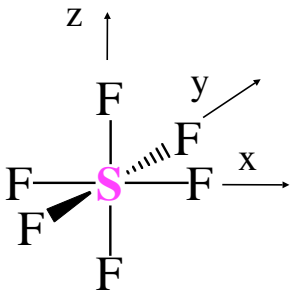
Molecular Orbital Diagrams of more complicated molecules

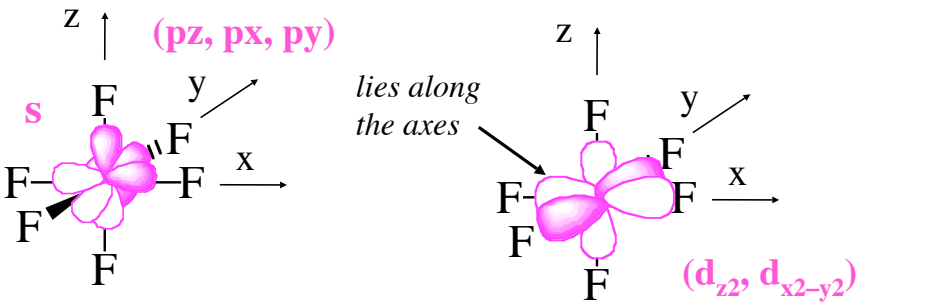
- √ XH_2 ($D_{\infty h}$)
- √ H_2O (C_{2v})
- → SF_6 (O_h)

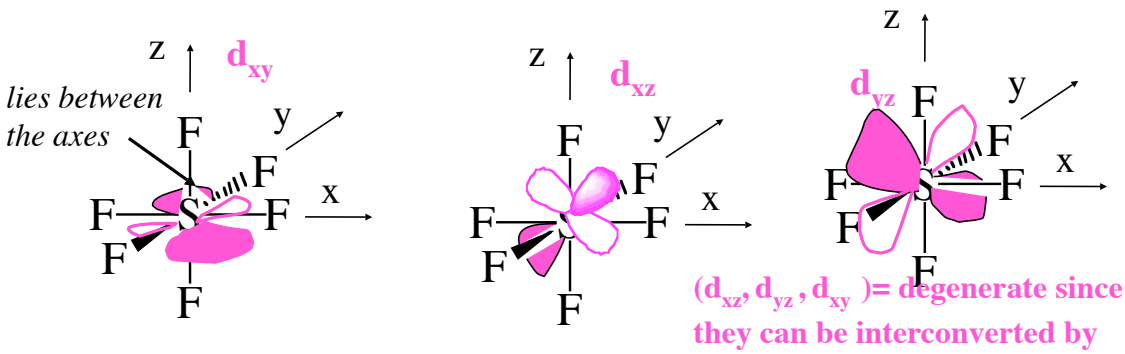
First let's consider the **sulfur** orbitals

