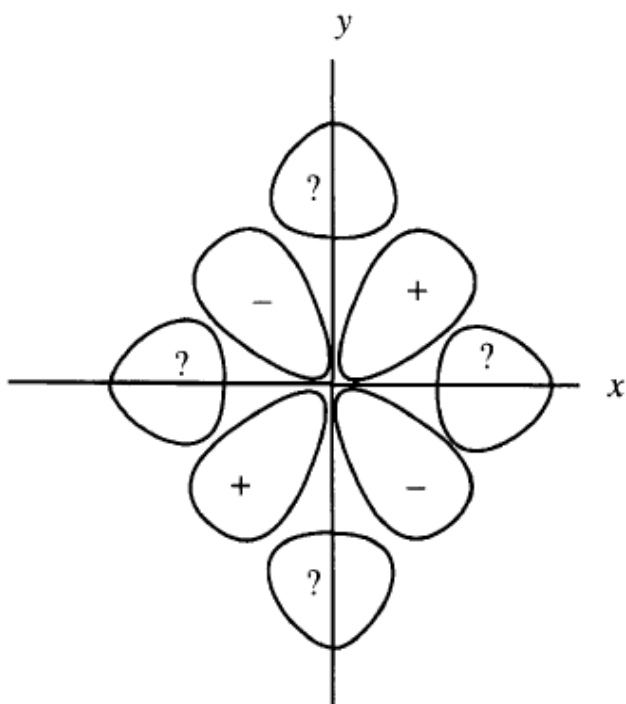
. Bonding and antibonding t_{1u}^x, t_{1u}^y combinations are similar but with orbital densities along the x or y axes respectively.



Interaction with the metal $d_{x^2-y^2}$ and d_{z^2} orbitals.

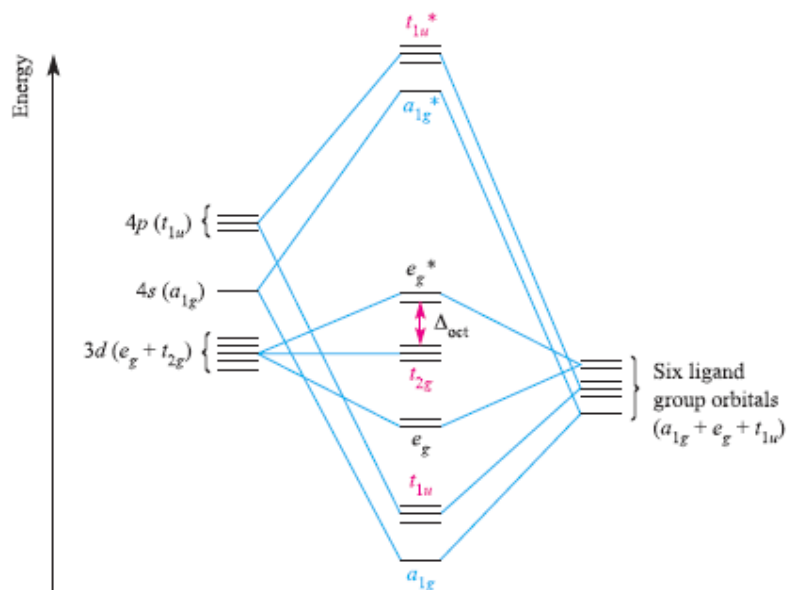


Impossible symmetry matching of ligand σ orbitals with metal d_{xy} . Similar results apply for the xz and yz planes.



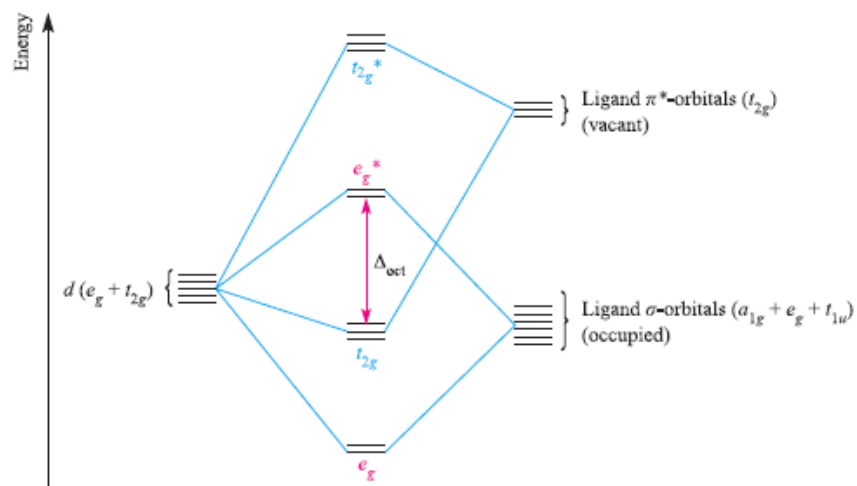
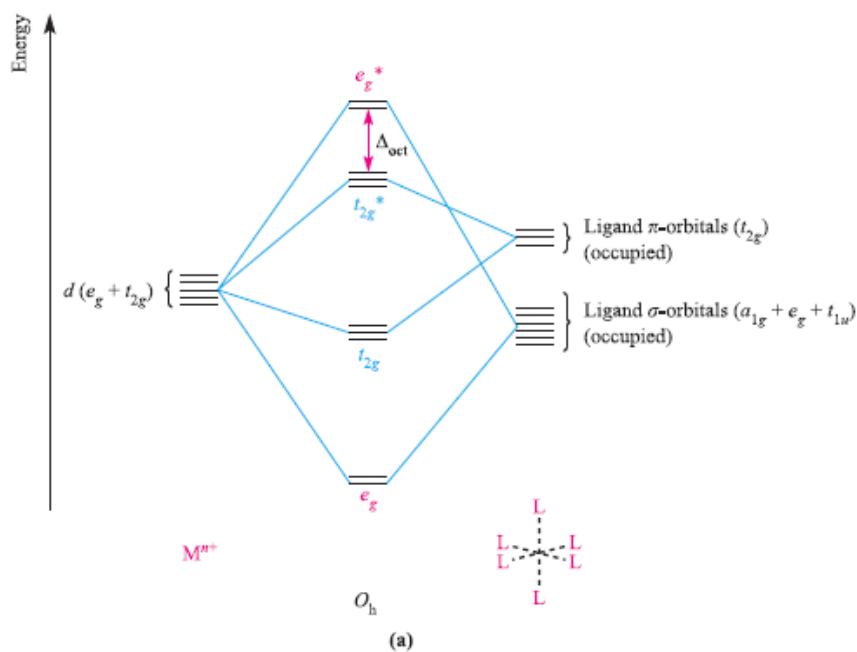
Schematic m.o. diagram for metal and σ -bonding ligands in O_h symmetry.

