Cluster Chemistry and Wade's Rules

For some main group (as well as some transition metal) compounds, we often encounter electron deficient structures, meaning we cannot simply form normal 2-center 2-electron bonds.

↳ need to develop holistic approach using MO theory / Projection Operator Method to describe multi-center 2-electron bonds / MOs.

The result of such a treatment is collectively known as Wade's Rules.

1) Count the number of e^- available for cluster bonding.
   a) B-H has $4e^-$, $2e^-$ for B-H bond
      $2e^-$ for cluster bonding
   b) C-H has $5e^-$, $2e^-$ for C-H bond
      $3e^-$ for cluster bonding.
   c) Zintl phase: Sb → $2s\,e^-$, non-contributing
      $3p\,e^-$, valence for cluster bonding.

2) Of the total number e^- for cluster bonding, $2e^-$ always for delocalized MO (generally the completely symmetric A_1, A_{1g} ... irr. rep.), i.e. if I have 20 e^- for cluster bonding, only 18 e^- to form the skeleton.

3) The remaining e^- are available to form the cluster skeleton bonds.

4) Each skeleton cluster e^- pair forms/corresponds to one vertex of a ~~[illegible]~~ regular polyhedra.

5) Fill in each vertex w/ your nuclei (there might be vacancies. Rules for which vertices are vacant follow the closo, nido, arachno, hypno, klado structures, though there are many deviations).

N.B. there are many exceptions to Wade's rules, but it serves as a good first order approximation, and can be refined through experiment and looking at/deriving the MO diagram.

Example: $[Ge_9]^{4-}$

1) Each Ge contributes 2 4p e^-, plus the 4 e^- for the anionic charge gives 22 e^-.

2) 2 e^- for delocalized cluster bonding. 20 e^- (10 e^- pairs) to form the skeleton.

3)/4) We start w/ a 10 vertex polyhedra.

5) Occupy 9 of the vertices (1 vacancy) → nido structure. (see Pset solutions for structure).

MO Theory of Cluster Compounds:

Use Projection Operator Method to come up w/ MO diagram for clusters. Can come up w/ Walsh-type diagrams to determine which structures are the most favorable → Wade's Rules (+ modifications).

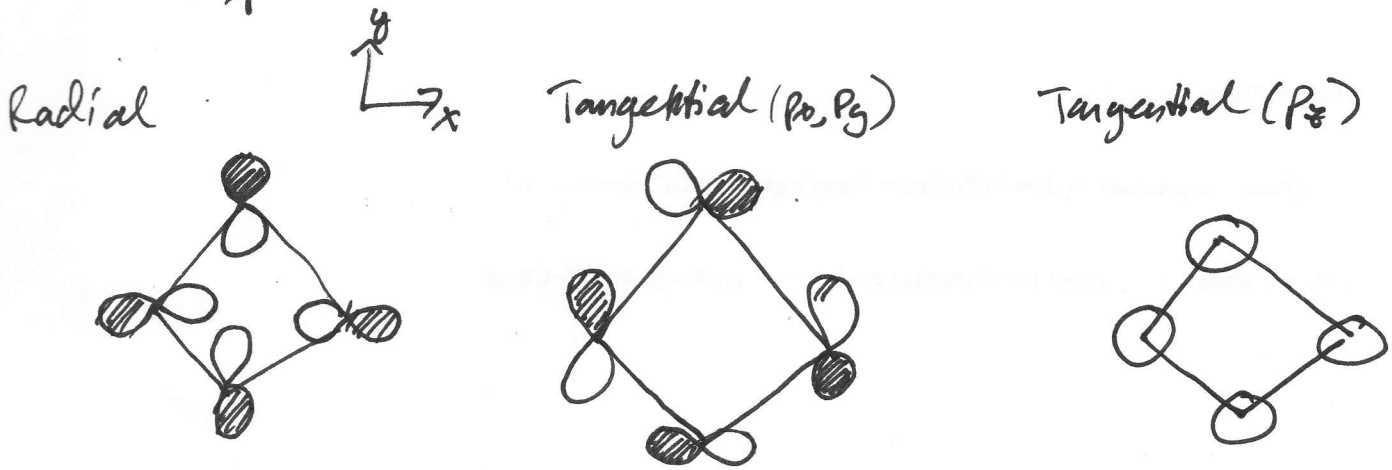
Let's compare the species $[Sb_4]^{2-}$ and $[Sn_4]^{2-}$.

