Post-VBSCF Methods
&
VB Methods for Solvation Effect

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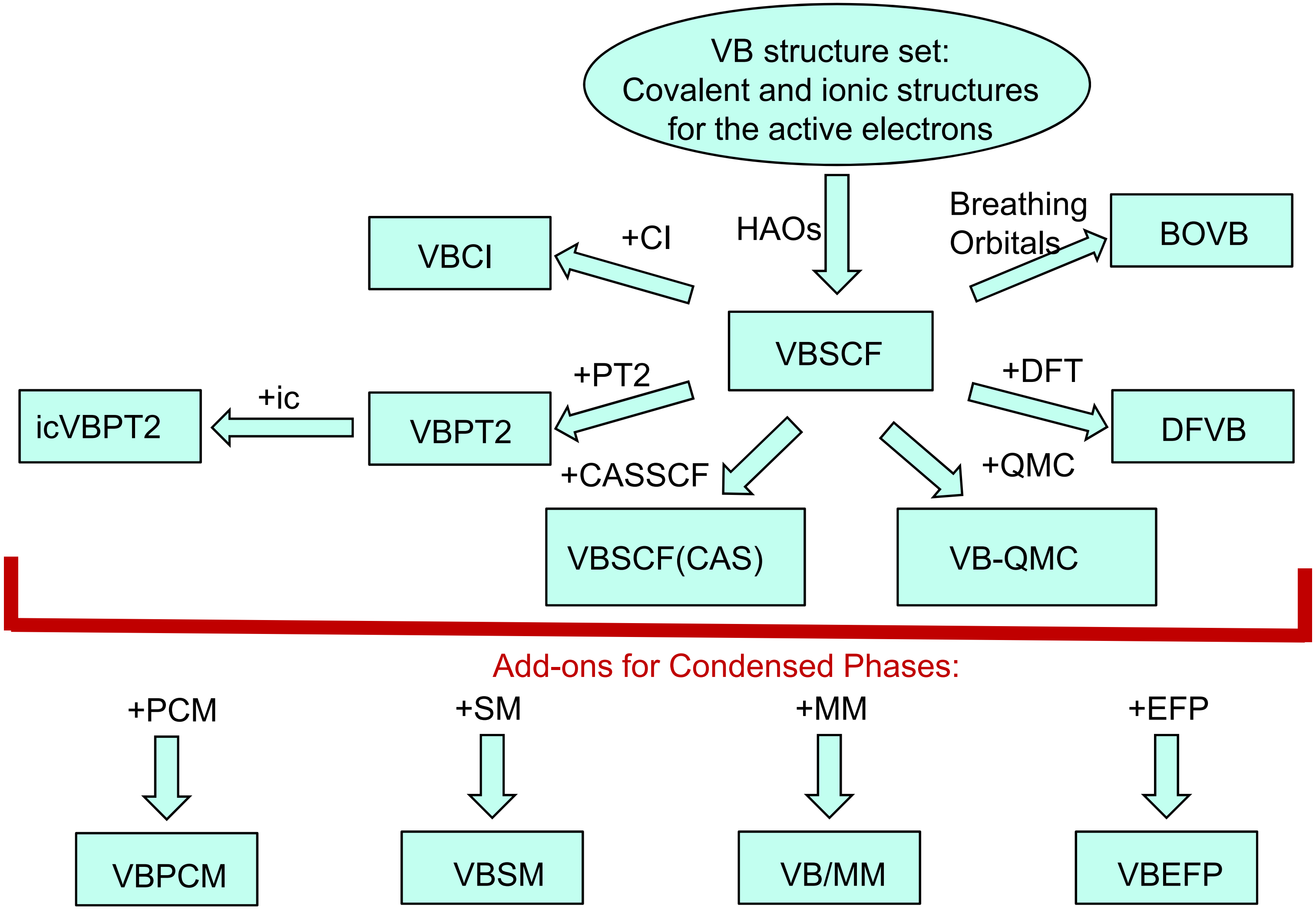
July 16, 2012 Paris



VB structure set:
Covalent and ionic structures
for the active electrons

HAOs

VBSCF

+CI

VBCI

Breathing Orbitals

BOVB

+PT2

VBPT2

+ic

icVBPT2

+DFT

DFVB

+CASSCF

VBSCF(CAS)

+QMC

VB-QMC

Add-ons for Condensed Phases:

+PCM

VBPCM

+SM

VBSM

+MM

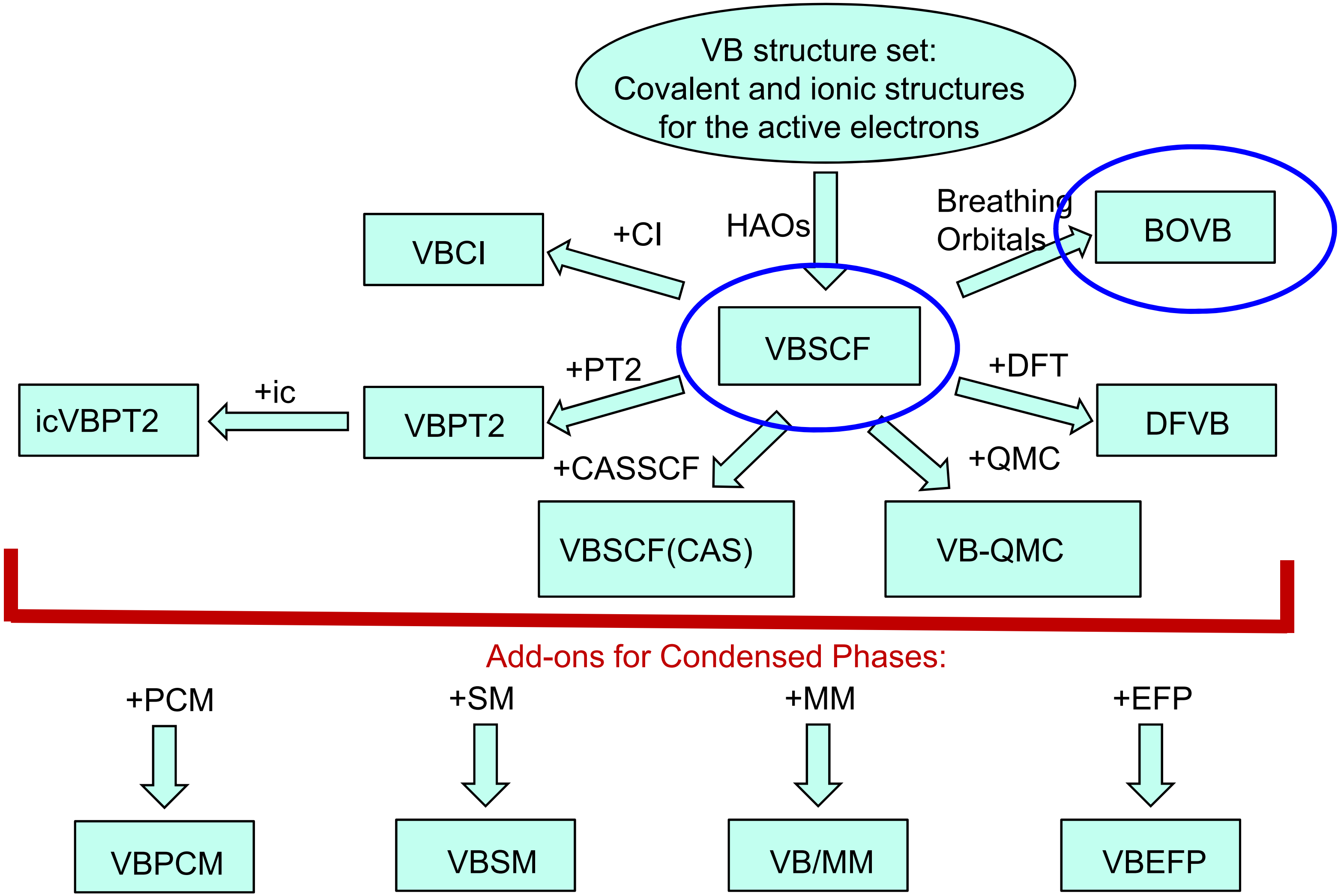
VB/MM

+EFP

VBEFP

The tree of VB methods that are based on classical VB theory.

Wu; Su; Shaik; Hiberty, **Chem. Rev.** 2011. 111, 7557-7593.



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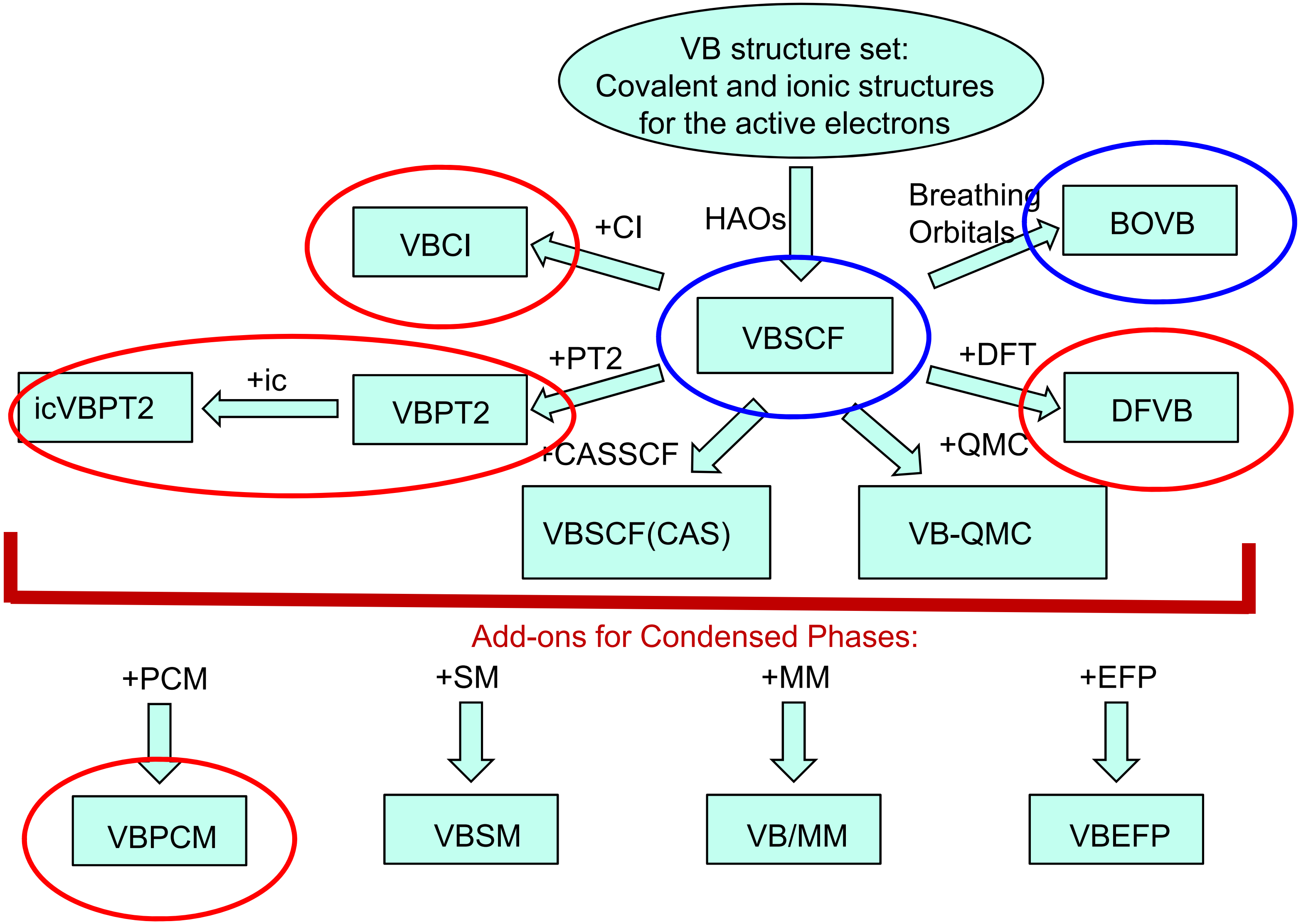

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Covalent and ionic structures
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Orbitals

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DFVB

+CASSCF

VBSCF(CAS)

+QMC

VB-QMC

Add-ons for Condensed Phases:

+PCM

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+MM

VB/MM

+EFP

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The tree of VB methods that are based on classical VB theory.

