The Orbital Optimization in Classical Valence Bond Theory
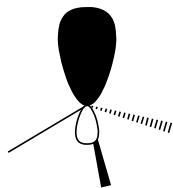
Zhenhua Chen

Xiamen University

March 27, 2017 Paris
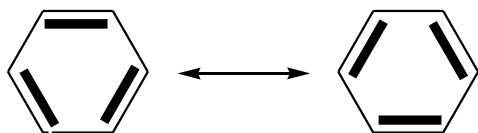
The Elements of Classical Valence Bond Theory
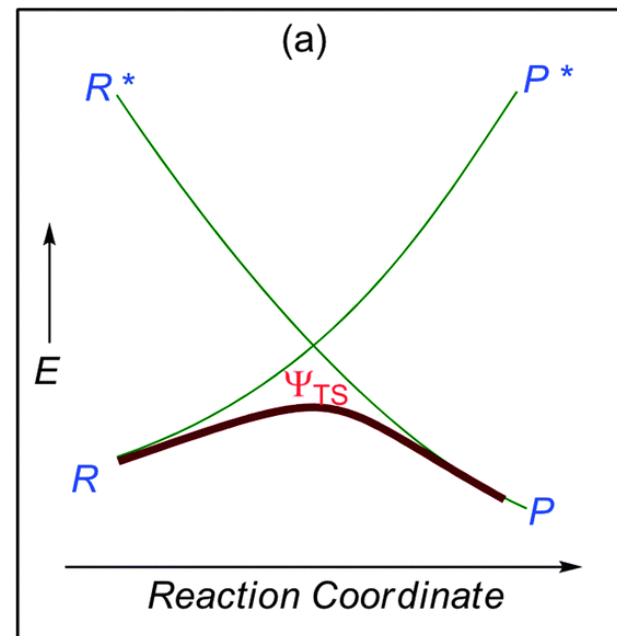
Strict Localized orbital

hybridization

Spin-adapted HLSP

resonance

Energy of individual structure

VB diagram

Roots of Valence Bond Theory

J. Am. Chem. Soc. **38**, 762 (1916).

The Atom and the Molecule

Lewis' electron-pair bonding and octet rule.

G. N. Lewis

L. Pauling
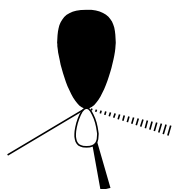
hybridization   resonance

$A\!\bullet\!\!-\!\!\bullet B \longleftrightarrow A\!:\!^{\ominus} \quad ^{\oplus}B \longleftrightarrow A^{\oplus} \quad ^{\ominus}\!:\!B$

$A\!\!-\!\!B$
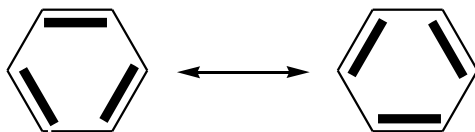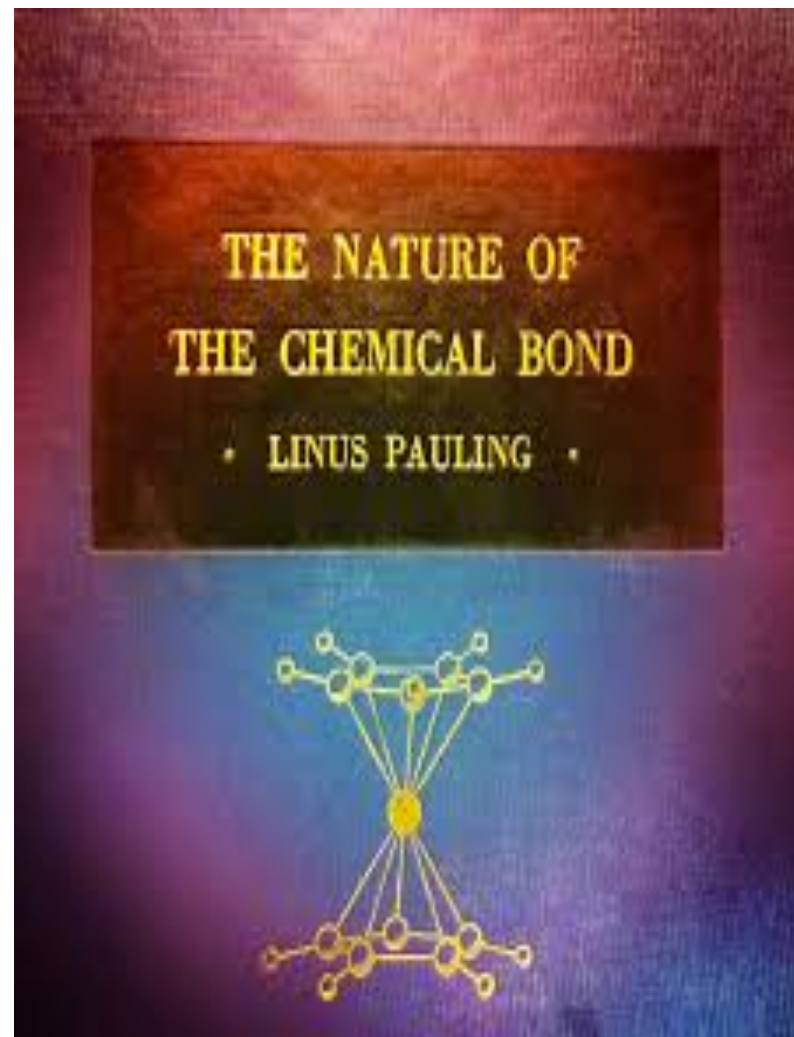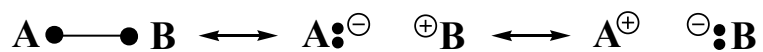
The Nature of the Chemical Bond, Cornell University Press, Ithaca New York,1939 (3rd Edition, 1960).

(a) ethane

- QC state
- covalent structure
- ground state

E(kcal/mol)

R_{C-C}(Å)

42.3

59.8

36.3

1.55 Å

(b) [1.1.1]propellane

E(kcal/mol)

- QC state
- covalent structure
- ground state

46

25

11

72

57

R_{C-C}(Å)

1.60Å   1.8Å
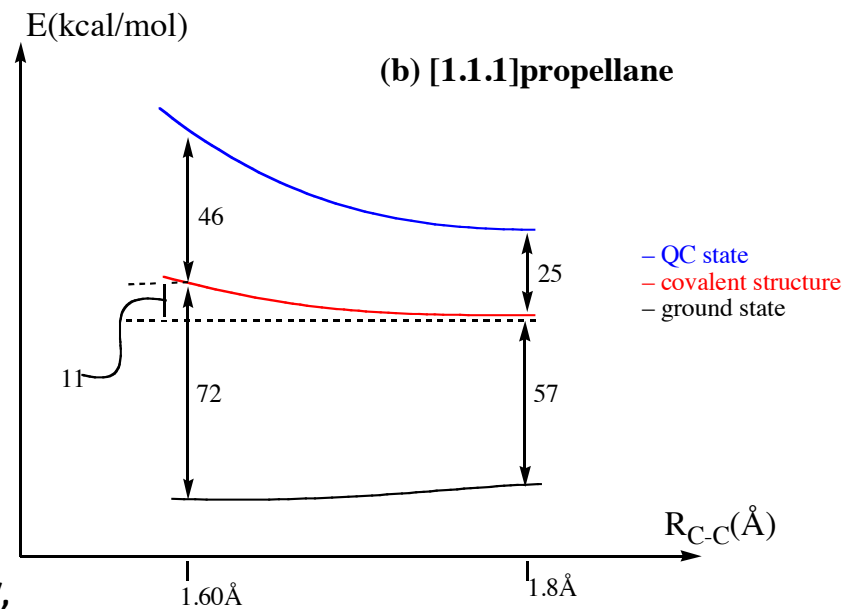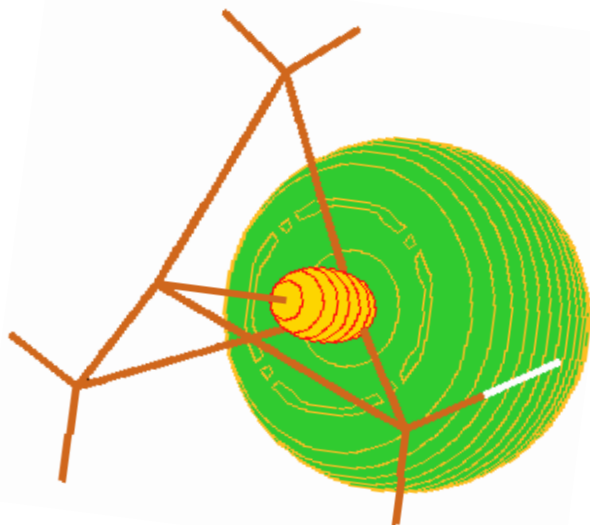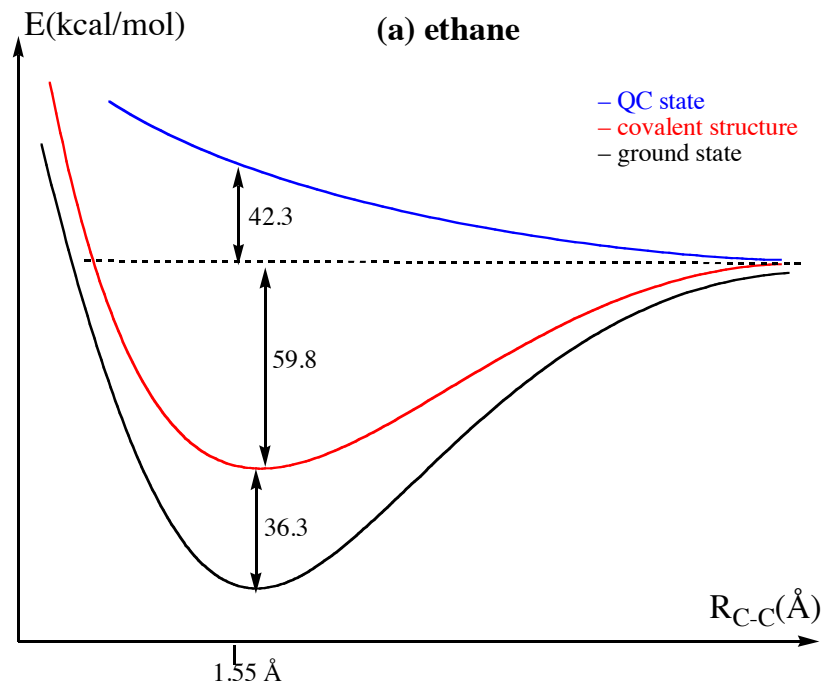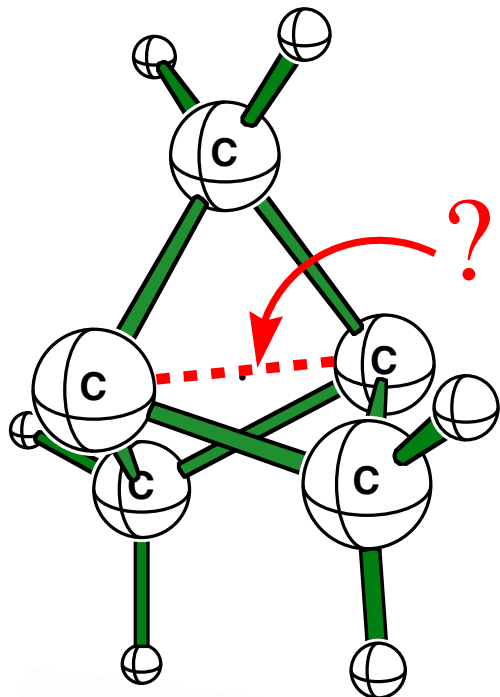
W. Wu, J. Gu, J. Song, S. Shaik, and P. Hiberty, Angew. Chem., 2009, 121, 1435.