We might predict either a square planar or tetrahedral compound. What do these MO diagrams look like?

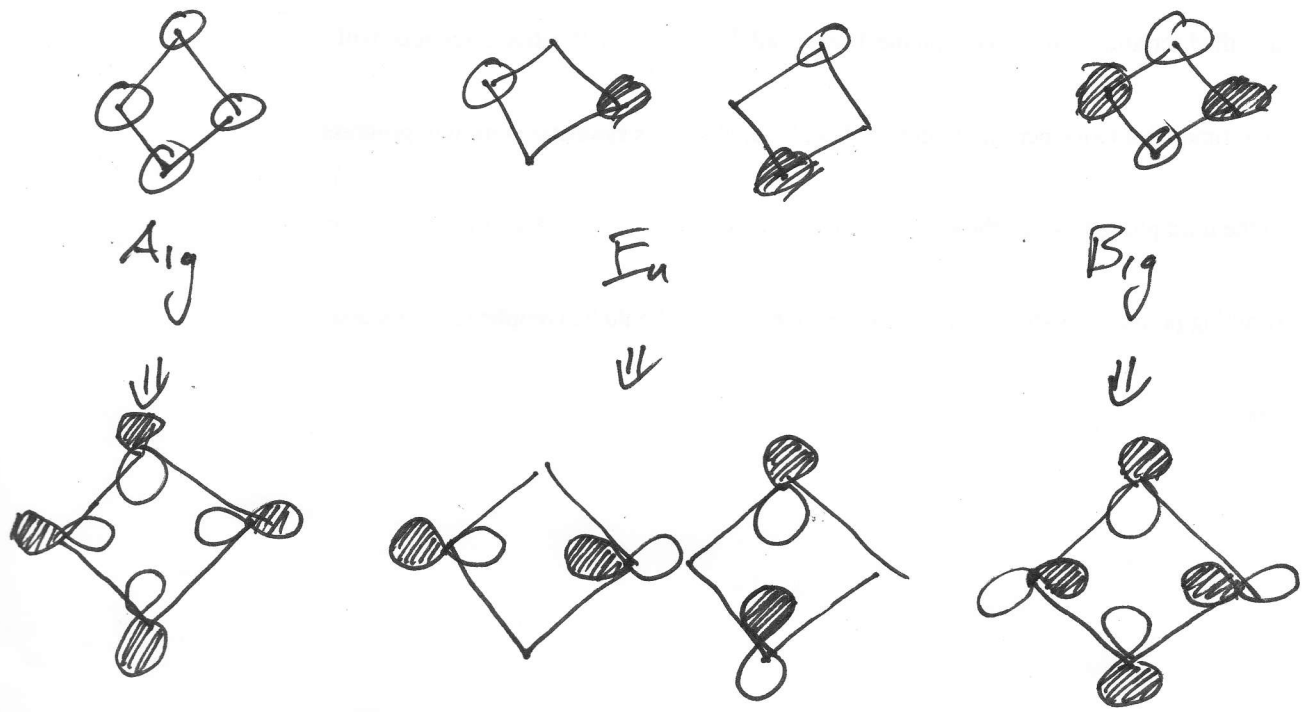
Square Planar:

Take 3 p orbitals for each atom, 4x3 orbitals.

We'll split the orbitals into 3 basises.



