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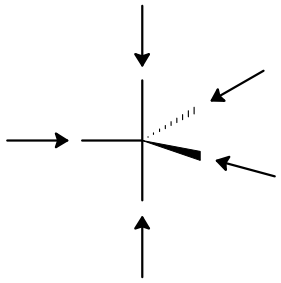
Chem 370 - Spring, 2019
Test II - Part 2
April 22 2019

4. (42 points) As noted in Part 1 of this test, $CuCl_5^{3-}$ is a trigonal bipyramidal structure (D_{3h}). In the following sections of this problem, you will construct a σ-only MO scheme for $CuCl_5^{3-}$, using only 4*s* and 3*d* orbitals on the central Cu^{2+} ion, and sigma SALCS from the pendant Cl^- ions, each of which contributes one pair of electrons to the scheme.

a. (16 points) Taking the five-vector model below as a basis, use the template below and the character table on the last page, to generate a reducible representation for the five chlorine σ-SALCs$^-$, Γ_{SALC}, and carry out the systematic reduction into its component irreducible representations to show the symmetries of the individual SALCs.



D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
Γ_{SALC}	5	2	1	3	0	3	Σ	Σ/*h*
A_1'	5	4	3	3	0	9	24	2
A_2'	5	4	-3	3	0	-9	0	0
E'	10	-4	0	6	0	0	12	1
A_1''	5	4	3	-3	0	-9	0	0
A_2''	5	4	-3	-3	0	9	12	1
E''	10	-4	0	-6	0	0	0	0

$$\Gamma_{SALC} = 2\,A_1' + E' + A_2'' \qquad d = 5\ \checkmark$$

b. (6 points) Give the symmetries of the individual *s* and *d* orbitals on the central Cu^{2+} ion.

$$s = A_1' \qquad d_{z^2} = A_1' \qquad (d_{x-y^2},\, d_{xy}) = E' \qquad (d_{xz},\, d_{yz}) = E''$$