5

Lone pair

FF bond
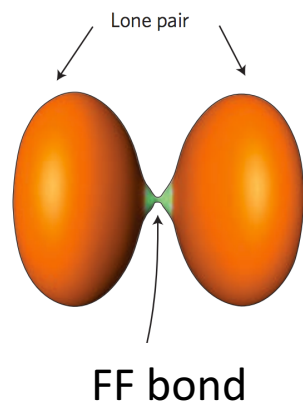
S. Shaik, D. Danovich, W. Wu, P. C. Hiberty, Nat. Chem., 2009, 1, 443.

Charge-shift bonding and its manifestations in chemistry

| 4 | 5 | 6 | 7 |
| 0.221 | 0.221 | 0.252 | 0.078 |

| 8 | 9 | 10 | 11 |
| 0.058 | 0.058 | 0.056 | 0.056 |
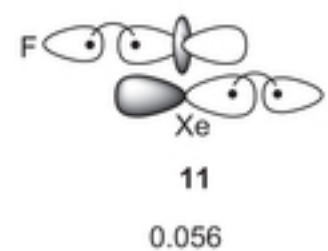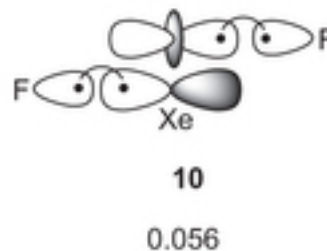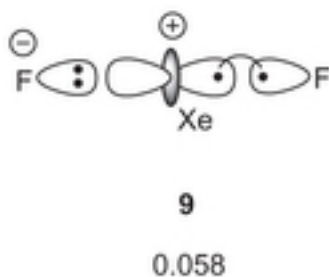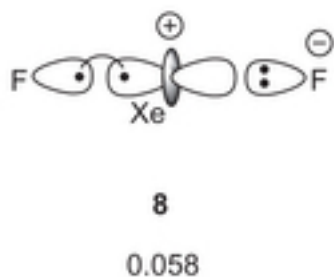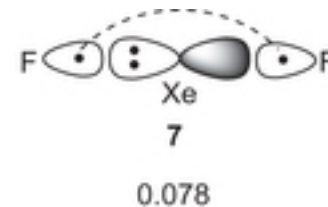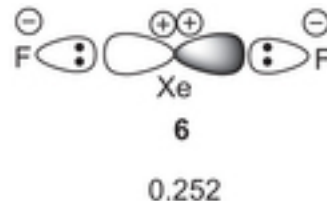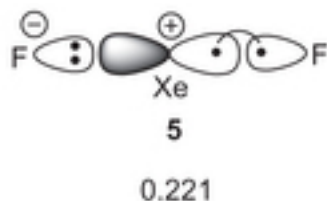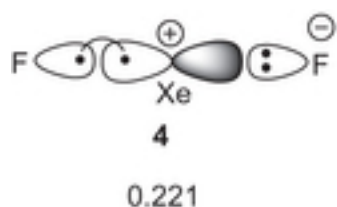
B. Braida, P. C. Hiberty, Nat. Chem. 2013, 5, 417.

The essential role of charge-shift bonding in hypervalent prototype XeF_2

6

Valence Bond Self-consistent Field (VBSCF)
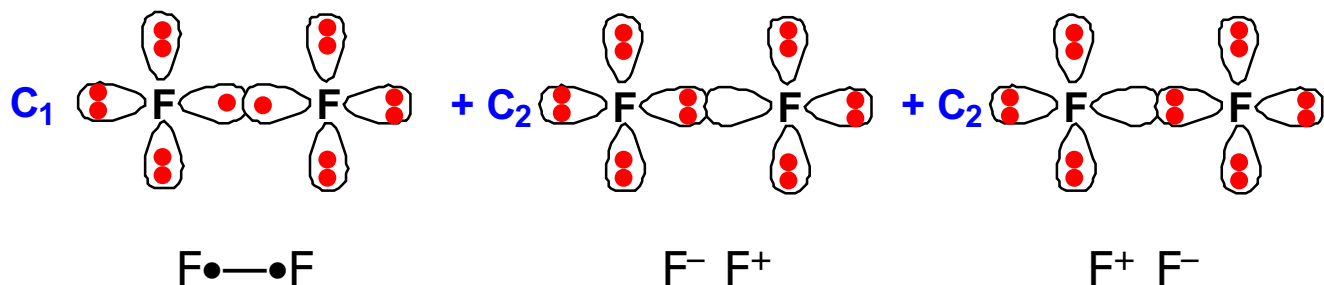
- VBSCF uses arbitrary VB structures based on localized orbitals.
- Both structural coefficients and VB orbitals are simultaneously optimized to minimize the total energy.
- VBSCF provides qualitative correct description for bond breaking/forming, but its accuracy is still wanting.
- VBSCF takes care of the static correlation, but lacks dynamic correlation.
- VBSCF wave function is adequate to serve as reference.

  van Lenthe and G. G. Balint-Kurti, J. Chem. Phys., 1983, 78, 5699.

Properties of determinant

Molecular Orbital Theory

Molecular orbitals based

- ✓ Orthogonal
- ✓ Delocalized

Valence Bond Theory

Atomic orbitals based

- ✓ Nonorthogonal
- ✓ Localized

Multi-determinant wave function

To find transformations:
- keep every VB determinants invariant.
- keep the full many-electron Hilbert space invariant.

Adding a scalar multiple of one column to another column, or more generally, non-singular linear combination of any columns, does not change the value of the determinant.

$$\Phi_K = \left| 1\bar{1}\cdots i\bar{i}\cdots tu\bar{v}\cdots \right\rangle$$

$$\Phi_L = \left| 1\bar{1}\cdots i\bar{i}\cdots xy\bar{z}\cdots \right\rangle$$

Inactive-Inactive electron separation

Any non-singular transformation within the inactive (or virtual) orbital sub-space keeps the VB determinant invariant.

The overlap of nonorthogonal orbitals is not unit.

$$s_{ij} = \langle i | j \rangle$$

After, Lowdin orthogonalization

$$|i'\rangle = \sum_j (\mathbf{s}^{-\frac{1}{2}})_{ij} |j\rangle$$

we have a set of orthogonal inactive orbitals

$$\langle i' | j' \rangle = (\mathbf{s}^{-\frac{1}{2}} \mathbf{s} \mathbf{s}^{-\frac{1}{2}})_{ij} = \delta_{ij}$$

Energy expression

Sum over the spin of the inactive orbitals, we have

inactive   inactive ---acitive

$$E = \sum_i \left\{ 2h_{ii} + \sum_j^{j>i} \left[2(ii \mid jj) - (ij \mid ij) \right] + 2\sum_{t,u} \left[(ii \mid tu) - (it \mid iu) \right] D_{tu} \right\}$$

$$+ \left\{ \sum_{tu} h_{tu} D_{tu} + \sum_{\substack{t<u \\ v<w}} \left[(tv \mid wu) - (tw \mid vu) \right] D_{tuvw} \right\}$$

active

P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, J. Chem. Phys., 1992, **97**, 7637.

Why not core-valence separation first, then orbital optimization?

Delocalized orthogonal orbitals can't be **strictly** localized by linear transformation.

$$s_{ij} = \left\langle i \middle| j \right\rangle$$

$$\left\langle i' \middle| j' \right\rangle = \delta_{ij}$$

C_1 F•——•F $+ C_2$ F^- F^+ $+ C_2$ F^+ F^-
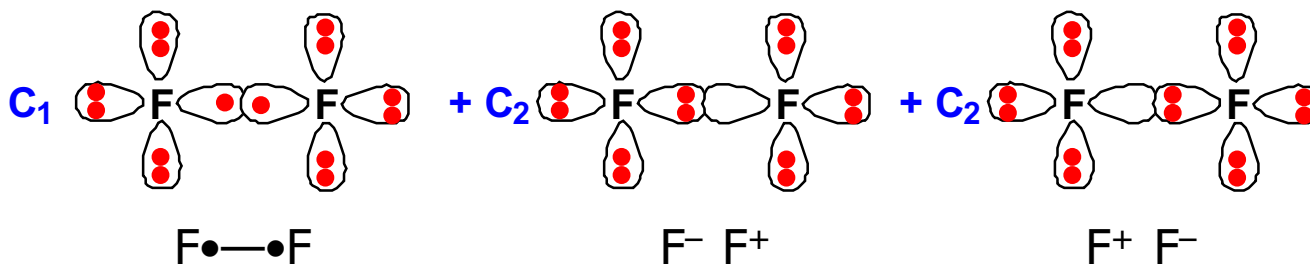
Inactive-Active electron separation

Adding a scalar multiple of one column to another column, does not change the value of the determinant.

Adding any components of inactive orbitals on to
any active orbitals keeps the VB determinant invariant

$$\left| t' \right\rangle = (1 - \sum_i \left| i \right\rangle \left\langle i \right|) \left| t \right\rangle$$

$$s'_{it} = \left\langle i \middle| t' \right\rangle = 0$$

Energy expression

After, the active-inactive electron separation, the energy expression can be reduced

$$E = \sum_i \left\{ 2h_{ii} + \sum_j^{j>i} \left[2(ii \mid jj) - (ij \mid ij) \right] \right\} \quad \text{inactive}$$

$$+ \left\{ \sum_{tu} f_{tu} D_{tu} + \sum_{\substack{t<u \\ v<w}} \left[(tv \mid wu) - (tw \mid vu) \right] D_{tuvw} \right\} \quad \text{active}$$

P. B. Karadakov, J. Gerratt, D. L. Cooper and M. Raimondi, J. Chem. Phys., 1992, **97**, 7637.

Energy gradients

$$\xi_p^{\bullet q} = 2\left\langle \Psi \middle| (H - E) \middle| \Psi_p^{\bullet q} \right\rangle$$

Inactive orbital to virtual orbital

$$\xi_a^{\bullet i} = 4(f^1)_{ia} + 2(G^2)_{ia}$$

Active orbital to active orbital

$$\xi_x^{\bullet t} = 2\sum_u (f^1)_{ux} D^{ut} + 2\sum_{uv} (f^1)_{uv} D_{\bullet x}^{v\bullet,ut} + 2\sum_{uvw} g_{wv,ux} D^{wv,ut}$$

$$+ g_{v_1 v_2, u_1 u_2} D_{\bullet \quad \bullet x}^{v_1 v_2 \bullet, u_1 u_2 t} - 2\left(E - E^1\right) D_x^{\bullet t}$$