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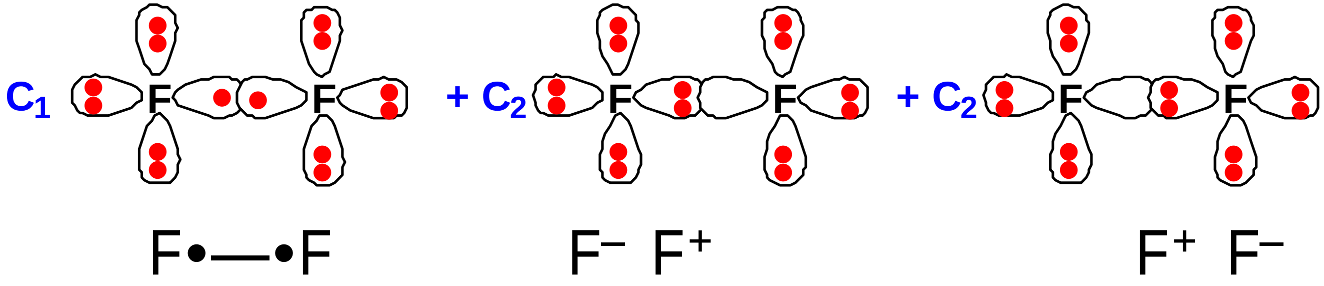
Outlines

- VBCI
- VBPT2 (icVBPT2)
- DFVB
- VBPCM

Valence Bond Self-Consistent Field (VBSCF)

Both structure coefficients and VB orbitals are optimized simultaneously to minimize the total energy.



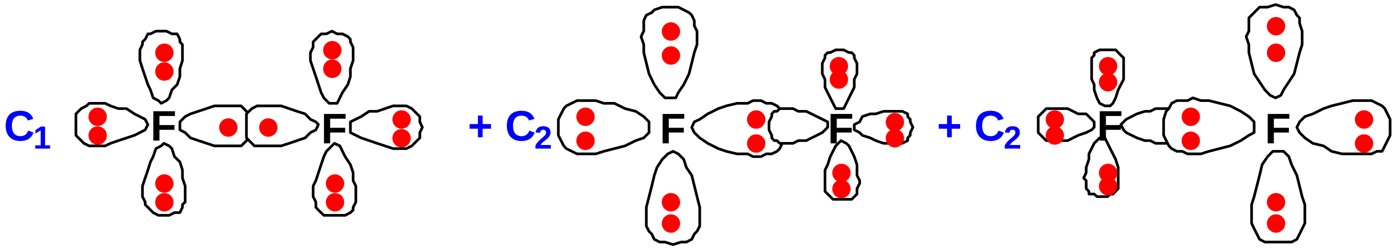
VBSCF provides qualitative correct description for bond breaking/forming, but its accuracy is still wanting.

VBSCF takes care of the static correlation, but lacks dynamic correlation.

van Lenthe; Balint-Kurti, *J. Chem. Phys.* 1983, *78*, 5699.

Breathing Orbital Valence Bond (BOVB)

- **Different orbital sets for different VB structures**



F•—•F F^- F^+ F^+ F^-

The degree of freedom introduces dynamic correlation with very compact wave function. It improves considerably the accuracy of the results.

Levels: L-BOVB; D-BOVB; SL-BOVB; SD-BOVB.

Hiberty, et al. *Chem. Phys. Lett.* **1992,** *189*, 259.

TABLE 1: Bond Energies (D) with Various Methods(kcal/mol)

molecule	D^{HF}	D^{B3LYP}	D^{CCSD}	D^{VBSCF}	$D^{L\text{-}BOVB}$	D^{VBCIS}	D^{VBCISD}
H_2	84.6	111.7	105.9	95.8	96.0	96.0(11)	105.9(55)
LiH	32.5	57.2	49.5	42.4	43.0	42.8(27)	49.6(118)
HF	94.9	132.4	127.2	105.1	115.9	125.0(40)	126.0(274)
HCl	77.6	103.1	99.1	85.8	89.9	92.0(40)	98.0(274)
F_2	-33.1	41.4	28.3	10.9	31.5	40.4(81)	33.9(1089)
Cl_2	14.5	48.4	41.6	26.2	35.6	38.9(81)	42.1(1089)

Note that BOVB values may be improved by using higher BOVB levels.

Post-HF in MO theory

For single-reference, post Hartree-Fock methods, such as CI, MP2, and CC;

For multi-reference, CASPT2, MRCI, etc.

Can we have post-VBSCF methods?

VBCI & VBPT2

Post-VBSCF Wave Function

$$\left|\Psi^{\text{Post-VBSCF}}\right\rangle = \left|\Psi^{\text{VBSCF}}\right\rangle + \sum_{R} C_R \left|\Phi_R\right\rangle$$

Φ_R Excited VB structures

How to define localized VB orbitals (HAOs)?

$$\{\chi_\alpha\} = \{\chi_1^A, \chi_2^A, \cdots, \chi_{m_A}^A; \chi_1^B, \chi_2^B, \cdots, \chi_{m_B}^B; \chi_1^C, \chi_2^C \cdots, \chi_{m_C}^C; \cdots\}$$

A: atom or fragment

Localized occupied VB orbitals

$$\phi_i^A = \sum_\beta c_{\beta i}^A \chi_\beta^A$$

Occupied VB orbitals are obtained by VBSCF calculations.
Virtual orbitals are not necessary in VBSCF.

How to define virtual orbitals?

Scheme 1:

Schmidt Orthogonalization to occupied orbitals on their own fragments

$$\chi'_{\mu,A} = \left.\left(\chi_\mu - S_{\mu\nu} T_n^{\mu} S^{nm} \phi_m\right)\right|_{\mu,\nu\in A}$$

Localized

Used in VBCI

Scheme 2:

Schmidt Orthogonalization to all occupied orbitals

$$\chi'_{\mu} = \chi_\mu - S_{\mu\nu} T_n^{\mu} S^{nm} \phi_m$$

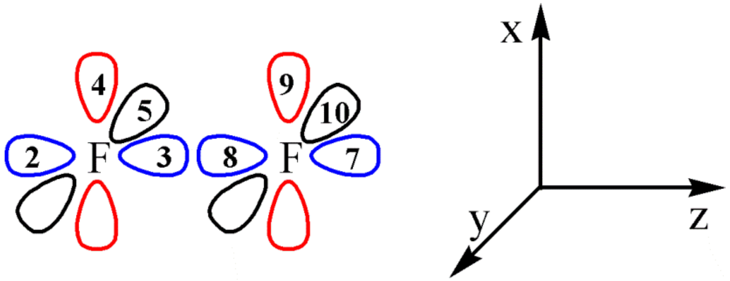
Delocalized

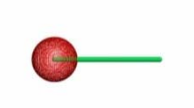
Used in VBPT2

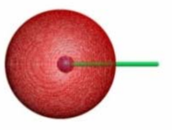
Note:

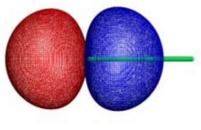
- Virtual basis functions are not linearly independent.
- To remove the redundant basis functions, one may diagonalize the overlap matrix of the transformed basis functions.

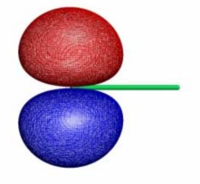
Occupied orbitals of F_2

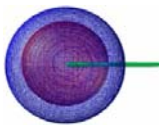


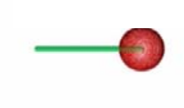

$$1\phi_{\sigma}^{A} = 1s$$

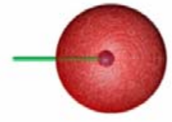

$$2\phi_{\sigma}^{A} = 2s$$

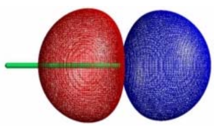

$$3\phi_{\sigma}^{A} = 2p_z$$

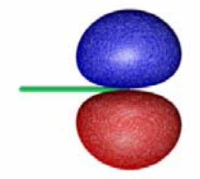

$$4\phi_{\pi}^{A} = 2p_x$$

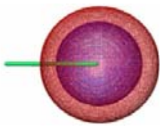

$$5\phi_{\pi}^{A} = 2p_y$$


$$6\phi_{\sigma}^{B} = 1s$$

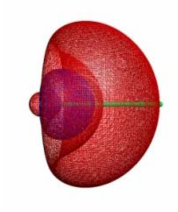

$$7\phi_{\sigma}^{B} = 2s$$


$$8\phi_{\sigma}^{B} = 2p_z$$

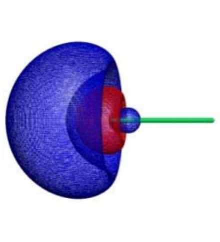

$$9\phi_{\pi}^{B} = 2p_x$$


$$10\phi_{\pi}^{B} = 2p_y$$

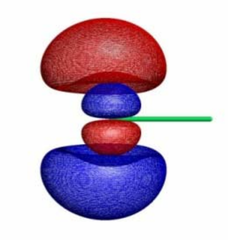
Virtual Orbitals from Scheme 1



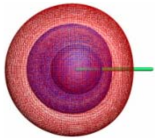
$11\phi_{\sigma}^{\mathrm{A}}$



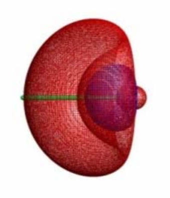
$12\phi_{\sigma}^{\mathrm{A}}$



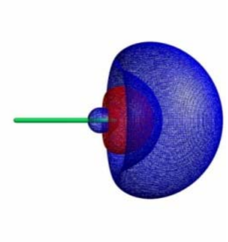
$13\phi_{\pi}^{\mathrm{A}}$



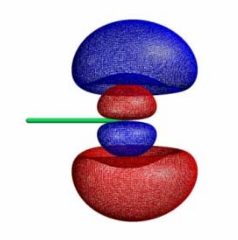
$14\phi_{\pi}^{\mathrm{A}}$



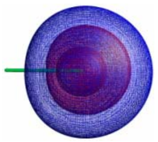
$15\phi_{\sigma}^{\mathrm{B}}$



$16\phi_{\sigma}^{\mathrm{B}}$

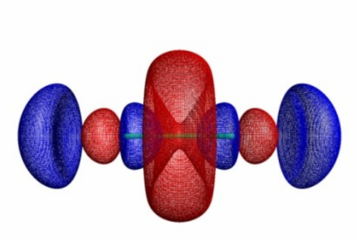


$17\phi_{\pi}^{\mathrm{B}}$

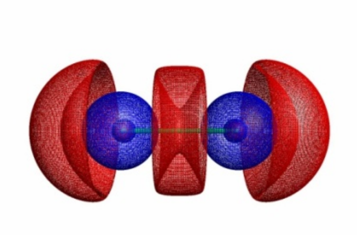


$18\phi_{\pi}^{\mathrm{B}}$

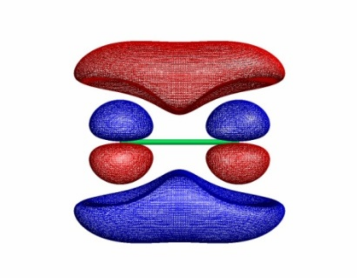
Virtual Orbitals from Scheme 2



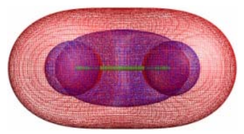
$11\phi_\sigma$



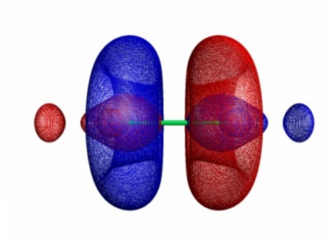
$12\phi_\sigma$



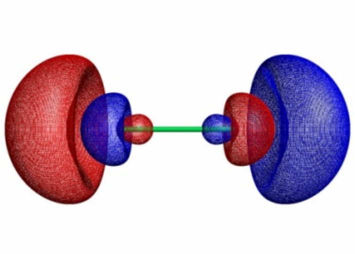
$13\phi_\pi$



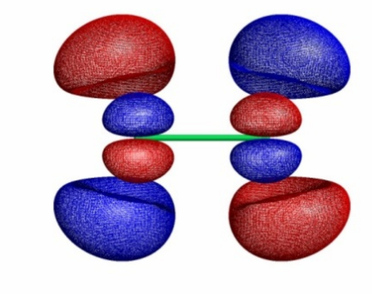
$14\phi_\pi$



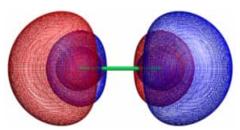
$15\phi_\sigma$



$16\phi_\sigma$



$17\phi_\pi$



$18\phi_\pi$

1. Valence Bond Configuration Interaction (VBCI)

Excited VB structures

$$\Psi^{\mathrm{VBSCF}} = \sum_K C_K^{\mathrm{SCF}} \Phi_K^{\mathrm{SCF}}$$

An excited VB structure Φ_K^i is built from Φ_K^{SCF} by replacing occupied ϕ_j^A with virtual orbital ϕ_α^A.