We can either assemble the irr. rep.s by inspection by comparing w/ the isolated case we derived for the H_4 cluster:



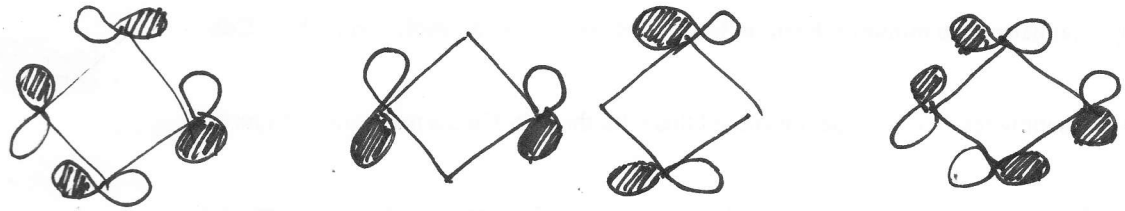
Or, come up w/ red. rep. → find irr. rep.

* note, because the sign of the p orbital can change upon acting w/ a symmetry operation, we can/will get negative integers for the red. rep.

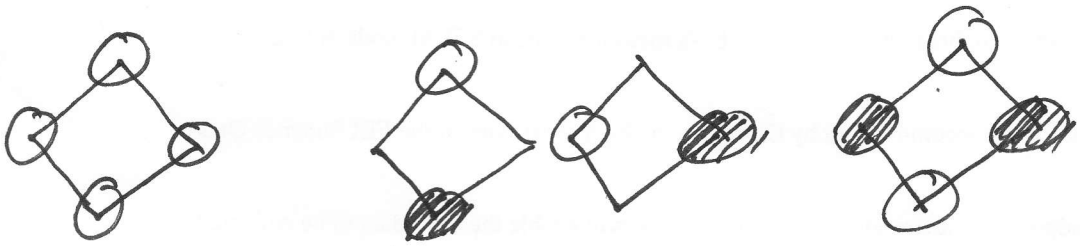
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{radial}	4	0	0	2	0	0	0	4	2	0
$\Gamma_{x,y}$	4	0	0	-2	0	0	0	4	-2	0
Γ_z	4	0	0	-2	0	0	0	-4	2	0

$\Gamma_{radial} = A_{1g} + B_{1g} + E_u$ $\quad \Gamma_{x,y} = A_{2g} + B_{2g} + E_u$ $\quad \Gamma_z = A_{2u} + B_{2u} + E_g$

