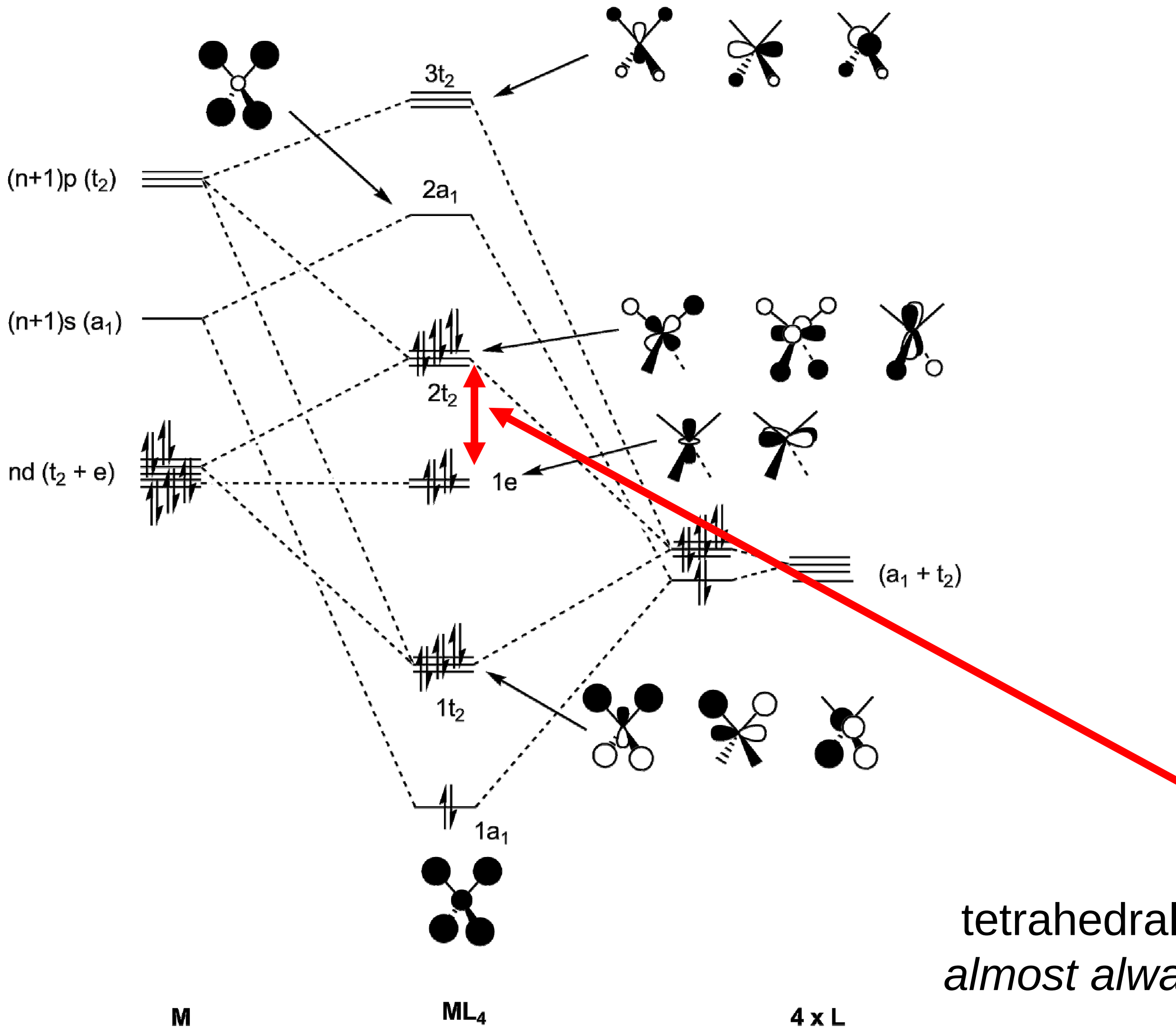
Bonding in Molecules

Lecture 6

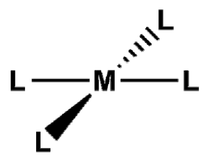
4 coordinate complexes, summary, typical exam questions

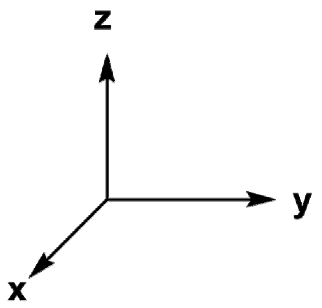


$\Delta_t = 4/9\ \Delta_o$

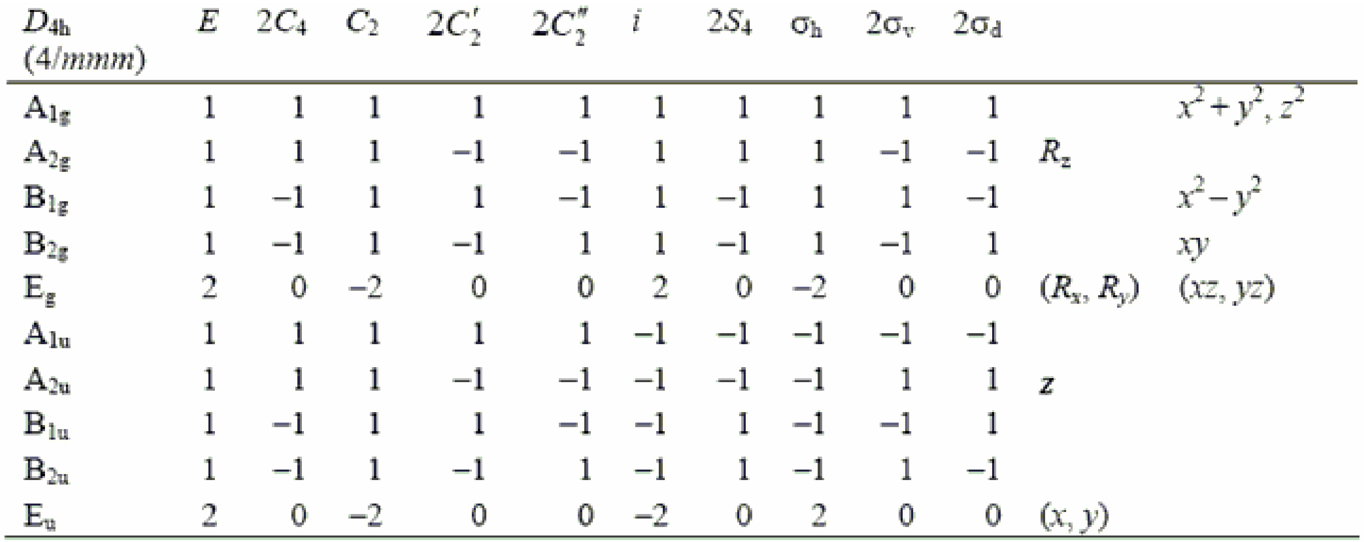
tetrahedral complexes
almost always high-spin

Square planar complexes e.g $[Ni(CN)_4]^{2-}$, $[PtCl_4]^{2-}$

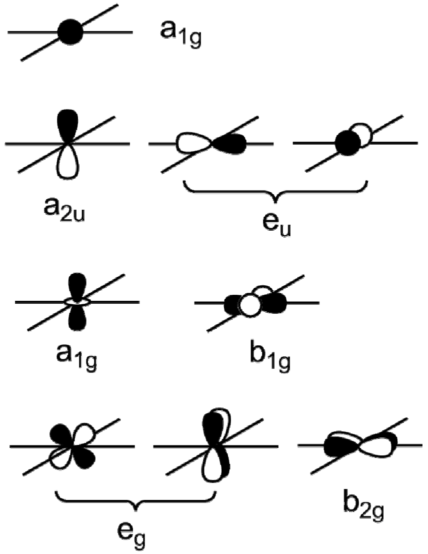


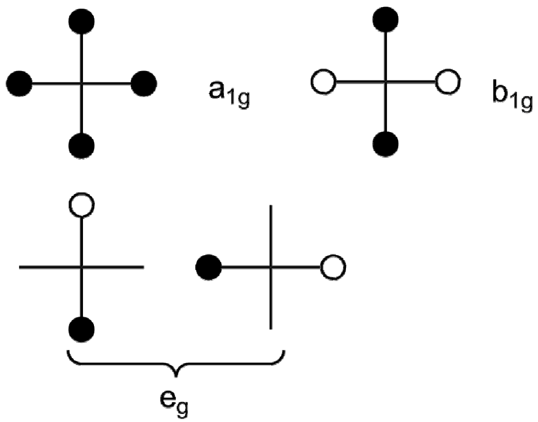


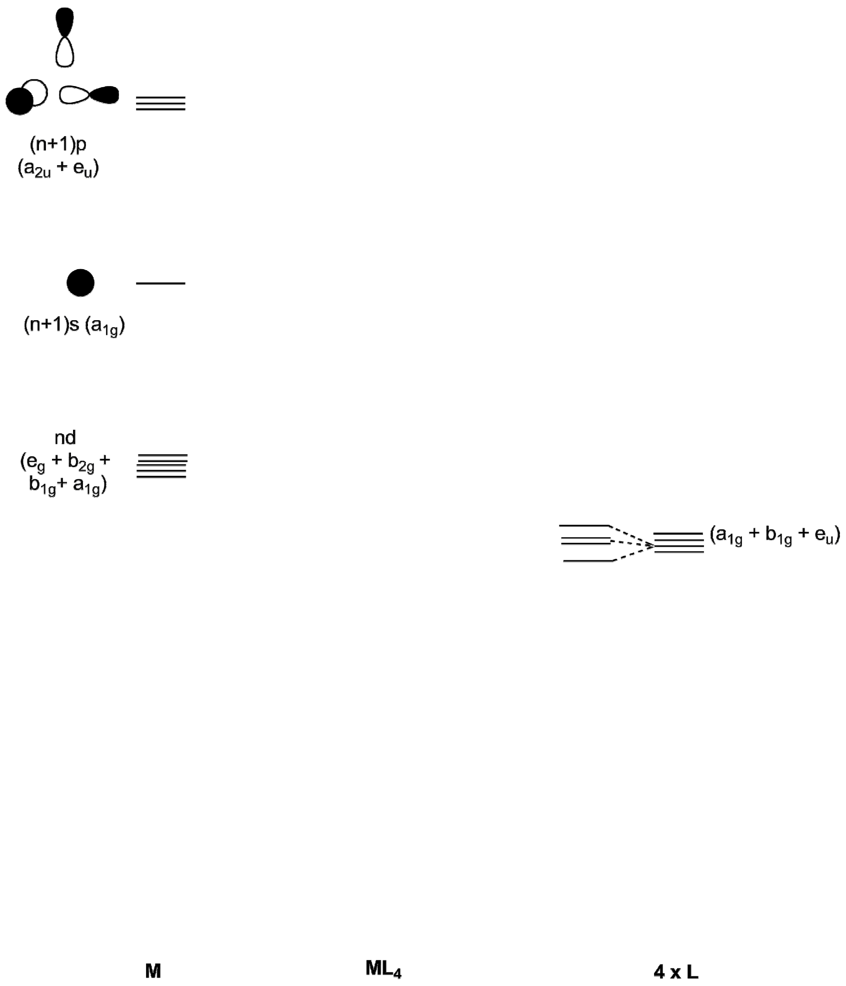
Symmetry analysis (σ-only)