Z. Chen, X. Chen and W. Wu, J. Chem. Phys., 2013, 138, 164120.

The VBSCF procedure in XMVB program package

1. Read initial guess for the occupied orbitals.

2. Evaluate matrix elements between VB structures.

3. Solve the secular equation to obtain the VB structural coefficients and the total energy.

4. Calculate n-RDMs of the auxiliary active orbitals.

5. Evaluate energy gradients.

6. Use LBFGS (Limited-memory Broyden–Fletcher–Goldfarb–Shanno) algorithm to update orbitals.

7. If converged, print final results; otherwise go back to step (1).

Diels-Alder reaction of 1, 3-butadiene and ethylene
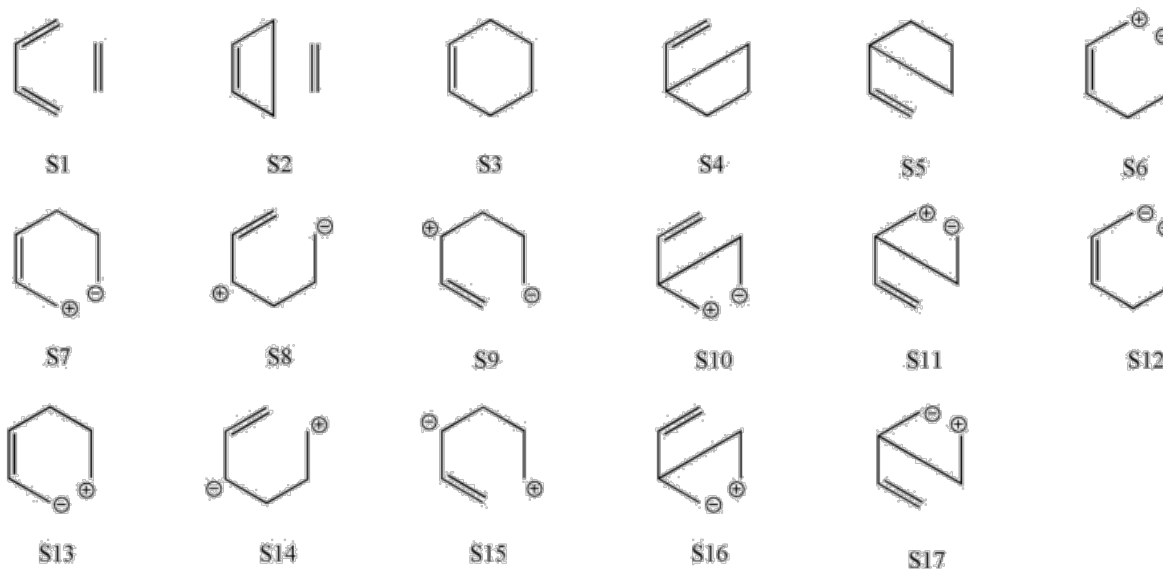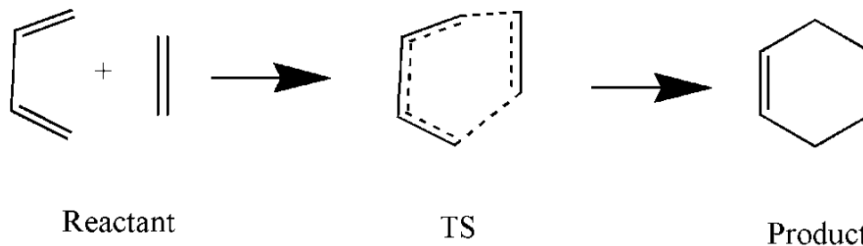
Fundamental VB structures used in VB calculations

Performance

Table 3.1 The CPU time (second) of different VBSCF algorithms

Molecule	Number of basis functions	Algorithm		
		Numberical gradients	$SSMW^a$	This work
$C_4H_6+C_2H_4(TS，5str)^b$	104	1348.0	183.9	**1.33**
$C_4H_6+C_2H_4(TS，175str)$	104	239528.7	—	**1.70**
$Fe(CO)_4C_2H_4(20str)$	170	22326.8	1765.3	**15.99**

a. Song, L., Song, J., Mo, Y., Wu, W., *J. Comput. Chem*., **2009**, 30, 399.

b. Diels-Alder reaction, trasition state, five Rumer structures.

VBSCF Orbital Optimization

Test calculations
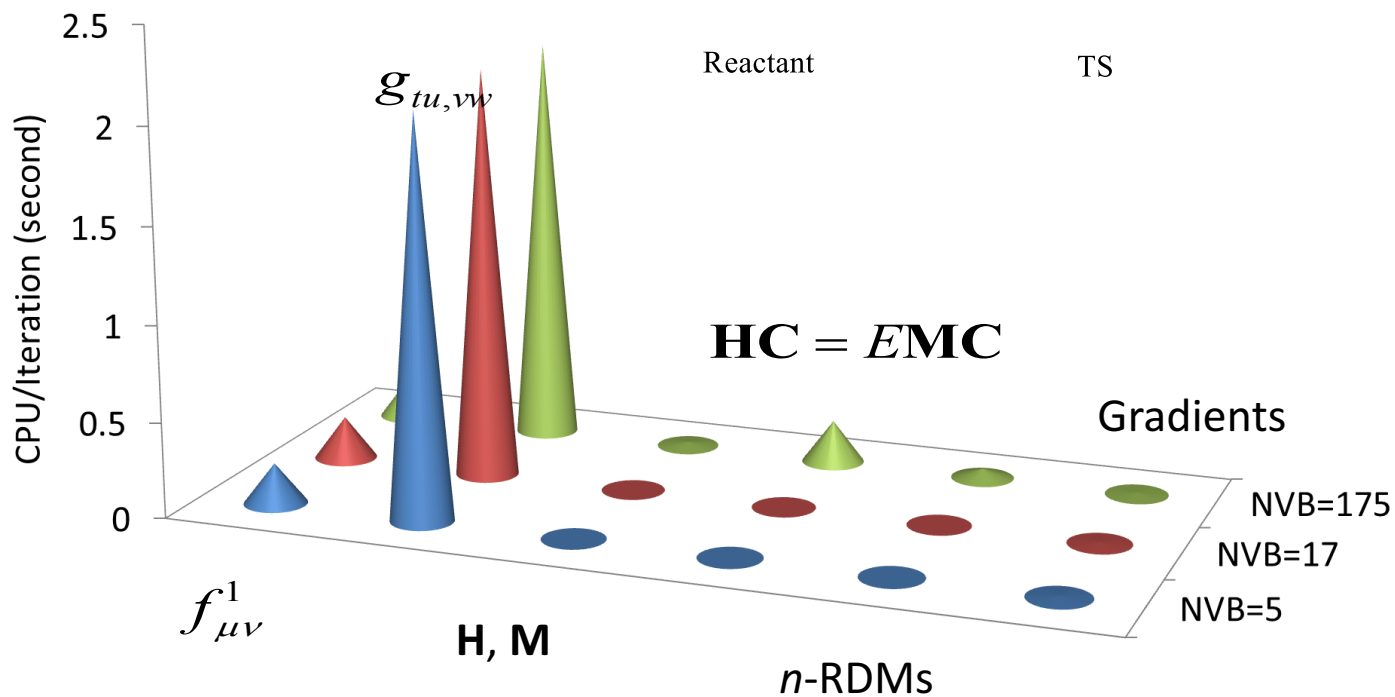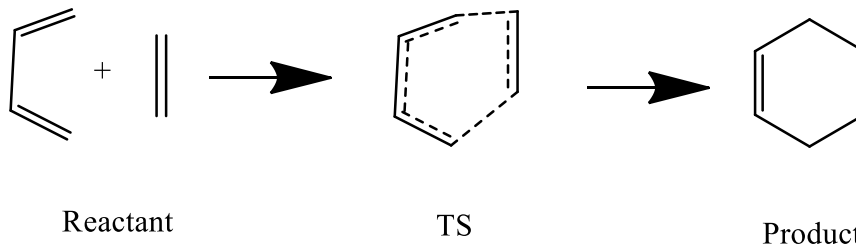
Z. Chen, X. Chen and W. Wu, J. Chem. Phys., 2013, 138, 164120.

How about
the active nonorthogonal orbitals?

Tensor Analysis and Second Quantization

Basis function sets $\{e_i\}$ and $\{\widetilde{e}_i\}$

Transformation $\quad \widetilde{e}_i = R_{\bullet i}^{j} e_j \qquad$ Einstein convention

The indices of a tensor are either covariant or contravariant.

placehold

Contravariant

$$\widetilde{T}_{i_1 i_2}^{\bullet\bullet i_3 i_4} = R_{\bullet i_1}^{j_1} R_{\bullet i_2}^{j_2} (R^{-1})_{j_3}^{\bullet i_3} (R^{-1})_{j_4}^{\bullet i_4} T_{j_1 j_2}^{\bullet\bullet j_3 j_4}$$

Covariant

Index i_1 ($\boldsymbol{i}_3$) transform on the change of basis function sets in the same (inverse) way as the basis functions do.

Tensor Analysis and Second Quantization

Basis $\{e_i\}$ 　　　 Dual Basis $\{e^i\}$

Metric Tensor 　　　　 Inner Product

Covariant $g_{ij} = \langle e_i | e_j \rangle$ 　　 Contravariant $g^{ij} = \langle e^i | e^j \rangle$

$$g_{ik} g^{kj} = \delta_i^{\bullet j}$$

Lower, Rise Indices

$$e^i = g^{ij} e_j \qquad e_i = g_{ij} e^j$$

$$\widetilde{T}_{i_1 \bullet i_3}^{\bullet i_2 \bullet i_4} = g^{i_2 j_2} g_{i_3 j_3} T_{j_1 j_2}^{\bullet\bullet j_3 j_4}$$

D. A. Danielson, *Vectors and Tensors in Engineering and Physics*. (Westview, Perseus, 1997).

Tensor Analysis and Second Quantization

Basis $\{\chi_\mu\}$

Metric tensor $\quad s_{\mu\nu} = \left\langle \chi_\mu \middle| \chi_\nu \right\rangle$

$$\left| \chi^\mu \right\rangle = s^{\mu\nu} \left| \chi_\nu \right\rangle \qquad \left| \chi_\mu \right\rangle = s_{\mu\nu} \left| \chi^\nu \right\rangle$$

Creation and annihilation operators

$$a_{p\sigma}^+ \left| vac \right\rangle = \left| \phi_{p\sigma} \right\rangle \qquad a^{p\sigma} \left| \phi_{q\omega} \right\rangle = \delta_{\bullet q}^p \delta_{\bullet \omega}^\sigma \left| vac \right\rangle$$

$$a^{p\sigma+} = a_{q\omega}^+ s^{pq} \delta^{\sigma\omega} \qquad a_{p\sigma} = a^{q\omega} s_{pq} \delta_{\sigma\omega}$$

Tensor Analysis and Second Quantization

Anticommutation Relations

$$\left\{a^{p\sigma+},a^{q\omega+}\right\}=\left\{a^{p\sigma},a^{q\omega}\right\}=0 \qquad \left\{a_{p\sigma}^{+},a_{q\omega}^{+}\right\}=\left\{a_{p\sigma},a_{q\omega}\right\}=0$$

$$\left\{a^{p\sigma},a_{q\omega}^{+}\right\}=\left\{a^{p\sigma+},a_{q\omega}\right\}=\delta_{\bullet q}^{p}\delta_{\bullet\omega}^{\sigma}$$

$$\left\{a^{p\sigma},a^{q\omega+}\right\}=\left\{a^{p\sigma+},a^{q\omega}\right\}=s^{pq}\delta^{\sigma\omega} \qquad \left\{a_{p\sigma},a_{q\omega}^{+}\right\}=\left\{a_{p\sigma}^{+},a_{q\omega}\right\}=s_{pq}\delta_{\sigma\omega}$$

