MO Diagram for CO$_2$

C 2p
C 2s

CO$_2$ MOs

antibonding MOs

non-bonding

bonding MOs

1σ$_u$
1σ$_g$

3σ$_u$
3σ$_g$
2π$_u$
1π$_g$

2σ$_u$
2σ$_g$

3σ$_g$
2π$_g$
1π$_u$

2σ$_u$
2σ$_g$
1σ$_u$
1σ$_g$
Molecular Orbitals in SF₆

The Lewis structure of SF₆ 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.

Four S AOs:

The six F 2s orbitals give linear combinations that transform as a₁g, e₁g, and t₁u, but they are very low in energy and remain effectively non-bonding. The eighteen F 2p orbitals give linear combinations transforming as a₁g, e₁g, t₁g, t₂g, and t₁u. Most of these remain non-bonding, but four combinations, a₁g and one of the t₁u 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 SF₆

The 48 valence electrons of SF₆ 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.
Molecular Orbitals: Octahedral TM Complex

antibonding

non-bonding

bonding

M

ML₆

6 L σ