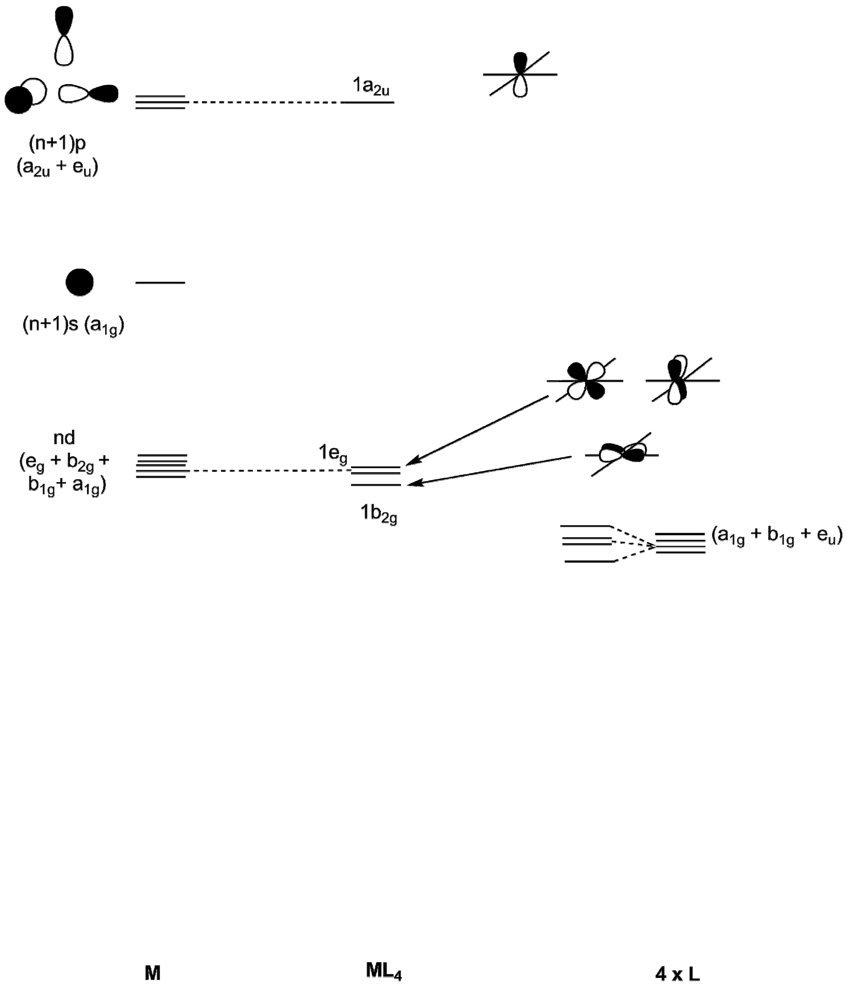


D_{4h} (4/mmm)	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1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

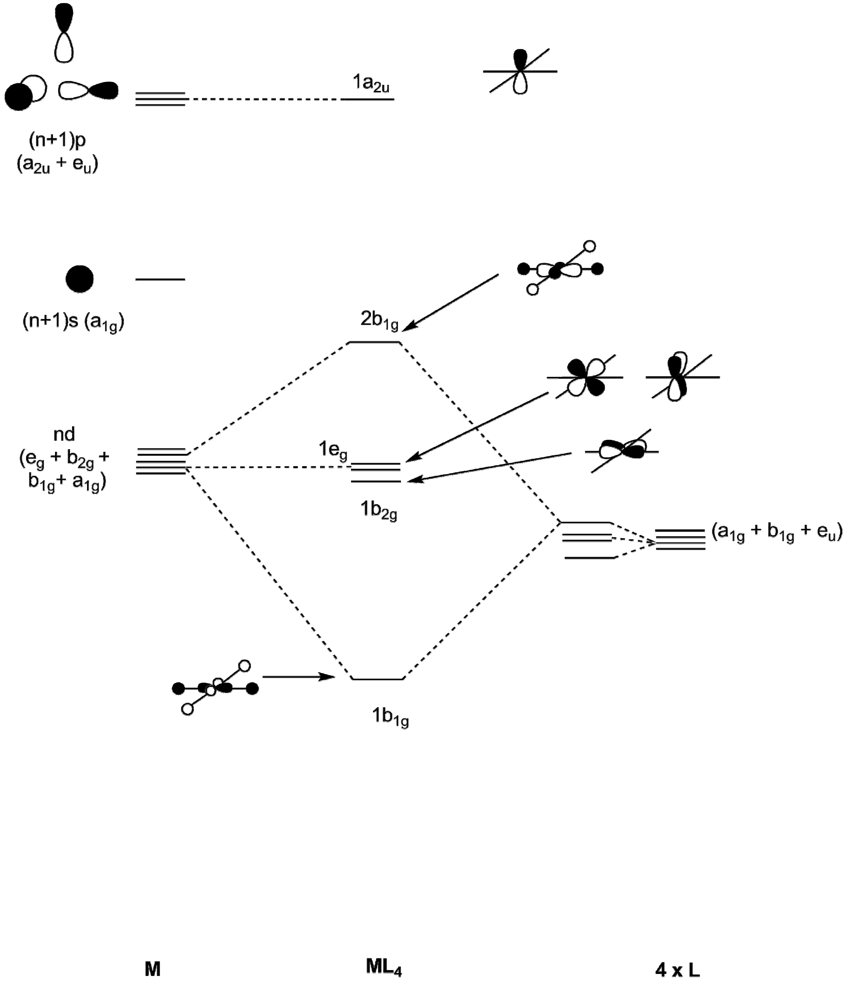


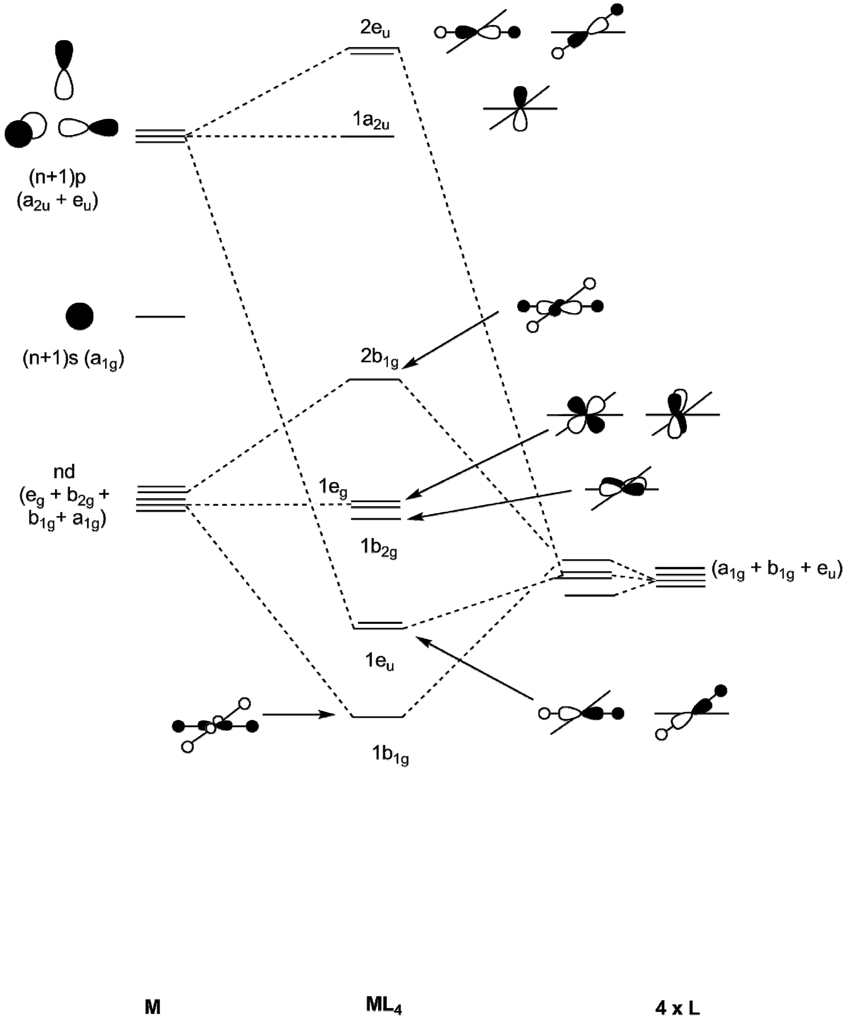


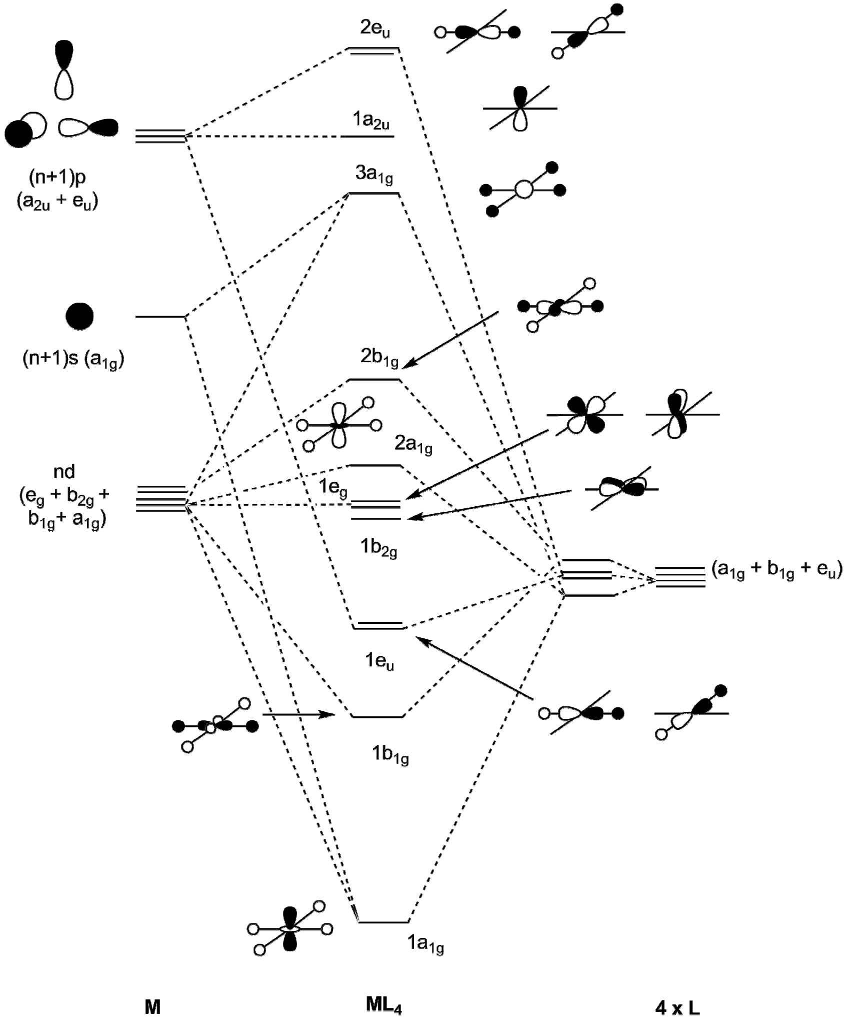

(n+1)p
(a2u + eu)
(n+1)s (a1g)
nd
(eg + b2g +
b1g+ a1g)
(a1g + b1g + eu)
M
ML4
4 x L

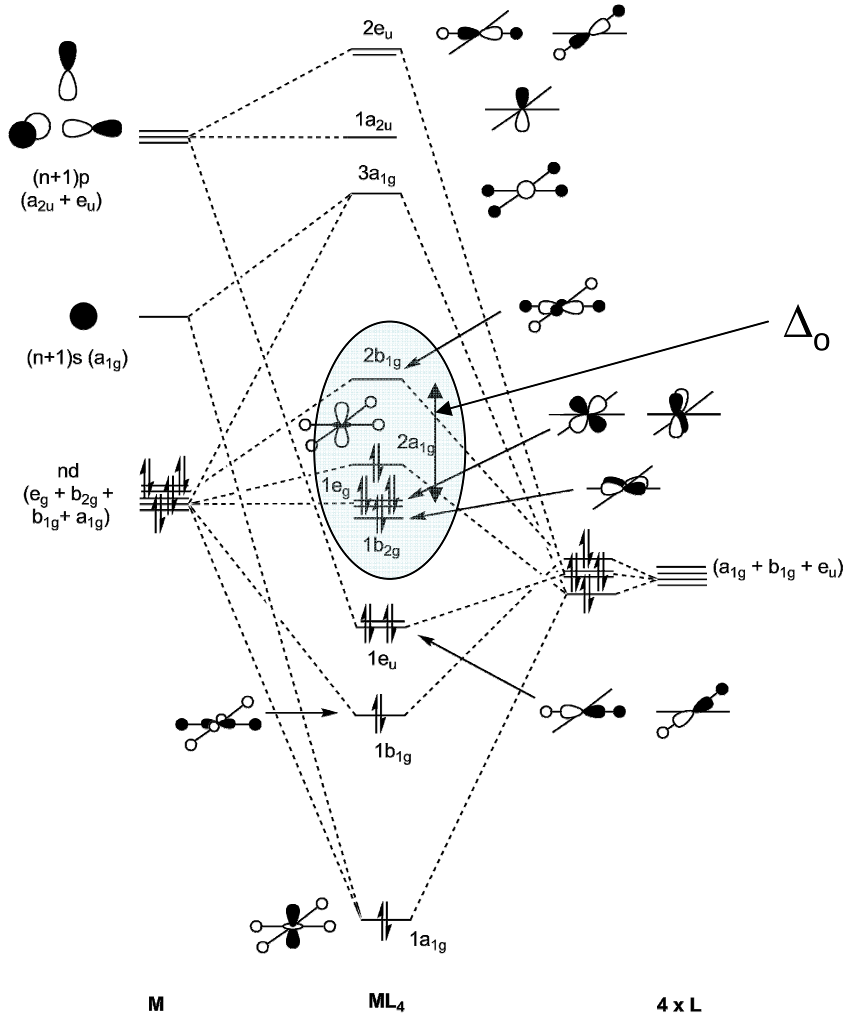


1a$_{2u}$
(n+1)p
(a$_{2u}$ + e$_u$)
(n+1)s (a$_{1g}$)
nd
(e$_g$ + b$_{2g}$ +
b$_{1g}$+ a$_{1g}$)
1e$_g$
1b$_{2g}$
(a$_{1g}$ + b$_{1g}$ + e$_u$)
M
ML$_4$
4 x L

