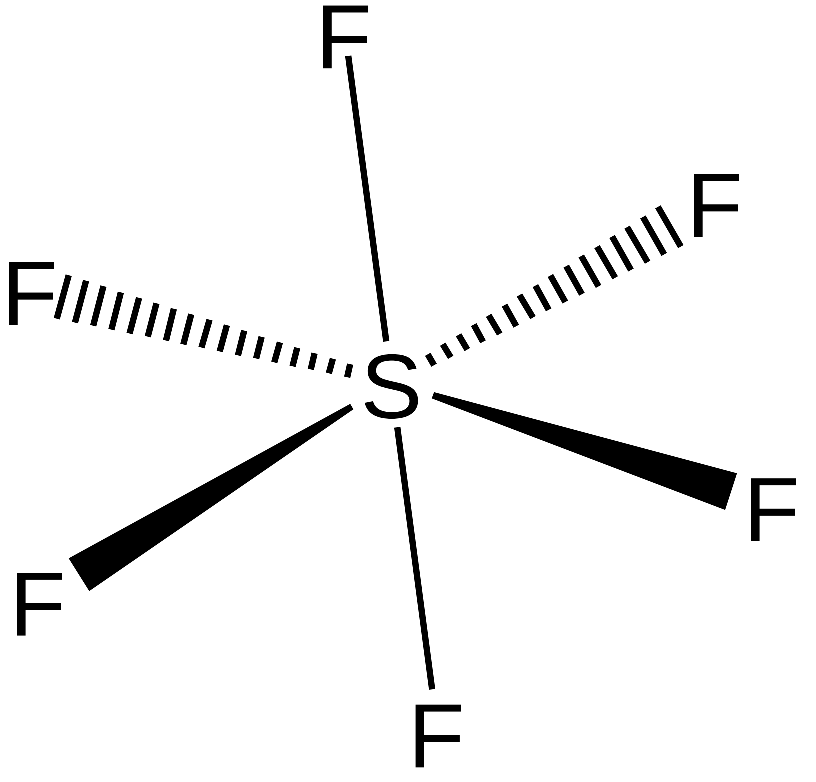
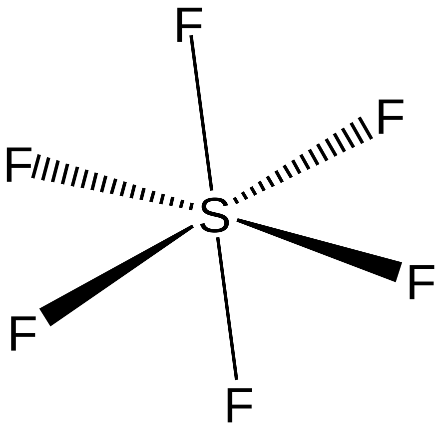
Predicting the SALCs of SF_6

