COMPUTATIONS WITH XMVB@XACS

Chen Zhou

Xiamen University

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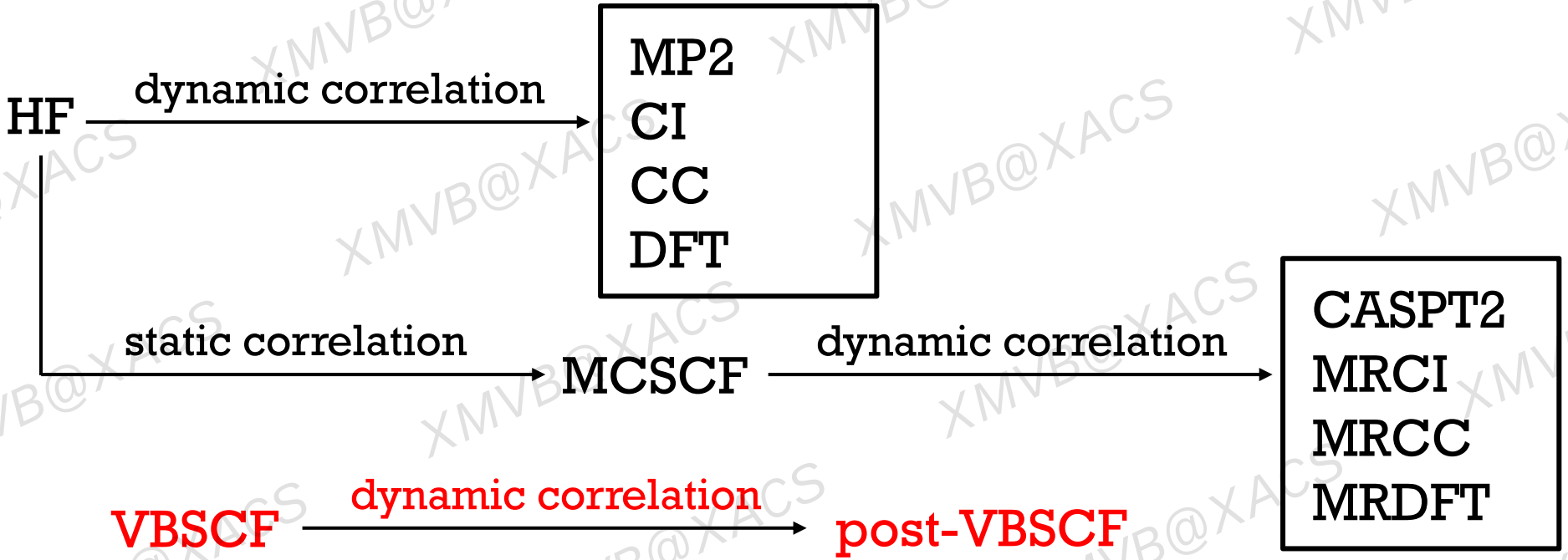
POST-VBSCF METHOD

$$E^{\text{corr}} = E^{\text{HF}} - E^{\text{FCI}}$$

Dynamic correlation　　Static correlation

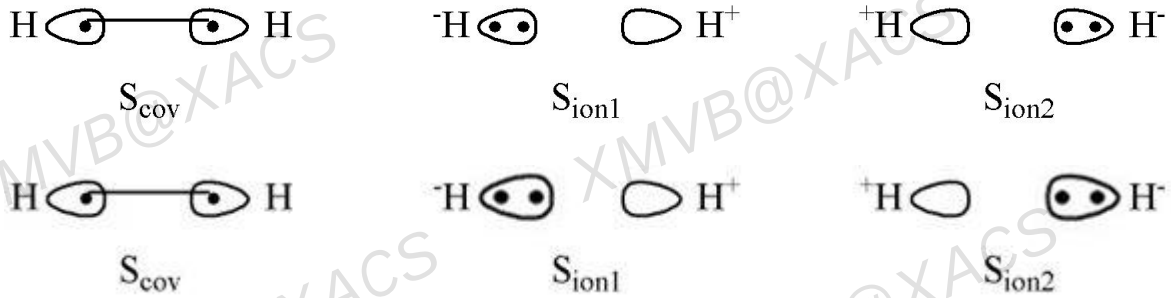


POST-VBSCF METHOD

- VBCIS or VBCISD
- BOVB

$$\Psi^{\mathrm{VBSCF}} = C_1\left(\left|\phi_a\bar{\phi}_b\right| - \left|\bar{\phi}_a\phi_b\right|\right) + C_2\left|\phi_a\bar{\phi}_a\right| + C_3\left|\phi_b\bar{\phi}_b\right|$$

$$\Psi^{\mathrm{BOVB}} = C_1\left(\left|\phi_a\bar{\phi}_b\right| - \left|\bar{\phi}_a\phi_b\right|\right) + C_2\left|\phi_a'\bar{\phi}_a'\right| + C_3\left|\phi_b'\bar{\phi}_b'\right|$$



- VBPT2

No weight analysis in VBPT2.

- Hc-DFVB=functional

Currently, LDA, GGA and their hybrid form can be used in XMVB@XACS

F_2

- 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 ($2p_z$)

ORBTYP=HAO
FRGTYP=SAO

```
$FRAG
1*6
SPZDXXDYYDZZ 1
SPZDXXDYYDZZ 2
PXDXZ 1
PXDXZ 2
PYDYZ 1
PYDYZ 2
$END
$ORB
1*10
1
2
1
2
3
4
5
6
1
2
$END
```

=

```
$ORB
8*4 3*4 8*2
1-3    6  9 10 13 15
16-19 21 24 25 28 30
1-3    6  9 10 13 15
16-19 21 24 25 28 30
 4  7 12
19 22 27
 5  8 14
20 23 29
1-3    6  9 10 13 15
16-19 21 24 25 28 30
$END
```

ORBTYP=HAO
FRGTYP=ATOM

```
$ORB
1*10
1   # 1s of F1
2   # 1s of F2
1   # 2s of F1
2   # 2s of F2
1   # 2px of F1
2   # 2px of F2
1   # 2py of F1
2   # 2py of F2
1   # 2pz of F1
2   # 2pz of F2
$END
```

=

```
$ORB
15*10
 1-15
16-30
 1-15
16-30
 1-15
16-30
 1-15
16-30
 1-15
16-30
$END
```

MENSHUTKIN REACTION: COMPUTING OF REACTION BARRIER

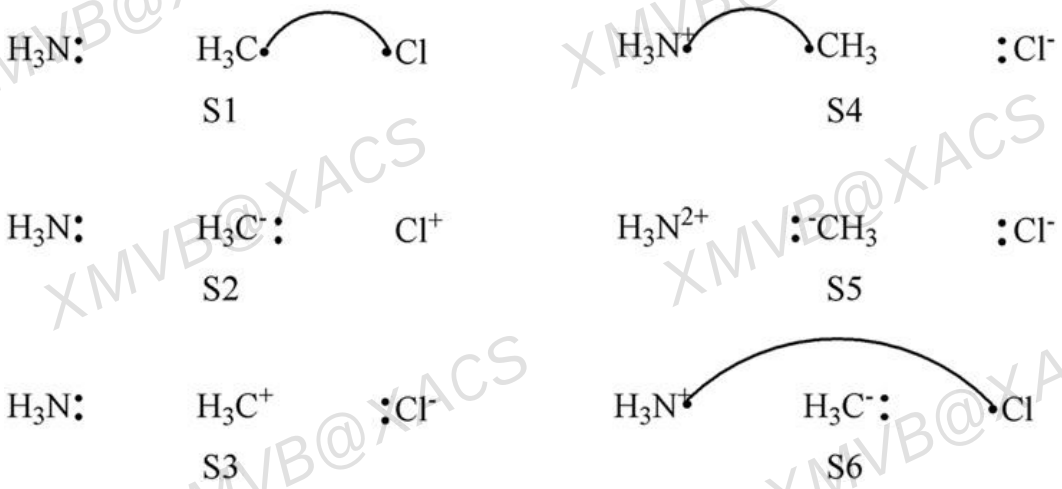
$$NH_3 + CH_3Cl \rightarrow [NH_3CH_3]^+ + Cl^-$$

