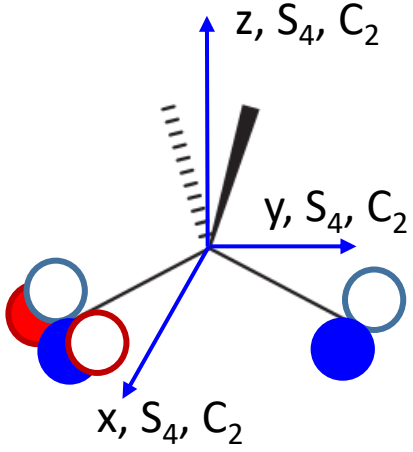
Symmetry & Bonding

Answers to the Questions 25(f,g),26(optional)

Ex. 25(f,g) Suppose that each ligand also contributes two *p* orbitals arranged at right angles to the M–L bond. Determine and reduce the representation generated by these eight orbitals.



$p_{\pi,x} \| \sigma_d$

$p_{\pi,y} \perp \sigma_d$

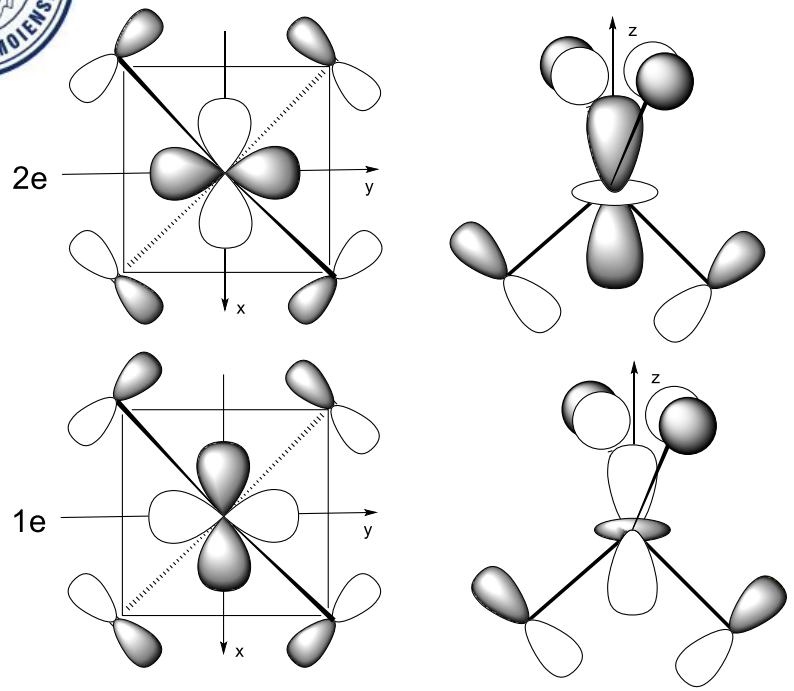
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1
Γ	8	-1	0	0	2-2

