Department of Chemistry, Michigan State University

CEM 993, Spring 2023

Midterm Exam

Deadline for Emailing Solutions to the Instructor: April 7, 2023, 11:59 pm EDT

Name (Last, First, Middle Initial):
Student ID Number:

INSTRUCTIONS

- The maximum number of points that you can earn in this exam is 50. 50 points earned in this exam are equivalent to 30 % of the final grade.
- Check that your booklet contains all 18 pages.
- Write your name and student ID number in the spaces provided above.
- Answer in the spaces provided. Use the extra pages 16-18 for additional space, if necessary. If you have technical difficulties with directly using this exam booklet, write down and scan your solutions, as you normally do in the case of homework assignments, but *do not forget to write your name and student ID number on the first page of your exam.* Email your exam (this booklet or your own pages) to the instructor using the deadline described above. Late exams will not be accepted.
- Show ALL your work. Insufficient justification will result in a loss of points.
- Do not write anything in the score table given below.

Problem	Score
1	/8
2	/12
3	/18
4	/6
5	/6
Total	/50

1. (8 pts.) Calculate the following normal products without or with contractions:

(a) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(b) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(c) $n[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$,

(d) $N[X_a X_b X_c^\dagger X_i^\dagger X_j X_d^\dagger]$.

Solution

2. (12 pts.) (a) Let Z_N be a one-body operator in the normal-product form,

$$Z_N = \sum_{p,q} \langle p|z|q\rangle N[X_p^\dagger X_q],$$

and let T_2 be a two-body particle-hole excitation operator,

$$T_2 = \frac{1}{4} \sum_{j,k,b,c} \langle bc|t_2|jk\rangle_{\mathcal{A}} N[X_b^\dagger X_j X_c^\dagger X_k].$$

Use the hole-particle variant of Wick's theorem to derive the formula for

$$\langle \Phi_i^a|\, [Z_N, T_2]\, |\Phi\rangle \tag{1}$$

in terms of matrix elements $\langle p|z|q\rangle$ and $\langle bc|t_2|jk\rangle_{\mathcal{A}}$. Here, [,] is the commutator, $|\Phi\rangle$ is the Fermi vacuum state, and $|\Phi_i^a\rangle$ is the singly excited determinant relative to $|\Phi\rangle$. [8 pts.]
(b) Use the diagrammatic method based on drawing the Hugenholtz (and Brandow) diagrams to calculate the matrix element given by Eq. (1). Compare the results obtained in (a) and (b). [4 pts.]

Solution

3. (18 pts.) Use the diagrammatic method based on drawing Goldstone diagrams to calculate $V_N\, C_1|\Phi\rangle$, where $V_N = \frac{1}{2} \sum_{p,q,r,s} \langle pq|v|rs\rangle\, N[X_p^\dagger X_r X_q^\dagger X_s]$ is a two-body part of the normal-ordered form of the Hamiltonian and $C_1 = \sum_{a,i} \langle a|c_1|i\rangle\, N[X_a^\dagger X_i]$ is a single excitation operator, in terms of matrix elements $\langle pq|v|rs\rangle$ and $\langle a|c_1|i\rangle$. In deriving the relevant Goldstone diagrams, go through the Hugenholtz skeletons and diagrams as intermediate steps. Remember, however, that the final resulting diagrams must be of the Goldstone type.

Solution

(*solution of Problem 3 continued*)

4. (6 pts.) Consider the expression $\langle\Phi|V_N C_2|\Phi\rangle$ for a $(2n)$-electron closed-shell system described by a spin-orbital basis $|p\rangle$ obtained by multiplying spatial functions (orbitals) $|P\rangle$ by the spin-up and spin-down states, $|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ and $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$, respectively, so that $|p\rangle = |P\rangle \otimes |\sigma_p\rangle$, where $|\sigma_p\rangle = |\alpha\rangle$ or $|\beta\rangle$. As you know from our lectures, $\langle\Phi|V_N C_2|\Phi\rangle$ results in two Goldstone diagrams. Assuming that the Fermi vacuum state $|\Phi\rangle$ is built from n doubly occupied orbitals $|I\rangle$, where $I = 1, \ldots, n$, and that the two-body part of the normal-ordered form of the Hamiltonian, V_N, and the double excitation operator C_2 are both spin-free operators, use the Goldstone diagrams representing $\langle\Phi|V_N C_2|\Phi\rangle$ to derive the spin-free form of it in terms of spin-independent matrix elements $\langle PQ|v|RS\rangle$ and $\langle AB|c_2|IJ\rangle$ of V_N and C_2. If you remember the two Goldstone diagrams corresponding to $\langle\Phi|V_N C_2|\Phi\rangle$, you do not have to rederive them. You do, however, have to convert them into the corresponding and properly labeled orbital diagrams, which must be shown as part of your solution, before deriving and reporting the final spin-free formula for $\langle\Phi|V_N C_2|\Phi\rangle$.

Solution

5. (6 pts.) Use the diagrammatic method based on drawing Hugenholtz/Brandow diagrams to derive the relationship between the standard and normal-ordered forms of a two-body operator, V and V_N, respectively.

Solution