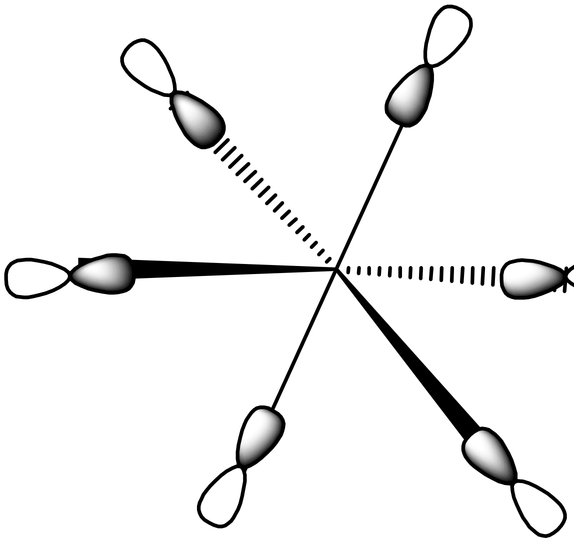


Predicting the SALCs of SF_6

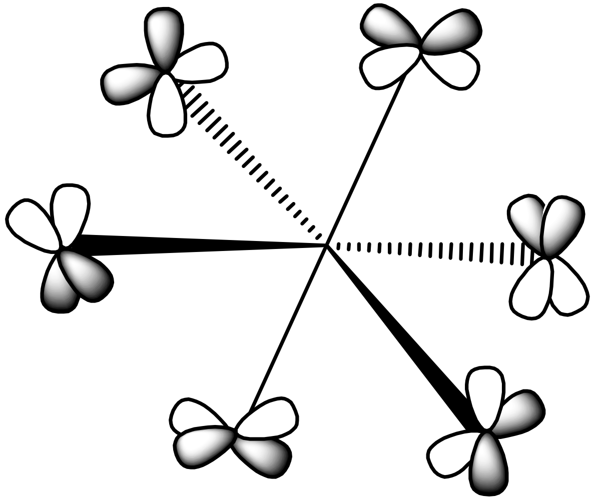


Using a 2p-orbital basis for the fluorine atoms and considering only the 3s- and 3p-orbitals for sulfur. Write down the SALCs of the F atoms. Match those SALCs with orbitals of appropriate symmetry on sulfur. Classify the SALCs as either bonding or non-bonding. NOTE: The bonding SALCs assume that the phase of the orbital on sulfur is matched to the SALC. Reversing the sign on sulfur will give the anti-bonding combination. Note that it is convenient to divide the F p-orbitals into σ-bonding and π-bonding sets.

Reducible representation of F p-orbital basis



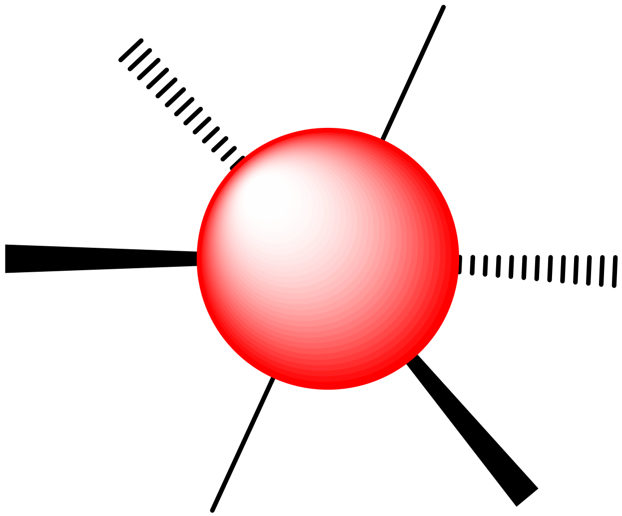
p-σ set



p-π set

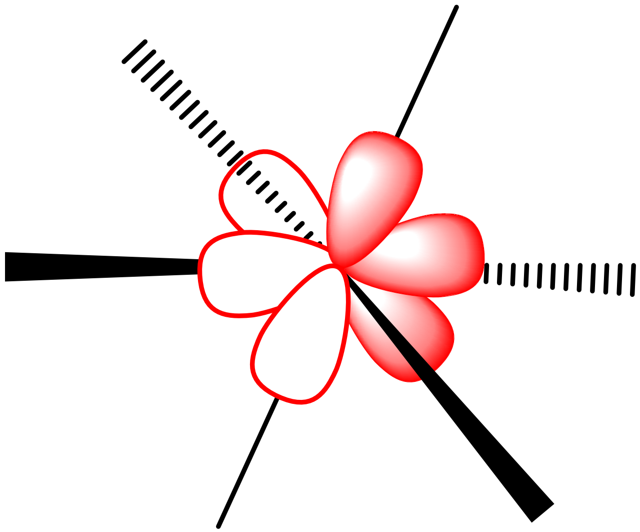
	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2
Γ_π	12	0	0	0	-4	0	0	0	0	0

