COURSE 5

4/22/2015

Restricted and unrestricted HF formalisms

Topics
- RHF & UHF formalisms
- E (H_i, J_{ij}, K_{ij})
- spin contamination
- Hartree-Fock-Roothaan equations
- Population analysis

RHF & UHF formalisms

Spin orbitals: - monoelectronic functions

$\chi = \phi \cdot \eta$

η → spin function: $\eta = \eta(\sigma)$ < α, β

ϕ → spatial function: $\phi = \phi(\vec{r})$

$\chi = \chi(\vec{x})$, $\vec{x} = \{\vec{r}, \sigma\}$

Cases:

(A) The same ϕ for a pair of electrons

$$\Rightarrow \quad \begin{aligned} &a)\ \chi_1(\vec{x}) = \phi_r(\vec{r}) \cdot \alpha \\ &b)\ \chi_2(\vec{x}) = \phi_r(\vec{r}) \cdot \beta \end{aligned} \qquad (1)$$

$\langle \chi_1 | \chi_2 \rangle = 0$ - orthogonal wfs.

Restricted Slater determinant

- an SD constructed with spin-orbitals of type (1)

$$\begin{matrix} \chi_1 & \longrightarrow & \chi_2 & \equiv \\ \downarrow & & & \\ \phi_1 \alpha & & \phi_1 \beta & \\ \downarrow & & \downarrow & \\ \phi_1 & & \bar{\phi}_1 & \end{matrix}$$

$\Rightarrow$

Total wavefunction:

$$\Psi = |\chi_1 \chi_2 \cdots \chi_N\rangle = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_{N/2} \bar{\phi}_{N/2}\rangle$$

spatial functions

$\phi_i \to \phi_1 \cdot \alpha$

$\bar{\phi}_i \to \phi_i \cdot \beta$

RHF formalism

- all the electrons are paired

$\longrightarrow$ "closed-shell" system

Monoelectronic integrals for RHF

$\langle \phi_i | h | \bar{\phi}_i \rangle = \langle \bar{\phi}_i | h | \phi_i \rangle = 0$ (because $\langle \alpha | \beta \rangle = 0$)

↳ antiparallel spins

$\langle \phi_i | h | \phi_i \rangle = \langle \bar{\phi}_i | h | \bar{\phi}_i \rangle \neq 0$ ($\langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$)

$\rightarrow$ spatial integration only (spin has already been integrated)

Bielectronic integrals

$\langle \phi_i \phi_j | \frac{1}{r_{12}} | \phi_i \phi_j \rangle$ — $J \neq 0$, $K \neq 0$ — $i(1\alpha)\, j(2\alpha)$, $i(1\alpha)\, j(2\alpha)$

$= \langle \phi_i \bar{\phi}_j | \frac{1}{r_{12}} | \phi_i \bar{\phi}_j \rangle$ — $J \neq 0$, $K = 0$

$= \langle \bar{\phi}_i \phi_j | \frac{1}{r_{12}} | \bar{\phi}_i \phi_j \rangle$ — $J \neq 0$, $K = 0$

$= \langle \bar{\phi}_i \bar{\phi}_j | \frac{1}{r_{12}} | \bar{\phi}_i \bar{\phi}_j \rangle$ — $J \neq 0$, $K \neq 0$

4 J_{ij} identical terms $\neq 0$

2 K_{ij} identical terms $\neq 0$

J: $i(1\alpha) j(2\beta) \frac{1}{r_{12}} i(1\alpha) j(2\beta) \neq 0$

K: $i(1\alpha) j(2\beta) \frac{1}{r_{12}} (i 2\alpha) j(1\beta) = 0$

$\Rightarrow$ general case (UHF): $E_{UHF} = \sum_{i=1}^{N} H_i + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (J_{ij} - K_{ij})$

RHF case: $E_{RHF} = 2 \sum_{i=1}^{N/2} H_i + \sum_{i=1}^{N/2} \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})$

Having 2 electrons described by ϕ_1 & ϕ_2

$\Rightarrow$:

$\phi_1 \bar{\phi}_2$ or $\bar{\phi}_1 \phi_2$: $E(\uparrow\downarrow) = h_1 + h_2 + J_{12}$

$\phi_1 \phi_2$ or $\bar{\phi}_1 \bar{\phi}_2$: $E(\uparrow\uparrow) = h_1 + h_2 + J_{12} - K_{12}$

$\Rightarrow E(\uparrow\downarrow) > E(\uparrow\uparrow)$

(for different spatial orbitals)

RHF equations

RHF Fock operator:

$$\hat{F}_i = \hat{h}(i) + \sum_{j=1}^{N/2} \left[2\hat{J}_j(i) - \hat{K}_j(i) \right]$$

$$\Rightarrow \boxed{\hat{F}_i \phi_i(i) = \varepsilon_i \phi_i(i)}$$

$$\boxed{\varepsilon_i = H_i + \sum_{j=1}^{N/2} (2J_{ij} - K_{ij})}$$

Summary

Given a set of K spatial orbitals (MO orbitals)

ϕ_i, $i = \overline{1,K}$

$\Rightarrow$ $2K$ spin-orbitals χ_i, $i = \overline{1,2K}$

with

$\chi_{2i-1}(\vec{x}) = \phi_i(\vec{r})\,\alpha(\omega)$

$\chi_{2i}(\vec{x}) = \phi_i(\vec{r})\,\beta(\omega)$ $\quad i = \overline{1,K}$

$\rightarrow$ restricted MOs $\rightarrow$ restricted Ψ

Example

Li atom

$\uparrow$ ϕ_{2s}

$\uparrow\downarrow$ ϕ_{1s}

restricted MOs

$$|\Psi_{RHF}\rangle = |\phi_{1s} \bar{\phi}_{1s} \phi_{2s}\rangle$$

? Is it a good idea to use restricted MOs ?