(36-4)/2=16

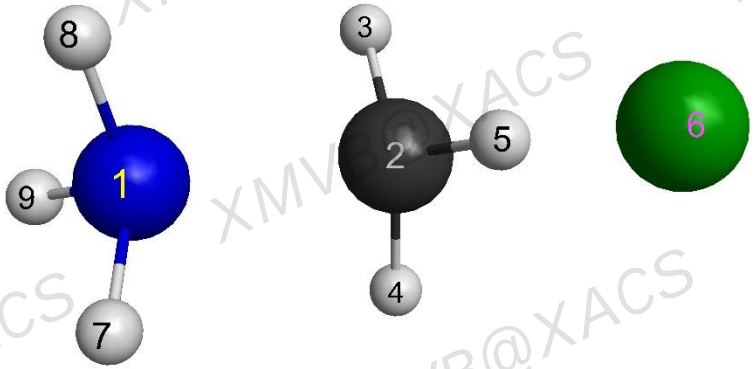
36: number of total electrons; 4: number of active electrons

- Spaces:
  - Inactive space: m=32 n=16 (the core orbitals of N, C and Cl, 3 N-H bonds, 3 C-H bonds, and 3*s*, 3p_x and 3p_y orbitals on Cl)
  - Active space: m=4 n=3 (the lone pair on NH_3 and the C-Cl bond in the reactants)

- VB structures



DEFINITION OF FRAGMENTS



fratyp=atom: each fragment is defined as one atom; no $frag section is needed.

- Spaces:
  - Inactive space: m=32 n=16 (the core orbitals of N, C and Cl, 3 N-H bonds, 3 C-H bonds, and 3*s*, 3p_x and 3p_y orbitals on Cl)
  - Active space: m=4 n=3 (the lone pair on NH_3 and the C-Cl bond in the reactants)

```
$orb
1*5 4 4 1*3 4*3 4*3 4 4 1
①  6
②  6
③  6
④  6
⑤  6
⑥  1 7 8 9
⑦  2 3 4 5
⑧  6
⑨  6
⑩  6
⑪  1 7 8 9
⑫  1 7 8 9
⑬  1 7 8 9
⑭  2 3 4 5
⑮  2 3 4 5
⑯  2 3 4 5
⑰  1 7 8 9 → lone pair on NH3
⑱  2 3 4 5 → part of C-Cl bond
⑲  6 → part of C-Cl bond
$end
```

Inactive: ①–⑯

① ② ③ ④ ⑤: 1s, 2s, 2p_x , 2p_y and 2p_z orbitals on Cl

⑥ ⑦: 1s orbitals on N and C

⑧ ⑨ ⑩: 3s, 3p_x and 3p_y orbitals on Cl

⑪ ⑫ ⑬: 3 N-H bonds

⑭ ⑮ ⑯: 3 C-H bonds

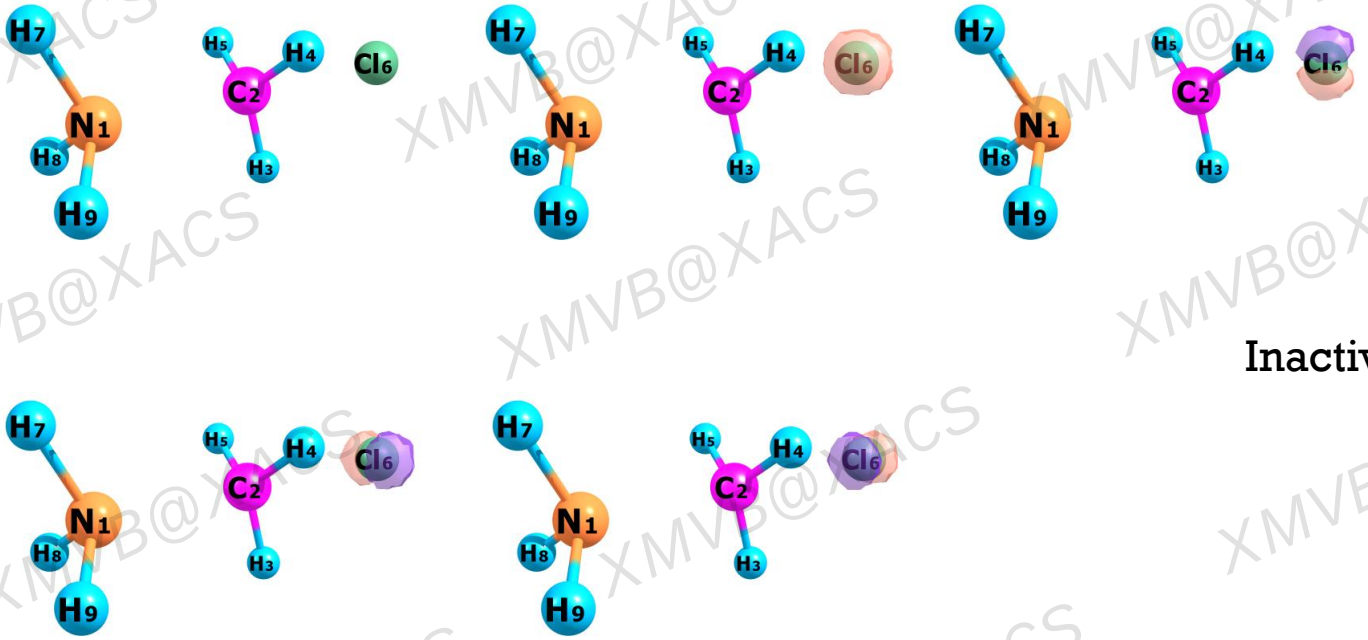
Active: ⑰–⑲

⑰ lone pair on NH_3

⑱ part of C-Cl bond

⑲ part of C-Cl bond

DEFINITION OF FRAGMENTS




```
$orb
1*5 4 4 1*3 4*3 4*3 4 4 1
```

Inactive

① 6
② 6
③ 6
④ 6
⑤ 6
— 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on Cl

⑥ 1 7 8 9
⑦ 2 3 4 5
— 1s orbitals on N and C

⑧ 6
⑨ 6
⑩ 6
— 3s, $3p_x$ and $3p_y$ orbitals on Cl

⑪ 1 7 8 9
⑫ 1 7 8 9
⑬ 1 7 8 9
— 3 N-H bonds

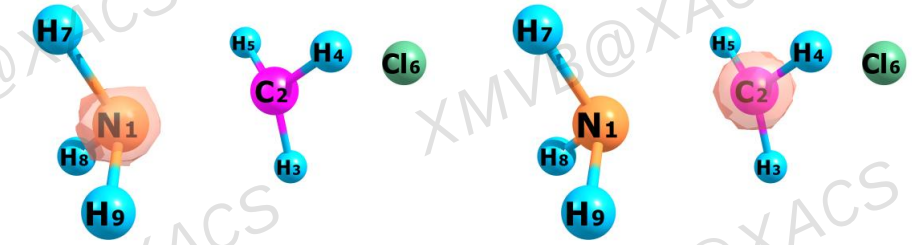
⑭ 2 3 4 5
⑮ 2 3 4 5
⑯ 2 3 4 5
— 3 C-H bonds

