# Programming Project 7 Theory

## *Deriving CIS matrix elements in Kutzelnigg-Mukherjee tensor notation*

The electronic Hamiltonian can be expressed as follows.

$$H_e = E_{\mathrm{HF}} + H_c \qquad E_{\mathrm{HF}} = \langle\Phi|H_e|\Phi\rangle \qquad H_c = f_p^q \tilde{a}_q^p + \tfrac{1}{4}\overline{g}_{pq}^{rs}\tilde{a}_{rs}^{pq} \tag{1}$$

Assuming Brillouin's theorem is satisfied and $\langle\Phi|H_e|\Phi_i^a\rangle = f_i^a = 0$, the CIS ground state eigenpair is simply the Hartree-Fock solution: the root is $E_{\mathrm{HF}}$ and the wavefunction is $\Phi$. Therefore, excitation energies from the ground state are eigenvalues of the matrix $\langle\Phi_i^a|H_e - E_{\mathrm{HF}}|\Phi_j^b\rangle = \langle\Phi_i^a|H_c|\Phi_j^b\rangle$. Applying Wick's theorem in $\Phi$-normal ordering gives

$$\begin{aligned}\langle\Phi_i^a|H_c|\Phi_j^b\rangle &= f_p^q\langle\Phi|\tilde{a}_a^i\tilde{a}_q^p\tilde{a}_j^b|\Phi\rangle + \tfrac{1}{4}\overline{g}_{pq}^{rs}\langle\Phi|\tilde{a}_a^i\tilde{a}_{rs}^{pq}\tilde{a}_j^b|\Phi\rangle \\ &= f_p^q(\tilde{a}_a^i\tilde{a}_q^p\tilde{a}_j^b)_{\text{f.c.}} + \tfrac{1}{4}\overline{g}_{pq}^{rs}(\tilde{a}_a^i\tilde{a}_{rs}^{pq}\tilde{a}_j^b)_{\text{f.c.}}\end{aligned} \tag{2}$$

where the subscript f.c. denotes the sum over fully contracted terms in these Wick expansions.

$$(\tilde{a}_a^i\tilde{a}_q^p\tilde{a}_j^b)_{\text{f.c.}} = \vdots\, a_{a\circ}^{i\bullet} a_{q\circ\circ}^{p\circ} a_{j\bullet}^{b\circ\circ}\,\vdots + \vdots\, a_{a\circ}^{i\bullet} a_{q\bullet}^{p\bullet\bullet} a_{j\bullet\bullet}^{b\circ}\,\vdots = \gamma_j^i\eta_a^p\eta_q^b - \gamma_q^i\gamma_j^p\eta_a^b \tag{3}$$

$$(\tilde{a}_a^i\tilde{a}_{rs}^{pq}\tilde{a}_j^b)_{\text{f.c.}} = \vdots\,\tilde{a}_{a\circ}^{i\bullet}\tilde{a}_{r\bullet s\circ\circ}^{p\circ q\bullet\bullet}\tilde{a}_{j\bullet\bullet}^{b\circ\circ}\,\vdots + \vdots\,\tilde{a}_{a\circ}^{i\bullet}\tilde{a}_{r\circ\circ s\bullet}^{p\circ q\bullet\bullet}\tilde{a}_{j\bullet\bullet}^{b\circ\circ}\,\vdots + \vdots\,\tilde{a}_{a\circ}^{i\bullet}\tilde{a}_{r\bullet s\circ\circ}^{p\bullet\bullet q\circ}\tilde{a}_{j\bullet\bullet}^{b\circ\circ}\,\vdots + \vdots\,\tilde{a}_{a\circ}^{i\bullet}\tilde{a}_{r\circ\circ s\bullet}^{p\bullet\bullet q\circ}\tilde{a}_{j\bullet\bullet}^{b\circ\circ}\,\vdots = \hat{P}_{(r/s)}^{(p/q)}\gamma_r^i\eta_a^p\gamma_j^q\eta_s^b \tag{4}$$

Plugging equations 3 and 4 into equation 2 gives the final working equation for the CIS matrix elements.

$$\langle\Phi_i^a|H_c|\Phi_j^b\rangle = f_a^b\gamma_j^i - f_j^i\eta_a^b + \overline{g}_{aj}^{ib} = f_a^b\delta_j^i - f_j^i\delta_a^b + \overline{g}_{aj}^{ib} \tag{5}$$

For a canonical Hartree-Fock reference, the Fock matrix is diagonal: $f_a^b = \epsilon_a\delta_a^b$ and $f_j^i = \epsilon_j\delta_j^i$.