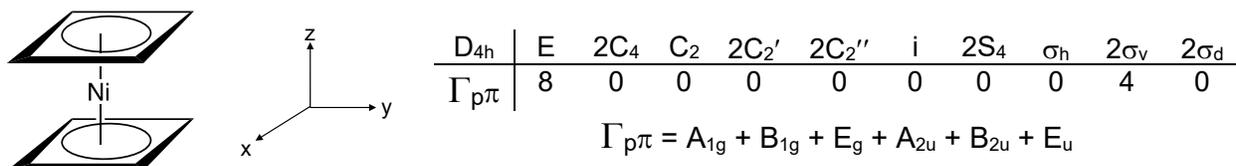


Chemistry 6330
Problem Set 5 Answer Key

(1)

(a)



Remember that for cyclobutadiene (from PS5) $\Gamma_{p\pi} = A_{2u} + B_{2u} + E_u$

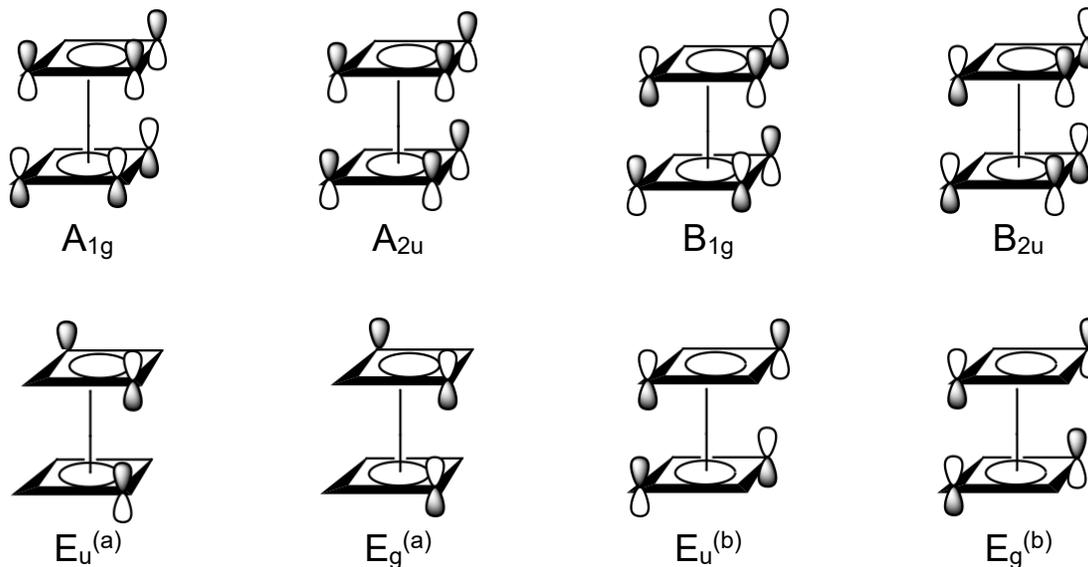
$$\Psi_1(a_{2u}) = \frac{1}{2}[\phi_1 + \phi_2 + \phi_3 + \phi_4]$$

$$\Psi_2(b_{2u}) = \frac{1}{2}[\phi_1 - \phi_2 + \phi_3 - \phi_4]$$

$$\Psi_3(e_u) = \frac{\sqrt{2}}{2}[\phi_1 - \phi_3]$$

$$\Psi_4(e_u) = \frac{\sqrt{2}}{2}[\phi_4 - \phi_2]$$

If we allow these orbitals to interact with each other, this will give us the orbitals for the bis(cyclobutadienyl) fragment of the molecule above.



(b)