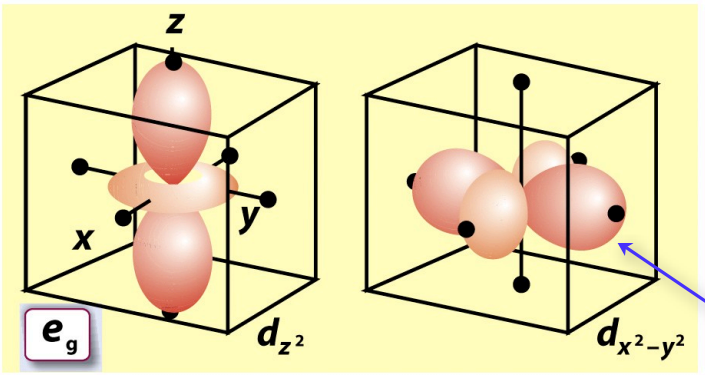


The fluorines lie along the axes

- we need to consider their symmetry
- and, we need to consider their energy

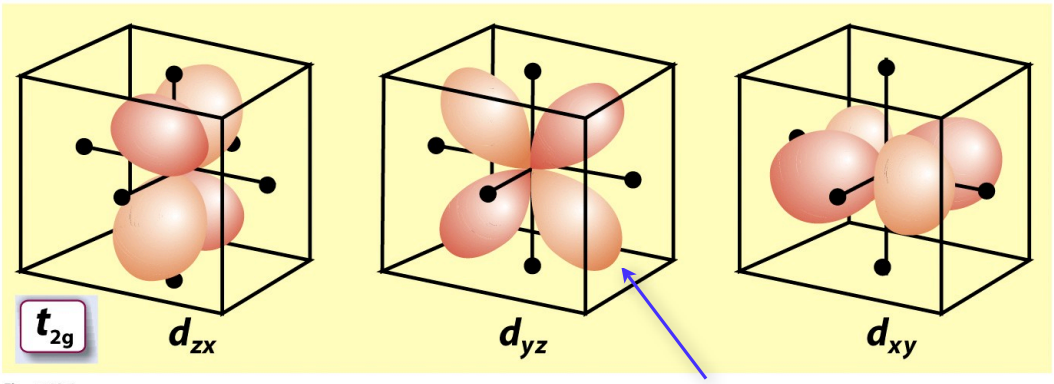






The d–orbitals

point along the axes



point between the axes

Figure 19-1
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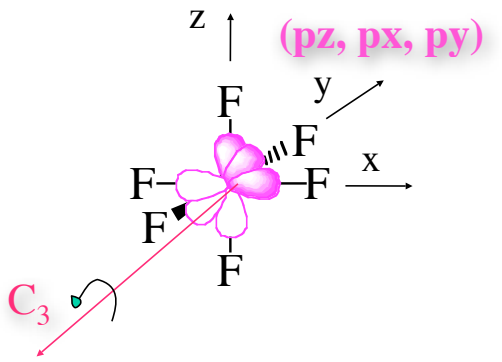
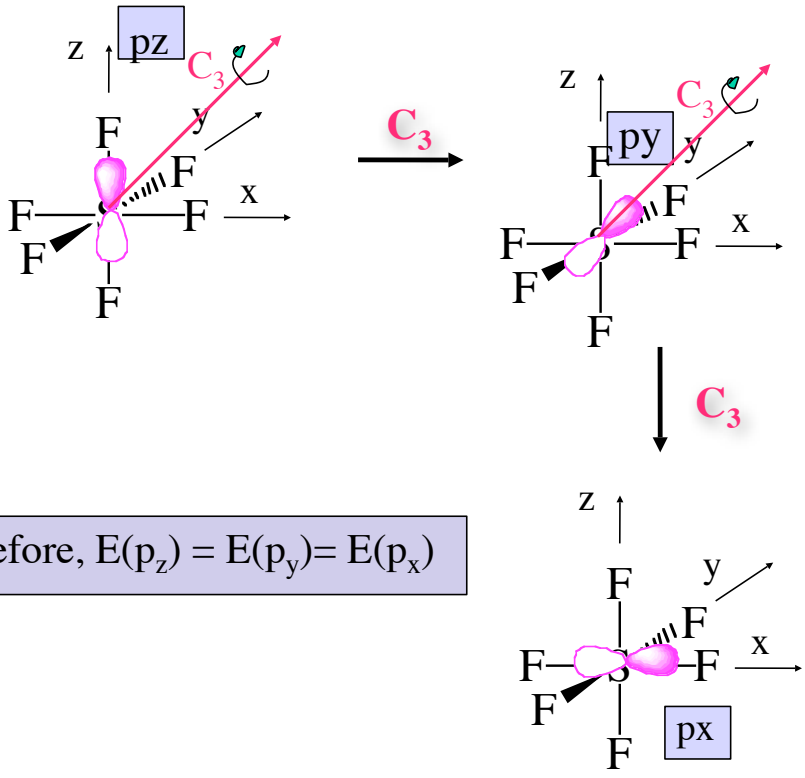
For orbitals to possess the same energy (ie, be degenerate), there has to be a symmetry element which interconverts them





