



Symmetry & Bonding

Answers to the Questions 22(optional), 23-24



Ex.22

考虑一个八面体过渡金属配合物，关注其金属基非键 $1t_{2g}$ 和反键 $2e_g$ 分子轨道，金属提供的d电子将填充在这些分子轨道组中。

- (a) 针对0到10个d电子的情况，制作表格显示 $1t_{2g}$ 和 $2e_g$ 分子轨道的电子排布情况，并采用常规符号（即" \uparrow "和" \downarrow "）标注电子自旋方向。当存在两种可能排布时，需分别列出低自旋与高自旋的排布方式。
- (b) 设 $1t_{2g}$ MO的能量为0， $2e_g$ MO的能量为 Δ_o ，假设每对平行自旋会使能量降低 K 值。请在原有表格中增加使用这些参数计算出的各构型能量。
- (c) 假设 $K = 1$ & $\Delta_o = 1/2$ （任意单位），画图表示电子排布能量随d电子数变化的关系，必要处需同时绘制高、低自旋排布的数据点。
- (d) 现假设 $K = 1$ & $\Delta_o = 4$ （任意单位），重新计算各电子排布能量，重新画图。
- (e) 根据上述图形对高低自旋态的倾向性进行评述。



Ex.22

(a-d) 考虑一个八面体过渡金属配合物，关注其金属基非键 $1t_{2g}$ 和反键 $2e_g$ 分子轨道，金属提供的d电子将填充在这些分子轨道组中。

	d ¹	d ²	d ³	d ⁴	d ⁵	d ⁶	d ⁷	d ⁸	d ⁹	d ¹⁰
HS $2e_g$				↑	↑ ↑	↑ ↑	↑ ↑	↑ ↑	↑↓ ↑	↑↓ ↑↓
$1t_{2g}$	↑	↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑ ↑ ↑	↑↓ ↑ ↑	↑↓ ↑↓ ↑	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓
E	0	-K	-3K	$-6K + \Delta_o$	$-10K + 2\Delta_o$	$-10K + 2\Delta_o$	$-11K + 2\Delta_o$	$-13K + 2\Delta_o$	$-16K + 3\Delta_o$	$-20K + 4\Delta_o$
K=1, $\Delta_o = 1/2$	0	-1	-3	-5.5	-9	-9	-10	-12	-14.5	-18
K=1, $\Delta_o = 4$	0	-1	-3	-2	-2	-2	-3	-5	-4	-4
LS $2e_g$							↑			
$1t_{2g}$				↑↓ ↑ ↑	↑↓ ↑↓ ↑	↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓			
E	-	-	-	-3K	-4K	-6K	$-9K + \Delta_o$	-	-	-
K=1, $\Delta_o = 1/2$				-3	-4	-6	-8.5			
K=1, $\Delta_o = 4$				-3	-4	-6	-5			



ex23



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

$$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ B.M.}$$

		d ⁴	d ⁵	d ⁶	d ⁷
HS	n	4	5	4	3
	$\mu_{\text{eff}}/\text{BM}$	4.90	5.92	4.90	3.87
LS	n	2	1	0	1
	$\mu_{\text{eff}}/\text{BM}$	2.83	1.41	0.00	1.41



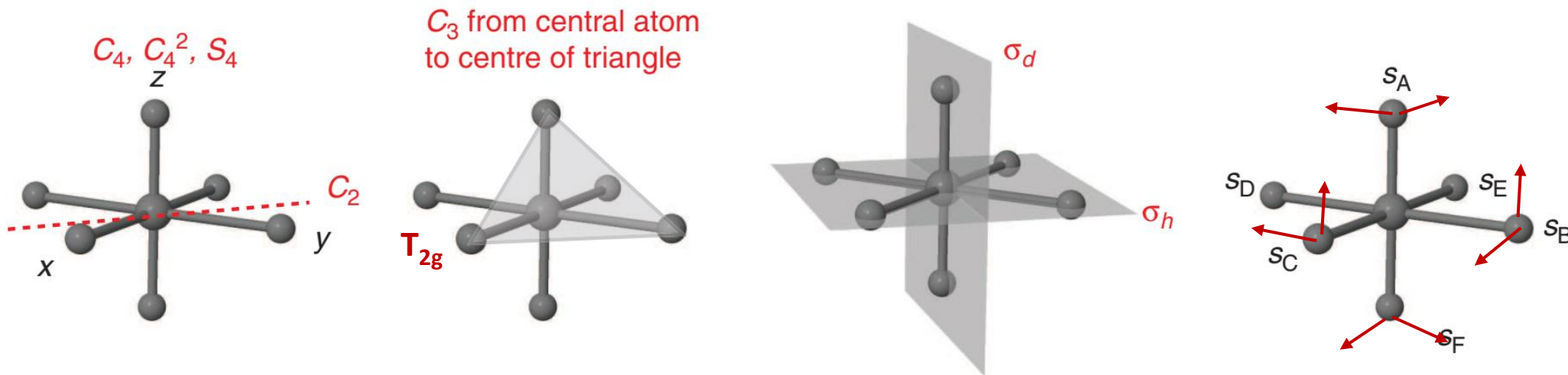
- (b) Use the following experimentally measured values of μ_{eff} to determine whether the given octahedral complex is high or low spin. (Be aware that the spin-only formula is not expected to give precise agreement with experimental data; in the complex $[\text{Co}(\text{NO}_2)_6]^{4-}$ the ligands are $[\text{NO}_2]^-$).