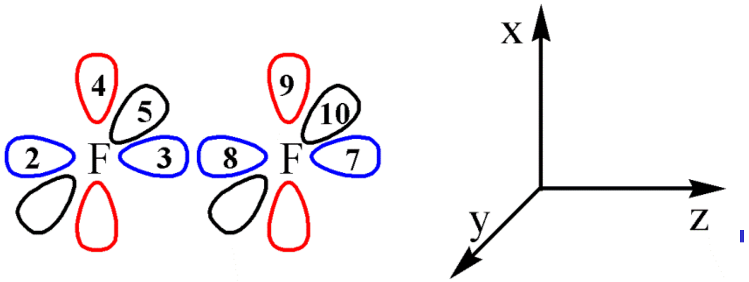
Φ_K^i *and* Φ_K^{SCF} *describe the* ***same*** *classical VB structure*.

By collecting all Φ_K^i, we have a wave function corresponding to VB structure *K*.

$$\Phi_K^{CI} = \sum_i C'_{Ki} \Phi_K^i$$

Corresponding to a VB structure.

VBCI Wave Function



CI wave function	Covalent	Ionic
Fundamental (VBSCF) +	$3\phi_\sigma^A — 8\phi_\sigma^B$	$3\phi_\sigma^A\, 3\phi_\sigma^A$
Single Excitation +	$3\phi_\sigma^A — 15\phi_\sigma^B$	$3\phi_\sigma^A 11\phi_\sigma^A$
Double Excitation +	$12\phi_\sigma^A — 15\phi_\sigma^B$	$12\phi_\sigma^A 11\phi_\sigma^A$
….		

$$\begin{aligned}\Psi^{VBCI} &= \sum_{K} C_{K}^{CI} \Phi_{K}^{CI} \\ &= \sum_{K} \sum_{i} C_{Ki} \Phi_{K}^{i}\end{aligned}$$

$$\Psi^{VBSCF} = \sum_{K} C_{K}^{SCF} \Phi_{K}^{SCF}$$

$$E^{VBCI} = \frac{\sum_{K,L} \sum_{i,j} C_{Ki} C_{Lj} \left\langle \Phi_{K}^{i} \middle| H \middle| \Phi_{L}^{j} \right\rangle}{\sum_{K,L} \sum_{i,j} C_{Ki} C_{Lj} \left\langle \Phi_{K}^{i} \middle| \Phi_{L}^{j} \right\rangle}$$

Condensed matrix elements and weights

$$H_{KL}^{CI} = \sum_{i,j} C_{Ki} C_{Lj} \left\langle \Phi_K^i \middle| H \middle| \Phi_L^j \right\rangle$$

$$M_{KL}^{CI} = \sum_{i,j} C_{Ki} C_{Lj} \left\langle \Phi_K^i \middle| \Phi_L^j \right\rangle$$

$$W_K = \sum_i W_{Ki}$$

$$W_{Ki} = \sum_{L,j} C_{Ki} \left\langle \Phi_K^i \middle| \Phi_L^j \right\rangle C_{Lj}$$

All formulas are similar to those of VBSCF, and compact.

Levels of VBCI Method

VBCI(A,I), A= D, S; I = D, S

A = Active electrons that are involved in a chemical process
I = Inactive electrons that are NOT involved in …

VBCI(D,D) = VBCISD

VBCI(S,S) = VBCIS

VBCI(D,S)

The “inactive” electrons play an indirect role in a chemical process, and the dynamic correlation of inactive electrons is quasi constant during the process.

Davidson Correction of VBCISD

Size inconsistency problem is one of the most undesirable drawbacks in truncated CI methods.

$$\Delta E_Q = (1 - \sum_K W_K)\Delta E_D$$

to estimate the contribution of quadruple excitations that are product of double excitations

TABLE 1: Bond Energies (D) with Various Methods(kcal/mol)

molecule	D^{HF}	D^{B3LYP}	D^{CCSD}	$\mathrm{D}^{\mathrm{VBSCF}}$	$D^{\mathrm{L\text{-}BOVB}}$	D^{VBCIS}	D^{VBCISD}
H_2	84.6	111.7	105.9	95.8	96.0	96.0(11)	105.9(55)
LiH	32.5	57.2	49.5	42.4	43.0	42.8(27)	49.6(118)
HF	94.9	132.4	127.2	105.1	115.9	125.0(40)	126.0(274)
HCl	77.6	103.1	99.1	85.8	89.9	92.0(40)	98.0(274)
F_2	-33.1	41.4	28.3	10.9	31.5	40.4(81)	33.9(1089)
Cl_2	14.5	48.4	41.6	26.2	35.6	38.9(81)	42.1(1089)

Table 2. Weights of the VB structures for various VB methods

	H2	LiH	HF	HCl	F_2	Cl_2
VBSCF	0.8074	0.8919	0.5829	0.6708	0.7933	0.6949
	0.0963	0.0028	0.0106	0.0725	0.1033	0.1531
	0.0963	0.1053	0.4066	0.2567	0.1033	0.1520
BOVB	0.7606	0.8756	0.5182	0.6486	0.7012	0.6513
	0.1197	-0.0062	0.0637	0.0998	0.1494	0.1744
	0.1197	0.1306	0.4181	0.2516	0.1494	0.1744
VBCISD	0.7727	0.8799	0.5515	0.6547	0.7395	0.6637
	0.1137	-0.0137	0.0191	0.0847	0.1305	0.1681
	0.1137	0.1338	0.4293	0.2606	0.1300	0.1682

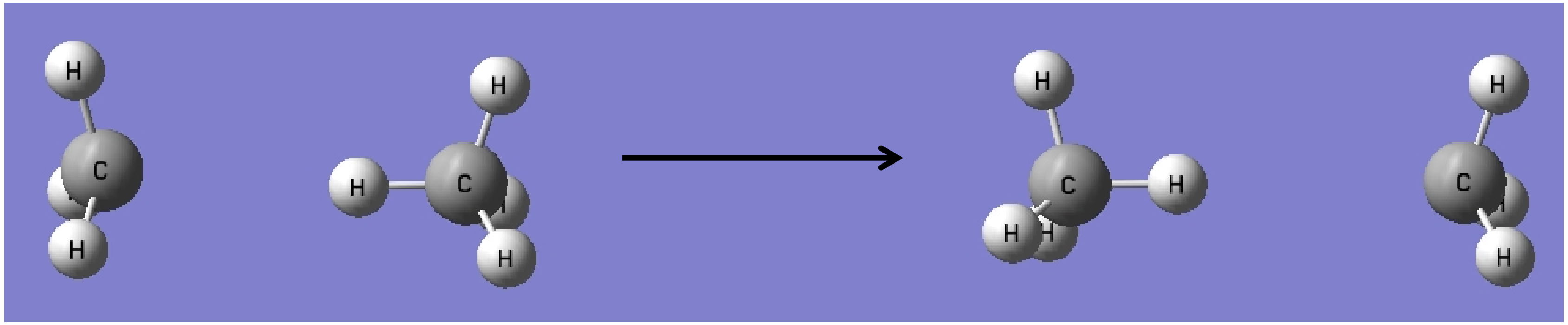
VBCI method provides significant improvement in accuracy from VBSCF method but still preserves the important feature of VB method.

Table 1. Bond Dissociation Energies Calculated with Valence Bond Methods[180]

		D_e (kcal/mol)			
bond	basis set	BOVB	VBCISD[a]	CCSD(T)	exptl
F−F	6-31G*	36.2	32.3	32.8	
	cc-pVTZ	37.9	36.1	34.8	38.3
Cl−Cl	6-31G*	40.0	41.6	40.5	
	cc-pVTZ	50.0	56.1	52.1	58.0
Br−Br	6-31G*	41.3	44.1	41.2	
	cc-pVTZ	44.0	50.0	48.0	45.9
F−Cl	6-31G*	47.9	49.3	50.2	
	cc-pVTZ	53.6	58.8	55.0	60.2
H−H	6-31G**	105.4	105.4	105.9	109.6
Li−Li	6-31G*	20.9	21.2	21.1	24.4
H_3C-H	6-31G**	105.7	113.6	109.9	112.3
H_3C-CH_3	6-31G*	94.7	90.0	95.6	96.7
HO−OH	6-31G*	50.8	49.8	48.1	53.9
H_2N-NH_2	6-31G*	68.5	70.5	66.5	75.4 ± 3
H_3Si-H	6-31G**	93.6	90.2	91.8	97.6 ± 3
H_3Si-F	6-31G*	140.4[b]	151.1	142.6	160 ± 7
H_3Si-Cl	6-31G*	102.1	101.2	98.1	113.7 ± 4

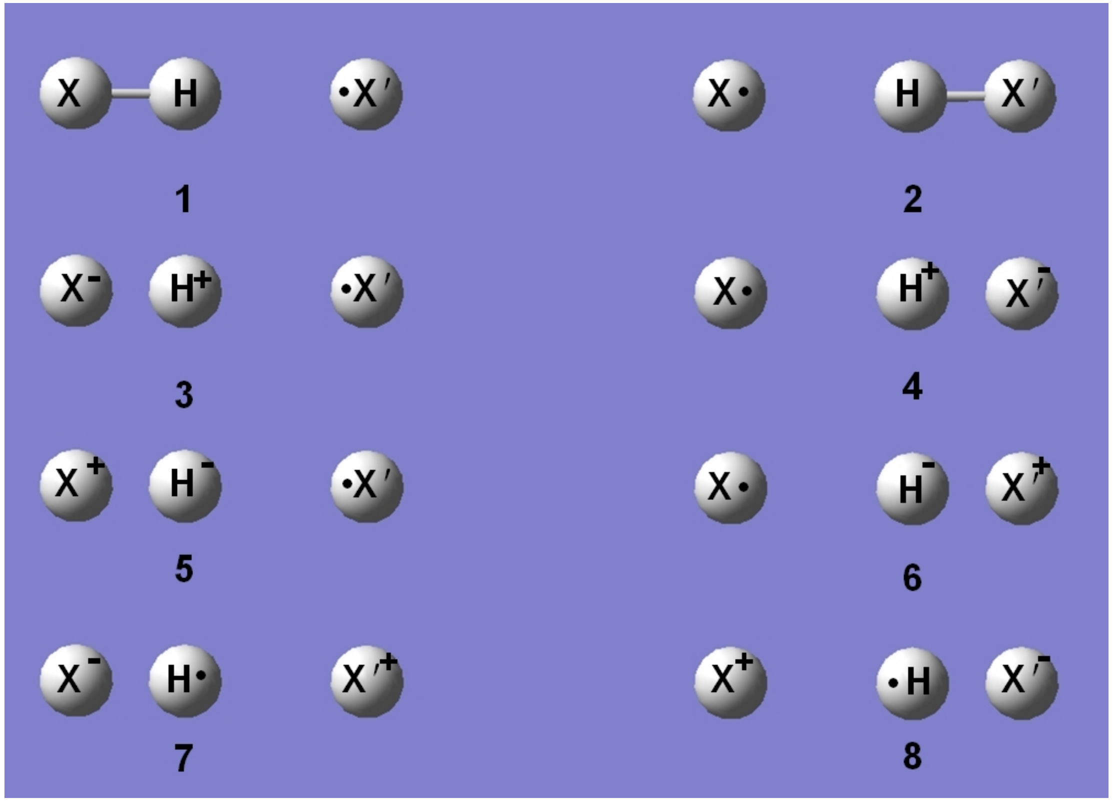
[a] With Davidson correction.[116] [b] Two-structure calculations ($H_3Si^-F^+$ is omitted).