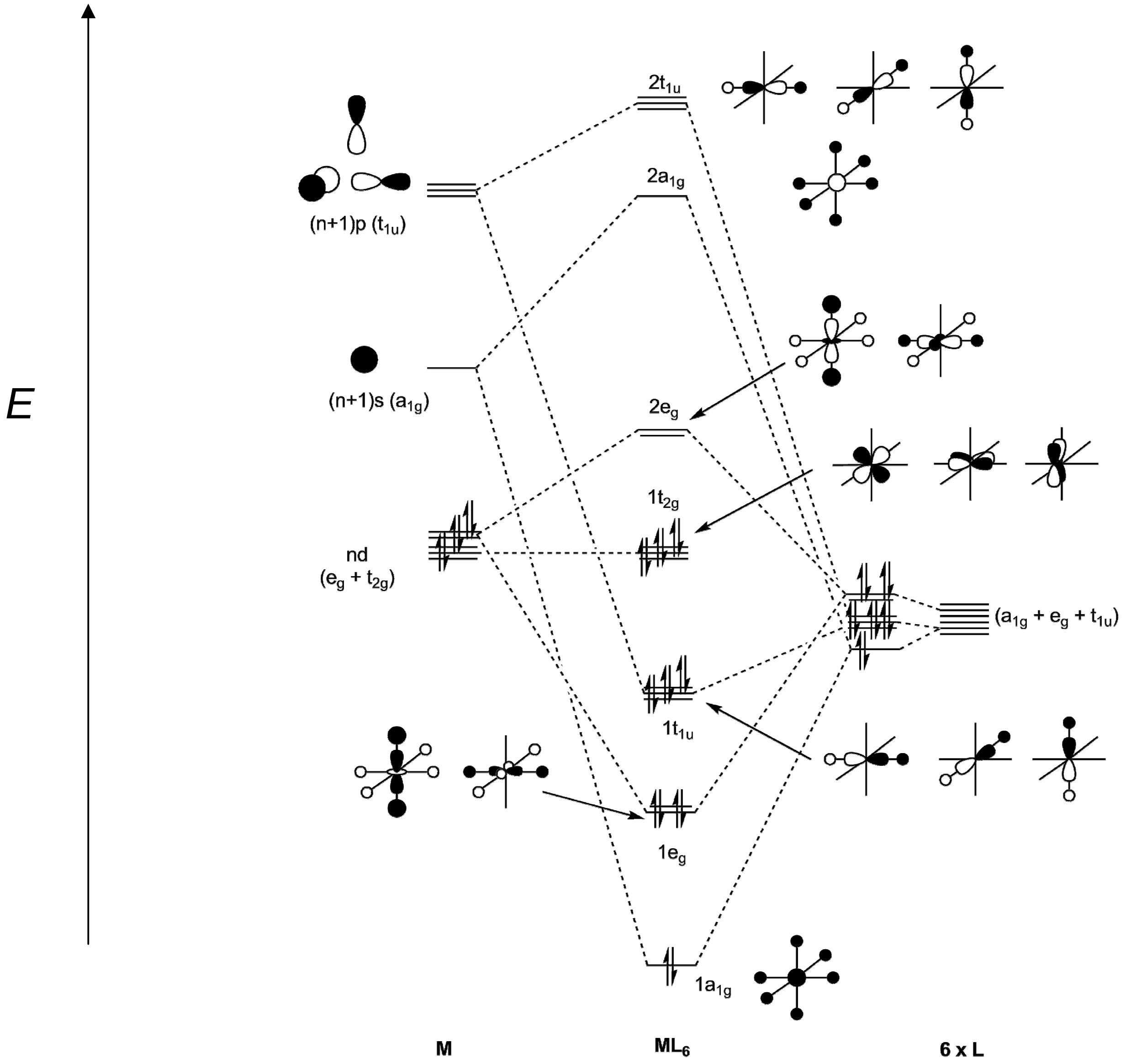

(n+1)p
(a_{2u} + e_u)
$1a_{2u}$
(n+1)s (a_{1g})
$2b_{1g}$
nd
(e_g + b_{2g} +
b_{1g}+ a_{1g})
$1e_g$
$1b_{2g}$
(a_{1g} + b_{1g} + e_u)
$1b_{1g}$
M
ML_4
4 x L


2e$_u$
1a$_{2u}$
(n+1)p
(a$_{2u}$ + e$_u$)
(n+1)s (a$_{1g}$)
2b$_{1g}$
nd
(e$_g$ + b$_{2g}$ +
b$_{1g}$+ a$_{1g}$)
1e$_g$
1b$_{2g}$
(a$_{1g}$ + b$_{1g}$ + e$_u$)
1e$_u$
1b$_{1g}$
M
ML$_4$
4 x L


$2e_u$
$1a_{2u}$
$3a_{1g}$
$(n+1)p$
$(a_{2u} + e_u)$
$(n+1)s\ (a_{1g})$
$2b_{1g}$
$2a_{1g}$
nd
$(e_g + b_{2g} +$
$b_{1g} + a_{1g})$
$1e_g$
$1b_{2g}$
$(a_{1g} + b_{1g} + e_u)$
$1e_u$
$1b_{1g}$
$1a_{1g}$
M
ML_4
4 x L

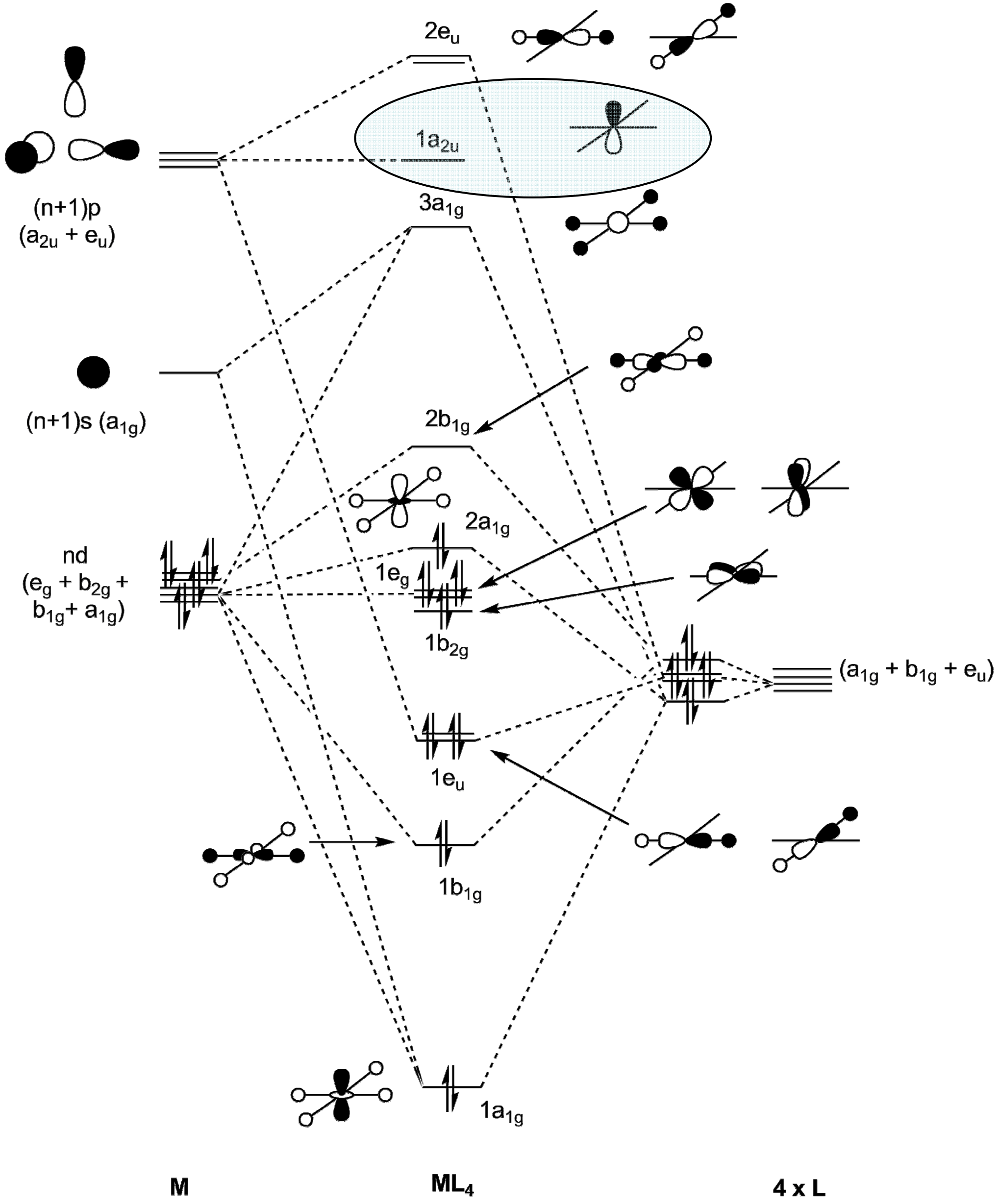

$2e_u$
$1a_{2u}$
$3a_{1g}$
$(n+1)p$
$(a_{2u} + e_u)$
$(n+1)s\ (a_{1g})$
$2b_{1g}$
Δ_o
$2a_{1g}$
$1e_g$
nd
$(e_g + b_{2g} +$
$b_{1g} + a_{1g})$
$1b_{2g}$
$(a_{1g} + b_{1g} + e_u)$
$1e_u$
$1b_{1g}$
$1a_{1g}$
M
ML_4
4 x L