The bonding only involves M-L σ -interactions.



For example $[\text{Co}(\text{NH}_3)_6]^{+3}$ σ -donor

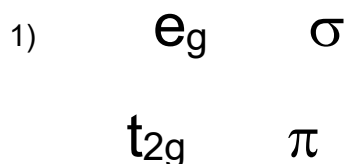
Approximate partial MO diagrams for metal-ligand π -bonding in an octahedral complex (a) with π -donor ligands and (b) with π -acceptor ligands. In addition to the MOs shown σ -bonding in the complex involves the a_{1g} and t_{1u} MOs.



For example (a) $[\text{CoF}_6]^{3-}$ π -donor

For example (b) $[\text{Fe}(\text{CN})_6]^{3-}$ π -acceptor

Note:



2) HOMO: **highest occupied molecular orbital**

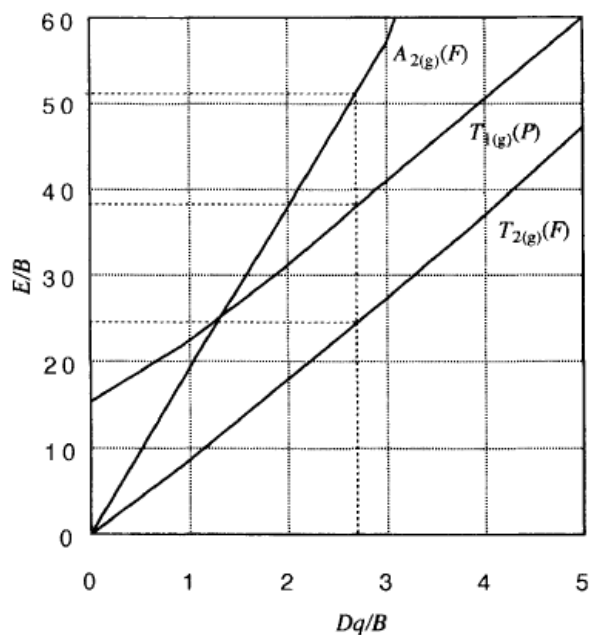
3) LUMO: **lowest unoccupied molecular orbital**

4) **More symmetry, less intensity, Cis more stable than Trans.**

5)

$$(500 \text{ nm} = 20000 \text{ cm}^{-1} = \Delta_o = 10 Dq, \quad \frac{1}{\lambda} = \tilde{\nu} \text{).}$$

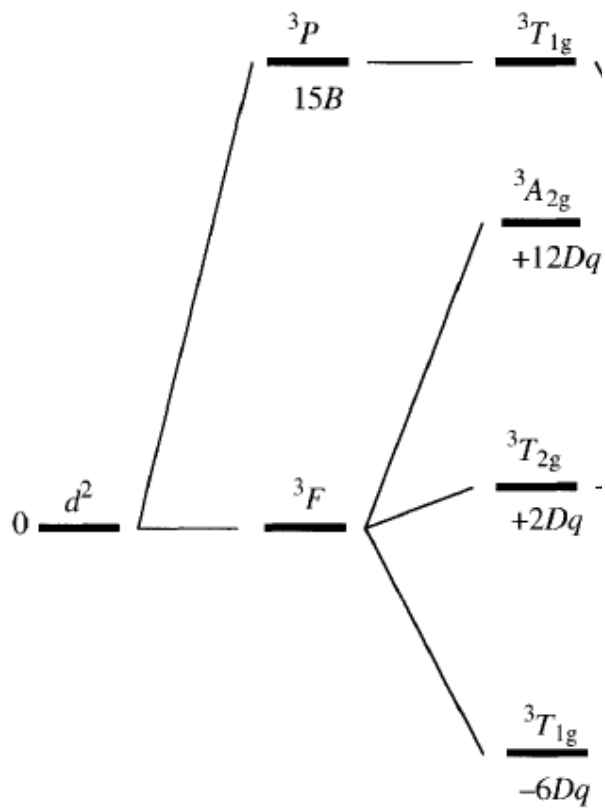
The figure below abstracts just the spin-triplet part of the Tanabe-Sugano diagram in the previous box. Suppose we have recorded the electronic 'd-d' spectrum of $[\text{V}(\text{H}_2\text{O})_6]^{2+}$ and identified two out of the three possible 'spin-allowed' (triplet-triplet) bands at energies $17,200 \text{ cm}^{-1}$ and $25,600 \text{ cm}^{-1}$



The question arises 'to which of the transitions ${}^3T_{1g} \rightarrow {}^3T_{2g}, \rightarrow {}^3A_{2g}, \rightarrow {}^3T_{1g}(P)$ do these bands correspond?'

