Numerical Evidence Invalidating Finite-Temperature Many-Body Perturbation Theory

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Low-order perturbation corrections to the electronic grand potential, internal energy, chemical potential, and entropy of a gas of noninteracting, identical molecules at a nonzero temperature are determined numerically as the $\lambda$-derivatives of the respective quantity calculated exactly (by thermal full configuration interaction) with a perturbation-scaled Hamiltonian, $\hat{H}_0 + \lambda \hat{V}$. The data thus obtained from the core definition of any perturbation theory serve as a benchmark against which analytical formulas can be validated. The first- and second-order corrections from finite-temperature many-body perturbation theory disagree with these benchmark data. The theory is incorrect as it neglects the variation of chemical potential with $\lambda$, thereby failing to converge at the exact, full-interaction ($\lambda = 1$) limit, unless the exact chemical potential is known in advance. The renormalized finite-temperature perturbation theory [S. Hirata and X. He, J. Chem. Phys., 138, 204112 (2013)] is also found to be incorrect.

I. INTRODUCTION

In 1960, Kohn and Luttinger wrote that the finite-temperature Brueckner–Goldstone perturbation theory (discussed in many contemporary textbooks) is “in general not correct.” This was based on their finding that its second-order correction contains the so-called “anomalous diagram,” whose value is nonzero in a gapless system even as the temperature tends to zero, thereby contradicting the established zero-temperature many-body perturbation theory. Luttinger and Ward pointed out that these anomalous diagrams emerge because the zeroth-order chemical potential ($\mu^{(0)}$) in a non-interacting system differs from the exact value ($\mu$) in the fully interacting system. The latter $\mu$ enters the zeroth-order Hamiltonian in their perturbation theory.

One of the present authors with a co-author proposed an alternative finite-temperature perturbation theory, which does not suffer from this inconsistency. The new formula was defined by a straightforward application of thermal Wick’s theorem to molecular integrals appearing in both the numerator and denominator of the Rayleigh–Schrödinger-like perturbation theory formula, which we call the renormalized finite-temperature perturbation theory (as opposed to the conventional finite-temperature perturbation theory). Kobayashi and Taketsugu showed that either expression is postulated from a density-matrix formulation of perturbation theory. The renormalized theory is only intuitively defined but not rigorously derivable and has thus been criticized.

Which is the correct finite-temperature perturbation theory that converges at the exact limit? Here, we give a definitive answer to this question on the basis of numerical calculations obtained by returning to the core definition of any perturbation theory.

II. NUMERICAL VALIDATION

The $n$th-order correction, $X^{(n)}$, of a converging perturbation series of quantity $X$ is defined as the $n$th derivative with respect to $\lambda$ of the same quantity calculated with the exact method, i.e., the full configuration interaction (FCI), using a perturbation-scaled Hamiltonian, $\hat{H} = \hat{H}_0 + \lambda \hat{V}$ ($\lambda = 1$ in the fully interacting system of interest):

$$X^{(n)} = \frac{1}{n!} \frac{\partial^n X}{\partial \lambda^n} \bigg|_{\lambda=0}. \tag{1}$$

Thermodynamic quantities such as the grand potential ($\Omega$), internal energy ($U$), chemical potential ($\mu$), and entropy ($S$) are calculated for a molecule unambiguously and exactly with thermal FCI (Ref. [1]) at any temperature ($T$) in a basis set with $m$ functions.

First, the zero-temperature FCI furnishes the exact energies, $E_{1}^{(N,S)}$, of all states of a molecule with any number of electrons ($N$) and any $S$, quantum number. Second, the grand partition function, $\Xi$, is obtained by evaluating

$$\Xi = \sum_{N=0}^{2m} \sum_{S} \sum_{\Omega} \exp \left[ -\beta \left( E_{1}^{(N,S)} - \mu \Omega \right) \right] \tag{2}$$

with

$$\tilde{N} = \frac{1}{\beta \mu} \ln \Xi. \tag{3}$$

These two are the equations of state to be solved for $\Xi$ and $\mu$ simultaneously with given $\beta = (k_B T)^{-1}$ and average number of electrons $\tilde{N}$, which is typically chosen so as to keep the system electrically neutral. Third, exact $U$ and $\Omega$ for the same $\beta$ and $\tilde{N}$ are calculated using

$$\Omega = -\frac{1}{\beta} \ln \Xi, \tag{4}$$

$$U = -\frac{\partial}{\partial \beta} \ln \Xi + \mu \tilde{N}. \tag{5}$$

$\Xi$ and $\mu$ (as well as $\Omega$, $U$, and $S$) vary with the strength of perturbation $\lambda$. Numerically differentiating these with respect to $\lambda$, one can obtain benchmark results for their several low-order perturbation corrections, against which analytical perturbation formulas can be tested and judged for their validity. There is a minimal risk of formulation or programming errors in this $\lambda$-variation method. One should only be mindful of the precision in finite-difference numerical differentiations. The $\lambda$-variation method was used to generate several low-order perturbation corrections of many-body perturbation theory.
theory, Hirschfelder–Certain degenerate perturbation theory, and Feynman–Dyson perturbation series in Green’s function theory.\(^\text{16}\)