complex	$\mu_{\text{eff}} / \text{B.M.}$	complex	$\mu_{\text{eff}} / \text{B.M.}$
$[\text{Co}(\text{NO}_2)_6]^{4-}$	1.9	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	3.8
$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	4.8	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	5.9
$[\text{Fe}(\text{CN})_6]^{3-}$	2.3	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	5.3

- b
- i) $[\text{Co}(\text{NO}_2)_6]^{4-}$: Co^{2+} d^7 & $n = 1$ ($\mu_{\text{eff}} = 1.9$) \rightarrow LS
 - ii) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$: Cr^{2+} d^4 & $n = 4$ ($\mu_{\text{eff}} = 4.8$) \rightarrow HS
 - iii) $[\text{Fe}(\text{CN})_6]^{3-}$: Fe^{3+} d^5 & $n = 1$ ($\mu_{\text{eff}} = 2.3$) \rightarrow LS
 - iv) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$: Cr^{3+} d^3 & $n = 3$ ($\mu_{\text{eff}} = 3.8$) \rightarrow no HS/LS issue
 - v) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$: Mn^{2+} d^5 & $n = 5$ ($\mu_{\text{eff}} = 5.8$) \rightarrow HS
 - vi) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: Fe^{2+} d^6 & $n = 4$ ($\mu_{\text{eff}} = 5.3$) \rightarrow HS



S&B **Ex. 24(a)** Considering an octahedral complex in which each ligand is a single anion, such as Cl^- . Suppose that each ligand also contributes two p orbitals arranged at right angles to the M–L bond. Find the representation generated by these **12** orbitals and show it reduces to $\mathbf{T}_{1g} \oplus \mathbf{T}_{2g} \oplus \mathbf{T}_{1u} \oplus \mathbf{T}_{2u}$



Use local axis system for each ligand! 每个配体有两个垂直键轴的p轨道

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
Γ	12	0	-4	0	0	0	0	0	0	0
			-2-2					4-4		

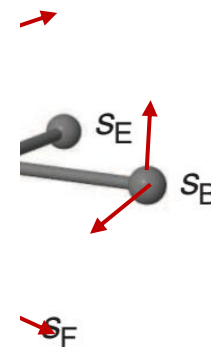
(xz, xy, yz)

这些配体p轨道组成的 \mathbf{T}_{2g} SOs



S&B **Ex. 24(a)** Considering an octahedral complex in which each ligand is a single anion, such as Cl^- . Suppose that each ligand also contributes two p orbitals arranged at right angles to the M–L bond. Find the representation

O_h	E	$8C_3$	$3C_4^2$	$6C_4$	$6C_2$	i	$8S_6$	$3\sigma_h$	$6S_4$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
E_g	2	-1	2	0	0	2	-1	2	0	0
T_{1g}	3	0	-1	1	-1	3	0	-1	1	-1
T_{2g}	3	0	-1	-1	1	3	0	-1	-1	1
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	2	0	0	-2	1	-2	0	0
T_{1u}	3	0	-1	1	-1	-3	0	1	-1	1
T_{2u}	3	0	-1	-1	1	-3	0	1	1	-1



$$\Gamma \quad 12 \quad 0 \quad \begin{matrix} -4 \\ -2-2 \end{matrix} \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad \begin{matrix} 0 \\ 4-4 \end{matrix} \quad 0 \quad 0 \quad = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$$



Ex. 24(b) With the aid of a suitable diagram explain why the presence of low-lying (in energy terms) filled π -type orbitals on the ligands generally results in a decrease in Δ_o .

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

(b) 配体上 π 轨道组合成的 T_{2g} SOs可与金属基的 T_{2g} SOs (即金属 d_{xy}, d_{xz}, d_{yz})组合成 $1t_{2g}$ 成键和 $2t_{2g}$ 反键分子轨道(如下左图)。当配体 π 轨道为占据轨道时, 金属基 t_{2g} 轨道为反键轨道, 能量升高, 与 $2e_g$ 间的能差缩小, 即配位场分裂能 Δ_o 降低 (如下右图) ;

(c) 当配体 π 轨道为空轨道时, 金属基 t_{2g} 轨道为成键轨道, 能量降低, 与 $2e_g$ 间的能差增大, 即配位场分裂能 Δ_o (如下右图) 增大。

