COMPUTATIONS WITH XMVB@XACS

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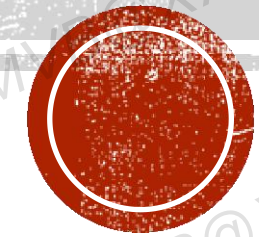

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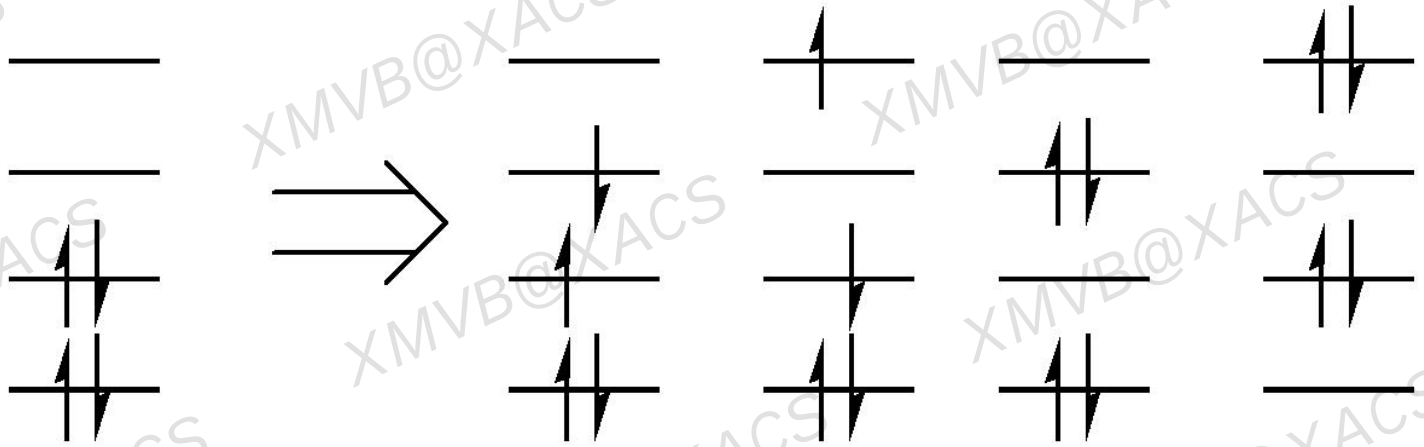
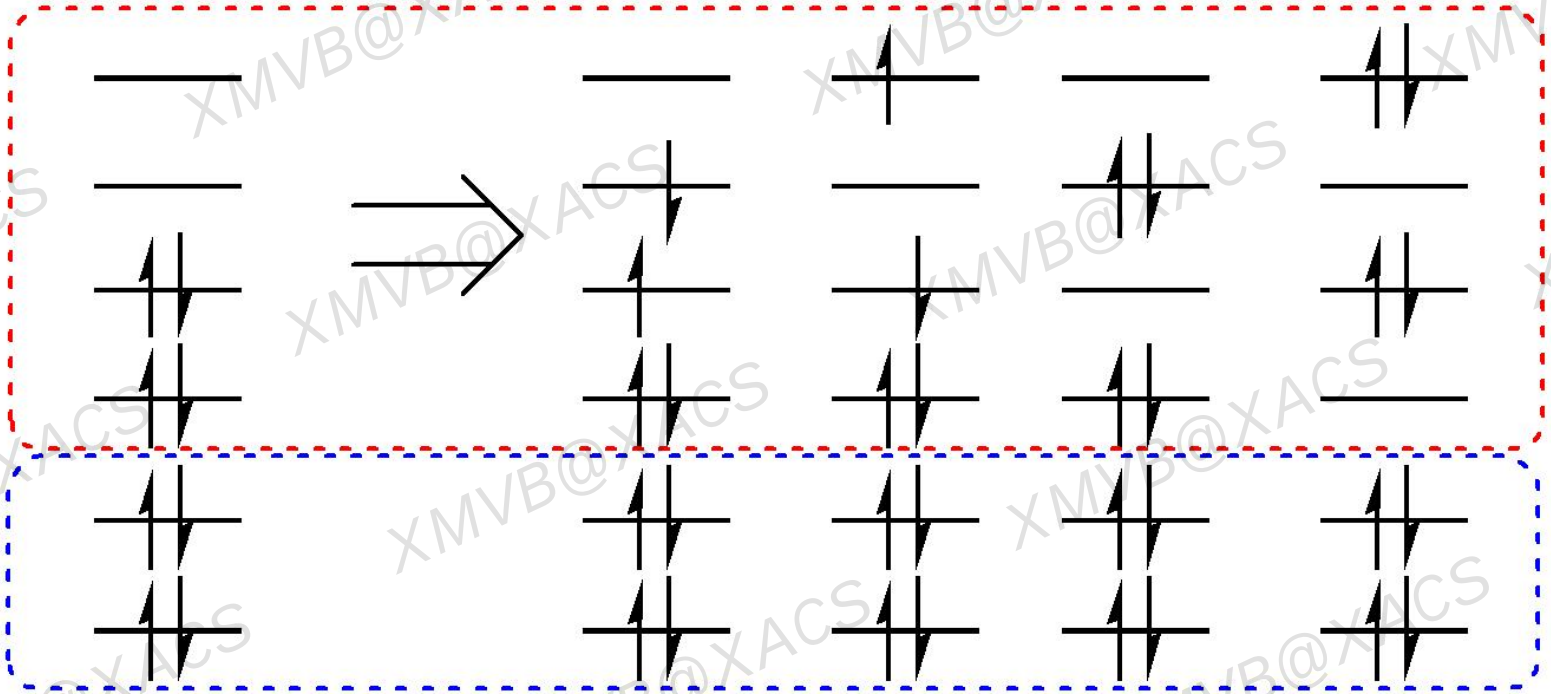
ACTIVE SPACE