We adopt the grand canonical ensemble in line with the analytical formula to be tested. It does not depend on a particular partitioning or reference wave function. Here, we employ the Møller–Plesset partitioning, where \(\hat{H}_0\) is the zero-temperature Fock operator, and the corresponding reference is the \(N\)-electron ground-state canonical Hartree–Fock (HF) wave function at \(T = 0\). Its orbitals and orbital energies are held fixed throughout the calculations. Insofar as both the \(\lambda\)-variation method and analytical formulas use the identical partitioning and reference wave function, the comparison is valid and it can verify or invalidate analytical formulas. It is applied to a gas of noninteracting, identical molecules at a nonzero electronic temperature (ignoring vibrational or rotational motions).

The thermal FCI program was verified against an independent code and several well-tested zero-temperature FCI programs. The \(\lambda\)-variation program used seven-point finite-difference formulas centered at \(\lambda = 0\) with the grid spacing of \(\Delta \lambda = 0.01\), and reproduced the Møller–Plesset perturbation energies at \(T = 0\). At each value of \(\lambda\), chemical potential \(\mu\) is determined by solving Eq. (3) by a bisection method. As \(T \to 0\), this determination becomes increasingly technically difficult, and extended-precision arithmetic was used to counter this problem.

### A. Zeroth order

In the zeroth-order finite-temperature perturbation theory, the energy of each state is the sum of the energies \(\epsilon_p\) of orbitals occupied by electrons plus the nuclear-repulsion energy, \(E_{\text{nuc}}\). The additivity of the state energies simplifies \(\Omega\) and \(U\) into the forms

\[
\begin{align*}
\Omega^{(0)} &= E_{\text{nuc}} + \frac{1}{\beta} \sum_p \ln f_p^+, \quad (6) \\
U^{(0)} &= E_{\text{nuc}} + \sum_p \epsilon_p f_p^- 
\end{align*}
\]

where \(p\) runs over all spin-orbitals spanned by the basis set, \(f_p^+ = [1 + \exp(\beta(\epsilon_p - \mu^{(0)}))]^{-1}\) is the Fermi–Dirac occupancy, and \(f_p^- = 1 - f_p^+\) is the Fermi–Dirac vacancy. Superscript ‘(0)’ denotes a zeroth-order quantity. The chemical potential, \(\mu^{(0)}\), is determined by solving

\[
\bar{N} = \sum_p f_p^+. \quad (8)
\]

There is no question whatsoever about the validity of this Fermi–Dirac theory for a system with additive state energies. Table II attests to the numerically exact agreement between the analytical (Fermi–Dirac) and numerical (\(\lambda\)-variation) values of \(\Omega^{(0)}\) and \(U^{(0)}\) at all temperatures. The agreement also underscores the validity of comparison and of thermodynamics applied to a gas of noninteracting, identical molecules.

### B. First order

The first-order finite-temperature perturbation correction to \(\Omega\) is given\(^{3,4,7,15,19}\) as

\[
\Omega^{(1)}_C = \sum_p F_{pp}(T) f_p^- - \frac{1}{2} \sum_{p,q} \langle pq|pq \rangle f_p^- f_q^- 
\]

where \(\langle pq|pq \rangle\) denotes an anti-symmetrized two-electron integral and

\[
F_{pq}(T) = H_{pq}^{\text{core}} + \sum_r \langle pr|qr \rangle f_r^- - \epsilon_p \delta_{pq}, \quad (10)
\]

which is the thermal shift of the Fock matrix.