$$A_{1g} \Rightarrow s, dz^2$$

$$B_{1g} \Rightarrow dx^2-y^2$$

$$E_u \Rightarrow (p_x, p_y)$$

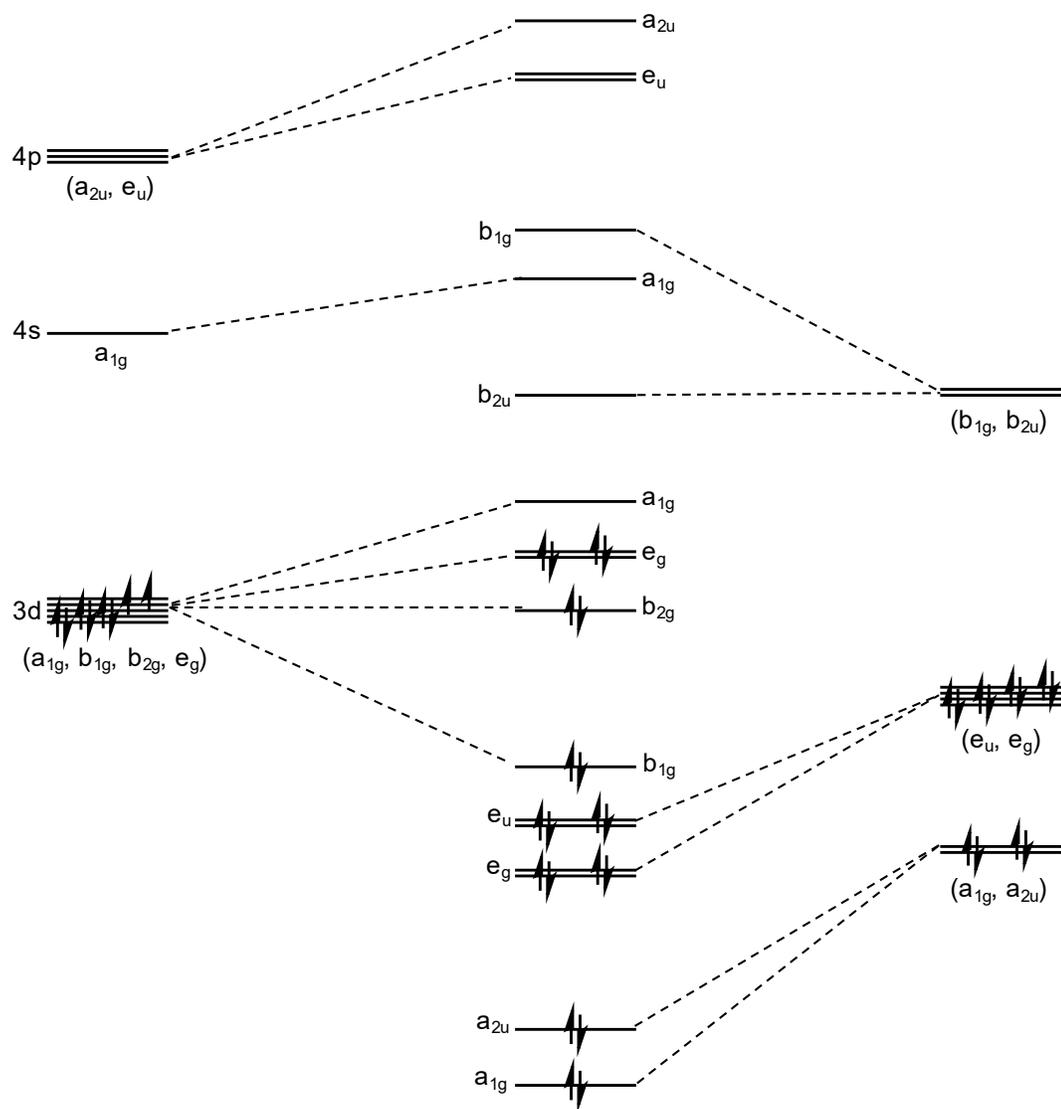
$$A_{2u} \Rightarrow p_z$$

$$B_{2u} \Rightarrow \text{None}$$

$$E_g \Rightarrow (dxz, dyz)$$

(c)

Interaction	Strength	Comments
A_{1g} with s	Moderate	s is small and spherical (not much directionality)
A_{1g} with dz^2	Strong	Well directed for overlap
A_{2u} with p_z	Strong	Well directed for overlap
B_{1g} with dx^2-y^2	Strong	Not as well directed but overlaps with all 8 p orbitals
E_u with (p_x, p_y)	Moderate	Not as well directed at the p- π orbitals
E_g with (dxz, dyz)	Strong	Well directed for overlap

Ni²⁺ - d⁸[Ni(cyclobutadiene)₂]²⁻2 x (cyclobutadiene)²⁻

(d)

Since all of the orbitals are completely filled or completely empty, the symmetry of the ground state would be ${}^1A_{1g}$, the totally symmetric representation for the D_{4h} point group.

Examination of the D_{4h} character table shows the dipole moment operator has symmetries of A_{2u} (z) and E_u (x,y).

The two lowest lying allowed excited states would be:

$$\begin{aligned} (b_{2g})^2(e_g)^3(a_{1g})^0(b_{2u})^1 & \quad {}^1E_u \\ (b_{2g})^1(e_g)^4(a_{1g})^0(b_{2u})^1 & \quad {}^1A_{1u} \end{aligned}$$

The electronic transitions would be:

$$\begin{aligned} (b_{2g})^2(e_g)^4(a_{1g})^0(b_{2u})^0 & \rightarrow (b_{2g})^2(e_g)^3(a_{1g})^0(b_{2u})^1 & \quad {}^1A_{1g} \rightarrow {}^1E_u \\ (b_{2g})^2(e_g)^4(a_{1g})^0(b_{2u})^0 & \rightarrow (b_{2g})^1(e_g)^4(a_{1g})^0(b_{2u})^1 & \quad {}^1A_{1g} \rightarrow {}^1A_{1u} \end{aligned}$$

$$\Gamma_{GS} \times \Gamma_{\mu} \times \Gamma_{ES} \Rightarrow \text{Must contain } A_{1g}$$

$$A_{1g} \times A_{2u} \times E_u = E_g$$

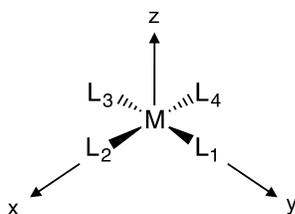
$$A_{1g} \times E_u \times E_u = \boxed{A_{1g}} + A_{2g} + B_{1g} + B_{2g} \quad \text{Allowed}$$

$$A_{1g} \times A_{2u} \times A_{1u} = A_{2g}$$

$$A_{1g} \times E_u \times A_{2u} = E_g$$

(e) These allowed transitions are MLCT transitions and would have ϵ values in the range of 5,000 – 50,000 $M^{-1}cm^{-1}$. The possible d-d transitions are all forbidden.