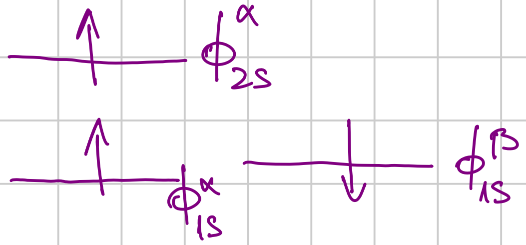
For Li, $K_{1s(\alpha)2s(\alpha)} \neq 0$ while $K_{1s(\beta)2s(\alpha)} = 0$

$\Rightarrow$ $1s(\alpha)$ and $1s(\beta)$ electrons feel a different electrostatic potential

$\Rightarrow$ paired electrons would be better described by different spatial functions

Li atom

$$|\Psi_{UHF}\rangle = |\phi_{1s}^{\alpha}\ \bar{\phi}_{1s}^{\beta}\ \phi_{2s}^{\alpha}\rangle$$



$\hookrightarrow$ unrestricted MOs

Obs. $E_{1s\beta} > E_{1s\alpha}$ because:

Coulomb repulsion $(J-K)$ contributes positively to E_e and $E^{rep}_{1s_\alpha 2s_\alpha} < E^{rep}_{1s_\beta 2s_\alpha}$

ϕ^α and ϕ^β are normalized:

$$\langle \phi_i^\alpha | \phi_j^\alpha \rangle = \delta_{ij}$$

$$\langle \phi_i^\beta | \phi_j^\beta \rangle = \delta_{ij}$$

but $\langle \phi_i^\alpha | \phi_j^\beta \rangle \neq 0$
$= S_{ij}^{\alpha\beta}$

The same basis set is used to expand the $\{\phi^\alpha\}$ and $\{\phi^\beta\}$ functions

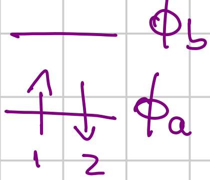
How to write E_e in terms of H_i, J_{ij} and K_{ij}?

$$E_e = \sum_i H_i + \frac{1}{2}\sum_i\sum_j (J_{ij} - K_{ij})$$

$$\varepsilon_i = H_i + \sum_j (J_{ij} - K_{ij})$$

Examples

(1)



$$E_{UHF} = H_1 + H_2 + \frac{1}{2}\Big[\overbrace{J_{11} - K_{11}}^{=0} + J_{12} - \underbrace{K_{12}}_{=0} + J_{21} - \underbrace{K_{21}}_{=0} + \overbrace{J_{22} - K_{22}}^{=0}\Big]$$

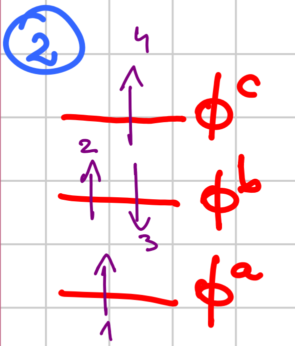
$$= H_1 + H_2 + \frac{1}{2}(J_{12} + \underbrace{J_{21}}_{= J_{12}})$$

$$= H_1 + H_2 + J_{12}$$

$$= H_a + H_a + J_{ab}$$

$$\boxed{E = 2H_a + J_{ab}}$$

2



(triplet state)

$$E = H_1+H_2+H_3+H_4 + \frac{1}{2}\Big[\cancel{J_{11}-K_{11}} + J_{12}-K_{12} + J_{13} - \cancel{K_{13}} + J_{14} - K_{14}$$

$$+ J_{21} - K_{21} + \cancel{J_{22}-K_{22}} + J_{23} - \cancel{K_{23}} + J_{24} - K_{24}$$

$$+ J_{31} - \cancel{K_{31}} + J_{32} - \cancel{K_{32}} + \cancel{J_{33}-K_{33}} + J_{34} - \cancel{K_{34}}$$

$$+ J_{41} - K_{41} + J_{42} - K_{42} + J_{43} - \cancel{K_{43}} + \cancel{J_{44}-K_{44}}\Big]$$

$$E = \underbrace{H_1+H_2+H_3+H_4}_{} + \frac{1}{2}\Big[2J_{12} + 2J_{13} + 2J_{14} + 2J_{23} + 2J_{24} + 2J_{34} - 2K_{12} - 2K_{14} - 2K_{24}\Big]$$

$$E = H_a + 2H_b + H_c + \frac{1}{2}\Big[2J_{ab} + 2J_{ab} + 2J_{ac} + 2J_{bb} + 2J_{bc} + 2J_{bc} - 2K_{ab} - 2K_{ac} - 2K_{bc}\Big]$$

$$\boxed{E = H_a + 2H_b + H_c + 2J_{ab} + J_{ac} + J_{bb} + 2J_{bc} - K_{ab} - K_{ac} - K_{bc}}$$

Homework

1) Calculate the energy of the electronic system given above the singlet state

2) What is the energetic order for the following 3 systems?

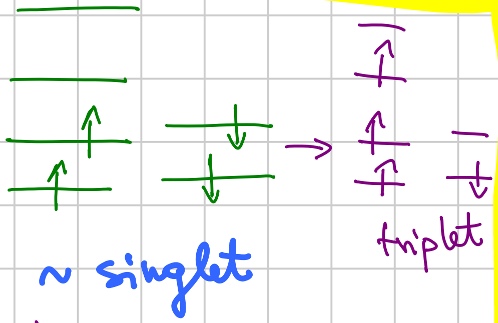
a) b) c)

UHF wavefunction and spin contamination

UHF wfs

- eigenfunctions of $\hat{S}_z$
- they are not eigenfunctions of $\hat{S}^2$

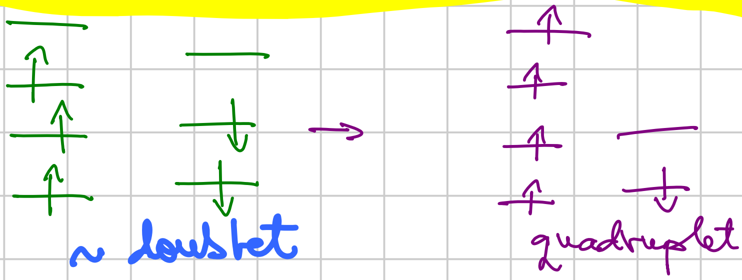
→ spin contamination



$|^1\Psi\rangle = C_1^2|1\rangle + C_3^2|3\rangle + \dots$

$|1\rangle$ exact singlet state

$|3\rangle$ —"— triplet state



$|^2\Psi\rangle = C_2^2|2\rangle + C_4^2|4\rangle + \dots$

$|2\rangle$ – exact doublet state

- - -

$$\langle S^2\rangle_{UHF} = \langle S^2\rangle_{exact} + N_\beta - \sum_i\sum_j |S_{ij}^{\alpha\beta}|^2$$

$$\langle S^2\rangle_{exact} = \left(\frac{N_\alpha - N_\beta}{2}\right)\left(\frac{N_\alpha - N_\beta}{2} + 1\right) = S(S+1)$$

