Department of Chemistry, Michigan State University

CEM 993, Spring 2023, Final Exam

Deadline for Emailing Solutions to the Instructor: May 5, 2023, 11:59 pm EDT

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

INSTRUCTIONS

- Write your name and student ID number in the spaces provided above. Check that your booklet contains all 20 pages.
- The maximum number of points that you can earn in this exam *by solving Problems 1–4* is 50. 50 points earned in this exam are equivalent to 35 % of the final grade.
- You may receive an extra performance-based bonus if the number of points that you obtain by solving Problems 1–4 is large enough. Thus, if you receive 30.0–34.5 points, you will automatically earn an extra 1 % toward the final course grade (the smallest partial credit in grading the exam is 0.5 pts.). If you receive 35.0–39.5 points, you will automatically earn an extra 2 % toward the final course grade. If you receive 40.0–44.5 points, you will automatically earn an extra 3 % toward the final course grade. If you receive 45.0–49.5 points, you will automatically earn an extra 4 % toward the final course grade. If you receive a perfect score of 50.0 points, you will automatically earn an extra 5 % of the final grade. The final grade determined after adding this performance-based bonus cannot exceed 100 %.
- Answer in the spaces provided. Use the extra pages 18–20 for additional space, if necessary. If you have technical difficulties with directly using this exam booklet, write down and scan your solutions, as some students did in the case of homework assignments and midterm exam, 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 may result in a loss of points.
- Do not write anything in the score table given below.

Problem	Score
1	/12
2	/12
3	/14
4	/12
Total	/50

Additional % will be added to your final grade

1. (12 pts.) (a) Let V_N be a two-body operator in the normal-product form,

$$V_N = \tfrac{1}{2} \sum_{p,q,r,s} \langle pq|v|rs\rangle N[X_p^\dagger X_q^\dagger X_s X_r],$$

and let T_1 be a one-body particle-hole excitation operator,

$$T_1 = \sum_{j,b} \langle b|t_1|j\rangle N[X_b^\dagger X_j].$$

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

$$\langle \Phi_i^a | \, [V_N, T_1] \, | \Phi \rangle$$

in terms of matrix elements $\langle pq|v|rs\rangle$ and $\langle b|t_1|j\rangle$. 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 Goldstone diagrams to calculate the matrix element

$$\langle \Phi_i^a | \, (V_N T_1)_C \, | \Phi \rangle,$$

where subscript C indicates the connected part of the corresponding operator expression. Compare the result with the formula for $\langle \Phi_i^a | \, [V_N, T_1] \, | \Phi \rangle$ obtained in part (a). Briefly comment on your findings. In deriving the relevant Goldstone diagrams, go through the Hugenholtz skeletons and diagrams as intermediate steps, which must be shown too. Remember, however, that the final resulting diagrams must be of the Goldstone type. [4 pts.]

Solution

2. (12 pts.) We showed in class that the third-order MBPT correction to the energy, $k_0^{(3)}$, can be written as a sum of the following four terms:

$$\begin{aligned}
k_0^{(3)}(A) &= \langle\Phi_0|V_N R^{(0)} V_N R^{(0)} V_N|\Phi_0\rangle, \\
k_0^{(3)}(B) &= \langle\Phi_0|Q_N R^{(0)} V_N R^{(0)} V_N|\Phi_0\rangle \\
&\quad +\langle\Phi_0|V_N R^{(0)} Q_N R^{(0)} V_N|\Phi_0\rangle \\
&\quad +\langle\Phi_0|V_N R^{(0)} V_N R^{(0)} Q_N|\Phi_0\rangle, \\
k_0^{(3)}(C) &= \langle\Phi_0|Q_N R^{(0)} Q_N R^{(0)} V_N|\Phi_0\rangle \\
&\quad +\langle\Phi_0|Q_N R^{(0)} V_N R^{(0)} Q_N|\Phi_0\rangle \\
&\quad +\langle\Phi_0|V_N R^{(0)} Q_N R^{(0)} Q_N|\Phi_0\rangle, \\
k_0^{(3)}(D) &= \langle\Phi_0|Q_N R^{(0)} Q_N R^{(0)} Q_N|\Phi_0\rangle,
\end{aligned}$$

where Q_N and V_N are the usual one- and two-body parts of the perturbation operator W and $R^{(0)}$ is the MBPT reduced resolvent. Use the Hugenholtz (and Brandow) diagrams to derive the explicit formula for $k_0^{(3)}(B)$ in terms of the relevant matrix elements and MBPT denominators. Assign weights (w_R), signs (s_R), and appropriate scalar factors to the Hugenholtz (Brandow) diagrams and write the complete algebraic expression for $k_0^{(3)}(B)$.