18 vs 16-electron rules



‘18 electron’ rule

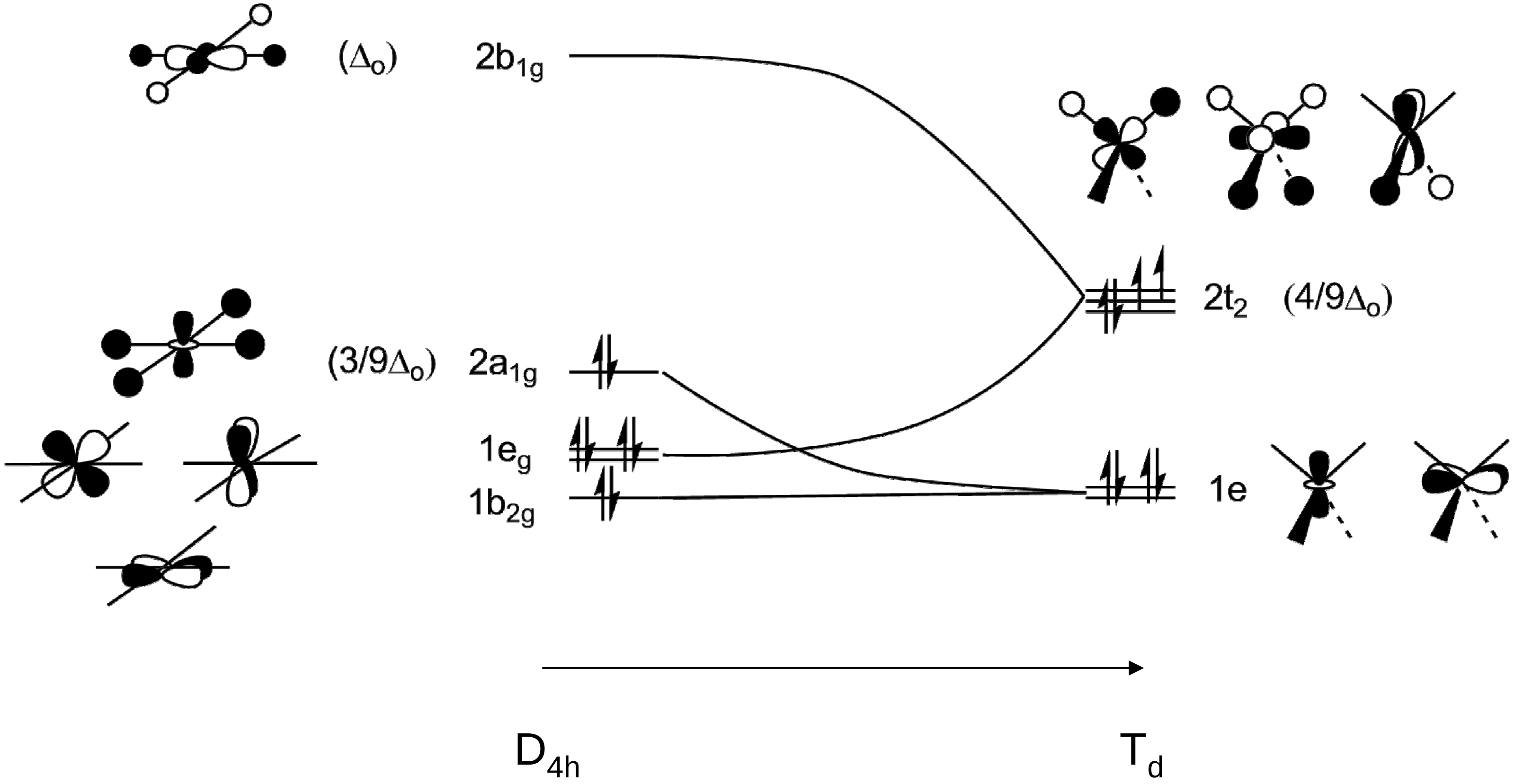
use *all* available s, p and d orbitals to accommodate electrons



‘16 electron’ rule

which orbital is not being used?

Walsh diagram for D_{4h} → T_d



n.b steric factors always favour T_d (angles 109.5)

Typical bond lengths

Bond	Square planar	Tetrahedral
Ni–N	1.68 Å	1.96 Å
Ni–P	2.14 Å	2.28 Å
Ni–S	2.15 Å	2.28 Å
Ni–Br	2.30 Å	2.36 Å
	2 (weakly) antibonding electrons	4 (weakly) antibonding electrons

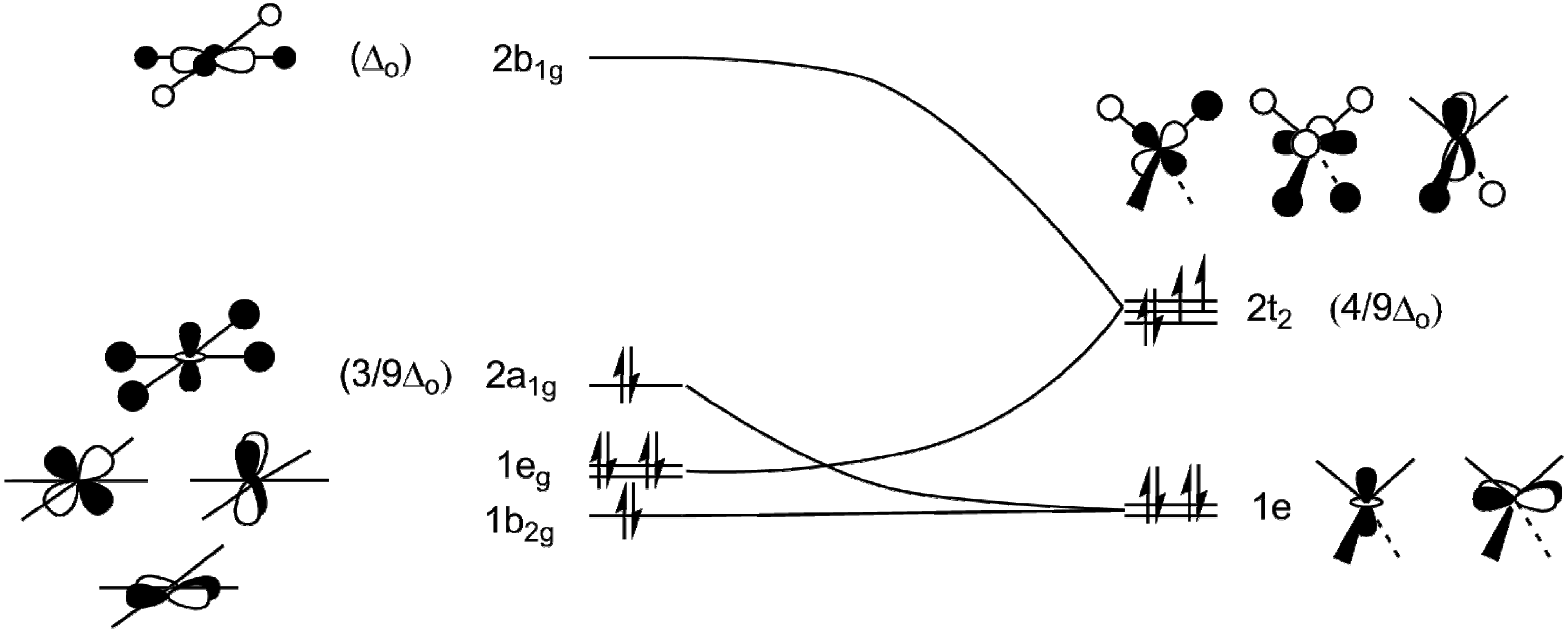
Factors controlling geometry

1) **Sterics** – large ligands favour T_d

2) **Electronics** – for d^8, large Δ (Δ_o/Δ_t) favours D_{4h}

D_{4h} destabilisation 2 x (3/9 Δ_o) = 6/9 Δ_o

T_d destabilisation = 4 x Δ_t= 4 x 4/9 x Δ_o= 16/9 x Δ_o



$[NiCl_4]^{2-}$	T_d	Sterics dominate
$[Ni(CN)_4]^{2-}$	D_{4h}	Electronics dominate
$[PdCl_4]^{2-}$	D_{4h}	Electronics dominate
$[PtCl_4]^{2-}$	D_{4h}	

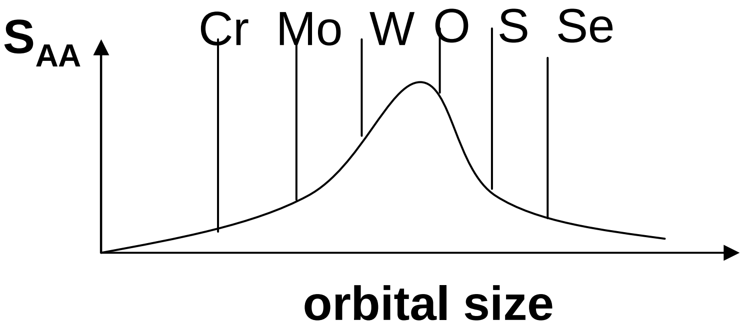
Recap

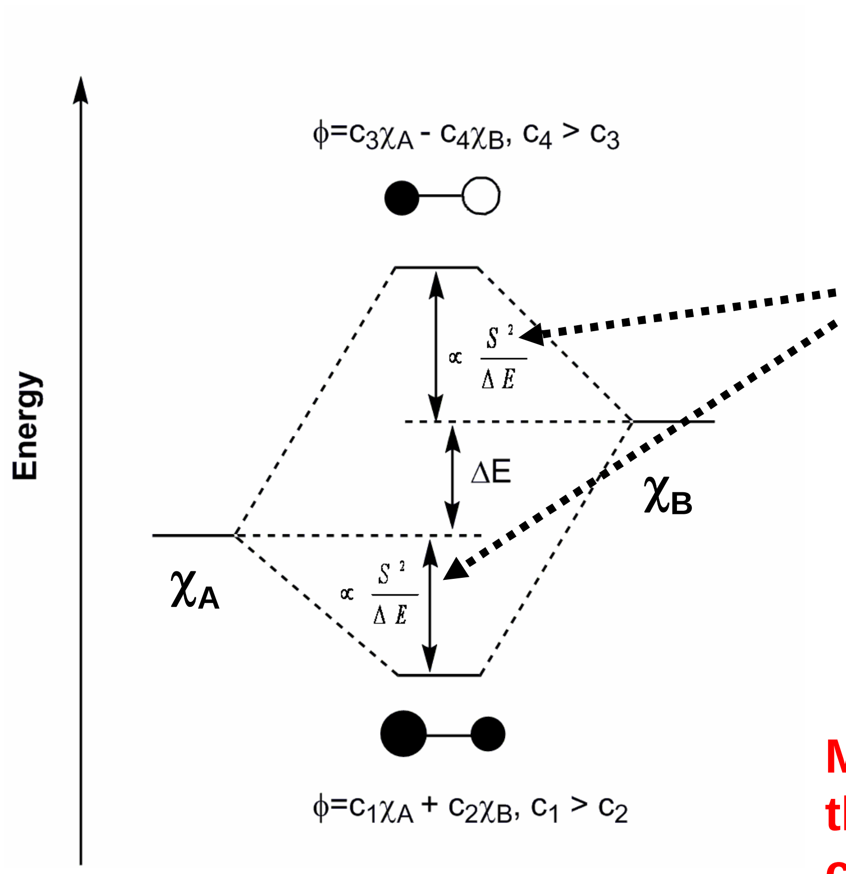
Interaction between two orbitals on different atoms:

$\propto S_{AB}$ for degenerate case

$\propto \dfrac{S^2_{AB}}{\Delta E}$ for non-degenerate case

Factors controlling S_{AB}: $\sigma > \pi > \delta$





interaction $\propto \frac{S^2_{AB}}{\Delta E}$

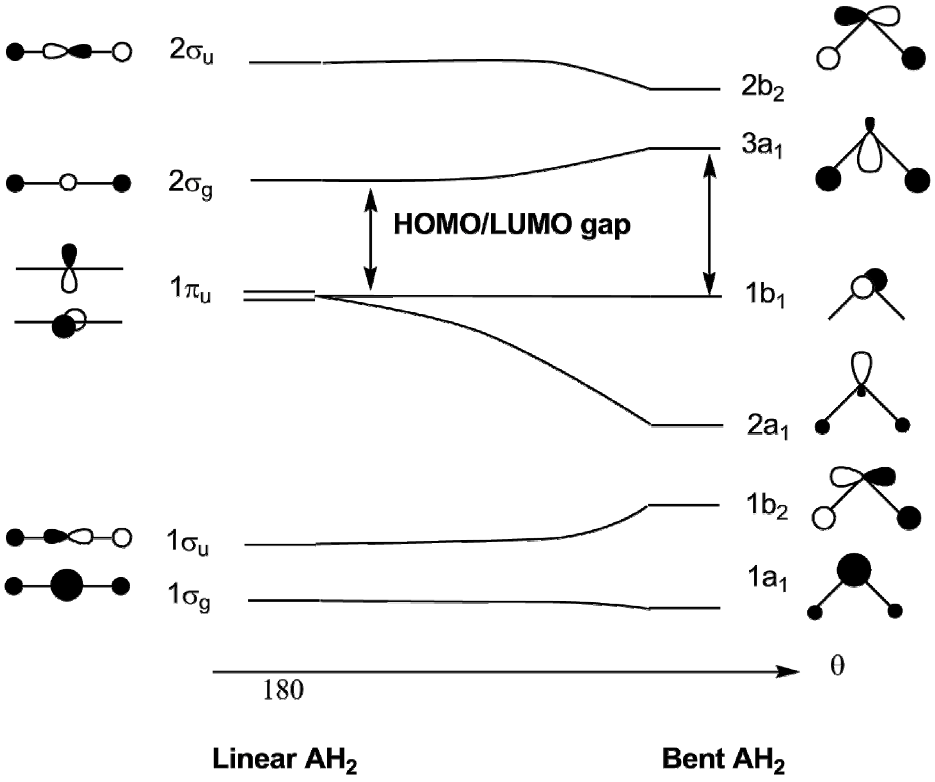
Molecular orbital 'resembles' the atomic orbital to which it lies closest in energy

