

# Quadratically Convergent VBSCF method

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# Introduction

$$\text{VB wavefunction} = \Psi_{VB} = \sum_i c_i \Phi_i$$

$$\Phi = \sum_j \alpha_j \Delta_j$$

$$\Delta = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3 \cdots \phi_k \phi_l|$$

$\phi_i$ 's are spin-orbitals

# Orbital Optimisation In VBSCF

- ▶ To get a consistent answer, that does not depend on the start
- ▶ Not really very different from orthogonal case

Based on Generalised Brillouin Theorem

$\Psi_0$  will not mix with singly excited states  $\Psi_{ij}$  :

$$\langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{ij} \rangle = 0$$

# Super-CI Method

$$\Psi_0 = |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3|$$

► infinitesimal

$$\phi_1 \rightarrow \phi_1 + \delta\gamma_{1 \rightarrow 4} \phi_4$$

$$\begin{aligned} |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3| &\rightarrow |(\phi_1 + \gamma_{1 \rightarrow 4} \phi_4)(\bar{\phi}_1 + \gamma_{1 \rightarrow 4} \bar{\phi}_4) \phi_2 \bar{\phi}_3| \\ &= |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3| + \delta\gamma_{1 \rightarrow 4} |\phi_4 \bar{\phi}_1 \phi_2 \bar{\phi}_3| \\ &\quad + \delta\gamma_{1 \rightarrow 4} |\phi_1 \bar{\phi}_4 \phi_2 \bar{\phi}_3| + \cancel{\delta\gamma_{1 \rightarrow 4}^2 |\phi_4 \bar{\phi}_4 \phi_2 \bar{\phi}_3|} \\ &= |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3| + \delta\gamma_{1 \rightarrow 4} \cdot \mathbf{C}_{1 \rightarrow 4} |\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_3| \\ &= \Psi_0 + \delta\gamma_{1 \rightarrow 4} \cdot \mathbf{C}_{1 \rightarrow 4} \Psi_0 \end{aligned}$$

$\mathbf{C}_{i \rightarrow j}$  Replaces orbital  $i$  by orbital  $j$ , once for  $\alpha$  spin and once for  $\beta$  spin in the complete function

$$\Psi_0 \rightarrow \Psi_0 + \sum_{i \neq j} \delta\gamma_{i \rightarrow j} \mathbf{C}_{i \rightarrow j} \Psi_0 = \Psi_0 + \sum_{i \neq j} \delta\gamma_{i \rightarrow j} \Psi_{ij}$$

where  $\Psi_{ij}$ 's are Brillouin States (singly excited states)

# Super-CI Method

Expand the wave function as linear combination of  $\Psi_0$  and all of the Brillouin state functions  $\Psi_{ij}$  and find that linear combination of these functions which minimises the energy

$$\Psi_{superCI} = \gamma_0 \Psi_0 + \sum \delta\gamma_{i \rightarrow j} \Psi_{ij}$$

by solving a set of secular equations

$$\begin{bmatrix} \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_0 \rangle \\ \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{ij} \rangle & \langle \Psi_{kl} | \mathbf{H} - E_0 | \Psi_{ij} \rangle \end{bmatrix} \vec{\gamma} = 0$$

Singly substituted configurations are absorbed into the orbitals so that  $\Psi_0$  approaches to  $\Psi_{superCI}$  to first order:

$$\phi_i \rightarrow \gamma_0 \phi_i + \sum_{j \neq i} \delta\gamma_{ij} \phi_j$$

# Newton-Raphson Method

$$\begin{aligned} |\delta\mathbf{c}\rangle &= -[\nabla^2.E]^{-1}\nabla.E \\ &= -\mathcal{H}^{-1}.g \end{aligned}$$

$\mathcal{H}$  is the second derivative with respect to all variational parameters

$$\begin{aligned} \mathbf{G}_{(ij,kl)} &= \frac{\partial^2 E}{\partial\gamma_{kl}\partial\gamma_{ij}} = 2.\langle\Psi_{kl}|\mathbf{H} - E_0|\Psi_{ij}\rangle \\ &\quad + 2.\langle\Psi_0|\mathbf{H} - E_0|\Psi_{ij,kl}\rangle \\ &\quad - 4.\langle\Psi_0|\mathbf{H} - E_0|\Psi_{ij}\rangle\langle\Psi_{kl}|\Psi_0\rangle \\ &\quad - 4.\langle\Psi_0|\mathbf{H} - E_0|\Psi_{kl}\rangle\langle\Psi_{ij}|\Psi_0\rangle \end{aligned}$$

$$\mathbf{C}_{i\rightarrow j}\Psi_0 \rightarrow \Psi_{ij} : \mathbf{C}_{k\rightarrow l}\Psi_{ij} \rightarrow \Psi_{ij,kl}$$