Therefore, $E(p_z) = E(p_y) = E(p_x)$

Therefore, $E(d_{xz}) = E(d_{yz})$

ie, they are degenerate

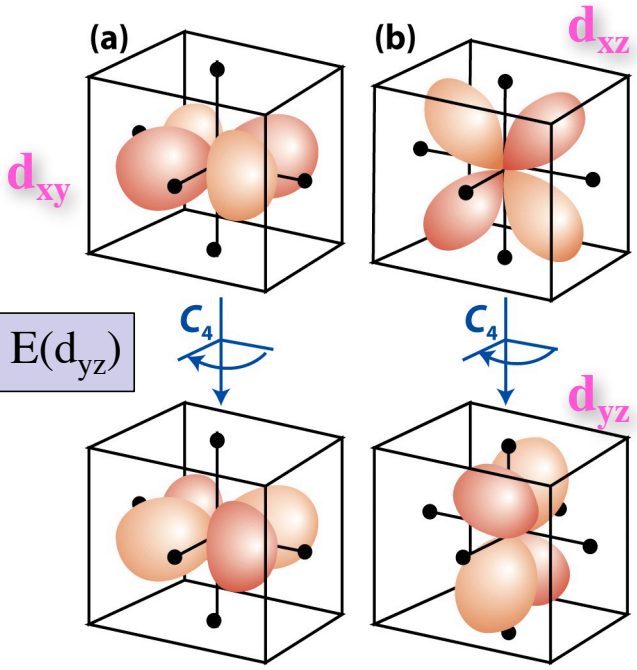


Figure 19-22
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What symmetry do these orbitals have?

The cubic groups (continued)

the central atom's atomic orbitals

doubly degenerate

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($= C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h = 48$
											Sulfur s-orbital
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	**Sulfur d-orbitals (σ)**
E_g	2	−1	0	0	2	2	0	−1	2	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	$(R_x, R_y R_z)$
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	**Sulfur d-orbitals (π-type)**
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_u	2	−1	0	0	2	−2	0	1	−2	0	**Sulfur p-orbitals**
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	

triply degenerate

triply degenerate

(originally all five d-orbitals were degenerate)

notice how the degeneracy of the sulfur's d–orbitals is "lifted" upon interaction with the six F's

What about the relative energies of these orbitals? Most importantly, how does their energy compare with the fluorine orbitals?

Upon interaction with the F's, the d–orbitals will no longer be equivalent, but divide up into one set of three (t_{2g}), and another set of two (e_g)

$3d_x$ d_y d_x d_z d_{x2-y2}

t_{2g} e_g

$3p_z$ p_x p_y

t_{1u}

$3s$

a_{1g}

- What about the symmetry of the fluorine AO's?
- How do the AOs combine to form LGO's in this molecule?

Sulfur AO's (atomic orbitals)

$2p_z$ p_x p_y

Fluorine's AO's

too low in E to interact with the sulfur orbitals → $2s$

The Fluorine LGO's (σ–bonding only)

O_h

a_{1g}

s *antibonding MO is pictured here*

LGO(1)

- **Sulfur p–orbitals have t_{1u} symmetry & thus match LGO(2)–LGO(4)**
- **Sulfur s–orbital has a_{1g} symmetry & thus matches LGO(1)**
- **two of the Sulfur d–orbitals have e_g symmetry & thus match LGO(5) & LGO(6)**

e_g

d_{z2} d_{x2-y2}

LGO(5) LGO(6)

t_{1u}

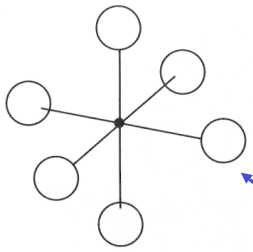
overlaps with the sulfur's

p_z p_x p_y

LGO(2) LGO(3) LGO(4)