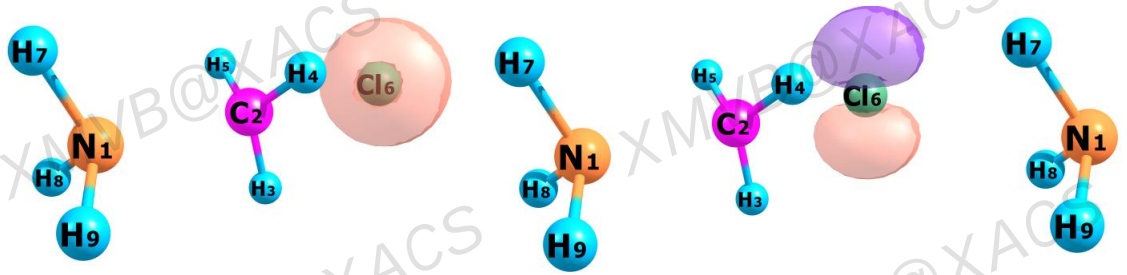
Active

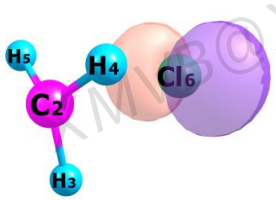
⑰ 1 7 8 9 → lone pair on NH_3
⑱ 2 3 4 5 → part of C-Cl bond
⑲ 6 → part of C-Cl bond

```
$end
```

DEFINITION OF FRAGMENTS








```
$orb
1*5 4 4 1*3 4*3 4*3 4 4 1
```

Inactive

① 6
② 6
③ 6
④ 6
⑤ 6

1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on Cl

⑥ 1 7 8 9
⑦ 2 3 4 5

1s orbitals on N and C

⑧ 6
⑨ 6
⑩ 6

3s, $3p_x$ and $3p_y$ orbitals on Cl

⑪ 1 7 8 9
⑫ 1 7 8 9
⑬ 1 7 8 9

3 N-H bonds

⑭ 2 3 4 5
⑮ 2 3 4 5
⑯ 2 3 4 5

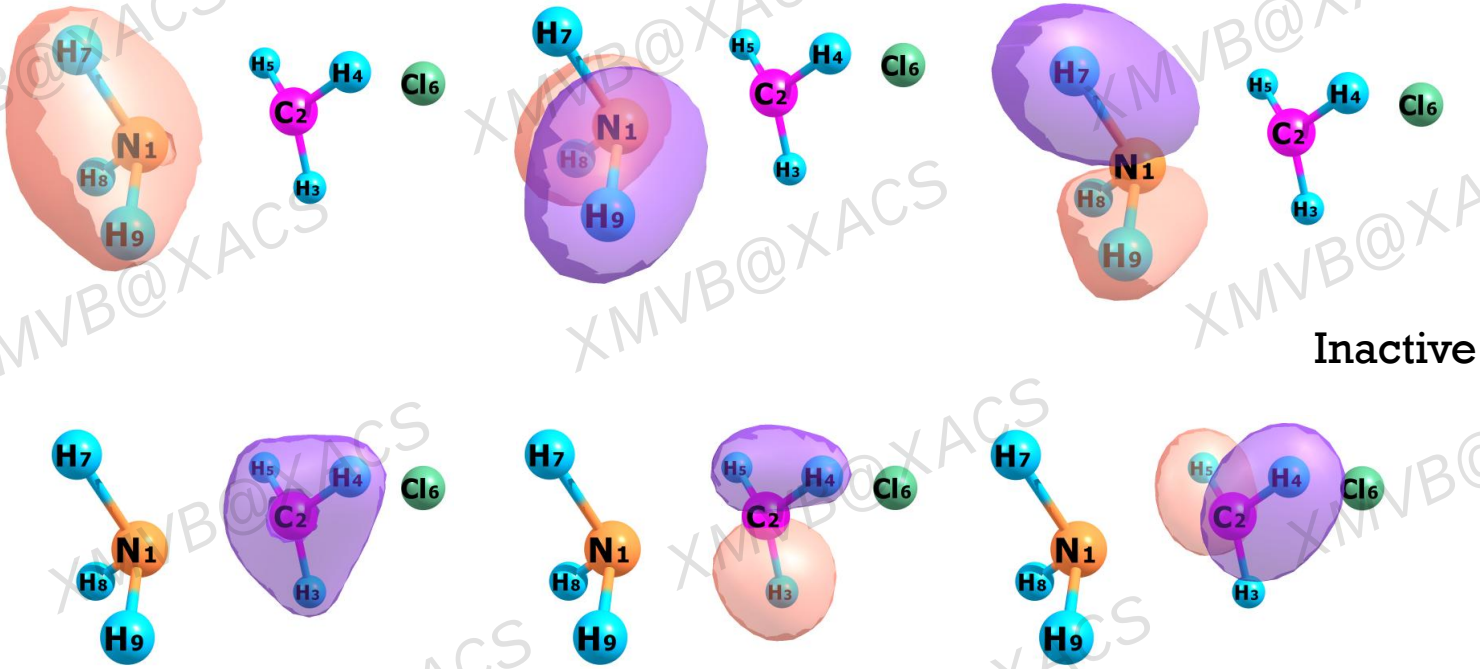
3 C-H bonds

Active

⑰ 1 7 8 9 → lone pair on NH_3
⑱ 2 3 4 5 → part of C-Cl bond
⑲ 6 → part of C-Cl bond

```
$end
```

DEFINITION OF FRAGMENTS




```
$orb
1*5 4 4 1*3 4*3 4*3 4 4 1
```

Inactive

① 6
② 6
③ 6
④ 6
⑤ 6

1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on Cl

⑥ 1 7 8 9
⑦ 2 3 4 5

1s orbitals on N and C

⑧ 6
⑨ 6
⑩ 6

3s, $3p_x$ and $3p_y$ orbitals on Cl

⑪ 1 7 8 9
⑫ 1 7 8 9
⑬ 1 7 8 9

3 N-H bonds

⑭ 2 3 4 5
⑮ 2 3 4 5
⑯ 2 3 4 5

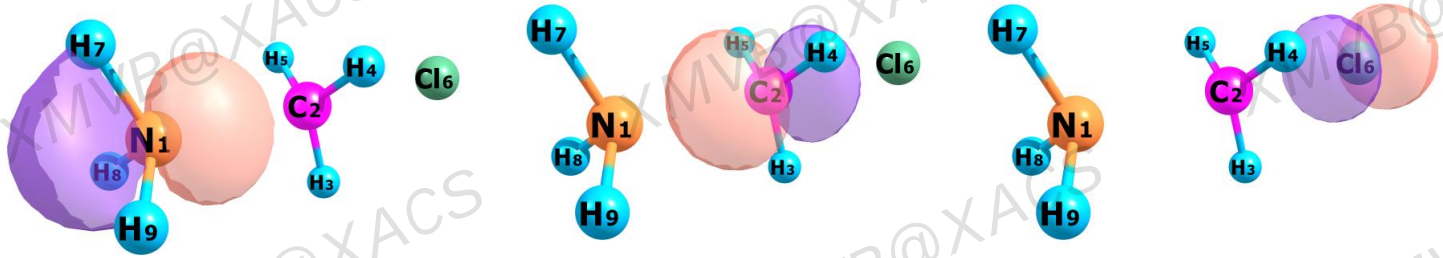
3 C-H bonds

Active

⑰ 1 7 8 9 → lone pair on NH_3
⑱ 2 3 4 5 → part of C-Cl bond
⑲ 6 → part of C-Cl bond

```
$end
```

DEFINITION OF FRAGMENTS




```
$orb
1*5 4 4 1*3 4*3 4*3 4 4 1
① 6
② 6
③ 6
④ 6
⑤ 6
⑥ 1 7 8 9
⑦ 2 3 4 5
⑧ 6
⑨ 6
⑩ 6
⑪ 1 7 8 9
⑫ 1 7 8 9
⑬ 1 7 8 9
⑭ 2 3 4 5
⑮ 2 3 4 5
⑯ 2 3 4 5
⑰ 1 7 8 9
⑱ 2 3 4 5
⑲ 6
$end
```

