The Kohn–Luttinger conundrum redux: Failure of finite-temperature many-body perturbation theory at low temperatures

So Hirata

Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

(Dated: June 2, 2020)

It is shown analytically and numerically that the finite-temperature many-body perturbation theory in the grand canonical ensemble has zero radius of convergence at zero temperature when the energy of the ground state as a function of the perturbation strength either touches or crosses the energy function of an excited state. Contrary to earlier assertions concerning the role played by the chemical potential, this nonconvergence, first suspected by W. Kohn and J. M. Luttinger, is caused by the nonanalytic nature of the Boltzmann factor \( e^{-E/T} \) at \( T = 0 \), plaguing the canonical ensemble also. These findings reveal serious flaws in quantum field theory for thermodynamics, which are deeply rooted in the fundamental limitation of the power series expansion of pathlogical functions and are hard to resolve.

I. INTRODUCTION

In 1960, Kohn and Luttinger\(^\text{1} \) discovered a mathematical inconsistency between the finite-temperature perturbation theory\(^\text{2–5} \) and its zero-temperature counterpart\(^\text{6–9} \). They found that the second-order grand potential \( \Omega^{(2)} \) at \( T = 0 \) and second-order energy \( E^{(2)} \) of many-body perturbation theory (MBPT)\(^\text{10–13} \) can differ from each other by divergent “anomalous” contributions for a degenerate, nonisotropic reference wave function. On this basis, they concluded that “the BG [Brueckner–Goldstone perturbation] series is therefore in general not correct.”\(^\text{14} \) For isotropic systems (i.e., systems with spherical symmetry) such as a homogeneous electron gas (HEG), they showed that the difference is exactly compensated for by the terms containing the chemical potential \( \mu \). This partial solution was generalized by Luttinger and Ward\(^\text{14} \) and by Balian, Bloch, and De Dominicis\(^\text{2} \).

The question posed by Kohn and Luttinger\(^\text{1} \) and the partial solution for isotropic systems are, however, not entirely satisfactory for the following three reasons: First, \( \Omega \) and \( E \) are separate thermodynamic functions and are not expected to agree with each other at \( T = 0 \); instead, the internal energy \( U \) at \( T = 0 \) is more rigorously compared with \( E \). Second, perturbation correction formulas for \( U \) were unknown until recently\(^\text{15,16} \) as the perturbation theory for \( \Omega \) of Bloch and coworkers\(^\text{17} \) described in many contemporary textbooks\(^\text{17,18} \) and an excellent review\(^\text{19} \) was plagued by an unequal treatment\(^\text{17,18} \) of \( \Omega, U, \) and \( \mu \). Third, \( E^{(2)} \) of MBPT may be already divergent in a degenerate, extended system such as a HEG, obscuring the comparison with the finite-temperature perturbation theory; \( E^{(2)} \) for a degenerate molecule evaluated by the Hirschfelder–Certa degenerate perturbation theory (HCPT)\(^\text{20} \) should be used as the correct zero-temperature limit, which is always finite.

In short, the inconsistency may persist for nonisotropic degenerate systems, implying that the finite-temperature perturbation theory is possibly still incorrect in a general sense.

Recently, we introduced\(^\text{15,16} \) a finite-temperature perturbation theory for electrons in the grand canonical ensemble, in which \( \Omega, U, \) and \( \mu \) are expanded in power series on an equal footing. Two types of analytical formulas were obtained for up to the second-order corrections to these quantities in a time-independent, algebraic (nondiagrammatic) derivation: sum-over-states (“SoS”) and sum-over-orbitals (“reduced”) formulas. They reproduce numerically exactly the correct benchmark data\(^\text{21} \) obtained as the \( \lambda \)-derivatives of the corresponding thermodynamic functions evaluated by the thermal full-configuration-interaction (FCI)\(^\text{22} \) with a perturbation-scaled Hamiltonian \( \hat{H} = \hat{H}_0 + \lambda \hat{V} \). They permit a rigorous comparison of the zero-temperature limit of \( U^{(n)} \) against \( E^{(n)} \) of HCPT both analytically and numerically. We can repeat this comparison for the finite-temperature perturbation theory in the canonical ensemble, whose SoS formulas for the Helmholtz energy \( F \) and internal energy \( U \) have been reported up to the third order\(^\text{19} \).