(2)



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
$\Gamma_{p\pi}$	8	0	0	-4	0	0	0	0	0	0
Γ_{σ}	4	0	0	2	0	0	0	4	2	0

$$\Gamma_{p\pi} = A_{2g} + B_{2g} + E_g + A_{2u} + B_{2u} + E_u$$

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

Metal orbital symmetries:

$$A_{1g} : s, dz^2$$

$$E_g : (dxy, dyz)$$

$$B_{1g} : dx^2-y^2$$

$$A_{2u} : pz$$

$$B_{2g} : dxy$$

$$E_u : (px, py)$$

Ligand SALC's:

σ :

$$\Psi(a_{1g}) = \frac{1}{2}[\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4]$$

$$\Psi(b_{1g}) = \frac{1}{2}[\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4]$$

$$\Psi(e_u^{(a)}) = \frac{1}{\sqrt{2}}[\sigma_1 - \sigma_3]$$

$$\Psi(e_u^{(b)}) = \frac{1}{\sqrt{2}}[\sigma_2 - \sigma_4]$$

π :

$$\Psi(a_{2g}) = \frac{1}{2}[p_x^1 + p_x^2 + p_x^3 + p_x^4]$$

$$\Psi(a_{2u}) = \frac{1}{2}[p_y^1 + p_y^2 + p_y^3 + p_y^4]$$

$$\Psi(b_{2g}) = \frac{1}{2}[p_x^1 - p_x^2 + p_x^3 - p_x^4]$$

$$\Psi(b_{2u}) = \frac{1}{2}[p_y^1 - p_y^2 + p_y^3 - p_y^4]$$

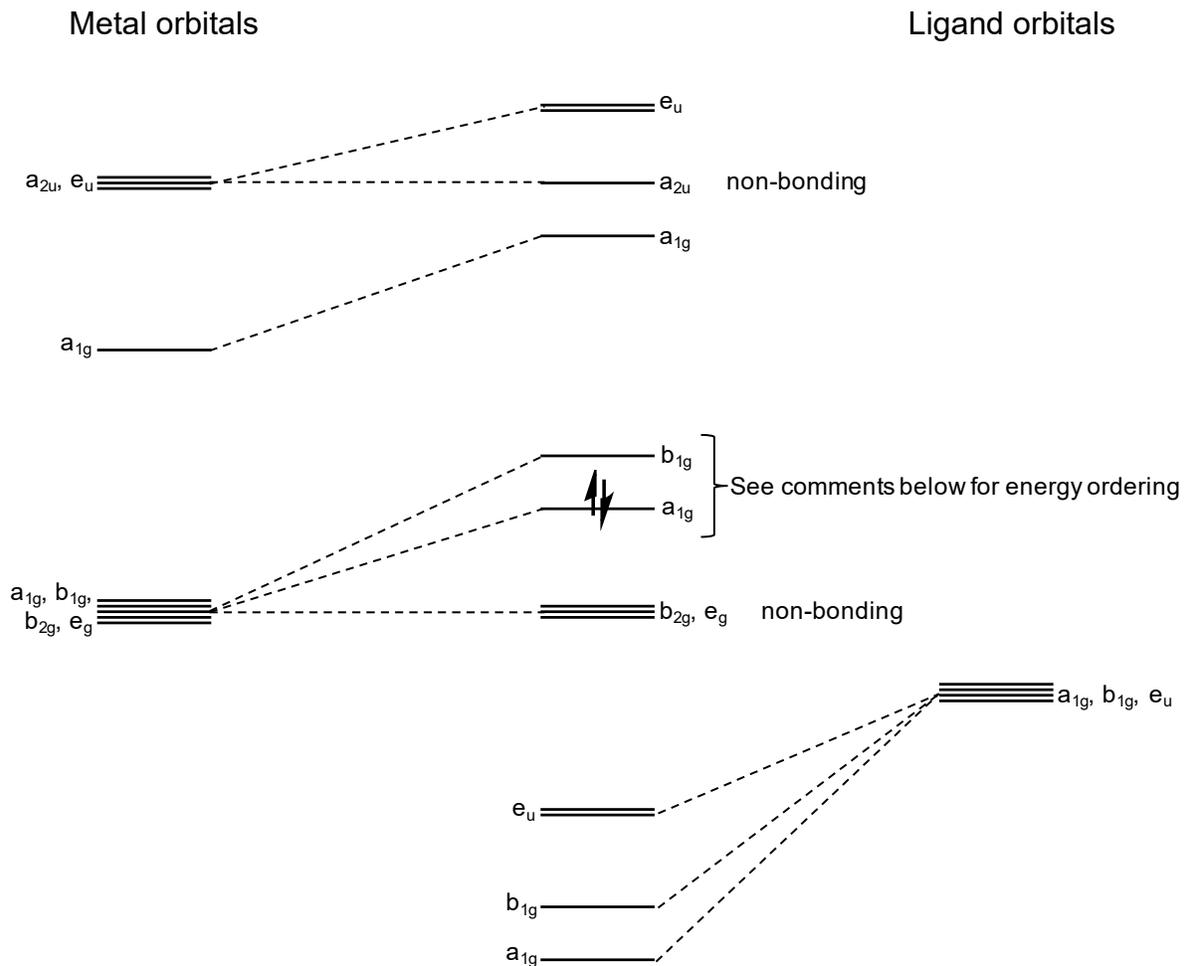
$$\Psi(e_u^{(a)}) = \frac{1}{\sqrt{2}}[p_x^1 - p_x^3]$$

$$\Psi(e_u^{(b)}) = \frac{1}{\sqrt{2}}[p_x^2 - p_x^4]$$

$$\Psi(e_g^{(a)}) = \frac{1}{\sqrt{2}}[p_y^1 - p_y^3]$$

$$\Psi(e_g^{(b)}) = \frac{1}{\sqrt{2}}[p_y^2 - p_y^4]$$

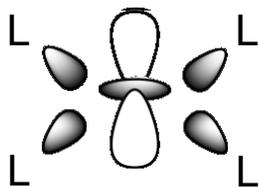
(a) σ -only MO diagram



There are two possible types of interactions involving these orbitals:

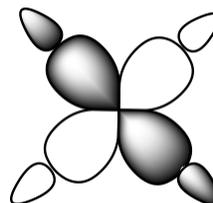
a_{1g} : d_{z^2} + 4 ligands

This is a very weak overlap

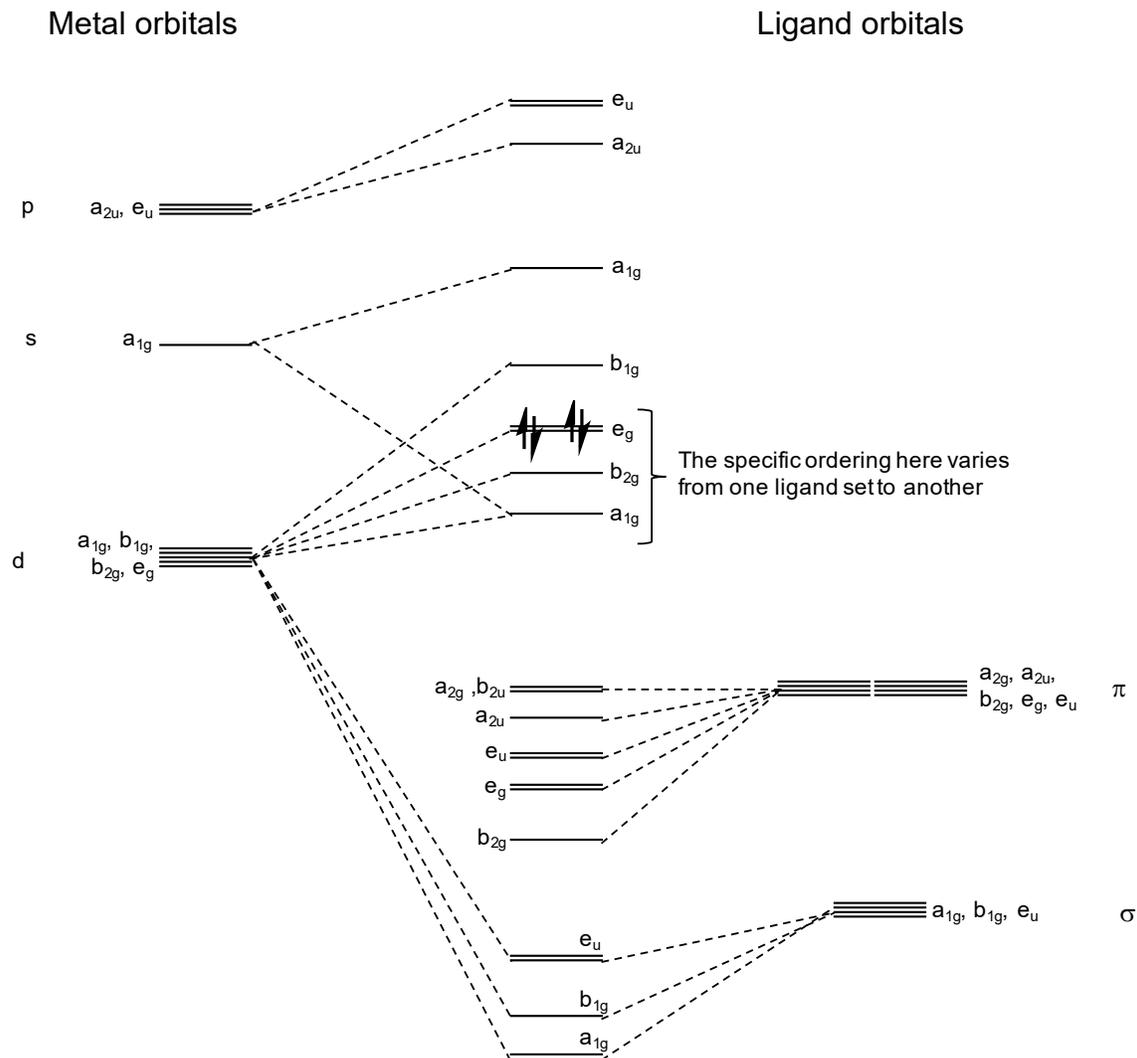


b_{1g} : $d_{x^2-y^2}$ + 4 ligands

This is very good overlap



(c) π -donor MO diagram:

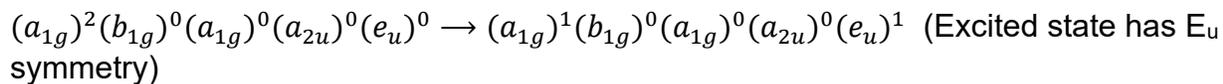
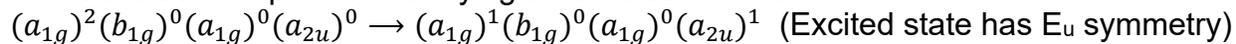


(d)

σ -only MO diagram:

Once again, under D_{4h} symmetry the dipole moment operator has symmetries of A_{2u} and E_u . Since the ground state has A_{1g} symmetry, the excited state must have A_{2u} or E_u symmetry for the transition to be allowed.