Inactive

1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals on Cl

1s orbitals on N and C

3s, $3p_x$ and $3p_y$ orbitals on Cl

3 N-H bonds

3 C-H bonds

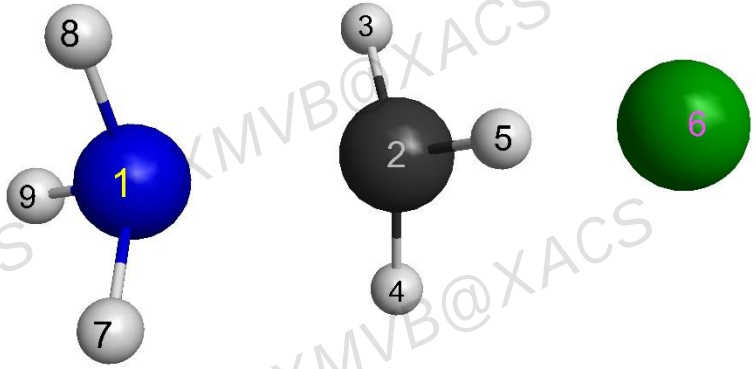
Active

⑰ → lone pair on NH_3

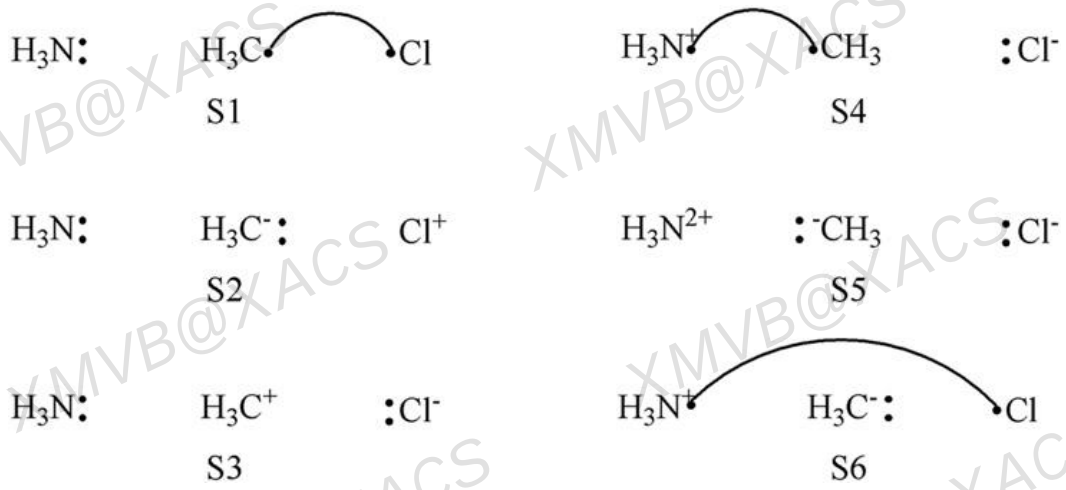
⑱ → part of C-Cl bond

⑲ → part of C-Cl bond

WRITING VB STRUCTURES



Active
- 17 1 7 8 9 → lone pair on NH_3
- 18 2 3 4 5 → part of C-Cl bond
- 19 6 → part of C-Cl bond



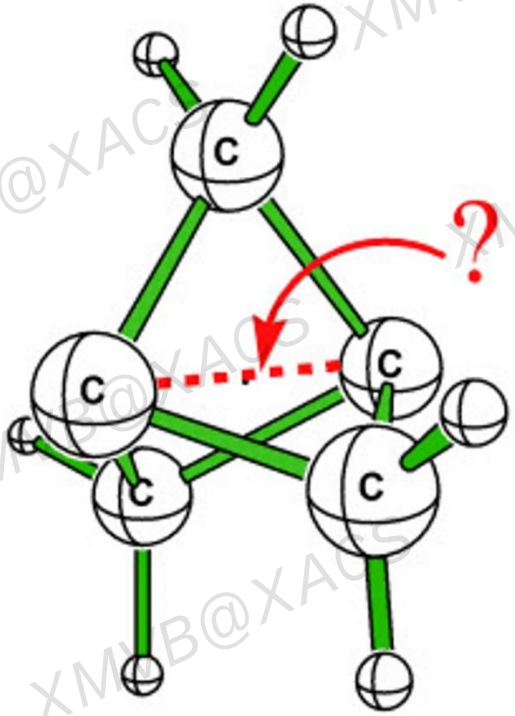
- S1 1:16 17 17 18 19
- S2 1:16 17 17 18 18
- S3 1:16 17 17 19 19
- S4 1:16 19 19 17 18
- S5 1:16 18 18 19 19
- S6 1:16 18 18 17 19

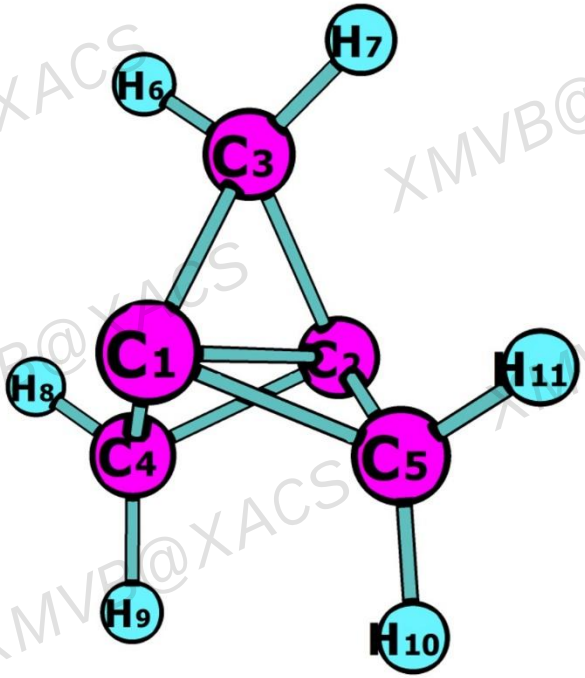
READING ORBITAL GUESS

- Initial orbital guess is always needed in SCF calculation. A good initial orbital guess will greatly increase the computational efficiency and convergence.
- Use keyword "GUESS=READ" in $CTRL section to read orbital guess from $VEC section.
- A good initial orbital guess is the optimal orbitals of previous VBSCF calculation.
- The optimal orbitals are stored in the **.orb** file after a VB calculation finished. The data in the **.orb** file can be directly pasted to the $VEC section.

CHARGE-SHIFT BONDING IN PROPELLANE

螺桨烷



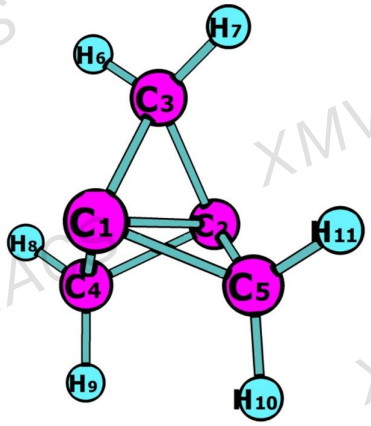


What's the nature of the C-C bridge bond? Is it charge-shift bond?

