

# **Valence bond based multi-reference DFT method**

**Peifeng Su**

**supi@xmu.edu.cn**

**Xiamen University**

# Electronic correlation

Many electrons interact simultaneously and their motion is correlated, which can not be described by mean field approximation (HF method)

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

**According to the different origin, there are two kinds of electronic correlation: dynamic and static correlations. They can not be separated exactly!**

# Methods for electronic correlation

## Multi-reference wave function method

- MCSCF (CASSCF)
- VBSCF

$$\Psi = \sum_K C_K \Phi_K^{\text{CSF}}$$

lack of dynamic correlation

## KS-DFT

mimics electron-correlation effects at a independent particle level with  $E_{\text{XC}}$  functional.

$$E^{\text{KS-DFT}}(\rho) = T_S[\rho] + J[\rho] + E_{\text{Ne}}[\rho] + E_{\text{XC}}[\rho]$$

Single reference

lack of static correlation

Static  
correlation

Dynamic  
correlation

**Multi-reference PT, CI and CC methods**

**Accurate but expensive**

**Static  
correlation**

**Dynamic  
correlation**

**Multi-reference SCF + DFT = MRDFT**

# MRDFT

## Multi-reference wave function method + DFT functionals

CAS-DFT  
BLW-DFT  
MC-PDFT  
DFVB  
...

Grimme S, Savin A, Roos B, Head-Gordon M, Cremer D, Yamaguchi K, Filatov M, Shaik S, Wu Q, Gao J, MO Y, Clementi E, Truhlar D, Fromager E, Jensen H,....

**The double counting error**

## Strategy 1

# Energy of MR wavefunction plus correction from DFT

$$E(\text{WF}) + \Delta E(\text{DFT})$$

Let the active space of MR wave function or the DFT correction as small as possible.

Semiempirical treatment of  $\Delta E(\text{DFT})$ .

## dc-DFVB

$$E^{\text{dc-DFVB}}[\rho^{\text{VB}}] = E^{\text{VBSCF}} + E_{\text{C}}[\rho^{\text{VB}}]$$

Ying, F.; Su, P.; Chen, Z.; Shaik, S.; Wu, W. *J. Chem. Theory Comput.* **2012**, 8, 1608

## MC-PDFT

$$E = V_{\text{nn}} + \langle \Psi | T + V_{\text{ne}} | \Psi \rangle + V_{\text{C}}[\rho] + E_{\text{ot}}[\rho, \Pi]$$

$E_{\text{ot}}[\rho, \Pi]$  is on-top electronic density functional

Olsen, J and Truhlar, D et al *J. Chem. Theory Comput.* 2014, 10, 3669

## CAS-DFT

Gräfenstein, J.; Cremer, D. *Mol. Phys.* 2005, 103, 279.

Takeda, R.; Yamanaka, S. and Yamaguchi, K. *Int. J. Quant. Chem.* 2004, 96, 463.



## Strategy 2

# Modified Hamiltonian matrix elements by DFT using configuration interaction scheme

## DFT/MRCI

$$\langle \omega W | \hat{H}^{\text{DFT}} - E^{\text{DFT}} | \omega W \rangle$$

$$\langle \omega W | \hat{H}^{\text{DFT}} - E^{\text{DFT}} | \omega' W' \rangle$$

Semiempirical formula

Grimme, S.; Waletzke, M. *J. Chem. Phys.* **1999**, *111*, 5645

Cembran, A.; Song, L.; Mo, Y.; Gao, J. *J. Chem. Theory Comput.* 2009, *5*, 2702

$$E^{\text{hc-DFVB}} = \sum_{K,L} C_K C_L H_{KL}^{\text{hc-DFVB}} = E^{\text{VBSCF}} + E^{\text{corr}}$$

Hamiltonian matrix elements are defined as:

$$H_{KL}^{\text{hc-DFVB}} = H_{KL}^{\text{VBSCF}} + H_{KL}^{\text{corr}}$$

$$H_{KL}^{\text{corr}} = \sum_{\kappa,\lambda} d_{\kappa K} d_{\lambda L} H_{\kappa\lambda}^{\text{corr}}$$



The correlation correction matrix elements of determinants

$$H_{\kappa\lambda}^{\text{corr}}$$

**The diagonal elements**  $k = l$

$$H_{kk}^{\text{corr}} = E^{\text{corr}} [r_k] = E_C [r_k] + (1-a) (E_X [r_k] - W_k)$$