$$S_{ij}^{\alpha\beta} = \langle \phi_i^\alpha | \phi_i^\beta \rangle$$

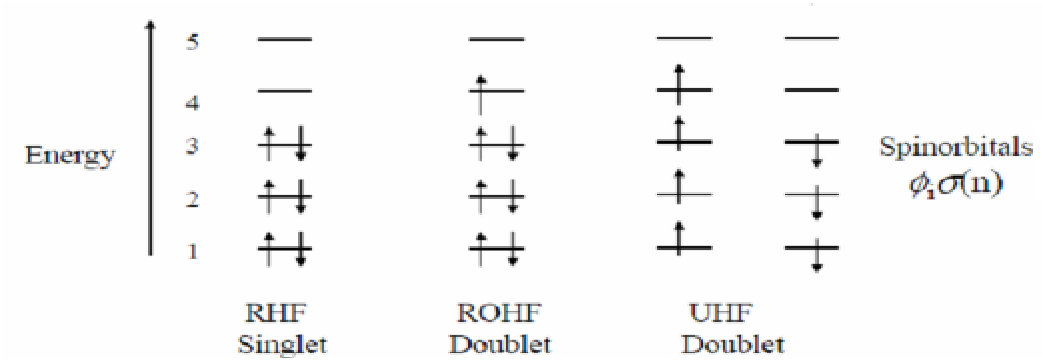
State	S	M=2S+1	$\langle S^2\rangle_{exact} \to S(S+1)$
singlet	0	1	0.0
doublet	1/2	2	0.75
triplet	1	3	2.0
----	3/2	4	3.75

! if $\langle S^2\rangle \neq S(S+1)$ by less than 10% → OK

Else

- check the wf
- remove spin-contamination
  - spin projection procedure
    - generate correct spin states by applying projection operators that interchange the spin of electrons

Comparison of the R(O)HF and UHF formalisms



R(O)HF	UHF
Spin-orbitals for pairs of electrons with α and β spin are constrained to have the same spatial dependence	Spin-orbitals for electrons with α and β spins have different spatial parts
Wavefunction is an eigenfuction of the $\mathbf{S}^2$ operator	Wavefunction is not an eigenfuction of the $\mathbf{S}^2$ operator; Spin-contamination
Not suitable for the calculation of spin-dependent properties	Yields qualitatively correct spin densities
	$E_{UHF} \leq E_{R(O)HF}$
	Different density matrices for the two sets of electrons; their sum gives the electronic density, while their difference gives the spin density

Hartree - Fock Roothaan equations

HF equations: $\hat{F}_i \phi_i = \varepsilon_i \phi_i$

ϕ_i - elements of ψ^{SD}:

$$\psi^{SD} = \begin{vmatrix} \phi_1(1) & \phi_2(2) & \dots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \dots & \phi_N(2) \\ \dots \end{vmatrix} \qquad \underline{\underline{\phi = \sum BFi}} \qquad \begin{vmatrix} \sum_1 BFi(1) & \sum_2 BF_i(2) & \dots \\ \dots \end{vmatrix}$$

$$\underline{\underline{BFi = \sum GTOi}} \qquad \begin{vmatrix} \sum\sum GTOi & \dots \\ \dots \end{vmatrix}$$

$\phi \to LCAO$

Given $\{f_\mu\}$ $\mu = \overline{1,K}$ a set of know functions (basis functions) forming a basis set

$$\phi_i = \sum_{\mu=1}^{K} c_{\mu i} f_\mu \quad , i = \overline{1,K} \qquad (1)$$

– independent linear combinations of basis functions

$\Rightarrow$ finding ϕ_i means finding $c_{\mu i}$

$c_{\mu i}$ – give the contributions of f_μ to ϕ_i MO

$\sum_\mu c_{\mu i}^2 = 1$ because $\{f_\mu\}$ - orto-normalized set

Find $c_{\mu i}$

Start with HF eq.:

$$\hat{F}_i \phi_i = \varepsilon_i \phi_i \qquad (2)$$

Use (1):

$$\hat{F}_i \sum_\mu c_{\mu i} f_\mu(k) = \varepsilon_i \sum_\mu c_{\mu i} f_\mu(k) \qquad (3)$$

Multiply (1) by $f_\nu^*(k)$ and integrate:

$$\Rightarrow \sum_i c_{\mu i} \int f_\nu^*(k) \hat{F}_i f_\mu(k) \, d\tau_k = \varepsilon_i \sum_\mu c_{\mu i} \int f_\nu^*(k) f_\mu(k) \, d\tau_k \qquad (4)$$

Notations:

$F_{\mu\nu} = \int f_\nu^* \hat{F}_i f_\mu \, d\tau$ – Fock matrix elements

– Hermitian square matrix (conjugate = transpose)

$S_{\mu\nu} = \int f_\nu^* f_\mu \, d\tau$ – overlap matrix elements
$(0 \leq S_{\mu\nu} \leq 1)$

$$\Rightarrow \boxed{\sum_\mu F_{\mu\nu} C_{\mu i} = \varepsilon_i \sum_\mu S_{\mu\nu} C_{\mu i}}$$

$i = \overline{1,K}$

$K = \#$ BFs $= \#$ MOs

- HFR equations

Matrix form: $\boxed{F C = S C \varepsilon}$ $C = \{C_{\mu i}\}$; $F = \{F_{\mu\nu}\}$

$$C = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ - & - & - & - \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix} \qquad \varepsilon = \begin{pmatrix} \varepsilon_1 & 0 & \cdots & 0 \\ 0 & \boxed{\varepsilon_2} & \cdots & 0 \\ 0 & 0 & \cdots & \varepsilon_K \end{pmatrix}$$

→ ϕ_K

→ corresponds to ϕ_2

→ ϕ_1

OM normalization condition:

$\phi_i = \sum_\mu c_{\mu i} f_\mu \qquad \phi_j = \sum_\nu c_{\nu j} f_\nu$

$\langle \phi_i | \phi_j \rangle = \delta_{ij} \Longrightarrow$

$$\sum_\mu \sum_\nu \int C_{\mu i} f_\mu C_{\nu j} f_\nu \, d\tau = \sum_\mu \sum_\nu \left[c_{\mu i} c_{\nu j} \int f_\mu f_\nu \, d\tau \right] = \delta_{ij}$$

$$\Rightarrow \boxed{\sum_\mu \sum_\nu c_{\mu i} c_{\nu j} S_{\mu\nu} = \delta_{ij}}$$

- MOs ortonormalization means the ortonormalization of $c_{\mu i}$ through $S_{\mu\nu}$

Solving the HFR equations

Start from: $FC = SC\varepsilon$ (1)

S – Hermitian matrix

$\Rightarrow \exists\ S^{1/2}$ and $S^{-1/2}$ so that $S^{-1/2} S^{+1/2} = \mathbb{1}$

and $S^{1/2} S^{1/2} = S$

$S^{1/2}$?

if a matrix A is diagonal:

$$f(A) = \begin{pmatrix} f(a_1) & \cdots & \\ \vdots & f(a_2) & \cdots \\ & \cdots & \end{pmatrix}$$