F. A. Matsen, in *Adv. Quantum Chem.*, edited by P.-O. Löwdin (Academic Press, 1964), Vol. 1, pp. 59-114.

Tensor Analysis and Second Quantization

Spin-Free *N*-Body Reduced Density Operators (RDOs)

$$E^{pq} \equiv \sum_{\sigma} a^{p\sigma+} a^{q\sigma} \qquad E^{pq,rs} \equiv \sum_{\sigma_1,\sigma_2} a^{p\sigma_1+} a^{q\sigma_2+} a^{s\sigma_2} a^{r\sigma_1}$$

Spin-Free *N*-Body Reduced Density Matrices (RDMs)

$$D^{pq} \equiv \langle \Psi | E^{pq} | \Psi \rangle \qquad D^{pq,rs} \equiv \langle \Psi | E^{pq,rs} | \Psi \rangle$$

Tensor Analysis and Second Quantization

Spin-Free Hamiltonian

Tensor
Contraction

Contravariant

$$H = h_{pq} E^{pq} + \frac{1}{2} g_{pq,rs} E^{pq,rs}$$

Covariant

VBSCF Orbital Optimization

Algorithms

Gradient

Exact Hessian

Approximate Hessian
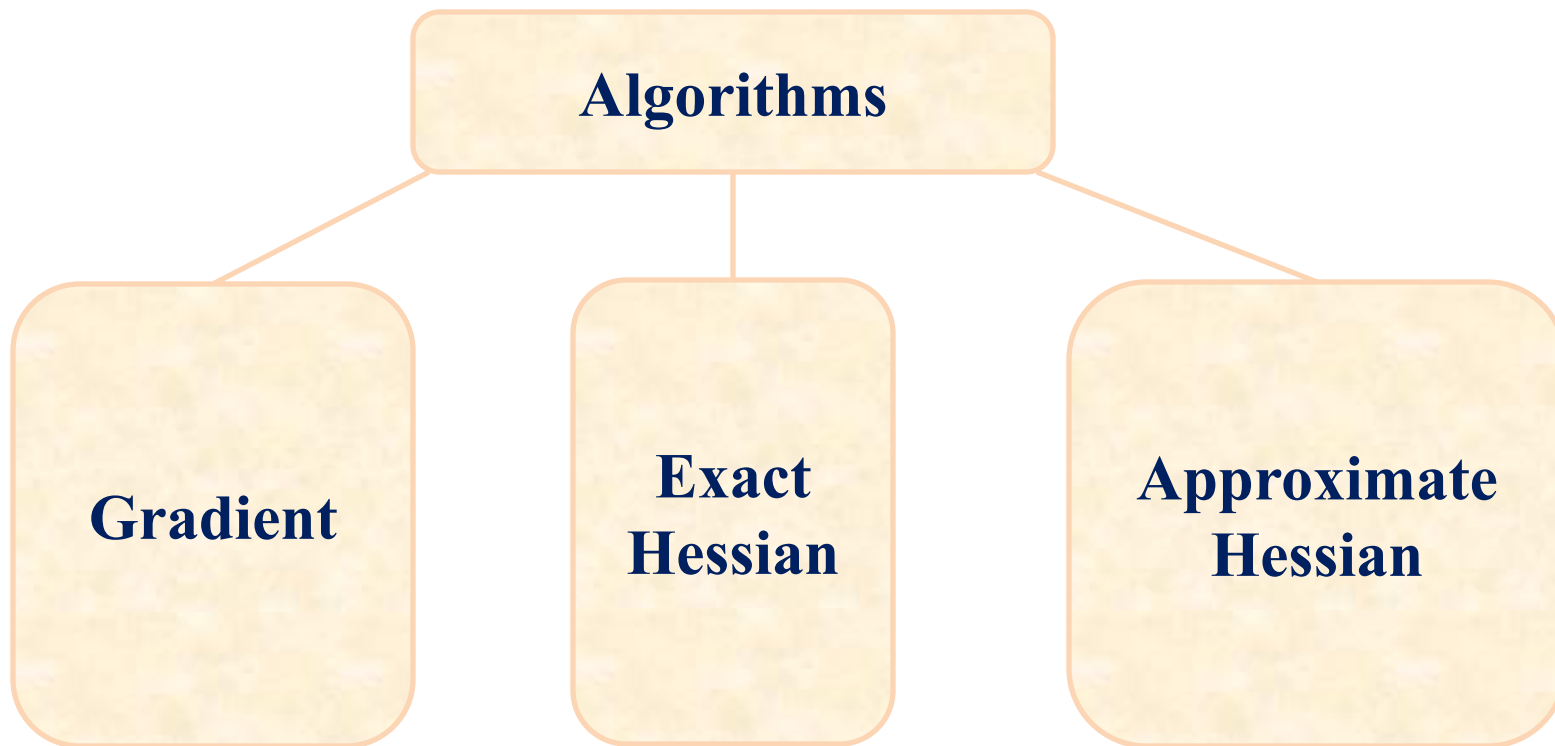
Gradient Algorithm

The energy gradient with respect to orbital excitation can be written as

$$\xi_p^{\bullet q} = 2\left\langle \Psi \middle| (H - E) \middle| \Psi_p^{\bullet q} \right\rangle$$

$$H = h_{pq} E^{pq} + \tfrac{1}{2} g_{pq,rs} E^{pq,rs}$$

Internally contracted excited wave function

$$\left| \Psi_{p_1 p_2 \cdots p_n}^{\bullet\bullet\cdots\bullet, q_1 q_2 \cdots q_n} \right\rangle = E_{p_1 p_2 \cdots p_n}^{\bullet\bullet\cdots\bullet, q_1 q_2 \cdots q_n} \left| \Psi \right\rangle$$

VBSCF: Hessian Algorithm

The orbital Hessian is written as

$$\Xi_{qs}^{\bullet\bullet\,pr} = 2\left(\left\langle \Psi_q^{\bullet p}\left|\hat{H}-E^{(0)}\right|\Psi_s^{\bullet r}\right\rangle + \left\langle \Psi^{(0)}\left|\hat{H}-E^{(0)}\right|\Psi_{qs}^{\bullet\bullet\,pr}\right\rangle\right)$$

$$-4\left\langle \Psi^{(0)}\left|\hat{H}-E^{(0)}\right|\Psi_s^{\bullet r}\right\rangle\left\langle \Psi^{(0)}\left|\Psi_q^{\bullet p}\right.\right\rangle$$

$$-4\left\langle \Psi^{(0)}\left|\hat{H}-E^{(0)}\right|\Psi_q^{\bullet p}\right\rangle\left\langle \Psi^{(0)}\left|\Psi_s^{\bullet r}\right.\right\rangle$$

Four kinds of matrix elements need to evaluate:

$$\left\langle \Psi_q^{\bullet p}\left|\Psi_s^{\bullet r}\right.\right\rangle \qquad\qquad \left\langle \Psi^{(0)}\left|\hat{H}\right|\Psi_{qs}^{\bullet\bullet\,pr}\right\rangle$$

$$\left\langle \Psi^{(0)}\left|\Psi_{qs}^{\bullet\bullet\,pr}\right.\right\rangle \qquad\qquad \left\langle \Psi_q^{\bullet p}\left|\hat{H}\right|\Psi_s^{\bullet r}\right\rangle$$

$$\left\langle E_{p_1 p_2 \cdots, q_1 q_2 \ldots} E_{r_1 r_2 \cdots, s_1 s_2 \cdots} \cdots E_{x_1 x_2 \cdots, y_1 y_2 \cdots} \right\rangle = \quad \textbf{?}$$

Enhanced Wick's Theorem

$$E_{p_1 p_2 \cdots, q_1 q_2 \cdots} E_{r_1 r_2 \cdots, s_1 s_2 \cdots} \cdots E_{x_1 x_2 \cdots, y_1 y_2 \cdots}$$

$$= E_{p_1 p_2 \cdots r_1 r_2 \cdots x_1 x_2 \cdots, q_1 q_2 \cdots s_1 s_2 \cdots y_1 y_2 \cdots}$$

$$+ \sum\nolimits_{Single} s_{r_j q_i} E_{\cdots p_i \cdots r_1 \cdots x_1 x_2 \cdots, \cdots q_j \cdots s_1 \cdots y_1 y_2 \cdots}$$

$$+ \sum\nolimits_{Double} s_{r_j q_i} s_{x_l s_k} E_{\cdots p_i \cdots r_k \cdots x_1 \cdots, \cdots q_j \cdots y_l \cdots y_1 \cdots}$$

$$+ etc.$$

Product of any number of RDOs based on nonorthogonal orbitals

Enhanced Wick's Theorem

$$E_{pr}E_{qs} = E_{pq,rs} + s_{qr}E_{ps}$$

$$E_{p_1q_1}\,E_{p_2q_2}E_{p_3q_3} = E_{p_1p_2p_3,q_1q_2q_3} + s_{p_2q_1}E_{p_1p_3,q_2q_3} + s_{p_3q_1}E_{p_1p_2,q_3q_2}$$
$$+ s_{p_3q_2}E_{p_1p_2,q_1q_3} + s_{p_2q_1}s_{p_3q_2}E_{p_1q_3}$$

$$E_{p_1p_2,q_1q_2}E_{p_3p_4,q_3q_4} = E_{p_1p_2p_3p_4,q_1q_2q_3q_4} + s_{p_3q_1}E_{p_1p_2p_4,q_3q_2q_4} + s_{p_4q_1}E_{p_1p_2p_3,q_4q_2q_3}$$
$$+ s_{p_3q_2}E_{p_1p_2p_4,q_1q_3q_4} + s_{p_4q_2}E_{p_1p_2p_3,q_1q_4q_3} + s_{p_3q_1}s_{p_4q_2}E_{p_1p_2,q_3q_4}$$
$$+ s_{p_4q_1}s_{p_3q_2}E_{p_1p_2,q_4q_3}$$

Z. Chen, X. Chen and W. Wu, J. Chem. Phys., 2013, 138, 164119.

Automatic Formula/Code Generator

Matrix Element → Automatic Formula Generator → Formula → Automatic Code Generator → XMVB Program

Matrix elements formulas

$$\left\langle \Psi_{n_1}^{\bullet m_1} \middle| H \middle| \Psi_{n_2}^{\bullet m_2} \right\rangle, \left\langle \Psi_{n_1}^{\bullet m_1} \middle| \Psi_{n_2}^{\bullet m_2} \right\rangle, \left\langle \Psi \middle| \Psi_{n_2 n_1}^{\bullet\bullet m_2 m_1} \right\rangle, \left\langle \Psi \middle| H \middle| \Psi_{n_2 n_1}^{\bullet\bullet m_2 m_1} \right\rangle, \cdots$$

Automatic Formula Generator

result formulas

$$< \Psi_A^{\cdot T} | \hat{H} | \Psi_Y^{\cdot J} > = - P_{\cdot Y}^{T \cdot tu} g_{\cdot Aut}^J + D^{Tt} G_{Y A \cdot t}^{\cdot\cdot J}$$

$$< \Psi_A^{\cdot I} | \hat{H} | \Psi_B^{\cdot T} > = - \delta_{AB} P^{Ttuv} g_{\cdot vut}^I + D^{Tt} G_{AB \cdot t}^{\cdot\cdot I} - \delta_{AB} D^{Tt} F_{\cdot t}^I$$

Automatic Code Generator

result codes

Cal_AJH0KL.F90
Cal_H0IUKW.F90
Cal_HIJKW.F90
Cal_AJH0VL.F90
......