# Newton-Raphson Method

## CI Block

$$\begin{aligned} \mathbf{G}_{(c_k, c_l)} &= \frac{\partial^2 E}{\partial c_k \partial c_l} = 2 \cdot \langle \Phi_k | \mathbf{H} - E_0 | \Phi_l \rangle \\ &\quad - 4 \cdot \langle \Psi_0 | \mathbf{H} - E_0 | \Phi_k \rangle \langle \Phi_l | \Psi_0 \rangle \\ &\quad - 4 \cdot \langle \Psi_0 | \mathbf{H} - E_0 | \Phi_l \rangle \langle \Phi_k | \Psi_0 \rangle \end{aligned}$$

## CI-Orbital Block

$$\begin{aligned} \mathbf{G}_{(c_k, ij)} &= \frac{\partial^2 E}{\partial c_i \partial \gamma_{ij}} = 2 \cdot \langle \Phi_i | \mathbf{H} - E_0 | \Psi_{ij} \rangle \\ &\quad + 2 \cdot \langle \Psi_0 | \mathbf{H} - E_0 | (\Phi_i)_{ij} \rangle \\ &\quad - 4 \cdot \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{ij} \rangle \langle \Phi_i | \Psi_0 \rangle \\ &\quad - 4 \cdot \langle \Psi_0 | \mathbf{H} - E_0 | \Phi_k \rangle \langle \Psi_{ij} | \Psi_0 \rangle \end{aligned}$$

# Newton-Raphson Method

$$\mathcal{H} = \left[ \begin{array}{c|c} \mathbf{G}_{(ij,kl)} & \mathbf{G}_{(c_k,ij)} \\ \hline \mathbf{G}_{(c_k,ij)} & \mathbf{G}_{(c_k,c_l)} \end{array} \right]$$
$$|\delta\mathbf{c}\rangle = -\mathcal{H}^{-1} \cdot g$$

can be solved

- ▶ in a single step (inverting the  $\mathcal{H}$ )
- ▶ iteratively (Conjugate Gradient Method)

Convergence will be quadratic close to the minima.

$$\phi_i \rightarrow c_0 \phi_i + \sum_{j \neq i} c_{ij} \phi_j \quad (\text{by setting } c_0 = 1)$$

- ▶ Due to the  $\langle \Psi | \Psi \rangle = 1$  condition,  $\mathcal{H}$  has at least one zero eigenvalue (CI-block).
- ▶ A positive definite  $\mathcal{H}$  is required.



# 1 - Stabilised Newton-Raphson Method\*†

$$|\delta\mathbf{c}\rangle = -(\mathcal{H} + \alpha\mathbf{I})^{-1} \cdot g$$

$$\text{where } \alpha = -\epsilon_0 + R \cdot \langle g|g\rangle$$

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\* J. Gerratt and M. Raimondi; *Proc. R. Soc. Lond. A* **1980**, 371, 525-552

† S. M. Goldfeld, R. E. Quandt and H. F. Trotter; *Econometrica*, **1966**, 34, 541-551 

## 2 - Back to Super-CI

$$\begin{aligned} \mathbf{G}_{(ij,kl)} &= \frac{\partial^2 E}{\partial \gamma_{kl} \partial \gamma_{ij}} = 2. \langle \Psi_{kl} | \mathbf{H} - E_0 | \Psi_{ij} \rangle \\ &\quad + 2. \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{ij,kl} \rangle \\ &\quad - 4. \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{ij} \rangle \langle \Psi_{kl} | \Psi_0 \rangle \\ &\quad - 4. \langle \Psi_0 | \mathbf{H} - E_0 | \Psi_{kl} \rangle \langle \Psi_{ij} | \Psi_0 \rangle \end{aligned}$$