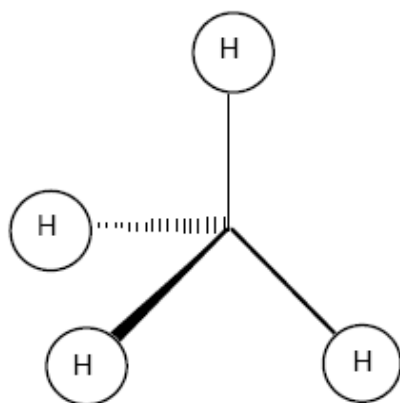
We proceed by determining at what value of Dq/B on the abscissa is the ratio $256/172 = 1.49$ reproduced by the plot: this is shown by the vertical broken line in the figure. Then we construct the horizontal broken lines to meet, as shown. For ν_a we find E/B on the ordinate as 25.9, and for ν_b we get $E/B = 38.7$. From either we find, therefore, that $B = 665 \text{ cm}^{-1}$. On referring back to the vertical line we thus find $10Dq = 18,600 \text{ cm}^{-1}$. At the same time we have established that ν_a corresponds to the transition $\rightarrow {}^3T_{2g}(F)$ and ν_b to $\rightarrow {}^3T_{1g}(P)$. The transition $\rightarrow {}^3A_{2g}(F)$ is predicted to lie at ca. $36,000 \text{ cm}^{-1}$.

In Oh system



Using a group theoretical approach, construct a MO energy level diagram for tetrahedral CH₄. Include appropriate symmetry labels and discuss the logic used as well as any assumptions made in the construction of the MO diagram.

First, identify valence orbitals of the atoms involved in the bonding: the valence orbitals of the Carbon atom are $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals while each hydrogen atom has a $1s$ orbital. Next, figure out the symmetry of the orbitals involved. Thus, we make SALC's of the hydrogen $1s$ orbitals

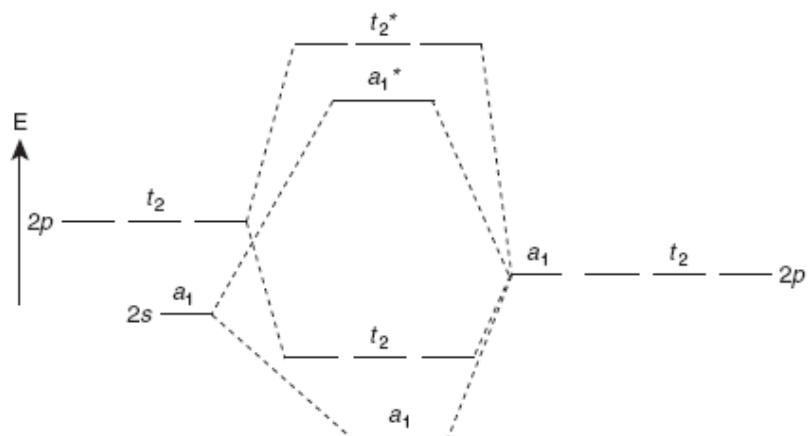


T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_{1s}	4	1	0	0	2

Which reduces to $\Gamma_{1s} = A_1 + T_2$

Looking in the character table, we see that for nitrogen:
 $2s$ orbital has a_1 symmetry
 $2p_x$, $2p_y$, and $2p_z$ orbitals have t_2 symmetry

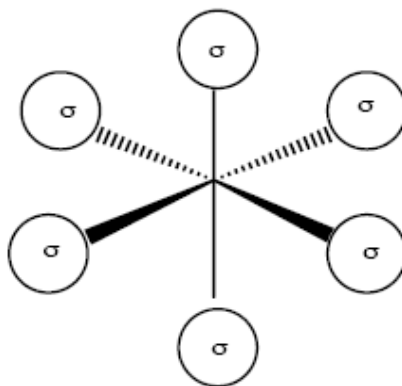
Recognizing that carbon is more electronegative than hydrogen, we can suspect that the hydrogen SALC's will have the higher energy and that the a_1 SALC is slightly lower than the t_2 SALC's because of the nodal surfaces that exist although the atoms are not formally bonded. Thus, we get the diagram below:



Qualitative orbital energy level diagram for T_d AX_4 molecule

Using group theory, construct a MO energy level diagram showing sigma bonding only for $[\text{Ti}(\text{CO})_6]^{2-}$. Include appropriate symmetry labels for all orbitals and discuss the logic used as well as any assumptions made in constructing your MO diagram. Draw the MO diagram using the template labeled $[\text{Ti}(\text{CO})_6]^{2-}$.

First, identify valence orbitals of the atoms involved in the bonding. The valence orbitals of the titanium atom are the five $3d$ -, $4s$ -, and three $4p$ orbitals. The CO ligands form sigma bonds through their 3σ HOMO. Next, we figure out the symmetry of the orbitals involved. Thus, we make SALC's of the CO donor sigma orbitals:



O_h	E	$8 C_3$	$6 C_2$	$6 C_4$	$3 C_4^2$	i	$6 S_4$	$8 S_6$	$3 \sigma_h$	$6 \sigma_d$
Γ_{Co}	6	0	0	2	2	0	0	0	4	2

Which reduces to $\Gamma_{CO} = A_{1g} + E_g + T_{1u}$

Looking in the character table, we see that for titanium:

4s orbital has a_{1g} symmetry

$3d_{z^2}$ and $3dx^2-y^2$ have e_g symmetry

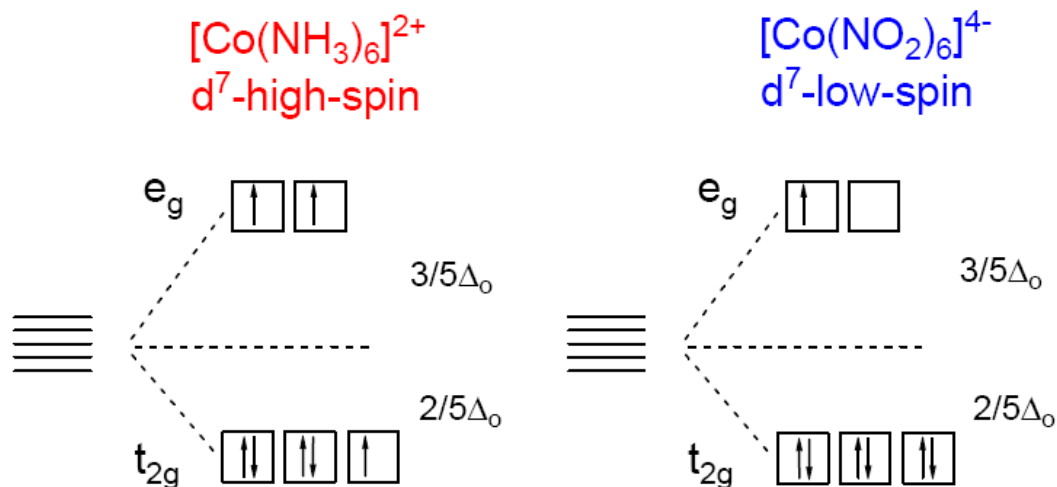
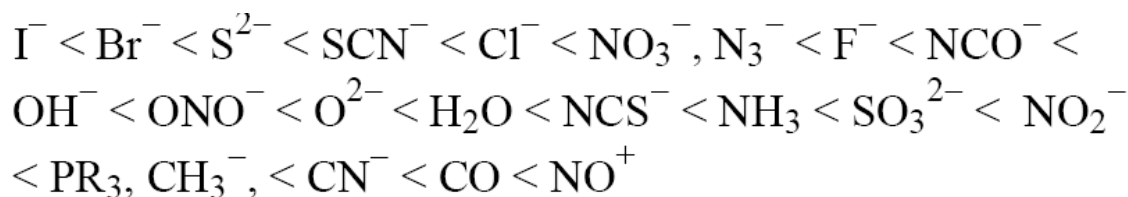
$3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ have t_{2g} symmetry

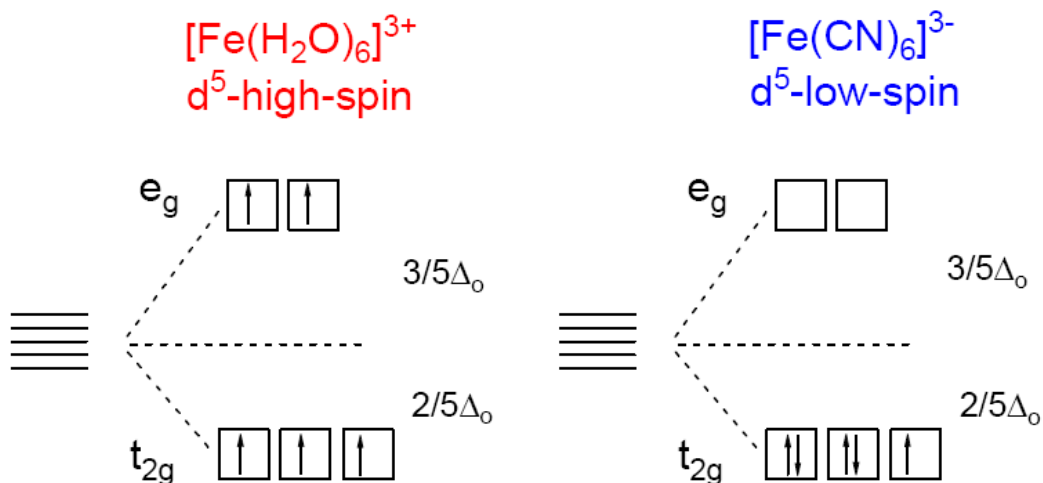
$4p_x$, $4p_y$, and $4p_z$ orbitals have t_{1u} symmetry

Recognizing that the CO donor electrons must be at lower energy than the titanium acceptor orbitals (CO carbon is more electronegative than titanium).

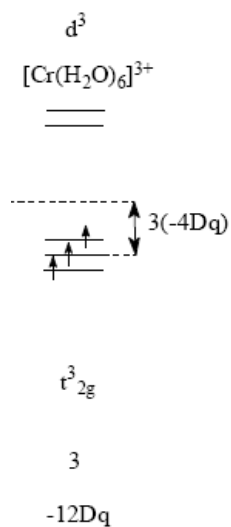
We see that the t_{1u} orbitals are lower

in energy than the e_g , this is because the e_g orbitals point directly at the ligands and are raised in energy due to repulsive interaction.





Q1 For $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ show the effect in Oh environment and determine ground state:



For d^3 High spin. $t_{2g}^1 \times t_{2g}^1 \times t_{2g}^1$

Q1 * *

t_{2g}^3 is on octahedral environment

Oh	E	$8C_2$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
$T_{2g} \times T_{2g} \times T_{2g}$	27	0	1	-1	-1	27	-1	0	-1	1

We make reduction

$$\# A_{1g} = \frac{1}{48} [27 + 0 + 6 - 6 - 3 + 27 - 6 + 0 - 3 + 6] = 1$$

$$\# A_{2g} = \frac{1}{48} [27 + 0 - 6 + 6 - 3 + 27 + 6 + 0 - 3 - 6] = 1$$

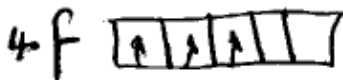
$$\# E_g = \frac{1}{48} [54 + 0 + 0 + 0 - 6 + 54 + 0 + 0 - 6 + 0] = 2$$

$$\# T_{1g} = \frac{1}{48} [81 + 0 + -6 + 6 + 3 + 81 - 6 + 0 + 3 - 6] = 3$$

$$\# T_{2g} = \frac{1}{48} [81 + 0 + 6 + 6 + 3 + 81 + 6 + 0 + 3 + 6] = 4$$

$$t_{2g} \times t_{2g} \times t_{2g} = A_{1g} + A_{2g} + 2E_g + 3T_{1g} + 4T_{2g}$$

For d^3



$$ml \quad +2 \quad +1 \quad 0 \quad -1 \quad -2$$

$$\sum ml = 2 + 1 + 0 = 3$$

$$L = 3 \quad F$$

$$\text{multiplicity } 2 \times \frac{3}{2} + 1 = 4$$

$4F$

$4A_{2g}$ ground state.