Fortran Compiler

result program

xmvb.exe

Automatic Formula/Code Generator

Example

$$\left\langle \Psi_{n_1}^{\bullet m_1} \left| H \right| \Psi_{n_2}^{\bullet m_2} \right\rangle$$

input.txt

```
Psi_N1^M1|H|Psi_N2^M2
```

Sample input

The formulas should be represented in plain text, so we have the following "rules" for the input file:

- Underscore "**_**" indicates that the following letters are **subscript**

- "**^**" indicates that the following letters are **superscript**

- Ψ is written as "Psi"

Example: Generate formulas and codes for matrix element $\left\langle \Psi_{n_1}^{\bullet m_1} \left| H \right| \Psi_{n_2}^{\bullet m_2} \right\rangle$

output.txt

```
Psi_I^U|H|Psi_K^W =
D^UW * g_IK^i_i
-D^UW * g_IKi^i
-2 * D^UW * g_IiK^i
2 * D^UW * g_I^i_Ki
P^UtWu * g_ItKu
-P^UtWu * g_IuKt


Psi_I^U|H|Psi_K^D = 0


Psi_I^U|H|Psi_V^L = 0


Psi_I^U|H|Psi_V^W =
-D^UW * g_IVi^i
D^UW * g_IV^i_i
2 * D^UW * g_I^i_Vi
-2 * D^UW * g_IiV^i
P^UtWu * g_ItVu
-P^UtWu * g_IuVt
-0.5 * s_Vt * L^UtuvWw * g_Iuvw
0.5 * s_Vt * L^UutvwW * g_Iuvw


……………
```

Automatic Formula Generator

Sample output formulas

(in plain text)

Example: Generate formulas and codes for matrix element $\left\langle \Psi^{\bullet m_1}_{n_1} \middle| H \middle| \Psi^{\bullet m_2}_{n_2} \right\rangle$

$$< \Psi_A^{\cdot I} | \hat{H} | \Psi_Y^{\cdot J} > = - \delta^{IJ} P_Y^{\cdot tuv} g_{Atuv} + 2 G_{\cdot\cdot AY}^{IJ} - D_Y^{\cdot t} G_{\cdot\cdot At}^{IJ} + \delta^{IJ} D^{tu} G_{YtAu} + $$
$$2 \delta^{IJ} F_{YA} - \delta^{IJ} D_Y^{\cdot t} F_{At}$$

$$< \Psi_A^{\cdot T} | \hat{H} | \Psi_Y^{\cdot J} > = - P_{\cdot Y}^{T \cdot tu} g_{\cdot Aut}^J + D^{Tt} G_{YA \cdot t}^{\cdot\cdot J}$$

$$< \Psi_A^{\cdot I} | \hat{H} | \Psi_B^{\cdot T} > = - \delta_{AB} P^{Ttuv} g_{\cdot vut}^I + D^{Tt} G_{AB \cdot t}^{\cdot\cdot I} - \delta_{AB} D^{Tt} F_{\cdot t}^I$$

$$< \Psi_X^{\cdot T} | \hat{H} | \Psi_Y^{\cdot I} > = - P_{\cdot Y}^{T \cdot tu} g_{\cdot Xut}^I - \Gamma_{\cdot Y \cdot X}^{T \cdot t \cdot uv} g_{\cdot tuv}^I - s_{XY} P^{Ttuv} g_{\cdot tuv}^I + D^{Tt} G_{YX \cdot t}^{\cdot\cdot I} + $$
$$P_{\cdot\cdot X}^{Tt \cdot u} G_{Yt \cdot u}^{\cdot\cdot I} + 2 D_{\cdot X}^T F_{\cdot Y}^I - P_{\cdot YX}^{T \cdot \cdot t} F_{\cdot t}^I - s_{XY} D^{Tt} F_{\cdot t}^I$$

$$< \Psi_X^{\cdot T} | \hat{H} | \Psi_A^{\cdot I} > = D^{Tt} G_{AX \cdot t}^{\cdot\cdot I} + P_{\cdot\cdot X}^{Tt \cdot u} G_{At \cdot u}^{\cdot\cdot I} + 2 D_{\cdot X}^T F_{\cdot A}^I$$

$$< \Psi_X^{\cdot T} | \hat{H} | \Psi_A^{\cdot U} > = P^{TtUu} g_{XtAu} + P^{TtuU} g_{XAut} + \Gamma_{\cdot\cdot\cdot X}^{Ttu \cdot vU} g_{Atuv} + D^{TU} F_{XA} + $$
$$P_{\cdot\cdot X}^{Tt \cdot U} F_{At}$$

....

Automatic Formula Generator

Sample output formulas (to LaTeX input file first, and compiled to pdf)

Example: Generate formulas and codes for matrix element $\left\langle \Psi_{n_1}^{\bullet m_1} \middle| H \middle| \Psi_{n_2}^{\bullet m_2} \right\rangle$

37

Automatic Code Generator

codes.F90

```fortran
! -delta^IJ * s_tY * P^tuvw * g_Auvw
subroutine Cal_term1(Ni,Na,Nv)
    ! Variables declaration
    integer :: delta_rank
    …………
    ! Variables initialization
    delta_rank = 2
    …………
    ! contract tensors
    Call
SortContractTensor(delta,delta_rank,delta_bounds, &
delta_size,Perm_delta, &
s,s_rank,s_bounds,s_size,Perm_s, &
deltas_isum, &
deltas,deltas_rank,deltas_bounds,deltas_size)

    …………
End subroutine Cal_term1
```

Sample output codes (Fortran subroutines)

Example: Generate formulas and codes for matrix element $\left\langle \Psi_{n_1}^{\bullet m_1} \left| H \right| \Psi_{n_2}^{\bullet m_2} \right\rangle$

The Newton optimization method

$$E(\Delta \mathbf{X} + \mathbf{X}^{(0)}) = \mathbf{E}^{(0)} + \Delta \mathbf{X}\mathbf{E}^{(1)} + \frac{1}{2}\Delta \widetilde{\mathbf{X}}\mathbf{E}^{(2)}\Delta \mathbf{X} + \ldots$$

$$\frac{\partial E(\Delta \mathbf{X} + \mathbf{X}^{(0)})}{\partial X} = \mathbf{E}^{(1)} + \frac{1}{2}\left(\mathbf{E}^{(2)}\Delta \mathbf{X} + \Delta \widetilde{\mathbf{X}}\mathbf{E}^{(2)}\right) = \mathbf{E}^{(1)} + \mathbf{E}^{(2)}\Delta \mathbf{X} \equiv 0$$

$$\mathbf{E}^{(2)}\Delta \mathbf{X} = -\mathbf{E}^{(1)}$$

$$\partial E(\mathbf{X}^*) = 0$$

VBSCF Orbital Optimization

	Analytical gradient, LBFGS method (iopt=5)			Analytical gradient and Hessian, Newton method (iopt=6)		
	number of iteration	total time(s)	time per iteration(s)	number of iteration	total time(s)	time per iteration(s)
Li_2(sto-6g)	8	0.001	0.000	5	0.03	0.006
F_2(sto-3g)	5	0.001	0.000	3	0.15	0.050
F_2(6-31g*)	25	0.07	0.003	5	2.08	0.416
N_2(6-31g*)	44	0.26	0.006	5	14.96	2.992
H_2O_2(6-31g*)	102	0.5	0.005	6	9.99	1.665
C_2H_6(6-31g*)	67	0.76	0.011	5	13.67	2.734
C_2H_6(6-31+g**)	125	20.5	0.164	5	146.23	29.246
C_2H_4(6-31g*)	112	0.7	0.006	6	9.96	1.660
H_2O(cc-pvdz)	68	0.19	0.003	6	1.93	0.322

Reduced Density Matrix Approach for VB Theory

Nonorthogonal orbital based *N*-body reduced density matrices and their applications to valence bond theory. I. Hamiltonian matrix elements between internally contracted excited valence bond wave functions

Zhenhua Chen, Xun Chen, and Wei Wu[a]

Nonorthogonal orbital based *N*-body reduced density matrices and their applications to valence bond theory. II. An efficient algorithm for matrix elements and analytical energy gradients in VBSCF method

Zhenhua Chen, Xun Chen, and Wei Wu[a]

Nonorthogonal orbital based *n*-body reduced density matrices and their applications to valence bond theory. III. Second-order perturbation theory using valence bond self-consistent field function as reference

Zhenhua Chen, Xun Chen, Fuming Ying, Junjing Gu, Huaiyu Zhang, and Wei Wu[a]

Nonorthogonal orbital based *N*-body reduced density matrices and their applications to valence bond theory. IV. The automatic implementation of the Hessian based VBSCF method

Xun Chen, Zhenhua Chen, and Wei Wu[a]

Valence Bond Coupled Cluster Theory?

Enhanced Wick's Theorem

$$E_{p_1 p_2 \cdots, q_1 q_2 \cdots} E_{r_1 r_2 \cdots, s_1 s_2 \cdots} \cdots E_{x_1 x_2 \cdots, y_1 y_2 \cdots}$$

$$= E_{p_1 p_2 \cdots, q_1 q_2 \cdots s_1 s_2 \cdots y_1 \cdots}$$

$$+ \sum_{Single} \cdots _i \cdots r_1 \cdots x_1 x_2 \cdots,$$

$$+ \sum_{Double} s_{r_j q_i} s_{x_l s_k} E_{\cdots p_i \cdots r_k \cdots x_1 \cdots, \cdots q_j \cdots y_l \cdots y_1 \cdots}$$

$$+ etc.$$

Automatic Formula Generator

Automatic Code Generator

MVB 2.1

An ab initio Non-orthogonal Valence Bond Program

Lingchun Song, Zhenhua Chen, Fuming Ying, Jinshuai Song, Xun Chen, Peifeng Su, Yirong Mo, Qianer Zhang, Wei Wu*

Xiamen University,
Xiamen, Fujian 361005, CHINA

Chen; Ying; Chen; Song; Su; Song; Mo; Zhang; Wu,
Int. J. Quant. Chem., 2015, 115, 731.