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

RRE > 50% : Charge-Shift Bond

COMPUTING OF RESONANCE ENERGY



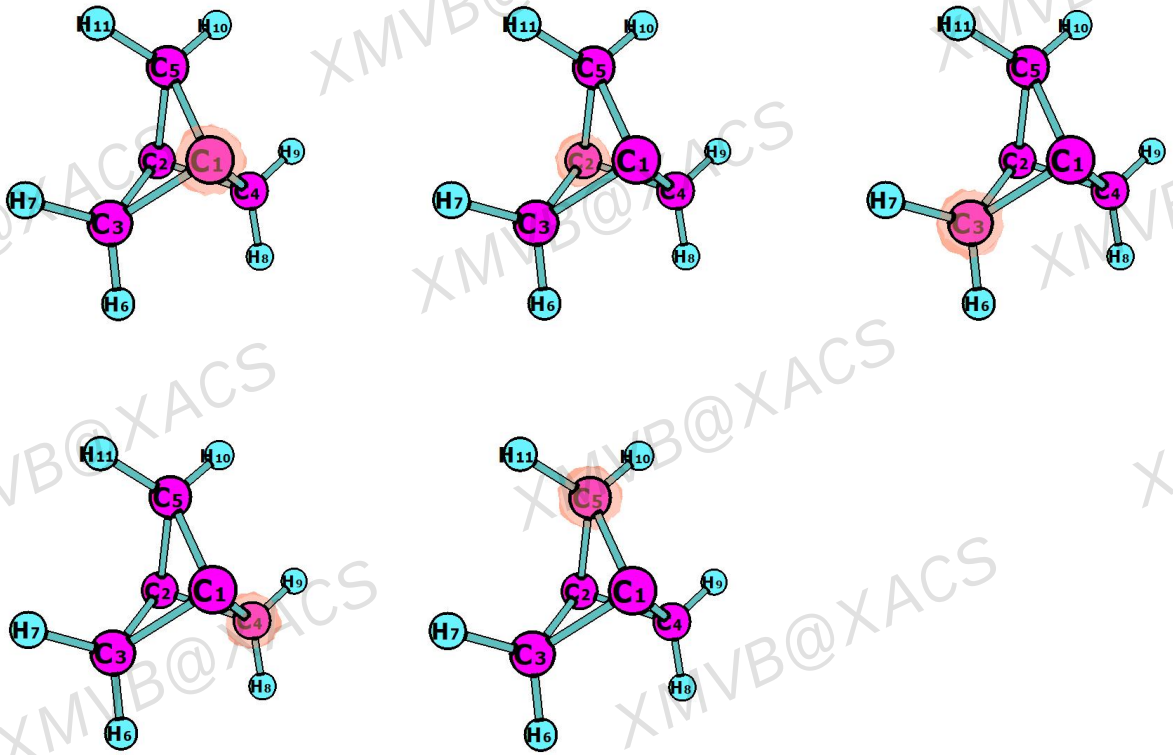
- VB method: BOVB
- Fratyp=atom
- Spaces:
  - Inactive space: m=34 n=17 (the core orbitals of, 6 C-C bonds (except the bridge bond), 6 C-H bonds)
  - Active space: m=2 n=2 (the C-C bridge bond)
- VB Structures

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

```
$ORB
1*5 2*12 1*2
1    # 1  C1     1s
2    # 2  C2     1s
3    # 3  C3     1s
4    # 4  C4     1s
5    # 5  C5     1s
1 3  # 6  C1-C3  sigma
2 3  # 7  C2-C3  sigma
1 4  # 8  C1-C4  sigma
2 4  # 9  C2-C4  sigma
1 5  # 10 C1-C5  sigma
2 5  # 11 C2-C5  sigma
3 6  # 12 C3-H6  sigma
3 7  # 13 C3-H7  sigma
4 8  # 14 C4-H8  sigma
4 9  # 15 C4-H9  sigma
5 10 # 16 C5-H10 sigma
5 11 # 17 C5-H11 sigma

1    # 18 C1-C2  sigma C1
2    # 19 C1-C2  sigma C2
$END
```

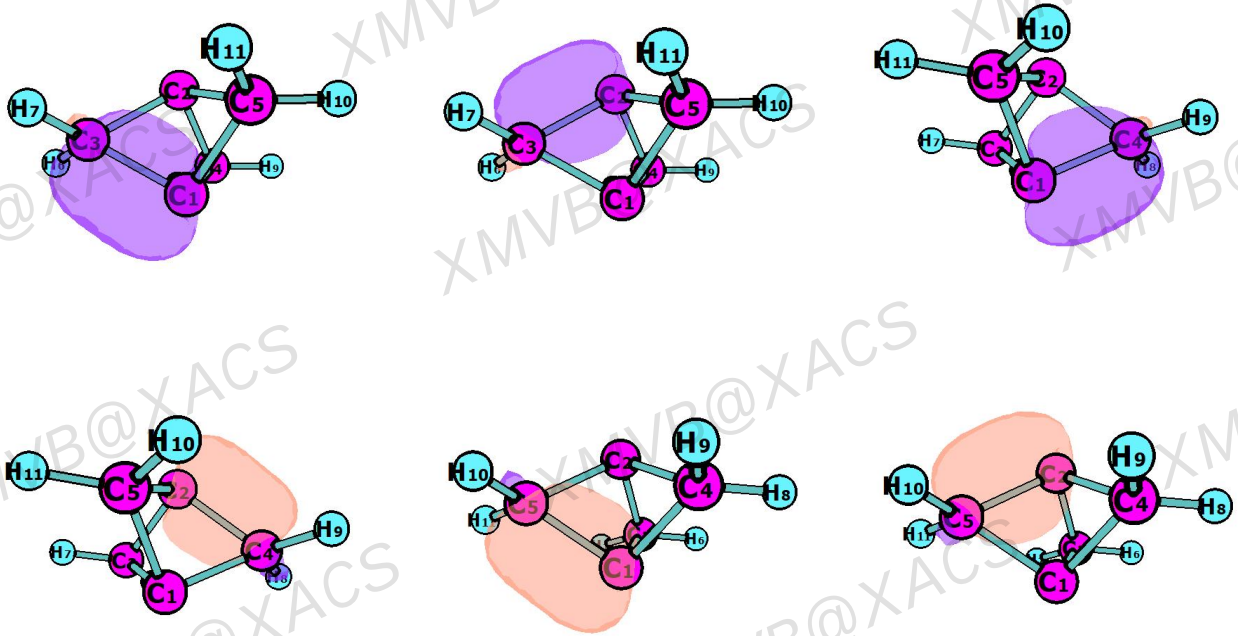
COMPUTING OF RESONANCE ENERGY




```
$ORB
1*5 2*12 1*2
1     # 1  C1      1s
2     # 2  C2      1s
3     # 3  C3      1s
4     # 4  C4      1s
5     # 5  C5      1s
1 3   # 6  C1-C3   sigma
2 3   # 7  C2-C3   sigma
1 4   # 8  C1-C4   sigma
2 4   # 9  C2-C4   sigma
1 5   # 10 C1-C5   sigma
2 5   # 11 C2-C5   sigma
3 6   # 12 C3-H6   sigma
3 7   # 13 C3-H7   sigma
4 8   # 14 C4-H8   sigma
4 9   # 15 C4-H9   sigma
5 10  # 16 C5-H10  sigma
5 11  # 17 C5-H11  sigma

1     # 18 C1-C2  sigma C1
2     # 19 C1-C2  sigma C2
$END
```