Note:

Totally symmetric representation, A_1 , with all characters = 1

Q2) Show the transition $A_1 \rightarrow B_1$ in D_{2d} in Z-direction and X,Y-direction:

Q2 **

(a) $A_1 \rightarrow B_1$ in D_{2d}

$$A_1 \times B_1 = 1 \quad -1 \quad 1 \quad -1 = B_1$$

to Determine in Z-direction

$$B_1 \times B_2 = 1 \quad 1 \quad 1 \quad -1 \quad -1 = A_2$$

forbidden in Z-direction, because is not equal to total symmetric representation and is not contain it.

to Determine in x,y - direction

$$B_1 \times E = 2 \quad 0 \quad -2 \quad 0 \quad 0 = E$$

The Transition is forbidden in x,y - direction, because is not equal to total symmetric representation and is not contain it.

b) $A_1g \rightarrow A_{2u}$ in D_{3d}

$$A_1g \times A_{2u} = 1 \quad 1 \quad -1 \quad -1 \quad -1 \quad 1 = A_{2u}$$

$$A_1g \times A_{2u} = A_{2u}$$

to Determine in x,y - direction

$$A_{2u} \times E_u = 2 \quad -1 \quad 0 \quad 2 \quad -1 \quad 0$$

The reduction

$$A_1g = \frac{1}{12} [2 - 2 + 0 + 2 - 2 + 0] = 0$$

is not contain total symmetric A_1g and the transition is forbidden in x,y - direction

(Z-) direction or operator A_{2u}

$$A_{2u} \times A_{2u} = 1 \quad 1 \quad 1 \quad 1 \quad 1 \quad 1 = A_1g$$

is equal to Total symmetric representation and transition is allowed in Z - direction

Q3 : Show the transition B₂ to E in C_{4v} in Z-direction and X,Y-direction:

a)

$$B_2 \rightarrow E \text{ in } C_{4v}$$

$$B_2 \times E = 2 \quad 0 \quad -2 \quad 0 \quad 0$$

in z-direction

$$E \times A_1 = E$$

$A_1 = \frac{1}{8} [2 + 0 + -2 + 0] = 0$ is not contain total symmetric representation and is forbidden in z-direction.

in x,y-direction

$$E \times E = 4 \quad 0 \quad 4 \quad 0 \quad 0$$

$A_1 = \frac{1}{8} [4 + 0 + 4 + 0] = 1$ is allowed in x,y-direction contain total symmetric representation.

b) Show the transition A_{1u} to T_{1g} in O_h and X,Y,Z-direction:

$$A_{1u} \rightarrow T_{1g} \text{ in } O_h$$

in (x,y,z) direction \Rightarrow operation

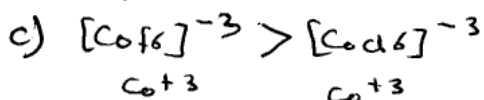
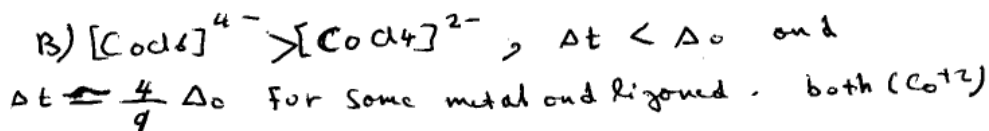
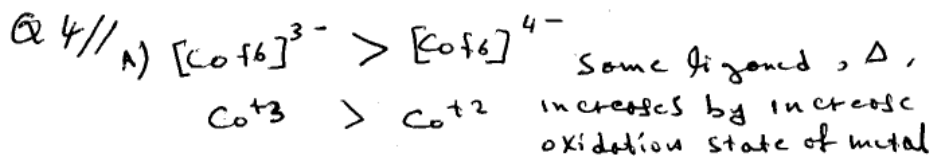
$$A_{1u} \times T_{1g} \times T_{1u} = 9 \quad 0 \quad 11 \quad 19 \quad 10 \quad 11$$

$$\# A_{1g} = \frac{1}{48} [9 + 0 + 6 + 6 + 3 + 9 + 6 + 0 + 3 + 6] = 1$$

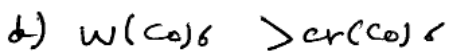
is allowed in (x,y,z) direction because direct product is contain total symmetric representation.

Q4) which of the following molecules more Δ :

Q5 Determine the kind of transition allowed or forbidden in the following molecules:

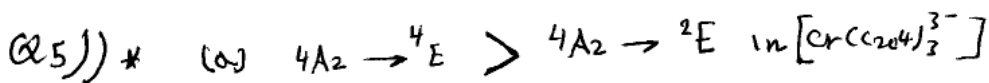
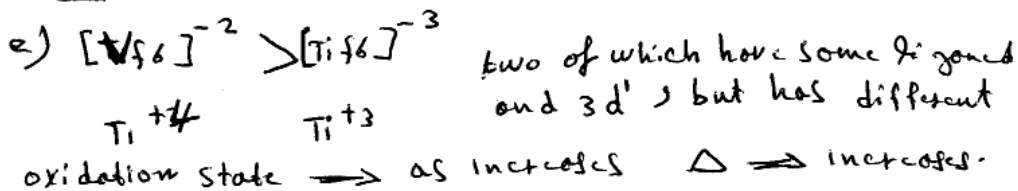


F^- is strong field ligand than Cl^-
 and Δ for F^- is larger.

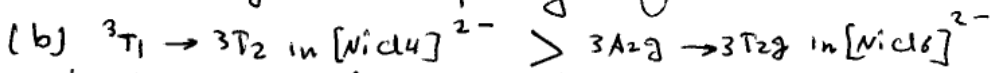


5d 3d as we go down in the Group

(Δ) increases



because the transition $4A_2 \rightarrow {}^2E$ is spin-forbidden
 due to change in multiplicity. 0



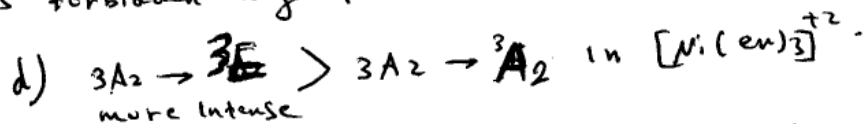
The intensity of the $[\text{NiCl}_4]^{2-}$ is the bond greater,
 because Tetrahedral (Td) is not having centrosymmetric
 or inversion center, but (Oh) have inversion center
 or centrosymmetric, this meaning (Oh) is forbidden
 transition by Laporte Rule, but the transition
 is possible by vibronic coupling for (Oh) (u-g or g-u).

by Laporte Rule g-g or d-d is forbidden.