- Multiconfigurational methods:
  - CASSCF/RASSCF
  - VB
  - ...
- Generating multiple determinants/configurations by excitations:



ACTIVE SPACE

- Spaces in Multiconfigurational wave function:
  - Inactive space: orbitals are always doubly occupied
  - Active space: orbitals are arbitrarily occupied



ACTIVE SPACE IN MULTICONFIGURATIONAL COMPUTATIONS

- 3 parameters to define an active space
  - Number of active electrons, m
  - Number of active orbitals, n
  - Multiplicity, S (same as multiplicity of the molecule)
- In VB computations, the interested bonds, unpaired electrons and corresponding orbitals (S > 1) should be included in the active space

ACTIVE SPACE: SOME EXAMPLES

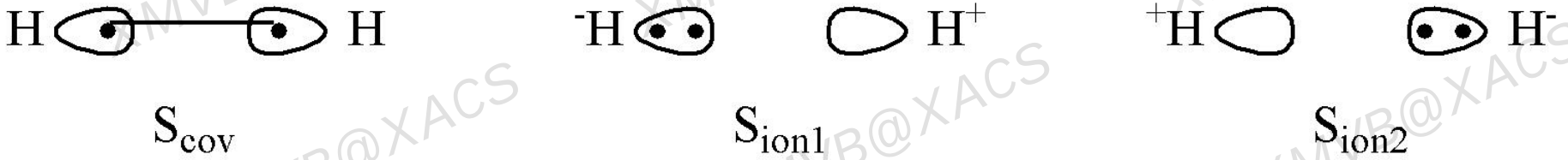
- H_2
  - m=2, n=2, S=1 (H-H bond)
- O_2
  - m=8, n=6, S=3 (p_x, p_y and p_z orbitals)
- Benzene
  - m=6, n=6, S=1 (π orbitals)

H_2: BASIC CONCEPTS

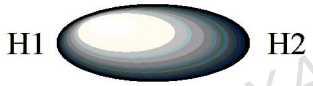
- The basic concepts of VB Theory:
  - Active space
  - VB structures and determinants
  - VB orbitals
- How to run VB computation:
  - Basic keywords
  - How to define active space
  - How to define VB orbitals
- Difference between DFT, CASSCF and VB

H_2: BASIC CONCEPTS

- VB Structures



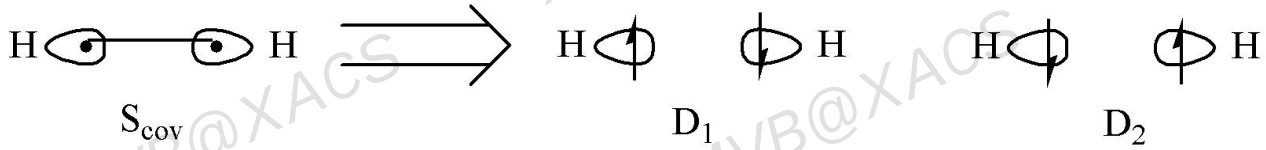
- VB Orbitals
  - s orbitals on each H atoms
- Spaces
  - No inactive space
  - Active space: m=2, n=2, S=1



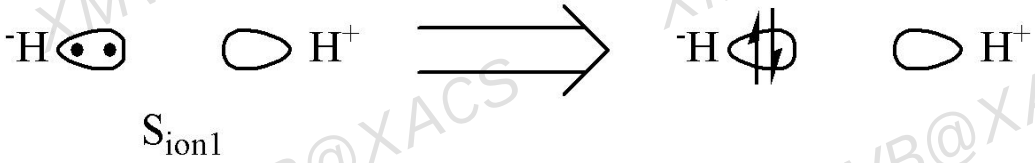
H_2: BASIC CONCEPTS

- Wave Function

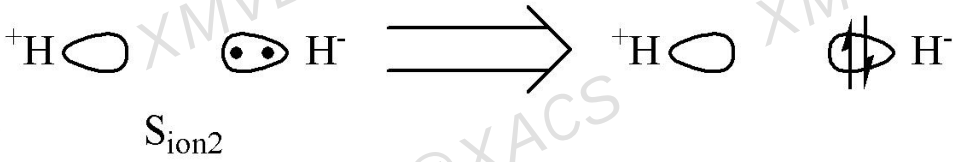
$$\Phi_{cov} = \frac{1}{\sqrt{2+2S_{ab}}}(|\phi_a\overline{\phi_b}| - |\overline{\phi_a}\phi_b|)$$



