CIS equations

Derivation in KM tensor notation

The electronic Hamiltonian can be expressed as follows.

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

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

$$\begin{aligned} \langle \Phi^a_i | H_c | \Phi^b_j \rangle &= f^q_p \langle \Phi | \tilde{a}^i_a \tilde{a}^p_q \tilde{a}^b_j | \Phi \rangle + \tfrac{1}{4} \overline{g}^{rs}_{pq} \langle \Phi | \tilde{a}^i_a \tilde{a}^{pq}_{rs} \tilde{a}^b_j | \Phi \rangle \\ &= f^q_p (\tilde{a}^i_a \tilde{a}^p_q \tilde{a}^b_j)_{\mathrm{f.c.}} + \tfrac{1}{4} \overline{g}^{rs}_{pq} (\tilde{a}^i_a \tilde{a}^{pq}_{rs} \tilde{a}^b_j)_{\mathrm{f.c.}} \end{aligned} \tag{2}$$

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

$$(\tilde{a}^i_a \tilde{a}^p_q \tilde{a}^b_j)_{\mathrm{f.c.}} = \vdots\, a^{i\bullet}_{a\circ} a^{p\circ}_{q\circ\circ} a^{b\circ\circ}_{j\bullet} \,\vdots + \vdots\, a^{i\bullet}_{a\circ} a^{p\bullet\bullet}_{q\bullet} a^{b\circ}_{j\bullet\bullet} \,\vdots = \kappa^i_j \eta^p_a \eta^b_q - \kappa^i_q \kappa^p_j \eta^b_a \tag{3}$$

$$(\tilde{a}^i_a \tilde{a}^{pq}_{rs} \tilde{a}^b_j)_{\mathrm{f.c.}} = \vdots\, \tilde{a}^{i\bullet}_{a\circ} \tilde{a}^{p\circ q\bullet\bullet}_{r\bullet s\circ\circ} \tilde{a}^{b\circ\circ}_{j\bullet\bullet} \,\vdots + \vdots\, \tilde{a}^{i\bullet}_{a\circ} \tilde{a}^{p\circ q\bullet\bullet}_{r\circ\circ s\bullet} \tilde{a}^{b\circ\circ}_{j\bullet\bullet} \,\vdots + \vdots\, \tilde{a}^{i\bullet}_{a\circ} \tilde{a}^{p\bullet\bullet q\circ}_{r\bullet s\circ\circ} \tilde{a}^{b\circ\circ}_{j\bullet\bullet} \,\vdots + \vdots\, \tilde{a}^{i\bullet}_{a\circ} \tilde{a}^{p\bullet\bullet q\circ}_{r\circ\circ s\bullet} \tilde{a}^{b\circ\circ}_{j\bullet\bullet} \,\vdots = \hat{P}^{(p/q)}_{(r/s)} \kappa^i_r \eta^p_a \kappa^q_j \eta^b_s \tag{4}$$

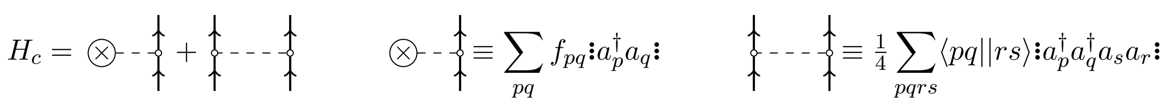
Plugging equations 3 and 4 into equation 2 gives the final working equation for the CIS matrix elements.

$$\langle \Phi^a_i | H_c | \Phi^b_j \rangle = f^b_a \kappa^i_j - f^i_j \eta^b_a + \overline{g}^{ib}_{aj} = f^b_a \delta^i_j - f^i_j \delta^b_a + \overline{g}^{ib}_{aj} \tag{5}$$

For a canonical Hartree-Fock reference, the Fock matrix is diagonal: $f^b_a = \epsilon_a \delta^b_a$ and $f^i_j = \epsilon_j \delta^i_j$.