Hydrogen Abstraction Reactions



X• + HX' -> XH + X'• (X = X' = CH_3, SiH_3, GeH_3, SnH_3, PbH_3)

VB structures (3 electrons/3 orbitals system)



(X = X’ = CH_3, SiH_3, GeH_3, SnH_3, PbH_3)

Table 4. 6-31G* Barriers for the Hydrogen Eaxhange Reactions, X• + X'H -> XH + X'• (X = CH_3, SiH_3, GeH_3, SnH_3, PbH_3) (kcal/mol)

Molecule	HF	CCSD	VBSCF	BOVB	VBCIS	VBCISD	VBCI(D,S)	VBCIPT
CH_3	35.1	26.5	33.0	23.1	26.7(266)	25.8(4156)	28.8(2788)	25.5(765)
SiH_3	25.2	19.3	25.5	19.1	19.2(266)	19.7(4156)	19.4(2788)	19.0(794)
GeH_3	22.0	16.6	25.5	18.0	18.9(266)	18.1(4156)	17.9(2788)	17.0(791)
SnH_3	18.5	13.5	20.5	14.9	15.5(266)	15.3(4156)	15.1(2788)	14.1(565)
PbH_3	15.2	13.0	17.3	12.3	12.7(266)	12.5(4156)	12.3(2788)	11.5(573)
CH_3[a]							19.7(17.3)[17.7]	

The seven σ valence electrons are set into CI window, where three are active, and four are inactive.

This barrier was calculated with the mixed basis set and no valence orbitals are frozen. The result 19.7 is obtained with the set of 8 fundamental VB structures (Scheme 3). In parentheses is CCSD(T) barrier. In the square brackets is the result obtained by adding the VB structures that can be generated by admitting all the s-electrons (seven) into the active space. There are additional 32 structures and their effect was evaluated without orbital optimization.
(aug-cc-pVDZ for C, cc-pVDZ for the exchanged H atom and 6-31G for H atoms)

Summary 1

- VBCI method covers dynamic correlation with a minimal number of effective structures.
- The VBCIS results are in good agreement with those of BOVB.
- The VBCISD results match CCSD results.

2. Valence Bond Second Order Perturbation Theory (VBPT2)

As one of post-VBSCF methods, VBCI incorporates dynamic correlation without further SCF procedure.

However, though the VBCI space is much smaller than those of MO-based methods. VBCI method is computational demanding.

Can we have a VB method that is accurate and cheap?

Valence Bond Second Order Perturbation Theory (VBPT2)

$$\left|\Psi\right\rangle = \left|\Psi^{(0)}\right\rangle + \left|\Psi^{(1)}\right\rangle \qquad \left|\Psi^{(0)}\right\rangle = \left|\Psi^{SCF}\right\rangle = \sum_K C_K^{SCF}\left|\Phi_K\right\rangle$$

$$\Psi^{(1)} = \sum_{R\in V_{SD}} C_R^{(1)}\left|\Phi_R\right\rangle$$

$$\left\langle\Psi^{(0)}\middle|\Psi^{(1)}\right\rangle = 0 \qquad \left\langle\Psi^{(0)}\middle|\Psi\right\rangle = 1$$

Excited VB structures:

Excited structures are generated from the VBSCF structures by replacing occupied orbitals with virtual orbitals.

Scheme 2 is used for virtual orbitals, which are not localized. Thus, excited structures are not “classical”.

The zeroth-order Hamilton:

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_K \hat{F} \hat{P}_K + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \cdots$$

$$\hat{F} = \sum_i \hat{f}(i)$$

$$\hat{f}(i) = \hat{h}(i) + \sum_{m,n} D_{mn}^{SCF} (\hat{J}_{nm}(i) - \hat{K}_{nm}(i))$$

$$f_{pq} = h_{pq} + \sum_{m,n} D_{mn}^{SCF} \left[(pq|mn) - \frac{1}{2}(pm|qn) \right]$$

The first-order wave function: $\Psi^{(1)} = \sum_{R \in V_{SD}} C_R^{(1)} \left| \Phi_R \right\rangle$

$$\boxed{\mathbf{C}^{(1)} = (\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}\mathbf{H}^{10}\mathbf{C}^{(0)}}$$

$$(H_0^{11})_{RS} = \left\langle \Phi_R \left| \hat{H}_0 \right| \Phi_S \right\rangle$$

$$(H^{01})_{KR} = \left\langle \Phi_K \left| \hat{H} \right| \Phi_R \right\rangle$$

$$(H^{10})_{RK} = \left\langle \Phi_R \left| \hat{H} \right| \Phi_K \right\rangle$$

$$(M^{11})_{RS} = \left\langle \Phi_R \middle| \Phi_S \right\rangle$$

The second-order energy:

$$\boxed{E^{(2)} = \mathbf{C}^{(0)+}\mathbf{H}^{01}(\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}\mathbf{H}^{10}\mathbf{C}^{(0)}}$$

The most time-consuming part:

$$(\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}$$

which is block diagonalized, due to the block-orthogonality between different orbital blocks.

If the occupation numbers of inactive or virtual orbitals are different in the two excited structures, the corresponding matrix element is zero.

VBPT2 is much cheaper than VBCI.

The structure weights in VBPT2 method:

$$\Phi_K^{PT} = N_K(\Phi_K + \sum_R X_{RK}\Phi_R) \qquad \mathbf{X} = (\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}\mathbf{H}^{10}$$

$$\Psi^{VBPT} = \sum_K C_K^{PT}\Phi_K^{PT}$$

$$C_K^{PT} = C_K^{(0)} / N_K \qquad N_K = (1 + \sum_{R,S} X_{RK}M_{RS}^{11}X_{SK})^{-1/2}$$

$$W_K^{PT} = \sum_L C_K^{PT}M_{KL}^{PT}C_L^{PT}$$

$$E_{KL}^{(2)} = \sum_{R,S} H_{KR}^{01}(\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})_{RS}^{-1}H_{SL}^{10}$$

$$H_{KL}^{PT} = H_{KL}^{SCF} + E_{KL}^{(2)}$$

Bond Dissociation Energy (Error to FCI)

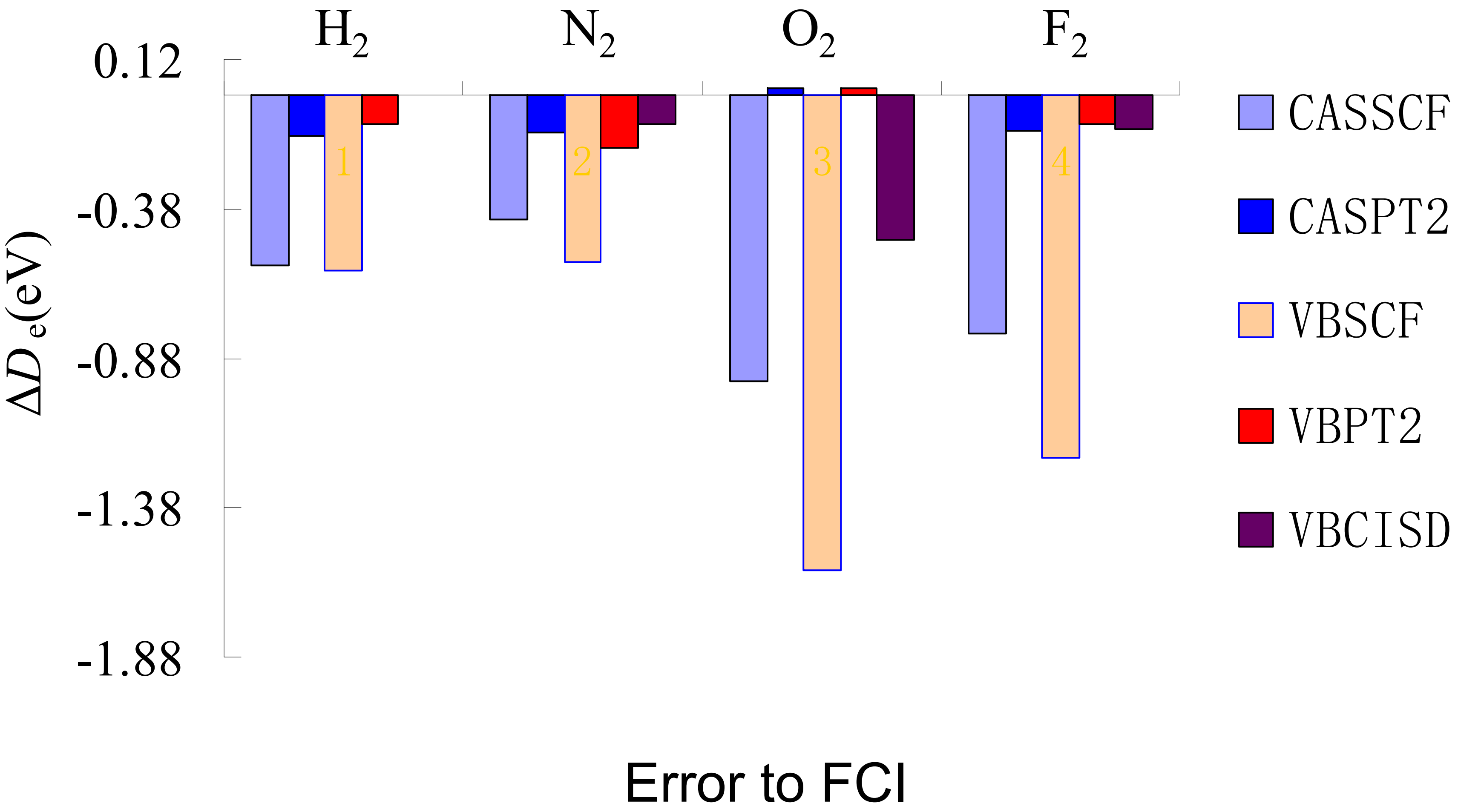


Table 6. Weights of the VB structures and resonance energy (RE) of F_2 , at an F-F distance of 2.70 a_0

Method	W_{cov}	W_{ion1}/W_{ion2}	RE (kcal/mol)
VBSCF	0.785	0.108	46.28
L-BOVB	0.695	0.152	71.46
VBCISD	0.730	0.135	60.68
VBPT2	0.778	0.111	60.02

The VBPT2 results are in very good agreement with CASPT2.

The VBPT2 results are in very good agreement with CASPT2.

Disadvantage of VBPT2

The dimension of excited VB structures increases dramatically, when the number of VB structures in VBSCF is large.

Solution

Internally contraction strategy

$$\left|\Psi\right\rangle = \left|\Psi^{(0)}\right\rangle + \left|\Psi^{(1)}\right\rangle$$

$$\left|\Psi^{(0)}\right\rangle = \left|\Psi^{\mathrm{SCF}}\right\rangle = \sum_{K} C_K^{(0)} \left|\Phi_K\right\rangle$$

The first-order wave function: a linear combination of the internally constracted excitated configurations.

$$\left|\Psi^{(1)}\right\rangle = \sum_{pqrs} t_{pr}^{qs} \left|\Psi_{qs}^{pr}\right\rangle = \sum_{pqrs} t_{pr}^{qs} E_s^{\bullet r} E_q^{\bullet p} \left|\Psi^{(0)}\right\rangle$$

Spin averaged orbital excitation operator

$$E_q^{\bullet p} = a_{q\alpha}^{+} a^{p\alpha} + a_{q\beta}^{+} a^{p\beta}$$

The expansion coefficients of first-order wave function

$$\mathbf{t} = (\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}\mathbf{V}$$

The second-order energy

$$E^{(2)} = \mathbf{V}^{+}(\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1}\mathbf{V}$$

$$(H_0^{11})_{\alpha\beta} = \left\langle \Psi_\alpha^{(1)} \middle| \hat{H}_0 \middle| \Psi_\beta^{(1)} \right\rangle$$

$$V_\alpha = \left\langle \Psi_\alpha^{(1)} \middle| \hat{H} \middle| \Psi^{(0)} \right\rangle$$

$$(M^{11})_{\alpha\beta} = \left\langle \Psi_\alpha^{(1)} \middle| \Psi_\beta^{(1)} \right\rangle$$

Various types of excitations

$$\left|\Psi_{xy}^{ij}\right\rangle = E_{y}^{\bullet j} E_{x}^{\bullet i}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{ta}^{ij}\right\rangle = E_{a}^{\bullet j} E_{t}^{\bullet i}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{ab}^{ij}\right\rangle = E_{b}^{\bullet j} E_{a}^{\bullet i}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{xy}^{ti}\right\rangle = E_{y}^{\bullet i} E_{x}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{xa}^{ti}\right\rangle = E_{a}^{\bullet i} E_{x}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{ab}^{ti}\right\rangle = E_{b}^{\bullet i} E_{a}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{ax}^{tu}\right\rangle = E_{x}^{\bullet u} E_{a}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

$$\left|\Psi_{ax}^{tu}\right\rangle = E_{x}^{\bullet u} E_{a}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