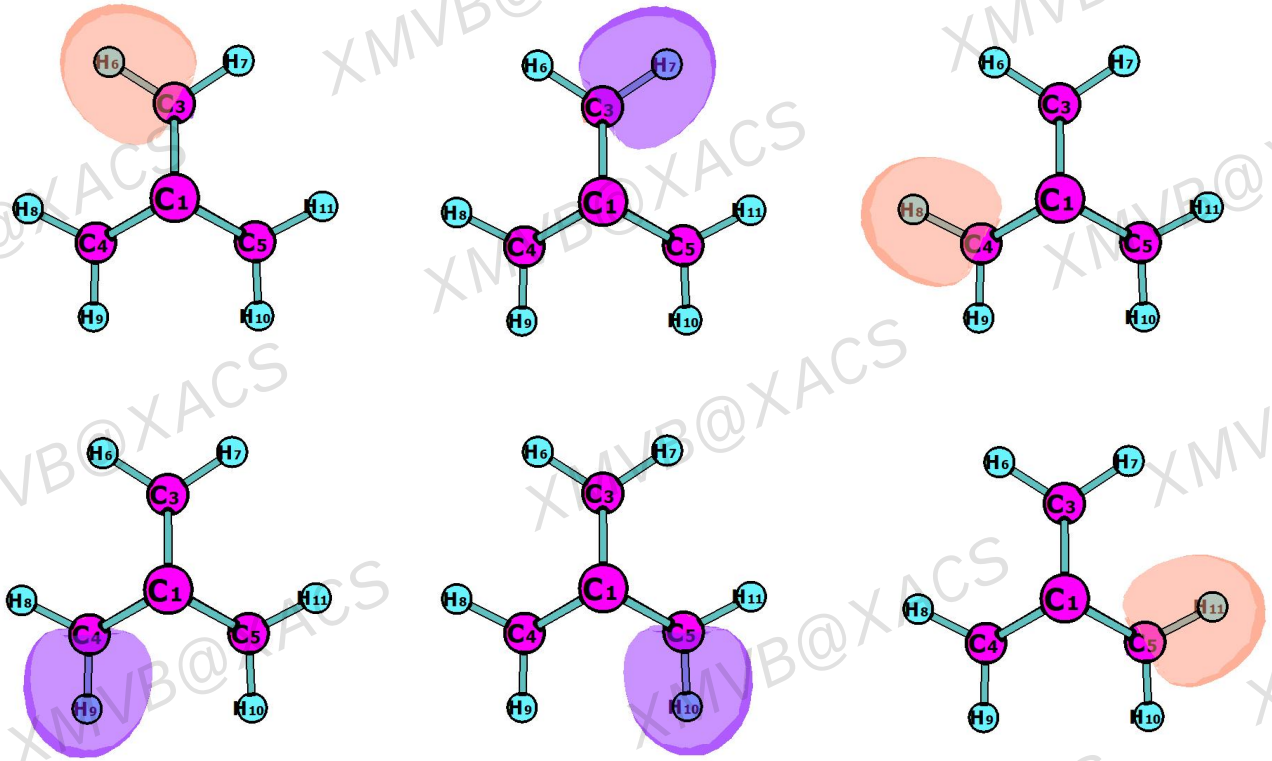
COMPUTING OF RESONANCE ENERGY



```
$ORB
1*5 2*12 1*2
1     # 1  C1     1s
2     # 2  C2     1s
3     # 3  C3     1s
4     # 4  C4     1s
5     # 5  C5     1s
1 3   # 6  C1-C3  sigma
2 3   # 7  C2-C3  sigma
1 4   # 8  C1-C4  sigma
2 4   # 9  C2-C4  sigma
1 5   # 10 C1-C5  sigma
2 5   # 11 C2-C5  sigma
3 6   # 12 C3-H6  sigma
3 7   # 13 C3-H7  sigma
4 8   # 14 C4-H8  sigma
4 9   # 15 C4-H9  sigma
5 10  # 16 C5-H10 sigma
5 11  # 17 C5-H11 sigma

1     # 18 C1-C2  sigma C1
2     # 19 C1-C2  sigma C2
$END
```

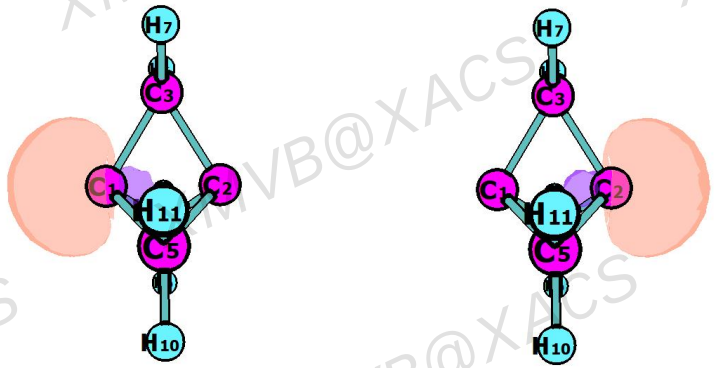
COMPUTING OF RESONANCE ENERGY




```
$ORB
1*5 2*12 1*2
1     # 1  C1     1s
2     # 2  C2     1s
3     # 3  C3     1s
4     # 4  C4     1s
5     # 5  C5     1s
1 3   # 6  C1-C3  sigma
2 3   # 7  C2-C3  sigma
1 4   # 8  C1-C4  sigma
2 4   # 9  C2-C4  sigma
1 5   # 10 C1-C5  sigma
2 5   # 11 C2-C5  sigma
3 6   # 12 C3-H6  sigma
3 7   # 13 C3-H7  sigma
4 8   # 14 C4-H8  sigma
4 9   # 15 C4-H9  sigma
5 10  # 16 C5-H10 sigma
5 11  # 17 C5-H11 sigma

1     # 18 C1-C2  sigma C1
2     # 19 C1-C2  sigma C2
$END
```

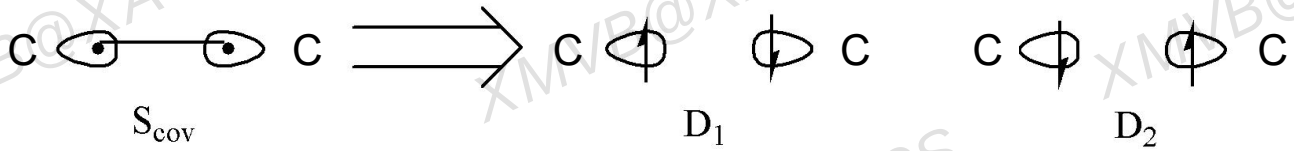
COMPUTING OF RESONANCE ENERGY




```
$ORB
1*5 2*12 1*2
1     # 1  C1      1s
2     # 2  C2      1s
3     # 3  C3      1s
4     # 4  C4      1s
5     # 5  C5      1s
1 3   # 6  C1-C3   sigma
2 3   # 7  C2-C3   sigma
1 4   # 8  C1-C4   sigma
2 4   # 9  C2-C4   sigma
1 5   # 10 C1-C5   sigma
2 5   # 11 C2-C5   sigma
3 6   # 12 C3-H6   sigma
3 7   # 13 C3-H7   sigma
4 8   # 14 C4-H8   sigma
4 9   # 15 C4-H9   sigma
5 10  # 16 C5-H10  sigma
5 11  # 17 C5-H11  sigma

1     # 18 C1-C2   sigma C1
2     # 19 C1-C2   sigma C2
$END
```

