Finite-temperature many-body perturbation theory in the grand canonical ensemble

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A finite-temperature many-body perturbation theory is presented that expands the electronic grand potential, chemical potential, internal energy, and entropy on an equal footing. Sum-over-states and sum-over-orbitals analytical formulas for the second-order perturbation corrections to these thermodynamic properties are obtained in a time-independent, nondiagrammatic, algebraic derivation, relying on the sum rules of the Hirschfelder–Certain degenerate perturbation energies in a degenerate subspace as well as nine algebraic identities for zeroth-order thermal averages of one- through four-indexed quantities and products thereof. They reproduce numerically exactly the benchmark data obtained as the numerical derivatives of the thermal-full-configuration-interaction results for a wide range of temperature, and are, therefore, the correct analytical theory for electronic thermodynamics.

I. INTRODUCTION

It is of interest to establish a finite-temperature many-body perturbation theory for electrons that expands in perturbation series the grand potential (Ω), chemical potential (µ), internal energy (U), and entropy (S) on an equal footing.

Recently, we derived sum-over-states and reduced analytical formulas for the first-order corrections to these quantities of such a perturbation theory. Our formulas are based on, and thus agree numerically exactly with, the postulate of a canonical perturbation theory because the order of perturbation corrections to these thermodynamic properties are obtained in a time-independent, nondiagrammatic, algebraic derivation, relying on the sum rules of the Hirschfelder–Certain degenerate perturbation energies in a degenerate subspace as well as nine algebraic identities for zeroth-order thermal averages of one- through four-indexed quantities and products thereof. They reproduce numerically exactly the benchmark data obtained as the numerical derivatives of the thermal-full-configuration-interaction results for a wide range of temperature, and are, therefore, the correct analytical theory for electronic thermodynamics.

II. THEORY

Here, we are exclusively concerned with thermodynamics of electrons in the grand canonical ensemble. For the sake of completeness and because higher-order perturbation corrections are given in terms of lower-order corrections, we reiterate the derivations of the zeroth13–16 and first-order17 perturbation theory formulas as succinctly as possible. For the electronic thermodynamics in the canonical ensemble, see Ref. 27.

The grand partition function Ξ is defined by

\[ \Xi = \sum_I e^{-\beta E_I + \beta \mu N_I}, \]  

where \( \beta = (k_B T)^{-1} \) is the inverse temperature, \( E_I \) is the exact energy of the \( I \)th state, and \( N_I \) is the number of electrons of the same state. In the following capital-letter indices \( I \) and \( J \) run over all \( 2^n \) states (where \( n \) is the number of spinorbitals), while lower-letter indices refer to spinorbitals. The exact chemical potential \( \mu \) is determined by solving the equation,

\[ \bar{N} = \frac{1}{\beta \mu} \ln \Xi \]

or

\[ \bar{N} \sum_I e^{-\beta E_I + \beta \mu N_I} = \sum_I N_I e^{-\beta E_I + \beta \mu N_I}, \]

where \( \bar{N} \) is the correct average number of electrons that keeps the system electrically neutral.

Once \( \Xi \) is determined, we can extract from it various thermodynamic properties such as the exact \( \Omega, U, \) and \( S \):

\[ \Omega = -\frac{1}{\beta} \ln \Xi, \]

\[ U = -\frac{\partial}{\partial \beta} \ln \Xi + \mu \bar{N} \]

or

\[ S = T^{-1} \left( U - \mu \bar{N} - \Omega \right). \]
By “exact,” we mean that they are determined by thermal FCI within a basis set. In this procedure, it is Eqs. (5) and (23) [not Eqs. (4) or (3)] that we actually use when numerically determining \( \mu \) and \( U \) (our thermal FCI program does not perform numerical differentiation with respect to \( \mu \) or \( \beta \)), even though they are mathematically equivalent. Since \( S \) is readily inferred from \( \Omega, \mu, \) and \( U \), we will not discuss it any further.

In our finite-temperature many-body perturbation theory, all thermodynamic properties are expanded in perturbation series on an equal footing:

\[
\mu = \mu^{(0)} + \lambda \mu^{(1)} + \lambda^2 \mu^{(2)} + \lambda^3 \mu^{(3)} + \ldots, \tag{11}
\]

\[
\Omega = \Omega^{(0)} + \lambda \Omega^{(1)} + \lambda^2 \Omega^{(2)} + \lambda^3 \Omega^{(3)} + \ldots, \tag{12}
\]

\[
U = U^{(0)} + \lambda U^{(1)} + \lambda^2 U^{(2)} + \lambda^3 U^{(3)} + \ldots, \tag{13}
\]

which are equivalent to Eq. (1) with \( X = \mu, \Omega, \) or \( U \), where \( \lambda \) is the scaling parameter of the perturbation operator in the partitioned Hamiltonian:

\[
\hat{H} = \hat{H}_0 + \lambda \hat{V}. \tag{14}
\]

In what follows, we adopt the so-called Møller–Plesset partitioning of the Hamiltonian,

\[
\hat{H}_0 = E_{\text{nuc.}} + \sum_p \epsilon_p \hat{p}_p, \tag{15}
\]

where \( E_{\text{nuc.}} \) is the nuclear-repulsion energy, \( \epsilon_p \) is the canonical Hartree–Fock (HF) energy of the \( p \)th spinorbital, and \( \hat{p}_p \) (\( \hat{p}^\dagger \)) are the creation (annihilation) operator of an electron in the \( p \)th spinorbital. With this choice of \( \hat{H}_0 \), the perturbation expansions of the \( \kappa \)th-order energy

\[
E_{\kappa} = E_{\kappa}^{(0)} + \lambda E_{\kappa}^{(1)} + \lambda^2 E_{\kappa}^{(2)} + \lambda^3 E_{\kappa}^{(3)} + \ldots, \tag{16}
\]

are given by the Hirschfelder–Certain degenerate perturbation theory (HCPT), which reduces to the Møller–Plesset perturbation theory (MPPT) for nondegenerate states. Our theory is not fundamentally limited to this partitioning and can be adjusted (if not directly used) for other cases (such as a finite-temperature HF reference).

The following Taylor expansions are implicitly used in the subsequent sections:

\[
e^{a+b} = e^a + e^b + e^{\frac{b^2}{2!}} + e^{\frac{b^3}{3!}} + \ldots, \tag{17}
\]

\[
\ln(a + b) = \ln a + \frac{b}{a} - \frac{b^2}{2a^2} + \frac{b^3}{3a^3} + \ldots, \tag{18}
\]

where \( a \gg b \).

The following benefitted from an excellent review by Santra and Schirmer, described in many textbooks, which differs from the one presented here at the first order and higher.

### III. Zeroth Order

The zeroth-order theory is the Fermi–Dirac theory. The zeroth-order grand partition function is

\[
\Xi^{(0)} = \sum_I e^{-\beta E_I^{(0)} + \beta \mu^{(0)} N_I}, \tag{19}
\]

with

\[
E_I^{(0)} = E_{\text{nuc.}} + \sum_I \epsilon_i, \tag{20}
\]

\[
N_I = \sum_I 1, \tag{21}
\]

where \( \Sigma_I \) means that \( i \) runs over all spinorbitals that are occupied in the \( I \)th state, which is a Slater determinant. Henceforth, we use letters \( i, j, \) and \( k \) for spinorbitals occupied in the \( I \)th Slater determinant, \( a, b, \) and \( c \) for those unoccupied in the same determinant, and \( p, q, r, \) and \( s \) for either.

#### A. Grand potential

Substituting these into Eq. (7), we obtain a sum-over-states formula for \( \Omega^{(0)} \) as

\[
\Omega^{(0)} = -\frac{1}{\beta} \ln \Xi^{(0)} = -\frac{1}{\beta} \ln \sum_I e^{-\beta E_I^{(0)} + \beta \mu^{(0)} N_I}, \tag{22}
\]

\[
\Omega^{(0)} = E_{\text{nuc.}} + \frac{1}{\beta} \ln \sum_I e^{\Sigma_I \nu_I}, \tag{23}
\]

where \( \nu_I = -\beta (\epsilon_i - \mu^{(0)}) \), where \( \mu^{(0)} \) is discussed in the next subsection.