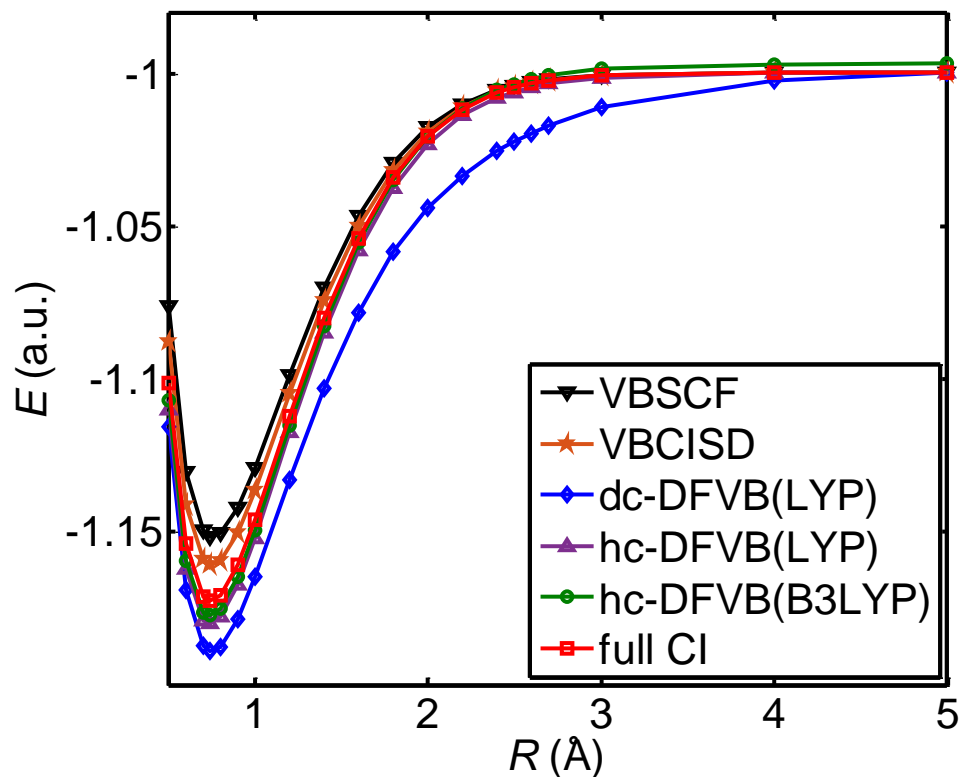
$W_k$  : exact exchange energy of determinant  $\kappa$

**The off-diagonal elements**  $\kappa \neq \lambda$

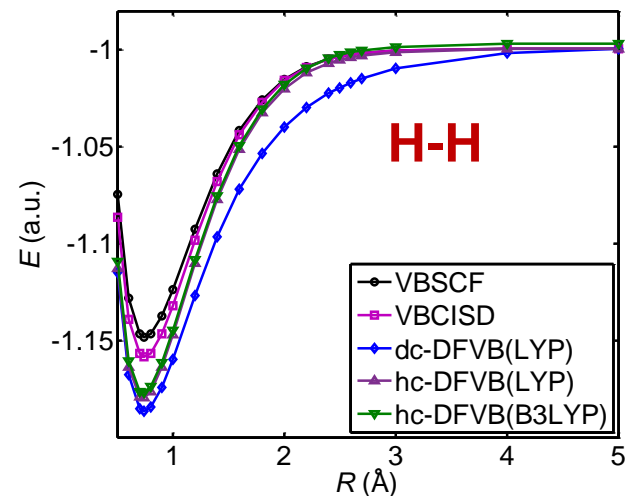
$$H_{\kappa\lambda}^{\text{corr}} \approx \left( \frac{H_{\kappa\lambda}^{\text{VBSCF}}}{H_{\kappa\kappa}^{\text{VBSCF}} + H_{\lambda\lambda}^{\text{VBSCF}}} \right) (E^{\text{corr}} [\rho_\kappa] + E^{\text{corr}} [\rho_\lambda])$$

$$H_{\kappa\lambda}^{\text{corr}} \approx \frac{1}{2} S_{\kappa\lambda} (E^{\text{corr}} [\rho_\kappa] + E^{\text{corr}} [\rho_\lambda])$$

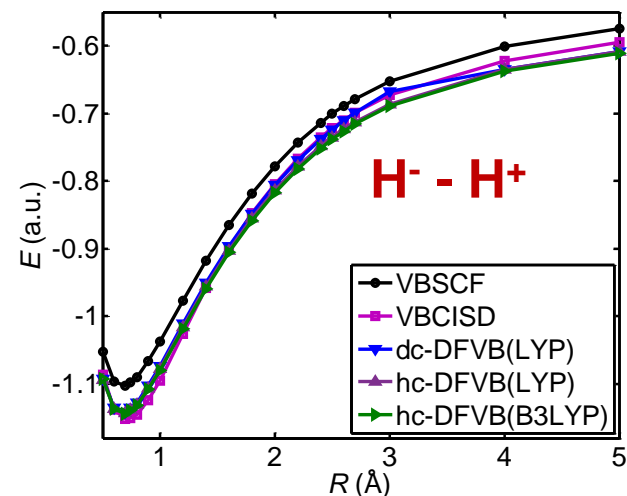
**Figure 1.** The potential energy surfaces of  $H_2$



(a)



(b)



Accuracy: hc-DFVB  $\approx$  Full CI, VBCISD(MRCI)  
Each diabatic (structure) has its own correction.