*S*inglet excitation operator

$$\left|\Psi_{ax}^{ti}\right\rangle = E_{x}^{\bullet i} E_{a}^{\bullet t}\left|\Psi^{(0)}\right\rangle$$

Orbitals:

- Inactive. i, j, k, l (orthogonal)
- Active. t, u, v, w, x, y, z (non-orthogonal)
- Virtual. a, b, c
- Any. p, q, r, s
- Any occupied. m, n

$$
\begin{aligned}
&\left\langle \Psi^{ij}_{x_1y_1} \middle| \hat{H}_0 \middle| \Psi^{ij}_{x_2y_2} \right\rangle = \left(E^{(0)}_{inact} - \varepsilon_i - \varepsilon_j\right)\left\langle \Psi^{ij}_{x_1y_1} \middle| \Psi^{ij}_{x_2y_2} \right\rangle \\
&+ \Big\{\Big(4s_{x_2x_1}s_{y_2y_1} - 2s_{y_2x_1}s_{x_2y_1}\Big)E^{(0)}_{act} \\
&+ 4f_{x_2x_1}s_{y_2y_1} + 4f_{y_2y_1}s_{x_2x_1} - 2f_{x_2y_1}s_{y_2x_1} - 2f_{y_2x_1}s_{x_2y_1} \\
&+ \Big[\Big(f_{tx_1}s_{x_2y_1}s_{y_2u} + f_{ty_1}s_{y_2x_1}s_{x_2u} - 2f_{tx_1}s_{y_2y_1}s_{x_2u} - 2f_{ty_1}s_{x_2x_1}s_{y_2u}\Big) \\
&+ \Big(f_{tx_2}s_{y_2x_1}s_{y_1u} + f_{ty_2}s_{x_2y_1}s_{x_1u} - 2f_{tx_2}s_{y_2y_1}s_{x_1u} - 2f_{ty_2}s_{x_2x_1}s_{y_1u}\Big) \\
&+ \Big(f_{y_2x_1}s_{y_1u}s_{x_2t} + f_{x_2y_1}s_{x_1u}s_{y_2t} - 2f_{x_2x_1}s_{y_1u}s_{y_2t} - 2f_{y_2y_1}s_{x_1u}s_{x_2t}\Big)\Big]D^{tu} \\
&+ \Big[f_{tu}\Big(s_{y_2x_1}s_{x_2v}s_{y_1w} + s_{x_2y_1}s_{y_2v}s_{x_1w} - 2s_{y_2y_1}s_{x_2v}s_{x_1w} - 2s_{x_2x_1}s_{y_2v}s_{y_1w}\Big) \\
&+ \Big(f_{tx_1}s_{x_2u}s_{y_1v}s_{y_2w} + f_{ty_1}s_{y_2u}s_{x_1v}s_{x_2w} + f_{tx_2}s_{y_2v}s_{x_1u}s_{y_1w} + f_{ty_2}s_{x_2v}s_{y_1u}s_{x_1w}\Big)\Big]\Pi^{tv,uw} \\
&+ f_{tu}s_{y_2v_1}s_{x_2w_1}s_{y_1v_2}s_{x_1w_2}\Gamma^{tv_1w_1,uv_2w_2}\Big\} \\
&+ \delta^{ij}\Big\{\Big(4s_{x_2y_1}s_{y_2x_1} - 2s_{x_2x_1}s_{y_2y_1}\Big)E^{(0)}_{act} \\
&+ 4f_{x_2y_1}s_{y_2x_1} + 4f_{y_2x_1}s_{x_2y_1} - 2s_{x_2x_1}f_{y_2y_1} - 2f_{x_2x_1}s_{y_2y_1} \\
&+ \Big[\Big(f_{tx_2}s_{y_2y_1}s_{x_1u} + f_{ty_2}s_{x_2x_1}s_{y_1u} - 2f_{ty_2}s_{x_2y_1}s_{x_1u} - 2f_{tx_2}s_{y_2x_1}s_{y_1u}\Big) \\
&+ \Big(f_{ty_1}s_{x_2x_1}s_{y_2u} + f_{tx_1}s_{y_2y_1}s_{x_2u} - 2f_{ty_1}s_{y_2x_1}s_{x_2u} - 2f_{tx_1}s_{x_2y_1}s_{y_2u}\Big) \\
&+ \Big(f_{y_2y_1}s_{x_1u}s_{x_2t} + f_{x_2x_1}s_{y_1u}s_{y_2t} - 2f_{x_2y_1}s_{x_1u}s_{y_2t} - 2f_{y_2x_1}s_{y_1u}s_{x_2t}\Big)\Big]D^{tu} \\
&\Big[+ f_{tu}\Big(s_{y_2y_1}s_{x_2v}s_{x_1w} + s_{x_2x_1}s_{y_2v}s_{y_1w} - 2s_{x_2y_1}s_{y_2v}s_{x_1w} - 2s_{y_2x_1}s_{x_2v}s_{y_1w}\Big) \\
&+ \Big(f_{ty_1}s_{x_2u}s_{x_1v}s_{y_2w} + f_{tx_1}s_{y_2u}s_{y_1v}s_{x_2w} + f_{tx_2}s_{y_1u}s_{y_2v}s_{x_1w} + f_{ty_2}s_{x_1u}s_{x_2v}s_{y_1w}\Big)\Big]\Pi^{tv,uw} \\
&+ f_{tu}s_{y_2v_1}s_{x_2w_1}s_{x_1v_2}s_{y_1w_2}\Gamma^{tv_1w_1,uv_2w_2}\Big\}
\end{aligned}
$$

The expressions for matrix elements are complicated due to use of non-orthogonal orbitals.

In implementation, the following techniques are applied

1. Second Quantization Technique for non-orthogonal orbitals;
2. Tensor Analysis;
3. Automatic Formula/Code Generator.

Example 1. The Spectroscopic Constants of H_2

Method	r_e (a_0)	ω_e (cm^{-1})	D_e (kcal/mol)
FCI	1.405	4421	108.56
CASSCF[a]	1.427	4255	95.48
CASPT2N[a]	1.410	4407	105.40
VBSCF	1.429	4193	95.04
VBPT2	1.408	4376	106.30
icVBPT2	1.407	4379	106.09
VBCISD	1.405	4421	108.56

---

[a] J. Phys. Chem., 1990, 94, 5483., where ANO(4s3p2d) basis set was used and orbitals $1\sigma_g$ and $1\sigma_u$ are taken as active orbitals.

Example 2. The Spectroscopic Constants of N_2

Method	r_e (a_0)	ω_e (cm^{-1})	D_e (kcal/mol)
FCI[a]	2.123	2341	201.75
VBSCF(17)[b]	2.109	2388	186.49
VBPT2(17)[b]	2.115	2373	194.21
icVBPT2(17)[b]	2.115	2367	195.25
VBSCF(175)[c]	2.114	2364	188.88
VBPT2(175)[c]	2.120	2344	197.72
icVBPT2(175)[c]	2.120	2345	197.65
VBCISD(17)[b]	2.121	2330	199.52
CASSCF[d]	2.119	2337	192.18
CASPT2N[d]	2.122	2342	198.82

a. J. Chem. Phys. 86, 5595 (1987).

b. 17 fundamental VB structures are used.

c. 175 fundamental VB structures are used, but the orbitals are optimized using 17 VB structures.

d. J. Chem. Phys. 96, 1218 (1992).

Example 3. The Spectroscopic Constants of F_2

Method	r_e (a_0)	ω_e (cm^{-1})	D_e (kcal/mol)
VBSCF	2.784	552.7	10.05
VBPT2	2.683	905.3	35.72
icVBPT2	2.708	900.0	33.67
VBCISD	2.689	886.8	35.35
L-BOVB	2.700	892.7	33.32
CASSCF[a]	2.755	803.1	19.62
CASPT2[a]	2.691	899.1	35.19
MRCI[a]	2.680	889.5	32.81
Expt[b]	2.668	917	38.0

a. The MOLPRO package is used for the CASSCF(2,2), CASPT2 and MRCI calculations. MOLPRO, version 2006.1, a package of ab initio programs, Werner, H.-J, etc.

b. Chase, M. W. Jr. NIST-JANAF Thermochemical table, 4th ed,; J. Phys. Chem. Ref. Data, Monogr. 1998, 9, pp1-1951.

Example 4. Total energies (a.u.) of H_2O as a function of the symmetric stretching from the equilibrium OH distance R_e

Method	R_e	1.5*R_e	2.0*R_e	2.5*R_e	3.0*R_e	8.0*R_e
FCI[a]	-76.2419	-76.0723	-75.9517	-75.9180	-75.9119	-75.9103
CASSCF(8,6)[a]	0.1640	0.1500	0.1336	0.1263	0.1247	
CASPT2[a]	0.0128	0.0108	0.0081	0.0080	0.0083	
VBSCF[b]	0.1857	0.1626	0.1380	0.1272	0.1250	0.1242
VBPT2(occ)[c]	0.0353	0.0374	0.0381	0.0394	0.0397	0.0397
VBPT2(all)[d]	0.0274	0.0266	0.0268	0.0283	0.0287	0.0287
icVBPT2	0.0201	0.0121	0.0093	0.0097	0.0099	0.0099

a. Olsen, J., Jorgensen, P., Koch, H., Balkova, A. Bartlett, R. J. J. Chem. Phys. 1996, 104, 8007.
b. 20 structures are used in VB calculations.
c. Only excitations from occupied orbitals to virtual ones are included.
d. All excitations are included, involving excitations from inactive orbitals to active ones.

Summary 2

- icVBPT2 provides a cheaper ab initio VB tool to cover dynamical correlation.
- Test calculation shows that both VBPT2 and icVBPT2 results are in good agreement with CASPT2 ones.
- Due to the use of delocalized virtual orbitals, excited structures are not classically physical any more.

3. DFVB: A VB Method with Density Functional Energy Correction

DFT: Single reference based method

VBSCF: lack of dynamic correlation

VB + DFT

From KS-DFT to DFVB

KS-DFT

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

$$E_{\text{XC}} = \left(T[\rho] - T_S[\rho]\right) + \left(E_{\text{ee}}[\rho] - J[\rho]\right)$$

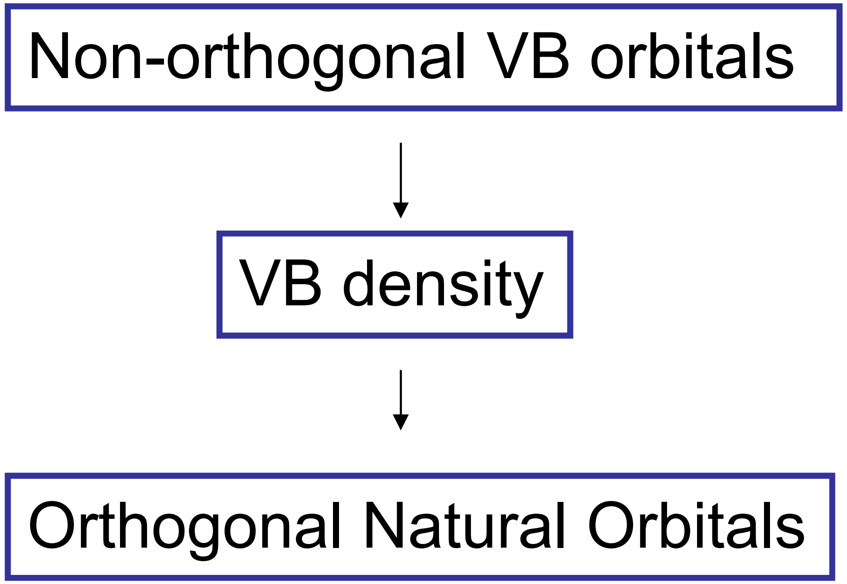
DFVB

$$E^{\text{DFVB}}\left[\rho^{\text{VB}}\right] \approx E^{\text{VBSCF}} + E_{\text{C}}\left[\rho^{\text{VB}}\right]$$

Approximate

Problem:
How to handle non-orthogonal VB orbitals in KS-DFT?

