

The Hypervalent SX_4 Molecules

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Outline

- 1 Is the Octet Rule Violated for Hypervalent Molecules?
- 2 Qualitative MO Diagram

Consider a Seesaw Geometry for the SH_4 Molecule



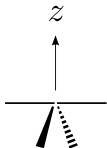
- We choose the z axis of our coordinate system to coincide with the principal rotation axis

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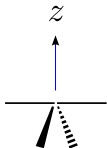
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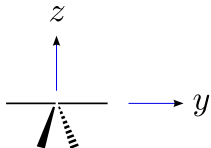
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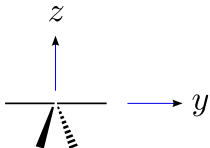
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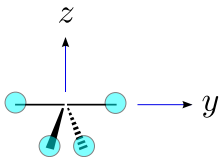
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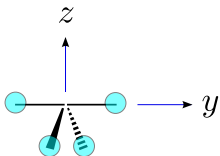
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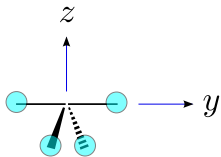
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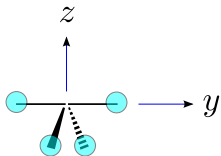
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C_{2v}	E^s	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
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- Identify sets of symmetry-related hydrogen 1s atomic orbitals

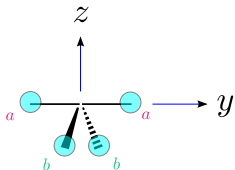
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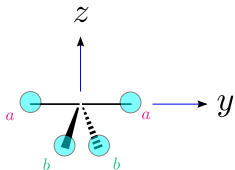
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- Use the set labeled a as the basis for a reducible representation

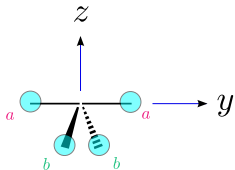
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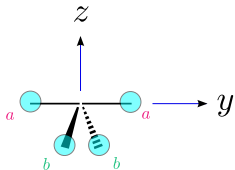


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$$\Gamma_{red}(a) = 2 \ 0 \ 0 \ 2$$

- See that it reduces to $A_1 + B_2$

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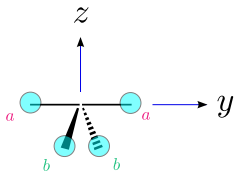


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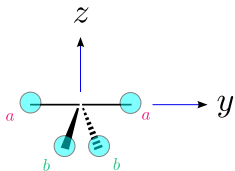


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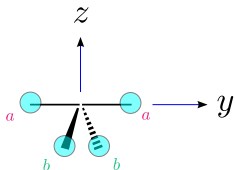


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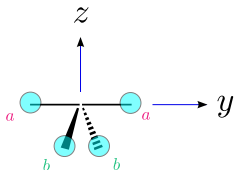
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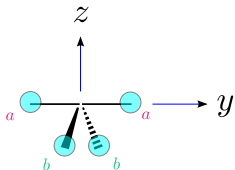
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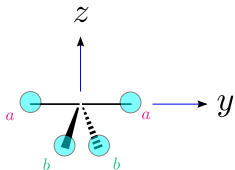
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- The sulfur $3s$ orbital (-20.7 eV) belongs to the totally symmetric representation
- The sulfur $3p$ orbitals (-11.6 eV) transform as A_1 (p_z), B_1 (p_x), and B_2 (p_y)

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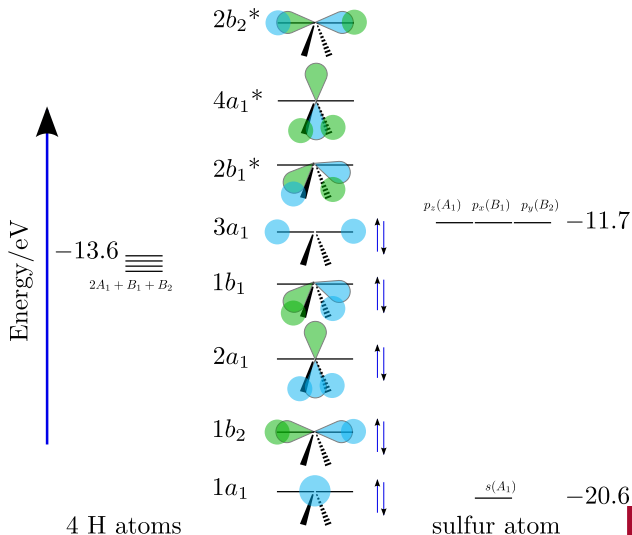
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Qualitative MO Diagram for SH₄ in C_{2v}



Analysis of the MO Diagram for SH₄ in C_{2v}

- The 1a₁ MO is a nonbonding 3s electron “lone pair” on sulfur
- The 2a₁, 1b₁, and 1b₂ MOs are bonding MOs between the sulfur 3p orbitals and symmetry adapted combinations of H 1s orbital functions
- The 3a₁ MO is a nonbonding “lone pair” of electrons localized on the H atoms on the y axis
- The MOs marked with “*” are antibonding counterparts to the three bonding MOs
- Three bonding MOs and one lone pair satisfy the octet rule for sulfur
- Inspect the MOs for SH₄ also in C_{4v} symmetry: [click here for the applet!](#)

Analysis of the MO Diagram for SH_4 in C_{2v}

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