<u>In-Class Problems / Self-study Problems / Test Preparation: Lecture 5</u>

- **In-Class P1** determine the number of times the E' and A_1" irreducible representations contribute to the reducible representation of H_3. Show your working.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1"	1	1	1	-1	-1	-1
$\Gamma(H_3)$	3	0	1	3	0	1

$$n_{A_1''} = \frac{1}{12}\left[(1\bullet1\bullet3)+(2\bullet1\bullet0)+(3\bullet1\bullet1)+(1\bullet\text{-}1\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet\text{-}1\bullet1)\right]$$

$$n_{A_1''} = \frac{1}{12}\left[3 + 0 + 3 - 3 + 0 - 3\right] = 0$$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
E'	2	-1	0	2	-1	0
$\Gamma(H_3)$	3	0	1	3	0	1

$$n_{E'} = \frac{1}{12}\left[(1\bullet2\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet0\bullet1)+(1\bullet2\bullet3)+(2\bullet\text{-}1\bullet0)+(3\bullet0\bullet1)\right]$$

$$n_{E'} = \frac{1}{12}\left[6 + 0 + 0 + 6 + 0 + 0\right] = 1$$

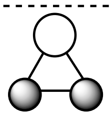
Figure 1 In class practice reduction tables

- **In-Class P2** You try! Determine the wavefunction for one of the components of the degenerate e' MOs, fill in the projection table.

		$2C_3$		$3C_2$				$2S_3$		3σ		
D_{3h}	E	C_3^1	C_3^2	C_2	C_2'	C_2''	σ_h	S_3^1	S_3^{-1}	σ_v	σ_v'	σ_v''
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2	s_1	s_2	s_3	s_1	s_3	s_2
E'	2	-1	-1	0	0	0	2	-1	-1	0	0	0
$\chi^{E'}(Q) \bullet Q \bullet [s_1]$	$2s_1$	$-s_2$	$-s_3$	-	-	-	$2s_1$	$-s_2$	$-s_3$	-	-	-

$$P_{E'}[s_1] = \frac{1}{12}\left[2s_1 - s_2 - s_3 + 2s_1 - s_2 - s_3\right]$$

$$P_{E'}[s_1] = \frac{1}{12}\left[4s_1 - 2s_2 - 2s_3\right] = \frac{1}{6}\left[2s_1 - s_2 - s_3\right]$$



$$\psi_{e'} = \frac{1}{6}\left[2\phi_{s_1} - \phi_{s_2} - \phi_{s_3}\right]$$

Figure 2 In class practice projection tables

- **Q1** Where would you put the FOs for a MO diagram of $MgCl_2$? Draw out the fragments and the FOs (don't complete the diagram, just set it up). Use the fragments "Cl_2" Cl–•–Cl and •–Mg–• for Cl–Mg–Cl
  - What are the valence orbitals of Mg? 3s and 3p. Mg is in the third row so 3s3p3d however Mg 3d AOs are very high in energy, we generally only consider the 3s and 3p for the valence of Mg
  - What relative energy will the valence orbitals of Mg have (and why)? Mg is a main group metal and electropositive, the orbitals will be high in energy. Mg lies to the left of the periodic table and will have a small sp gap. In MO theory we start always with the neutral fragment.
  - What relative energy will the valence orbitals of Cl have (and why)? Cl is an electronegative element, the orbitals will be deep in energy. Cl lies to the right of the PT and thus the sp gap will be large
  - When we form the Cl–•–Cl fragment how large will the interaction energy of the MOs be? The fragment orbitals are far apart and overlap will be small therefor the energy of stabilisation and destabilisation will be small. The fragment orbital diagram will look like that of O_2 because Cl is electronegative and has a large sp gap. If there is very little overlap, it doesn't matter how close in energy the orbitals are, they will not interact. So overlap is very important here.