There are several possible low lying allowed transitions:



$(e_g)^4(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0 \rightarrow (e_g)^3(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (Excited state symmetry includes A_{2u})

$(e_g)^4(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \rightarrow (e_g)^3(a_{1g})^2(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^1$ (Excited state symmetry includes A_{2u})

These are all metal-centered transitions (d→p), meaning that the ϵ values will be around $1,000 \text{ M}^{-1}\text{cm}^{-1}$.

π -acceptor MO diagram:

The ground state of this molecule is still A_{1g} and the dipole moment operator still has A_{2u} and E_u symmetry. Now however, there are the ligand π^* based orbitals which can be involved in the transitions. There are several possible low lying transitions. These include the same 4 d-p metal based transitions discussed in the σ -only case. There is also now the possibility of the allowed d- π^* transitions that would have an expected ϵ value of around $5,000\text{-}50,000 \text{ M}^{-1}\text{cm}^{-1}$. These include:

$(a_{1g})^2(b_{1g})^0 \dots (a_{2u}(\pi^*))^0 \rightarrow (a_{1g})^1(b_{1g})^0 \dots (a_{2u}(\pi^*))^1$ (ES = A_{2u})
 $(a_{1g})^2(b_{1g})^0 \dots (e_u(\pi^*))^0 \rightarrow (a_{1g})^1(b_{1g})^0 \dots (e_u(\pi^*))^1$ (ES = E_u)

$(e_g)^4(a_{1g})^2(b_{1g})^0 \dots (a_{2u}(\pi^*))^0 \rightarrow (e_g)^3(a_{1g})^1(b_{1g})^0 \dots (a_{2u}(\pi^*))^1$ (ES = E_u)
 $(e_g)^4(a_{1g})^2(b_{1g})^0 \dots (e_u(\pi^*))^0 \rightarrow (e_g)^3(a_{1g})^1(b_{1g})^0 \dots (e_u(\pi^*))^1$ (ES includes A_{2u})

$(b_{2g})^2(e_g)^4(a_{1g})^2(b_{1g})^0 \dots (e_u(\pi^*))^0 \rightarrow (b_{2g})^1(e_g)^4(a_{1g})^1(b_{1g})^0 \dots (e_u(\pi^*))^1$ (ES = E_u)

π -donor MO diagram:

Once again there are several metal-centered transitions possible. These would include:

$(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \rightarrow (e_g)^3(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = E_u)
 $(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \rightarrow (e_g)^3(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^1$ (ES includes A_{2u})

$(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \rightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = A_{2u})
 $(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0 \rightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1$ (ES = A_{2u})
 $(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^0(e_u)^0 \rightarrow (a_{1g})^1(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0(a_{2u})^1(e_u)^1$
 (ES = E_u)

Now there are also several possible ligand-to-metal charge-transfer transitions. These allowed transitions would be expected to have ϵ -values around $5,000\text{-}50,000 \text{ M}^{-1}\text{cm}^{-1}$.

They include:

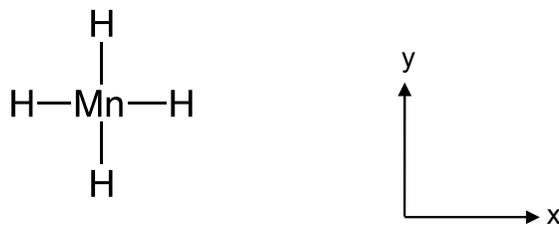
$(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0 \rightarrow (a_{2g})^2(b_{2u})^1(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^1$ (ES = A_{2u})

$(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0 \rightarrow (a_{2u})^1(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^1$
 (ES = A_{2u})

$$(e_u)^4(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^0 \rightarrow (e_u)^3(a_{2u})^2(a_{2g})^2(b_{2u})^2(a_{1g})^2(b_{2g})^2(e_g)^4(b_{1g})^0(a_{1g})^1$$

(ES = E_u)

(3) (a)



Under D_{4h} symmetry:

Mn orbitals:

$$3d \rightarrow A_{1g} + B_{1g} + B_{2g} + E_g$$

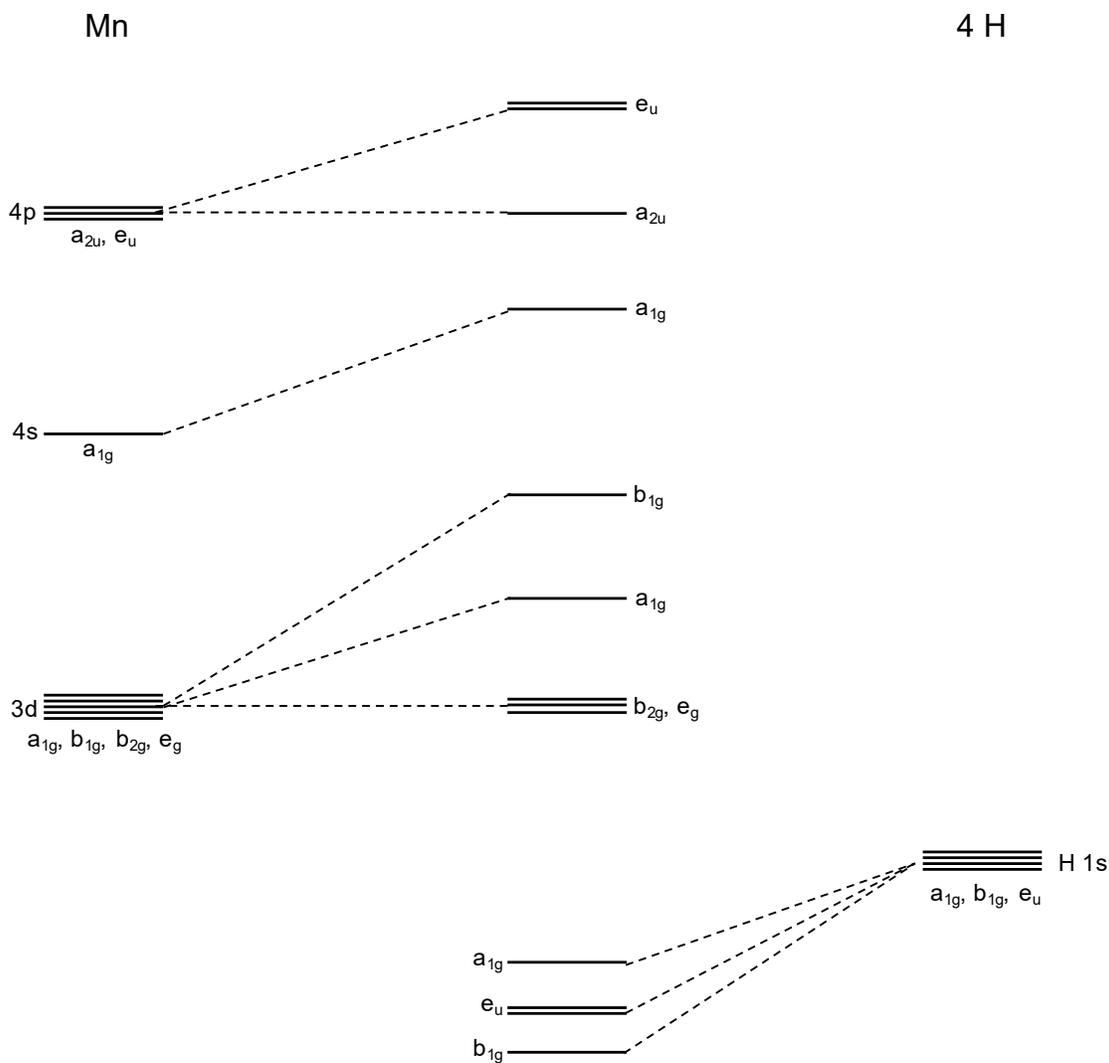
$$4s \rightarrow A_{1g}$$

$$4p \rightarrow A_{2u} + E_u$$

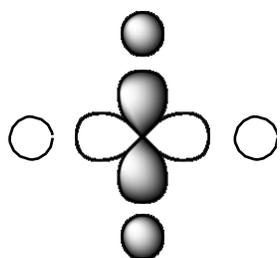
D _{4h}	E	2C ₄	C ₂	2C _{2'}	2C _{2''}	i	2S ₄	σ _h	2σ _v	2σ _d
Γ _(H1s)	4	0	0	2	0	0	0	4	2	0

$$\Gamma_{(H1s)} = A_{1g} + B_{1g} + E_u$$

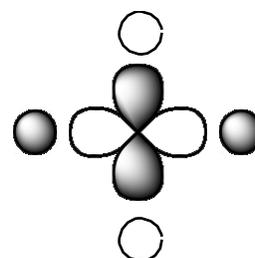
Because H bonded to metal atoms is assigned a formal oxidation state of (-1), we will assume the H 1s orbitals lie lower in energy than the Mn 3d orbitals. The MO diagram is then straightforward.



*Note that the strongest Mn-H interactions are in the b_{1g} orbitals, which are the bonding and antibonding interactions between the H 1s b_{1g} SALC and the Mn $3dx^2-y^2$ orbital.



Bonding b_{1g} orbital



Antibonding b_{1g} orbital

The metal a_{1g} $3dz^2$ orbital is destabilized slightly because of poor overlap – the H 1s orbitals must overlap with the torus (or “doughnut”) of the dz^2 orbital.