In what follows, we will show analytically and numerically that for an ideal gas of identical molecules with a degenerate ground state \( U^{(1)} \) converges at a finite, but wrong zero-temperature limit that differs from \( E^{(1)} \) of HCPT for the true ground state, whereas the zero-temperature limit of \( U^{(2)} \) is divergent and again wrong. While the chemical potentials \( \mu^{(n)} \) \((1 \leq n \leq 2)\) converge at the correct zero-temperature limits, the grand potentials \( \Omega^{(n)} \) \((1 \leq n \leq 2)\) display the same nonconvergent behaviors as \( U^{(n)} \). Taken together, these findings establish that the original concern of Kohn and Luttinger is well founded and the finite-temperature perturbation theory in the grand canonical ensemble is indeed incorrect; beyond the zeroth-order Fermi–Dirac theory, the perturbation theory for \( U \) and \( \Omega \) has zero radius of convergence at \( T = 0 \) and becomes increasingly inaccurate at lower temperatures whenever the reference wave function differs qualitatively from the true ground state.

The root cause of the failure does not have much to do with the chemical potential \( \mu \) (as implied by Kohn and Luttinger\(^\text{1} \) by Luttinger and Ward\(^\text{14} \) and by Balian \textit{et al.}\(^\text{2} \)) but with the smooth nonanalytic nature of the Boltzmann factor \( e^{-E/\lambda T} \) at \( T = 0 \). The nonconvergence, therefore, persists in the canonical ensemble also\(^\text{19} \) which does not involve \( \mu \). It casts doubt on the soundness of perturbation theories for thermodynamics or, by extension, of quantum field theory (QFT) in certain applications, which also suffers from more notorious divergence problems in its application to quantum electrodynamics.\(^\text{23} \)
II. ILLUSTRATIONS

Before going into the analytical formulas of \( U^{(n)} \) and their numerical behavior for a molecule in the next sections, we will use three simple models to illustrate the essence of the failure of the perturbation theory. Nonconvergence is ultimately caused by the nonanalytic nature of \( U \) at \( T = 0 \) for a degenerate reference or by a qualitatively wrong reference (zeroth-order) wave function, both preventing \( U \) from being expanded in a converging power series. This is ultimately ascribed to the nonanalytic nature of \( e^{-E/\beta T} \) at \( T = 0 \), a problem unseen in the zero-temperature perturbation theory\(^{24}\) or variational finite-temperature theory\(^{25}\) but reminiscent of the theory of superconductivity whose interaction operator has the same two-state system, whose energies are expanded in a converging power series. This is ultimately ascribed to the nonanalytic nature of \( e^{-E/\beta T} \) at \( T = 0 \), a problem unseen in the zero-temperature perturbation theory\(^{24}\) or variational finite-temperature theory\(^{25}\) but reminiscent of the theory of superconductivity whose interaction operator has the similar form, \( \delta e^{-1/\beta T} \). Therefore, this is caused by a fundamental mathematical limitation in the power series expansions of pathological functions, which lies at the core of perturbation theory (and QFT by extension) and may be hard to eliminate or resolve.