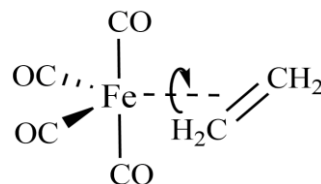
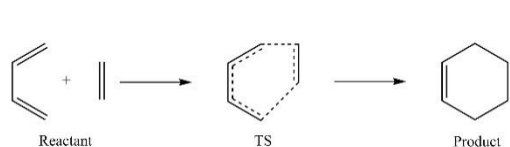
Table 1. The BDE (in kcal/mol) of diatomic molecules by different methods. (Deviation values are shown)

$D_e$	Expt	VBSCF	B3LYP	M06	revTPSS	hc-DFVB		
						B3LYP	M06	revTPSS
Li <sub>2</sub>	24.4	-14.2	-3.7	0.2	11.4	-4.9	-8.4	0.9
F <sub>2</sub>	38.2	-21.4	2.3	-3.2	11.4	-3.0	-2.4	4.8
C <sub>2</sub>	148.0	-35.9	-17.9	-20.9	-17.3	-8.8	-9.2	-5.4
N <sub>2</sub>	228.5	-58.4	3.1	-6.3	3.3	-8.2	-8.5	-6.3
O <sub>2</sub>	120.3	-53.0	4.3	-0.2	8.8	-14.3	-5.8	-7.4
Cu <sub>2</sub>	46.4	-28.6	-3.2	1.4	6.6	-6.0	-0.7	0.3
Ag <sub>2</sub>	41.0	-25.4	-6.1	0.1	1.6	-7.3	-1.1	-1.0
Au <sub>2</sub>	53.0	-30.2	-11.0	-5.8	-0.8	-13.0	-8.6	-5.1
MAE		<b>33.4</b>	<b>6.5</b>	<b>4.8</b>	<b>7.7</b>	<b>8.2</b>	<b>5.6</b>	<b>3.9</b>

Accuracy: hc-DFVB  $\approx$  DFT > VBSCF

Transit metal systems:

Table 2. The barriers (in kcal/mol) of the chemical reactions (kcal/mol)



Method		$\Delta E^\ddagger$	
		D-A	Rotation
<b>CASSCF</b>		<b>41.3</b>	<b>13.9</b>
<b>CASPT2</b>		<b>23.5</b>	<b>15.5</b>
<b>VBSCF</b>		<b>44.0</b>	<b>10.6</b>
<b>DFT</b>	B3LYP	<b>21.3</b>	<b>10.0</b>
	M06	<b>19.7</b>	<b>9.4</b>
	revTPSS	<b>13.0</b>	<b>10.2</b>
<b>hc-DFVB</b>	B3LYP	<b>29.3</b>	<b>14.1</b>
	M06	<b>23.3</b>	<b>19.1</b>
	revTPSS	<b>21.5</b>	<b>14.1</b>
<b>Expt.</b>		<b>23.3 ± 2</b>	

Accuracy: hc-DFVB  $\approx$  CASPT2 > CASSCF, VBSCF, DFT

## Strategy 3

Range-separated treatments (Decompose the Coulombic electron-electron interaction into long-range and short-range components)

a long-range (lr) electron-electron interaction determined by parameter  $\mu$  in the error function

$$E = \min_{\Psi} \left\{ \langle \Psi | \hat{T} + \hat{V}_{ne} + \hat{W}_{ee}^{\text{lr}} | \Psi \rangle + E_{\text{Hxc}}^{\text{sr}} [n_{\Psi}] \right\}$$

the corresponding  $\mu$ -dependent short-range (sr) Hartree-exchange-correlation (Hxc) density functional

The parameter  $\mu$  in the error function controls the range of the separation

The rs-DFVB energy is represented as

$$H_{KL}^{\lambda\text{-DFVB}} = H^{\lambda} + \widehat{V}^{\lambda}[\rho]$$

$$H^{\lambda} = \widehat{T} + \lambda\widehat{V}_{ee} + \widehat{V}_{ne}$$

$$\widehat{V}^{\lambda}[\rho] = (1-\lambda)v_{\text{H}}[\rho] + (1-\lambda)v_{\text{X}}[\rho] + v_{\text{C}}[\rho]$$