We place subscript ‘C’ (standing for the conventional finite-temperature theory) to distinguish this from the true first-order correction \(\Omega^{(1)}\) obtainable numerically from the \(\lambda\)-variation method. Across textbooks and research articles, there seems general agreement about the right-hand-side expression, but there is much confusion over which thermodynamic property it corresponds to. Blaizot and Ripka, Thouless, and Thouless, for instance, clearly assign it to a correction to the grand potential, whereas Mattuck\(^4\) e.g., Eq. (14.48) in page 249) and Fetter and Walecka\(^\text{4}\) e.g., Eq. (27.15) in page 258) seem to relate it to an internal energy and add it to \(U^{(0)}\) of Eq. (7) to obtain an energy expression isomorphic to the HF energy at \(T = 0\). Table III shows that \(\Omega^{(1)}_C\) disagrees with either \(\Omega^{(1)}\) or \(U^{(1)}\) determined by the benchmark \(\lambda\)-variation method at high temperatures, implying that the first-order formula \(\text{Eq. (9)}\) is incorrect and corresponds to neither the grand potential nor the internal energy.

The conventional theory is incorrect because it neglects the fact that \(\mu\) varies with \(\lambda\) to maintain the average number of electrons at \(\bar{N}\) at all \(\lambda\) (see the next paragraph). Table IV shows that such variations are significant, reflected by nonzero values of \(\mu^{(1)}\) and \(\mu^{(2)}\). Only at \(T = 0\), \(\Omega^{(1)} = U^{(1)}\) as both \(\mu^{(1)}\) and \(S^{(1)}\) vanish (and generally \(\Omega^{(1)} = U^{(1)} - TS^{(1)} - \mu^{(1)}\bar{N}\)), as seen in Table V. In fact, in both low- and high-temperature limits, \(S\) vanishes (\(n \geq 1\)) analytically, which was confirmed numerically by the \(\lambda\)-variation method. However, at higher temperatures, owing to the neglect of the variation in \(\mu\), \(\Omega^{(1)}_C\) is actually closer to \(U^{(1)}\) than \(\Omega^{(1)}\).

White and Chan\(^{19}\) showed that \(\Omega^{(1)}_C\) agrees numerically exactly with the \(\lambda\)-variation \(\Omega^{(1)}\) obtained by holding \(\mu\) fixed at \(\bar{N}\) or some other arbitrary value (such as 0 \(E_h\)), which we numerically reproduced. Such corrections are not a part of a perturbation series convergent at the exact limit, i.e., thermal FCI with full perturbation strength (\(\lambda = 1\)). The only situation in which the series does converge at the exact limit is when one somehow knows the exact \(\mu\) value (at \(\lambda = 1\)) and uses it in the zeroth-order Hamiltonian (or the Fermi–Dirac functions). This defeats the purpose of a perturbation theory because the exact \(\mu\) value needs to be obtained by solving Eq. (3) for a given average number of electrons, \(\bar{N}\), by the very thermal FCI procedure with \(\lambda = 1\). Nor is such a perturbation theory useful if \(\mu\) is chosen arbitrarily at the expense of allowing \(\bar{N}\) to fluctuate. In a solid, liquid, or gas, \(\bar{N}\) is usually fixed at the value that maintains overall charge neutrality, without
TABLE I. Comparison of the analytical [Eqs. (6) and (7)] and numerical (λ-variation) zeroth-order grand potential (Ω(0)) and internal energy (U(0)) as a function of temperature (T) for the hydrogen fluoride molecule (0.9168 Å) in the STO-3G basis set.

| T/K | Analytical [Eq. (6)] | Numerical [Eq. (1)] | Analytical [Eq. (7)] | Numerical [Eq. (1)] |
|-----|----------------------|----------------------|----------------------|----------------------|
| 10^3 | 53.41122             | 53.41122             | -52.57490            | -52.57490            |
| 10^4 | 53.51172             | 53.51172             | -52.57490            | -52.57490            |
| 10^5 | 55.63653             | 55.63653             | -52.01660            | -52.01660            |
| 10^6 | 105.94707            | 105.94707            | -50.59635            | -50.59635            |
| 10^7 | -686.7029            | -686.7029            | -45.78913            | -45.78913            |
| 10^8 | -6804.938            | -6804.938            | -42.36405            | -42.36405            |
| 10^9 | -68084.45            | -68084.45            | -41.94527            | -41.94527            |

a Recalculated based on the formula and data reported originally by White and Chan.[12]

TABLE II. Comparison of the analytical [Eq. (9)] and numerical (λ-variation) first-order grand potential (Ω(1)) and internal energy (U(1)) as a function of temperature (T) for the hydrogen fluoride molecule. The numerical (not analytical) data are the correct benchmark.