$$\Phi_{ion1} = |\phi_a\overline{\phi_a}|$$



$$\Phi_{ion2} = |\phi_b\overline{\phi_b}|$$

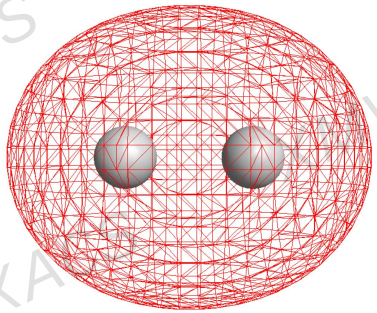


$$\Psi = \sum_K C_K\Phi_K = C_{cov}\Phi_{cov} + C_{ion1}\Phi_{ion1} + C_{ion2}\Phi_{ion2} = C_{cov}\Phi_{cov} + C_{ion}(\Phi_{ion1} + \Phi_{ion2})$$

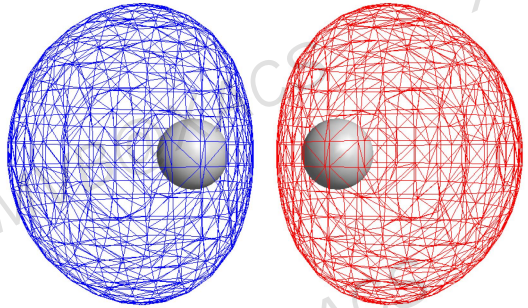
H_2: BASIC CONCEPTS

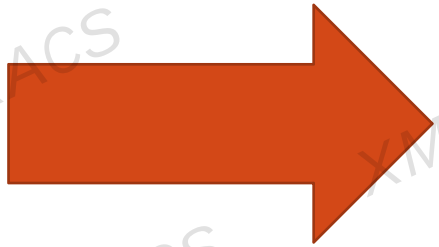
CASSCF Orbitals

ϕ_g

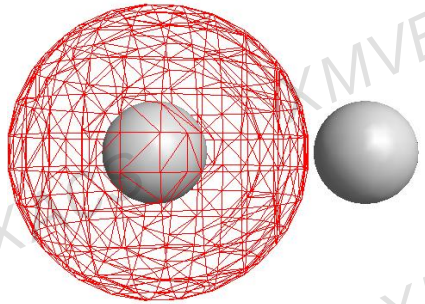


ϕ_u

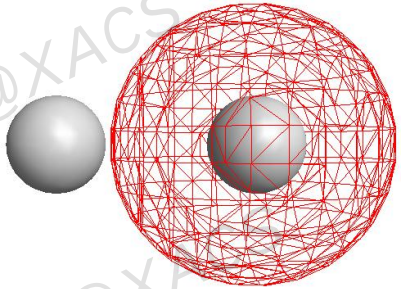




VB Orbitals



ϕ_{H_1}



ϕ_{H_2}

H_2: BASIC CONCEPTS

Energies (in a.u.) of H_2 by various methods

Methods	Energy
HF	-1.128743
B3LYP	-1.166743
CASSCF	-1.147207
VBSCF	-1.146944

H_2: BASIC CONCEPTS

Coefficents by CASSCF

Configurations	Coefficients
$\lvert\phi_g\overline{\phi_g}\rvert$	0.994
$\lvert\phi_g\overline{\phi_u}\rvert - \lvert\overline{\phi_g}\phi_u\rvert$	0.000
$\lvert\phi_u\overline{\phi_u}\rvert$	-0.110

Coefficents by VBSCF

Structure	Coefficients
S_{cov}	-0.835
S_{ion1}	-0.100
S_{ion2}	-0.100

F_2: BDE AND RESONANCE ENERGY

- Computations of bond dissociation energy (BDE) and resonance energy (RE)
  - How to compute BDE
  - How to compute RE
  - Definition of charge-shift (C-S) bond

F_2: BDE AND RESONANCE ENERGY

- Bond Dissociation Energy (BDE):