Using the identity,

\[
\sum_I e^{\Sigma_I \nu_I} = \prod_p \left( 1 + e^{\nu_p} \right) = \prod_p \frac{1 + e^{\nu_p}}{1 - e^{-\nu_p}} = \prod_p \frac{1}{1 - e^{-\nu_p}}, \tag{24}
\]

where \( I_m \) stands for a state with \( m \) electrons \((0 \leq m \leq n)\) and \( f_p^+ (f_p^-) \) is the Fermi–Dirac vacancy (occupancy) given by

\[
f_p^+ = \frac{1}{1 + e^{\beta(\epsilon_p - \mu^{(0)})}}, \tag{25}
\]

\[
f_p^- = \frac{1}{1 + e^{\beta(\epsilon_p - \mu^{(0)})}}, \tag{26}
\]

we obtain a sum-over-orbitals (‘reduced’) formula for \( \Omega^{(0)} \) as

\[
\Omega^{(0)} = E_{\text{nuc.}} + \frac{1}{\beta} \sum_p \ln f_p^+, \tag{27}
\]

where \( p \) runs over all spinorbitals. While the sum-over-states formula [Eq. (22)] involves an exponentially long \( 2^n \) summation, the reduced formula [Eq. (27)] sums only \( n \) terms.

#### B. Chemical potential

The sum-over-states equation to be solved for \( \mu^{(0)} \) is

\[
\Xi = \sum_I N_I e^{-\beta E_I^{(0)} + \beta \mu^{(0)} N_I} = \sum_I e^{-\beta E_I^{(0)} + \beta \mu^{(0)} N_I} \equiv \langle N_I \rangle, \tag{28}
\]

with

\[
\Xi^{(0)} = \sum_I N_I^0 e^{-\beta E_I^{(0)} + \beta \mu^{(0)} N_I}, \tag{29}
\]

where \( \Xi^{(0)} \) stands for a state with \( m \) electrons \((0 \leq m \leq n)\).
where we have introduced a shorthand notation of a zeroth-order thermal average:

\[
\langle X_i \rangle \equiv \frac{\sum_i X_i e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}}{\sum_i e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}}.
\] (30)

It can be reduced to a sum-over-orbitals expression by rewriting the right-hand side of Eq. (29) as

\[
\tilde{N} = \frac{\sum_i \sum_{\nu} a_i e^{\nu_i} + \sum_i \sum_{i<j} (a_i + a_j) e^{\nu_i} e^{\nu_j} + \ldots}{\Pi_p (1 + e^{\nu_p})} = \sum_p f_p^-, \quad \text{(31)}
\]

where \(a_i = 1, \nu_i = -\beta(\epsilon_i - \mu^{(0)})\) and the common factor of \(e^{-\beta E_{\text{nuc}}^{(0)}}\) has been canceled between the numerator and denominator. The second equality follows immediately from the Boltzmann-sum identity I of Appendix A.

Alternatively, comparing Eq. (23) and Eq. (29), we find

\[
\tilde{N} = \frac{1}{\beta} \frac{\partial}{\partial \mu^{(0)}} \ln \Xi^{(0)} = -\frac{\partial \Omega^{(0)}}{\partial \mu^{(0)}} = \sum_p f_p^-, \quad \text{where the last equality used Eq. (28) and}
\]

\[
\frac{\partial f_p^+}{\partial \mu^{(0)}} = \mp \beta f_p^- f_p^+. \quad \text{(35)}
\]

\[
\text{C. Internal energy}
\]

The sum-over-states formula for \(U^{(0)}\) is given by

\[
U^{(0)} = \frac{\sum_i E_i^{(0)} e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}}{\sum_i e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}} = \langle E_i^{(0)} \rangle.
\] (36)

Setting \(a_i = \epsilon_i\) and \(\nu_i = -\beta(\epsilon_i - \mu^{(0)})\) and using the Boltzmann-sum identity I of Appendix A, we obtain the reduced formula,

\[
U^{(0)} = E_{\text{muc.}} + \frac{\sum_i \sum_{\nu} a_i e^{\nu_i} + \sum_i \sum_{i<j} (a_i + a_j) e^{\nu_i} e^{\nu_j} + \ldots}{\Pi_p (1 + e^{\nu_p})} = E_{\text{muc.}} + \sum_p \epsilon_p f_p^-.
\] (37)

Comparing the sum-over-states formulas of \(\Omega^{(0)}\) [Eq. (23)] and \(U^{(0)}\) [Eq. (36)], we notice that they are related by

\[
U^{(0)} = -\frac{\partial \ln \Xi^{(0)}}{\partial \beta} + \mu^{(0)} \tilde{N} + \beta \frac{\partial \Xi^{(0)}}{\partial \beta} \tilde{N} = \Omega^{(0)} + \mu^{(0)} \tilde{N} + \beta \left( \frac{\partial \Omega^{(0)}}{\partial \beta} \right) \tilde{N},
\] (38)

where the subscript \(\mu^{(0)}\) indicates that it is held fixed when the partial derivative with respect to \(\beta\) is taken. While \(f_p^+\) and \(\mu^{(0)}\) vary with \(\beta\), the \(\beta\)-derivative must precede the \(\lambda\)-derivative (or the perturbation expansion), and, thus, \(\partial \mu^{(0)} / \partial \beta\) should not appear. Substituting Eq. (28) into the above as well as using

\[
\frac{\partial f_p^+}{\partial \mu^{(0)}} = \pm (\epsilon_p - \mu^{(0)}) f_p^- f_p^+,
\] (40)

we arrive at the same reduced formula for \(U^{(0)}\) given by Eq. (33).

\[
\text{IV. FIRST ORDER}
\]

Using Eq. (17), we obtain the sum-over-states formula for \(\Xi^{(1)}\) as

\[
\Xi^{(1)} = \sum_i (\beta E_i^{(1)} + \beta \mu^{(1)} N_i) e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}.
\] (41)

\[
\text{A. Grand potential}
\]

Equations (7) and (18) lead to the sum-over-states formula,

\[
\Omega^{(1)} = -\frac{1}{\beta} \frac{\Xi^{(1)}}{\Xi^{(0)}} = \langle E_i^{(1)} - \mu^{(1)} N_i \rangle = \langle E_i^{(1)} \rangle - \mu^{(1)} \tilde{N},
\] (42)

where \(\langle N_i \rangle = \tilde{N}\) according to Eq. (29).

At first glance, reducing \(E_i^{(1)}\) into a sum-over-orbitals formula may appear implausible because there is no closed expression for \(E_i^{(1)}\) given in terms of molecular integrals when its zeroth-order energy \(E_i^{(0)}\) is degenerate. However, the sum of all \(E_i^{(1)}\) in a degenerate subspace does have a closed formula specifically, Eq. (B2) of Appendix B. Because these \(E_i^{(1)}\) in the degenerate subspace are summed with an equal weight of \(e^{-\beta E_i^{(0)} + \beta \mu^{(0)} N_i}\), we can in fact reduce \(E_i^{(1)}\) by using this sum rule without knowing individual \(E_i^{(1)}\) for each state.