A. Nondegenerate, correct reference

Let us consider a function \( U(T) \), which is a weighted average of \( E \) with an exponential weight:

\[
U(T) = \frac{E_0 e^{-E_0/T} + E_1 e^{-E_1/T}}{e^{-E_0/T} + e^{-E_1/T}}. \tag{1}
\]

This function is meant to capture the essential mathematical features of the internal energy (thermal average of energy) \( U \) as a function of temperature \( T \) in the canonical ensemble of a two-state system with energies \( E_0 \) and \( E_1 \). Let \( E_0 \) and \( E_1 \) be functions of \( \lambda \) given by

\[
E_0 = -1.1 - 0.1 \lambda - 0.1 \lambda^2, \tag{2}
\]

\[
E_1 = 0.9 + 0.1 \lambda + 0.1 \lambda^2, \tag{3}
\]

which are plotted as a function of \( \lambda \) in Fig. 1. They simulate the energies of the two states as a function of the perturbation strength \( \lambda \), which are nondegenerate and correct at the zeroth order (at \( \lambda = 0 \)). By “correct,” we mean that the energy ordering of the ground state and first excited state is unchanged in \( 0 \leq \lambda \leq 1 \), with the zeroth-order ground state \( (E_0 = -1.1) \) and excited state \( (E_1 = 0.9) \) smoothly morphing into the true ground state \( (E_0 = -1.3) \) and true excited state \( (E_1 = -0.7) \), respectively, in the fully interacting (physical) limit of \( \lambda = 1 \).

A Taylor series of \( U \) at \( \lambda = 0 \) is

\[
U(T) = U^{(0)} + U^{(1)} \lambda + U^{(2)} \lambda^2 + \ldots \tag{4}
\]

\[
= -0.9 e^{0.9/T} + 1.1 e^{1.1/T} -0.04 e^{2/1/T} + 0.17 e^{1.8/T} - 0.1 T e^{2.2/T} + \ldots \tag{5}
\]

Figure 1 plots \( U \) with \( \lambda = 1 \) (i.e., in the real physical situation) as a function of \( T \) as well as its zeroth- through third-order Taylor-series approximations. Exact \( U \) is a smooth function starting with \( E_0 = -1.3 \) at \( T = 0 \) (where 100% weight is on the ground state), while its high-\( T \) limit is the simple average of \( E_0 \) and \( E_1 \) and is equal to \(-1 = (-1.3 - 0.7)/2\).

The Taylor-series approximations to \( U(T) \) are finite and convergent at the exact \( U(T) \) everywhere including \( T = 0 \). Reflecting the fact that \( E_0 \) is a quadratic function of \( \lambda \) and \( U(0) = E_0 \), the second- and higher-order Taylor-series approximations of \( U(T) \) become exact at \( T = 0 \). To put it in the physics context, a perturbation theory for the internal energy \( U \) is valid at all temperatures and converges at the correct zero-temperature limit, \( E_0 \), if the reference chosen is nondegenerate and correct.

B. Degenerate reference

Next, we consider a similar function \( U'(T) \),

\[
U'(T) = \frac{E'_0 e^{-E'_0/T} + E'_1 e^{-E'_1/T}}{e^{-E'_0/T} + e^{-E'_1/T}}, \tag{6}
\]

with

\[
E'_0 = -1 - 0.1 \lambda - 0.2 \lambda^2, \tag{7}
\]

\[
E'_1 = -1 + 0.1 \lambda + 0.2 \lambda^2, \tag{8}
\]

which are plotted in Fig. 2. At \( \lambda = 1 \), \( E'_0 = E_0 = -1.3 \) and \( E'_1 = E_1 = 0.7 \), and therefore \( U'(T) \equiv U(T) \). Here, however, we elect to write \( E'_0 \) and \( E'_1 \) as functions of \( \lambda \) that start from the same value of \(-1.0 \) at \( \lambda = 0 \). Hence, \( U'(T) \) is meant to model the internal energy \( U \) in the canonical ensemble of the same two-state system, whose energies are expanded in a perturbation series with a degenerate reference. More precisely, a “degenerate” reference means that the degree of degeneracy of the true ground state \( (E_0) \) is partially or fully lifted as \( \lambda = 0 \to 1 \).