If A is non-diagonal:

- find a matrix B that diagonalizes A: $A' = BAB^{-1}$

$|A'| = |A|$

Thus:

If S – non-diagonal $\Rightarrow$ diagonalize S

Then, multiply (1) by $S^{-1/2}$ (to left):

$$S^{-1/2}FC = S^{-1/2}SC\varepsilon \qquad (2)$$

Multiply (2) by $S^{-1/2}S^{1/2}$ in front of C:

$$\underbrace{S^{-1/2}FS^{-1/2}}_{F'}\underbrace{S^{1/2}C}_{C'} = \underbrace{S^{-1/2}SS^{-1/2}}_{\mathbb{1}}\underbrace{S^{1/2}C}_{C'}\varepsilon$$

$$\Rightarrow \boxed{F'C' = C'\varepsilon}$$

Algorithm

0. start with C^0
1. calculate $F^0_{\mu\nu}$
2. calculate S
3. diagonalize S
4. calculate $S^{1/2}$
5. calculate $F' = S^{-1/2}FS^{-1/2}$
6. diagonalize F'
7. calculate C' and ε
8. calculate $C = S^{-1/2}C'$
9. calculate E_e
10. convergence test

Population analysis

Assume a "closed-shell" molecule:
Charge density:

$$\rho(r) = 2\sum_i^{N/2} |\phi_i(r)|^2$$

ρ - integrates to N and $\phi_i = \sum_{\mu=1}^{K} c_{\mu i} f_\mu$

$$\Rightarrow \rho = 2\sum_{i=1}^{N/2} \phi_i^*(r)\phi_i(r) = 2\sum_{i=1}^{N/2}\sum_\mu^K c_{\mu i}^* f_\mu^*(r) \sum_\nu^K c_{\nu i} f_\nu(r) =$$

$$= \sum_\mu^K \sum_\nu^K \underbrace{\left[2\sum_{i=1}^{N/2} c_{\mu i}^* c_{\nu i}\right]}_{D_{\mu\nu}} f_\mu^*(r) f_\nu(r)$$

Notation: $D_{\mu\nu} = 2\sum_i^{N/2} c_{\mu i}^* c_{\nu i}$ - density matrix elements

$$\Rightarrow \int \rho(r)\,dr = \int \sum_\mu^K \sum_\nu^K D_{\mu\nu} f_\mu^*(r) f_\nu(r)\,dr =$$

$$= \sum_\mu^K \sum_\nu^K D_{\mu\nu} \underbrace{\int f_\mu^*(r) f_\nu(r)\,dr}_{S_{\mu\nu}}$$

S - is symmetric

$$= \sum_\mu^K \sum_\nu^K D_{\mu\nu} S_{\mu\nu} = \sum_\mu \sum_\nu D_{\mu\nu} S_{\nu\mu} = N$$

$$\Rightarrow \boxed{\sum_\mu^K \sum_\nu^K D_{\mu\nu} S_{\mu\nu} = N} = \sum_\mu^K \sum_\nu^K (\underbrace{DS}_{P})_{\mu\nu} = \sum_\mu^K \sum_\nu^K (P_{\mu\nu})$$

- electronic charge distribution can be decomposed in contributions associated with the basis functions

Example

$$\phi_i = c_{ij} f_j + c_{ik} f_k$$

Probability density associated with ϕ_i is:

$$\phi_i^2 = c_{ij}^2 f_j^2 + c_{ik}^2 f_k^2 + 2c_{ij}c_{ik} f_j f_k$$

Integrating (taken into account that f_i - normalized):

$$1 = c_{ij}^2 + c_{ik}^2 + 2c_{ij}c_{ik}S_{jk} \quad \text{with } S_{jk} = \langle f_j | f_k \rangle$$

Interpretation

One e^- from ϕ_i contributes:

- c_{ij}^2 to the charge in φ_j
- c_{ik}^2 — " — φ_k
- $2c_{ij}c_{ik}S_{jk}$ to the electronic charge in the overlap region between φ_j & φ_k.

$\Rightarrow$ c_{ij}^2, c_{ik}^2 - atomic orbitals populations

$2c_{ij}c_{ik}S_{jk}$ - overlap populations

$\longrightarrow$ >0 - bonding orbital

<0 - antibonding orbital

$=0$ - non-bonding orbital

$D_{\mu\nu}S_{\mu\nu}$ - nondiagonal elements

$\mu \neq \nu$ - overlap electronic population of φ_μ & φ_ν

- suggest the contribution to the chemical bond for the two functions φ_μ & φ_ν centered on two different atoms

$D_{\mu\mu}S_{\mu\mu}$ - diagonal elements

- net electronic charge in φ_μ

$$\sum_{\nu=1}^{K}\sum_{\mu\in A} D_{\mu\mu}S_{\mu\mu} = q_M(A)$$ - Mulliken charge of atom A

$$2D_{\mu\nu}S_{\mu\nu} = Q_{\mu\nu} \quad (\mu \neq \nu)$$

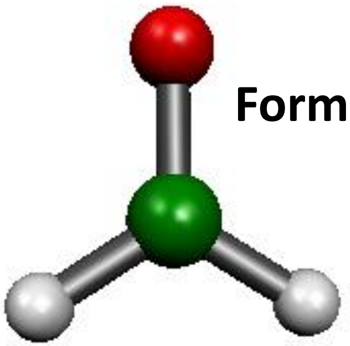
- overlap population associated with 2 BFs centered on two different atoms

$$q_A^{net} = Z_A - \sum_{\nu}^{K}\sum_{\mu\in A} D_{\mu\nu}S_{\mu\nu}$$ - net charge of atom A

$$q_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} Q_{\mu\nu}$$ - overlap population between atoms A & B

Population analysis gives:

- partial atomic charges, gross populations
- dipole, quadrupole, ... moments
- MEP
- electrofilicity, nucleofilicity



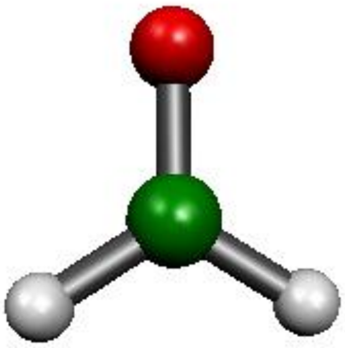
Formaldehyde (CH_2O) (aqueous solution: formol)

- an important precursor to many chemical compounds, especially for polymers.
- gas at room temperature which converts readily to a variety of derivatives.
- annual world production: more than 21 million tonnes.
- intermediate in the oxidation (or combustion) of methane as well as other carbon compounds (forest fires, automobile exhaust, tobacco smoke).
- can be produced in the atmosphere by the action of sunlight and oxygen on atmospheric methane and other hydrocarbons (part of smog).
- the first polyatomic organic molecule detected in the interstellar medium (Zuckerman, B.; Buhl, D.; Palmer, P.; Snyder, L. E., *Observation of interstellar formaldehyde*, *Astrophys. J.* 160 (1970) 485) → used to map out kinematic features of dark clouds
- mechanism of formation: hydrogenation of CO ice:

  $H + CO \rightarrow HCO$ $\quad\quad$ $HCO + H \rightarrow H_2CO$ (low reactivity in gas phase)

Due to its widespread use, toxicity and volatility, exposure to formaldehyde is very important for human health. It is used to make the hard pill coatings that dissolve slowly and deliver a more complete dosage.