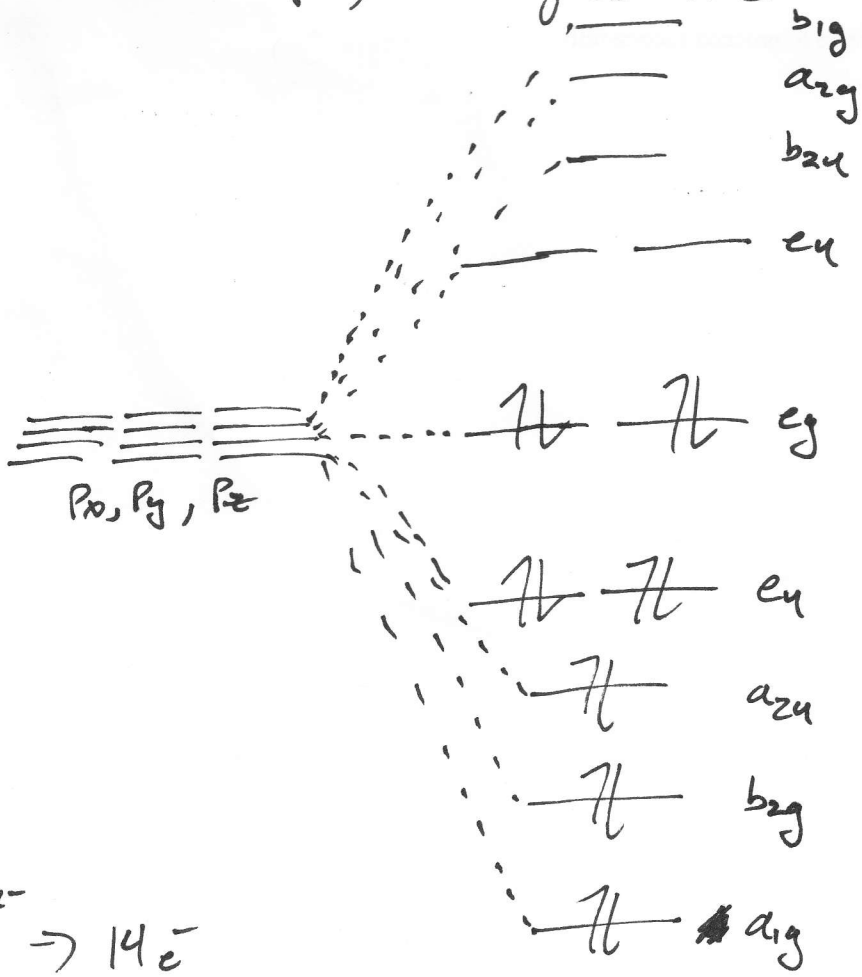
Tangential (x,y): A_{2g} E_u B_{2g}



Tangential (z): A_{2u} E_g B_{2u}



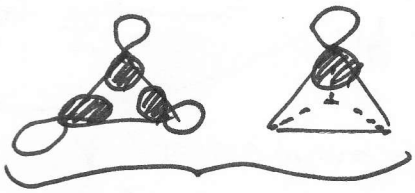
Since these irr. rep.s are close together (orbitals have appreciable overlap) energies are not degenerate.



For $[Sb_4]^{2-} \rightarrow 14e^-$

For the tetrahedral case, we can similarly define different basis sets.

Radial:



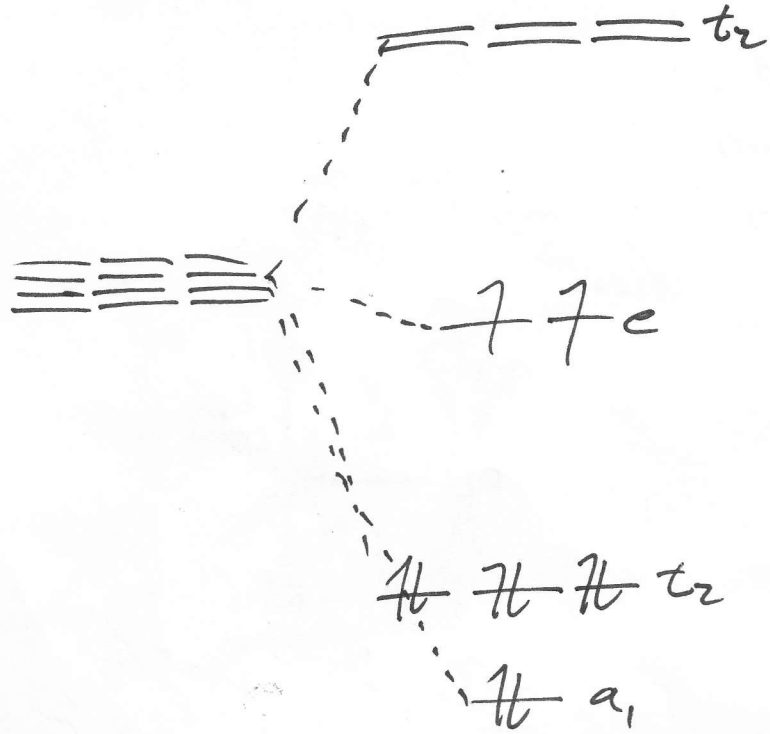
3X2 tangential:

1X2 tangential:

As before, we can derive the irr. rep. orbital shapes in many ways. (Proj. operator, isolobal analogies)
use carefully