A Taylor expansion of \( U'(T) \) with respect to \( \lambda \) is

\[
U'(T) = U'^{(0)} + U'^{(1)} \lambda + U'^{(2)} \lambda^2 + U'^{(3)} \lambda^3 + \ldots \tag{9}
\]

\[
= -1 + 0.\lambda - \frac{0.01}{T} \lambda^2 - \frac{0.04}{T} \lambda^3 + \ldots \tag{10}
\]

Figure 2 plots \( U'(T) \) with \( \lambda = 1 \) as a function of \( T \) as well as its zeroth- through third-order Taylor-series approximations. \( U'(T) \) behaves exactly the same way as \( U(T) \) because they define the identical function at \( \lambda = 1 \); \( U'(T) \) is a smooth function going from \(-1.3 \) at \( T = 0 \) to \(-1 \) as \( T \to \infty \).

The zeroth- and first-order approximations \( U'^{(0)} \) and \( U'^{(0)} + U'^{(1)} \) are constant \((-1) \) and finite everywhere, but the second- and all higher-order approximations are divergent at \( T = 0 \). Unlike \( U(T) \), the radius of convergence of the Taylor series of \( U' \) is zero at \( T = 0 \), implying that \( U' \) is a smooth nonanalytic function of \( \lambda \), which are infinitely differentiable yet not expandable in a Taylor series in \( \lambda \) at \( T = 0 \). To put this in the language of physics, a perturbation theory of the internal energy \( U \) is always divergent at \( T = 0 \) and increasingly inaccurate at low \( T \), when the reference is degenerate.
C. Nondegenerate, incorrect reference

As the third case, we consider the function,

$$U''(T) = \frac{E''_0 e^{-E''_0/T} + E''_1 e^{-E''_1/T}}{e^{-E''_0/T} + e^{-E''_1/T}}.$$  \hspace{1cm} (11)

with

$$E''_0 = -0.9 - 0.2\lambda - 0.2\lambda^2,$$  \hspace{1cm} (12)

$$E''_1 = -1.1 + 0.2\lambda + 0.2\lambda^2,$$  \hspace{1cm} (13)

as drawn in Fig. 3. Since $E''_0 = E_0$ and $E''_1 = E_1$ at $\lambda = 1$, $U''(T)$ is again identical to $U(T)$ or $U'(T)$ at $\lambda = 1$, but the ordering of $E''_0$ and $E''_1$ reverses at $\lambda \approx 0.366$, making $E''_1$ the more negative of the two at $\lambda = 0$. Physically, this corresponds to a perturbation theory with a qualitatively wrong reference, which is the ground state only in the zeroth-order description ($\lambda = 0$), but it actually evolves into the first excited state in the fully interacting limit ($\lambda = 1$).

A Taylor expansion of $U''(T)$ around $\lambda = 0$ reads

$$U''(T) = U''(0) + U''(1)\lambda + U''(2)\lambda^2 + \ldots$$  \hspace{1cm} (14)

$$= -0.9e^{0.9/T} - 1.1e^{1.1/T} + 0.08e^{2.1/T} - 0.2Te^{1.8/T} + 0.2Te^{2.2/T} + \ldots$$  \hspace{1cm} (15)

the various truncations of which are plotted in Fig. 3 as a function of $T$. They remain finite, but converge at $E''_1 = -0.7$ at $T = 0$ (at the second and higher orders) instead of the correct $T = 0$ limit of $E''_0 = -1.3$.

Therefore, $U''(T)$ is also a smooth nonanalytic function that has zero radius of convergence at $T = 0$. A perturbation theory for the internal energy becomes increasingly inaccurate at low temperatures and fails to converge at the zero-temperature perturbation theory when the reference is qualitatively wrong and does not smoothly transform into the true ground state as $\lambda = 0 \rightarrow 1$. 

FIG. 1. (a) $E_0$ and $E_1$ as a function of $\lambda$. (b) $U$ as a function of $T$ at $\lambda = 1$ and its Taylor-series approximations.