ESTIMATION OF BONDING ENERGY



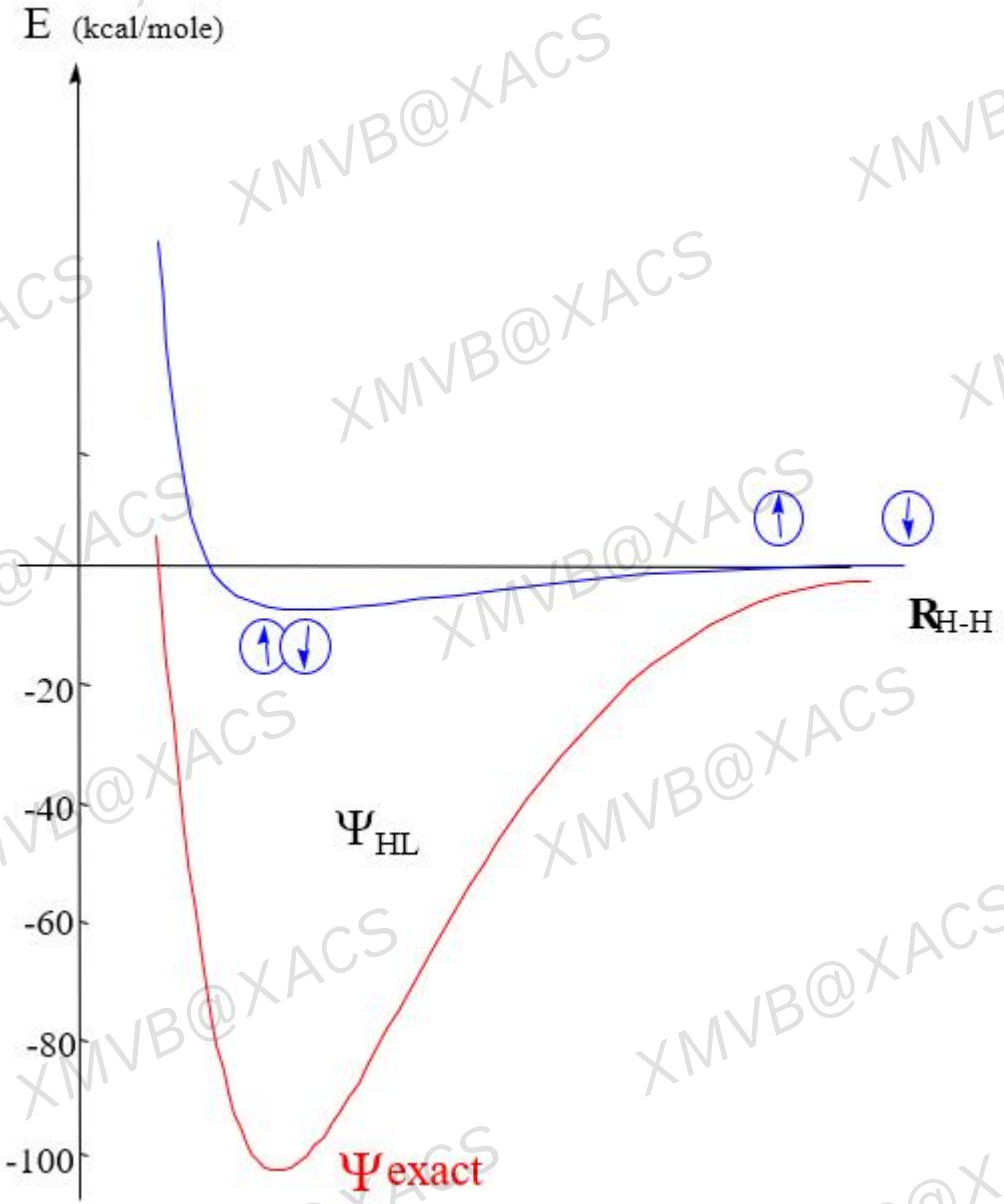
Covalent structure Quasi-classical state Quasi-classical state

The covalent bonding energy comes from the interaction of the two quasi-classical states.

The "in-situ" bonding energy can be an approximation of the bonding energy.

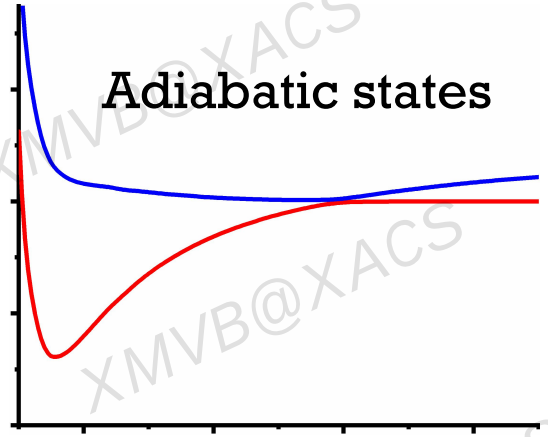
$$BDE \approx D_{\text{in-situ}} = E(D_1) - E(\Psi)$$

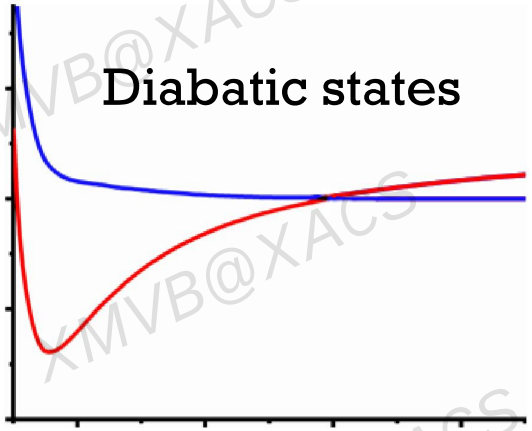
- S_{cov}: 1:17 18 19
- D_1: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 ⟶ Occupied α orbitals
  1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 19 ⟶ Occupied β orbitals



COMPUTING OF DIABATIC STATES WITH VB THEORY

- Adiabatic state: eigenstates of electronic Hamiltonian
- Diabatic state: states whose non-adiabatic couplings are 0 or sufficiently small; not uniquely defined.





Diabatization schemes with VB theory:

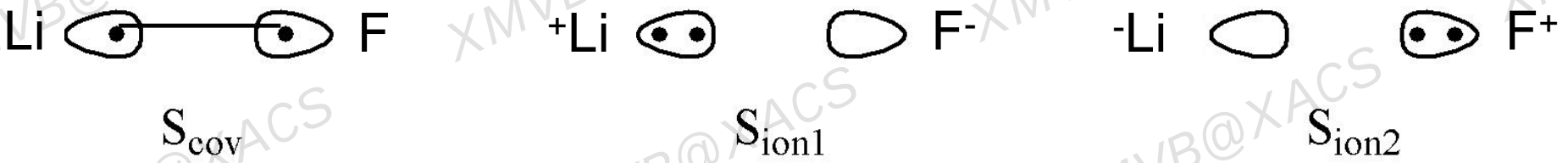
- The VB block-diagonalization approach (VBBDA)
- According to the chemical insights of VB structures
- The valence-bond-based compression approach for diabatization (VBCAD)

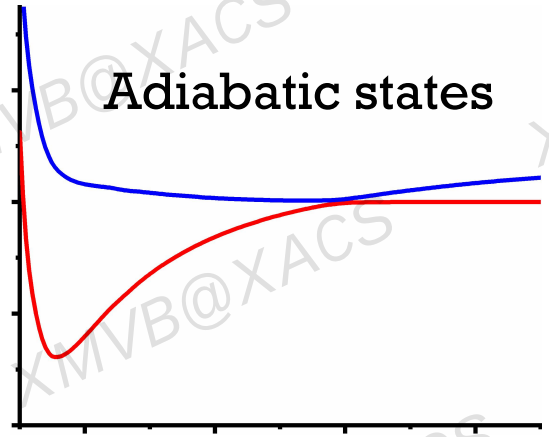
LIF MOLECULE

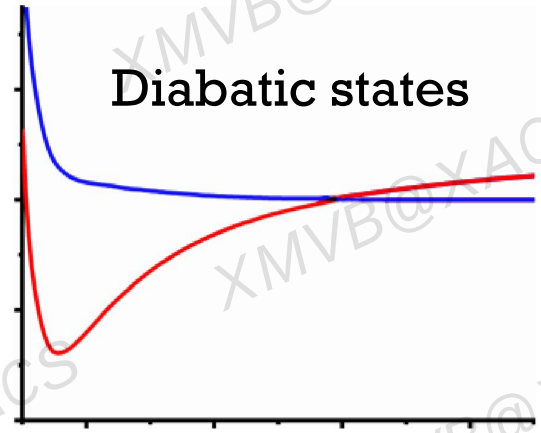
- Spaces:
  - Inactive space: m=10 n=5 (1s of Li; 1s, 2s, $2p_x$, $2p_y$ of F)
  - Active space: m=2 n=2 (2s of Li; $2p_z$ of F)