$$E^{BDE} = E^{\infty} - E^{eq}$$

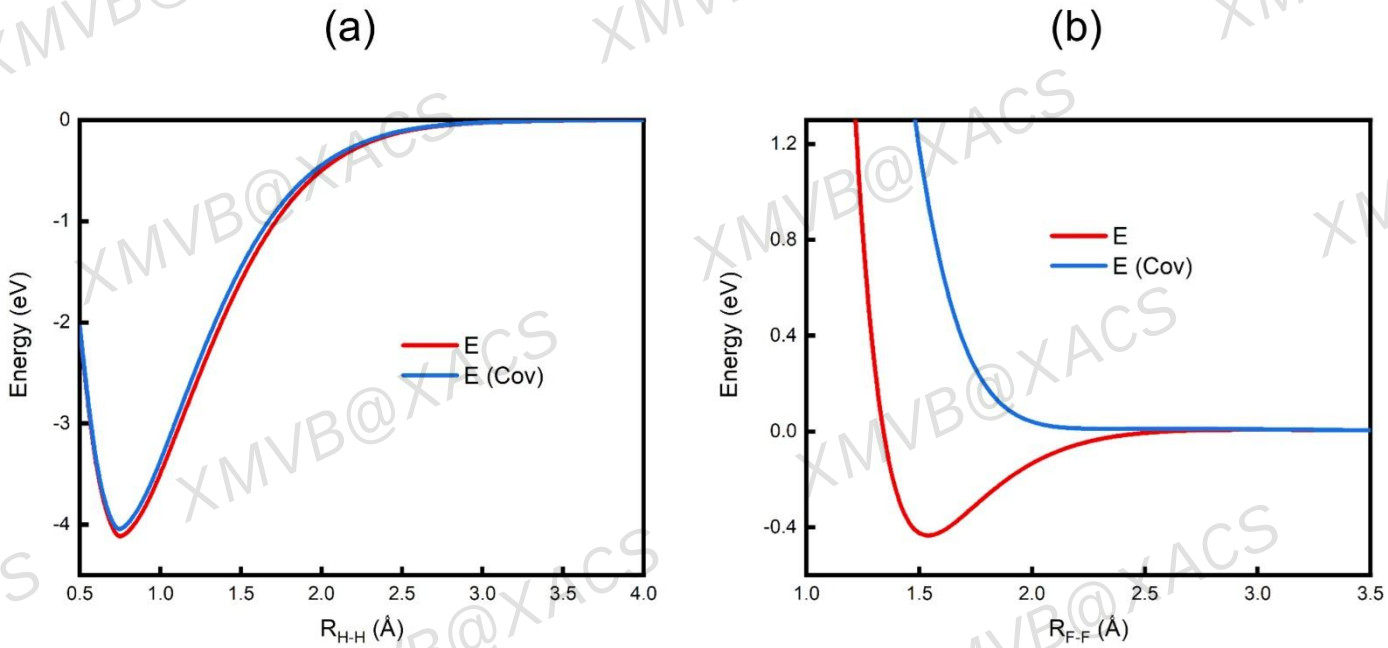
- Resonance Energy (RE):

$$E^{RE} = E^{FULL} - E^{K}$$

- Relative Resonance Energy (RRE):

$$RRE = \frac{E^{RE}}{E^{BDE}} \times 100\%$$

RRE > 50% : Charge-Shift Bond



F_2: BDE AND RESONANCE ENERGY

- VB Structures

S_{cov} S_{ion1} S_{ion2}

- Spaces:
  - Inactive space: m=16 n=8 (1s, 2s, $2p_x$, $2p_y$)
  - Active space: m=2 n=2 ($2p_z$)