FIG. 2. (a) $E'_0$ and $E'_1$ as a function of $\lambda$. (b) $U'$ as a function of $T$ at $\lambda = 1$ and its Taylor-series approximations.
III. ZERO-TEMPERATURE LIMIT OF $U$

The internal energy $U$ in the grand canonical ensemble of electrons is the thermal average of energy,

$$U = \sum_i E_i e^{-\beta E_i + \beta \mu N_i} / \sum_i e^{-\beta E_i + \beta \mu N_i},$$

where $I$ runs over all states with any number of electrons, $\beta = (k_B T)^{-1}$, $\mu$ is the chemical potential, and $E_i$ and $N_i$ are respectively the exact (FCI) energy and number of electrons in the $I$th state.

A perturbation expansion of $U$ means that

$$U = U^{(0)} + \lambda U^{(1)} + \lambda^2 U^{(2)} + \lambda^3 U^{(3)} + \ldots,$$

with

$$U^{(n)} = \frac{1}{n!} \left. \frac{\partial^n U(\lambda)}{\partial \lambda^n} \right|_{\lambda = 0},$$

where $U(\lambda)$ is given by Eq. (16) with $E_i$ being the $I$th eigenvalue of a perturbation-scaled Hamiltonian, $\hat{H}_0 + \lambda \hat{V}$.

Carrying through the $\lambda$-differentiation of Eq. (16), we obtain the SoS analytical formulas for the zeroth-, first- and second-order perturbation corrections of $U$ as

$$U^{(0)} = \langle E_1^{(0)} \rangle,$$

$$U^{(1)} = \langle E_1^{(1)} \rangle - \beta \langle F_1^{(0)} F_1^{(1)} \rangle + \beta \langle F_1^{(0)} \rangle \langle F_1^{(1)} \rangle,$$

$$U^{(2)} = \langle E_1^{(2)} \rangle - \beta \langle F_1^{(0)} F_1^{(2)} \rangle + \beta \langle F_1^{(1)} \rangle \langle F_1^{(1)} \rangle - \langle F_1^{(0)} \rangle \langle F_1^{(2)} \rangle + \frac{\beta^2}{2} \langle F_1^{(0)} \rangle^2 \left( - \frac{\beta^2}{2} \langle F_1^{(0)} \rangle \langle F_1^{(1)} \rangle \right)^2 - \beta \langle F_1^{(0)} \rangle \langle F_1^{(1)} \rangle \langle F_1^{(1)} \rangle^2 + \beta^2 \langle F_1^{(0)} \rangle^2 \langle F_1^{(1)} \rangle^2,$$

where $\langle X_i \rangle$ stands for the zeroth-order thermal average,

$$\langle X_i \rangle = \sum_i X_i e^{-\beta E_i^{(0)}} / \sum_i e^{-\beta E_i^{(0)}},$$

with

$$F_1^{(n)} = E_1^{(n)} - \mu^{(n)} N_1.$$ 

Here, $\mu^{(n)}$ is the $n$th-order correction to the chemical potential, discussed fully in the next section, which is shown to be finite at any temperature for $n \leq 2$.

On the other hand, $E_1^{(n)}$ is identified as the $n$th-order HCPT correction to the $I$th-state energy of a degenerate and nondegenerate reference, distinguished from the Møller–Plesset perturbation theory (MPPT). Since many zeroth-order (excited, ionized, etc.) states are degenerate, it is imperative to use a degenerate perturbation theory such as HCPT that computes energy corrections that match the definition:

$$E_1^{(n)} = \frac{1}{n!} \left. \frac{\partial^n E_1(\lambda)}{\partial \lambda^n} \right|_{\lambda = 0},$$

which remains finite for any state. In contrast, a nondegenerate perturbation theory such as MPPT diverges for a degenerate reference and is, therefore, inappropriate here, although HCPT reduces to MPPT for a nondegenerate reference. In this article, the acronyms MPPT, MBPT, and (diagrammatic) BG perturbation theories are used interchangeably, but in distinction to HCPT.