Is it carcinogen**?**



Formaldehyde
Mulliken population analysis

```
#P RHF/STO-3G scf(conventional) Iop(3/33=6) Extralinks=L316 Noraff
Symm=Noint Iop(3/33=1) pop(full)
```

Basis functions:

```
 1 1   O   1S
 2         2S
 3         2PX
 4         2PY
 5         2PZ
 6 2   C   1S
 7         2S
 8         2PX
 9         2PY
10         2PZ
11 3   H   1S
12 4   H   1S
```

$c_{\mu i}$

Molecular Orbital Coefficients

				1	2	3	4	5	6	7	8	9	10	11	12
				(A1)--O	(A1)--O	(A1)--O	(A1)--O	(B2)--O	(A1)--O	(B1)--O	(B2)--O	(B1)--V	(A1)--V	(B2)--V	(A1)--V
EIGENVALUES --				-20.31271	-11.12506	-1.33740	-0.80774	-0.63285	-0.54552	-0.44316	-0.35437	0.28196	0.62855	0.73426	0.91288
1	1	O	1S	0.99429	0.00013	-0.21937	0.09883	0.00000	-0.09380	0.00000	0.00000	0.00000	0.02812	0.00000	0.11576
2			2S	0.02593	-0.00571	0.76901	-0.42911	0.00000	0.49908	0.00000	0.00000	0.00000	-0.16162	0.00000	-0.86372
3			2PX	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.67589	0.00000	-0.76726	0.00000	0.00000	0.00000
4			2PY	0.00000	0.00000	0.00000	0.00000	0.44236	0.00000	0.00000	0.86988	0.00000	0.00000	-0.31859	0.00000
5			2PZ	-0.00562	0.00164	-0.17016	-0.16466	0.00000	0.67685	0.00000	0.00000	0.00000	0.24629	0.00000	0.92385
6	2	C	1S	0.00053	0.99263	-0.12253	-0.18563	0.00000	0.03302	0.00000	0.00000	0.00000	-0.20805	0.00000	-0.09473
7			2S	-0.00718	0.03289	0.27715	0.57744	0.00000	-0.10672	0.00000	0.00000	0.00000	1.30303	0.00000	0.63126
8			2PX	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.60935	0.00000	0.82111	0.00000	0.00000	0.00000
9			2PY	0.00000	0.00000	0.00000	0.00000	0.53317	0.00000	0.00000	-0.18211	0.00000	0.00000	1.14827	0.00000
10			2PZ	-0.00629	0.00052	0.15773	-0.22622	0.00000	-0.44752	0.00000	0.00000	0.00000	-0.44473	0.00000	1.17321
11	3	H	1S	0.00019	-0.00651	0.03174	0.26454	0.30023	0.15896	0.00000	-0.35922	0.00000	-0.88918	-0.83976	0.15496
12	4	H	1S	0.00019	-0.00651	0.03174	0.26454	-0.30023	0.15896	0.00000	0.35922	0.00000	-0.88918	0.83976	0.15496

$$D_{\mu\nu} = \boxed{2} \sum_{i=1}^{oc} c_{\mu i} c_{\nu i}$$

DENSITY MATRIX.

				1	2	3	4	5	6	7	8	9	10	11	12
1	1	O	1S	2.11060											
2			2S	-0.46428	2.05059										
3			2PX	0.00000	0.00000	0.91365									
4			2PY	0.00000	0.00000	0.00000	1.90474								
5			2PZ	-0.09605	0.55490	0.00000	0.00000	1.02847							
6	2	C	1S	0.01217	-0.00750	0.00000	0.00000	0.15078	2.07173						
7			2S	-0.00170	-0.17657	0.00000	0.00000	-0.42877	-0.22405	0.84555					
8			2PX	0.00000	0.00000	0.82370	0.00000	0.00000	0.00000	0.00000	0.74260				
9			2PY	0.00000	0.00000	0.00000	0.15489	0.00000	0.00000	0.00000	0.00000	0.63487			
10			2PZ	-0.04248	-0.01029	0.00000	0.00000	-0.58492	0.01680	-0.07818	0.00000	0.00000	0.55274		
11	3	H	1S	0.00892	-0.01946	0.00000	-0.35934	0.11724	-0.10842	0.28875	0.00000	0.45099	-0.25196	0.63097	
12	4	H	1S	0.00892	-0.01946	0.00000	0.35934	0.11724	-0.10842	0.28875	0.00000	-0.45099	-0.25196	-0.24576	0.63097

Example

$$D_{51} = 2(c_{51}c_{11} + c_{52}c_{12} + \ldots + c_{58}c_{18})$$

DENSITY MATRIX.

				1	2	3	4	5	6	7	8	9	10	11	12
1	1	O	1S	2.11060											
2			2S	-0.46428	2.05059										
3			2PX	0.00000	0.00000	0.91365									
4			2PY	0.00000	0.00000	0.00000	1.90474								
5			2PZ	-0.09605	0.55490	0.00000	0.00000	1.02847							
6	2	C	1S	0.01217	-0.00750	0.00000	0.00000	0.15078	2.07173						
7			2S	-0.00170	-0.17657	0.00000	0.00000	-0.42877	-0.22405	0.84555					
8			2PX	0.00000	0.00000	0.82370	0.00000	0.00000	0.00000	0.00000	0.74260				
9			2PY	0.00000	0.00000	0.00000	0.15489	0.00000	0.00000	0.00000	0.00000	0.63487			
10			2PZ	-0.04248	-0.01029	0.00000	0.00000	-0.58492	0.01680	-0.07818	0.00000	0.00000	0.55274		
11	3	H	1S	0.00892	-0.01946	0.00000	-0.35934	0.11724	-0.10842	0.28875	0.00000	0.45099	-0.25196	0.63097	
12	4	H	1S	0.00892	-0.01946	0.00000	0.35934	0.11724	-0.10842	0.28875	0.00000	-0.45099	-0.25196	-0.24576	0.63097

