1 Basics

Orbital transformation:

$$|\psi_p\rangle = \sum_\mu C_{\mu p}|\phi_\mu\rangle \tag{1}$$

$$\langle\psi_p| = |\psi_p\rangle^\dagger = \sum_\mu \langle\phi_\mu|C^*_{\mu p} \tag{2}$$

Note that $C_{\mu p}$ is just a number, taking the Hermitian conjugate will just give the complex conjugate. In matrix notation:

$$\boldsymbol{\psi} = \boldsymbol{\phi}\mathbf{C} \tag{3}$$

$$\boldsymbol{\psi}^\dagger = \mathbf{C}^\dagger\boldsymbol{\phi}^\dagger \tag{4}$$

$$\begin{aligned} h_{pq} &= \langle\psi_p|\hat{h}|\psi_q\rangle \\ &= \langle\sum_\mu C_{\mu p}\phi_\mu|\hat{h}|\sum_\nu C_{\nu q}\phi_\nu\rangle \\ &= \sum_{\mu\nu} C^*_{\mu p}\langle\phi_\mu|\hat{h}|\phi_\nu\rangle C_{\nu q} \\ &= \sum_{\mu\nu} C^*_{\mu p}h_{\mu\nu}C_{\nu q} \end{aligned} \tag{5}$$

2 UHF

3 RHF

3.1 Singlet Excitation Operators

Generally, the one- and two-body excitation operators are defined as:

$$E^p_q = \hat{p}^\dagger_\alpha\hat{q}_\alpha + \hat{p}^\dagger_\beta\hat{q}_\beta \tag{6}$$

$$e^{pq}_{rs} = \sum_{\sigma\tau}\hat{p}^\dagger_\sigma\hat{q}^\dagger_\tau\hat{s}_\tau\hat{r}_\sigma \tag{7}$$

By:

$$[\hat{p}^\dagger, \hat{q}]_+ = \hat{\delta}_{pq} \tag{8}$$

the two-body singlet excitation operator could be written as:

$$\begin{aligned} e^{pq}_{rs} &= \sum_{\sigma\tau}\hat{p}^\dagger_\sigma\hat{q}^\dagger_\tau\hat{s}_\tau\hat{r}_\sigma \\ &= -\sum_{\sigma\tau}\hat{p}^\dagger_\sigma\hat{q}^\dagger_\tau\hat{r}_\sigma\hat{s}_\tau \\ &= -\sum_{\sigma\tau}\hat{p}^\dagger_\sigma(\delta_{qr}\delta_{\sigma\tau} - \hat{r}_\sigma\hat{q}^\dagger_\tau)\hat{s}_\tau \\ &= \sum_{\sigma\tau}\hat{p}^\dagger_\sigma\hat{r}_\sigma\hat{q}^\dagger_\tau\hat{s}_\tau - \sum_{\sigma\tau}\delta_{qr}\delta_{\sigma\tau}\hat{p}^\dagger_\sigma\hat{s}_\tau \\ &= \hat{p}^\dagger_\alpha\hat{r}_\alpha\hat{q}^\dagger_\alpha\hat{s}_\alpha + \hat{p}^\dagger_\alpha\hat{r}_\alpha\hat{q}^\dagger_\beta\hat{s}_\beta + \hat{p}^\dagger_\beta\hat{r}_\beta\hat{q}^\dagger_\alpha\hat{s}_\alpha + \hat{p}^\dagger_\beta\hat{r}_\beta\hat{q}^\dagger_\beta\hat{s}_\beta - \delta_{qr}(\hat{p}^\dagger_\alpha\hat{s}_\alpha + \hat{p}^\dagger_\beta\hat{s}_\beta) \\ &= E^p_rE^q_s - \delta_{qr}E^p_s \end{aligned} \tag{9}$$

Note, conventionally, the indices for the two-body operator are written in Chemists' notation.

Considering the nature of excitation operators, the following expressions are often more useful:

$$E_i^a = \hat{a}_\alpha^\dagger \hat{i}_\alpha + \hat{a}_\beta^\dagger \hat{i}_\beta \tag{10}$$

$$e_{ij}^{ab} = \sum_{\sigma\tau} \hat{a}_\sigma^\dagger \hat{b}_\tau^\dagger \hat{j}_\tau \hat{i}_\sigma = E_i^a E_j^b \tag{11}$$