Solution

(*solution of Problem 2 continued*)

(*solution of Problem 2 continued*)

3. (14 pts.) (a) Draw the complete set of non-oriented Hugenholtz skeletons and Hugenholtz diagrams (with oriented lines and indices) 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, $W = V_N$. Identify the Hugenholtz diagrams that describe the triply excited contributions to $|\Psi_0^{(2)}\rangle$ (i.e., the contributions to $|\Psi_0^{(2)}\rangle$ that are linear combinations of the triply excited determinats relative to the reference state $|\Phi_0\rangle$). Draw the corresponding Brandow diagrams and write the resulting algebraic expressions. [10 pts.]
(b) One can always determine the MBPT corrections to the energy using the formula

$$k_0^{(n+1)} = \langle \Phi_0 | W | \Psi_0^{(n)} \rangle,$$

where $|\Phi_0\rangle$ is the zeroth-order independent-particle-model state and $|\Psi_0^{(n)}\rangle$ is the nth-order correction to the wave function. This means that

$$k_0^{(3)} = \langle \Phi_0 | W | \Psi_0^{(2)} \rangle.$$

Assuming that the perturbation operator W consists of only two-body part, i.e., $W = V_N$, identify a subset of the Hugenholtz diagrams representing $|\Psi_0^{(2)}\rangle$ that contribute to $k_0^{(3)}$. Provide a clear justification of your diagram selection. What kinds of excited contributions to $|\Psi_0^{(2)}\rangle$ are represented by the diagrams you have selected? What is this telling us about the physical content of $k_0^{(3)}$? [4 pts.]

Solution

(*solution of Problem 3 continued*)

(*solution of Problem 3 continued*)

(*solution of Problem 3 continued*)

4. (12 pts.) (a) Let $|\Psi_0^{(m)}\rangle$ be the <u>*lowest-order*</u> MBPT wave function correction that contains a T_1T_2 contribution. We use the notation in which T is the cluster operator, which generates the connected wave function diagrams, and T_k is the k-body component of T. What is the value of the lowest order m, as defined above, assuming that the Hamiltonian contains up to two-body interactions and the perturbation operator W consists of only two-body part, $W = V_N$? Provide a clear justification of your answer, referring, in particular, to the oriented or non-oriented Hugenholtz skeletons representing the low-order MBPT contributions to the T_1 and T_2 clusters. What is the formula for the m-th order contribution to T_1T_2 in terms of perturbative contributions to T_1 and T_2 ($T_1^{(p)}$ and $T_2^{(q)}$, respectively), where m is the lowest MBPT order for T_1T_2 that you have determined? [2 pts.]
(b) A direct comparison of the coupled-cluster (CC) wave function expansion,

$$|\Psi_0\rangle = e^T|\Phi_0\rangle, \quad T = T_1 + T_2 + \cdots + T_N,$$

with the full configuration interaction (CI) expansion for the exact wave function $|\Psi_0\rangle$, i.e.,

$$|\Psi_0\rangle = (1 + C)|\Phi_0\rangle, \quad C = C_1 + C_2 + \cdots + C_N,$$

shows that the many-body components of the full CI excitation operator C and the many-body components of the cluster operator T are related in the following way:

$$C_1 = T_1,$$

$$C_2 = T_2 + \tfrac{1}{2}(T_1)^2,$$

$$C_3 = T_3 + T_1T_2 + \tfrac{1}{6}(T_1)^3,$$

$$C_4 = T_4 + \tfrac{1}{2}(T_2)^2 + T_1T_3 + \tfrac{1}{2}(T_1)^2T_2 + \tfrac{1}{24}(T_1)^4, \text{ etc.}$$

Determine the lowest MBPT orders, in which the connected (T_3) and disconnected (T_1T_2 and $\frac{1}{6}(T_1)^3$) clusters included in C_3 contribute to the wave function, assuming that $|\Phi_0\rangle$ is the Hartree-Fock reference determinant and the Hamiltonian contains up to two-body terms. Order all connected and disconnected triply excited cluster components contributing to C_3 according to their significance in the MBPT wave function expansion. Justify your answer by drawing representative non-oriented Hugenholtz skeletons defining the lowest-order contributions to T_1, T_2, and T_3. [4 pts.]
(c) How would the ordering of the connected and disconnected triply excited clusters contributing to C_3 obtained in part (b) change if $|\Phi_0\rangle$ was a non-Hartree-Fock reference? As in part (b), justify your answer by determining the lowest MBPT orders of the connected and disconnected clusters contributing to C_3. [3 pts.]
(d) How would the relationships between the many-body components of C and T, C_n and T_n, respectively, where $n = 1 - 4$, change if $|\Phi_0\rangle$ was a Brueckner determinant? What would the relationship between the five-body component C_5 and many-body components of T be in this case? [3 pts.]

Solution