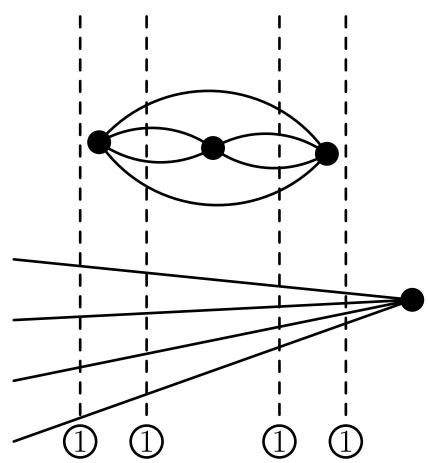
CEM 993 **Spring 2023**

Assignment No. 6 (20 pts.) **Due Date: April 28, 2023**

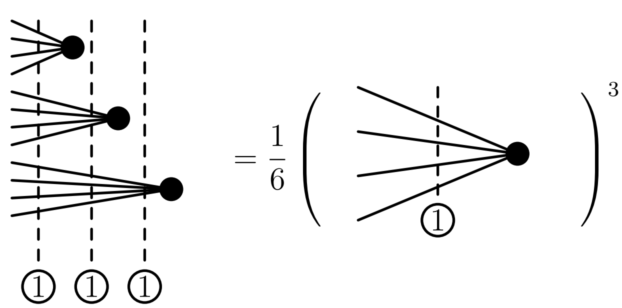
1. (8 pts.) Draw the Hugenholtz and Brandow diagrams for the second-order MBPT correction to the wave function, $|\Psi_0^{(2)}\rangle$, assuming that the perturbation operator W consists of only two-body part, $W = V_N$, and write the complete algebraic expression for each of the resulting diagrams. Distinguish between the wave function contributions corresponding to different excitation levels (i.e., the second-order MBPT corrections due to singly excited determinants, the second-order MBPT corrections due to doubly excited determinants, etc.).

2. (4 pts.) Among the unlinked contributions that originate from the principal term in the fourth-order MBPT correction to the wave function, $|\Psi_0^{(4)}\rangle$, there is a group of diagrams represented by the skeleton



and all time versions of the first kind associated with it. Perform suitable diagram factorization for this group and identify the specific renormalization term contributing to $|\Psi_0^{(4)}\rangle$ that this group cancels out.

3. (4 pts.) Prove the following diagram factorization:



4. (4 pts.) Let us assume that the reference determinant $|\Phi_0\rangle$ used in MBPT as the unperturbed wave function is a Hartree-Fock state, i.e., the perturbation operator

W consists of only two-body part, $W = V_N$. In this case, among the Hugenholtz diagrams representing the second-order MBPT correction to the wave function, $|\Psi_0^{(2)}\rangle$, there are two that correspond to the second-order estimate of the singly excited cluster operator T_1, i.e., $T_1^{(2)}$. Identify these diagrams and provide the corresponding algebraic expressions for them (you can copy this information from your solution of Problem 1 if you like). Use the resulting formula for $T_1^{(2)}$ in terms of the antisymmetrized matrix elements $v_{pq}^{rs} \equiv \langle pq|v|rs\rangle_{\mathcal{A}}$, unperturbed spin-orbital energies ε_p, and particle-hole excitation operators $E_i^a = X_a^\dagger X_i$ relevant to the problem to determine the explicit formula for the second-order MBPT estimate of the singly excited cluster amplitude $t_a^i \equiv \langle a|t_1|i\rangle$, i.e., ${}^{(2)}t_a^i \equiv \langle a|t_1^{(2)}|i\rangle$.