Orbital patterns:

2 orbitals:	1 bonding, 1 antibonding
3 orbitals	1 bonding, 1 non-bonding, 1 antibonding
	(details depend on relative energies)

Always break MO diagrams down into components based on symmetry

Walsh diagrams summarise changes in MO diagram wrt structure

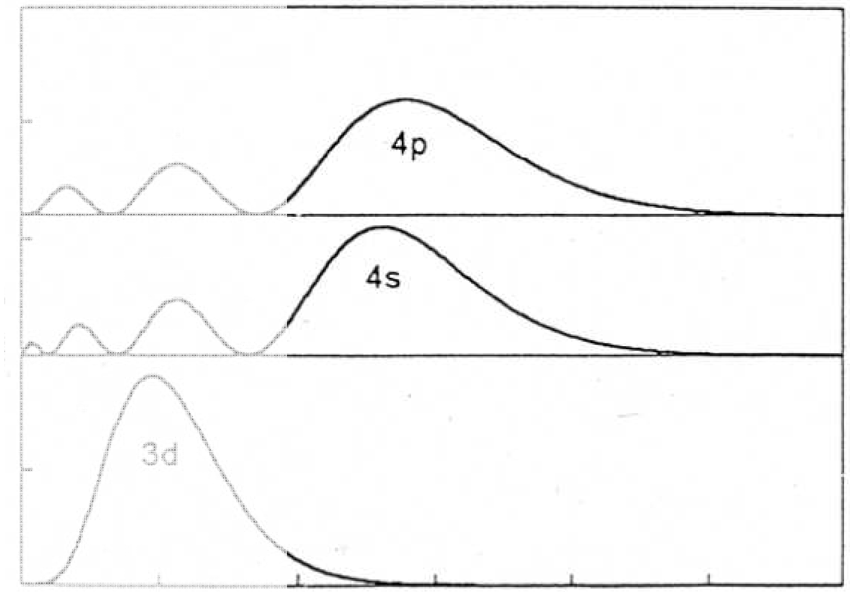


note a combination of **first** and **second** order effects

d orbitals

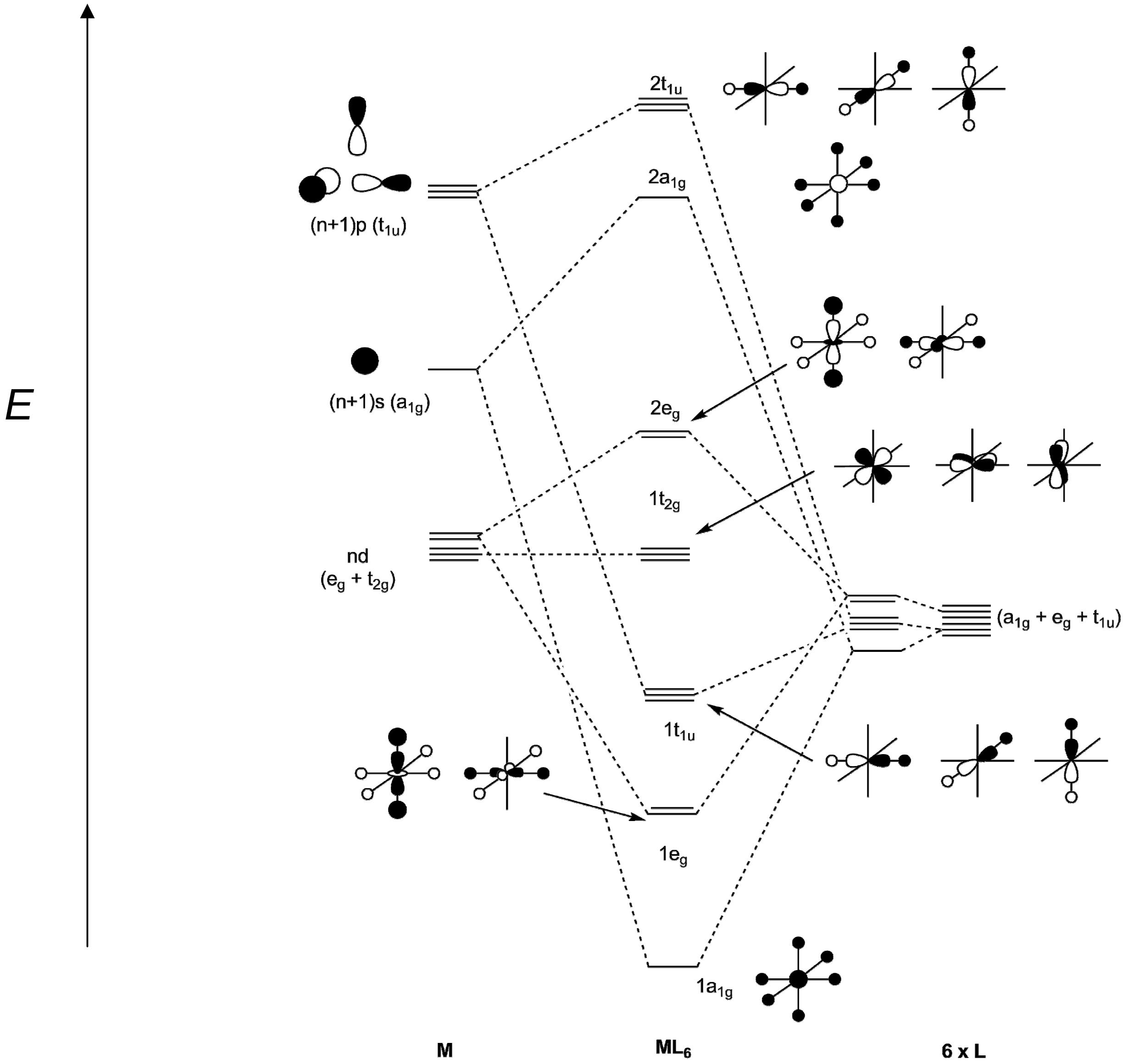
Less important in hypervalent main-group molecules such as XeF_2, SF_6 (recall ns < np < nd)

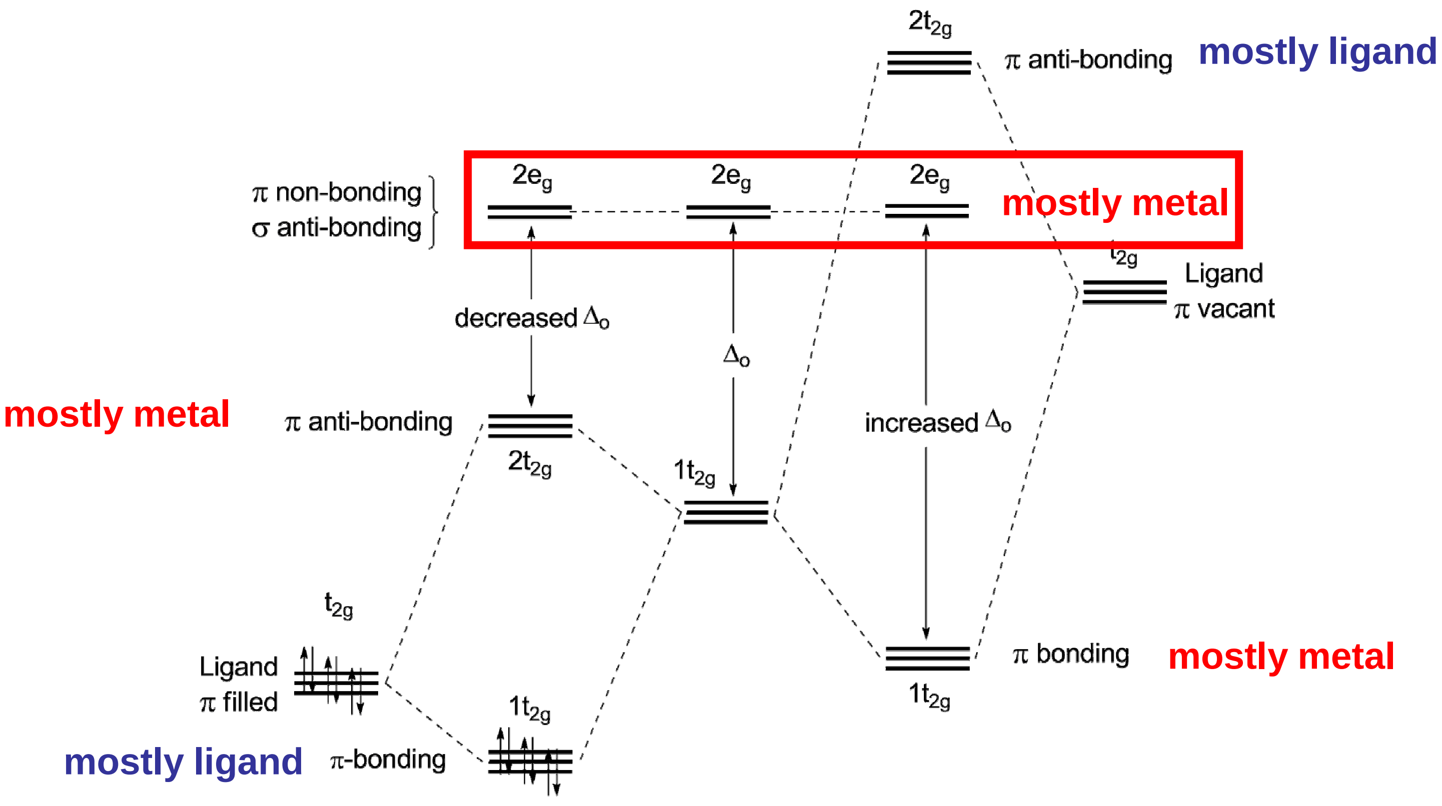
Critical in transition metals (recall nd < (n+1)s < (n+1)p)



d orbital overlap is weak
bonding mostly due to s/p

σ-only MO diagram for ML_6

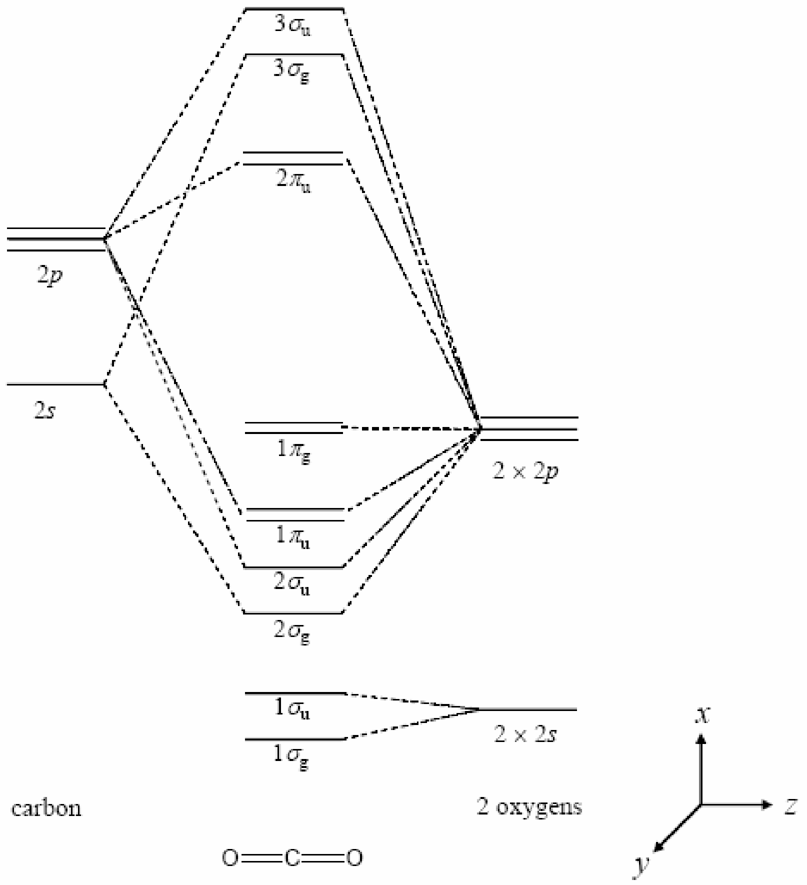




Ligand with filled π donor orbitals ⇦ Ligand with no π orbitals (σ-only) ⇨ Ligand with empty π acceptor orbitals