F_2: BDE AND RESONANCE ENERGY

Fragments

$FRAG
1*6
① SPZDXXDYYDZZ 1
② SPZDXXDYYDZZ 2
③ PXDXZ 1
④ PXDXZ 2
⑤ PYDYZ 1
⑥ PYDYZ 2
$END

6 fragments
1 atom in each

s, pz, dxx, etc on atom 1

px and dxz on atom 1

py and dyz on atom 1

Orbitals

$ORB
1*10
① 1
② 2
③ 1
④ 2
⑤ 3
⑥ 4
⑦ 5
⑧ 6
⑨ 1
⑩ 2
$END

10 orbitals
1 fragment in each

fragment 1 in orbital 1

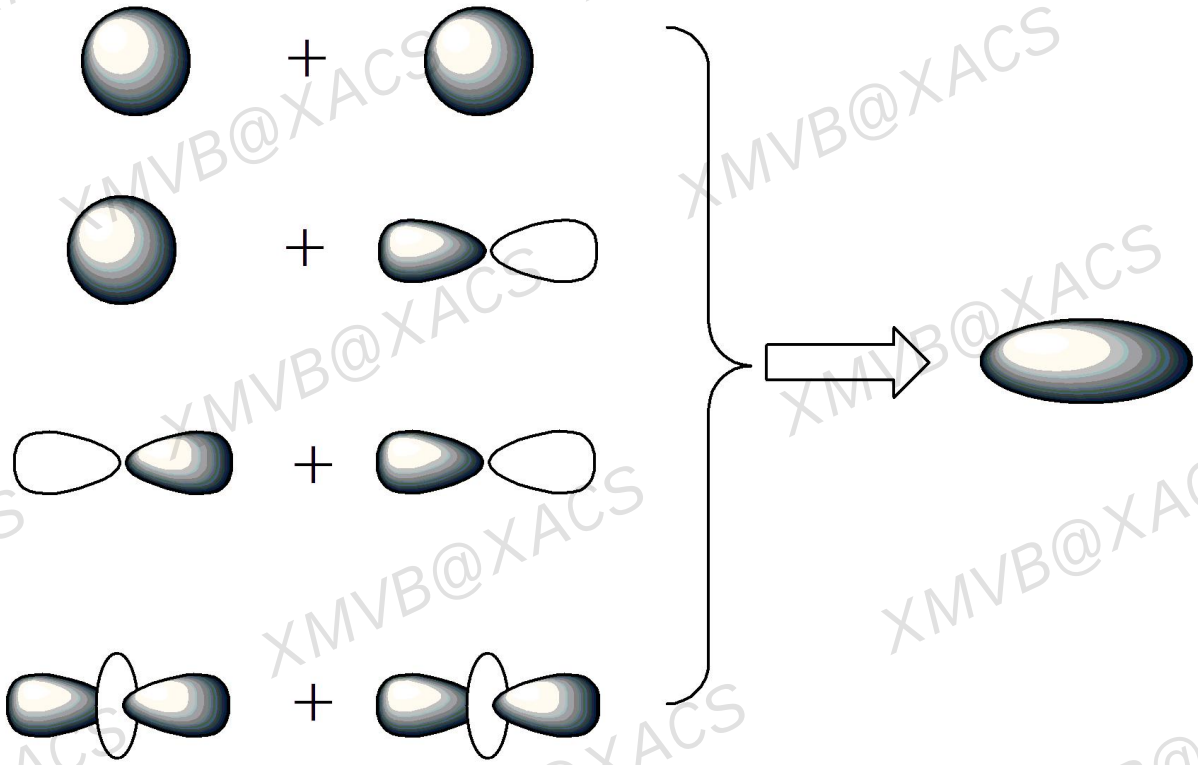
fragment 3 in orbital 5

Inactive space

Active space

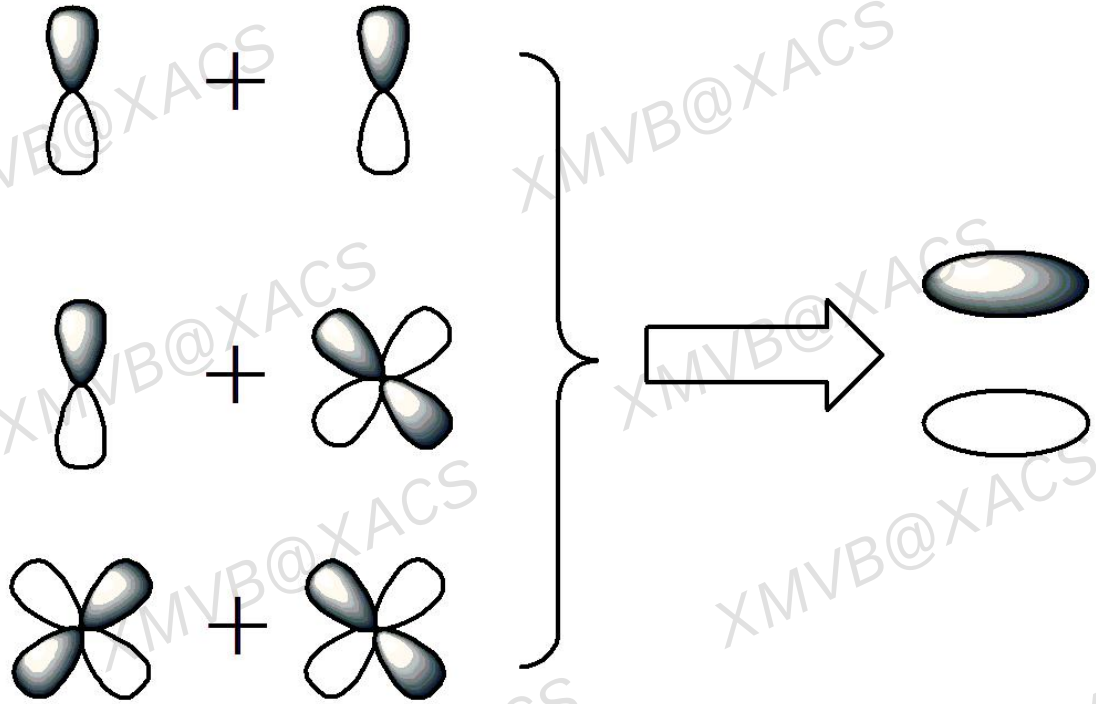
F_2: BDE AND RESONANCE ENERGY

- σ Bonding in F_2

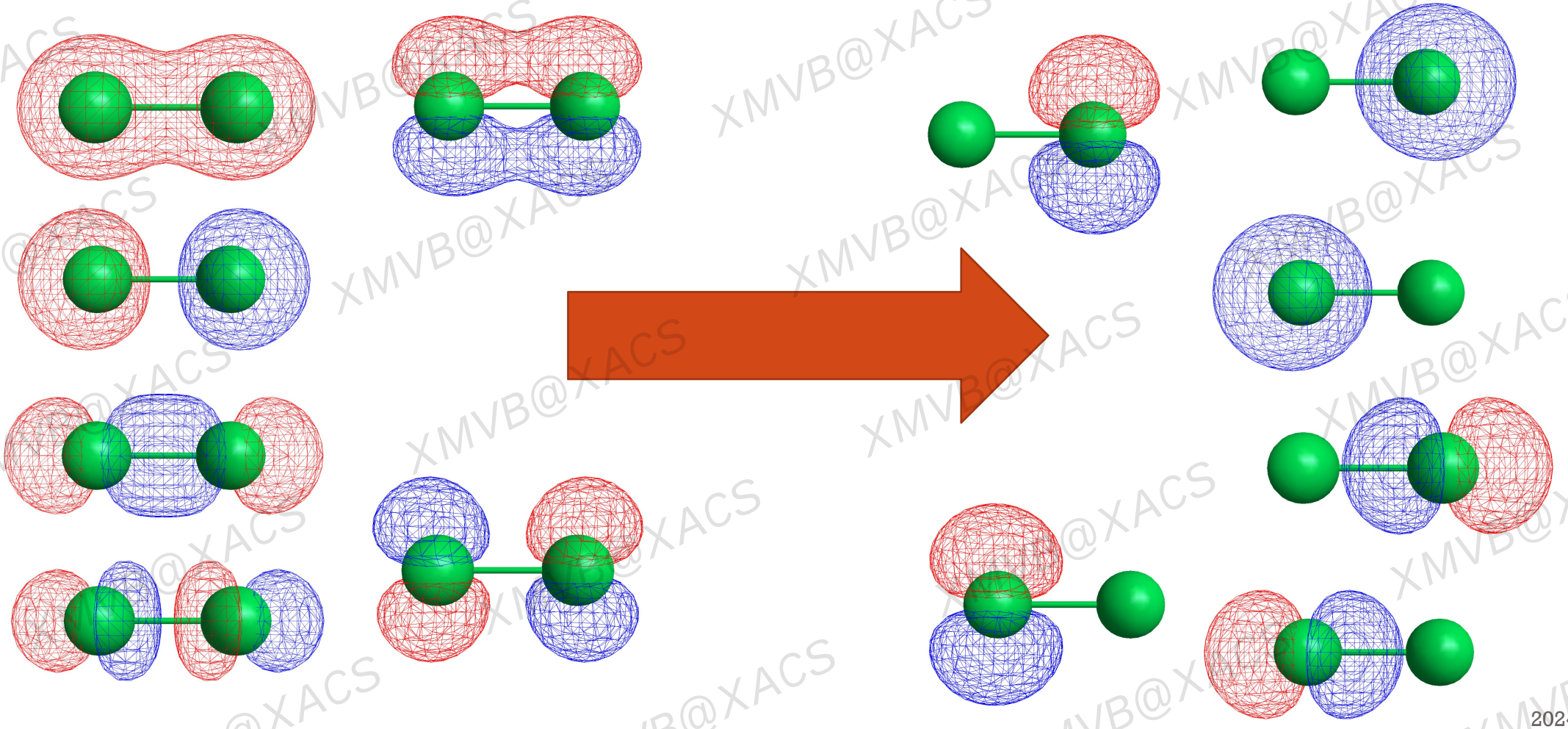


F_2: BDE AND RESONANCE ENERGY

- π Bondings in F_2



F_2: BDE AND RESONANCE ENERGY



F_2: BDE AND RESONANCE ENERGY