| T/K | Analytical [Eq. (9)] | Numerical [Eq. (1)] | Analytical [Eq. (7)] | Numerical [Eq. (1)] |
|-----|----------------------|----------------------|----------------------|----------------------|
| 10^3 | -45.99586            | -45.99586            | -45.99586            | -45.99586            |
| 10^4 | -45.99586            | -45.99586            | -45.99586            | -45.99586            |
| 10^5 | -46.02032            | -46.02032            | -45.94786            | -45.94786            |
| 10^6 | -46.21519            | -46.21519            | -46.17665            | -46.17665            |
| 10^7 | -46.18020            | -46.18020            | -46.23554            | -46.23554            |
| 10^8 | -46.10675            | -46.10675            | -46.11803            | -46.11803            |
| 10^9 | -46.09626            | -46.09626            | -46.09746            | -46.09746            |

TABLE III. Perturbation corrections to the chemical potential as a function of temperature (T) obtained by the λ-variation method for the hydrogen fluoride molecule.

| T/K | µ(0)/E_b | µ(1)/E_b | µ(2)/E_b |
|-----|----------|----------|----------|
| 10^3 | 0.083631 | 0.000000 | 0.041801 |
| 10^4 | 0.093681 | 0.000000 | 0.041510 |
| 10^5 | 0.272233 | -0.07188 | 0.231983 |
| 10^6 | 3.961266 | -0.16895 | 0.085092 |
| 10^7 | 47.149730| -0.29810 | 0.017745 |
| 10^8 | 505.060542| -0.41220 | 0.002486 |
| 10^9 | 5092.053478| -0.426987| 0.000257 |

a It tends to the midpoint of the highest occupied and lowest unoccupied orbital energies at T → 0.[12]

TABLE IV. Perturbation corrections to the entropy (S) as a function of temperature (T) obtained by the λ-variation method for the hydrogen fluoride molecule.

| T/K | S(0)/k_B | S(1)/k_B | S(2)/k_B |
|-----|----------|----------|----------|
| 10^3 | 0.000000 | 0.000000 | 0.000000 |
| 10^4 | 0.000003 | 0.000003 | 0.000003 |
| 10^5 | 2.834407 | 0.228809 | 1.136956 |
| 10^6 | 4.969719 | 0.012169 | 0.033614 |
| 10^7 | 5.349785 | -0.001748| 0.000413 |
| 10^8 | 5.406003 | -0.000036| 0.000008 |
| 10^9 | 5.406727 | 0.000000 | 0.000000 |

C. Second order

The second-order perturbation correction at a nonzero temperature[20,7,15,19] is given by

$$\Omega^{(2)}_{C1} = \frac{1}{4} \sum_{D>0} |\langle pq|rs\rangle|^2 f_p^* f_q^* f_r f_s \left( \epsilon_s + \epsilon_q - \epsilon_p - \epsilon_f \right) \frac{\beta}{8} \sum_{D>0} |\langle pq|rs\rangle|^2 f_p^* f_q^* f_r f_s$$

where D ≠ 0 (D = 0) indicates the summation is limited to the summands of which \( \epsilon_s + \epsilon_q - \epsilon_p - \epsilon_f \) is nonzero (zero).

Kohn and Luttinger[14] pointed out that there emerges an additional (“anomalous”) term in the second-order correction at T > 0, which is identified as the non-HF term in second-order Møller–Plesset perturbation theory. Adding this to the above, the second-order correction to the grand potential becomes[15,19]

$$\Omega^{(2)}_{C2} = \Omega^{(2)}_{C1} + \sum_{D>0} |F_{pq}(T)|^2 f_p^* f_q \left( \epsilon_q - \epsilon_p \right) \left( \epsilon_q - \epsilon_p \right)$$

where D ≠ 0 (D = 0) excludes (includes only) the summands with \( \epsilon_q - \epsilon_p = 0 \).

We proposed[20] yet another pair of second-order corrections which thermodynamics itself may break down.[20] The conventional finite-temperature perturbation theory is incorrect as it neglects to expand µ in a perturbation series and holds it fixed at an arbitrarily chosen value, thereby failing to converge to the exact limit, unless the exact µ is known a priori.

The change in grand potential from the zeroth-order theory to finite-temperature HF theory (not shown) is found to be numerically much closer but not identical to Ω(1) from our λ-variation calculation. This is because both include a thermal correction to µ, although not in the same fashion.
to the internal energy:

\[
U^{(2)}_{R1} = \frac{1}{4} \sum_{p,q,r,s} \langle pq|rs \rangle \left( f_{r} f_{s} f_{p} f_{q} - f_{r} f_{s} f_{p} f_{q} - f_{r} f_{s} f_{p} f_{q} - f_{r} f_{s} f_{p} f_{q} \right),
\]

\[
U^{(2)}_{R2} = \bar{U}^{(2)}_{R1} + \sum_{p,q} |f_{p} f_{q}|^{2} f_{r} f_{s} f_{p} f_{q} - f_{r} f_{s} f_{p} f_{q},
\]

which differ from the conventional formula in that the temperature effect is applied symmetrically on the interactions in the numerators and denominators. Divergent summands generally do not occur.

