1 Contravariant Space

By 2nd order perturbation theory, the most important contribution to the corrlation energy comes from the configuration Φ_I which spans the first-order interacting space:

$$\langle \Phi_I | \hat{H} | 0 \rangle \neq 0 \tag{1}$$

In RHF, $|0\rangle = |\Phi_{\text{HF}}\rangle$ is the HF determinant, and the singlet excitation operators are defined as:

$$\hat{E}_i^a = \sum_\sigma \hat{a}_\sigma^\dagger \hat{i}_\sigma \tag{2}$$

$$\hat{e}_{ij}^{ab} = \sum_{\sigma\tau} \hat{a}_\sigma^\dagger \hat{b}_\tau^\dagger \hat{j}_\tau \hat{i}_\sigma = \hat{E}_i^a \hat{E}_j^b \tag{3}$$

hence the singly and doubly excitation configurations are:

$$|\Phi_i^a\rangle = \hat{E}_i^a |0\rangle \tag{4}$$

$$|\Phi_{ij}^{ab}\rangle = \hat{E}_i^a \hat{E}_j^b |0\rangle \tag{5}$$

From Brillouin theorem, i.e. $f_{ai} = 0$, we know that the first-order wavefunction is a linear combination of the doubly excitation configurations:

$$|\Psi^{(1)}\rangle = \frac{1}{2} \sum_{ij,ab} T_{ij}^{ab} |\Phi_{ij}^{ab}\rangle \tag{6}$$

the $\frac{1}{2}$ arises due to the summation in spin (?).

It is convenient to define a set of contravariant configurations:

$$|\tilde{\Phi}_i^a\rangle = \frac{1}{2} \hat{E}_i^a |0\rangle = \frac{1}{2} |\Phi_i^a\rangle \tag{7}$$

$$|\tilde{\Phi}_{ij}^{ab}\rangle = \frac{1}{6} (2\hat{E}_i^a \hat{E}_j^b + \hat{E}_j^a \hat{E}_i^b) |0\rangle = \frac{1}{6} (2|\Phi_{ij}^{ab}\rangle + |\Phi_{ji}^{ab}\rangle) \tag{8}$$

As a result, some expressions become simpler:

$$\langle \tilde{\Phi}_{ij}^{ab} | \Phi_{kl}^{cd} \rangle = \delta_{ac}\delta_{bd}\delta_{ik}\delta_{jl} + \delta_{ad}\delta_{bc}\delta_{il}\delta_{jk} \tag{9}$$

$$\langle \tilde{\Phi}_{ij}^{ab} | \Psi^{(1)} \rangle = T_{ij}^{ab} \tag{10}$$

$$\langle \tilde{\Phi}_{ij}^{ab} | \hat{H} | \Psi^{(0)} \rangle = \langle ab | ij \rangle \tag{11}$$

Now $|\Psi^{(1)}\rangle$ becomes:

$$|\Psi^{(1)}\rangle = \frac{1}{2} \sum_{ij,ab} T_{ij}^{ab} |\Phi_{ij}^{ab}\rangle = \sum_{ij,ab} \tilde{T}_{ij}^{ab} |\tilde{\Phi}_{ij}^{ab}\rangle \tag{12}$$

where $\tilde{T}_{ij}^{ab} = 2T_{ij}^{ab} - T_{ji}^{ab}$.

*Derivation

Derivation for eqns. (9), (10) and (11):

$$\langle \tilde{\Phi}_{ij}^{ab} | \Phi_{kl}^{cd} \rangle = \langle 0 | \frac{1}{6} (2\hat{E}_i^a \hat{E}_j^b + \hat{E}_j^a \hat{E}_i^b) \hat{E}_k^c \hat{E}_l^d |0\rangle \tag{13}$$

in which:

$$\hat{E}_i^a \hat{E}_j^b = (\hat{a}_\alpha^\dagger \hat{i}_\alpha + \hat{a}_\beta^\dagger \hat{i}_\beta)(\hat{b}_\alpha^\dagger \hat{j}_\alpha + \hat{b}_\beta^\dagger \hat{j}_\beta)$$

$$=\hat{a}^\dagger_\alpha(\hat{i}_\alpha\hat{b}^\dagger_\alpha)\hat{j}_\alpha+\hat{a}^\dagger_\alpha(\hat{i}_\alpha\hat{b}^\dagger_\beta)\hat{j}_\beta+\hat{a}^\dagger_\beta(\hat{i}_\beta\hat{b}^\dagger_\alpha)\hat{j}_\alpha+\hat{a}^\dagger_\beta(\hat{i}_\beta\hat{b}^\dagger_\beta)\hat{j}_\beta \tag{14}$$

by $[\hat{p}^\dagger,\hat{q}]_+=\delta_{pq}$, we have:

$$\hat{E}^a_i\hat{E}^b_j=-\hat{a}^\dagger_\alpha\hat{b}^\dagger_\alpha\hat{i}_\alpha\hat{j}_\alpha-\hat{a}^\dagger_\alpha\hat{b}^\dagger_\beta\hat{i}_\alpha\hat{j}_\beta-\hat{a}^\dagger_\beta\hat{b}^\dagger_\alpha\hat{i}_\beta\hat{j}_\alpha-\hat{a}^\dagger_\beta\hat{b}^\dagger_\beta\hat{i}_\beta\hat{j}_\beta \tag{15}$$

Similarly:

$$\hat{E}^c_k\hat{E}^d_l=-\hat{c}^\dagger_\alpha\hat{d}^\dagger_\alpha\hat{k}_\alpha\hat{l}_\alpha-\hat{c}^\dagger_\alpha\hat{d}^\dagger_\beta\hat{k}_\alpha\hat{l}_\beta-\hat{c}^\dagger_\beta\hat{d}^\dagger_\alpha\hat{k}_\beta\hat{l}_\alpha-\hat{c}^\dagger_\beta\hat{d}^\dagger_\beta\hat{k}_\beta\hat{l}_\beta \tag{16}$$