$[\text{Co}(\text{en})_3]^{+3}$ is more intense because D_3 point group
 is not centrosymmetric (is not contain inversion center)

and The Transition is allowed by Laporte Rule (g-g, d-d)
but in Centrosymmetric which have inversion center (Oh)
is forbidden by Laporte and this is less intense.



$A_2 \times A_2 = A_1 \Rightarrow$ in z-direction $A_1 \times A_2 = A_2$ is forbidden
 \Rightarrow in x,y-direction $A_1 \times E = 2 \quad -1 \quad 0$

$\# A_1 = \frac{1}{6} [2 + -2 + 0] = 0$
in x,y-direction is forbidden

but $A_2 \times E = 2 \quad -1 \quad 0 = E$

in z-direction $E \times A_2 = 2 \quad -1 \quad 0$

$\# A_1 = \frac{1}{6} [2 + -2 + 0] = 0$ is forbidden

in x,y-direction $E \times E = 4 \quad 1 \quad 0$

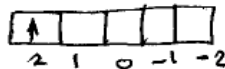
$\# A_1 = \frac{1}{6} [4 + 2 + 0] = 1$ is allowed in x,y-direction

$3A_2 \rightarrow 3E$ is more intense because is allowed
in x,y direction, but $3A_2 \rightarrow 3A_2$ is symmetry
forbidden and is less intense.

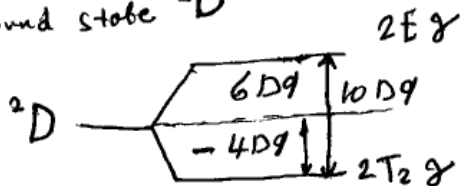
Q7: Describe the transition in Ti^{+3} :

07

$Ti^{+3} = d^1$ free ion



Ground state $2D$

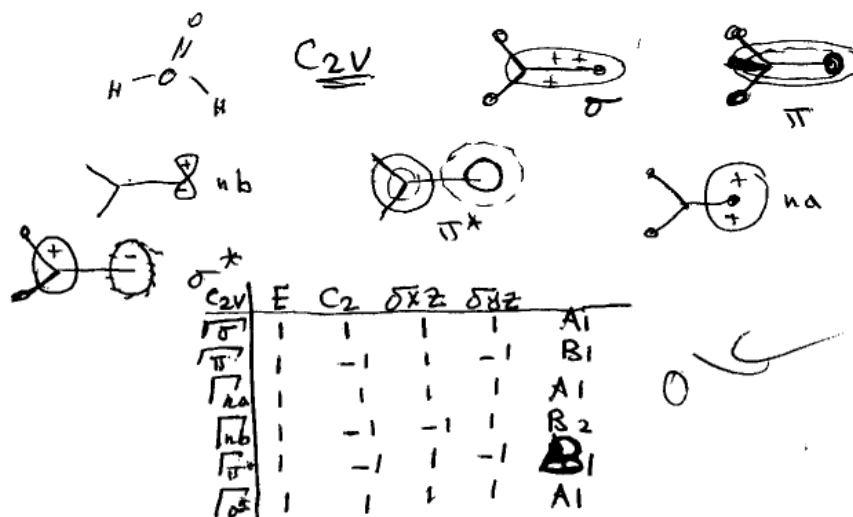


Transition $2T_{2g} \rightarrow 2E_g$

energy of the transition $2T_{2g} \rightarrow 2E_g$ is
equal $= 10Dq = 20,000 \text{ cm}^{-1}$

Q8: See the orbitals in the following scheme below and determine all the kind of the following transition in different direction, and also determine the number of modes in rotational, translational and vibration.

Q8



To Determine X-direction oscillator = B_1

$n_a \rightarrow \sigma^*$, $A_1 \times B_1 \times A_1 = B_1$ is forbidden

$n_a \rightarrow \pi^*$, $A_1 \times B_1 \times B_1 = A_1$ allowed

$\pi \rightarrow \sigma^*$, $B_1 \times B_1 \times A_1 = A_1$ allowed

$\pi \rightarrow \pi^*$, $B_1 \times B_1 \times B_1 = B_1$ forbidden

$n_b \rightarrow \sigma^*$, $B_2 \times A_1 \times B_1 = A_2$ forbidden

$nb \rightarrow \pi^*$, $B_2 \times B_1 \times B_1 = B_2$ is forbidden.

* y-direction B_2 .

- $na \rightarrow \sigma^*$ $A_1 \times A_1 \times B_2 = B_2$ forbidden.
- $na \rightarrow \pi^*$ $A_1 \times B_2 \times B_1 = A_2$ forbidden.
- $\pi \rightarrow \sigma^*$ $b_1 \times b_2 \times a_1 = A_2$ forbidden.
- $\pi \rightarrow \pi^*$ $B_1 \times B_1 \times B_2 = B_2$ forbidden.
- $nb \rightarrow \sigma^*$ $b_2 \times a_1 \times B_2 = A_1$ allowed.
- $nb \rightarrow \pi^*$ $b_2 \times b_1 \times b_2 = B_1$ forbidden.

In z-direction A_1 .