The zero-temperature limit of $U$ is $E_0$ (the FCI energy for the true ground state) according to Eq. (16), where the states are numbered in the ascending order of the FCI energy. Then, the correct zero-temperature limit of $U^{(n)}$ should be $E_0^{(n)}$, the latter being defined by HCPT for the true ground state according to FCI. We propose to refine the question raised by Kohn and Luttinger as follows:

$$\lim_{T \to 0} U^{(n)} = E_0^{(n)},$$

in a molecule for $0 \leq n \leq 2$, where $E_0^{(n)}$ is the $n$th-order HCPT energy correction for the lowest-energy neutral state of the molecule according to FCI. The revised question eliminates many of the confusions sown by the original question. First, we are no longer comparing the zero-temperature limit of $\Omega^{(n)}$
with $E^{(n)}_0$, which, even in the most ideal circumstance, differ from each other by $\mu^{(n)}(N_l)$, which is generally nonzero at $T = 0$. Second, $E^{(n)}_0$ is identified as the $n$th-order HCPT correction, and not as the diagrammatic BG perturbation correction or the $n$th-order MPPT correction, which is ill defined for a degenerate reference. Third, we apply the perturbation theory to an ideal gas of finite-sized molecules with a degenerate or nondegenerate reference (whose $E^{(n)}_0$ and $E_0$ are always finite) instead of a specific example of HEG, whose $\Omega^{(2)}$ and $E^{(2)}_0$ (according to the BG perturbation theory) are divergent for a multitude of reasons.

A. Nondegenerate, correct reference

Let us first establish analytically that the finite-temperature perturbation theory passes the Kohn–Luttinger test [Eq. (25)] for a nondegenerate, correct reference. By ‘correct’, we mean that the reference ($\lambda = 0$) wave function morphs into the true ground state of the neutral molecule as per FCI ($\lambda = 1$) as $\lambda = 0 \to 1$; there is no contact or crossing of the ground- and excited-state energies as functions of $\lambda$ in $0 \leq \lambda \leq 1$. Under these conditions, we can identify one and only one nondegenerate neutral reference state whose $E^{(n)}_0$ is the most negative. Then, each zeroth-order thermal average ($X_I$) reduces to $X_0$ at $T = 0$. Also, a thermal average of products $\langle X_1 Y_I \rangle$ becomes the single product $X_0 Y_0$ for the ground state at $T = 0$. Therefore, we have

$$\lim_{T \to 0} U^{(0)} = E^{(0)}_0,$$

$$\lim_{T \to 0} U^{(1)} = E^{(1)}_0 - \beta F^{(0)}_0 F^{(1)}_0 + \beta E^{(0)}_0 F^{(1)}_0$$

$$= E^{(1)}_0,$$

$$\lim_{T \to 0} U^{(2)} = E^{(2)}_0 - \beta F^{(0)}_0 F^{(1)}_0 + \beta E^{(0)}_0 F^{(1)}_0$$

$$- \beta F^{(0)}_0 F^{(2)}_0 + \beta E^{(0)}_0 F^{(2)}_0$$

$$+ \frac{\beta^2}{2} F^{(0)}_0 (F^{(1)}_0)^2 - \frac{\beta^2}{2} F^{(0)}_0 (F^{(1)}_0)^2$$

$$+ \beta^2 F^{(0)}_0 (F^{(1)}_0)^2 + \beta^2 F^{(0)}_0 (F^{(1)}_0)^2$$

$$= E^{(2)}_0,$$

satisfying Eq. (25) for $0 \leq n \leq 2$. These have been numerically verified also. We conclude that the Kohn–Luttinger conundrum does not exist for a nondegenerate, correct reference. This corresponds to the case of Sec. II A.

