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.

To 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 $\pi$ available for cluster bonding.
   a) B-H has 4 $\pi$, 2 $\pi$ for B-H bond
      2 $\pi$ for cluster bonding
   b) C-H has 5 $\pi$, 2 $\pi$ for C-H bond
      3 $\pi$ for cluster bonding.
   c) Zintl phase: Sb $\rightarrow$ 2 $\pi$, non-contributing
      3 $\pi^-$, valence for cluster bonding.

2) of the total number $\pi$ for cluster bonding, 2 $\pi$ always for delocalized MO (generally the completely symmetric A1, Alg ... irr. rep.), i.e. if I have 20 $\pi$ for cluster bonding, only 18 $\pi$ to form the skeleton.
3) The remaining $\varepsilon$ are available to form the cluster skeleton bonds.

4) Each skeleton cluster $\varepsilon$ pair forms/corresponds to one vertex of a deltahedral polyhedron.

5) Fill in each vertex of your nuclei. (there might be vacancies. Rules for which vertices are vacant follow the close, wide, arachno, hypno, klando structures, though there are many deviations).

-note- 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: \([Ge_7]^{4-}\)

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

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

3) We start w/ a 10 vertex polyhedra.

4) Occupy 9 of the vertices (1 vacancy) \(\Rightarrow\) nido structure.

(see Pset solutions for structure)
MO Theory of Cluster Compounds:

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

Let's compare the species \([56y]^2\) and \([6z_y]^2\).

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, \(4 \times 3\) orbitals.

We'll split the orbitals into 3 basises.

- Radial
- Tangential \((p_x, p_y)\)
- Tangential \((p_z)\)
We can either assemble the irr. rep. s by inspection by comparing
of the isodiral case we derived for the Hg cluster:

Or, come up w/ red. rep. => find irr. rep.
* note, because the sign of the p orbital can
change upon acting of asymmetry 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  3h  2D_2  2D_2

T_{radial}  4  0  0  2  0  0  0  0  4  2  0
T_{xy}  4  0  0  -2  0  0  0  0  4  -2  0
T_{z}  4  0  0  -2  0  0  0  0  4  2  0

T_{radial} = A_g + B_{1g} + E_u  T_{xy} = A_g + B_{2g} + E_u  T_{z} = A_{2u} + E_{2u} + E_{g}
Since these irr. rep. s are close together (orbitals have appreciable overlap) energies are not degenerate.

For $[Sby]^{2-} \rightarrow 14e^{-}$
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, kubelik analogies)

* see PS 5 HW solution for breakdown of these irr. rep. shapes.
At the end:

\[ [\text{GeH}]^- \rightarrow 10 \text{ e}^- \]

A Walsh-type Diagram:

Square planar

[\text{big}]
[\text{eq}]
[\text{ax}

For 19 e\text{-, }[\text{SiH}]^2 -, \text{ tetrahedral shape will start to fill anti-bonding MO's (unfavorable), while for 20 e\text{-, }[\text{GeH}]^2 -, \text{ tetrahedral is lower energy.}