*** Overlap *** $S_{\mu\nu}$

	1	2	3	4	5	6	7	8	9	10	11	12
1	0.100000D+01											
2	0.236704D+00	0.100000D+01										
3	0.000000D+00	0.000000D+00	0.100000D+01									
4	0.000000D+00	0.000000D+00	0.000000D+00	0.100000D+01								
5	0.000000D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.100000D+01							
6	0.108247D-05	0.357592D-01	0.000000D+00	0.000000D+00	-0.600792D-01	0.100000D+01						
7	0.364526D-01	0.361125D+00	0.000000D+00	0.000000D+00	-0.320209D+00	0.248362D+00	0.100000D+01					
8	0.000000D+00	0.000000D+00	0.208659D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.100000D+01				
9	0.000000D+00	0.000000D+00	0.000000D+00	0.208659D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.100000D+01			
10	0.612920D-01	0.440440D+00	0.000000D+00	0.000000D+00	-0.313477D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.000000D+00	0.100000D+01		
11	0.456968D-02	0.705422D-01	0.000000D+00	0.358513D-01	-0.701419D-01	0.606312D-01	0.484179D+00	0.000000D+00	0.389690D+00	-0.250597D+00	0.100000D+01	
12	0.456968D-02	0.705422D-01	0.000000D+00	-0.358513D-01	-0.701419D-01	0.606312D-01	0.484179D+00	0.000000D+00	-0.389690D+00	-0.250597D+00	0.151054D+00	0.100000D+01

$$\int \rho(r)dr = \sum_{\mu}^{oc}\sum_{\nu}^{oc} D_{\mu\nu}S_{\mu\nu} = N$$

$D_{\mu\nu}S_{\mu\nu} \rightarrow$ Population matrix

Full Mulliken population analysis:

				1	2	3	4	5	6	7	8	9	10	11	12
1	1	O	1S	2.11060											
2			2S	-0.10990	2.05059										
3			2PX	0.00000	0.00000	0.91365									
4			2PY	0.00000	0.00000	0.00000	1.90474								
5			2PZ	0.00000	0.00000	0.00000	0.00000	1.02847							
6	2	C	1S	0.00000	-0.00027	0.00000	0.00000	-0.00906	2.07173						
7			2S	-0.00006	-0.06376	0.00000	0.00000	0.13730	-0.05565	0.84555					
8			2PX	0.00000	0.00000	0.17187	0.00000	0.00000	0.00000	0.00000	0.74260				
9			2PY	0.00000	0.00000	0.00000	0.03232	0.00000	0.00000	0.00000	0.00000	0.63487			
10			2PZ	-0.00260	-0.00453	0.00000	0.00000	0.18336	0.00000	0.00000	0.00000	0.00000	0.55274		
11	3	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	0.63097	
12	4	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	-0.03712	0.63097

Full Mulliken population analysis:

				1	2	3	4	5	6	7	8	9	10	11	12
1	1	O	1S	2.11060	-0.10990	0.00000	0.00000	0.00000	0.00000	-0.00006	0.00000	0.00000	-0.00260	0.00004	0.00004
2			2S	-0.10990	2.05059	0.00000	0.00000	0.00000	-0.00027	-0.06376	0.00000	0.00000	-0.00453	-0.00137	-0.00137
3			2PX	0.00000	0.00000	0.91365	0.00000	0.00000	0.00000	0.00000	0.17187	0.00000	0.00000	0.00000	0.00000
4			2PY	0.00000	0.00000	0.00000	1.90474	0.00000	0.00000	0.00000	0.00000	0.03232	0.00000	-0.01288	-0.01288
5			2PZ	0.00000	0.00000	0.00000	0.00000	1.02847	-0.00906	0.13730	0.00000	0.00000	0.18336	-0.00822	-0.00822
6	2	C	1S	0.00000	-0.00027	0.00000	0.00000	-0.00906	2.07173	-0.05565	0.00000	0.00000	0.00000	-0.00657	-0.00657
7			2S	-0.00006	-0.06376	0.00000	0.00000	0.13730	-0.05565	0.84555	0.00000	0.00000	0.00000	0.13981	0.13981
8			2PX	0.00000	0.00000	0.17187	0.00000	0.00000	0.00000	0.00000	0.74260	0.00000	0.00000	0.00000	0.00000
9			2PY	0.00000	0.00000	0.00000	0.03232	0.00000	0.00000	0.00000	0.00000	0.63487	0.00000	0.17575	0.17575
10			2PZ	-0.00260	-0.00453	0.00000	0.00000	0.18336	0.00000	0.00000	0.00000	0.00000	0.55274	0.06314	0.06314
11	3	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	0.63097	-0.03712
12	4	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	-0.03712	0.63097

Gross orbital populations:

				1
1	1	O	1S	1.99812
2			2S	1.86939
3			2PX	1.08552
4			2PY	1.91130
5			2PZ	1.32361
6	2	C	1S	1.99361
7			2S	1.14299
8			2PX	0.91448
9			2PY	1.01868
10			2PZ	0.85524
11	3	H	1S	0.94353
12	4	H	1S	0.94353

= sum over the line (or column) corresponding to the C(1s) basis function

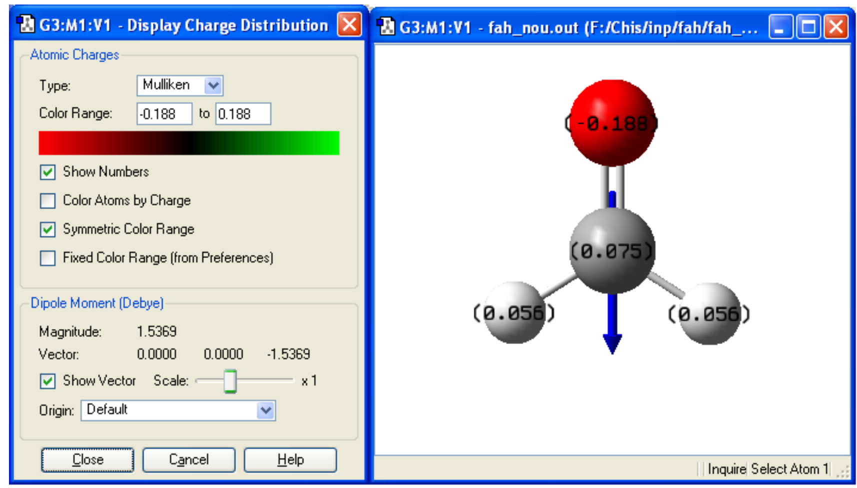
$$q_\mu = D_{\mu\mu} + \sum_\mu \sum_{\nu>\mu} D_{\mu\nu} S_{\mu\nu}$$