Problem:
How to handle non-orthogonal VB orbitals in KS-DFT?



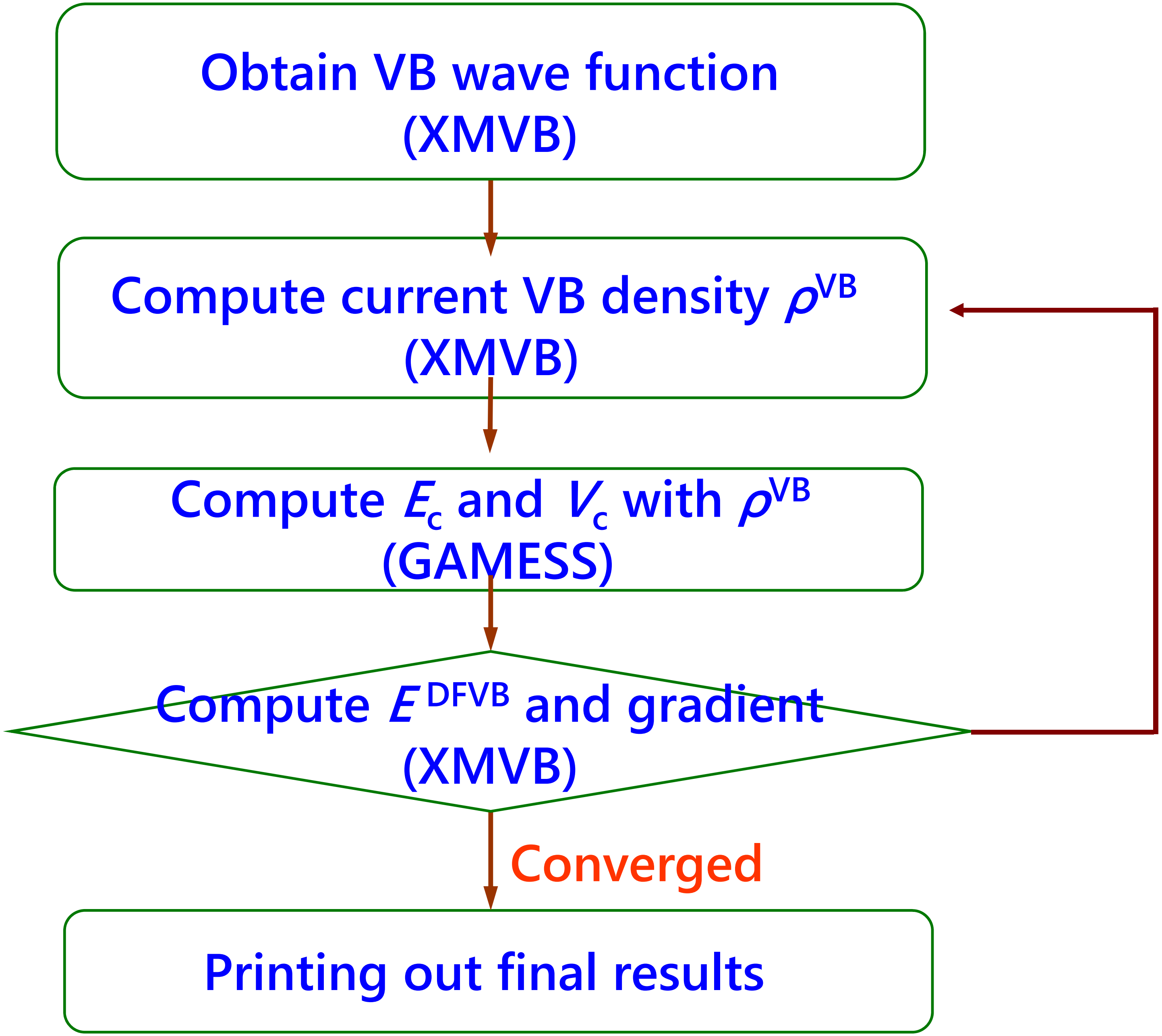
Non-orthogonal VB orbitals

↓

VB density

↓

Orthogonal Natural Orbitals



Obtain VB wave function (XMVB)

Compute current VB density ρ^{VB} (XMVB)

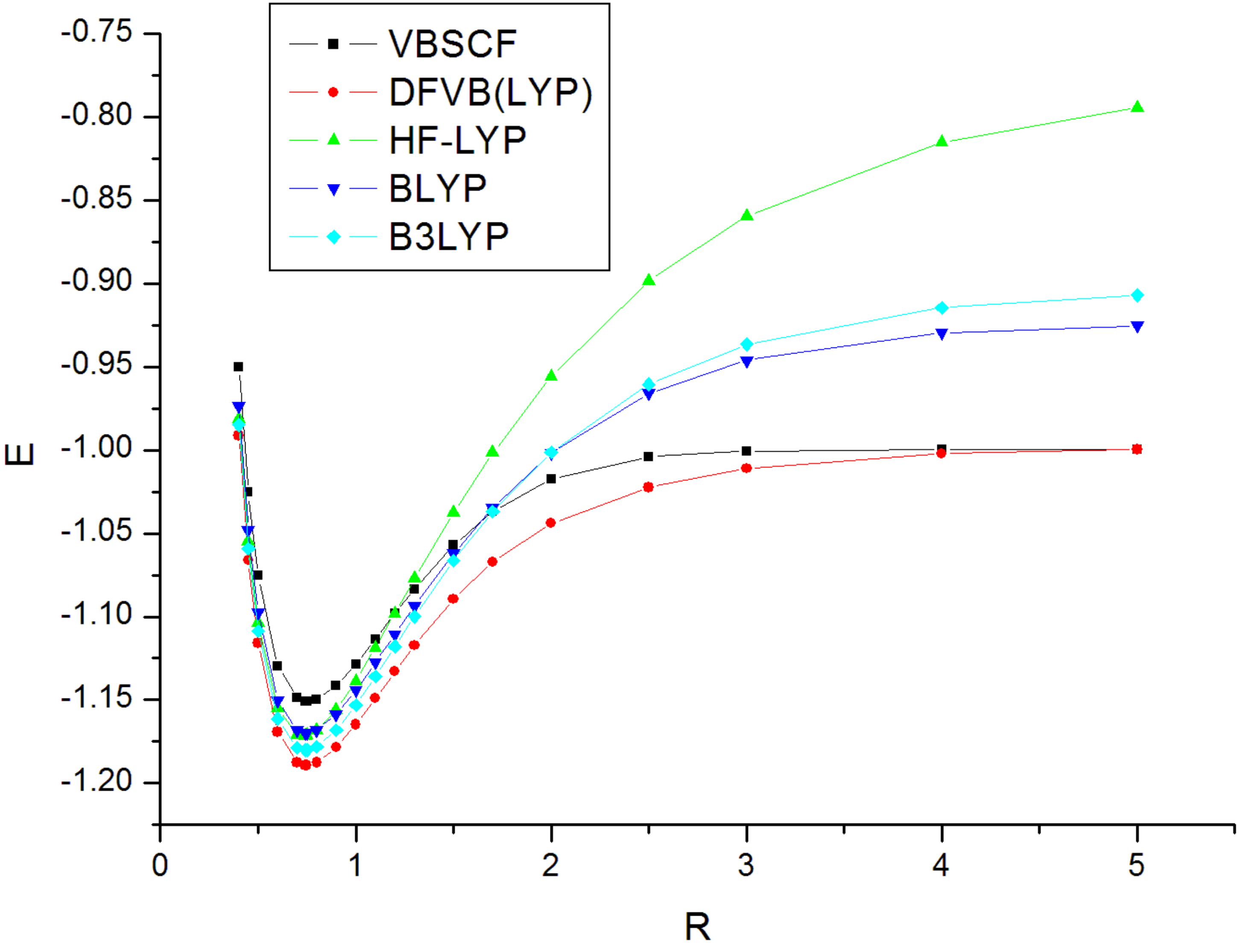
Compute E_c and V_c with ρ^{VB} (GAMESS)

Compute E^{DFVB} and gradient (XMVB)

Converged

Printing out final results

PEC of H_2 with Different Methods with cc-pVTZ



R_0 of diatomic molecules

Mol	**Exp**	**B3LYP**	**BLYP**	**PW91**	**VBSCF**	**DFVB**	
						LYP	**PW**
H_2	0.741	0.002	0.006	0.008	0.015	0.008	0.010
HF	0.917	0.005	0.016	0.012	-0.003	-0.010	-0.013
HCl	1.275	0.006	0.015	0.012	0.011	-0.001	-0.003
Li_2	2.673	0.028	0.038	0.054	0.272	0.157	0.197
N_2	1.098	-0.007	0.005	0.003	-0.003	-0.012	-0.014
O_2	1.208	-0.004	0.023	0.011	0.035	0.019	0.009
F_2	1.412	-0.016	0.019	0.000	0.065	0.016	-0.011
Cl_2	1.988	0.023	0.052	0.019	0.050	0.009	-0.016
ClF	1.628	0.012	0.044	0.022	0.031	-0.005	-0.023
NF	1.317	0.001	0.026	0.010	0.043	0.014	0.003
MAE		0.010	0.024	0.015	0.053	0.025	0.030

Frequency (ω_e) of diatomic molecules (Errors to experimental values)

Mol	**Exp**	**B3LYP**	**BLYP**	**PW91**	**VBSCF**	**DFVB**	
						LYP	**PW**
H_2	4401	18	-55	-69	-179	-92	-92
HF	4138	-13	-172	-116	15	122	177
HCl	2991	-20	-113	-69	-13	-4	63
Li_2	351	-7	-18	-18	-88	-53	-59
N_2	2359	91	-23	-1	14	73	95
O_2	1580	56	-91	-31	-76	1	60
F_2	917	139	51	90	-277	-135	-56
Cl_2	560	-18	-55	-20	57	-15	15
ClF	786	3	-56	-19	-95	-35	6
NF	1141	16	-59	-8	-86	10	52
MAE		38	69	44	90	54	68

BDE of diatomic molecules (Errors to experimental values)

Mol	D_e	B3LYP	BLYP	PW91	VBSCF	DFVB	
						LYP	PW
H_2	109.5	3.7	0.0	-4.3	-14.6	9.4	6.0
HF	141.3	-2.6	-1.2	0.5	-30.4	-4.9	-5.0
HCl	106.4	-0.3	-1.1	1.0	-17.0	5.2	6.1
Li_2	24.4	-3.7	-3.9	-4.5	-14.6	1.7	-1.2
N_2	228.5	3.1	13.8	16.1	-67.3	-5.8	-10.1
O_2	120.3	4.3	17.7	25.4	-45.3	-11.2	-9.3
F_2	38.2	2.3	14.4	18.7	-25.7	-6.9	-7.4
Cl_2	58.0	-0.2	2.2	10.0	-21.0	-2.5	2.3
ClF	60.2	2.4	8.9	14.5	-29.0	-8.6	-6.9
NF	70.4	14.0	23.6	27.5	-32.0	-2.5	-3.3
Au_2	53.0	-10.6	-7.2	-3.0	-32.9	-18.6	-18.2
MAE		4.3	8.5	11.4	30.0	7.0	6.9

S-T energy gaps of diradical systems (Errors to experimental values)

	Expt	Refs	CASPT2	B3LYP	BLYP	VBSCF	DFVB	
							LYP	PW
C	29.1[1]	1.3[5]	0.9	11.3	10.1	5.4	-4.5	-1.3
O	45.4[1]	-1.6[1]	0.9	17.0	15.5	4.9	-5.1	-1.7
O_2	22.7[2]	1.0[6]/0.7[7]	0.9	13.1	12.4	-2.4	-5.7	-5.1
NF	32.7[3]	2.6[3]	0.1	10.8	8.9	5.9	-3.0	-0.8
CH_2	32.9[1]	1.6[5]/-1.3[1]	-6.0	-25.5	-25.6	6.3	-7.0	-1.6
TMM	18.1[4]	-0.3[3]	2.0	25.7	16.6	3.4	-3.4	-0.4
MAE			1.8	17.2	14.9	4.7	4.8	1.8

[1] D.H. Ess, E.R. Johnson, X. Hu, et al., *J Phys Chem A*(2011) **115**(1), 76
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[3] G.S. Harbison, *J Am Chem Soc*(2001) **124**(3), 366
[4] XZ Li and J. Paldus, *J Chem Phys* (2008) **129**(17), 174101
[5] L.V. Slipchenko and A.I. Krylov, *J Chem Phys* (2002) **117**(10), 4694
[6] J. Pittner, P. Čársky and I. Hubač, *Int. J. Quantum Chem(*2002) **90**(3), 1031
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Summary 3

- DFVB method incorporates VB method to density functional theory.
- Test calculations show that DFVB improves VBSCF results, and overcomes the difficulty of DFT for diradical systems.
- Double-counting problem still exists and need to be corrected.