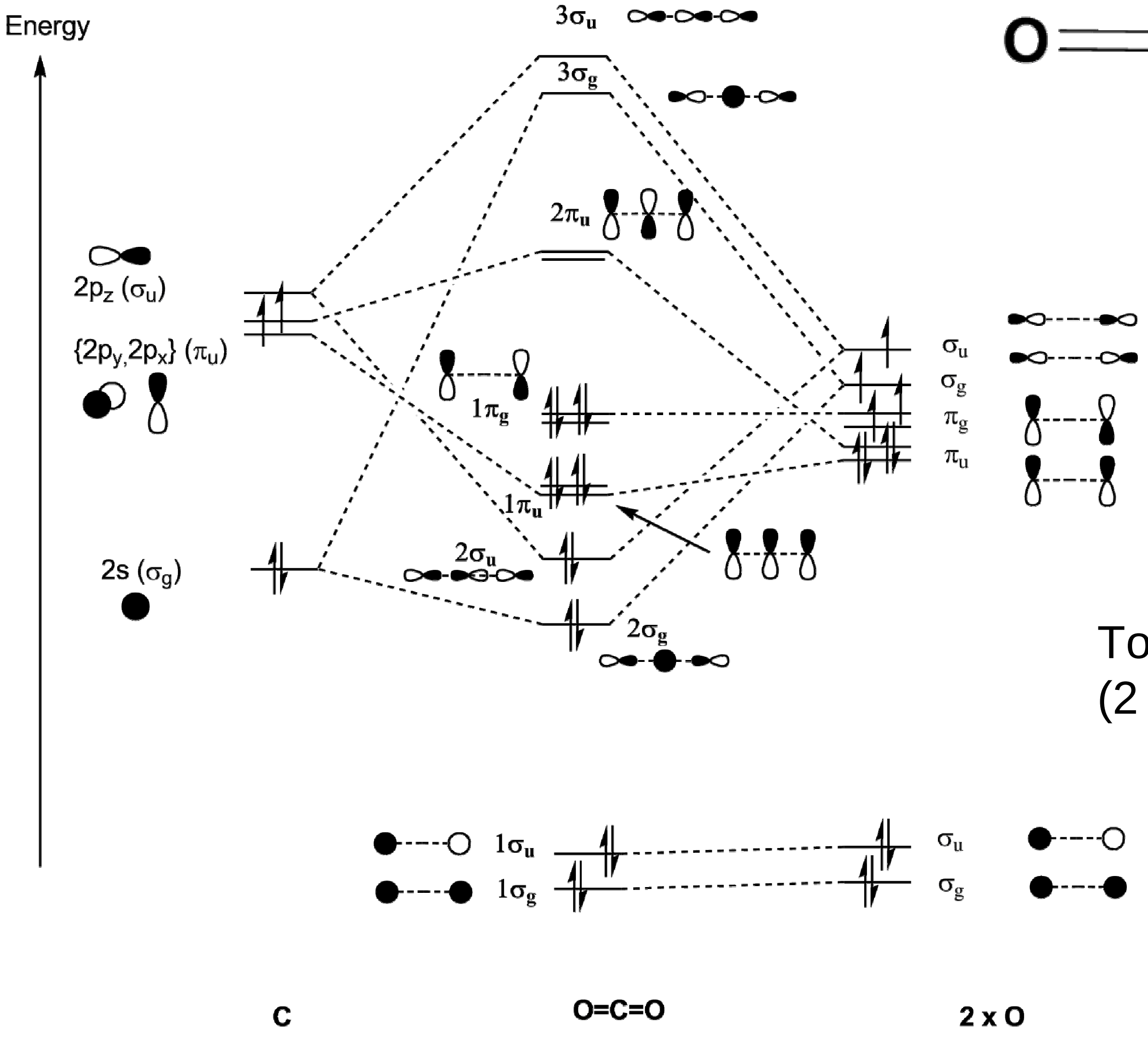
2008

(b) A molecular orbital energy level diagram for CO_2 is shown below. Inclusion of the oxygen 2*s* orbitals in bonding has minor effects on the energies of the molecular orbitals.



(i) Sketch the combination of atomic orbitals for the $2\sigma_g$, $2\sigma_u$, $1\pi_u$ and $1\pi_g$ molecular orbitals and discuss the nature of the bonding in each. **[6]**

$O=C=O$



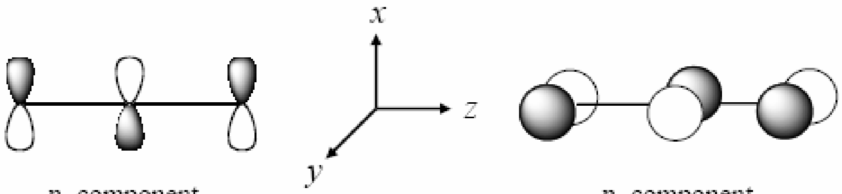
Total bond order 4
(2 per C=O bond)

(ii) Calculate the bond order of each Xe—F bond in the linear molecule XeF_2. It has been suggested that the Xe $5d_{z^2}$ orbital might be involved in bonding in XeF_2. Discuss which of the molecular orbitals in the diagram above might be involved and how Xe $5d_{z^2}$ participation might alter their energies. **[3]**

(c) (i) Show that the lowest energy unoccupied molecular orbital (LUMO) of CO_2 is the $2\pi_u$ orbital. **[1]**

(ii) The molecule NO_2 has a bent structure. A linear structure for NO_2 would have one electron in the $2\pi_u$ orbital. Assess the effect of bending the linear molecule in the xz plane on the overlap and thus energy of the p_x and p_y components of the $2\pi_u$ molecular orbital shown below. Hence rationalise why the bent structure of NO_2 is at a lower energy than the linear structure. **[5]**

[Detailed analysis of any changes in orbital mixing on bending is not required.]

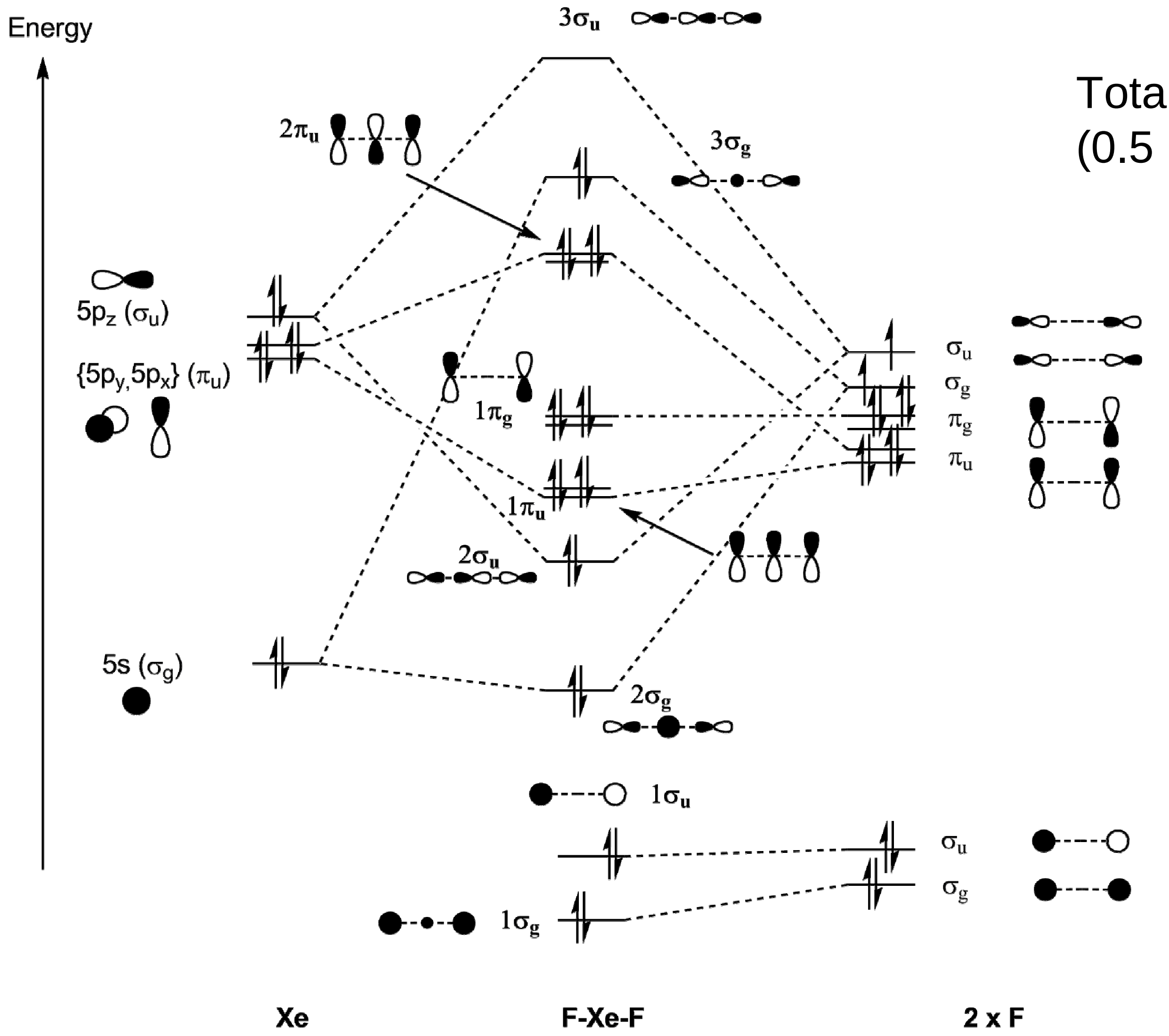


p_x component

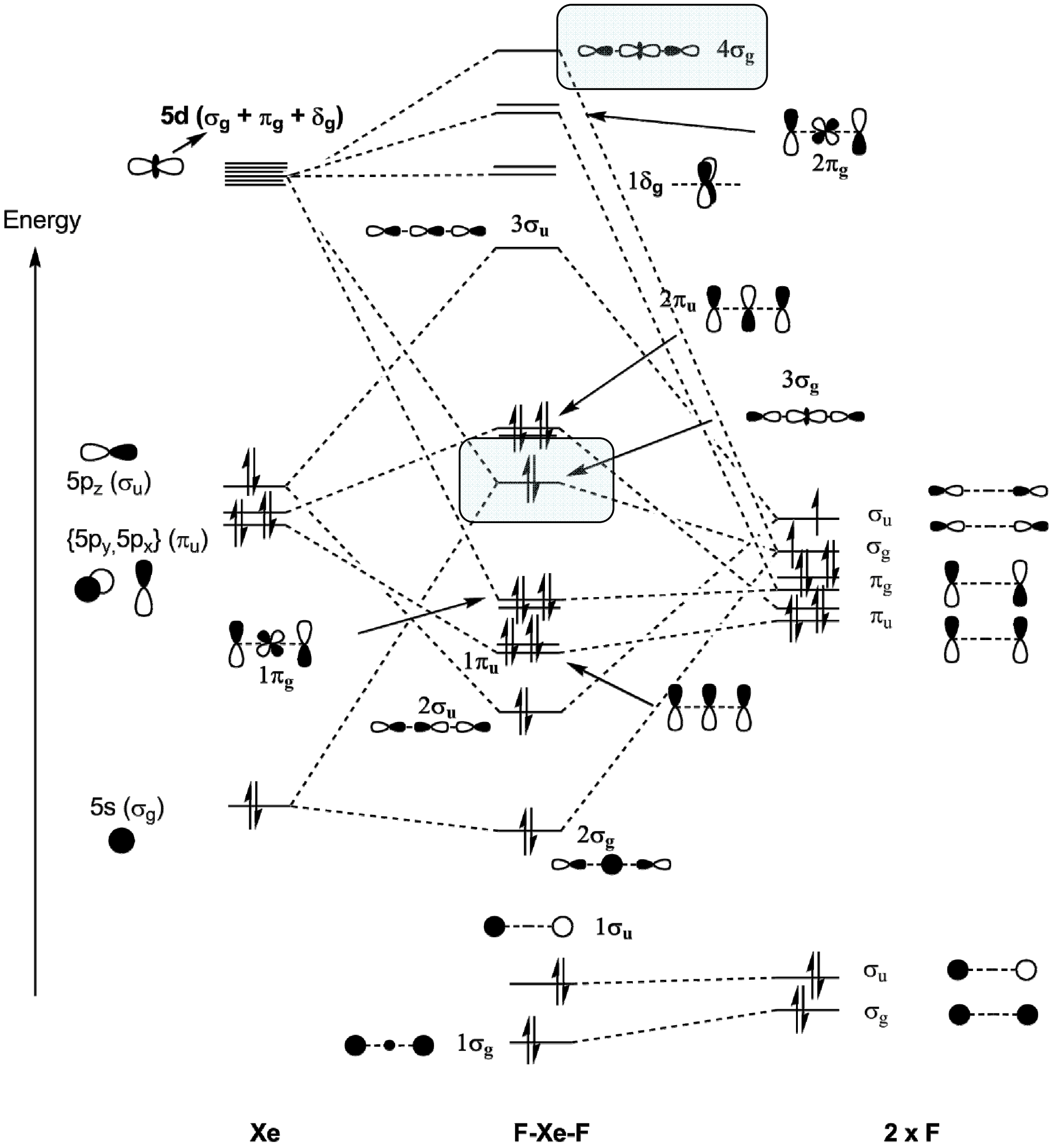
p_y component

(d) Use your answer to (c) to explain why ozone (O_3) has a bent structure and calculate the bond order of each O—O bond. **[2]**