Energies and BDEs of F_2 by various methods

Methods	Energies (a .u.)		BDE (kcal/mol)
	Equilibrium	Dissociated	
HF	-198.687494	-198.743865	-35.4
B3LYP	-199.447478	-199.385090	39.1
CASSCF	-198.761112	-198.743865	10.8
VBSCF	-198.751156	-198.743865	4.6
BOVB	-198.783180	-198.743865	24.7
VBCISD	-198.972549	-198.930888	26.1
CCSD	-199.093045	-199.057382	22.4

ref: 38.2 kcal/mol

F_2: BDE AND RESONANCE ENERGY

REs and RREs of F_2 by VBSCF and VBCISD

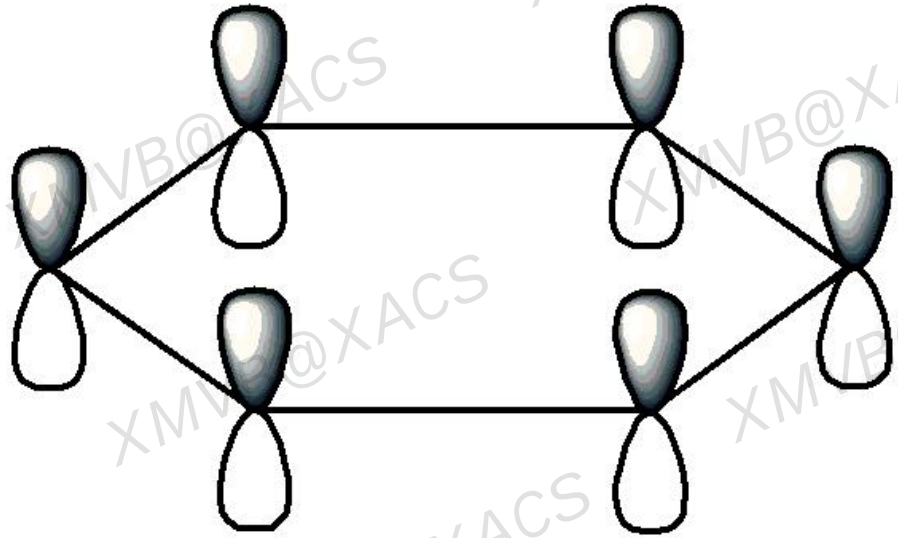
Methods	Energies (a .u.)		RE (kcal/mol)	BDE (kcal/mol)	RRE (%)
	Full	Cov			
VBSCF	-198.751156	-198.674860	47.9	4.6	1041.3
BOVB	-198.783180	-198.674860	68.0	24.7	275.0
VBCISD	-198.972549	-198.871326	63.5	26.1	243.3