Reducible representations of S s and p-orbitals



3s

A_{1g}



3p-set

T_{1u}

	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_{3s}	1	1	1	1	1	1	1	1	1	1
Γ_{3p}	3	0	-1	1	-1	-3	-1	0	1	1

Decomposition of the σ-set

Γ_σ	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Product
A_{1g}	6	0	0	2	2	0	0	0	4	2	48/48=1
A_{2g}	6	0	0	-2	2	0	0	0	4	-2	0
E_g	12	0	0	0	4	0	0	0	8	0	48/48=1
T_{1g}	18	0	0	2	-2	0	0	0	-4	-2	0
T_{2g}	18	0	0	-2	-2	0	0	0	-4	2	0
A_{1u}	6	0	0	2	2	0	0	0	-4	-2	0
A_{2u}	6	0	0	-2	2	0	0	0	-4	2	0
E_u	12	0	0	0	4	0	0	0	-8	0	0
T_{1u}	18	0	0	2	-2	0	0	0	4	2	48/48=1
T_{2u}	18	0	0	-2	-2	0	0	0	4	-2	0

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u}$$

Decomposition of the π-set

Γ_π	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	I	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Product
A_{1g}	12	0	0	0	-4	0	0	0	0	0	0
A_{2g}	12	0	0	0	-4	0	0	0	0	0	0
E_g	24	0	0	0	-8	0	0	0	0	0	0
T_{1g}	36	0	0	0	4	0	0	0	0	0	48/48=1
T_{2g}	36	0	0	0	4	0	0	0	0	0	48/48=1
A_{1u}	12	0	0	0	-4	0	0	0	0	0	0
A_{2u}	12	0	0	0	-4	0	0	0	0	0	0
E_u	24	0	0	0	-8	0	0	0	0	0	0
T_{1u}	36	0	0	0	4	0	0	0	0	0	48/48=1
T_{2u}	36	0	0	0	4	0	0	0	0	0	48/48=1

$$\Gamma_p = T_{1g} + T_{2g} + T_{1u} + T_{2u}$$

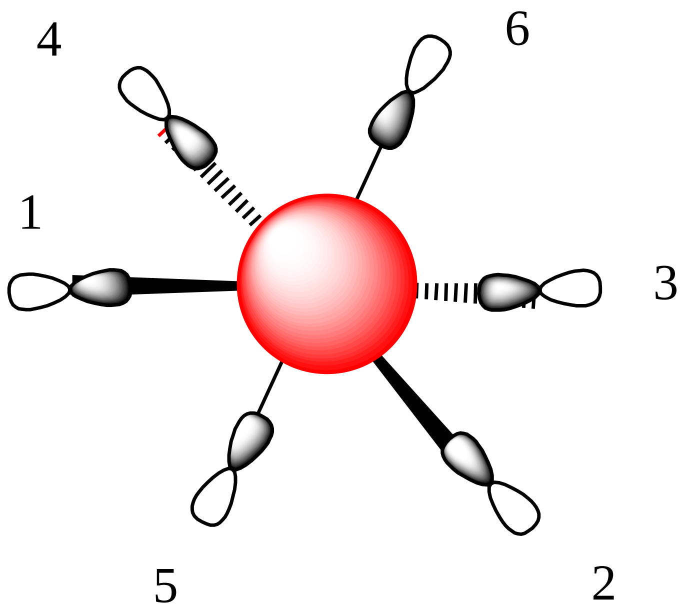
The σ-bonding set has two possible sets of SALCs based on the correspondence of both the S and F atoms. These are A_{1g} and T_{1u}. The SALCs for each are shown below.