Before calculating the  $\mathbf{G}_{(c_k,ij)}$  and  $\mathbf{G}_{(c_k,c_l)}$

- ▶ If  $\mathbf{G}_{(ij,kl)}$  Block is not positive definite.
- ▶ Super-CI ! (everything is available)

# TURTLE

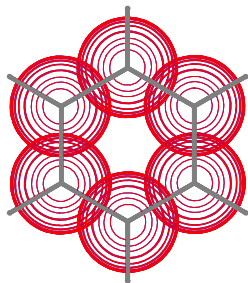
A gradient VB/VBSCF program available as part of  
GAMESS-UK

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      tttt   u  u   rrrrr   tttt   l          eee
      t      u  u   r  r   t      l          eeeee
      t  t   u  u   r      t  t   l  l       e
      ttt    uu    r      ttt    111       eee
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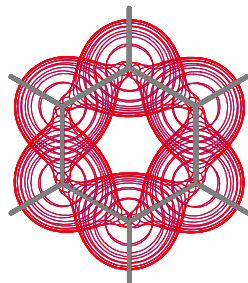
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# Test Calculations

Contours of the square of each  $p$ -orbital of the benzene molecule in VBSCF method



VBSCF-local



VBSCF-delocal

- ▶ In **VB-local** mixing between the basis functions which are on different atoms is not allowed (a restriction)
- ▶ In **VB-delocal** orbitals are optimized without *ANY* restriction (VB-delocal = SCVB)

# Test Calculations

## Benzene (VB-local)

(5 structures, 6 singly occupied, (18 doubly occupied and frozen), 6-31G basis)

Newton-Raphson				Super-CI		
it	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)
1	-230.5259178726	4.5E-02	0.61	-230.5259178726	4.5E-02	0.57
2	-0.0144672170	4.5E-05	1.00	-0.0144104380	2.9E-03	0.91
3	-0.0000000142	2.5E-10	1.38	-0.0000565700	1.8E-04	1.25
4	0.0000000000	3.3E-16	1.76	-0.0000002223	1.1E-05	1.60
5				-0.0000000009	7.3E-07	1.94
6				0.0000000000	4.6E-08	2.28

On 2.3 GHz intel Core i7 (single core)

# Test Calculations

## Benzene (VB-delocal)

(5 structures, 6 singly occupied, (18 doubly occupied and frozen), 6-31G basis)

Newton-Raphson				Super-CI		
it	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)
1	-230.5451395787	6.5E-02*	1.90	-230.53 14 43 62	6.5E-02	0.90
2	-0.1145683153	2.9E-02*	3.59	-0.1046599957	5.7E-02	1.59
3	-0.0280847844	9.8E-03*	5.29	-0.0288869095	3.3E-02	2.28
4	-0.0047150114	2.2E-03*	6.98	-0.0127044622	1.0E-02	2.98
5	-0.0003805415	2.3E-04	8.67	-0.0014916033	5.9E-04	3.67
6	-0.0000120653	1.8E-05	10.35	-0.0000174271	3.6E-05	4.35
7	-0.0000000471	3.2E-07	12.04	-0.0000002928	5.8E-06	5.04
8	0.0000000000	5.1E-11	13.72	-0.0000000578	2.8E-06	5.72
⋮				⋮	⋮	⋮
12				-0.0000000001	1.4E-07	8.46
13				0.0000000000	6.6E-08	9.17

\* Hessian has (some) negative eigenvalues

# Test Calculations

## Naphthalene (VB-local)

(3 Kekulé structures, 10 singly occupied, (29 doubly occupied and frozen), 6-31G basis)

Newton-Raphson				Super-CI		
it	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)
1	-383.0470764886	4.8E-02	23.77	-383.0470764886	4.8E-02	8.61
2	-0.0235373623	3.4E-04	47.13	-0.0234656126	2.6E-03	16.08
3	-0.0000002905	1.4E-09	70.33	-0.0000717600	1.6E-04	23.52
4	0.0000000000	1.8E-15	93.38	-0.0000002790	1.0E-05	31.00
5				-0.0000000011	6.5E-07	38.43
6				0.0000000000	4.2E-08	45.89

# Test Calculations

## Naphthalene (VB-delocal)

(3 Kekulé structures, 10 singly occupied, (29 doubly occupied and frozen), 6-31G basis)