F——Xe——F

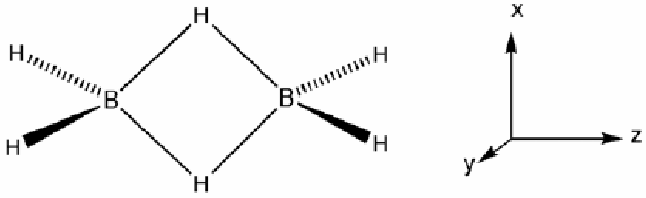


Total bond order = 1.0
(0.5 per Xe-F bond)

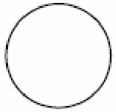

$4\sigma_g$
5d $(\sigma_g + \pi_g + \delta_g)$
$2\pi_g$
$1\delta_g$
Energy
$3\sigma_u$
$2\pi_u$
$3\sigma_g$
$5p_z\ (\sigma_u)$
$\{5p_y, 5p_x\}\ (\pi_u)$
σ_u
σ_g
π_g
π_u
$1\pi_g$
$1\pi_u$
$2\sigma_u$
5s (σ_g)
$2\sigma_g$
$1\sigma_u$
σ_u
σ_g
$1\sigma_g$
Xe
F-Xe-F
2 x F

2005

(a) The molecule B_2H_6 has D_{2h} symmetry. (Group Theory tables are available).



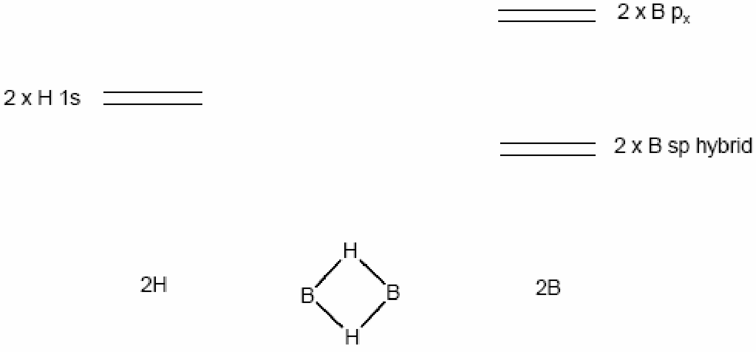
Construct molecular orbitals (MOs) for the B(μ-H_2)B bridge from symmetry adapted linear combinations (SALCs) of the two H 1*s* orbitals, two B *sp*$_z$ hybrids and two B *p*$_x$ orbitals.


H 1s

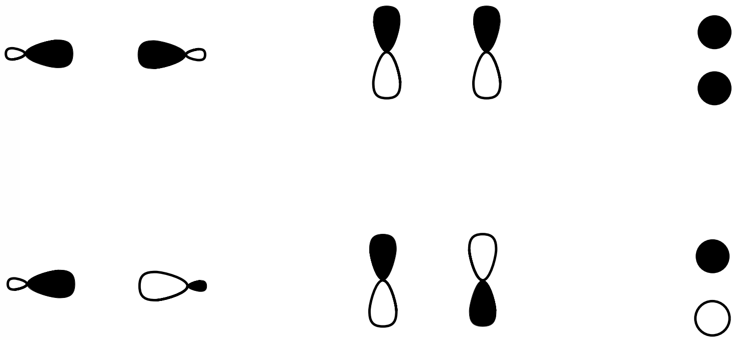

B sp hybrid

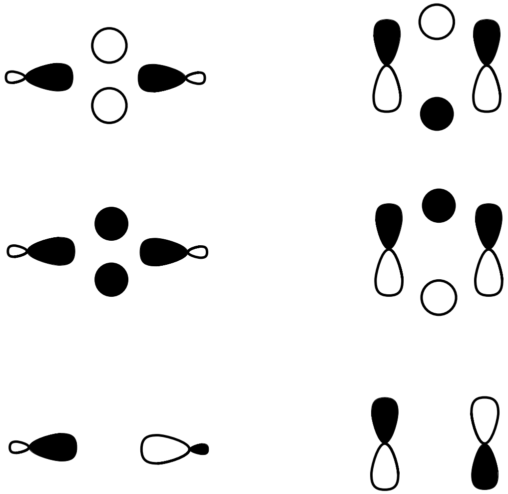

B p_x

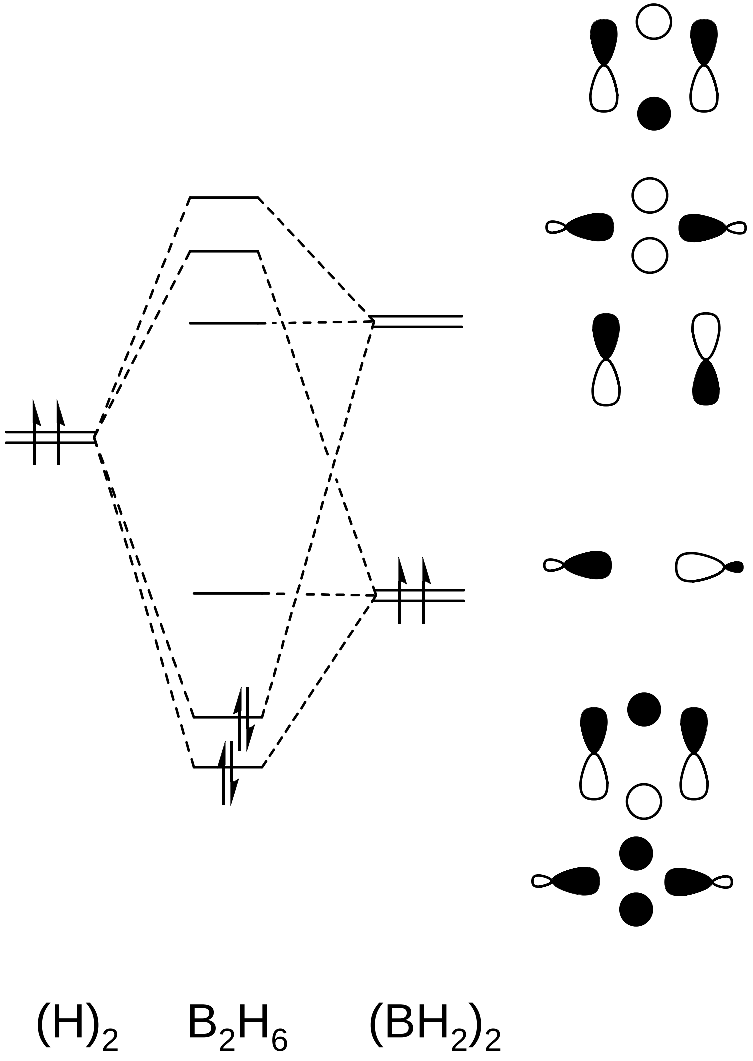
Complete the MO diagram given below giving symmetry labels to each MO and sketching the form of each MO. Indicate the electron occupancy of each MO. What bond order is assigned to the B–H bridging bonds?



[12]


SALCS


MOs



Total bond order 2

(0.5 per B-H bond)

2006

Answer *ALL* of the following parts (a) – (c).

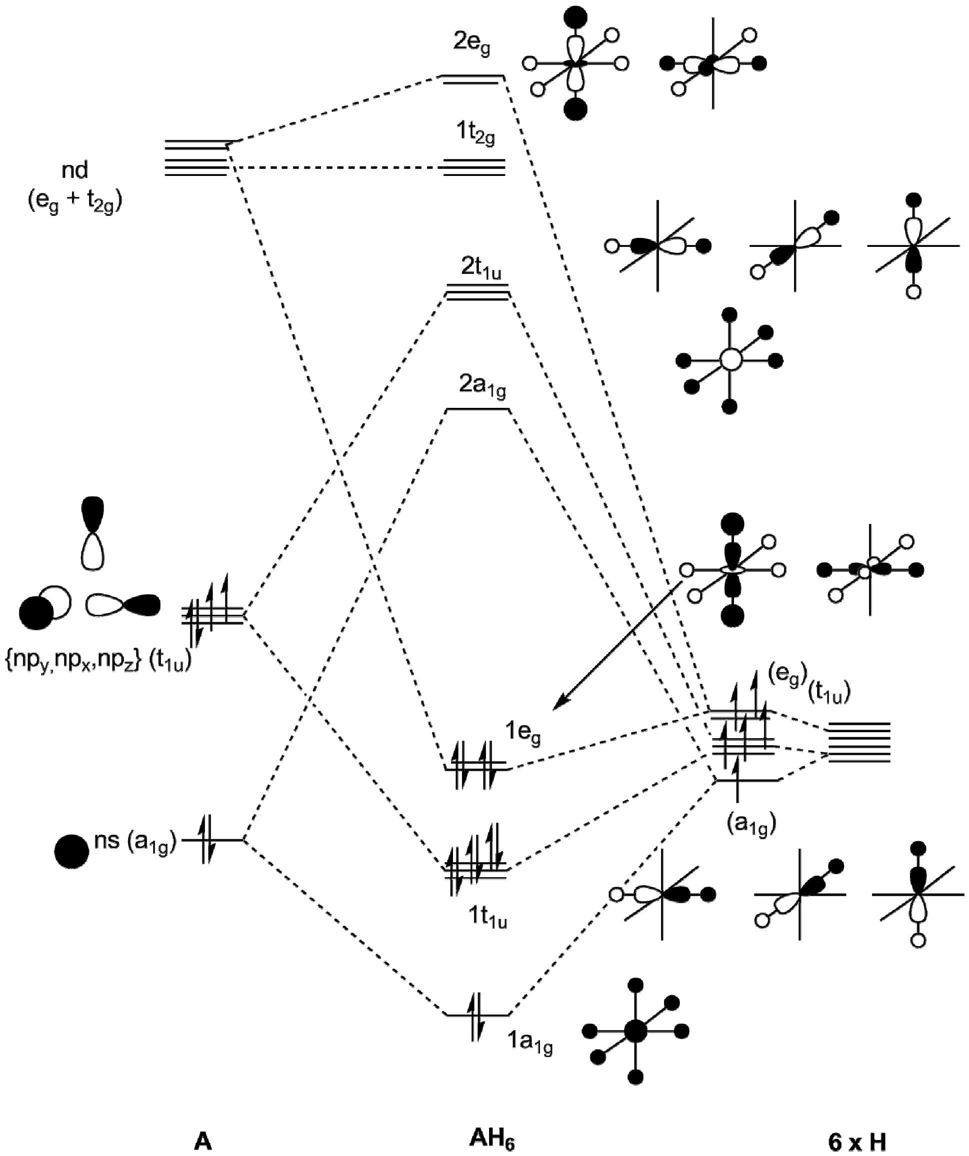
(a) Construct a molecular orbital energy level diagram describing the σ bonding in SF_6. You may neglect any participation of the 3*d* orbitals of sulfur. Comment on any points of interest in the bonding description you have given.[†] **[7]**