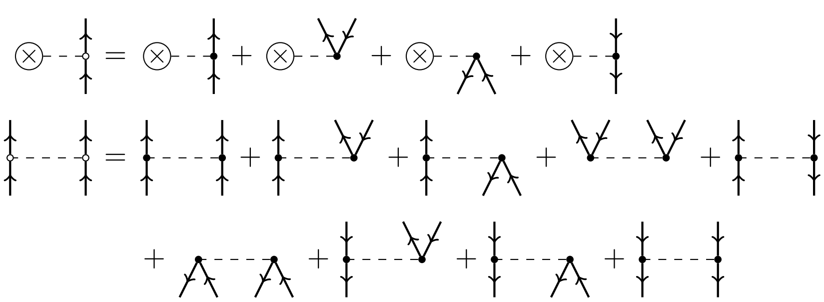
Derivation in diagrammatic notation

In diagrammatic notation, H_c is given by the following.



(6)

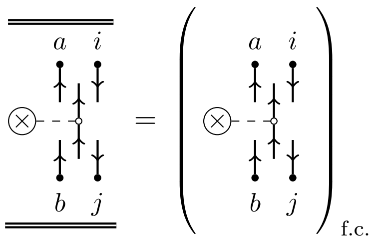
Expanding the one- and two-electron compnents in terms of quasiparticle operators $\{b_p\} = \{a^\dagger_i\} \cup \{a_a\}$ and $\{b^\dagger_p\} = \{a_i\} \cup \{a^\dagger_a\}$, indicated by black interaction points, gives



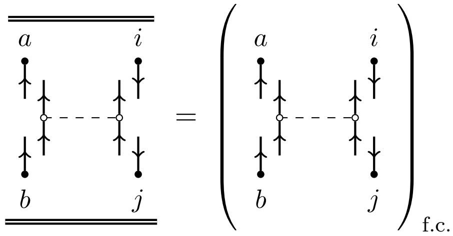
(7)

(8)

whose algebraic expressions are shown in the appendix (equations 13 and 14). The matrix elements $\langle \Phi_i^a | \vdots \boldsymbol{f} \vdots | \Phi_j^b \rangle$ and $\langle \Phi_i^a | \vdots \boldsymbol{\overline{g}} \vdots | \Phi_j^b \rangle$ are given by the following diagrammatic and algebraic expressions.

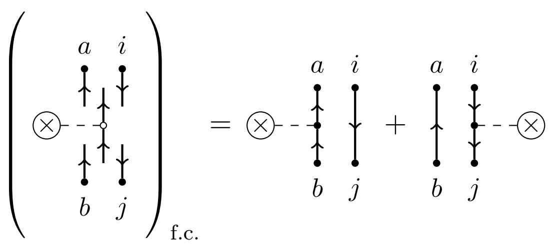


$$\sum_{pq} f_{pq} \langle \Phi | \vdots b_i b_a \vdots \vdots a_p^\dagger a_q \vdots \vdots b_b^\dagger b_j^\dagger \vdots | \Phi \rangle \\ = \sum_{pq} f_{pq} (\vdots b_i b_a \vdots \vdots a_p^\dagger a_q \vdots \vdots b_b^\dagger b_j^\dagger \vdots)_{\text{f.c.}} \tag{9}$$



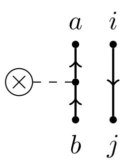
$$\frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle \langle \Phi | \vdots b_i b_a \vdots \vdots a_p^\dagger a_q^\dagger a_s a_r \vdots \vdots b_b^\dagger b_j^\dagger \vdots | \Phi \rangle \\ = \frac{1}{4} \sum_{pqrs} \langle pq || rs \rangle (\vdots b_i b_a \vdots \vdots a_p^\dagger a_q^\dagger a_s a_r \vdots \vdots b_b^\dagger b_j^\dagger \vdots)_{\text{f.c.}} \tag{10}$$

The matrix element of the one-electron interaction evaluates as follows

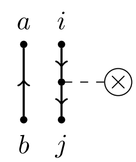


$$= f_{ab}\delta_{ij} - f_{ji}\delta_{ab} \tag{11}$$

where the signs can be determined by translating each diagram into its algebraic form.