For the purpose of simplifying \(E_i^{(1)}\), therefore, we can pretend

\[
E_i^{(1)} = \sum_i a_i + \sum_{i<j} b_{ij},
\] (43)

with \(a_i = H_{ii}^{\text{core}} - \epsilon_i\) and \(b_{ij} = \langle ij|ij \rangle\), where \(H_{ii}^{\text{core}}\) is the one-electron part of the Fock matrix and \(\langle pq|rs \rangle\) is an antisymmetrized two-electron integral. Combining these with the Boltzmann-sum identities I and III of Appendix A, we obtain
\[ \langle E^{(1)}_I \rangle = \frac{\sum_a a e^{\beta e^\nu} + \sum_{i,j} (a_i + a_j) e^{\nu e^\nu} + \ldots}{\prod_p (1 + e^{\nu})} + \frac{\sum_{i,j} b_{ij} e^{\nu e^\nu} + \sum_{i,j,k} (b_{ij} + b_{jk} + b_{ik}) e^{\nu e^\nu}}{\prod_p (1 + e^{\nu})} \]

where \( F \) is the finite-temperature Fock matrix,\textsuperscript{12} minus the diagonal zero-temperature Fock matrix,\textsuperscript{28}

\[ F_{pq} = H_{pq}^{\text{core}} + \sum_r \langle pr| qr \rangle f_r - \delta_{pq} e_p. \tag{47} \]

The reduced formula for \( \Omega^{(1)} \) is, therefore,

\[ \Omega^{(1)} = \sum_p F_{pp} f_p - \frac{1}{2} \sum_{p,q} \langle pq| pq \rangle f_p f_q - \mu^{(1)} \bar{N}, \tag{48} \]

which differs from the one found in the textbooks\textsuperscript{12,16} by the presence of the last term, but is the same as Eq. (46) of our earlier paper.\textsuperscript{1}

### B. Chemical potential

Expanding the electroneutrality condition [Eq. (6)] with the Taylor expansion of an exponential [Eq. (17)] and collecting the first-order corrections, we obtain

\[ \bar{N} \sum_I \left( -\beta E^{(1)}_I + \beta \mu^{(1)} N_I \right) e^{-\beta e^{\nu}} + \beta \mu^{(0)} N_I \]

\[ = \sum_I N_I \left( -\beta E^{(1)}_I + \beta \mu^{(1)} N_I \right) e^{-\beta e^{\nu}} + \beta \mu^{(0)} N_I, \tag{49} \]

or

\[ \bar{N} \langle E^{(1)}_I - \mu^{(1)} N_I \rangle = \langle N_I (E^{(1)}_I - \mu^{(1)} N_I) \rangle. \tag{50} \]

We can solve this for \( \mu^{(1)} \) and arrive at its sum-over-states formula:

\[ \mu^{(1)} = \frac{\langle E^{(1)}_I (\bar{N} - \bar{N}) \rangle - \langle E^{(1)}_I \rangle \bar{N}}{\langle N_I (\bar{N} - \bar{N}) \rangle - \langle N_I \rangle - \bar{N}^2}. \tag{51} \]

Using the Boltzmann-sum identities II and IV of Appendix A, we can simplify the numerator and denominator as

\[ \langle E^{(1)}_I \rangle - \langle E^{(1)}_I \rangle \bar{N} = \sum_p F_{pp} f_p^+ f_p^-, \tag{52} \]

\[ \langle N_I \rangle - \bar{N}^2 = \sum_p f_p^+ f_p^-, \tag{53} \]

leading to the reduced formula for \( \mu^{(1)} \) that reads

\[ \mu^{(1)} = \frac{\sum_p F_{pp} f_p^+ f_p^-}{\sum_p f_p^+ f_p^-}. \tag{54} \]

This is identified as Eq. (48) of our earlier paper.\textsuperscript{1}

Alternatively, differentiating Eq. (42) with respect to \( \mu^{(0)} \) (while holding \( \mu^{(1)} \) fixed) and using Eq. (50), we find

\[ \frac{\partial \Omega^{(1)}}{\partial \mu^{(0)}} = 0. \tag{55} \]

Substituting the reduced formula of \( \Omega^{(1)} \) [Eq. (48)] into this and noting \( \bar{N} = \sum_p f_p^+ \) as well as Eq. (55), we obtain the same reduced formula for \( \mu^{(1)} \) as Eq. (54).

### C. Internal energy

Expanding the definition of \( U \) [Eq. (9)] with the Taylor expansion of an exponential [Eq. (17)], we obtain the sum-over-states formula:

\[ U^{(1)} = \langle E^{(1)}_I \rangle - \beta (E^{(0)}_I (E^{(1)}_I - \mu^{(0)} N_I)) \]

\[ + \beta (E^{(0)}_I (E^{(1)}_I - \mu^{(1)} N_I)). \tag{56} \]

Expanding Eq. (8) [instead of Eq. (9)] can be misleading. As discussed in Sec. III C, since the \( \beta \)-derivative must precede the perturbation expansion, the derivative of \( \mu^{(0)} \) or \( \mu^{(1)} \) with respect to \( \beta \) should not be taken. This fact may be obscured if Eq. (8) were used as a starting point.

Keeping this in mind, however, we differentiate Eq. (42) and find

\[ \frac{\partial}{\partial \beta} \left( \beta \Omega^{(1)} \right) = \frac{\partial}{\partial \beta} \left( \Xi^{(1)} \right) \]

\[ = \langle E^{(1)}_I - \mu^{(1)} N_I \rangle \]

\[ - \beta \langle E^{(1)}_I - \mu^{(1)} N_I \rangle (E^{(0)}_I - \mu^{(0)} N_I) \]

\[ + \beta \langle E^{(1)}_I - \mu^{(1)} N_I \rangle (E^{(0)}_I - \mu^{(0)} N_I) \]

\[ + \beta^2 \frac{\partial \mu^{(0)}}{\partial \beta} \langle (E^{(1)}_I - \mu^{(1)} N_I) N_I \rangle \]

\[ - \beta^2 \frac{\partial \mu^{(0)}}{\partial \beta} \langle E^{(1)}_I - \mu^{(1)} N_I \rangle (N_I) - \beta \frac{\partial \mu^{(1)}}{\partial \beta} \langle N_I \rangle \]

\[ = \langle E^{(1)}_I - \beta (E^{(0)}_I (E^{(1)}_I - \mu^{(1)} N_I)) \]

\[ + \beta (E^{(0)}_I (E^{(1)}_I - \mu^{(1)} N_I)). \tag{57} \]

where Eq. (50) was used twice in the last equality. Comparing the last expression with Eq. (56), we notice that \( U^{(1)} \) and \( \Omega^{(1)} \)
are related to each other by

\[ U^{(1)} = \frac{\partial}{\partial \beta} \left( \beta \Omega^{(1)} \right) + \mu^{(1)} \bar{N} + \beta \frac{\partial \mu^{(1)}}{\partial \beta} \bar{N} \]

\[ = \Omega^{(1)} + \mu^{(1)} \bar{N} + \beta \left( \frac{\partial \Omega^{(1)}}{\partial \beta} \right) \mu^{(1)} \]  \hspace{1cm} (59)

\[ = \sum_p F_{p p} f_p^+ - \frac{1}{2} \sum_{p q} \langle pq \rangle f_p^+ f_q^- \]

\[ - \beta \sum_p \left( F_{p p} - \mu^{(1)} \right) \epsilon_p f_p^+ f_p^- , \]  \hspace{1cm} (60)

where the reduced formula for \( \Omega^{(2)} \) [Eq. (48)] was substituted in the last equality. Equation (60) is the reduced formula for \( U^{(1)} \) and is the same as Eq. (49) of Ref. [1].

Therefore, we can start with Eq. (8) and still obtain a useful relationship between \( U^{(1)} \) and \( \Omega^{(1)} \), insofar as care is exercised to ensure that \( \mu^{(0)} \) and \( \mu^{(1)} \) are held fixed in the partial differentiation with \( \beta \). Dropping \( \mu^{(0)} \) as a fixed variable is permitted because terms involving the derivative of \( \mu^{(0)} \) cancel with each other. It is, however, incorrect to drop \( \mu^{(1)} \) as a fixed variable.