The internal energy formulas in the canonical ensemble are the same as Eqs. (19)–(21) with each $E^{(n)}_0$ replaced by $E^{(n)}_I$ (in the definition of the thermal average $\langle X_I \rangle$ [Eq. (22)] also). Hence, they also pass the Kohn–Luttinger test [Eq. (25)] for a nondegenerate, correct reference for $0 \leq n \leq 3$.

An obvious issue with the foregoing conclusion is that one cannot know whether a reference is ‘correct’ until the FCI calculation is actually carried out, defeating the purpose of the perturbation theory as a converging approximation. To put it another way, the two cases discussed in Secs. II A and II C cannot be distinguished until the truncation order of the Taylor series reaches infinity.

B. Degenerate and/or incorrect reference

To understand the $T$-dependence of $U$ for a degenerate and/or incorrect reference, it is instructive to first analyze the HCPT energies. This may be facilitated by an example.

Figures 4 and 5 plot the exact (FCI) energies of the sixteen zeroth-order degenerate states of the square-planar $H_4$ molecule (0.8 Å) with the STO-3G basis set. HF stands for the zero-temperature limit of the thermal Hartree–Fock energy, whose wave function is a linear combination of two Slater determinants for the neutral, singlet ground state. MP1 refers to the first-order Möller–Plesset perturbation energy for the single Slater-determinant reference for the neutral, singlet ground state. See footnotes of Table I for more details.
The reduced analytical formula for \( U^{(0)} \) reads,\textsuperscript{15,16}
\[
U^{(0)} = E_{\text{nuc.}} + \sum_i \epsilon_i = E^{(0)}_0,
\]
where ‘occ.’ means that \( i \) runs over spinorbitals occupied in the reference Slater determinant. Therefore, both SoS and reduced analytical formulas for \( U^{(0)} \) reach the correct zero-temperature limit \( E^{(0)}_0 \). This is true even if the reference is incorrect insofar as it is degenerate with the correct reference at the zeroth order (which is the case with our \( \text{H}_4 \) example).

It is concluded that the zeroth-order (Fermi–Dirac) theory is correct at any temperature including \( T = 0 \) for a degenerate, incorrect reference as long as the correct reference belongs to the same zeroth-order degenerate subspace.

This conclusion is verified numerically in Fig. 6, whose selected data are compiled in Table I. For the square-planar \( \text{H}_4 \), which has a degenerate reference, \( U^{(0)} \) converges at its zero-temperature limit of 1.9980 \( E_0 \) at \( T = 10^2 \) K, which is equal to \( E^{(0)}_0 \) according to HCPT and MPPT as well as the corresponding energy component of the finite-temperature HF theory at \( T = 0 \).
is divergent and thus could not equal to the correct zero-temperature limit of the finite-temperature Hartree–Fock theory and is degenerate:

$$T / K$$ | $U^{(0)} / E_b$ | $U^{(1)} / E_b$ | $U^{(2)} / E_b$
---|---|---|---
0 (HCPT) | 1.9980 | −3.7015 | −0.0187
0 (HCPT)² | 1.9980 | −3.6966 | −0.0534
0 (MPPT) | 1.9980 | −3.5818 | −∞
0 (HF) | 1.9980 | −3.3771 | ...
$10^2$ | 1.9980 | −3.3771 | −343.9555
$10^3$ | 1.9980 | −3.3771 | −34.4176
$10^4$ | 1.9980 | −3.3771 | −3.4638
$10^5$ | 2.1568 | −3.3691 | −0.3002
$10^6$ | 3.7079 | −3.4831 | −0.1684

² The correct zero-temperature limit. The Hirschfelder–Certain degenerate perturbation theory for the triplet ground state. The FCI wave function of this state is

$-0.70(1a_1)^2(2e_α)^1(3e_β)^1(4h_1)^0 + 0.70(1a_1)^2(2e_β)^1(3e_α)^1(4h_1)^0.$

³ The Hirschfelder–Certain degenerate perturbation theory for the singlet ground state. The FCI wave function of this state is