4. Valence Bond Polarizable Continuum Model (VBPCM) Method

VBPCM Method

Solvation effects play a very important role in molecular energy, structures, and properties.

PCM is an efficient and economical tool for describing solvation problems.

The solvent is usually represented as a homogeneous medium that is characterized by a single dielectric constant.

The QM packages of PCM are widely applied to study solvent effect in ab initio level.

The PCM Model

In Vacuum:

$$H^0\Psi^0 = E^0\Psi^0$$

In Solution:

$$(H^0 + V_R)\Psi = E\Psi$$

$$V_R = V_{el} + V_{dis} + V_{rep}$$

Minimizing

$$G =< \Psi \,|\, H^0 \,|\, \Psi > + < \Psi \,|\, V_R'' \,|\, \Psi > + \frac{1}{2} < \Psi \,|\, V_R'(\Psi) \,|\, \Psi > + V_{NN} + G_{nel}$$

$$\mathbf{F}^{\mathbf{S}}\mathbf{C} = \mathbf{S}\mathbf{C}\,\varepsilon$$

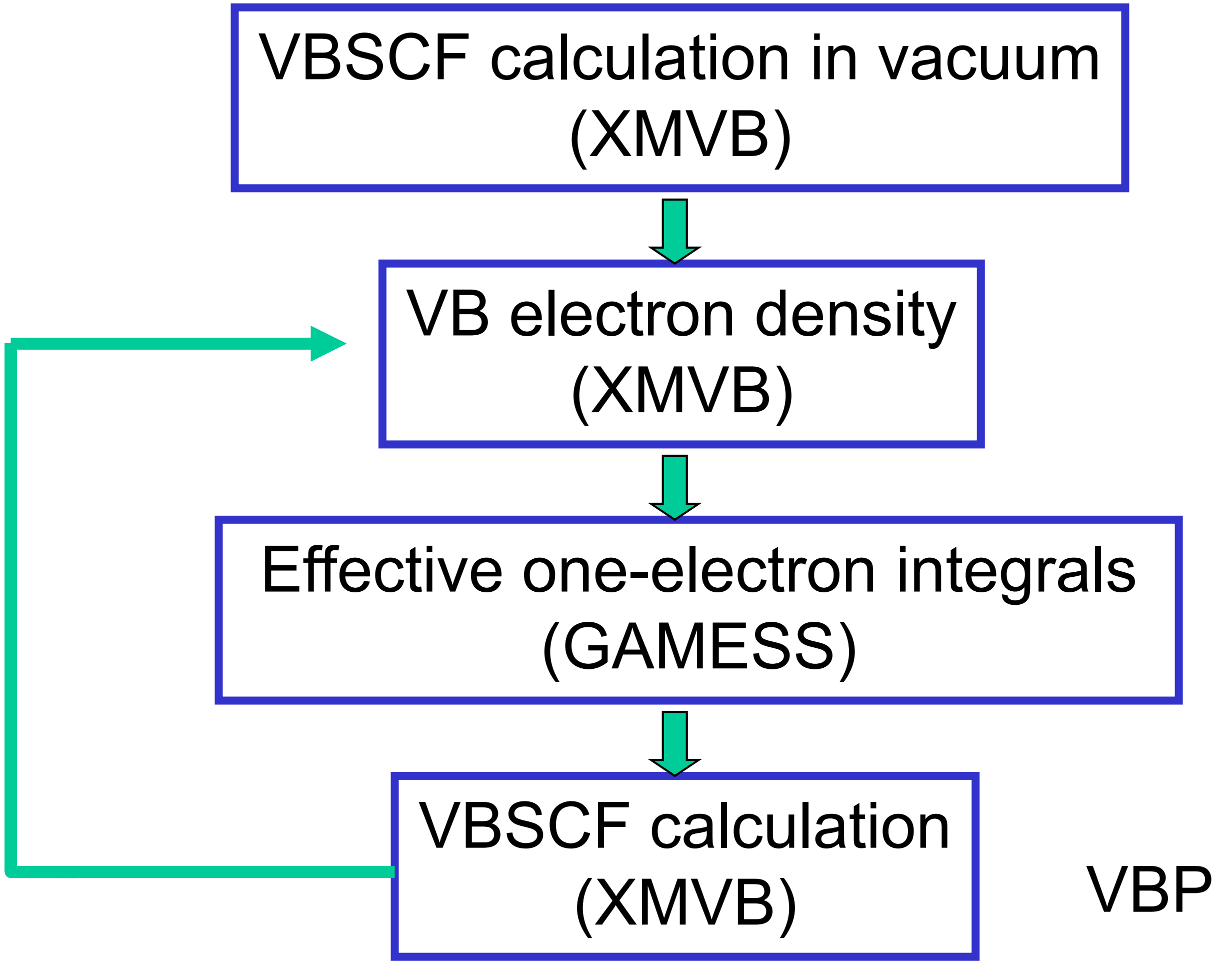
As one of QM method, essentially, PCM can be applied to VB method by the same strategy.

The difference between VB and MO-based methods is the form of wave function.

VBPCM method incorporates PCM into VB method by using VB density for the solvent-solute interaction potential, instead of MO-based density.

J. Phys. Chem. A, 108，6017-6024 (2004).

VBPCM Calculation



VBSCF calculation in vacuum
(XMVB)

VB electron density
(XMVB)

Effective one-electron integrals
(GAMESS)

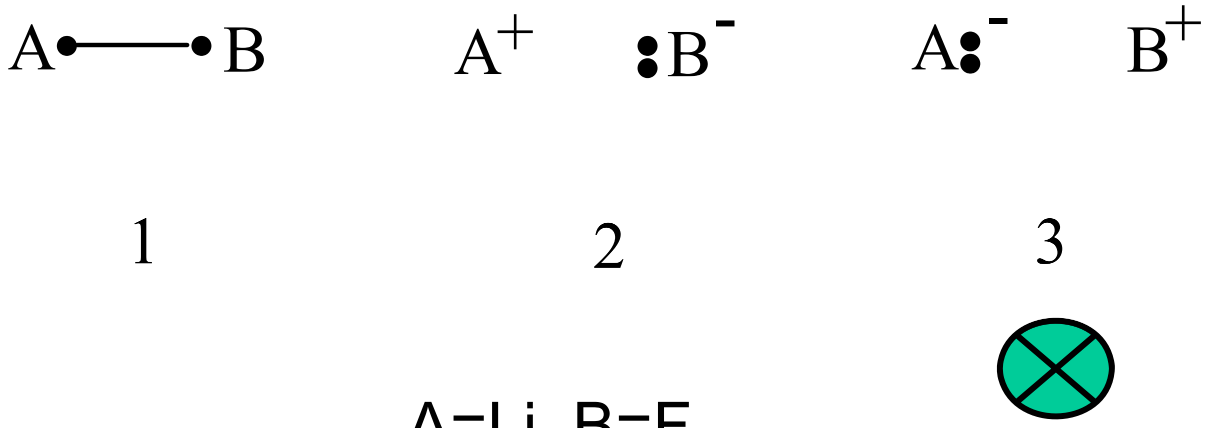
VBSCF calculation
(XMVB)

VBPCM/VBSCF

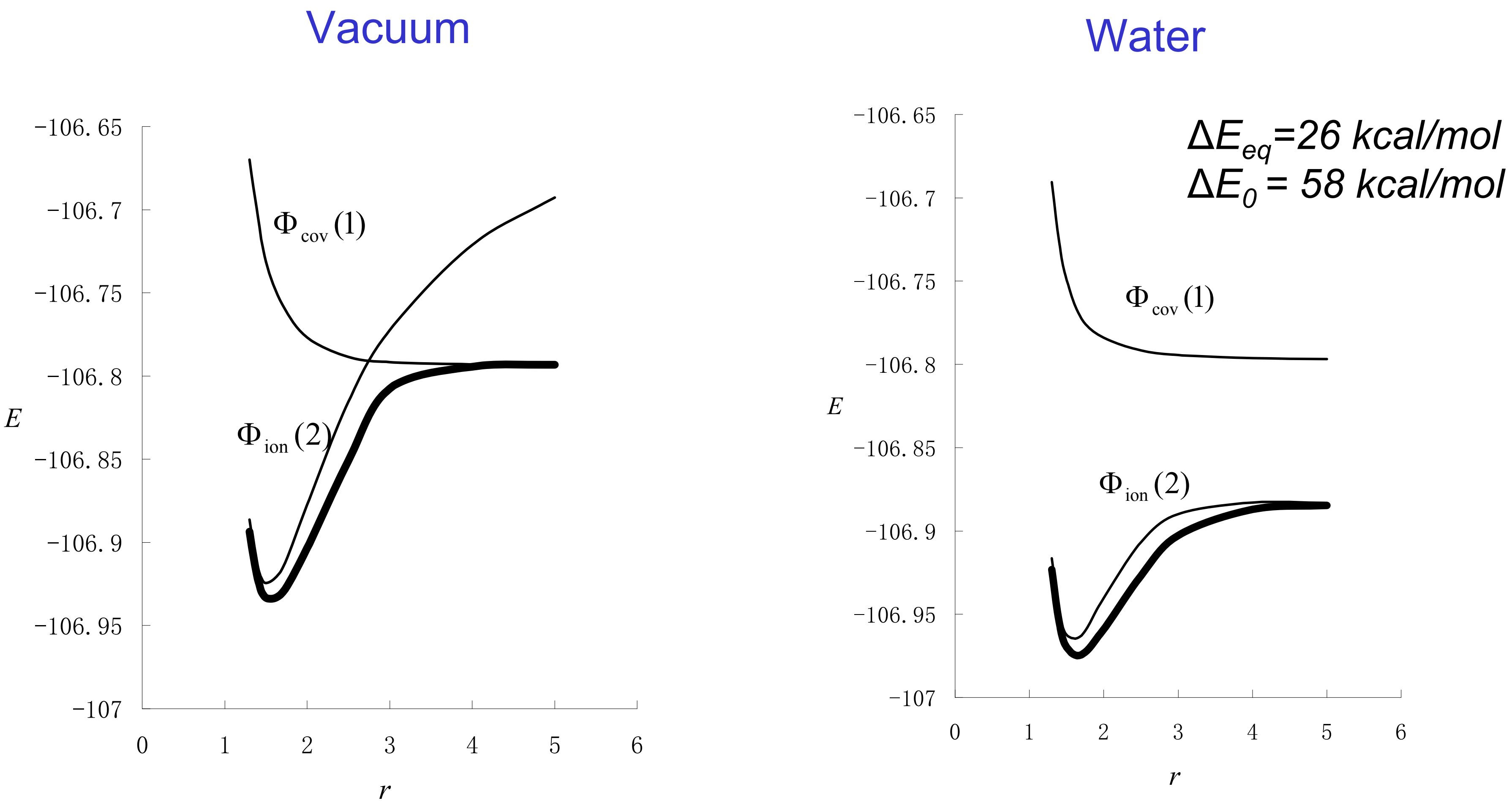
$$E = < \Psi \mid H^0 + \frac{1}{2} V_R \mid \Psi >$$

Dissociation of LiF

VBPCM//VBSCF 6-31G* and 6-31+G*



A=Li, B=F



Vacuum

Water

ΔE_{eq}=26 kcal/mol

ΔE_0 = 58 kcal/mol

Figure 1a. VBSCF/6-31G* dissociation energy profiles of LiF in vacuum. Adiabatic potentials are shown in bold curves. 1b. VBPCM//VBSCF/6-31G* dissociation energy profiles of LiF in H_2O.