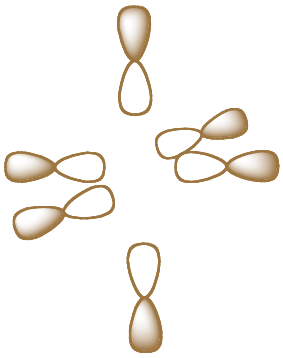
O_h

A_{1g}



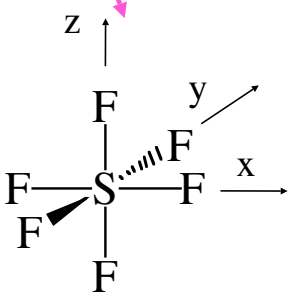
LGO's are contained in the appendices of numerous text books…….

Shown here is an abbreviation for the orbitals involved in bonding on the terminal atoms



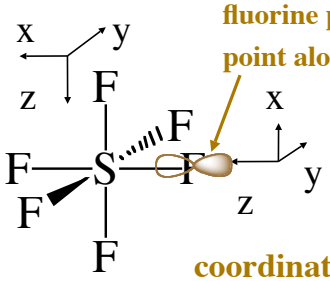
in the more specific case of SF_6, these terminal atom orbitals would be the F p_z–orbitals.

coordinate system for sulfur orbitals

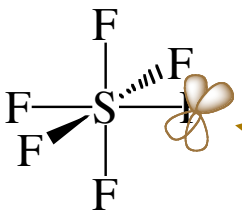


thus the F p_x and p_y–orbitals would have π–symmetry

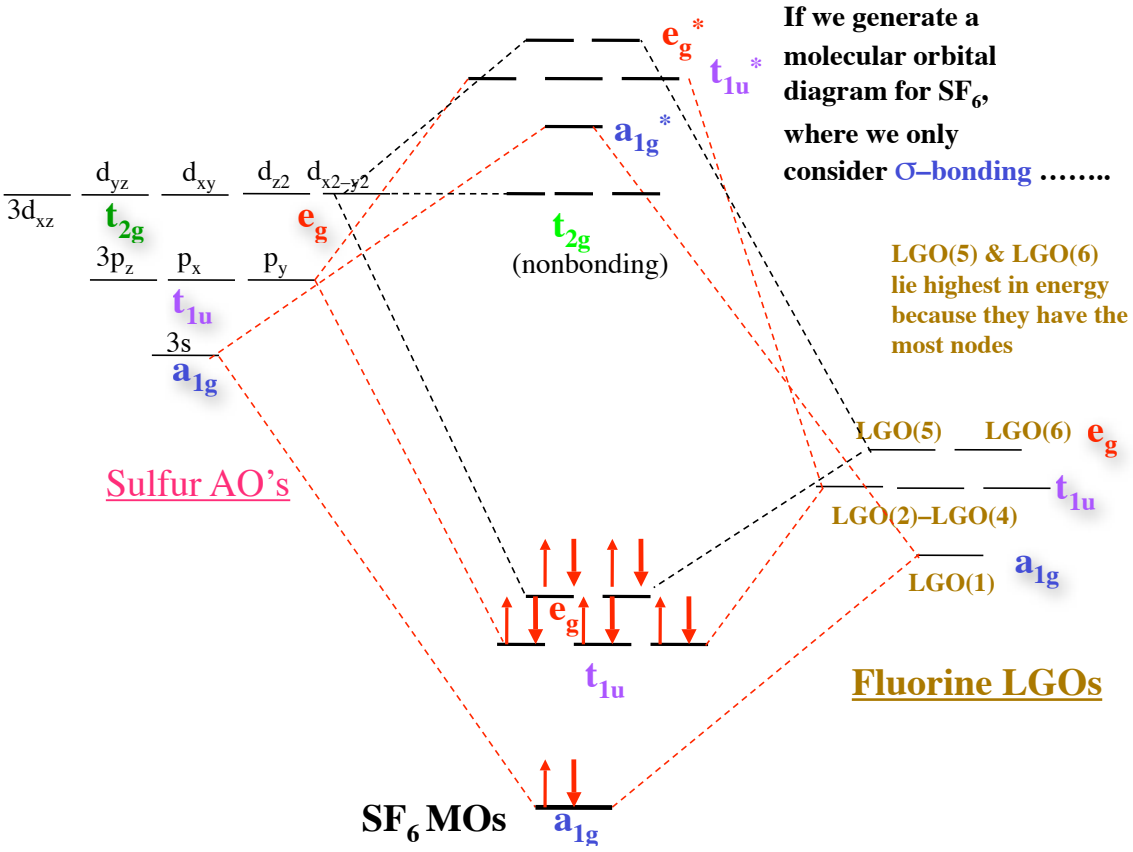
in contrast to the fluorine p_z which point along the axes