The Upper Limit of Classical Valence Bond Theory

Strict Localized orbital

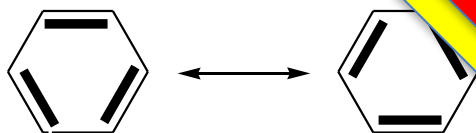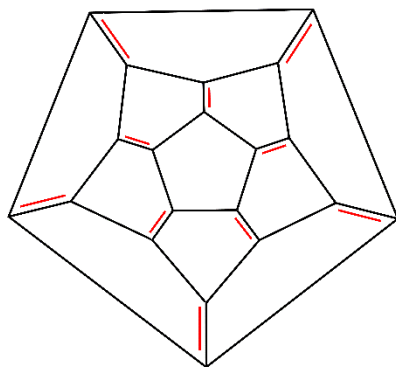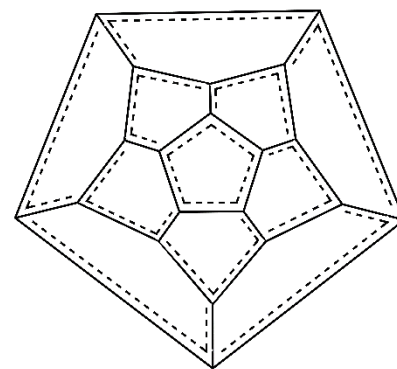**Spin-free HLSP**

resonance

Energy of individual structure

18+

(a)

VB diagram

Energy (kcal/mol)

C$_{20}$
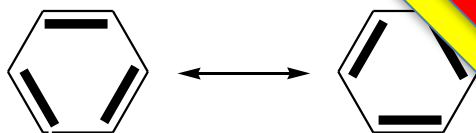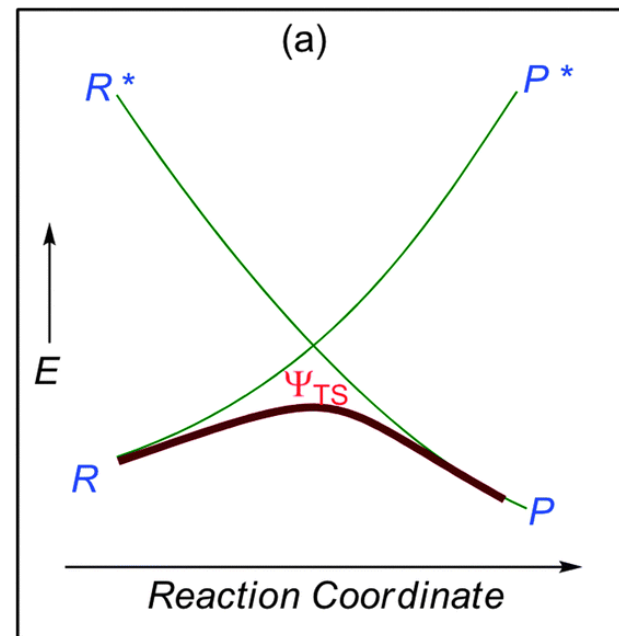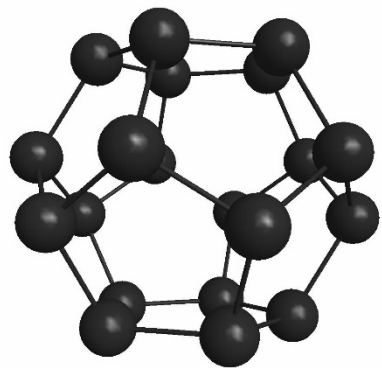
166.2

172.4

0.0

The Upper Limit of Classical Valence Bond Theory

Strict Localized orbital

Spin-free HLSP

21+

resonance

Energy of individual structure

(a)

R^*

P^*

E

Ψ_{TS}
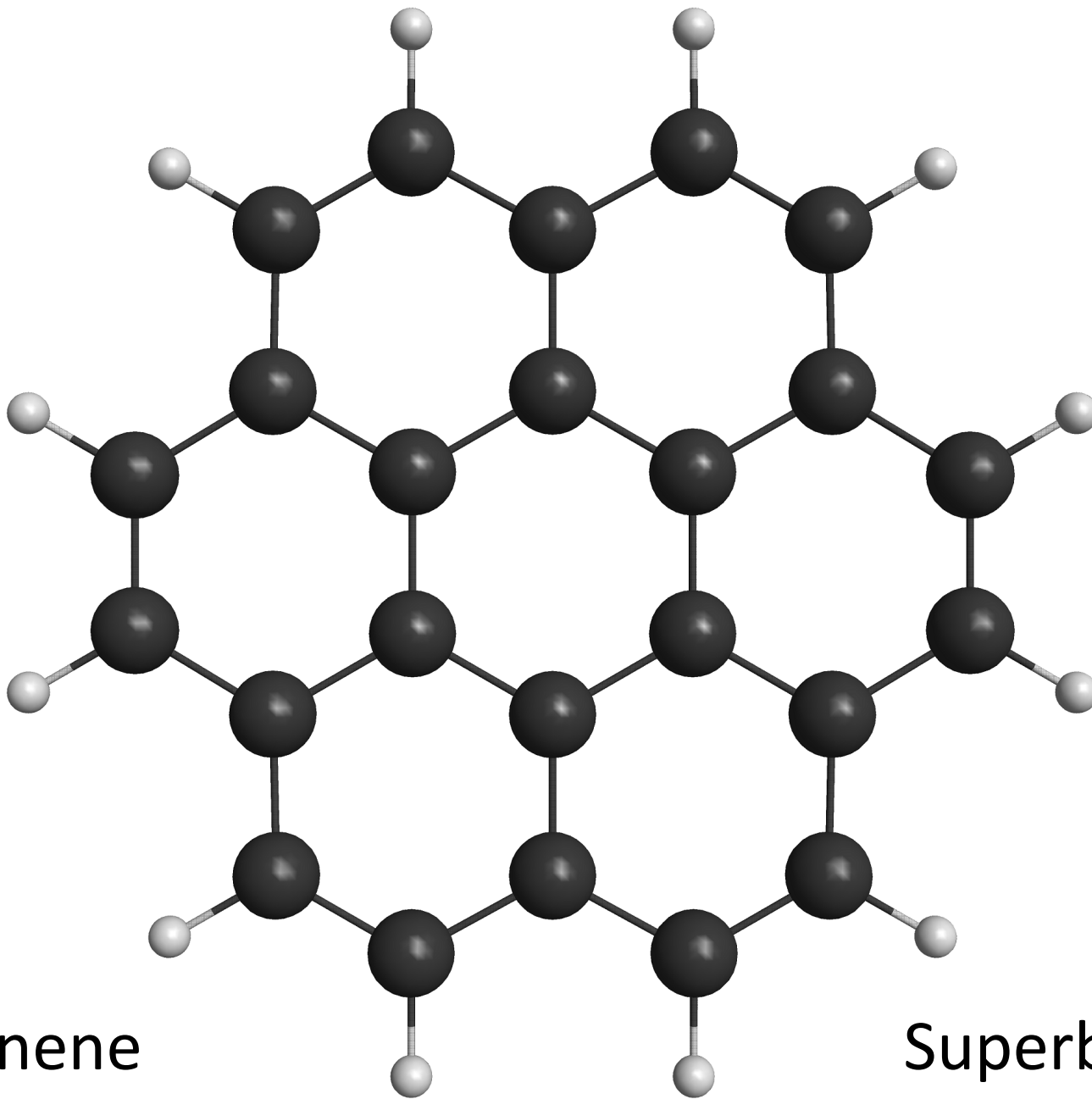
R

P

Reaction Coordinate
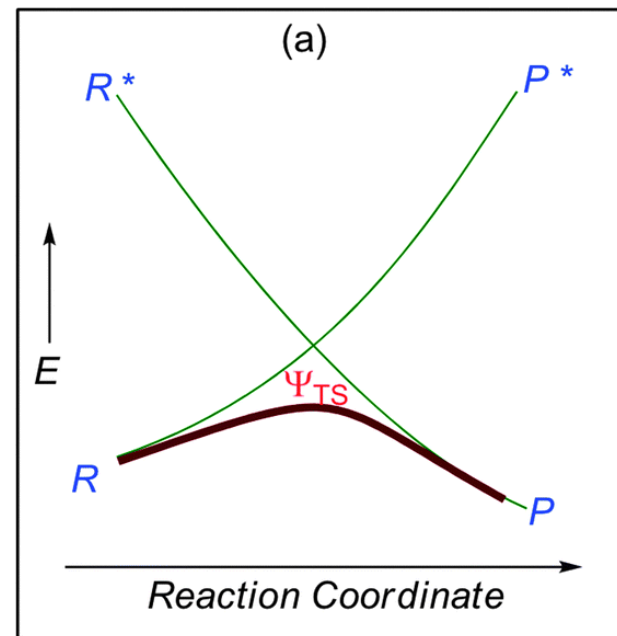
VB diagram
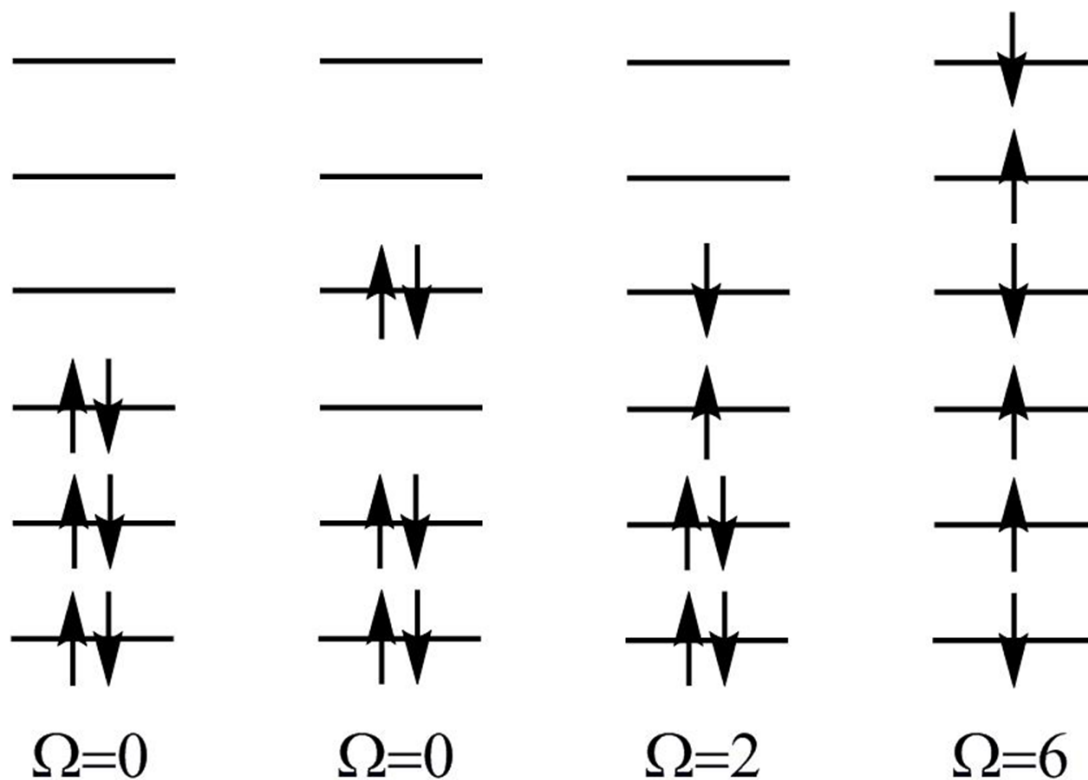
Coronene   Superbenzene

Seniority Number in Valence Bond Theory

The number of singly occupied orbitals

Determinants with various Ω values

# The performance of seniority number based CI methods

H$_8$

| R(Å)	Benchmark[a]	Deviation from the benchmark (millihartree)					
		$\Omega = 0$[b]	$\Omega = 0,2$[b]	$\Omega = 0,2,4$[b]	$n_{ph} = 2$[c]	$n_{ph} = 3$[c]	$n_{ph} = 4$[c]
		H$_8$ –linear chain, CI active space = [8 electrons in 8 orbitals]					
0.7	−4.166 794	33.247	8.357	0.136	2.224	0.837	0.013
1.0	−4.414 546	33.977	9.619	0.068	7.240	3.598	0.125
1.2	−4.355 115	34.027	9.497	0.441	15.071	8.566	0.524
1.5	−4.218 948	32.405	9.875	0.743	39.283	26.269	3.311
2.0	−4.064 602	20.854	5.803	0.193	122.692	95.757	25.790
2.2	−4.034 862	14.783	3.880	0.019	166.221	150.002	41.975
3.0	−3.997 913	2.054	0.468	0.092	323.970	182.952	6.802
NPE[d]	**0**	**31.923**	**9.151**	**0.675**	**321.746**	**182.115**	**41.962**

Strong correlation problem:
Seniority number based CI has **better convergence behavior** toward FCI limit than particle-hole number based CI. And thus smaller nonparallelity error (NPE) for PECs.