- $na \rightarrow \sigma^*$ $A_1 \times A_1 \times A_1 = A_1$ allowed
- $na \rightarrow \pi^*$ $A_1 \times B_1 \times A_1 = B_1$ forbidden
- $\pi \rightarrow \sigma^*$ $B_1 \times A_1 \times A_1 = B_1$ forbidden
- $\pi \rightarrow \pi^*$ $B_1 \times A_1 \times B_1 = A_1$ allowed
- $nb \rightarrow \sigma^*$ $B_2 \times A_1 \times A_1 = B_2$ forbidden
- $nb \rightarrow \pi^*$ $B_2 \times A_1 \times B_1 = A_2$ forbidden

orbitals
 σ_{yz} plane of molecule

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\sqrt{X_{yz}}$	12	-2	2	4

σ_{yz} plane of molecule

basis orbitals σ_{yz} plane of molecule
 σ_{yz} plane orbitals

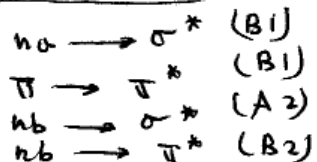
no. of normal mode = $3N - 6 = 12 - 6 = 6$

$A_1 = \frac{1}{4} [12 - 2 + 2 + 4] = 4$
 # $A_2 = \frac{1}{4} [12 - 2 - 2 - 4] = 1$
 # $B_1 = \frac{1}{4} [12 + 2 + 2 - 4] = 3$
 # $B_2 = \frac{1}{4} [12 + 2 - 2 + 4] = 4$

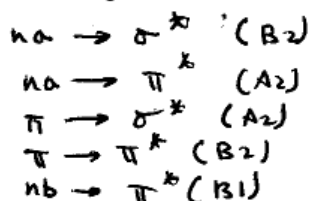
$\sqrt{X_{yz}} = 4A_1 + A_2 + 3B_1 + 4B_2$

3-Translational $A_1 + B_1 + B_2$
 3-Rotational $A_2 + B_1 + B_2$

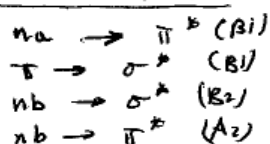
normal mode of vibration = $3A_1 + B_1 + 2B_2$

Vibronic CouplingX - directionvibronic coupling

allowed
 allowed
 forbidden
 allowed

for y - directionvibronic coupling

Allowed
 forbidden
 forbidden
 allowed
 allowed

In Z - directionVibronic coupling

Allowed
 Allowed
 Allowed
 forbidden

Q9) a) determine the number of modes in rotational, translational and vibration:

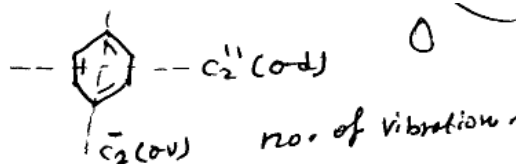
b) Determine the active and inactive in both Raman and IR:

c) Determine Γ_{C-C} , Γ_{C-H} and Γ_{C-C-H} :

Q10) The interaction of $[M(CO)_6]$ with triphenylphosphine gives two complexes with the formula $[M(CO)_4\{P(Ph)_3\}_2]$. Assign the isomers to point groups (treat the phosphines as point ligands – i.e., ignore their symmetry, Note: X: PPh_3). The carbonyl stretching frequencies at about 2000 cm^{-1} are well isolated from other vibrations in the molecules.

Derive the symmetry (Mulliken label) of each CO stretching frequency, and tell whether it is IR and/or Raman active

Q9



$$\begin{aligned} \text{no. of vibration mode} &= 3N - 6 \\ &= 3(12) - 6 \\ &= 30 \end{aligned}$$

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_6$	$2S_6^5$	$8C_2$	$3C_2$	$3C_2$	$3C_2$
χ_{12}	36	0	0	0	-4	0	0	0	0	12	0	0	4

$$\# A_{1g} = \frac{1}{24} [36 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 4] = 2$$

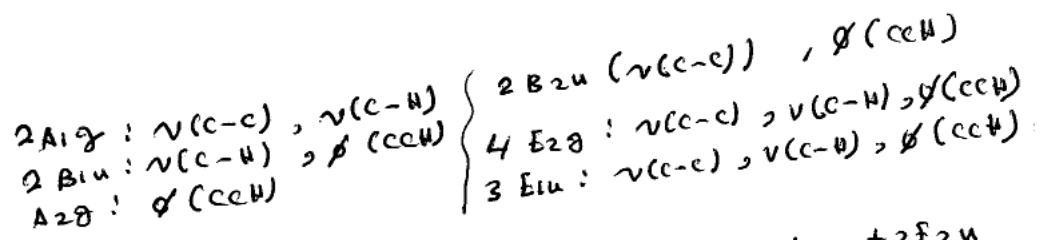
$$\# A_{2g} = \frac{1}{24} [36 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 4] = 2$$

$$\# B_{1g} = \frac{1}{24} [36 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 4] = 0$$

$$\# B_{2g} = \frac{1}{24} [36 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 0 + 0 + 12 + 0 + 0 + 4] = 2$$

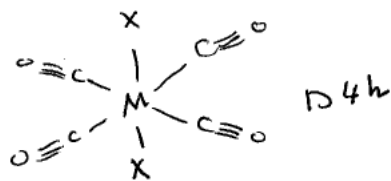
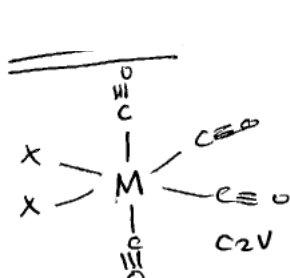
$$\# E_{1g} = \frac{1}{24} [72 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 24 + 0 + 0] = 2$$

$$\# E_{2g} = \frac{1}{24} [72 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 0 + 24 + 0 + 0] = 4$$



d) out of plane mode = $2B_{2g} + E_{1g} + A_{2u} + 2E_{2u}$
 The rest not included above.

Q10



C_{2v}	E	C_2	σ_{xz}	σ_{yz}
$\Gamma_{C\equiv O}$	4	0	2	2

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{C\equiv O}$	4	0	0	2	0	0	0	4	2	0

$$\Gamma_{C\equiv O} = 2A_1 + B_1 + B_2$$

$4 \nu(C\equiv O)$, all active
 in both, IR and Raman

$$\Gamma_{C\equiv O} = A_{1g} + B_{1g} + E_u$$

$$\Rightarrow 3 \nu(C\equiv O)$$

$E_u \Rightarrow$ IR active

$B_{1g}, E_u \Rightarrow$ Raman active

To distinguish between cis and trans

For cis - all of them $2A_1 + B_1 + B_2$ active in both
 IR and Raman.