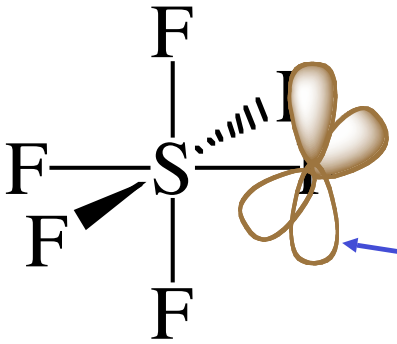


coordinate system for fluorine orbitals



fluorine p_x and p_y–orbitals are perpendicular to the S–F axis……& therefore π in character





Which sulfur orbitals do the fluorine p_x and p_y–orbitals interact with?

The d_{x2-y2} and d_{xy} orbitals are <u>orthogonal</u>

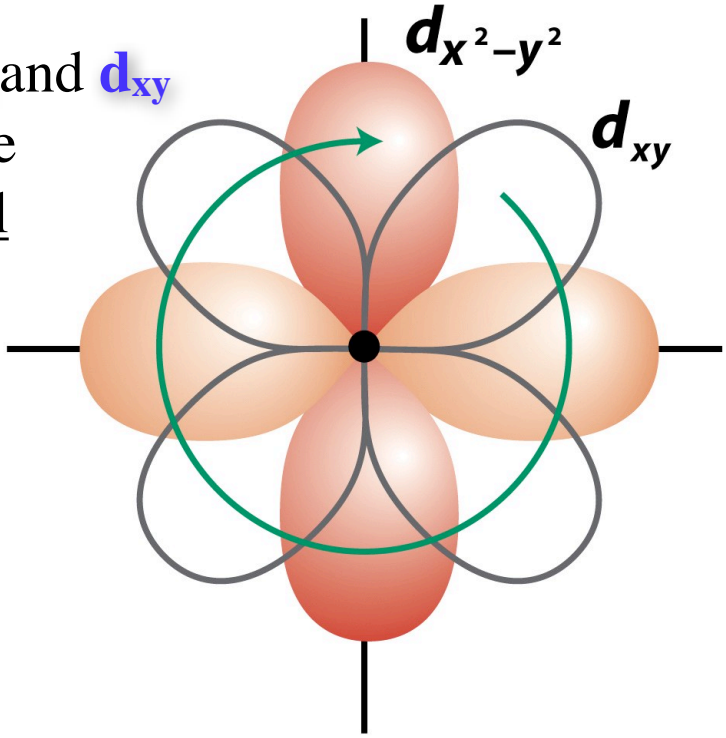


Figure 19-5
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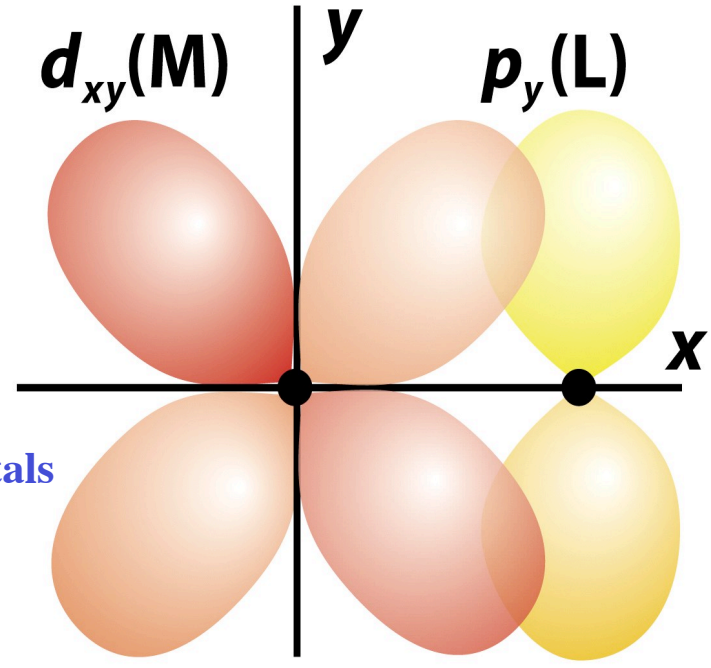
The p_y & d_{xy} orbitals are configured for π–overlap