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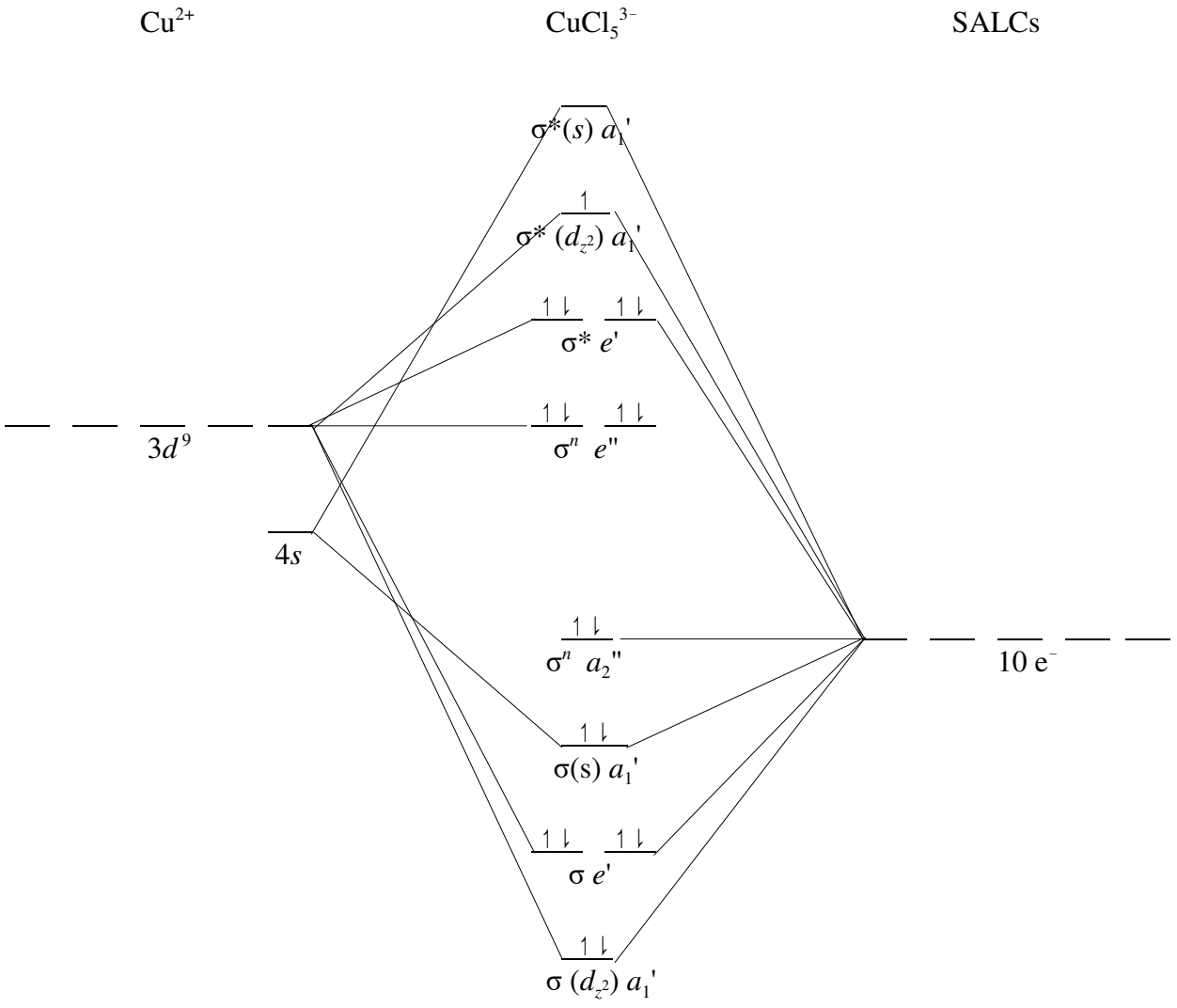
c. (12 points) Assume that Cu^{2+} only uses *s* and *d* orbitals for bonding in $CuCl_5^{3-}$. Using the skeletal MO scheme below, connect the SALC and AO levels with the MOs to which they contribute. Label all levels with the appropriate Mulliken symbols (lower case), and indicate the bond type of every MO level (σ, σ*, or σ^n). Show the filling of electrons in the MO scheme, assuming that Cu^{2+} ion contributes nine electrons and each Cl^- ligand contributes a pair of electrons. The labels for the MO levels formed from 4*s* AOs are already indicated for you. Add their Mulliken symbol. Remember that the pattern of filling of the highest electrons mirrors the CFT scheme of the transition metal ion, which you determined in Part 1 of this test.



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d. (8 points) The valence bond model of bonding in trigonal bipyramidal (*tbp*) complexes assumes the participation of *s*, *p*, and *d* orbitals on the central atom, forming appropriate hybrid orbitals. On the basis of symmetry, which specific combinations of *s*, *p*, and *d* orbitals could be combined to form sets of hybrid orbitals to account for *tbp* geometry about a central atom, such as Cu^{2+} in $CuCl_5^{3-}$? [Hint: The reducible representation Γ_{SALC}, which you generated in part a, would be the same as Γ_{hybrid} for five hybrid orbitals in a *tbp* arrangement.]

$$\Gamma_{SALC} = \Gamma_{hybrid} = 2\,A_1' + E' + A_2''$$

AOs with these symmetries:

$s, d_{z^2} = A_1'$
$(p_x, p_y), (d_{x-y^2}, d_{xy}) = E'$
$p_z = A_2''$

Note: No orbital of *E* "symmetry can be used in forming these hybrids, so the degenerate pair (d_{xz}, d_{yz}) are excluded. Also, two AOs of A_1' symmetry are required, so both *s* and d_{z^2} must be used in any set. Any set must use p_z.

Possible combinations:

$dsp^3 = d_{z^2} \pm s \pm p_x \pm p_y + p_z$
$d^3sp = d_{z^2} \pm d_{x-y^2} \pm d_{xy} \pm s \pm p_z$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

Note: Feel free to detach this page for use in working through the problems, but please do not write anything on this that you wish to have graded.