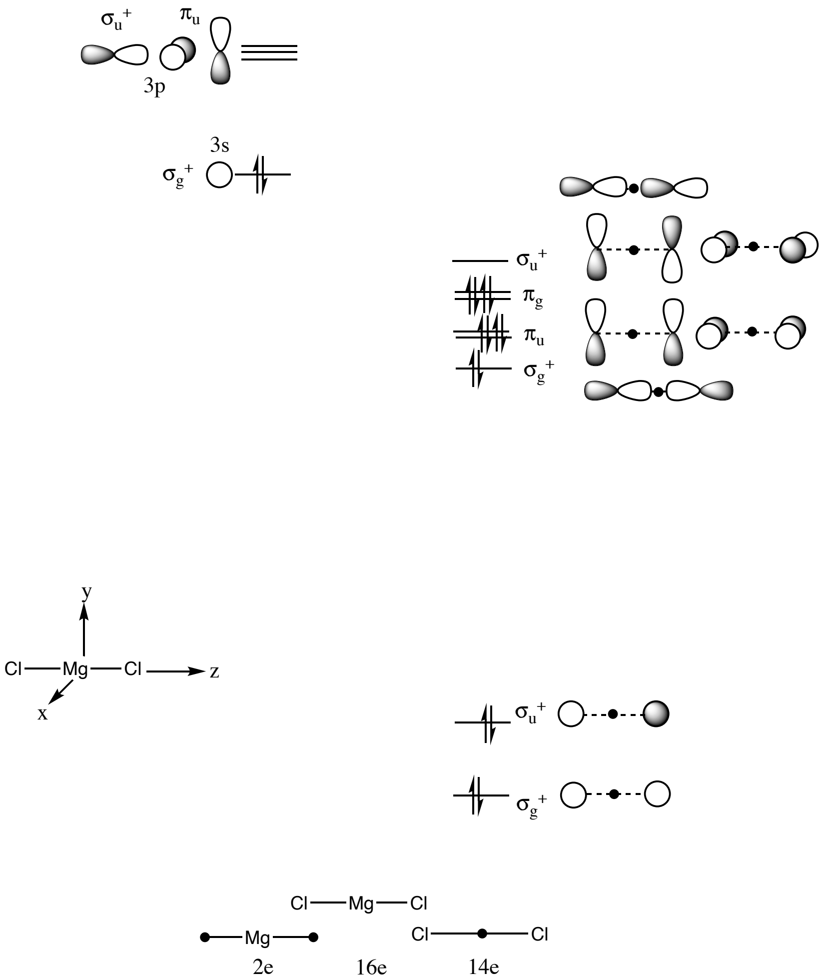


Figure 3 Fragments for the MO diagram of $MgCl_2$

- **Q2** The transition metal (M) complex ML_4 with 4 sigma ligands (L) belongs to the D_{4h} point group and is aligned as shown in **Figure 4**. In the following show your working
  - Determine the reducible representation ($\Gamma_{L\sigma}$) for the basis set consisting of 4 ligand σ-orbitals.

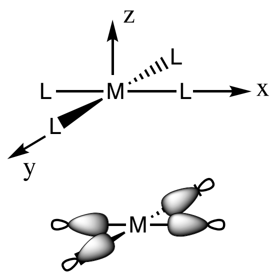


Figure 4 L_4 ligand σ-orbitals

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{L_σ}	4	0	0	2	0	0	0	4	2	0

Figure 5 reducible representation for $\Gamma_{L\sigma}$

  - The reducible representation $\Gamma_{L\sigma}$ has three irreducible components, one of which is E_u. Use the reduction formula and appropriate "short-cuts" to determine the remaining irreducible components of $\Gamma_{L\sigma}$.

try A_{1g} first because sAOs

D_{4h}	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
Γ_{L_σ}	4	0	0	2	0	0	0	4	2	0

$$n_{A_{1g}} = \frac{1}{16}\left[\underbrace{1\bullet 1\bullet 4}_{E} + 0 + \underbrace{2\bullet 1\bullet 2}_{C_2'} + 0 + \underbrace{1\bullet 1\bullet 4}_{\sigma_h} + \underbrace{2\bullet 1\bullet 2}_{\sigma_v} + 0\right]$$

$$n_{A_{1g}} = \frac{1}{16}\left[4+0+4+0+4+4+0\right] = \frac{16}{16} = 1$$

remove known E_u

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{L_σ}	4	0	0	2	0	0	0	4	2	0
E_u	2	0	-2	0	0	-2	0	2	0	0
$\Gamma_{L_\sigma} - E_u$	2	0	2	2	0	2	0	2	2	0

remove known A_{1g}

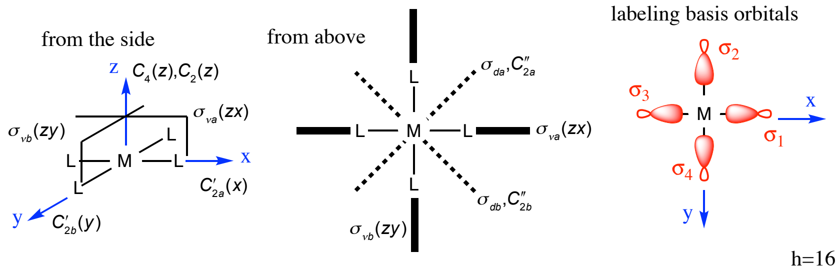
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{L_\sigma} - E_u$	2	0	2	2	0	2	0	2	2	0
A_{1g}	1	1	1	1	1	1	1	1	1	1
$\Gamma_{L_\sigma} - A_{1g}$	1	-1	1	1	-1	1	-1	1	1	-1

$=B_{1g}$

$$\Gamma_{L_\sigma} = A_{1g} + B_{1g} + E_u$$

Figure 6 reducible representation

- Use the projection formula to determine the wave function of the totally symmetric irreducible representation. The wavefunction does not need to be normalised.



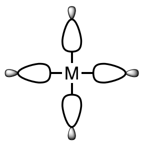
h=16

D_{4h}	E	C_4^1	C_4^2	C_2	C_{2a}'	C_{2b}'	C_{2a}''	C_{2b}''	i	S_4^1	S_4^{-1}	σ_h	σ_{va}	σ_{vb}	σ_{da}	σ_{db}
$Q[\sigma_1]$	σ_1	σ_2	σ_4	σ_3	σ_1	σ_3	σ_2	σ_4	σ_3	σ_2	σ_4	σ_1	σ_1	σ_3	σ_2	σ_4
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\chi^{A_{1g}}(Q) \bullet Q \bullet Q[\sigma_1]$	σ_1	σ_2	σ_4	σ_3	σ_1	σ_3	σ_2	σ_4	σ_3	σ_2	σ_4	σ_1	σ_1	σ_3	σ_2	σ_4

$$P_{A_{1g}}[\sigma_1] = \frac{1}{16}[\sigma_1 + \sigma_2 + \sigma_4 + \sigma_3 + \sigma_1 + \sigma_3 + \sigma_2 + \sigma_4 + \sigma_3 + \sigma_2 + \sigma_4 + \sigma_1 + \sigma_1 + \sigma_3 + \sigma_2 + \sigma_4]$$

$$= \frac{1}{16}[4\sigma_1 + 4\sigma_2 + 4\sigma_3 + 4\sigma_4]$$

$$= \frac{1}{4}[\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4]$$



$$\psi^{A_{1g}} = \frac{1}{4}[\phi_{\sigma_1} + \phi_{\sigma_2} + \phi_{\sigma_3} + \phi_{\sigma_4}]$$

Figure 7 energy level diagram with FOs and their equations