Newton-Raphson

Super-CI with  
DIIS (it = 4) and level shift (0.3)

it	$\Delta E_{(it,it-1)}$ (a.u.)	$g_{max}$	cpu(s)	$E$ (a.u.)	$g_{max}$	cpu(s)
1	-383.0706141415	8.5E-02*	783.52	-383.0706141415	8.5E-02	211.46
2	-0.1918307736	4.1E-02*	1565.06	-0.1859593315	5.0E-02	421.80
3	-0.0614601257	1.5E-02	2339.62	-0.0317196124	3.8E-02	633.92
4	-0.0115183023	5.1E-03	3114.62	-0.0145516610	3.0E-02	845.75
5	-0.0012003815	7.1E-04	3898.10	-0.0137721837	2.2E-02	1066.81
6	-0.0000304014	4.0E-05	4676.77	-0.0027824377	2.0E-02	1277.55
7	-0.0000002076	2.6E-06	5456.09	-0.0090676856	1.2E-02	1488.03
8	-0.0000000021	3.2E-07	6247.09	-0.0062508165	5.3E-03	1697.93
9	0.0000000000	4.1E-08	7032.38	-0.0004213629	4.6E-03	1909.54
⋮				⋮	⋮	⋮
16				-0.0000000069	6.2E-07	3403.21
17				0.0000000000	2.3E-07	3614.82



# Conclusion

- ▶ The quadratically convergent scheme for the simultaneous optimisation of orbitals and CI coefficients is very efficient with respect to convergence (but expensive in computational time).
- ▶ Simple with respect to the formalism and programming.
- ▶ In VB-local the method is quadratic from the very beginning (optimisation converges in 4 - 6 iterations).
- ▶ In VB-delocal it is quadratic close to the minima.

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- ▶ Netherlands Universities Foundation for International Cooperation (NUFFIC).



# TURTLE 1988-2012

## Orbital Optimisation

- ▶ With arbitrary restrictions, VB-local (atomic or optimal hybrid orbitals) , Bond Distorted (distortion on one side), BLW, RBLW (Resonating Block-localised wave function in a BOVB like fashion)
- ▶ Full Optimisation (without any restriction), VB-delocal = SCVB
- ▶ BOVB (VB-local/VB-delocal)
- ▶ Anything between VB-local and VB-delocal.

## Gradient Capabilities

- ▶ Geometry optimisation (combined with any of the above orbital optimisation) for single- or multi-structure VB wave function
- ▶ Frequency calculations

## Response Properties

polarisability and magnetisability, (Coupled VB).

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## AIVB (Atoms In Valence Bond) method<sup>†§</sup>

$$\Psi_{AIVB} = c_1 \begin{array}{c} O \quad H \\ \circ \quad \circ \\ 3P \quad 2S \end{array} + c_2 \begin{array}{c} O \quad H \\ \circ \quad \circ \\ 1D \quad 2S \end{array} \\ + c_3 \begin{array}{c} O \quad H \\ \circ \quad \circ \\ 1S \quad 2S \end{array} + c_4 \begin{array}{c} O \quad H^+ \\ \circ \quad \circ \\ 2P \quad \circ \end{array}$$

**AIVB wave function for OH radical**

available for  $s$  and  $p$  orbitals

<sup>†</sup>M. Zielinski and J. H. van Lenthe; *Chem. Phys. Lett.* **2010**, 500, 155-160

<sup>§</sup>J. H. van Lenthe and G. G. Balint-Kurti; *Chem. Phys. Lett.* **1980**, 76, 138-142

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## Available Methods/Algorithms For Orbital Optimisation

1. non-orthogonal Super-CI
2. non-orthogonal equivalent of the first-order Rayleigh-Schrödinger perturbation method
3. an automatic switching between the above two methods
4. Newton-Raphson method
5. an automatic switching between Super-CI and Newton-Raphson method

In addition some convergence accelerators like **DIIS** and **level shift** are available to help Super-CI or Perturbation method

# Massively Parallel

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t           t           l
tttt    u u   rrrrr  tttt    l           eee
t       u u   r   r   t       l           eeeee
t   t   u u   r       t   t   l   l       e
      ttt    uu     r       ttt    lll       eee
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J. Verbeek, J. H. Langenberg, C. P. Byrman, F. Dijkstra, R.  
W. A. Havenith, J. J. Engelberts, M. L. Zielinski, Z. Rashid  
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<http://tc5.chem.uu.nl>