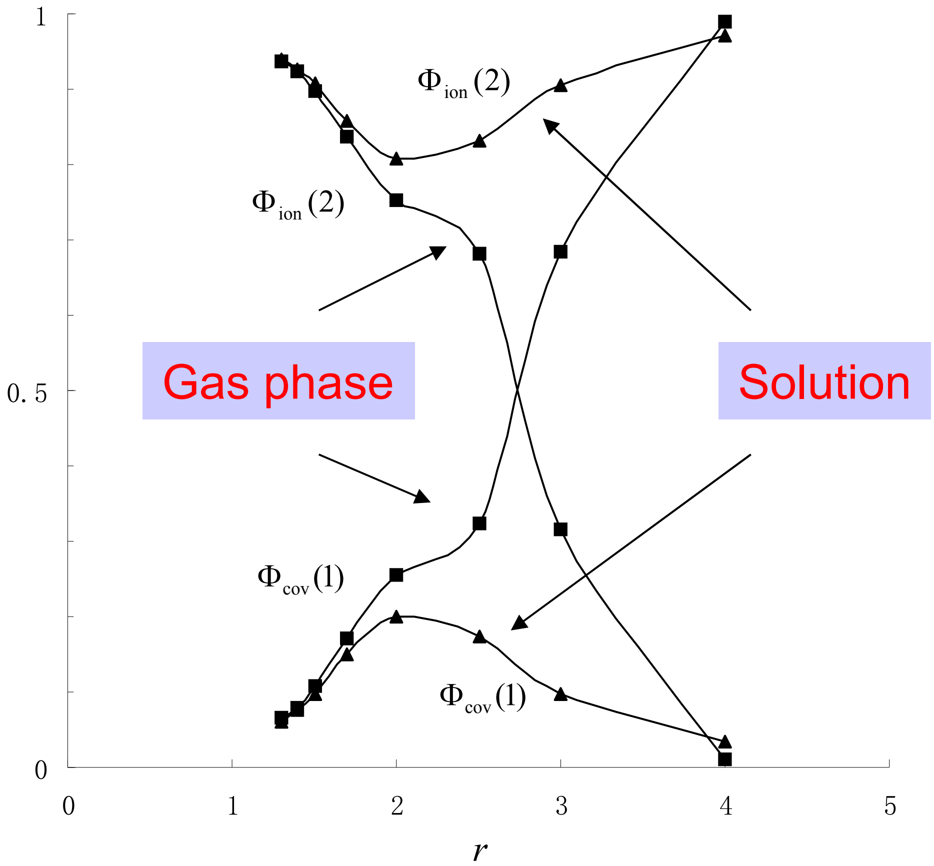
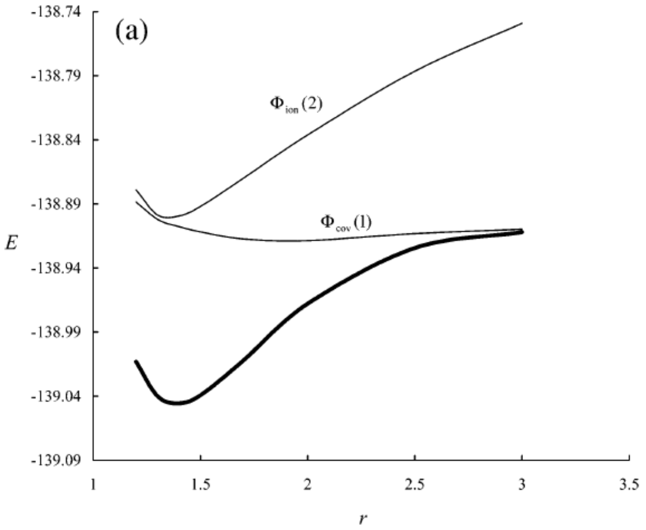


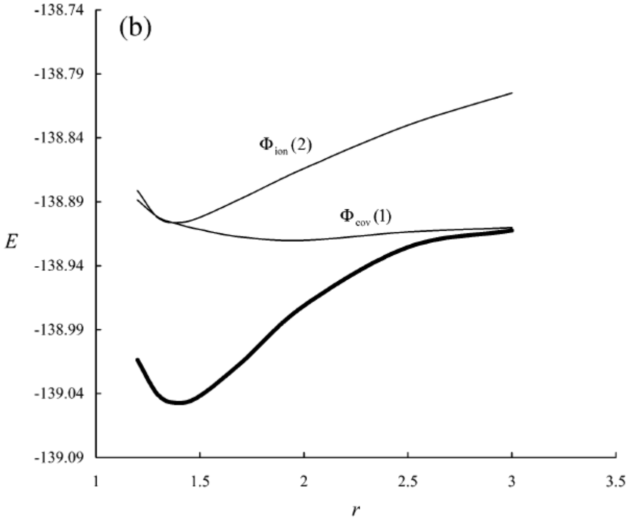
Figure 3. Weights of VB structures of LiF. VBSCF/6-31G* weights are annotated with bold squares and VBPCM//VBSCF/6-31G* weights with triangles.

Dissociation of CH_3F (polar-covalent bond)

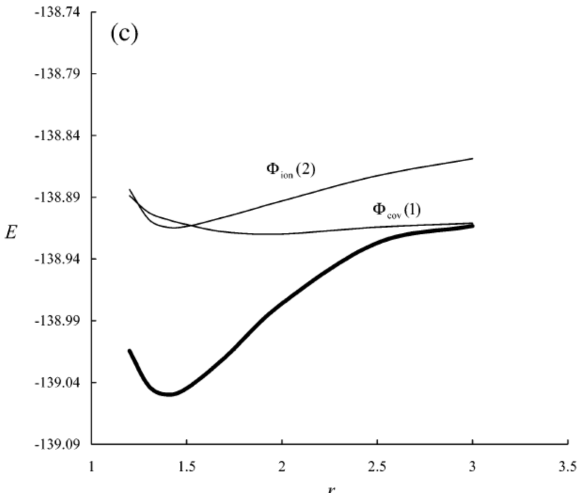


Vacuum

CCl_4



H_2O



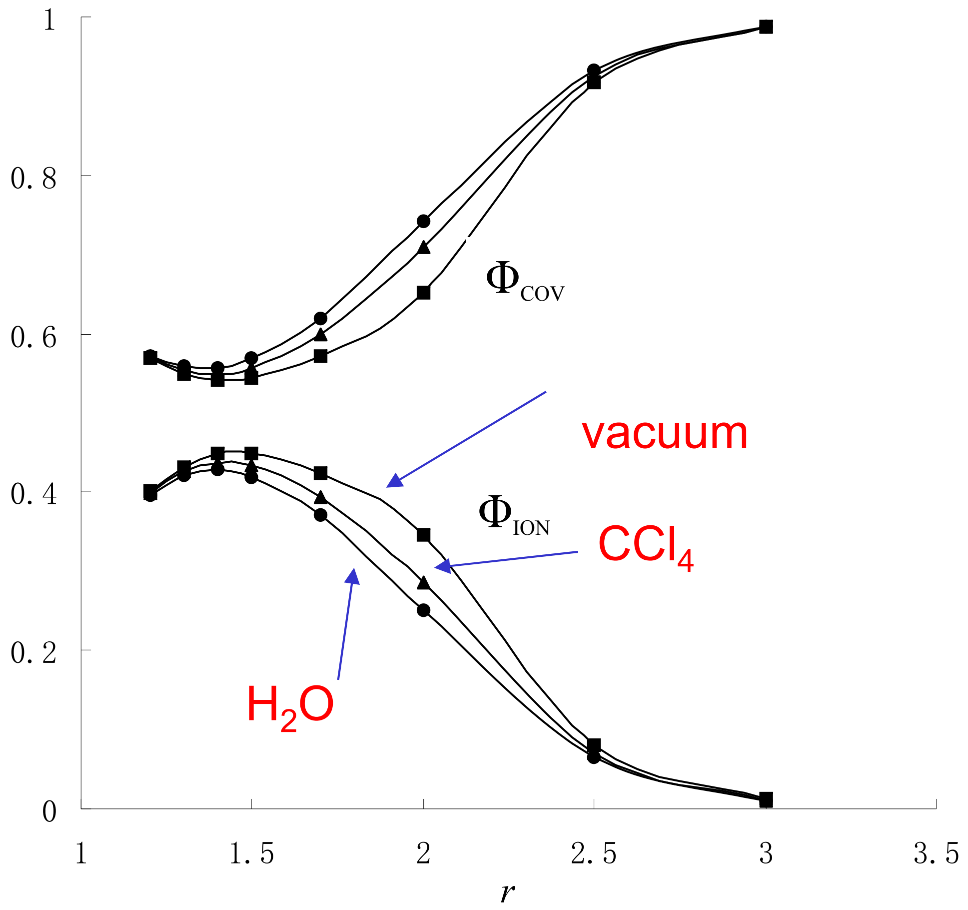


Figure 5. VBSCF/6-31G* and VBPCM//VBSCF/6-31G* weights of VB structures of CH_3F along the C-F dissociation coordinate. The curves in vacuum, CCl_4, H_2O are annotated with bold squares, triangles and circles respectively.

Summary 4

- VBPCM method enables us to compute the energy profile of the full state as well as of individual VB structures. Thus, it provides qualitative insights into the solvent effects of chemical problems.

- One-electron density plays a role as a bridge between the VB and the PCM methods: More general VBPCM methods can be presented by combining different VB methods and solvent models.

More VB Methods for Solvation Effects

Valence Bond Solvation Model (VBSM)

Su; Wu; Kelly; Cramer; Truhlar,J. Phys. Chem. A, 2008, 112, 12761.

Valence Bond Effect Fragment Potential (VBEFP)

Ying; Chang; Su; Wu, J. Phys. Chem., A, 2012, 116, 1846.

VB/EFP/PCM

Su; Ying; Wu, in preparation

Combined VB and MM method (VB/MM)

Shurki; Cromn, J. Phem. Chem. B, 2005, 109, 23638;
Sharir-Ivry; Crown; Wu; Shurki, J. Phys. Chem. A, 2008, 112, 2489

Explicit Solvation VB Method

Braida; Hiberty, Int. J. Quant. Chem. 2010, 110, 571.

Acknowledgements

Xiamen Group:
Zhenhua Chen, Peifeng Su, Fuming Ying, Jinshuai Song, Xun Chen, Lingchun Song, Qianer Zhang

Collaborators:
Prof. S. Shaik (Hebrew University, Jerusalem)
Prof. P. C. Hiberty (Université de Paris-Sud, Orsay)
Prof. Y. Mo (Western Michigan University)

$ Natural Science Foundation of China

Thank you!

Total Time Consuming by Various VB Methods

	VBSCF	VBCISD	VBPT2	DFVB(LYP)	DFVB(PW)
H_2	0.04	0.05	0.05	4.96	5.76
HF	0.10	14.18	0.10	80.76	126.49
F_2	0.52	5217.80	0.37	354.28	465.88
O_2	0.81	35506.17	0.67	390.40	441.10
N_2(17str)	1.02[a]	147163.48	0.74	917.64	1019.32
N_2(11str)	0.84[a]	101598.66	0.73	602.10	819.08

unit: second

[a] with GUESS=MO

Iscf=5 for VBSCF, Iscf=1 for DFVB

Computational costs of VBSCF, VBCISD, VBPT2, icVBPT2 and icVBCISD

The computational cost of integral transformation:

VBSCF Energy	VBSCF Gradient	VBSCF Hessian	VBCISD	VBPT2	icVBPT2	icVBCISD
$(N_{act})*(N_{bas})^4$	$(N_{act})*(N_{bas})^4$	$(N_{occ})*(N_{bas})^4$	$(N_{bas})^5$	$(N_{occ})*(N_{bas})^4$	$(N_{occ})*(N_{bas})^4$	$(N_{bas})^5$

N_{act}, N_{occ}, N_{bas} are the number of active, occupied orbitals and basis functions respectively.

VBCISD	VBPT2	icVBPT2[c]	icVBCISD[d]
$(N_{CISD}^{VB})^2(N_{ele})^4$	$(N_{PT2}^{VB})^2(N_{ele})^2$	$(N_{str}^{\alpha})^2(N_{act}^{\alpha})^8$ $+(N_{str}^{\beta})^2(N_{act}^{\beta})^8$ $+(N_{\det})^2(N_{act}^{\beta})^4$	$(N_{str}^{\alpha})^2(N_{act}^{\alpha})^{10}$ $+(N_{str}^{\beta})^2(N_{act}^{\beta})^{10}$ $+(N_{\det})^2(N_{act}^{\beta})^4$

a. string-based implementation

b. The computational cost of RDMs up to 3th-order.

c. The computational cost of RDMs up to 4th-order.

d. The computational cost of RDMs up to 5th-order.