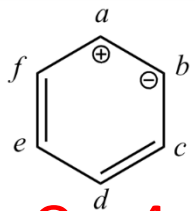# Heitler-London-Slater-Pauling (HLSP) Function
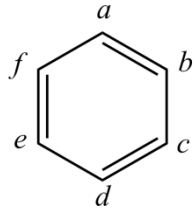
$$\Phi_1 = |a\bar{b}c\bar{d}e\bar{f}| - |\bar{a}bc\bar{d}e\bar{f}| - |a\bar{b}\bar{c}de\bar{f}| + |\bar{a}b\bar{c}de\bar{f}|$$

$$- |a\bar{b}c\bar{d}\bar{e}f| + |\bar{a}bc\bar{d}\bar{e}f| + |a\bar{b}\bar{c}d\bar{e}f| - |\bar{a}b\bar{c}d\bar{e}f|$$
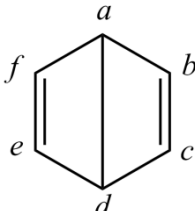
$\Omega = 6$

$$\Phi_2 = (|a\bar{d}b\bar{c}e\bar{f}| - |\bar{a}db\bar{c}e\bar{f}| - |a\bar{d}bce\bar{f}| + |\bar{a}d\bar{b}ce\bar{f}|$$

$$- |a\bar{d}b\bar{c}\bar{e}f| + |\bar{a}db\bar{c}\bar{e}f| + |a\bar{d}bc\bar{e}f| - |\bar{a}d\bar{b}c\bar{e}f|)$$

$\Omega = 6$

$$\Phi_3 = \left|b\bar{b}c\bar{d}e\bar{f}\right| - \left|b\bar{b}\bar{c}de\bar{f}\right| - \left|b\bar{b}c\bar{d}\bar{e}f\right| + \left|b\bar{b}\bar{c}d\bar{e}f\right|$$

$\Omega = 4$

$$\Phi_4 = \left|b\bar{b}d\bar{d}e\bar{f}\right| - \left|b\bar{b}d\bar{d}\bar{e}f\right|$$

$\Omega = 2$

50

Ω	6	4	2	0
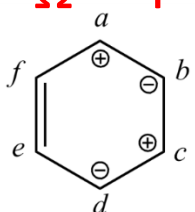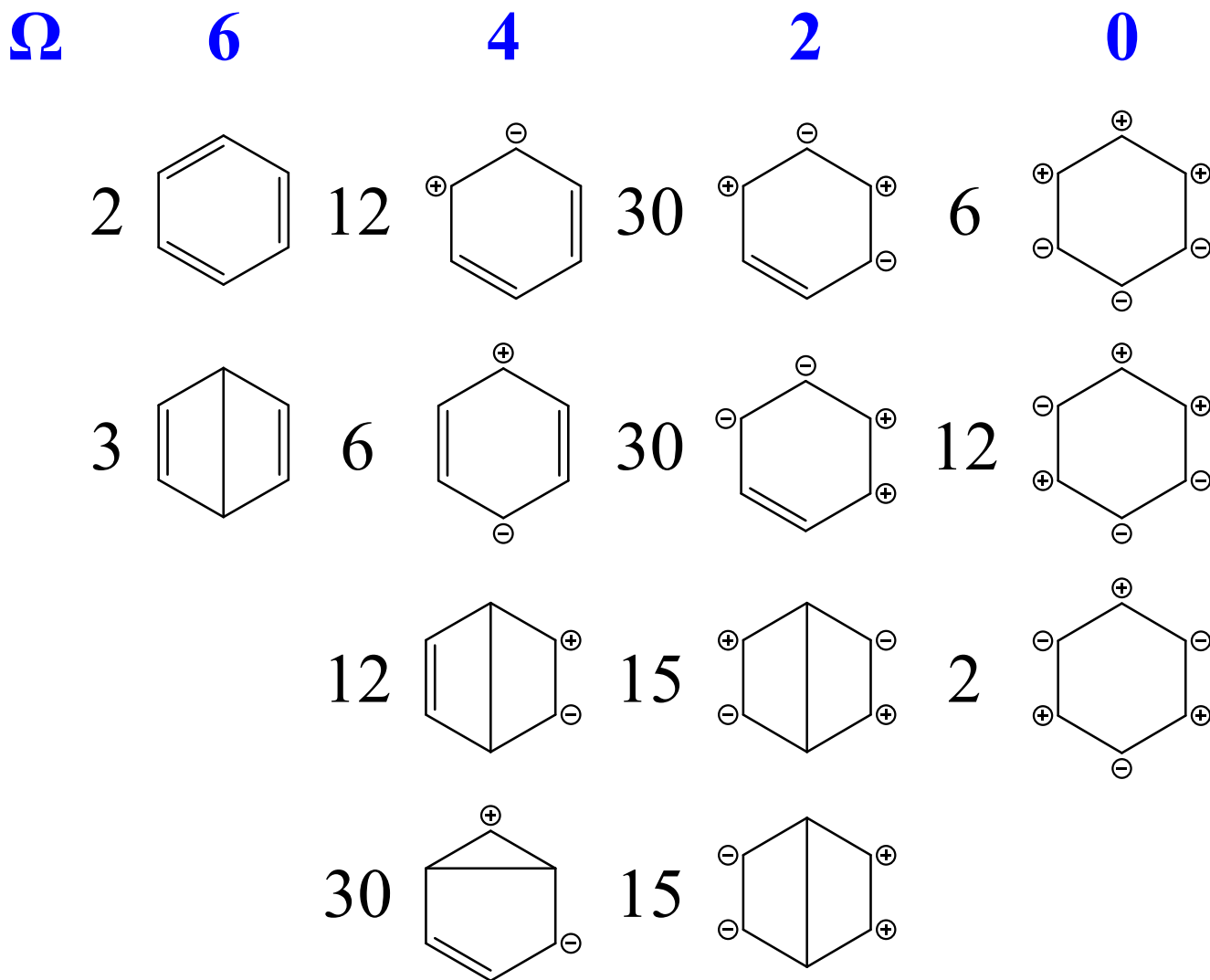
Seniority number (Ω) shares chemical interpretation:
Ionicity (ω) $\Omega + 2\omega = N$

51

$$\Psi = \sum_K C_K \Phi_K = \sum_\Omega \sum_A \sum_\kappa C_{\Omega A\kappa} \Phi_{\Omega A\kappa}$$

Ω is over $2S$, $2S+2$, …, Ω_{max} $\Omega_{max} = \begin{cases} N, & N \leq n \\ 2n - N, & N > n \end{cases}$

Ω: Seniority number
A: Orbital configuration which belongs to the given Ω
κ: Component of spin eigenfunction

Seniority based VB wave function

$$\Psi_{(\Lambda)} = \sum_\Omega \sum_A \sum_\kappa C_{\Omega A\kappa} \Phi_{\Omega A\kappa}, \quad (\Lambda = \Omega_{max}, \Omega_{max} - 2, \cdots, 2S)$$

Ω is over Λ, $\Lambda + 2$, …, Ω_{max}

The lowest level is $\Lambda = \Omega_{max}$, SCVB method.

Ω^{MO}	0	2	4	6	8
N^{CSF}	70	560	840	280	14
N^{DET}	70	1120	2520	1120	70
N^{VB}	14	280	840	560	70
Ω^{VB}	8	6	4	2	0

$N = 8$, $n = 8$

For the lowest level, ($n=N$, $S=0$)

$$\frac{N_{\Omega}^{MO}}{N_{\Omega}^{VB}} = N/2 + 1$$

H$_8$

Table 1. Total CASSCF energies, deviation from CASSCF, and non-parallelity errors (NPE) for H$_8$ linear chain molecule with seniority-based MCSCF. The CASSCF energies are in E_h, and the deviations are in mE_h. (Basis set: cc-pVDZ)

R (Å)	CASSCF[a]	Molecular Orbital Theory[a]			Valence Bond Theory		
		$\Omega=0$	$\Omega=(0,2)$	$\Omega=(0,2,4)$	$\Omega=8$	$\Omega=(8,6)$	$\Omega=(8,6,4)$
0.7	−4.166 794	33.247	8.357	0.136	12.232	0.814	0.158
1.0	−4.414 546	33.977	9.619	0.068	8.743	1.280	0.027
1.2	−4.355 115	34.027	9.497	0.441	5.933	1.112	0.021
1.5	−4.218 948	32.405	9.875	0.743	2.678	0.628	0.010
2.0	−4.064 602	20.854	5.803	0.193	0.420	0.190	0.000
2.2	−4.034 862	14.783	3.880	0.019	0.173	0.060	0.000
3.0	−3.997 913	2.054	0.468	0.092	0.003	0.000	0.000
NPE	0	31.923	9.151	0.675	12.229	1.280	0.158

[a]Scuseria, et al, J. Chem. Phys. 2011, 135, 044119.

Chen; Zhou; Wu, J. Chem. Theor. Comput. 2015, 11, 4102.

N$_2$

Table 3. Total CASSCF energies, deviation from CASSCF, and non-parallelity errors (NPE) for N$_2$ molecule with seniority-based MCSCF. The CASSCF energies are in E_h, the deviations and NPE are in mE_h. (Basis set: cc-pVDZ)

R (Å)	CASSCF[a]	Molecular Orbital Theory[a]			Valence Bond Theory		
		$\Omega=0$	$\Omega=(0,2)$	$\Omega=(0,2,4)$	$\Omega=6$	$\Omega=(6,4)$	$\Omega=(6,4,2)$
0.9	-108.889381	50.120	9.103	0.048	14.953	0.988	0.074
1.1	-109.103396	64.257	14.062	0.042	17.941	0.506	0.055
1.5	-108.943238	74.762	27.879	0.125	21.687	3.616	0.080
1.8	-108.827857	67.428	19.581	0.064	19.685	4.175	0.035
2.1	-108.786568	76.957	17.730	0.039	3.134	0.346	0.012
3.0	-108.777536	104.025	23.244	/	0.109	0.004	0.001
NPE	0	53.905	18.776	0.086	21.578	4.171	0.080

[a]Scuseria, et al, J. Chem. Phys. 2011, 135, 044119.