V. SECOND ORDER

Using the Taylor expansion of an exponential [Eq. (17)] to \( \Xi \), we find that the sum-over-states formula for \( \Xi^{(2)} \) reads

\[ \Xi^{(2)} = \sum \left\{ -\beta E_i^{(1)} + \mu^{(2)} N_l + \frac{1}{2} \left( -\beta E_i^{(1)} + \beta \mu^{(1)} N_l \right)^2 \right\} \]

\[ \times e^{-\beta E_i^{(0)} + \mu^{(0)} N_l}. \]  \hspace{1cm} (62)

A. Grand potential

Likewise, using the Taylor expansion of a logarithm [Eq. (18)], we obtain the sum-over-states formula for \( \Omega^{(2)} \) as

\[ \Omega^{(2)} = -\frac{1}{\beta} \Xi^{(2)} + \frac{1}{2 \beta} \left( \frac{\Xi^{(1)}}{\Xi^{(0)}} \right)^2 \]

\[ = \langle E_i^{(2)} - \mu^{(2)} N_l \rangle - \frac{\beta}{2} \langle (E_i^{(1)} - \mu^{(1)} N_l)^2 \rangle \]

\[ - \frac{\beta}{2} \langle E_i^{(1)} - \mu^{(1)} N_l \rangle. \]  \hspace{1cm} (63)

From this expression, combining the sum rules for \( E_i^{(2)} \) and \( (E_i^{(1)})^2 \) in Appendix A with the nine Boltzmann-sum identities in Appendix A, we can derive the following reduced formula (a complete derivation given in Appendix C):

\[ \Omega^{(2)} = \sum_{p,q} \frac{|F_{pq}|^2 f_p^+ f_q^-}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q,r,s} \frac{|\langle pq | rs \rangle|^2 f_p^+ f_q^- f_r^+ f_s^-}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ - \beta \sum_p |F_{pq}|^2 f_p^+ f_q^- \]

\[ - \frac{\beta}{8} \sum_{p,q,r,s} \langle pq | rs \rangle^2 f_p^+ f_q^- f_r^+ f_s^- \]

\[ - \mu^{(2)} \bar{N} + \beta \mu^{(1)} \sum_p F_{p p} f_p^+ f_p^- - \frac{\beta}{2} \langle \mu^{(1)} \rangle^2 \sum_p f_p^+ f_p^-, \]  \hspace{1cm} (65)

where “denom. \neq 0” in the first term means that the sums are taken over only \( p \) and \( q \) that satisfy \( \epsilon_p - \epsilon_q \neq 0 \), while the same in the second term demands \( \epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s \neq 0 \). In the third and fourth terms, the sums are taken over cases where \( \epsilon_p - \epsilon_q = 0 \) or \( \epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s = 0 \), respectively. The penultimate term is identified as \((-2\beta\mu^{(1)}\bar{N})\) times the last term and, therefore, the last two terms can be consolidated. However, we leave them separate to keep track of the origin of each factor for later use [in Eqs. (68) and (72), specifically].

This reduced formula differs from the one in textbooks [12-16] in the last three terms all involving perturbation corrections to \( \mu \). The first of these \((-\mu^{(2)}\bar{N})\) is expected, but the other two may not be.

The derivation of this formula is tedious but straightforward, using the identical strategy as that leading to \( \Omega^{(1)} \). It is documented in Appendix C.

B. Chemical potential

Collecting the second-order terms in the electroneutrality condition [Eq. (9)], we obtain

\[ \bar{N} \langle E_i^{(2)} - \mu^{(2)} N_l \rangle = \frac{\beta}{2} \langle (E_i^{(1)} - \mu^{(1)} N_l)^2 \rangle \]

\[ \langle N_l (E_i^{(2)} - \mu^{(2)} N_l) \rangle = \frac{\beta}{2} \langle N_l (E_i^{(1)} - \mu^{(1)} N_l)^2 \rangle, \]  \hspace{1cm} (66)

which can be solved for \( \mu^{(2)} \) to arrive at the sum-over-states formula:

\[ \mu^{(2)} = \frac{\langle E_i^{(2)} (N_l - \bar{N}) \rangle}{\langle N_l (N_l - \bar{N}) \rangle} \]

\[ - \frac{\beta}{2} \langle (E_i^{(1)} - \mu^{(1)} N_l)^2 (N_l - \bar{N}) \rangle. \]  \hspace{1cm} (67)

Differentiating Eq. (63) with respect to \( \mu^{(0)} \) (while holding \( \mu^{(1)} \) and \( \mu^{(2)} \) fixed) and using Eqs. (55) and (66), we find

\[ \frac{\partial \Omega^{(2)}}{\partial \mu^{(0)}} \bigg|_{\mu^{(1)}, \mu^{(2)}} = 0. \]  \hspace{1cm} (68)

Substituting the reduced formula of \( \Omega^{(2)} \) [Eq. (65)] into this and using the \( \mu^{(0)} \)-derivatives of the Fermi–Dirac functions [Eq. (13)], we obtain the reduced formula for \( \mu^{(2)} \) as
\[ \mu^{(2)} \sum_p f_p f_p^* = \sum_{p,q} \frac{|F_{pq}|^2 f_p f_q^* (f_p^* - f_q^*)}{\epsilon_p - \epsilon_q} + \sum_{p,q,r} \frac{(F_{qr}^* (\epsilon_r - \epsilon_q) f_p f_r^* f_r^* f_q^*)}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p f_q f_r f_s (f_p^* + f_q^* - f_r^* - f_s^*)}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} - \frac{\beta}{2} \sum_{p,q} \frac{|F_{pq}|^2 f_p f_q^* (f_p^* - f_q^*)}{\epsilon_p - \epsilon_q} \]

\[ - \frac{\beta}{2} \sum_{p,q,r} (F_{qr}^* (\epsilon_r - \epsilon_q) f_p f_r f_r^* f_q^*) - \frac{\beta}{8} \sum_{p,q,r,s} |(pq)(rs)| f_p f_q f_r f_s (f_p^* + f_q^* - f_r^* - f_s^*) \]

\[ + \beta \mu^{(1)} \sum_p f_{pp} f_{p^*} (f_p^* - f_p^*) + \beta \mu^{(1)} \sum_{p,q} |(pq)| f_p f_q (\epsilon_p f_q^* - \epsilon_q f_p^*) - \frac{\beta}{2} (\mu^{(1)})^2 \sum_p f_p f_p^* (f_p^* - f_p^*). \]  

(69)

Dropping \( \mu^{(1)} \) as a fixed variable is permitted and leads to the same result.

C. Internal energy

Collecting the second-order terms in \( U \) [Eq. (59)], we have the sum-over-states formula for \( U^{(2)} \) that reads

\[ U^{(2)} = \langle E^{(2)} \rangle - \beta \langle E^{(1)} I \rangle (\mu^{(1)} N_1) + \mu^{(1)} I \langle E^{(1)}(\epsilon^{(1)} - \mu^{(1)} N_1) \rangle \]

\[ - \beta \langle E^{(0)} (\mu^{(2)} N_1) + \beta \langle E^{(0)} (\mu^{(2)} N_1) \rangle \]

\[ + \frac{\beta^2}{2} \langle E^{(0)} (\mu^{(1)} N_1) \rangle (\mu^{(1)} N_1) \]

\[ - \beta^2 \langle E^{(0)} (\mu^{(1)} N_1) \rangle (\mu^{(1)} N_1) \]

\[ + \beta^2 \langle E^{(0)} (\mu^{(1)} N_1) \rangle. \]  

(70)

Comparing this with the \( \beta \)-derivative of Eq. (63), we find

\[ \frac{\partial}{\partial \beta} (\beta \Omega^{(2)}) = - \frac{\partial}{\partial \beta} \left( \Xi^{(2)} \right) + \frac{1}{2} \frac{\partial}{\partial \beta} \left( \Xi^{(1)} \right)^2 \]

\[ = U^{(2)} - \mu^{(2)} \Omega - \mu^{(1)} \Omega^{(1)} \Omega^{(1)} \]  