= sum over the line (or column) corresponding to the O(2px) basis function

$q_1=P_{11}+P_{12}S_{12}+P_{13}S_{13}+\ldots+P_{1\,12}S_{1\,12}$

Full Mulliken population analysis:

				1	2	3	4	5	6	7	8	9	10	11	12
1	1	O	1S	2.11060	-0.10990	0.00000	0.00000	0.00000	0.00000	-0.00006	0.00000	0.00000	-0.00260	0.00004	0.00004
2			2S	-0.10990	2.05059	0.00000	0.00000	0.00000	-0.00027	-0.06376	0.00000	0.00000	-0.00453	-0.00137	-0.00137
3			2PX	0.00000	0.00000	0.91365	0.00000	0.00000	0.00000	0.00000	0.17187	0.00000	0.00000	0.00000	0.00000
4			2PY	0.00000	0.00000	0.00000	1.90474	0.00000	0.00000	0.00000	0.00000	0.03232	0.00000	-0.01288	-0.01288
5			2PZ	0.00000	0.00000	0.00000	0.00000	1.02847	-0.00906	0.13730	0.00000	0.00000	0.18336	-0.00822	-0.00822
6	2	C	1S	0.00000	-0.00027	0.00000	0.00000	-0.00906	2.07173	-0.05565	0.00000	0.00000	0.00000	-0.00657	-0.00657
7			2S	-0.00006	-0.06376	0.00000	0.00000	0.13730	-0.05565	0.84555	0.00000	0.00000	0.00000	0.13981	0.13981
8			2PX	0.00000	0.00000	0.17187	0.00000	0.00000	0.00000	0.00000	0.74260	0.00000	0.00000	0.00000	0.00000
9			2PY	0.00000	0.00000	0.00000	0.03232	0.00000	0.00000	0.00000	0.00000	0.63487	0.00000	0.17575	0.17575
10			2PZ	-0.00260	-0.00453	0.00000	0.00000	0.18336	0.00000	0.00000	0.00000	0.00000	0.55274	0.06314	0.06314
11	3	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	0.63097	-0.03712
12	4	H	1S	0.00004	-0.00137	0.00000	-0.01288	-0.00822	-0.00657	0.13981	0.00000	0.17575	0.06314	-0.03712	0.63097



Condensed to atoms (all electrons):

		1	2	3	4
1	O	7.788259	0.444556	-0.022438	-0.022438
2	C	0.444556	4.736204	0.372121	0.372121
3	H	-0.022438	0.372121	0.630970	-0.037123
4	H	-0.022438	0.372121	-0.037123	0.630970

Off-diagonal elements represent the number of electrons shared between the pairs of atoms (overlap population)

! The total overlap population between oxygen and carbon is 2*(0.444556)

0.444556 is the population received by each of the two atoms for which the overlap population has been calculated.

Gross orbital populations:

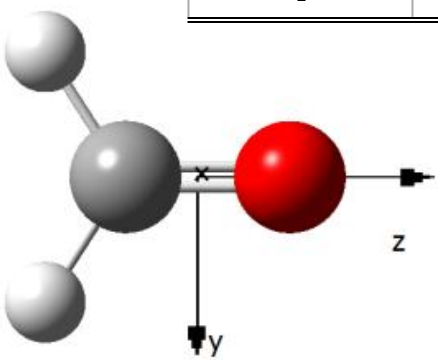
				1
1	1	O	1S	1.99912
2			2S	1.86939
3			2PX	1.08552
4			2PY	1.91130
5			2PZ	1.32361
6	2	C	1S	1.99361
7			2S	1.14299
8			2PX	0.91448
9			2PY	1.01868
10			2PZ	0.85524
11	3	H	1S	0.94353
12	4	H	1S	0.94353

Atomic populations (AP)		Total atomic charges (Q=Z-AP)	
1 O	8.186789	1 O	-0.186789
2 C	5.926642	2 C	0.073358
3 H	0.943285	3 H	0.056715
4 H	0.943285	4 H	0.056715

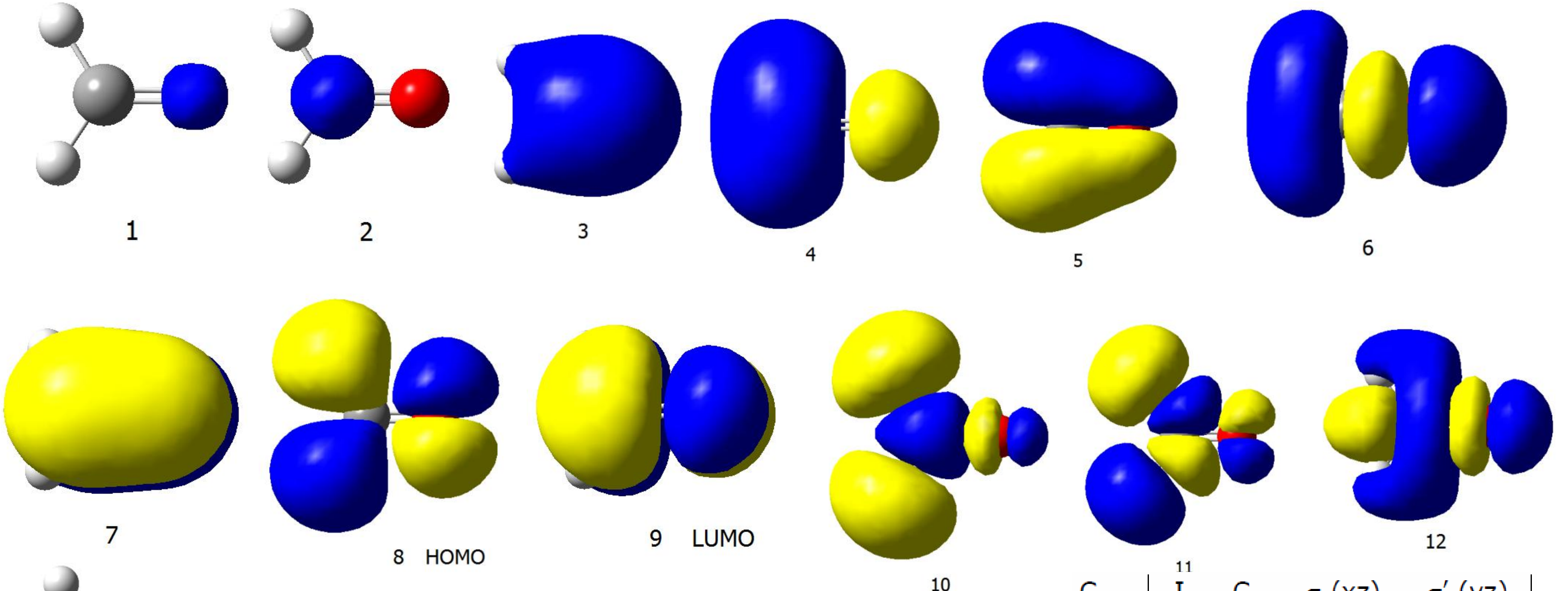
Notation for irreducible representations