Chen; Zhou; Wu, J. Chem. Theor. Comput. 2015, 11, 4102.
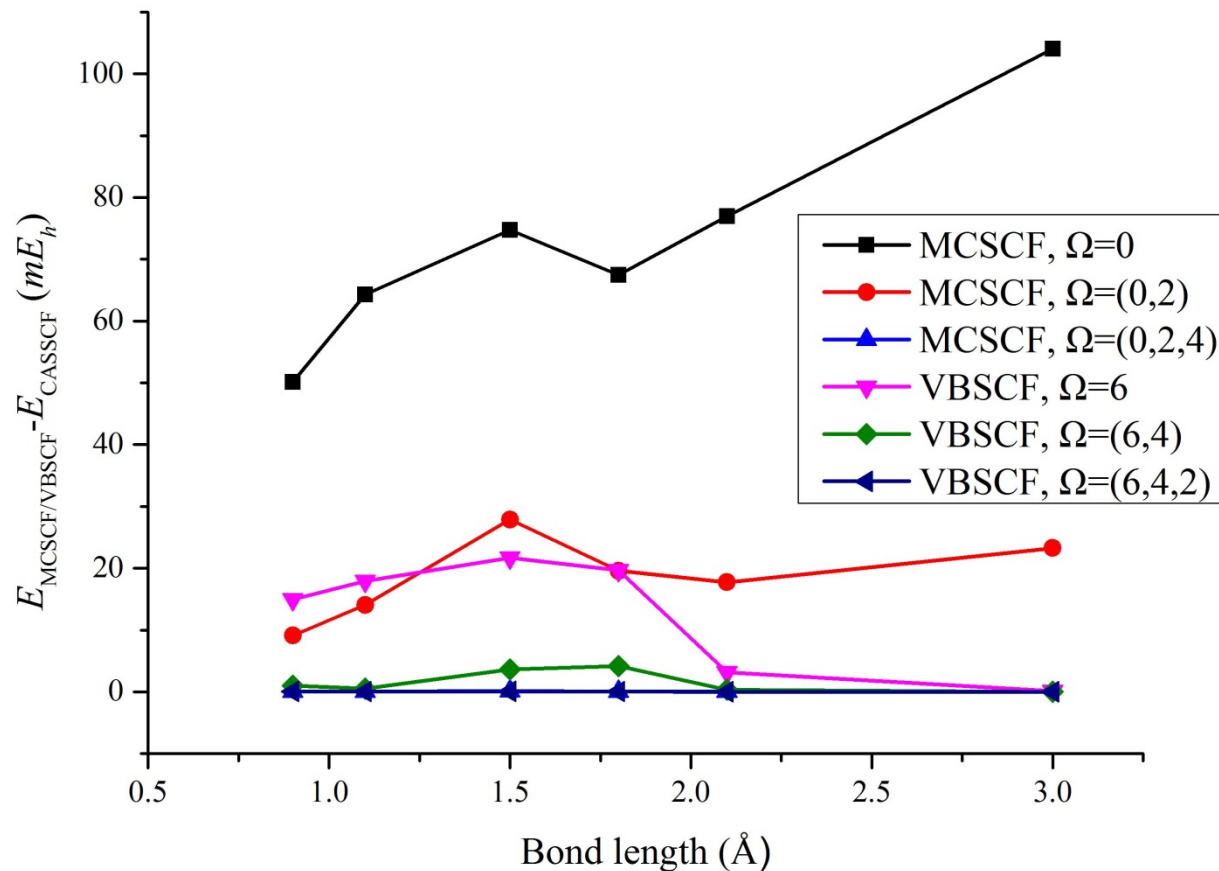
The ground state dissociation PECs for N_2 molecule by seniority-based MCSCF and VBSCF approaches. The error is defined as the energy difference of seniority-based method from the benchmark CASSCF result.

How to make seniority number based VB more efficient?

Active-Active Electron Separation

Any non-singular transformation within the active orbital sub-space keeps the full Hilbert space invariant. But, individual VB determinant changes.

The metric of nonorthogonal orbitals is not unit.

$$s_{tu} = \left\langle \phi_t \middle| \phi_u \right\rangle$$

Using the contravariant metric $\qquad \phi^t = s^{tu} \phi_u$

we have $\qquad \delta_t^u = \left\langle \phi_t \middle| \phi^u \right\rangle$

The transformation of rank-n determinant in seniority number restricted subspace

$$\Phi_P = \left| \cdots \phi_t \cdots \overline{\phi}_u \cdots \right\rangle$$

$$\Phi^Q = \left| \cdots \phi^v \cdots \overline{\phi}^w \cdots \right\rangle$$

Contravariant

$$\sum_Q C_Q \Phi^Q = \Psi = \sum_P C^P \Phi_P$$

Covariant

U

t

Covariant   Contravariant

Malmqvist P Å. Int. J. Quantum Chem. 1986, 30, 479.
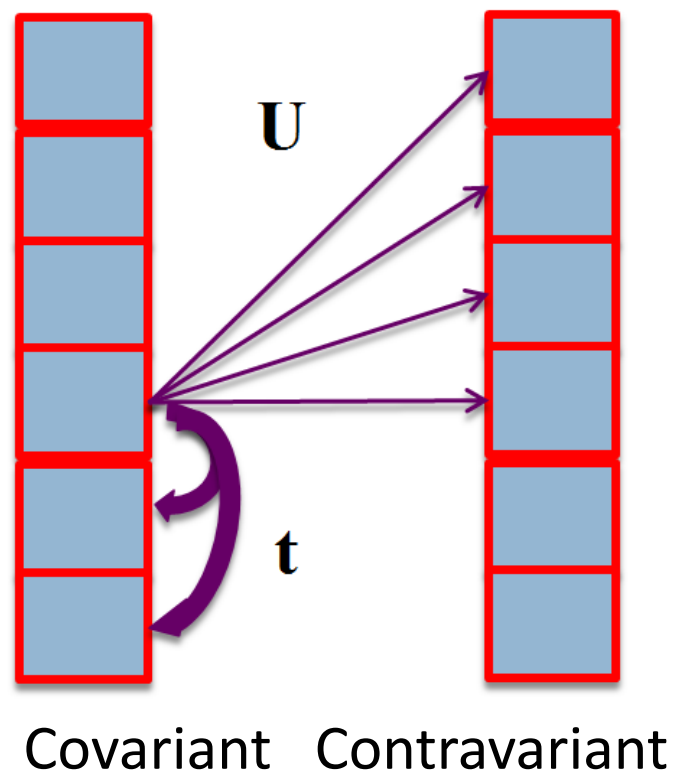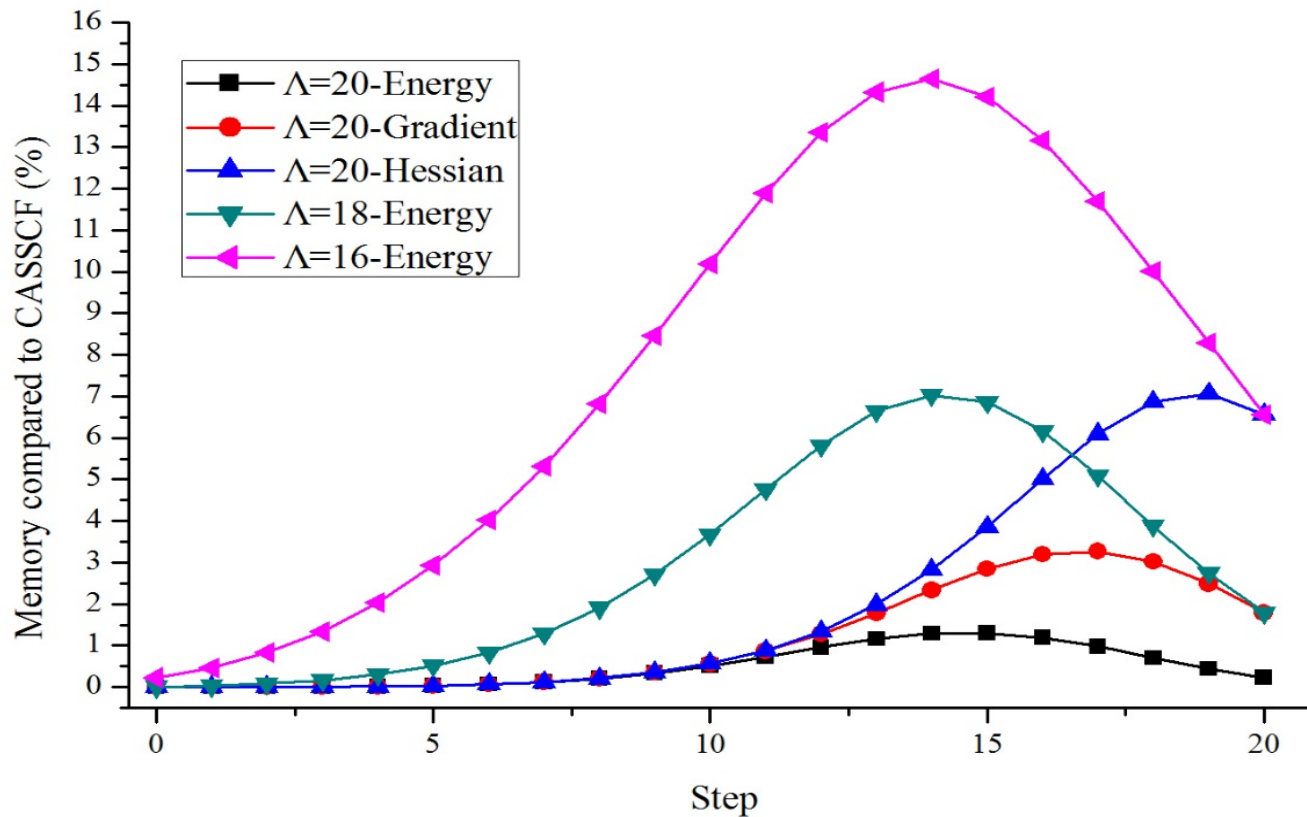
The memory cost of determinant transformation in seniority number based VB methods, as compared to CASCI calculation.

Energy (kcal/mol)

172.4

166.2
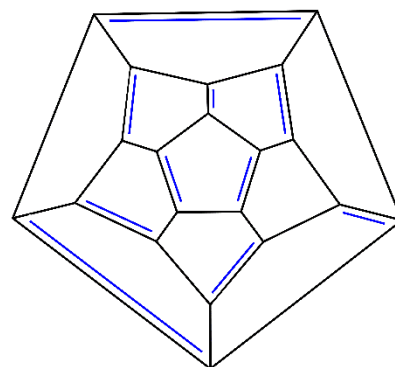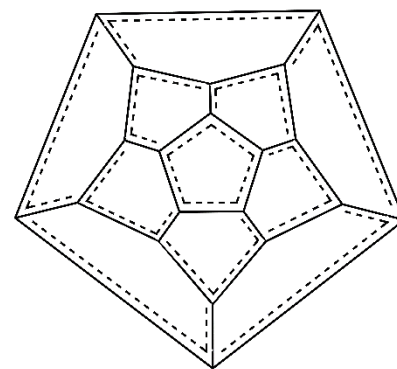
0.0
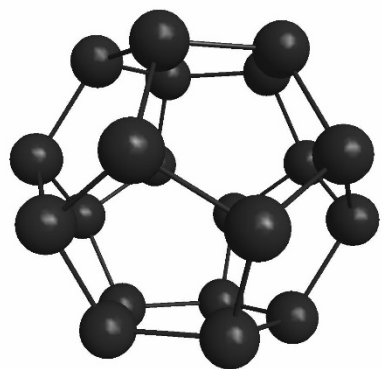
C_{20}

Acknowledgements

Prof. Wei Wu
Prof. Sason Shaik
Prof. Philippe Hiberty
Prof. Benoit Braida
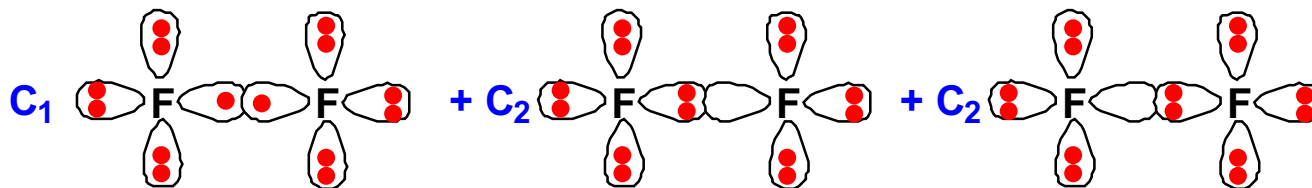**Dr. Fuming Ying**
Dr. Xun Chen
Mr. Chen Zhou

Thank you!

Points

- How to remove the redundant variables in classical VB wave function.

$$E = E(\mathbf{C}, \mathbf{T})$$

C is VB structural coefficient vector; **T** is the orbitals expansion matrix. They are coupled.

- Other gradient based optimization methods besides Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.