(71)

where Eqs. (50) and (66) were used for simplification analogous to the one leading to the corresponding formula at the first order [Eq. (58)]. Substituting the reduced formula of \( \Omega^{(2)} \) [Eq. (63)] into this and using the \( \beta \)-derivatives of the Fermi–Dirac functions [Eq. (40)], we obtain the reduced formula for \( U^{(2)} \) as

\[ U^{(2)} = \frac{\partial}{\partial \beta} (\beta \Omega^{(2)}) + \mu^{(2)} N + \beta \mu^{(2)} N = \Omega^{(2)} + \mu^{(2)} \Omega + \beta \left( \frac{\partial \Omega^{(2)}}{\partial \beta} \right) \mu^{(0), \mu^{(1)}, \mu^{(2)}} \]

\[ = \sum_{p,q} \frac{|F_{pq}|^2 f_p^* f_q^*}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} - \beta \sum_{p,q} \frac{|F_{pq}|^2 f_p^* f_q^*}{\epsilon_p - \epsilon_q} \]

\[ + \frac{1}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ + \frac{1}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ - \beta \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ + \frac{\beta^2}{2} \sum_{p,q} \frac{|F_{pq}|^2 f_p^* f_q^*}{\epsilon_p - \epsilon_q} \]

\[ + \frac{\beta^2}{2} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ + \frac{\beta^2}{8} \sum_{p,q,r,s} \frac{|(pq)(rs)| f_p^* f_q^* f_r^* f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \]

\[ - \beta^2 \mu^{(1)} \sum_{p,q} \frac{|pq||pq| f_p^* f_q^* (\epsilon_p f_q^* - \epsilon_q f_p^*)}{\epsilon_p - \epsilon_q} + \frac{\beta^2}{2} (\mu^{(1)})^2 \sum_{p,q} \frac{|pq||pq| f_p^* f_q^* (\epsilon_p f_q^* - \epsilon_q f_p^*)}{\epsilon_p - \epsilon_q} \]

\[ + \beta \mu^{(1)} \sum_{p,q} f_p f_p^* (\epsilon_p f_q^* - \epsilon_q f_p^*). \]  

(73)

(74)

where \( \mu^{(0)} \) and \( \mu^{(1)} \) may be dropped as fixed variables (giv- ing the same result), but \( \mu^{(2)} \) must be held fixed. If the last
two terms of $\Omega^{(2)}$ in Eq. 65 are consolidated into one, the $\beta$-derivative of $\mu^{(1)}$ must be considered. The $\mu^{(1)}$ factor in Eq. 40 that should accompany every $e_p$ can be shown to cancel with one another and disappear by virtue of Eq. 66.

VI. NUMERICAL VERIFICATION

Table I lists the numerical values of $\Omega^{(2)}$, $\mu^{(2)}$, and $U^{(2)}$ of the hydrogen fluoride molecule (0.9168 Å) in the STO-3G basis set as a function of temperature. They were computed by three different methods: the $\lambda$-variation method, which computes $X^{(n)}$ ($X = \Omega$, $\mu$, or $U$) by a finite-difference approximation for the $\lambda$-derivatives [Eq. (1)], the sum-over-states (“SoS”) analytical formulas, and the reduced (sum-over-orbitals) analytical formulas. They agree numerically exactly with one another in a wide range of temperature, attesting to their correctness (for a nondegenerate ground state).

See our previous paper 1 for the numerical verification of $\Omega^{(1)}$, $\mu^{(1)}$, and $U^{(1)}$.

VII. CONCLUSIONS

Unlike thermodynamics of vibrations, rotations, and translations, which are well understood, finite-temperature perturbation theory for electrons has been plagued with a controversy. 6,7,12,30,31 This is traced at least partly to the fact that electrons are charged particles. The chemical potential $\mu$ must be adjusted at each perturbation order to ensure the overall charge neutrality of the macroscopic system being described.

There are more than one way to make such adjustments, but expanding $\mu$ as well as $\Omega$, $U$, and $S$ in a consistent perturbation series is the most satisfactory route because it conforms to the canonical definition of a perturbation theory [Eq. (1)]. Given that only such canonical perturbation theories (MPPT for nondegenerate states, HCPT for degenerate states, and the Feynman–Dyson perturbation series for many-body Green’s function theory) tend to survive the test of time, a finite-temperature perturbation theory that expands $\Omega$, $\mu$, and $S$ on an equal footing is warranted.

In a previous article, 1 we presented the sum-over-states and reduced (sum-over-orbitals) analytical formulas of these properties at the first order of such a finite-temperature many-body perturbation theory. In this article, we extended this theory to the second order. The reduced analytical formula for $\Omega^{(2)}$ differs from the one found in the textbooks 12-16. To the authors’ knowledge, the analytical formulas for $\mu^{(2)}$ and $U^{(2)}$ were unknown until they are presented in this article for the first time.

They reproduce the benchmark data numerically exactly and are correct.

Equally important to these analytical formulas is the general and transparent (if tedious) strategy of their derivation. It is time-independent, nondiagrammatic, and algebraic, using elementary combinatorics and calculus with the only nontrivial step being the sum rules of HCPT. The latter is inevitable because the perturbation corrections to energies that are being thermally averaged come from HCPT, which is apparently hidden from view in the quantum-field-theoretical or density-matrix-based derivations. We hope that our derivation will serve to justify and perhaps generalize the diagrammatic logic as well as to sharpen and answer the question that is the basis of the aforementioned controversy. 22 We also expect that this work will help clarify the precise relationship between the finite-temperature many-body perturbation theory and other finite-temperature theories. 10,11,23,32-37

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Appendix A: Boltzmann-sum identities

Here, we list all the algebraic identities needed to derive the reduced analytical formulas in this article. These identities can be inferred from elementary combinatorics, and are not limited to the thermodynamics application insofar as an exponentially weighted sum is taken over all $2^n$ occupancies of $n$ slots. Equation 45 may be considered as Identity 0.

Index $I$ runs over all $2^n$ Slater determinants, where $n$ is the number of spinorbitals. Index $i$ in $\sum_i$ goes through all spinorbitals occupied by an electron in the $I$th state. Index $a$ in $\sum_a$ runs through all spinorbitals unoccupied in the $I$th state. We use letters $i$, $j$, and $k$ for an occupied spinorbital in the $I$th state, $a$ and $b$ for an unoccupied spinorbital in the same state, and $p$, $q$, $r$, and $s$ for a general spinorbital.

The first identity is

$$\sum_{I_1} \sum_{I_2} a_i e^{n_i} + \sum_{I_1} \sum_{i<j} (a_i + a_j) e^{n_i} e^{n_j} + \sum_{I_1} \sum_{i<j<k} (a_i + a_j + a_k) e^{n_i} e^{n_j} e^{n_k} + \ldots = \sum_p a_p f_p ; \text{ (Identity I),} \quad (A1)$$

where $\sum_{I_1}$ sums over all one-electron ($I_1$) Slater determinants, $\sum_{I_1}$ over all two-electron ($I_2$) determinants, etc. with “…” includes
the sum over up to all \(n\)-electron determinants (though there is only one). \(\Sigma_{i}^{l_{i}}\) means that \(i\) runs over all spinorbitals occupied in \(l\), whereas \(\prod_{p}\) takes the product over all spinorbitals. \(\alpha_{p}\) is a complex number and \(f_{p}^{-} = (1 + e^{\lambda_{p}})^{-1}\). The second identity reads