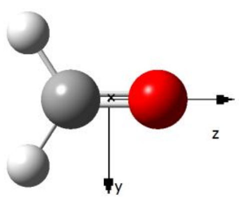
Dimension of the representation	Symbol
1	A, B
2	E
3	T (F)
4	G
5	H

Symmetry of the representation	Symbol			
	Rotation C_n	$C_2 \perp C_n$ or σ_v (σ_d)	σ_h	i
symmetric	A	1	'	g
antisymmetric	B	2	''	u



C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$			
A_1	1	1	1	1	z	x^2, y^2, z^2	$z^3, z(x^2-y^2)$
A_2	1	1	-1	-1	R_z	xy	xyz
B_1	1	-1	1	-1	x, R_y	xz	$xz^2, x(x^2-3y^2)$
B_2	1	-1	-1	1	y, R_x	yz	$yz^2, y(3x^2-y^2)$
$\Gamma_{x,y,z}$	3	-1	1	1			





C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
	3	-1	1	1

Molecular orbitals of formaldehyde (RHF/STO-3G)

Molecular Orbital Coefficients

				1	2	3	4	5	6	7	8	9	10	11	12
				(A1)--O	(A1)--O	(A1)--O	(A1)--O	(B2)--O	(A1)--O	(B1)--O	(B2)--O	(B1)--V	(A1)--V	(B2)--V	(A1)--V
EIGENVALUES --				-20.31271	-11.12506	-1.33740	-0.80774	-0.63285	-0.54552	-0.44316	-0.35437	0.28196	0.62855	0.73426	0.91288
1	1	O	1S	0.99429	0.00013	-0.21937	0.09883	0.00000	-0.09380	0.00000	0.00000	0.00000	0.02812	0.00000	0.11576
2			2S	0.02593	-0.00571	0.76901	-0.42911	0.00000	0.49908	0.00000	0.00000	0.00000	-0.16162	0.00000	-0.86372
3			2PX	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.67589	0.00000	-0.76726	0.00000	0.00000	0.00000
4			2PY	0.00000	0.00000	0.00000	0.00000	0.44236	0.00000	0.00000	0.86988	0.00000	0.00000	-0.31859	0.00000
5			2PZ	-0.00562	0.00164	-0.17016	-0.16466	0.00000	0.67685	0.00000	0.00000	0.00000	0.24629	0.00000	0.92385
6	2	C	1S	0.00053	0.99263	-0.12253	-0.18563	0.00000	0.03302	0.00000	0.00000	0.00000	-0.20805	0.00000	-0.09473
7			2S	-0.00718	0.03289	0.27715	0.57744	0.00000	-0.10672	0.00000	0.00000	0.00000	1.30303	0.00000	0.63126
8			2PX	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.60935	0.00000	0.82111	0.00000	0.00000	0.00000
9			2PY	0.00000	0.00000	0.00000	0.00000	0.53317	0.00000	0.00000	-0.18211	0.00000	0.00000	1.14827	0.00000
10			2PZ	-0.00629	0.00052	0.15773	-0.22622	0.00000	-0.44752	0.00000	0.00000	0.00000	-0.44473	0.00000	1.17321
11	3	H	1S	0.00019	-0.00651	0.03174	0.26454	0.30023	0.15896	0.00000	-0.35922	0.00000	-0.88918	-0.83976	0.15496
12	4	H	1S	0.00019	-0.00651	0.03174	0.26454	-0.30023	0.15896	0.00000	0.35922	0.00000	-0.88918	0.83976	0.15496

Excited state symmetry

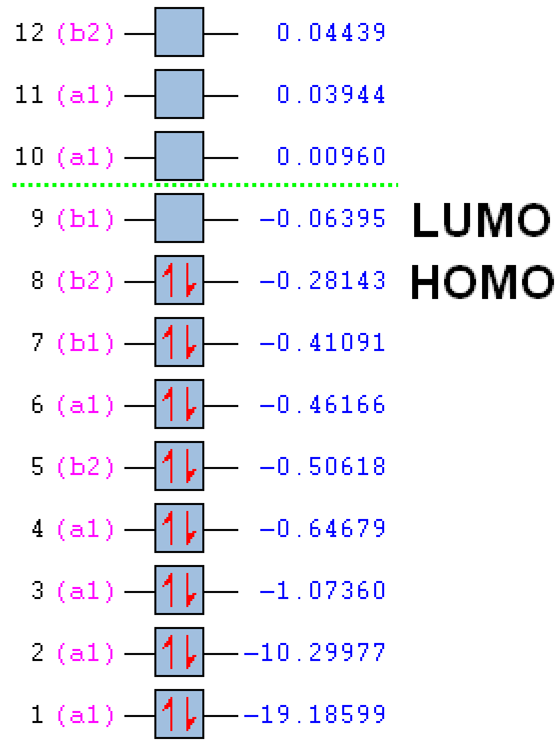
Formaldehyde

ground state:

$a_1^2\ a_1^2\ a_1^2\ a_1^2\ b_2^2\ a_1^2\ b_1^2\ b_2^2$

first excited state

$a_1^2\ a_1^2\ a_1^2\ a_1^2\ b_2^2\ a_1^2\ b_1^2\ b_2^1\ b_1^1$



C_{2v}	I	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$			
A_1	1	1	1	1	z	x^2, y^2, z^2	$z^3, z(x^2-y^2)$
A_2	1	1	-1	-1	R_z	xy	xyz
B_1	1	-1	1	-1	x, R_y	xz	$xz^2, x(x^2-3y^2)$
B_2	1	-1	-1	1	y, R_x	yz	$yz^2, y(3x^2-y^2)$
$\Gamma_{x,y,z}$	3	-1	1	1			

$B_2 x B_1$ = 1 1 -1 -1 $= A_2$

The symmetry of the first excited state of formaldehyde (as a result of HOMO-LUMO transition)

ground state	moment dipol component	excited state
A_1	A_1 (μ_z) B_1 (μ_x) B_2 (μ_y)	A_2

$$P = \int \Psi'^{*} \hat{\mu} \Psi \, d\tau$$

$A_1 x A_1 x A_2 = A_2$
$A_1 x B_1 x A_2 = B_2$
$A_1 x B_2 x A_2 = B_1$

Thus, HOMO-LUMO transition is not allowed!
Transitions HOMO-LUMO+1, HOMO-LUMO+2 are allowed