For Trans \Rightarrow only one IR active (E_u)
 and $A_{1g} + B_{1g}$ active in Raman

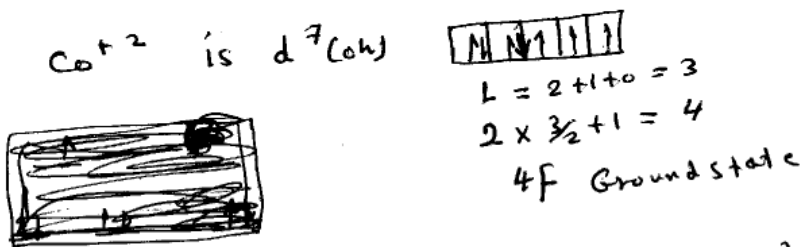
by using IR or Raman we distinguish
 between cis or trans.

The *trans* isomer has 3 $\nu(CO)$ absorptions: E_u is IR active; A_{1g} and B_{1g} are Raman active,

The *cis* isomer has 4 $\nu(CO)$ absorptions, all IR and Raman active

Q11) Show all transitions of Co^{+2} in Oh high spin:

Q11

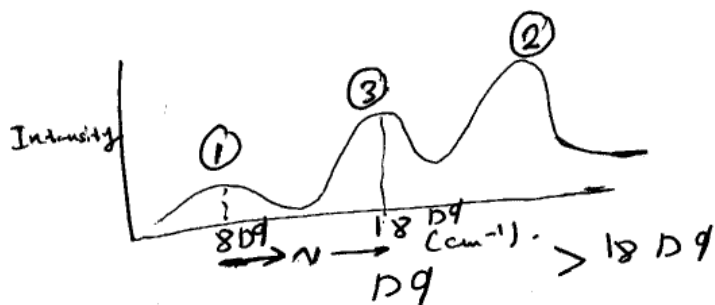


$\text{Co}^{+2} \rightarrow$ weak field ligand (high spin).



The transition

- ① $4T_{1g} \rightarrow 4T_{2g} \rightarrow 8Dq$
- ② $4T_{1g} \rightarrow 4T_{1g}(P) \rightarrow > 18Dq$
- ③ $4T_{1g} \rightarrow 4A_{2g} \rightarrow 18Dq$



In order of decreasing ν

② > ③ > ①

* Strong field ligand (low spin)

$2E_g =$ ground state

The transition

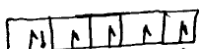
$2E_g \rightarrow 2T_{1g}$
 $2E_g \rightarrow 2T_{2g}$
 $2E_g \rightarrow 2A_{1g}$
 $2E_g \rightarrow 2A_{2g}$

We expect 3-bands and the fourth transition is highest in energy.

Q12) Show all transitions in the following 1) K_3CoF_6 2) Cr^{+3} (high spin in Oh) 3) Cr^{+2} (high spin in Oh) 4) Fe^{+2} (high spin in Oh) 5) Mn^{+2} (high spin in Oh) 6) Ti^{+3} (high spin in Oh) 7) V^{+3} (high spin in Oh):

Q12

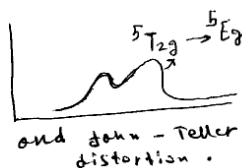
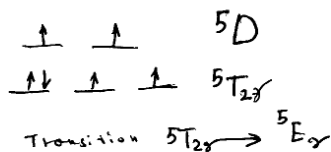
Co^{+3} is d^6 f^- is weak ligand \rightarrow
is high spin



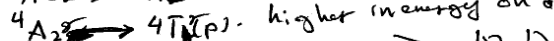
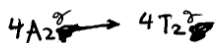
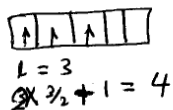
$$2 \quad 1 \quad 0 \quad -1 \quad -2$$

$$2 \times 2 + 1 = 5$$

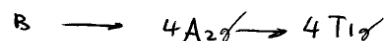
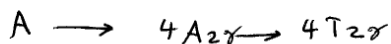
$$L = 2 \Rightarrow D$$

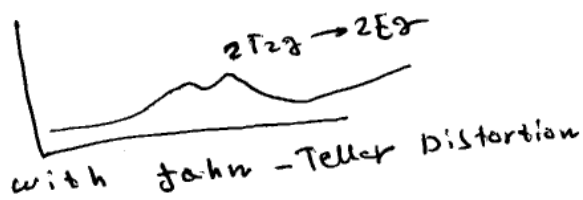
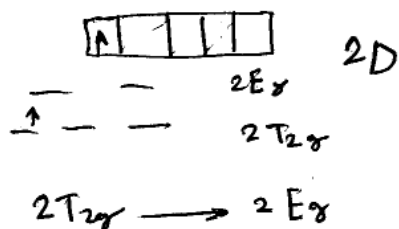


② $Cr^{+3} (d^3)$ Ground state $4F$



is not shown energy

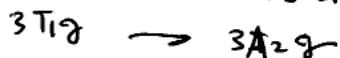
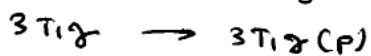
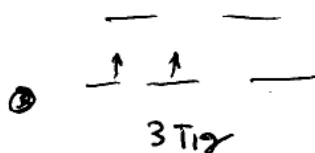


6) $Ti^{+3} (d^1)$ 7) $V^{+3} (d^2)$ Ground state $3f$ 

$$l = 3$$

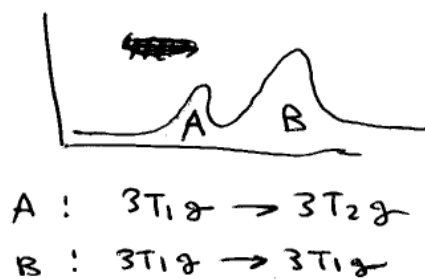
$$3F$$

$$2 \times 1 + 1 = 3$$



OK

we expect 3-Transition
but one is higher in energy and is
not shown



but third
Transition is
not shown
due to higher
energy
Transition

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