- Interested electronic states:
  - Adiabatic: the ground and first excited states
  - Diabatic: the covalent and ionic states

- VB structures







COMPUTING OF STATE-AVERAGED VBSCF

The state-averaged scheme is needed for the calculation of excited states in multiconfigurational methods. In state-averaged scheme, the wave function for each electronic state is optimized variationally to minimize the averaged energy (E) of interested N states as

$$E = \sum_{i=1}^{N} w_i E_i$$

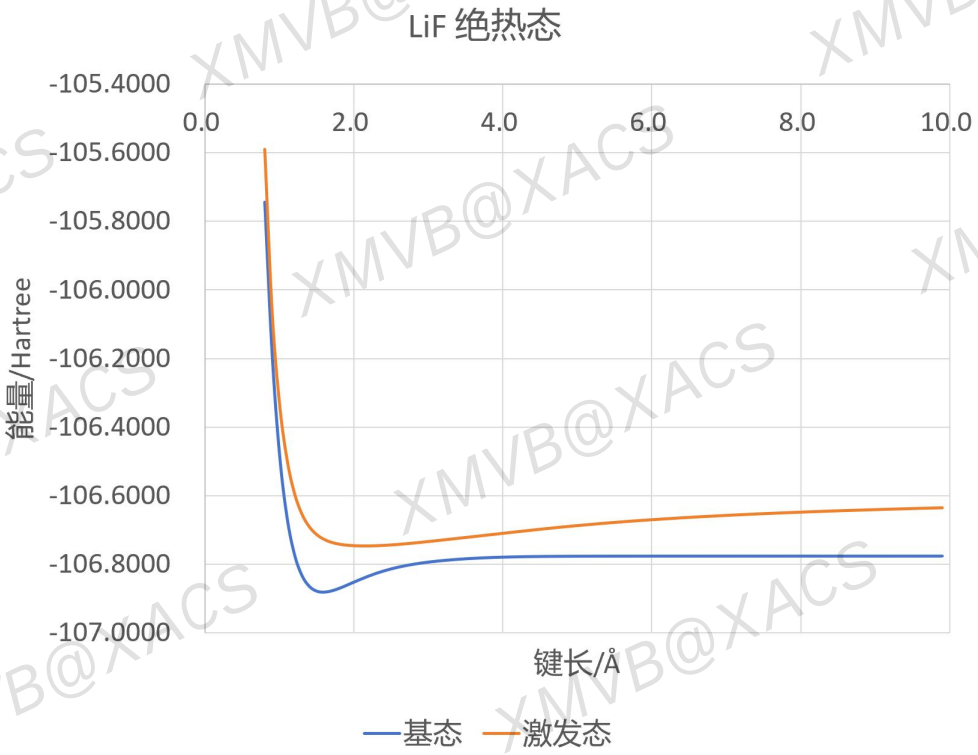
WSTATE(K)=w_1,w_2,…

the K^{th} state is averaged with weight w_1, the $(K+1)^{th}$ state is averaged with weight w_2, and so on.

WSTATE(1)=0.5,0.5

The first 2 low-lying states are averaged as E=0.5E_1+0.5E_2

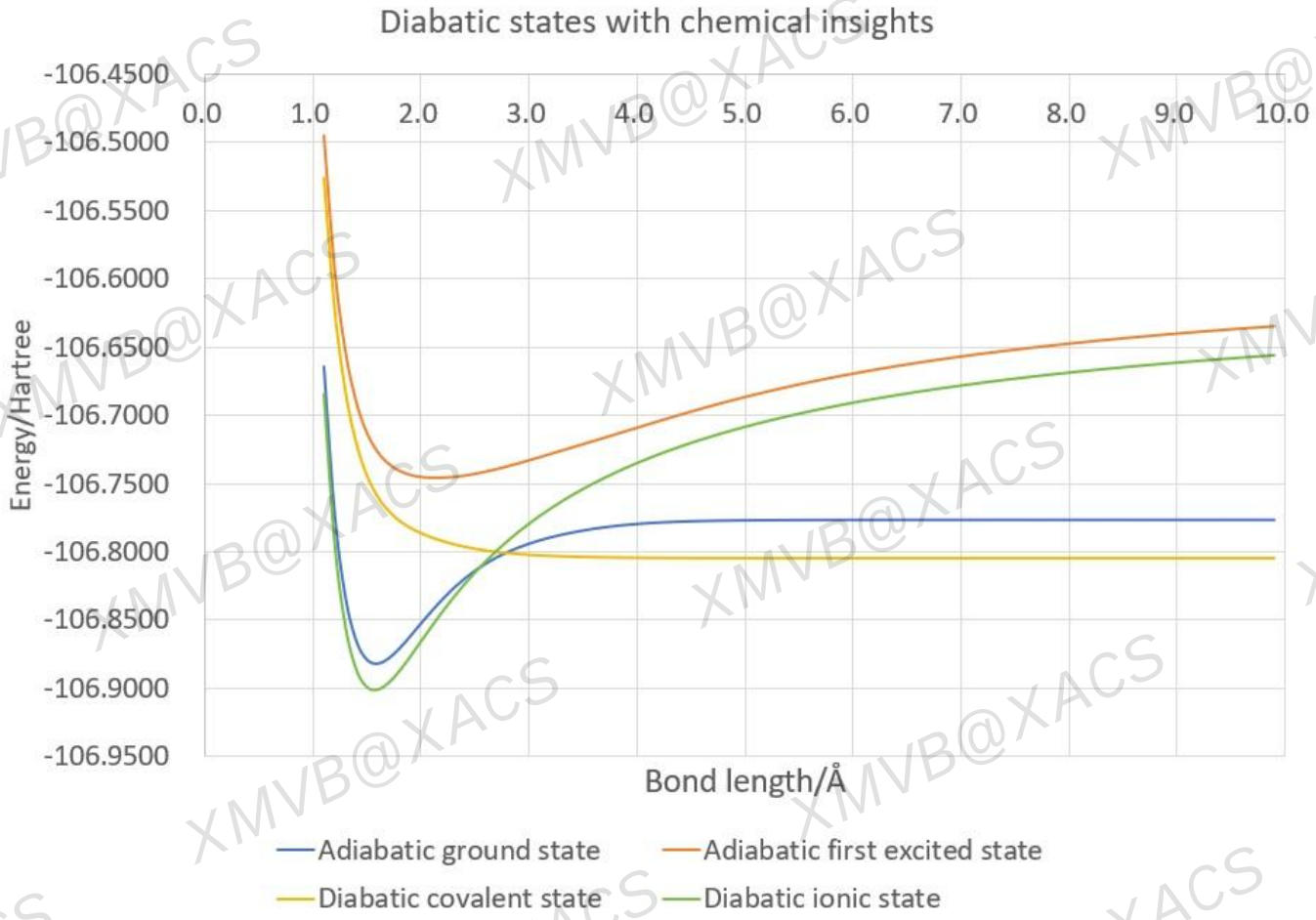
COMPUTING OF ADIABATIC STATES



Suggested bond length to plot the potential energy curve (Å):

1.0	1.2	1.4	1.6	1.8
2.0	2.2	2.4	2.6	2.8
3.0	4.0	5.0	6.0	7.0
8.0	9.0	10.0		

COMPUTING OF DIABATIC STATES WITH CHEMICAL INSIGHTS



COMPUTING OF DIABATIC STATES WITH VBCAD