π–type orbitals

Figure 19-16
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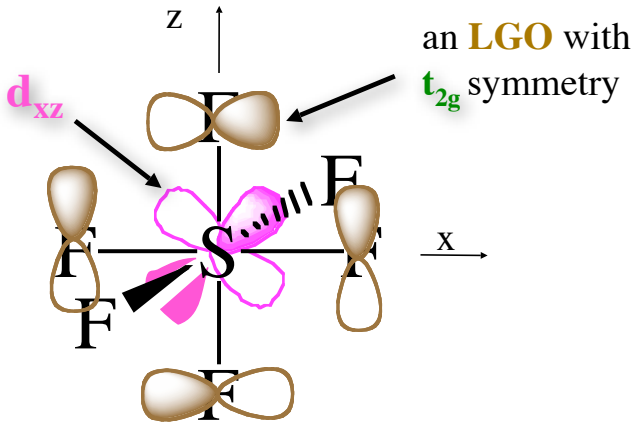
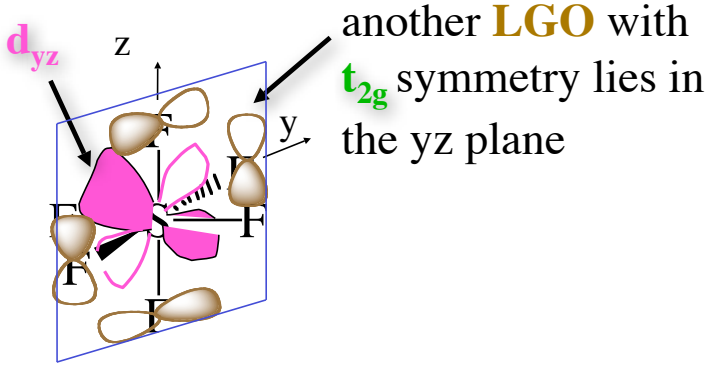
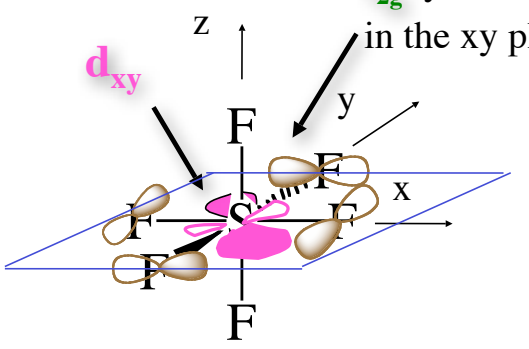


The **sulfur d_{xz}** only interacts with **fluorines** that lie along the x– and z–axes



The **sulfur d_{yz}** only interacts with **fluorines** that lie along the y– and z–axes

a third **LGO** with
t_{2g} symmetry lies
in the xy plane



The **sulfur d_{xy}** only interacts with **fluorines** that lie along the x– and y–axes