\[
\sum_{l_{i}}\sum_{i}^{l_{i}} \alpha_{p}^{3} e^{\nu_{p}} + \sum_{l_{i}}\sum_{j}^{l_{j}}(\alpha_{i}^{j} + \alpha_{j}^{i})e^{\nu_{i} + \nu_{j}} + \sum_{l_{i}}\sum_{j}^{l_{j}}(\alpha_{i}^{j} + \alpha_{j}^{i})e^{\nu_{i} + \nu_{j}} + \ldots
\]

\[
= \sum_{p} \alpha_{p}^{3} f_{p}^{-} f_{p}^{+} + \left(\sum_{p} \alpha_{p} f_{p}^{-}\right) \left(\sum_{p} \alpha_{p}^{3} f_{p}^{+}\right) ; \text{ (Identity II)}
\]

\[
\frac{1}{\prod_{p}(1 + e^{\lambda_{p}})} \cdot (A2)
\]

where \(\alpha_{p}\) and \(\alpha_{p}^{3}\) are two independent complex numbers, and \(f_{p}^{+} = 1 - f_{p}^{-}\). The third identity is

\[
\sum_{l_{i}}\sum_{k}^{l_{k}} b_{i} e^{\nu_{i}} e^{\nu_{k}} + \sum_{l_{i}}\sum_{j}^{l_{j}}(b_{ij} + b_{ik})e^{\nu_{i} e^{\nu_{j}} e^{\nu_{k}}} + \ldots
\]

\[
= \frac{1}{2} \sum_{p, q} b_{pq} f_{p}^{-} f_{q}^{+} ; \text{ (Identity III)}
\]

\[
\frac{1}{\prod_{p}(1 + e^{\lambda_{p}})} \cdot (A3)
\]

where \(b_{pq}\) is real and \(b_{pq} = b_{qp}\) as well as \(b_{pp} = 0\). The fourth identity is

\[
\sum_{l_{i}}\sum_{k}^{l_{k}} (a_{i} + a_{k})b_{i} e^{\nu_{i}} e^{\nu_{k}} + \sum_{l_{i}}\sum_{j}^{l_{j}}(a_{i} + a_{j})(b_{ij} + b_{ik})e^{\nu_{i} e^{\nu_{j}} e^{\nu_{k}}} + \ldots
\]

\[
= \frac{1}{2} \sum_{p, q} (a_{p} f_{p}^{-} + a_{q} f_{q}^{-})b_{pq} f_{p}^{-} f_{q}^{+} + \frac{1}{2} \sum_{p} a_{p} f_{p}^{-} \sum_{p, q} b_{pq} f_{p}^{-} f_{q}^{+} ; \text{ (Identity IV)}
\]

\[
\frac{1}{\prod_{p}(1 + e^{\lambda_{p}})} \cdot (A4)
\]

where \(a_{p}\) is complex, \(b_{pq}\) is real, \(b_{pq} = b_{qp}\), and \(b_{pp} = 0\). Identities I through IV were already presented in our earlier paper.

A new identity involves spinorbitals that are occupied (labeled by \(i\) and \(j\)) and unoccupied (labeled by \(a\)), and it reads

\[
\sum_{l_{i}}\sum_{j}^{l_{j}} b_{ia} e^{\nu_{i}} e^{\nu_{j}} + \sum_{l_{i}}\sum_{k}^{l_{k}}(b_{ia} + b_{ja})e^{\nu_{i} e^{\nu_{j}} e^{\nu_{k}}} + \ldots
\]

\[
= \sum_{p, q} b_{pq} f_{p}^{-} f_{q}^{+} ; \text{ (Identity V)}
\]

\[
\frac{1}{\prod_{p}(1 + e^{\lambda_{p}})} \cdot (A5)
\]

where \(b_{pq}\) is complex. The restriction \(q \neq p\) in the right-hand side comes from the fact that no spinorbital can be simultaneously occupied and unoccupied in any state.

The sixth identity is

\[
\sum_{l_{i}}\sum_{j}^{l_{j}} (b_{ij})^{2} e^{\nu_{i} e^{\nu_{j}}} + \sum_{l_{i}}\sum_{k}^{l_{k}}(b_{ij} + b_{ik})^{2} e^{\nu_{i} e^{\nu_{j}} e^{\nu_{k}}} + \ldots
\]

\[
= \frac{1}{2} \sum_{p, q} (b_{pq})^{2} f_{p}^{-} f_{q}^{+} + \sum_{p, q, r} b_{pq} b_{pr} f_{p}^{-} f_{q}^{+} f_{r}^{+} + \frac{1}{4} \sum_{p, q, r, s} b_{pq} b_{pr} f_{p}^{-} f_{q}^{+} f_{r}^{+} f_{s}^{+} ; \text{ (Identity VI)}
\]

\[
\frac{1}{\prod_{p}(1 + e^{\lambda_{p}})} \cdot (A6)
\]
The seventh identity reads

$$
\sum_{l} \sum_{i,j,a} c_{ija} e^{\epsilon_i} e^{\epsilon_j} + \sum_{l} \sum_{i,j,k,a,b} (c_{ija} + c_{ikab}) e^{\epsilon_i} e^{\epsilon_k} e^{\epsilon_j} e^{\epsilon_b} + \ldots = \sum_{p} \sum_{r \neq p} c_{pqr} f^+_p f^+_r f^+_q f^+_r ; \quad \text{(Identity VII),}
$$

where $c_{pqr}$ is complex and $c_{ppr} = c_{ppq} = 0$. The eighth is

$$
\sum_{l} \sum_{i,j,a} c_{ija} e^{\epsilon_i} e^{\epsilon_j} + \sum_{l} \sum_{i,j,k,a,b} e^{\epsilon_i} e^{\epsilon_j} e^{\epsilon_k} e^{\epsilon_b} + \ldots = \sum_{p} \sum_{r \neq p} \left( \sum_{q} c_{pqr} f^+_p f^+_r f^+_q + \sum_{p,q} c_{pqr} f^+_p f^+_r f^+_q f^+_r \right) ; \quad \text{(Identity VIII),}
$$

where $c_{pqr}$ is complex and $c_{ppr} = c_{ppq} = 0$.

The ninth identity for real $d_{ijab}$ is

$$
\sum_{l} \sum_{i,j,a,b,c} d_{ijabc} e^{\epsilon_i} e^{\epsilon_j} + \sum_{l} \sum_{i,j,k,a,b,c} (d_{ijabc} + d_{ikabc} + d_{abkbc} + d_{akbca} + d_{kabca} + d_{kabc}) e^{\epsilon_i} e^{\epsilon_j} e^{\epsilon_k} e^{\epsilon_b} + \ldots = \frac{1}{4} \sum_{p \neq q \neq r \neq s} d_{pqrs} f^+_p f^+_q f^+_r f^+_s ; \quad \text{(Identity IX),}
$$

where $d_{pqrs} = d_{qpqr} = d_{pqs r} = d_{pqsr}$ and $d_{pqrs} = d_{pqr s} = 0$ are presumed. Superscript “no coinc.” stands for excluding all cases where two or more indices are coincident, namely, $p = r$, $p = s$, $q = r$, or $q = s$, which ultimately arises from the fact that no spinorbital is simultaneously occupied and unoccupied in any state (the exclusion of $p = q$ or $r = s$ is effected by $d_{pqrs} = d_{pqr s} = 0$). Remarkably, such restrictions are systematically lifted in the final reduced formula of $\Omega^{(2)}$ (see Appendix C).

**Appendix B: Hirschfelder–Certain sum rules**

For a state whose zeroth-order energy is degenerate, a perturbation correction to energy $E^{(a)}_I$ cannot be written in a closed expression of molecular integrals (or diagrammatically); it is defined only procedurally by HCPT.\(^{21}\) This procedure, in turn, involves diagonalization of a matrix in the degenerate subspace, whose outcome is generally not expressible as a sum-of-products of integrals.