C_6H_6 : RESONANCE AND AROMATICITY

- Purpose:
  - VB computation for molecules with conjugate π orbitals
  - The relationship between resonance and aromaticity

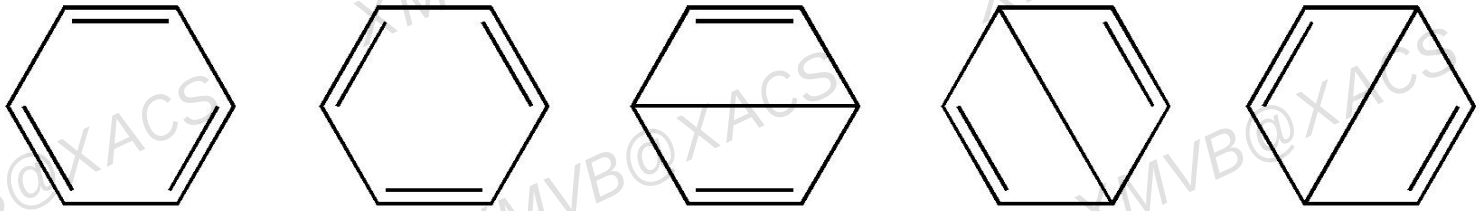
C_6H_6 : RESONANCE AND AROMATICITY

- Spaces:
  - Inactive: m=36 n=18 (all σ orbitals)
  - Active: m=6 n=6 (all π orbitals)

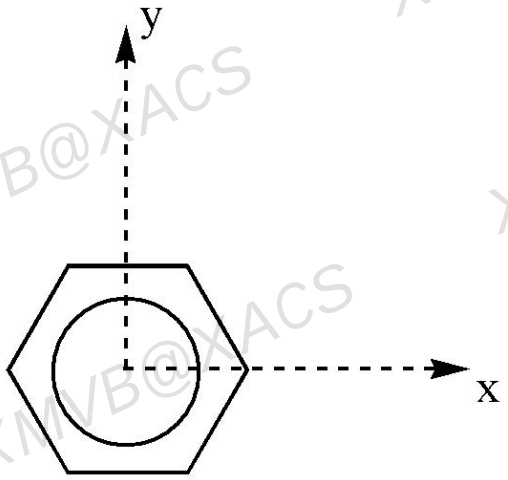


C_6H_6 : RESONANCE AND AROMATICITY

- Structures

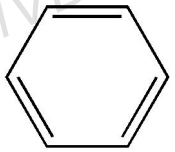


K1 K2 D1 D2 D3



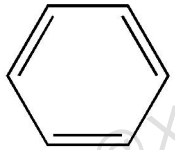
C_6H_6 : RESONANCE AND AROMATICITY

- Structures



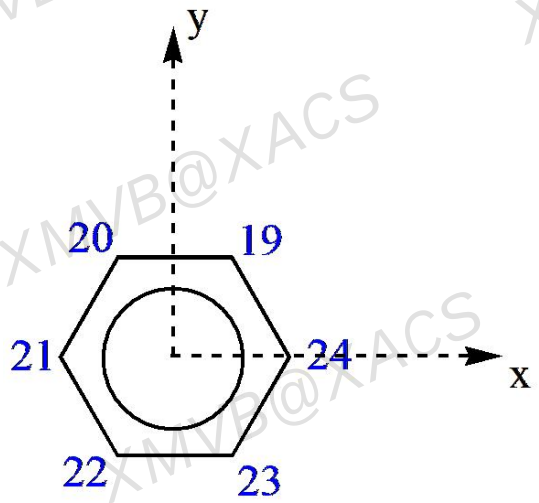
K1

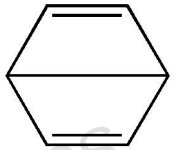
19 20 21 22 23 24



K2

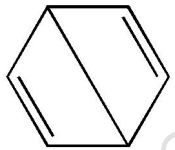
20 21 22 23 19 24





D1

19 20 22 23 21 24



D2

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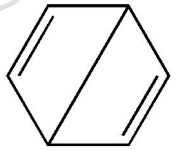