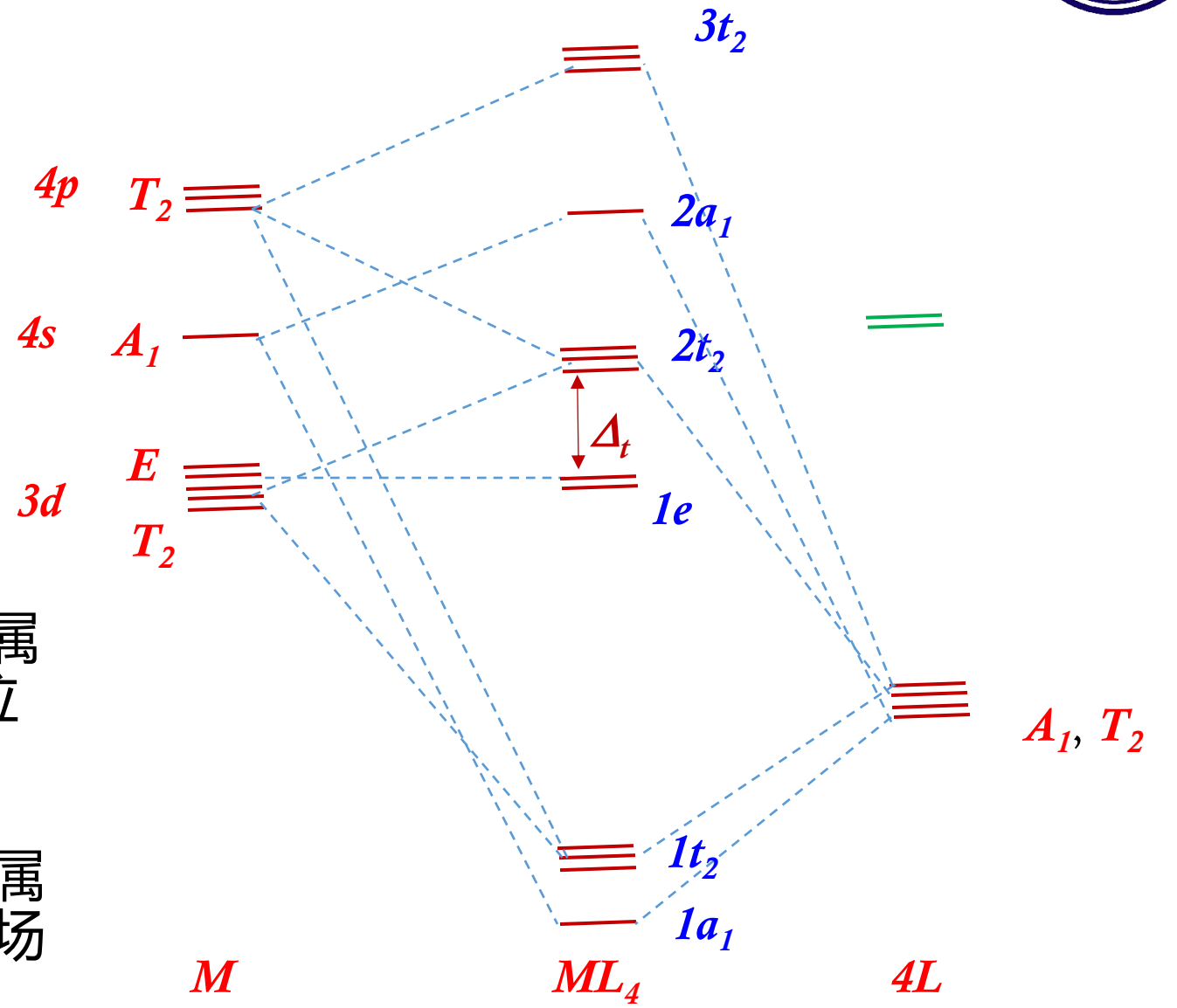
$E \oplus T_1 \oplus T_2$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	−1	1	1	−1	
E'	2	−1	0	2	−1	0	(x, y)
A_1''	1	1	1	−1	−1	−1	
A_2''	1	1	−1	−1	−1	1	z
E''	2	−1	0	−2	1	0	

- Each M-L bond axis is a C_3 axis. Therefore define a ***local axis system*** on each ligand with the M-L bond being z-axis and two $p_\pi(x,y)$ AOs perpendicular to this axis.
- For the effects of C_3 operation on the ligand p_π AOs, refer to the D_{3h} character table!

MO diagram of ML4





- 配体 π轨道(如Cl⁻ p_π)为占据轨道时, 金属基轨道为2e(反键)轨道, 能量升高, 配位场分裂能Δ_t降低!

- 配体 π轨道(如CO 2π*)为空轨道时, 金属基轨道为1e成键轨道, 能量降低, 配位场分裂Δ_t能增大!