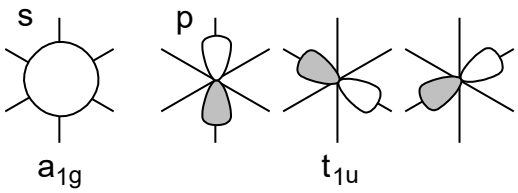
Molecular Orbitals in SF_6

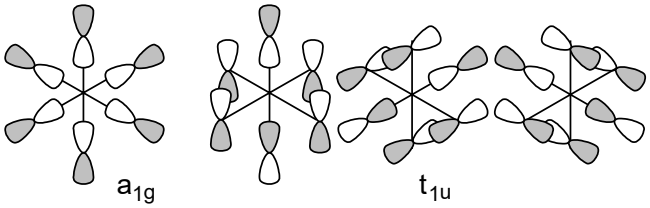
The Lewis structure of SF_6 describes six pairs of electrons as bond pairs, despite the availability of only four valence orbitals on sulphur. The valence bond description of this hypervalent complex must therefore invoke d-orbitals. However, high-level theoretical calculations suggest that the electronic structure involves not d-orbitals and six bonds, but instead only four bonds, each delocalized over all seven atoms.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1	
E_g	2	–1	0	0	2	2	0	–1	2	0	$(z^2,x^2–y^2)$
T_{1g}	3	0	–1	1	–1	–1	1	0	–1	–1	
T_{2g}	3	0	1	–1	–1	–1	–1	0	–1	1	(xy,xz,yz)
A_{1u}	1	1	1	1	1	1	–1	1	–1	–1	
A_{2u}	1	1	–1	–1	1	1	1	1	–1	1	
E_u	2	–1	0	0	2	2	0	–1	–2	0	
T_{1u}	3	0	–1	1	–1	–1	–1	0	1	1	(x,y,z)
T_{2u}	3	0	1	–1	–1	–1	1	0	1	–1	

Four S AOs:

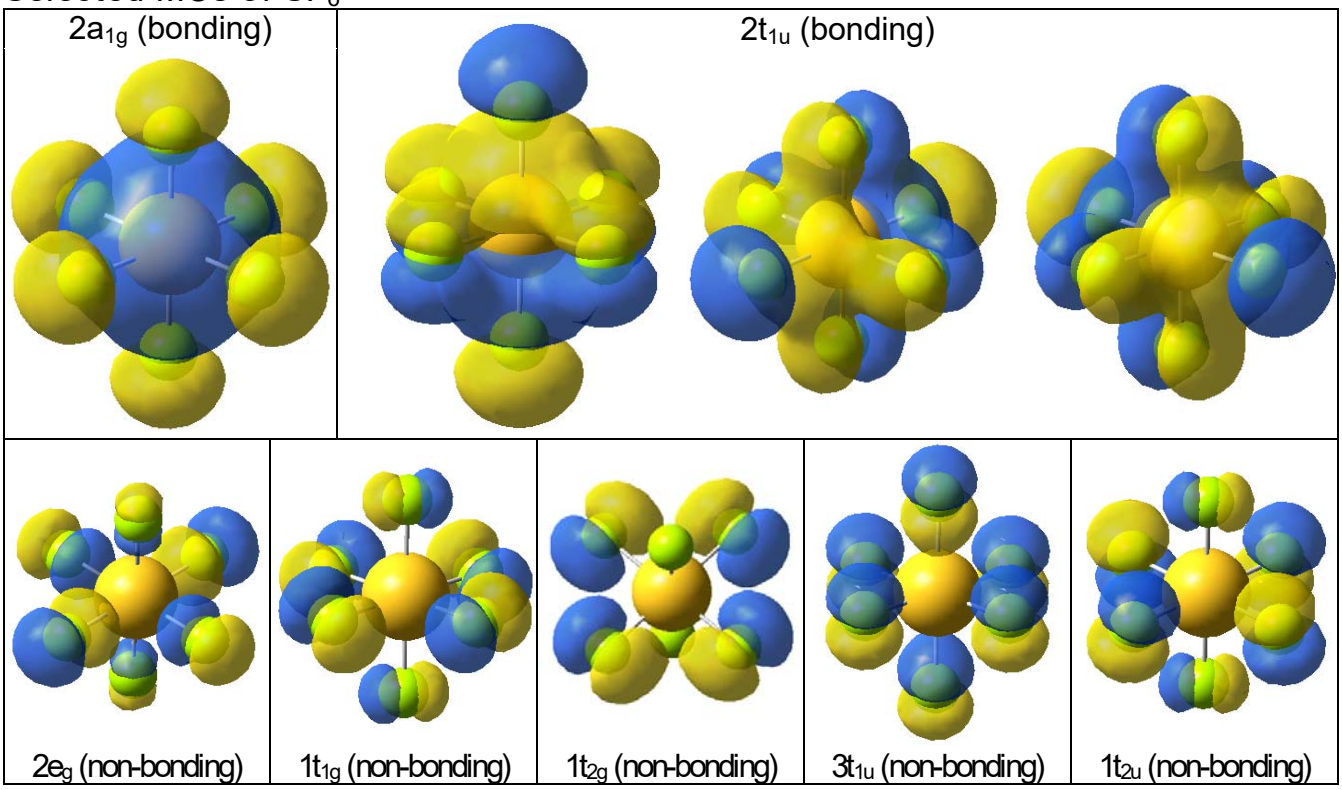


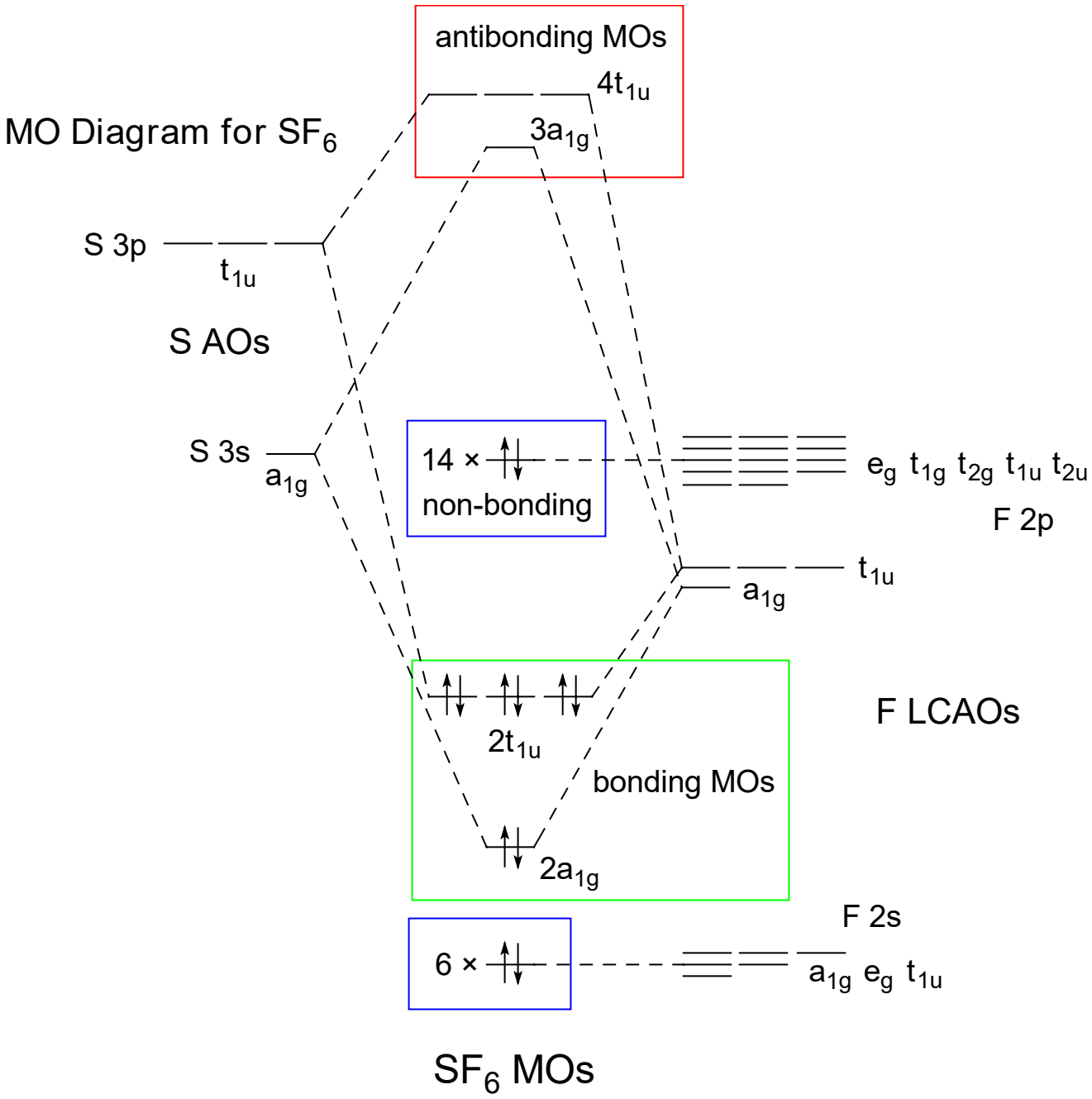
Four of the twenty-four F SALCAOs:



The six F 2s orbitals give linear combinations that transform as a_{1g} e_g and t_{1u}, but they are very low in energy and remain effectively non-bonding. The eighteen F 2p orbitals give linear combinations transforming as a_{1g} e_g t_{1g} t_{2g} $2\times t_{1u}$ and t_{2u}. Most of these remain non-bonding, but four combinations, a_{1g} and one of the t_{1u} sets, can overlap with the S AOs to give four bonding and four anti-bonding MOs. Shown below are all four bonding MOs and one of each symmetry of the F 2p non-bonding MOs.

Selected MOs of SF_6





The resulting MO diagram contains:

- 6 non-bonding MOs derived from F 2s AOs
- 4 bonding and 4 anti-bonding MOs of a_{1g} and t_{1u} symmetry, derived from F 2p AOs
- 14 non-bonding MOs, also derived from F 2p AOs

The 48 valence electrons of SF_6 fill the first 24 available MOs: 20 non-bonding and 4 bonding MOs. This leads to an interpretation that is different than that of the Lewis structure: not 18 LPs and 6 BPs, but 20 F-based lone pairs and only 4 bond pairs! The total bond order equals 4, or an "average" of only 2/3 bond per S-F interaction. In MOT, hypervalency manifests as electron-deficient bonding, with fewer than 2 bonding electrons per formal bonding interaction. Weird. Eerie.