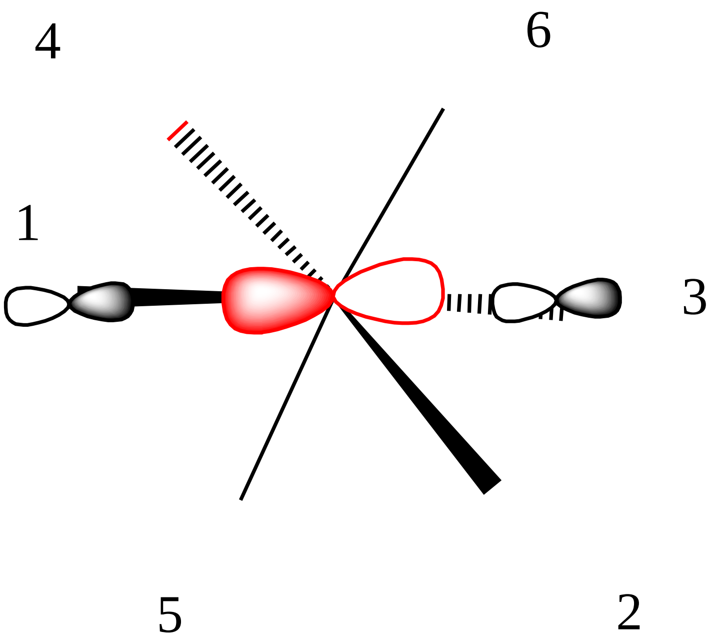
$$a_{1g} = \frac{1}{\sqrt{6}}\left(p_1 + p_2 + p_3 + p_4 + p_5 + p_6\right)$$

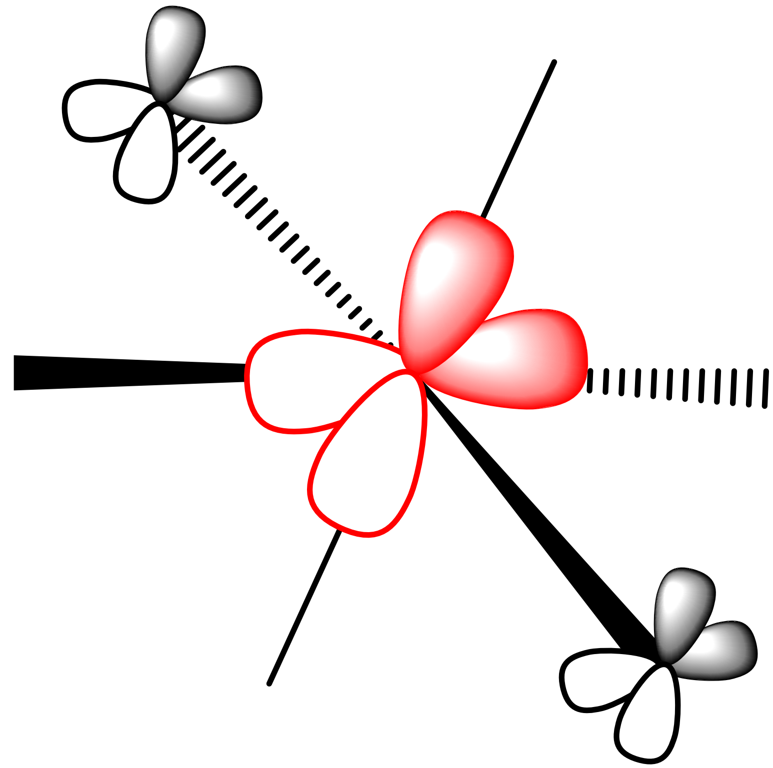
$$t_{1u}(1) = \frac{1}{\sqrt{2}}\left(p_1 - p_3\right)$$

$$t_{1u}(2) = \frac{1}{\sqrt{2}}\left(p_2 - p_4\right)$$

$$t_{1u}(3) = \frac{1}{\sqrt{2}}\left(p_5 - p_6\right)$$







There is also a set of T_{1u} orbitals of π-symmetry according to the analysis. This is an example of the T_{1u} combination that leads to bonding for the π-symmetry SALCs.   There are three of these orbitals.