Contents

1 Framework

Conventions:

- Greek letters τ and σ indicate spin functions.
- ϕ and lowercase subscript letters (p, q, r, s) indicate the non-orthogonal atomic orbitals.

Let us define $\hat{a}_p^\dagger$ and $\hat{a}_q$ as elementary creation and annihilation operators of an non-orthogonal spatial basis. Evaluating the anti-commutator on the vacuum state:

$$\begin{aligned}
\langle \text{vac} | [\hat{a}_p^\dagger, \hat{a}_q]_+ | \text{vac} \rangle &= \langle \text{vac} | \hat{a}_q \hat{a}_p^\dagger | \text{vac} \rangle && (1.1)\\
&= \langle \phi_q | \phi_p \rangle && (1.2)\\
&= S_{qp} && (1.3)\\
\left[\hat{a}_p^\dagger, \hat{a}_q\right]_+ &= S_{qp} && (1.4)
\end{aligned}$$

With spin in the picture the non-relativistic framework allows us to define elementary operators in the non-orthogonal spin orbitals basis as:

$$\begin{aligned}
\left[\hat{a}_{p\sigma}^\dagger, \hat{a}_{q\tau}\right]_+ &= S_{qp}\delta_{\sigma\tau} && (1.5)\\
\left[\hat{a}_{p\sigma}^\dagger, \hat{a}_{q\tau}^\dagger\right]_+ &= 0 && (1.6)\\
\left[\hat{a}_{p\sigma}, \hat{a}_{q\tau}\right]_+ &= 0 && (1.7)
\end{aligned}$$

A valence bond structure can then be expressed as a summation of creation operators on a vacuum state (with $k_{p\sigma}$ 0 if not occupied in the given state and 1 if occupied):

$$|\mathbf{k}\rangle = \prod_\sigma \prod_p^K (\hat{a}_{p\sigma}^\dagger)^{k_{p\sigma}} |\text{vac}\rangle \tag{1.8}$$

$$\psi_{\text{vb}} = \sum_k |\mathbf{k}\rangle \tag{1.9}$$

For given valence wave function we can then write:

$$\Psi_{\text{vb}} = \sum_i c_i \psi_i \tag{1.10}$$

The electronic Hamiltonian in restricted space can then be written as:

$$\hat{\mathcal{H}}_{\text{elec}} = \sum_{pq}^{K} h_{pq} \hat{E}_{pq} + \frac{1}{2} \sum_{pqrs}^{K} g_{pqrs} \hat{e}_{pqrs} \tag{1.11}$$

Where $\hat{E}_{pq}$ is the singlet one-electron excitation operator:

$$\hat{E}_{pq} = \hat{a}^\dagger_{p\alpha} \hat{a}_{q\alpha} + \hat{a}^\dagger_{p\beta} \hat{a}_{q\beta} \tag{1.12}$$

$$= \hat{E}^\alpha_{pq} + \hat{E}^\beta_{pq} \tag{1.13}$$

$$= \sum_\sigma \hat{a}^\dagger_{p\sigma} \hat{a}_{q\sigma} \tag{1.14}$$

And $\hat{e}_{pqrs}$ is a singlet two-electron excitation operator:

$$\hat{e}_{pqrs} = \hat{E}_{pq} \hat{E}_{rs} - \delta_{qr} \hat{E}_{ps} \tag{1.15}$$

$$= \sum_{\sigma\tau} \hat{a}^\dagger_{p\sigma} \hat{a}^\dagger_{r\tau} \hat{a}_{s\tau} \hat{a}_{q\sigma} \tag{1.16}$$

1.1 Butadiene

- P_z Middle carbon = ϕ_1
- P_z Outer neighbour = ϕ_3
- P_z Other middle carbon = ϕ_2
- P_z His neightbour = ϕ_4

All ONVs are also appended by a doubly occupied ONV and RHF based basis $|RHF\rangle$ this is omitted for convenience. All ONVs use integer $|1\rangle$ instead of $|\phi_1\rangle$. An example of an ONV is $|1_\alpha|2_\beta\rangle$ left side is always alpha, right side is always beta.

1.1.1 Covalent wave function

$$\psi_{cov} = (|1|3\rangle + |3|1\rangle) \bigotimes (|2|4\rangle + |4|2\rangle) \tag{1.17}$$

$$= |12|34\rangle + |14|23\rangle + |23|14\rangle + |34|12\rangle \tag{1.18}$$

1.1.2 Radical wave function

$$\psi_{rad} = (|1|2\rangle + |2|1\rangle) \bigotimes (|3|4\rangle + |4|3\rangle) \tag{1.19}$$

$$= |13|24\rangle + |14|23\rangle + |23|14\rangle + |24|13\rangle \tag{1.20}$$

1.1.3 other

1.2 Semi-localised orbitals

$$\phi_1' = \phi_1 + d_1\phi_3 \tag{1.21}$$

$$\phi_3' = d_2\phi_1 + \phi_3 \tag{1.22}$$

$$\phi_2' = \phi_2 + d_3\phi_4 \tag{1.23}$$

$$\phi_4' = d_4\phi_2 + \phi_4 \tag{1.24}$$

Replacing ϕs by ϕ's and rewriting it in terms of ϕ again yields the following vb state function:

$$\begin{aligned}\psi_{cov} =& 2(d_2\,|1|1\rangle + |1|3\rangle + d_1d_2\,|1|3\rangle + d_1\,|3|3\rangle) \bigotimes \\ & 2(d_4\,|2|2\rangle + |2|4\rangle + d_3d_4\,|2|4\rangle + d_3\,|4|4\rangle) \\ & \text{omit constant factors}\end{aligned} \tag{1.25}$$

$$\begin{aligned}\psi_{cov} =& d_2d_4\,|12|12\rangle + d_2\,|12|14\rangle + d_2d_3d_4\,|12|14\rangle + d_2d_3\,|14|14\rangle \\ & + d_4\,|12|23\rangle + |12|34\rangle + d_3d_4\,|12|34\rangle + d_3\,|14|34\rangle \\ & + d_1d_2d_4\,|12|23\rangle + d_1d_2\,|12|34\rangle + d_1d_2d_3d_4\,|12|34\rangle + d_1d_2d_3\,|14|34\rangle \\ & + d_1d_4\,|23|23\rangle + d_1\,|23|34\rangle + d_1d_3d_4\,|23|34\rangle + d_1d_3\,|34|34\rangle\end{aligned} \tag{1.26}$$

$$\begin{aligned}\psi_{cov} =& |12|34\rangle + d_1\,|23|34\rangle + d_2\,|12|14\rangle + d_3\,|14|34\rangle + d_4\,|12|13\rangle \\ & + d_1d_2\,|12|34\rangle + d_1d_3\,|34|34\rangle + d_1d_4\,|23|23\rangle \\ & + d_2d_3\,|14|14\rangle + d_2d_4\,|12|12\rangle + d_3d_4\,|12|34\rangle \\ & + d_1d_2d_3\,|14|34\rangle + d_1d_2d_4\,|12|23\rangle + d_1d_3d_4\,|23|34\rangle + d_2d_3d_4\,|12|14\rangle \\ & + d_1d_2d_3d_4\,|12|34\rangle\end{aligned} \tag{1.27}$$

1.3 Dislocation