D3

20 21 19 22 23 24

C_6H_6 : RESONANCE AND AROMATICITY

- Results

Structure	Coef.	Weight
K1	-0.40080	0.333
K2	-0.40080	0.333
D1	0.14218	0.111
D2	0.14218	0.111
D3	0.14218	0.111

$$RE = E^K - E^{cov}$$

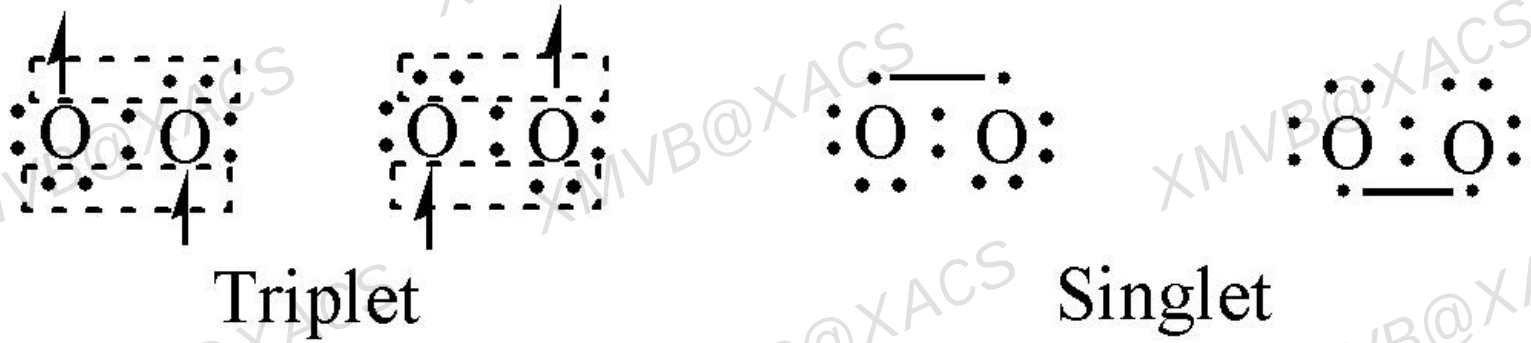
Computation	Energy (a.u.)	RE (kcal/mol)
5 Covalent Structures	-230.604424	--
2 Kekulé Structures	-230.599801	2.9
1 Kekulé Structure	-230.556432	30.1

O_2: SINGLET AND TRIPLET

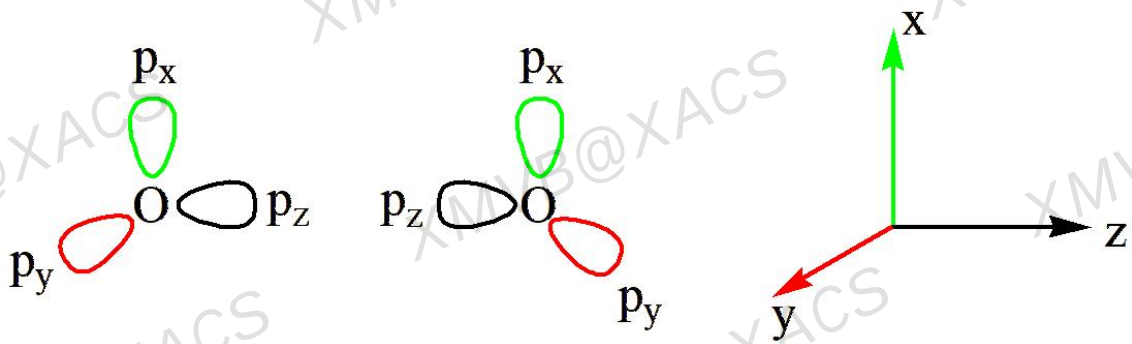
- Purposes:
  - VB computation for open-shell molecules
  - How to select structures
  - Computation for excited state

O_2: SINGLET AND TRIPLET

- Singlet and Triplet States

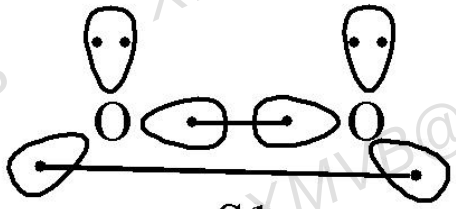


- Spaces:
  - Inactive: m=10 n=5
  - Active: m=6 n=4



O_2: SINGLET AND TRIPLET

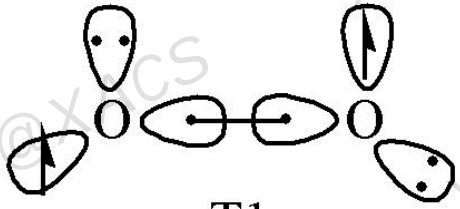
- Singlet Structures



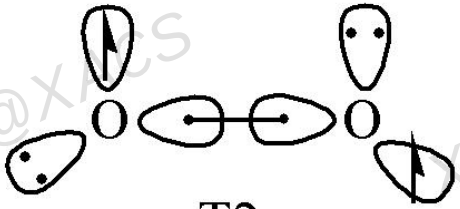
S1

S2

- Triplet Structures



T1



T2