Nevertheless, the sum of $E^{(0)}_I$ in a degenerate subspace can be written in a closed formula of integrals, as shown below. Since, in the zeroth-order thermal average, they are summed with an equal weight, $e^{-\beta E^{(0)}_I + \beta N_I}$, dictated by $E^{(0)}_I$ and $N_I$ (which are common within the degenerate subspace), it is the sums of $E^{(0)}_I$ in degenerate subspaces (rather than individual $E^{(0)}_I$) that we need in order to correctly evaluate the average. Here, we derive and document such sum rules.

For a nondegenerate state, HCPT reduces to MPPT, giving the closed formula for $E^{(1)}_I$.\(^{1,28}\)

$$
E^{(1)}_I = \sum_i H^{\text{core}}_{ii} + \sum_{i<j} V_{ij} - \sum_i \epsilon_i , \quad \text{(B1)}
$$

which is equal to $\langle \Phi_I | \hat{V} | \Phi_I \rangle$ evaluated by the Slater–Condon rules, where $\Phi_I$ is the $I$th Slater determinant and $V$ is the perturbation operator [Eqs. (14) and (15)].

For a degenerate subspace, we have\(^{1,28}\)

$$
\text{degen.} \sum_i E^{(1)}_I = \sum_i \left\{ \sum_{i<j} H^{\text{core}}_{ij} + \sum_{i<j} V_{ij} - \sum_i \epsilon_i \right\} , \quad \text{(B2)}
$$

where “degen.” means that $I$ runs over all Slater determinants in the degenerate subspace sharing the same $E^{(0)}_I$ and $N_I$.

Equation (B2) can be rationalized as follows. According to Eq. (37) of Hirschfelder and Certain,\(^{22,29}\) $E^{(3)}_I$ within a degenerate subspace are the eigenvalues of the matrix $V$ whose element is $V_{ij} = \langle \Phi_I | \hat{V} | \Phi_I \rangle$ (where $\Phi_I$ and $\Phi_J$ are two Slater determinants in the degenerate subspace). Owing to the similarity invariance of trace, the sum of the eigenvalues (the left-hand side of the above equation) is equal to the sum of the diagonal elements, readily evaluated by the Slater–Condon rules (the right-hand side).\(^{2,26}\)

For a nondegenerate state, $E^{(2)}_I$ has a well-known formula.\(^{28,29}\)

$$
E^{(2)}_I = \sum_{i,a} \frac{|H^{\text{core}}_{ia} + \sum_j (i||a) \epsilon_j |^2}{\epsilon_i - \epsilon_a} + \sum_{i<j,a,b,c} \frac{|(i||a) \epsilon_j - \epsilon_a - \epsilon_b |^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} ,
$$

where $i$ and $j$ run over spinorbitals occupied in the $I$th Slater determinant, while $a$ and $b$ refer to spinorbitals unoccupied in the same determinant. The first term is identified as the non-HF term with the numerator factor recognized as the $(ia)$th element of the zero-temperature Fock matrix of the $I$th state.

The sum rule for $E^{(2)}_I$ within a degenerate subspace is
where “I, denom. ≠ 0” means i, j (a, b) run over spinorbitals occupied (unoccupied) in the Ith state excluding the case with a vanishing denominator. In other words, \( E_i^{(2)} \) for a degenerate state accumulates the usual MPPT-type second-order corrections [Eq. (B3)] only from outside the degenerate subspace. This sum rule can be justified by Eqs. (49), (56), and (57) of Hirschfelder and Certain12 as well as the trace invariance.

The sum rule for \( (E_i^{(1)})^2 \) within a degenerate subspace reads

\[
\sum_{I} \text{deg. over all degenerate } \left( E_i^{(1)} \right)^2 = \sum_{I} \left( E_i^{\text{occ}} + E_i^{\text{ev}} + E_i^{\text{ce}} \right),
\]

(B5)

with

\[
E_i^{\text{occ}} = \left\{ \sum_{I, \text{denom. ≠ 0}} H_{\text{core}}^{\text{occ}} + \sum_{i < j} \langle i|j\rangle \right\}^2,
\]

E_i^{\text{ev}} = \sum_{I, \text{denom. ≠ 0}} \left( \sum_{a} H_{\text{core}}^{\text{ev}} + \sum_{i} \langle i|a\rangle \right)^2,
\]

E_i^{\text{ce}} = \sum_{i < j, \text{a}, \text{b}} |\langle i|j\rangle| |a|b|^2.
\]

(B6)

(B7)

(B8)

where “I, denom. = 0” in \( E_i^{\text{ce}} \) means that i and a run over all occupied and unoccupied spinorbitals in the Ith state that satisfy \( \epsilon_i = \epsilon_a = 0 \). The same in \( E_i^{\text{ce}} \) demands \( \epsilon_i + \epsilon_j = \epsilon_a + \epsilon_b = 0 \). Therefore, in contrast to the sum rule for \( E_i^{(2)} \) [Eq. (B4)], \( E_i^{\text{ev}} \) and \( E_i^{\text{ce}} \) accumulate denominatorless MPPT-type corrections only from inside the degenerate subspace. The unlinked-diagram term, \( E_i^{\text{ce}} \), does not have such restrictions.

This sum rule is rationalized as follows. Since \( E_i^{(1)} \) are the eigenvalues of the matrix \( V \), \( (E_i^{(1)})^2 \) are the eigenvalues of the matrix \( V^2 \). The trace invariance of the latter implies that the sum of \( (E_i^{(1)})^2 \) is equal to the sum of the diagonal elements of \( V^2 \), which can then be expanded as

\[
\sum_{I} \left( E_i^{(1)} \right)^2 = \sum_{I} \langle \Phi_I|\tilde{V}^{2}\Phi_I \rangle + \sum_{I, \text{denom. ≠ 0}} \langle \Phi_I|\tilde{V}|\Phi_I \rangle \sum_{I, \text{denom. ≠ 0}} \langle \Phi_I|\tilde{V}^{2}|\Phi_I \rangle
\]

\[
+ \sum_{I, \text{denom. ≠ 0}} \langle \Phi_I|\tilde{V}|\Phi_I \rangle \sum_{I, \text{denom. ≠ 0}} \langle \Phi_I|\tilde{V}^{2}|\Phi_I \rangle
\]

\[
(B9)
\]

where \( \Phi_i^p \) runs over all degenerate Slater determinants that are a one-electron replacement from \( \Phi_I \) (an electron in the ith spinorbital occupied in \( \Phi_I \) is promoted to the ith spinorbital unoccupied in \( \Phi_I \) with \( \epsilon_i = \epsilon_{a} \)). Similarly, \( \Phi_i^{\text{d}} \) runs over all degenerate Slater determinants that is a two-electron replacement from \( \Phi_I \) (with \( \epsilon_a + \epsilon_b = \epsilon_i + \epsilon_j \)). The Slater-Condon rules dictate that there are only these three terms12,22. The first term corresponds to an unlinked-diagram contribution and is identified as \( E_i^{\text{ec}} \) [Eq. (B6)], whereas the second and third terms are linked and are evaluated as \( E_i^{\text{ev}} \) [Eq. (B7)] and \( E_i^{\text{ce}} \) [Eq. (B8)], respectively.

Appendix C: Derivation of Eq. (65)

Using Eqs. (52) and (53), we can immediately partially reduce the sum-over-states formula of \( \Omega^{(2)} \) [Eq. (64)] to

\[
\Omega^{(2)} = \langle E_i^{(2)} \rangle - \frac{\beta}{2} \langle (E_i^{(1)})^2 \rangle + \frac{\beta}{2} \langle (E_i^{(1)})^2 - \mu^{(2)} \rangle
\]

\[
+ \beta \frac{1}{2} \sum_{p} f_p^+ f_p^\dagger - \frac{\mu^{(2)}}{2} \sum_{p} f_p^+ f_p^\dagger,
\]

(C1)

where \( \langle E_i^{(1)} \rangle \) was also already reduced to Eq. (46). The remaining task is, therefore, to evaluate and simplify \( \langle E_i^{(2)} \rangle \) and \( (E_i^{(1)})^2 \).