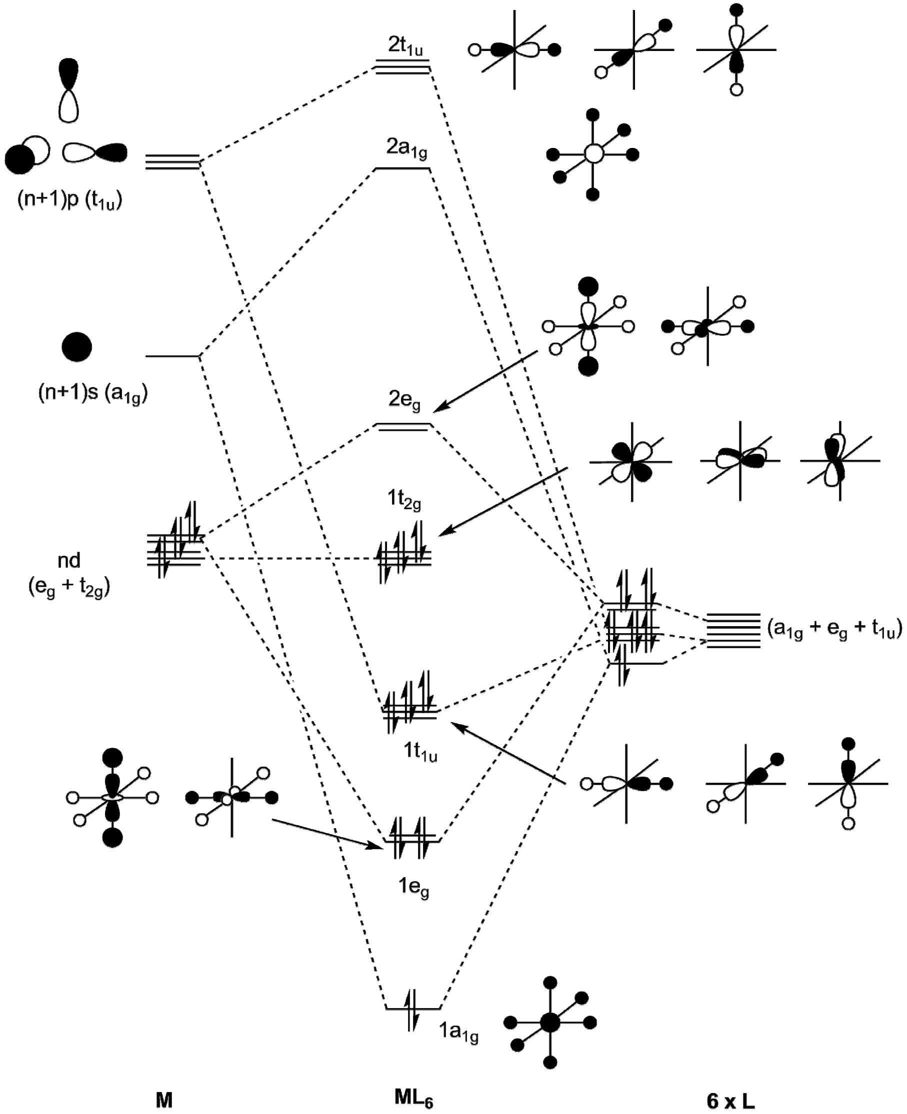
(b) Construct a molecular orbital energy level diagram describing the σ bonding in the hypothetical octahedral compound CrH_6. Describe the principal differences between the σ bonding situations in SF_6 and CrH_6.[†] **[5]**

(c) By referring to the molecular orbital energy level diagram you have constructed in part (b) above, and making any appropriate modifications, account for the following values of Δ_o for the octahedral complexes listed. **[8]**

Complex	Δ_o *(cm^{-1})*
$[Cr(H_2O)_6]^{3+}$	17,400
$[CrF_6]^{3-}$	15,060
$[Cr(CN)_6]^{3-}$	26,600
$[Fe(H_2O)_6]^{3+}$	14,000
$[Ru(H_2O)_6]^{2+}$	19,800
$[Ru(H_2O)_6]^{3+}$	28,600
$[Fe(CN)_6]^{4-}$	32,200
$[Fe(CN)_6]^{3-}$	35,000

[†] Group Theory Tables are available.
The σ donor Symmetry Adapted Linear Combinations (SALCs) of the $(F)_6$ and $(H)_6$ fragments transform as $a_{1g} + t_{1u} + e_g$ in the O_h point group.


$2e_g$
$1t_{2g}$
nd
$(e_g + t_{2g})$
$2t_{1u}$
$2a_{1g}$
$\{np_y, np_x, np_z\}$ (t_{1u})
(e_g)
(t_{1u})
$1e_g$
(a_{1g})
ns (a_{1g})
$1t_{1u}$
$1a_{1g}$
A
AH_6
6 x H


$2t_{1u}$
$2a_{1g}$
$(n+1)p\ (t_{1u})$
$(n+1)s\ (a_{1g})$
$2e_g$
$1t_{2g}$
nd
$(e_g + t_{2g})$
$(a_{1g} + e_g + t_{1u})$
$1t_{1u}$
$1e_g$
$1a_{1g}$
M
ML_6
6 x L

5. **Molecular orbital theory** **2004**

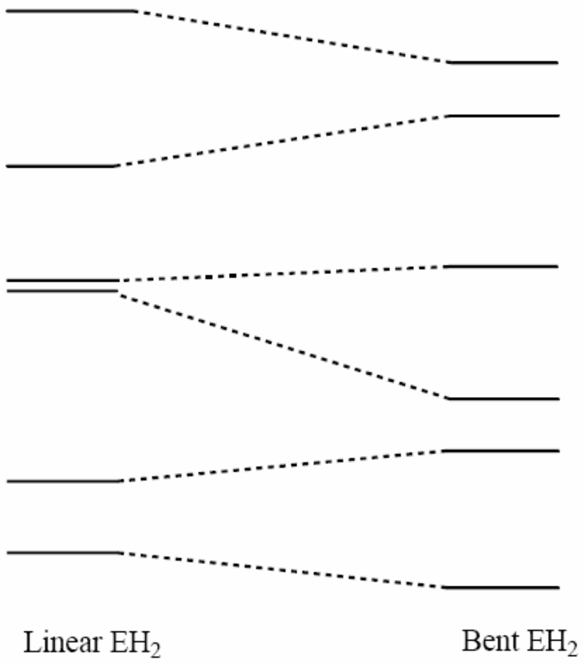
Answer *ALL* parts (a) – (f).

(a) Construct molecular orbital (MO) energy level diagrams for a molecule EH_2 (E = a second row element) for both linear and bent geometries given the data below. Use the outline Walsh diagram below to obtain relative MO ordering.

[8]

EH_2 linear: The atomic orbitals of E span the irreducible representations: 2s, σ_g; $2p_z$, σ_u; $2p_{x,y}$, π_u and the symmetry-adapted linear combinations (SALCs) for the two hydrogens span σ_u and σ_g.

EH_2 bent: The atomic orbitals of E span the irreducible representations: 2s, a_1; $2p_z$, a_1; $2p_x$, b_1; $2p_y$, b_2, and the SALCs for the two hydrogens span a_1 and b_2.



(b) What are the symmetry point groups of the two forms of the EH_2 molecule? **[2]**

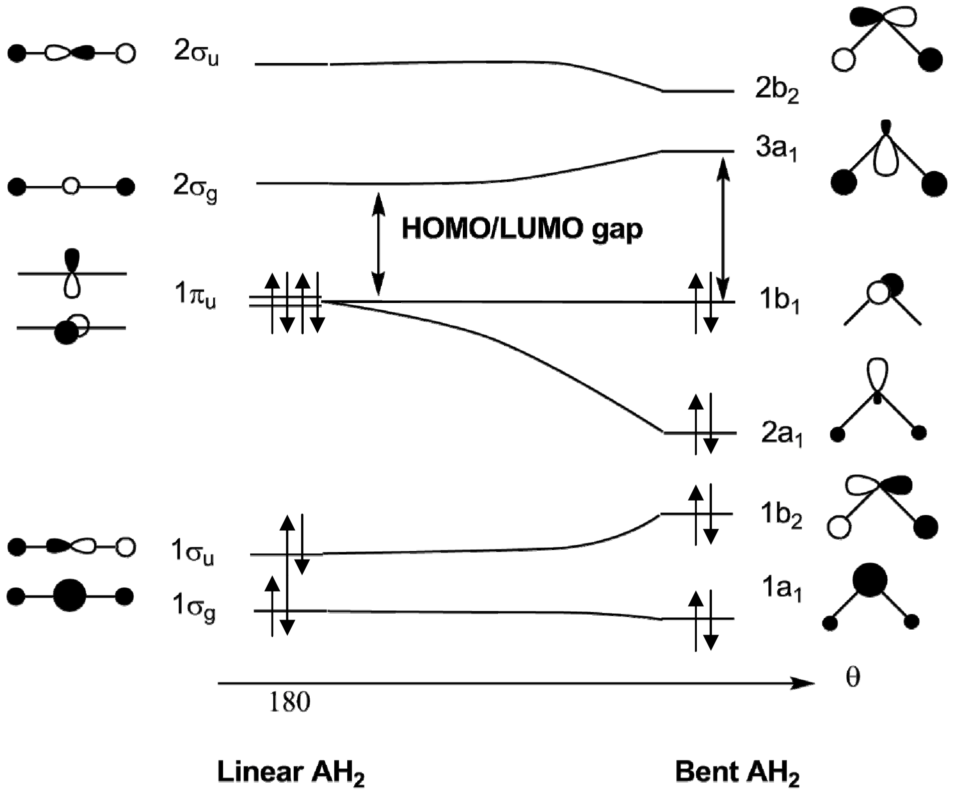
(c) What are the more stable geometries for E = O and E = Be ? Explain your reasoning. **[4]**

(d) The photoelectron spectrum for water shows four distinct bands. To which ionisations do these correspond? **[2]**

(e) What are the geometries you would predict for the ground and first electronic excited state configuration for CH_2 ? **[2]**

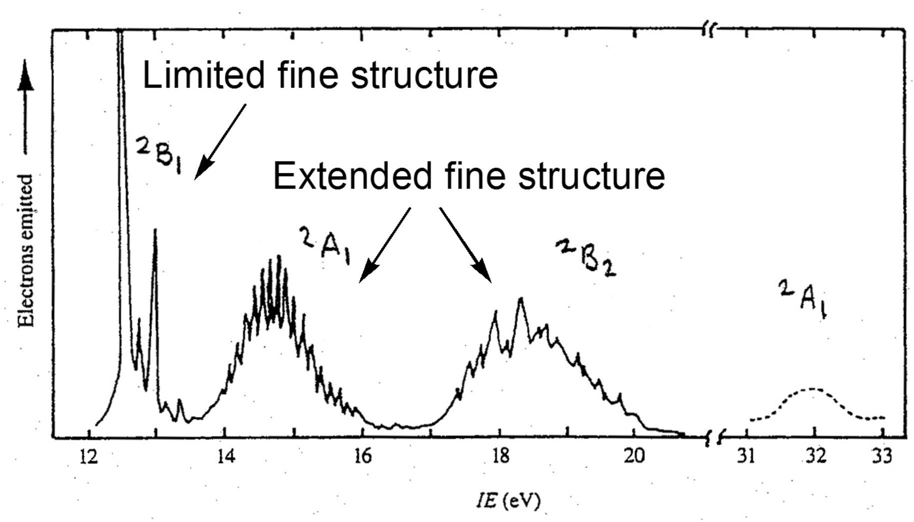
(f) What is the effect on the HEH angle of replacing O by S ? Provide a brief explanation for your answer. **[2]**

Walsh diagram



Known shape of some AH2 molecules		
Molecular species	No. of valence electrons	Shape
LiH_2^+	2	Bent
LiH_2, BeH_2^+	3	Linear
BeH_2, BH_2^+	4	Linear
BH_2, AlH_2, CH_2^+	5	Bent
CH_2, SiH_2, BH_2^-, NH_2^+	6	Bent
NH_2, PH_2, CH_2^-, OH_2^+	7	Bent
OH_2, SH_2, NH_2^-, FH_2^+	8	Bent

Recall: a molecule adopts the structure that best stabilises the HOMO.
If the HOMO is unperturbed by the structural change under consideration, then the occupied MO lying closest to it governs the geometric preference.



Limited fine structure

Extended fine structure