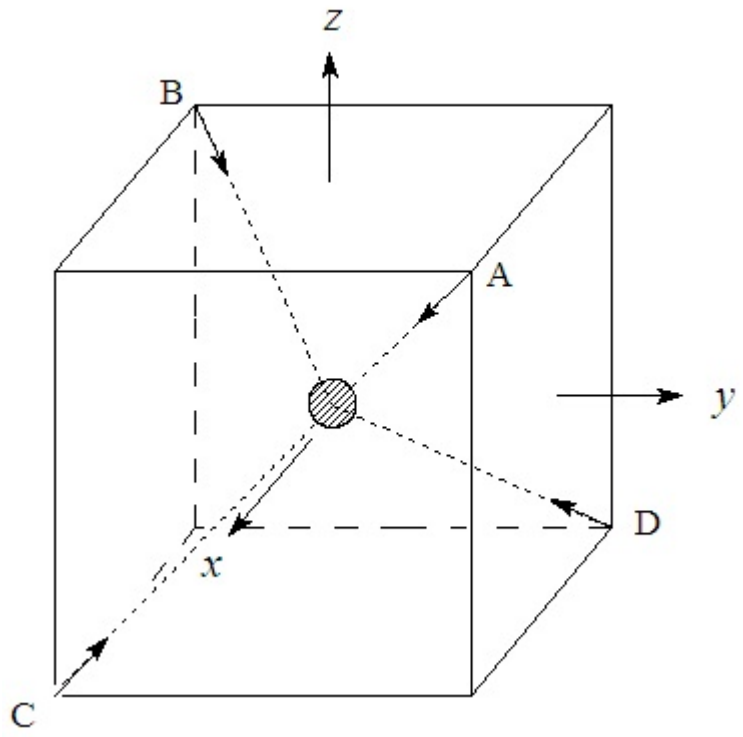
General MOs for CH_4

✔ The four pendant H atoms in their sigma interactions with central C AOs can be represented by a set of four tetrahedrally oriented vectors point toward the center of a cube.



✔ Counting nonshifted vectors after applying a representative operation from each class yields the following reducible representation:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_{SALC}	4	1	0	0	2

$$\Rightarrow A_1 + T_2$$

Forming the Hydrogen SALCs

✔ The following SALC equations have the requisite symmetries:

$$A_1: \quad \Phi_1 = \tfrac{1}{2}\{1s_A + 1s_B + 1s_C + 1s_D\}$$

$$T_2: \quad \Phi_2 = \tfrac{1}{2}\{1s_A + 1s_B - 1s_C - 1s_D\}$$
$$\Phi_3 = \tfrac{1}{2}\{1s_A - 1s_B - 1s_C + 1s_D\}$$
$$\Phi_4 = \tfrac{1}{2}\{1s_A - 1s_B + 1s_C - 1s_D\}$$

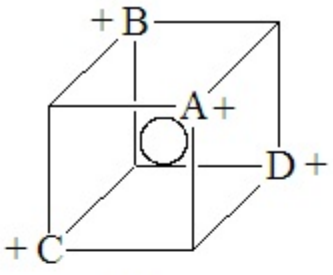
Carbon AO Symmetries

✔ From vector transformation properties listed in the T_d character table:

$$s = A_1 \qquad (p_x, p_y, p_z) = T_2$$

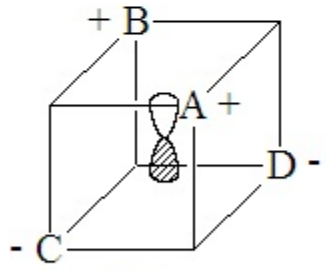
✔ Assuming 1*s* orbital on C is nonbonding, LCAOs are formed between 2*s* and 2*p* AOs on C with the four SALCs defined above.

Representations of Bonding LCAO-MOs of CH_4

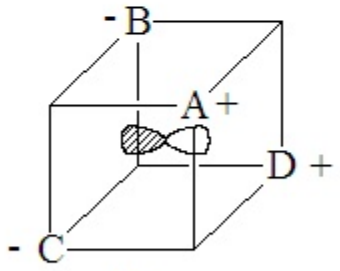


σ_2

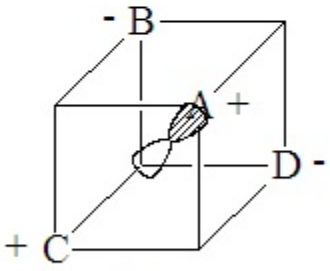
A_1



σ_3



σ_4



σ_5

T_2

LCAO MO Equations for CH_4

$\sigma_1^{\,n} = c_0(1s)$ nonbonding core (a_1)

a_1 MOs:

$\sigma_2 = c_1(2s) + c_2\Phi_1$ bonding
$\sigma_6^{\,*} = c_3(2s) - c_4\Phi_1$ antibonding

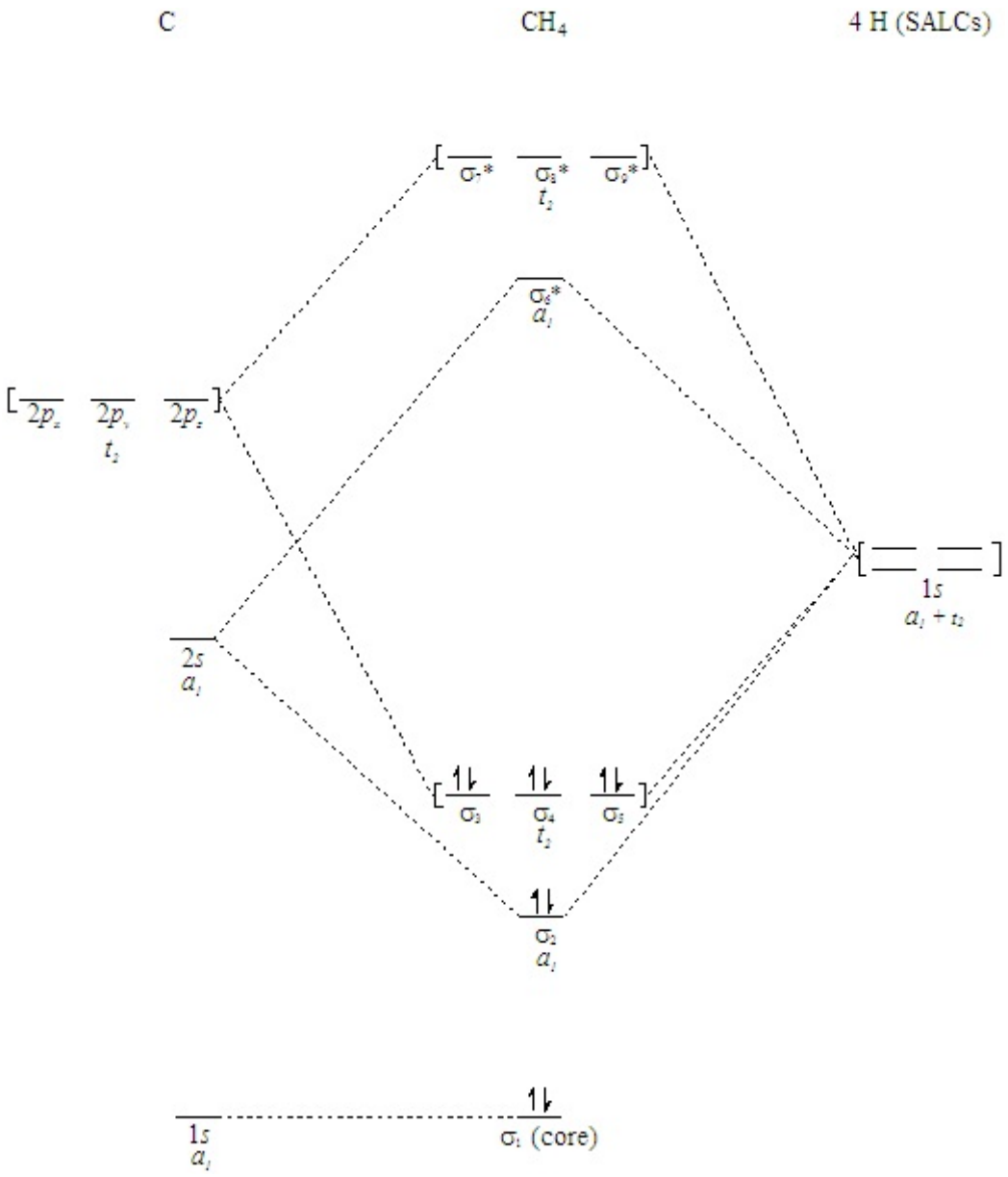
t_2 MOs:

$\sigma_3 = c_5(2p_z) + c_6\Phi_2$ bonding
$\sigma_7^{\,*} = c_7(2p_z) - c_8\Phi_2$ antibonding

$\sigma_4 = c_9(2p_y) + c_{10}\Phi_3$ bonding
$\sigma_8^{\,*} = c_{11}(2p_y) - c_{12}\Phi_3$ antibonding

$\sigma_5 = c_{13}(2p_x) + c_{14}\Phi_4$ bonding
$\sigma_9^{\,*} = c_{15}(2p_x) - c_{16}\Phi_4$ antibonding

Qualitative MO Scheme for CH_4



Photoelectron Spectrum of CH_4