For the purpose of reducing \( \langle E_i^{(2)} \rangle \), we can pretend that \( \langle E_i^{(2)} \rangle \) has the following closed expression for each (degenerate or nondegenerate) state:

\[
\langle E_i^{(2)} \rangle = \sum_{I, \text{denom. ≠ 0}} b_{ia} + \sum_{I, \text{denom. ≠ 0}} c_{ija} - \sum_{I, \text{denom. ≠ 0}} \sum_{I, \text{denom. ≠ 0}} \sum_{I, \text{denom. ≠ 0}} d_{ijab},
\]

(C2)

with

\[
b_{ia} = |H_{ia}|^2 / \epsilon_i - \epsilon_a,
\]

\[
c_{ija} = |H_{ia}^{\text{core}}| \langle i|a\rangle \langle j|f\rangle H_{ia}^{\text{core}} / \epsilon_i - \epsilon_a,
\]

\[
c_{ija} = |\langle i|f\rangle| \langle j|a\rangle / (\epsilon_a - \epsilon_j)^{1/2},
\]

\[
d_{ijab} = |\langle i|j\rangle|^2 / \epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b,
\]

(C3)

(C4)

(C5)

(C6)

which encompass both Eqs. (B3) and (B4). Since the Ith state in Eq. (B3) is nondegenerate, a vanishing denominator cannot occur and \( \sum_{I} \) in it can, therefore, be replaced by \( \sum_{I, \text{denom. ≠ 0}} \), justifying Eq. (C2).

Substituting these into the Boltzmann-sum identities V, VII,
VIII, and IX of Appendix A we obtain

\[
\langle E_1^{(2)} \rangle = \sum_{p,q \neq p} \frac{|F_{pq}|^2 f_p f_q^*}{\epsilon_p - \epsilon_q} + \sum_{p,q \neq p} \sum_r \frac{|pr||qr|^2 f_p f_q^* f_r f_r^*}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q \neq p} \sum_{r,s} \frac{|pq||rs|^2 f_p f_q^* f_r f_r^* f_s f_s^*}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s}.
\]

(C7)

In the first term of Eq. (C7), the restriction \( q \neq p \) is encompassed by the nonzero denominator condition ("denom. \( \neq 0 \)"") and can thus be lifted. The second term of Eq. (C7) was absorbed by the third term to eliminate the restriction ("no coinc."), that is, there is no index coincidence (\( p = r, \ p = s, q = r, \ \text{or} \ q = s \)). The exclusion of the contributions involving \( \langle pq||pq \rangle \) or \( \langle pq||qp \rangle \) is still in effect, but it is encompassed by the nonzero denominator condition, and is hence not explicitly demanded. This step, \( F \) (the finite-temperature Fock matrix minus the diagonal part of the zero-temperature Fock matrix) given by Eq. (47) naturally emerges.

Likewise, for the purpose of simplifying \( \langle E_1^{(1)} \rangle^2 \), we may write \( \langle E_1^{(1)} \rangle^2 \) for each (degenerate or nondegenerate) state as

\[
\langle E_1^{(1)} \rangle^2 = E_1^{0e} + E_1^{1e} + E_1^{2e},
\]

(C9)

where

\[
E_1^{0e} = \sum_i a_i \sum_{j \neq k} b_{jk} + \frac{1}{4} \sum_{i,j} b_{ij}^2,
\]

(C10)

\[
E_1^{1e} = \sum_i b_{ia} + \sum_{i,j,a} c_{ija} + \sum_{i,a} \sum_j c_{jia}^2,
\]

(C11)

\[
E_1^{2e} = \sum_{i < j, a < b} d_{ijab},
\]

(C12)

\[
\begin{align*}
\langle E_1^{(1)} \rangle^2 & = \sum_{p,q \neq p} |F_{pq}|^2 f_p f_q^* + \sum_{p,q \neq p} \sum_r |pr||qr|^2 f_p f_q^* f_r f_r^* + \frac{1}{4} \sum_{p,q \neq p} \sum_{r,s} |pq||rs|^2 f_p f_q^* f_r f_r^* f_s f_s^*, \\
& = \sum_{p,q \neq p} |F_{pq}|^2 f_p f_q^* + \sum_{p,q \neq p} \sum_r |pr||qr|^2 f_p f_q^* f_r f_r^* + \frac{1}{4} \sum_{p,q \neq p} \sum_{r,s} |pq||rs|^2 f_p f_q^* f_r f_r^* f_s f_s^*.
\end{align*}
\]

(C8)

For a nondegenerate state, \( \langle E_1^{(1)} \rangle^2 = \langle E_1^{0e} \rangle^2 \).

Following the identical strategy to obtain \( \langle E_1^{(2)} \rangle \) [Eq. (C8)], that is, applying the Bolzmann-sum identities V, VII, VIII, and IX to Eqs. (C11) and (C12), we obtain

\[
\langle E_1^{1e} \rangle = \sum_{p,q \neq p} |F_{pq}|^2 f_p f_q^* + \sum_{p,q \neq p} \sum_r |pr||qr|^2 f_p f_q^* f_r f_r^* + \frac{1}{4} \sum_{p,q \neq p} \sum_{r,s} |pq||rs|^2 f_p f_q^* f_r f_r^* f_s f_s^*,
\]

(C19)

which are nothing but Eq. (C7) stripped of the denominators. However, adding them together, we get

\[
\langle E_1^{0e} \rangle + \langle E_1^{1e} \rangle = \sum_{p,q \neq p} |F_{pq}|^2 f_p f_q^* + \frac{1}{4} \sum_{p,q \neq p} \sum_{r,s} |pq||rs|^2 f_p f_q^* f_r f_r^* f_s f_s^*,
\]

(C20)

which is not Eq. (C8) stripped of the denominators. Unlike in \( \langle E_1^{(2)} \rangle \), the \( q \neq p \) restriction in the first term is not lifted because \( \epsilon_p - \epsilon_q = 0 \) can still be true even when \( q \neq p \). Similarly, the second term of \( \langle E_1^{(1)} \rangle \) is absorbed by \( \langle E_1^{2e} \rangle \), turning the restriction on the index coincidence ("no coinc.") to only a weaker restriction ("no J or K") excluding the so-called J- and K-type integrals, \( \langle pq||pq \rangle \) and \( \langle pq||qp \rangle \), from the sum.

Next, applying the Bolzmann-sum identities II, IV, and VI to Eq. (C10), we find
Remarkably, the unlinked contribution \( \langle E_{1x}^{\text{lk}} \rangle \) is not canceled exactly by \( \langle E_{2x}^{\text{lk}} \rangle \). The small remainder exist, which are identified as anomalous diagrams of Kohn and Luttinger and they lift the restrictions on summation indices (both \( q \neq p \) and “no \( J \) or \( K' \)”) in Eq. (C21) for \( \langle E_{1x}^{\text{lk}} \rangle + \langle E_{2x}^{\text{lk}} \rangle \).

Combining Eqs. (C21) and (C22), therefore, we obtain

\[
\langle E_{1x}^{\text{lk}} \rangle = \langle E_{1x}^{\text{ex}} \rangle + \langle E_{1x}^{\text{lk}} \rangle + \langle E_{2x}^{\text{lk}} \rangle \quad \text{(C25)}
\]

Substituting this as well as Eq. (C8) into Eq. (C1), we arrive at the desired result [Eq. (63)].

\[
\langle E_{1x}^{\text{lk}} \rangle = \langle E_{1x}^{\text{ex}} \rangle + \sum_{p,q} |F_{pq}|^2 f_p f_q^+ + \sum_{p,q,r,s} \langle pq \rangle \langle rs \rangle f_p f_q f_r f_s^+.
\]  

\[\text{(C26)}\]
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