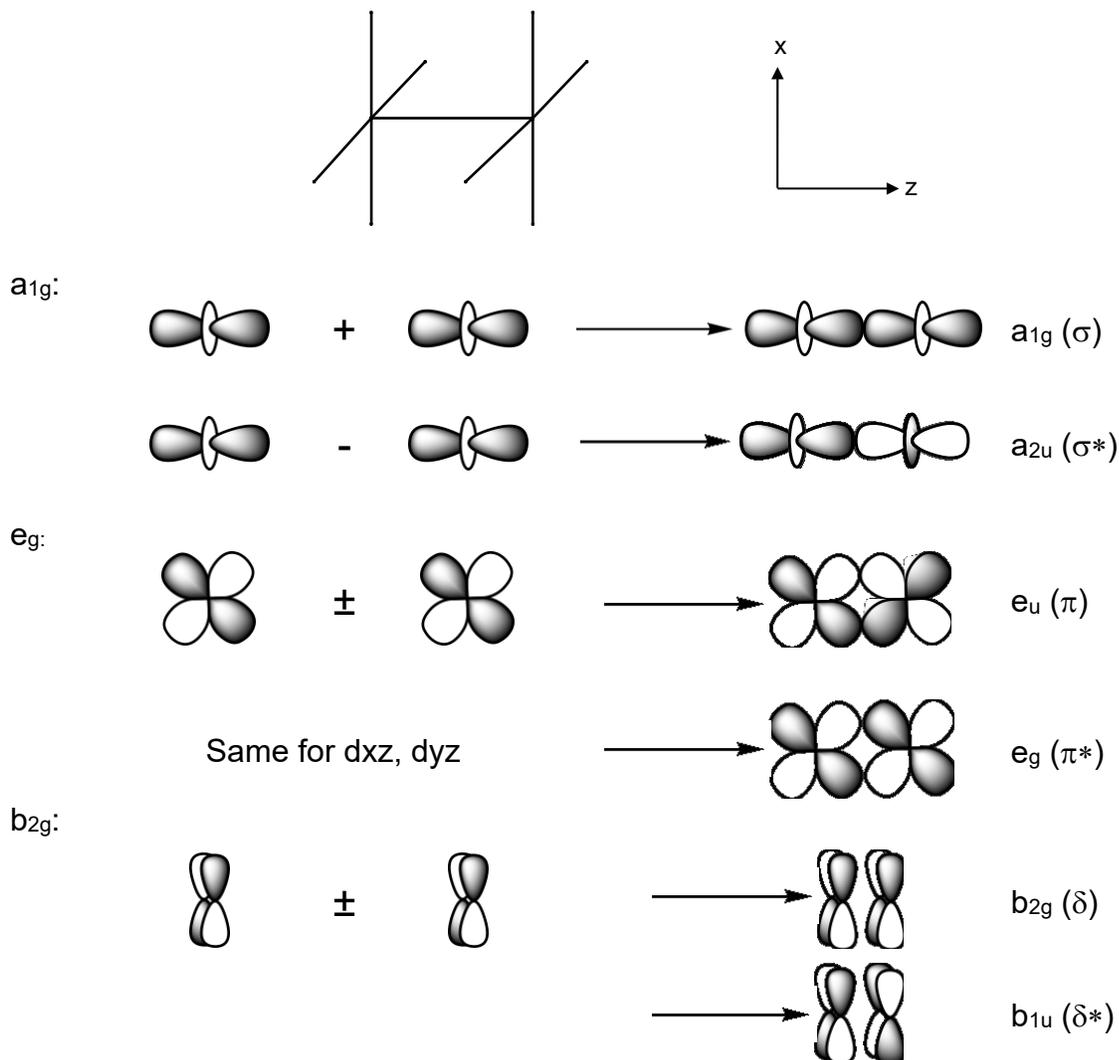
(b) As discussed above, the overlap between the H 1s a_{1g} SALC and the $3d_{z^2}$ metal orbital is poor. The other overlap between the a_{1g} SALC and the metal 4s orbital is better:

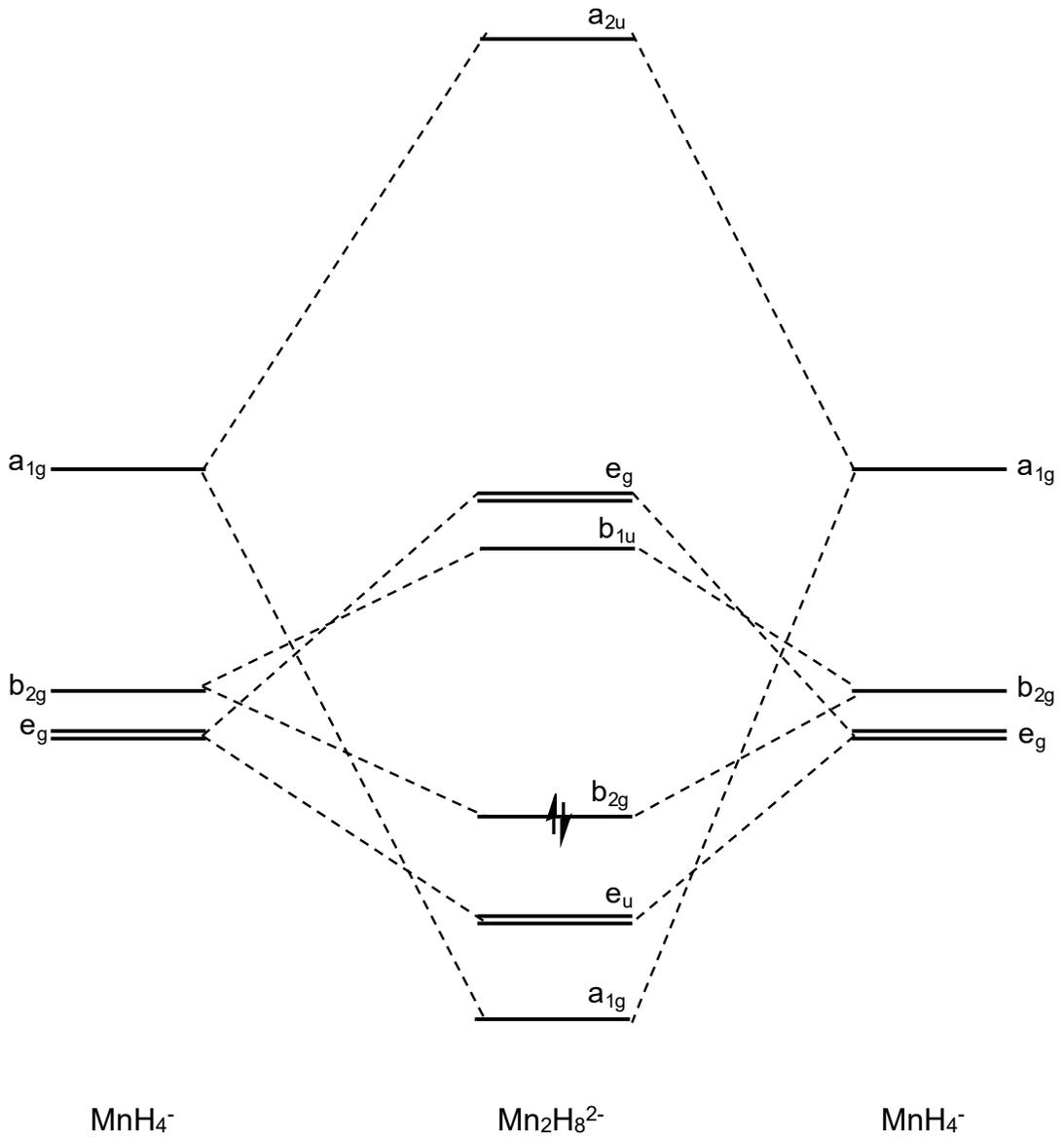


The $3d_{z^2}$ is better off energetically, however, to interact with the a_{1g} SALC. Thus it is difficult to decide which interaction will be stronger.

(c) As discussed above, the strongest Mn – H interaction (by far) involves the Mn $3d_{x^2-y^2}$ orbital. We will “throw out” this orbital.

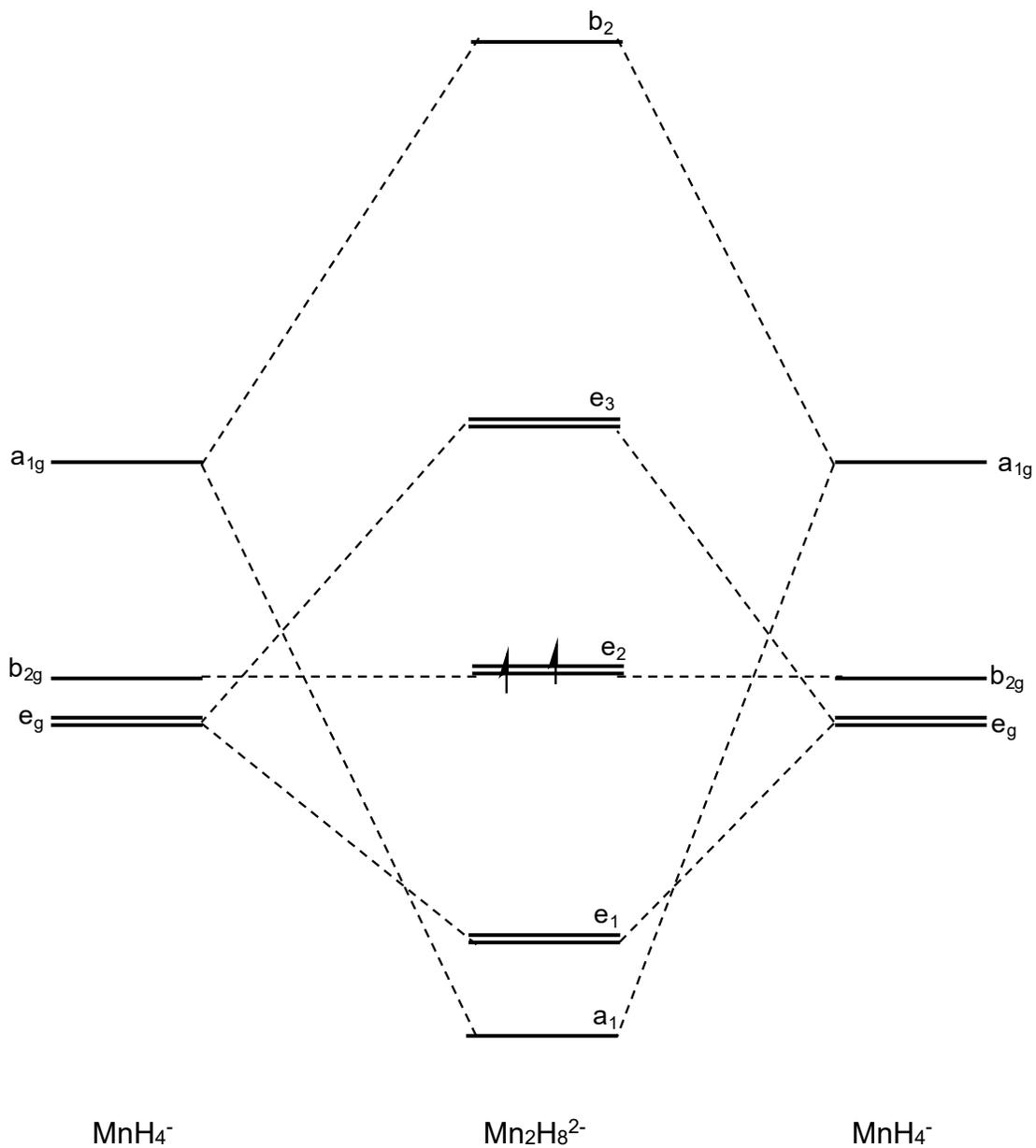
(d) We will consider only the four remaining Mn 3d orbitals on each MnH_4^- fragment.





Bond order = 4

(e) When the molecule is staggered, there is no overlap between the b_{2g} orbitals of MnH_4^- (the d_{xy} orbitals). Under D_{4d} symmetry, the two d_{xy} orbitals are a basis for the e_2 representation; they stay non-bonding.



Bond order = 3

The staggered conformation should be paramagnetic.