Table V shows unequivocally that all of the second-order formulas tested here are incorrect; none of them is a part of the converging perturbation series to the thermal FCI limits.

To be specific, \( \Omega^{(2)} \) does not agree with the benchmark \( \Omega^{(2)} \) values from the \( \lambda \)-variation method at any temperature, but instead tends to agree with \( U^{(2)} \) at low temperatures (which is expected from its mathematical form, but is still incorrect). \( \Omega^{(2)}_{C2} \) displays essentially the same behavior as \( \Omega^{(2)}_{C1} \) and does not agree with benchmark \( \Omega^{(2)} \) at any temperature.

White and Chan\cite{19} showed that \( \Omega^{(2)}_{C2} \) also agrees with the \( \lambda \)-variation \( \Omega^{(2)} \) only when \( \mu \) is held fixed at a constant (such as \( \mu^{(0)} \) in their calculations), which we reproduced. Therefore, the conventional second-order formula, \( \Omega^{(2)}_{C2} \), is again lacking in the sense that it is not a part of a perturbation series converging at the exact \( \lambda = 1 \) limit, where \( \mu \) is no longer \( \mu^{(0)} \). In other words, the conventional theory incorrectly assumes or imposes \( \mu^{(n)} = 0 \) \((n \geq 1)\). In fact, Table III shows that even at the lowest temperature tested \((T = 10^{3} \text{ K})\), \( \mu^{(2)} \) has a large value of 0.041801 \( E_{h} \), which explains the large difference between \( \Omega^{(2)} \) and \( U^{(2)} \), which are related to each other by the formula: \( \Omega^{(2)} = U^{(2)} - T S^{(2)} - \mu^{(2)} N \) \((\text{note } S^{(2)} = 0 \text{ and } N = 10)\). As a result of the faulty assumption \( \mu^{(2)} = 0 \), the conventional formula \( \Omega^{(2)}_{C2} \) and the \( \lambda \)-variation result of White and Chan at \( T = 10^{3} \text{ K} \) are far from the true \( \Omega^{(2)} \) and are closer to \( U^{(2)} \) (or to some arbitrary value if the fixed value of \( \mu \) was chosen arbitrarily). The persistent confusion about the identity of \( \Omega^{(n)}_{C} \) may stem partly from the fact that a large portion of the difference between \( \Omega^{(n)} \) and \( U^{(n)} \) arising from nonzero \( \mu^{(n)} \) is missing in \( \Omega^{(n)}_{C} \).

We also note that the sum of our benchmark \( \Omega^{(n)} \) (or any other quantity) over \( n = 0, 1, 2, 3 \) gives a close approximation to \( \Omega \) obtained by thermal FCI \((\lambda = 1)\) at each temperature. Such convergence is not expected in conventional finite-temperature perturbation theory or White and Chan’s \( \lambda \)-variation calculation, unless the exact \( \mu \) is known in advance and used in their zeroth-order Hamiltonian. It is rather doubtful if such a perturbation theory has much utility.

Our alternative formulas, \( U^{(2)}_{R1} \) and \( U^{(2)}_{R2} \), do not match \( U^{(2)} \) except at low temperatures and is completely different from \( \Omega^{(2)} \) at any temperatures studied. Therefore, the renormalized finite-temperature perturbation theory\cite{20} is also incorrect.

The self-consistent second-order Green’s function data at a nonzero temperature reported by Welden et al.\cite{21} are numerically more compatible (but still not in agreement) with our \( \lambda \)-variation results at the same order. This is because their calculation uses the value of \( \mu \) that guarantees the correct number of electrons in each iteration.

### III. CONCLUSIONS

The benchmark \( \lambda \)-variation calculations showed that the finite-temperature first- and second-order many-body perturbation theory formalisms proposed so far are incorrect. Exact numerical agreement at the zeroth order justifies the comparison itself. The conventional theory fails to account for a continuous change in \( \mu \) as the perturbation strength \( \lambda \) is raised to unity, whereupon the system becomes the real one of interest with the correct average number of electrons. The conventional theory does not converge at this exact limit unless the exact \( \mu \) is known in advance. While it may be argued that such a theory still has some use, the correct finite-temperature perturbation theory that expands both \( \Sigma \) and \( \mu \) in converging perturbation series should be developed for more realistic physics.

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