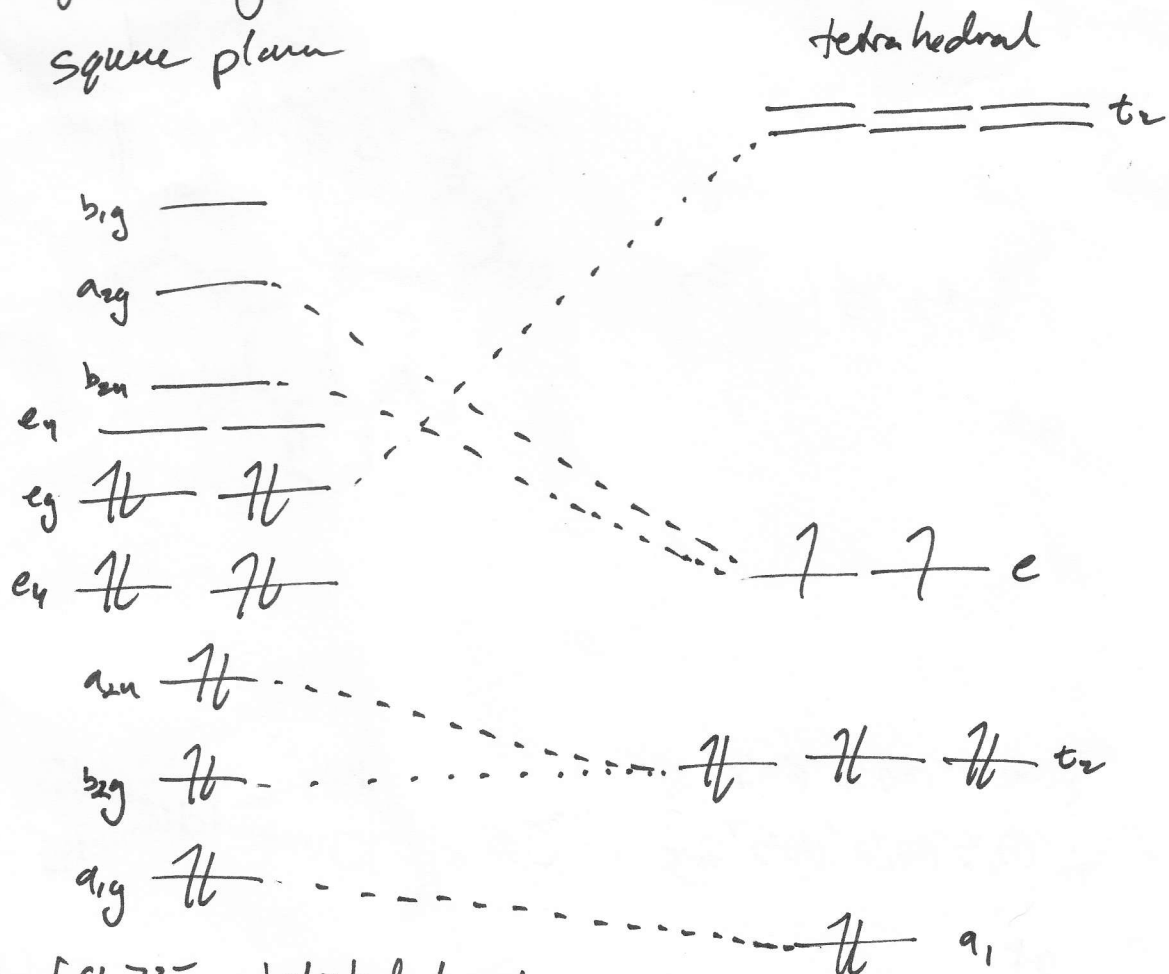
* see PS 5 HW solution for breakdown of these irr. rep. shapes.

At the end:



$[Ge_4]^{2-} \Rightarrow 10\,e^-$

A Walsh-type Diagram:



For $14\,e^-$, $[Sb_4]^{2-}$, tetrahedral shape will start to fill anti-bonding MOs (unfavorable), while for $10\,e^-$, $[Ge_4]^{2-}$, tetrahedral is lower energy.