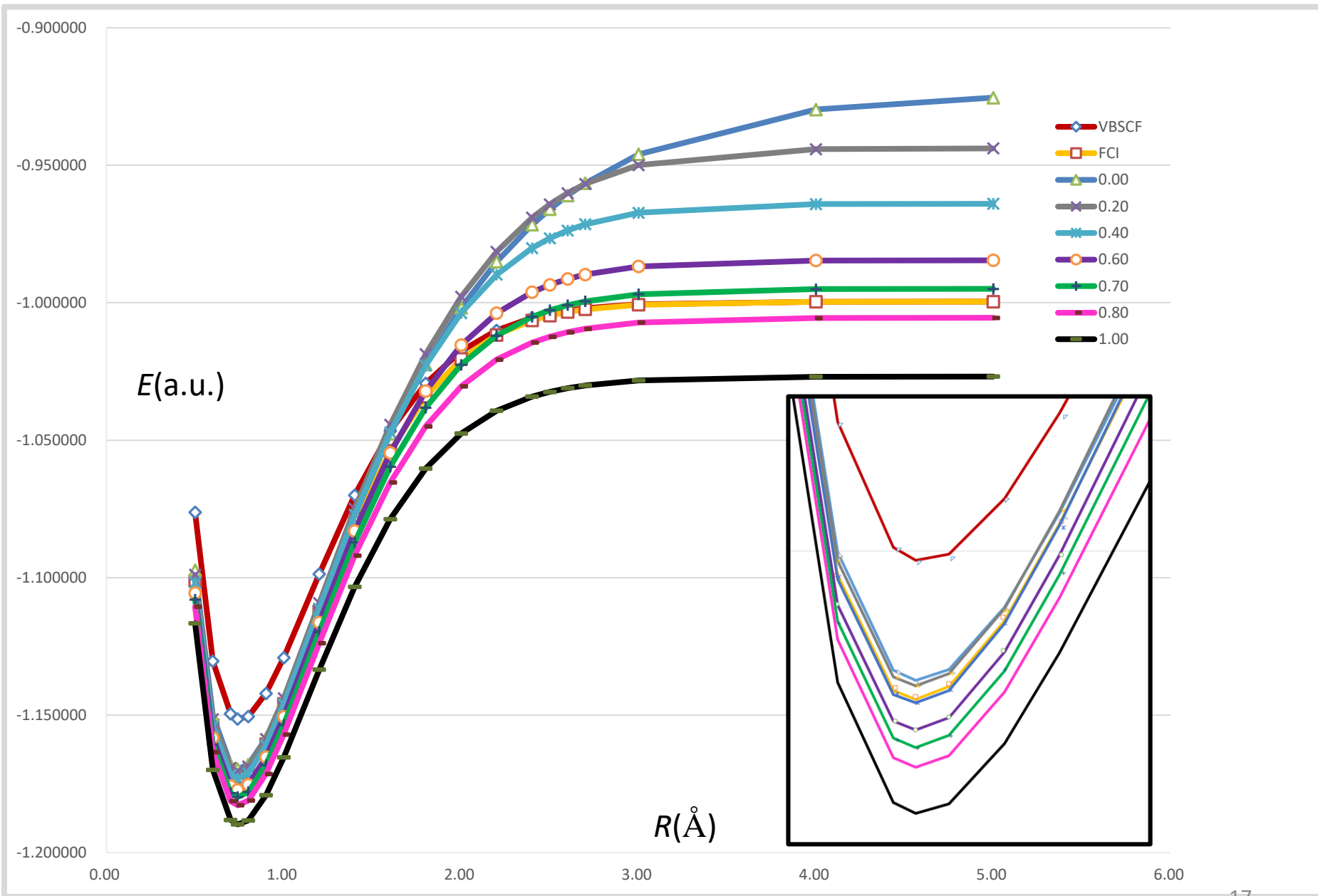
$$v_{\text{H}}[\rho] = \frac{\partial E_{\text{H}}}{\partial \rho} = \int dr' \rho(r')/|r-r'|$$

$$v_{\text{X}}[\rho] = \frac{\delta E_{\text{X}}[\rho]}{\delta \rho}$$

$$v_{\text{C}}[\rho] = \frac{\delta E_{\text{C}}[\rho]}{\delta \rho}$$



# rs-DFVB test, H2, BLYP/cc-pVTZ



# Summary

**correct the energy of multi-reference wave with dynamic correlation from DFT functional**

**modify the Hamiltonian matrix elements explicitly by DFT corrections**

**use the range-separated scheme, which decomposes the Coulombic electron-electron interaction into long-range and short-range components**

# Acknowledgements

---

Xiamen University

Prof. Wei Wu; Dr. Fuming Ying

Students: Yang Zhang, Chen Zhou



University of Strasbourg

Prof. Fromager Emmanuel

**Natural Science Foundation of China (Nos. 21573176, 21373165)**

*Thank you for your attention!*

# The correlation of MCSCF and VBSCF