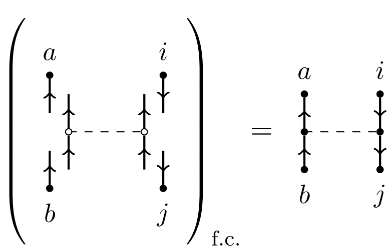


$$= \sum_{cd} f_{cd} \vdots b_i b_a b_c^\dagger b_d b_b b_j^\dagger \vdots = +f_{ab}\delta_{ij}$$



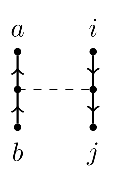
$$= \sum_{kl} f_{kl} \vdots b_i b_a b_k b_l^\dagger b_b^\dagger b_j^\dagger \vdots = -f_{ji}\delta_{ab}$$

For the two-electron interaction, one finds



$$= -\langle aj || bi \rangle \tag{12}$$

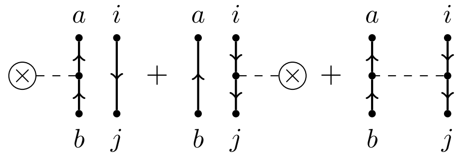
where the sign can be determined from the algebraic expression.



$$= \sum_{ckdl} \langle ck || dl \rangle \vdots b_i b_a b_c^\dagger b_k b_l^\dagger b_d b_b^\dagger b_j \vdots = -\langle aj || bi \rangle$$

Putting these results together gives

$$\langle \Phi_i^a | H_c | \Phi_j^b \rangle =$$



$$= f_{ab}\delta_{ij} - f_{ji}\delta_{ab} - \langle aj||bi \rangle$$

which is the same as equation 5.

Appendix: Quasiparticle expansion of one- and two-electron operators

$$\sum_{pq} f_{pq} :a_p^\dagger a_q: = \sum_{ab} f_{ab} :b_a^\dagger b_b: + \sum_{ai} f_{ai} :b_a^\dagger b_i^\dagger: + \sum_{ia} f_{ia} :b_i b_a: + \sum_{ij} f_{ij} :b_i b_j^\dagger: \tag{13}$$

$$\begin{aligned} \frac{1}{4}\sum_{pqrs} \langle pq||rs \rangle :a_p^\dagger a_q^\dagger a_s a_r: = & \frac{1}{4}\sum_{abcd} \langle ab||cd \rangle :b_a^\dagger b_b^\dagger b_d b_c: + \frac{1}{2}\sum_{abci} \langle ab||ci \rangle :b_a^\dagger b_b^\dagger b_i^\dagger b_c: + \frac{1}{2}\sum_{aibc} \langle ai||bc \rangle :b_a^\dagger b_i b_c b_b: \\ & + \frac{1}{4}\sum_{abij} \langle ab||ij \rangle :b_a^\dagger b_b^\dagger b_j^\dagger b_i^\dagger: + \sum_{aibj} \langle ai||bj \rangle :b_a^\dagger b_i b_j^\dagger b_b: + \frac{1}{4}\sum_{ijab} \langle ij||ab \rangle :b_i b_j b_b b_a: \\ & + \frac{1}{2}\sum_{iajk} \langle ia||jk \rangle :b_i b_a^\dagger b_k^\dagger b_j^\dagger: + \frac{1}{2}\sum_{ijka} \langle ij||ka \rangle :b_i b_j b_a b_k^\dagger: + \frac{1}{4}\sum_{ijkl} \langle ij||kl \rangle :b_i b_j b_l^\dagger b_k^\dagger: \end{aligned} \tag{14}$$