

# Internally Contracted Valence Bond Perturbation Theory

$$|\Psi\rangle = |\Psi^{(0)}\rangle + |\Psi^{(1)}\rangle \quad |\Psi^{(0)}\rangle = |\Psi^{\text{SCF}}\rangle = \sum_K C_K^{(0)} |\Phi_K\rangle$$

The first-order wave function: a linear combination of the internally contracted excited configurations.

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

The first-order wave function  $\mathbf{t} = (\mathbf{H}_0^{11} - E^{(0)}\mathbf{M}^{11})^{-1} \mathbf{V}$

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

- Efficient & accurate
- Spin-free
- Invariant of orbital rotation
- Near size-consistent
- Intruder state possible
- No VB weight yet

Z. Chen, J. Song, S. Shaik, P. C. Hiberty, W. Wu, *J. Phys. Chem. A*, 2009, 113, 11560.

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Bond dissociation energies ( $D_e$ , eV) of N<sub>2</sub>, O<sub>2</sub> and F<sub>2</sub>.

Molecule	N <sub>2</sub>		O <sub>2</sub>		F <sub>2</sub>
$N^{\text{VB}}$	17	175	12	105	3
<b>VBSCF</b>	8.086	8.190	2.999	3.045	<b>0.436</b>
<b>VBPT2</b>	8.421	8.573	4.327	4.661	<b>1.549</b>
<b>icVBPT2</b>	8.466	8.570	4.539	4.606	<b>1.460</b>
FCI/MRCI	8.748		4.637		<b>1.423</b>

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