$0.57(1a_1)^0(2e_α)^3(4h_1)^0 - 0.57(1a_1)^0(2e_β)^3(3e_α)^0(4h_1)^0 + 0.40(1a_1)^0(2e_α)^3(3e_β)^0(4h_1)^0 + 0.40(1a_1)^0(2e_β)^3(3e_α)^0(4h_1)^0.$

⁴ The Möller–Plesset perturbation theory for the singlet Slater-determinant reference: $(1a_1)^2(2e_α)^3(4h_1)^0.$

⁵ The zero-temperature limit of the finite-temperature Hartree–Fock theory. The wave function is not a single Slater determinant, but is a linear combination of the form

$2^{-1/2}(1a_1)^2(2e_α)^0(4h_1)^0 + 2^{-1/2}(1a_1)^2(2e_β)^0(3e_α)^0(4h_1)^0.$

Let us reproduce the SoS analytical formula of $U^{(1)}$ [Eq. (20)] for the reader’s convenience:

$$U^{(1)} = \langle E_f^{(1)} \rangle - \beta \langle T^{(0)} F_f^{(1)} \rangle + \beta \langle T^{(0)} F_f^{(1)} \rangle F_f^{(1)}.$$

The last two terms are alarming since $\beta \to \infty$ as $T \to 0$. If $\langle T^{(0)} F_f^{(1)} \rangle$ and $\langle T^{(0)} F_f^{(1)} \rangle F_f^{(1)}$ did not cancel with each other exactly at $T = 0$, the zero-temperature limit of $U^{(1)}$ would be divergent and thus could not equal to the correct zero-temperature limit of $E_f^{(1)}$, which is always finite.

As $T \to 0$, each of these thermal averages is dominated by the simple average in the zero-order degenerate subspace sharing the same lowest $F_f^{(0)}$ whose Boltzmann factor is exponentially greater. As discussed above, generally, the degeneracy of $E_f^{(n)}$ is gradually lifted as the perturbation order $n$ is raised and, therefore, the $E_f^{(1)}$ values of the zero-order degenerate states can have a distribution (e.g., Figs. 4 and 5). (The values of $E_f^{(1)}$ can also have a distribution arising from different ionic states.) Then, the sum of the last two terms can be viewed as a covariance (multiplied by $-\beta$) of two distributions, $F_f^{(0)}$ and $F_f^{(1)}$. In this case, however, $F_f^{(0)}$ has the same lowest value for all the zero-order degenerate states and thus zero variance, and, therefore, the covariance is also zero:

$$\text{cov} \left( F_f^{(0)}, F_f^{(1)} \right) = \langle F_f^{(0)} F_f^{(1)} \rangle - \langle F_f^{(0)} \rangle \langle F_f^{(1)} \rangle = 0,$$

at $T = 0$ and, therefore,

$$\lim_{T \to 0} U^{(1)} = \lim_{T \to 0} \langle E_f^{(1)} \rangle = E \left[ E_f^{(1)} \right],$$

where $E \left[ X_I \right]$ stands for the simple average of $X_I$ over the zero-order degenerate states $I$. This limit is finite.

Does this [Eq. (37)] mean that $U^{(1)}$ passes the Kohn–Luttinger test for a degenerate reference? The answer is no because $E_f^{(1)}$ in the zero-order degenerate subspace has a nonzero variance and its simple average differs from (is usually greater than) $E_f^{(0)}$ for the true (FCI) ground state, which is often (but not always) the most negative of $E_f^{(1)}$ in the degenerate subspace and is the correct zero-temperature limit. Hence, we write

$$\lim_{T \to 0} U^{(1)} = E \left[ E_f^{(1)} \right] \neq E_f^{(0)},$$

indicating that although the first-order finite-temperature perturbation theory remains finite and well defined as $T \to 0$, it fails to converge at the correct zero-temperature limit if the degeneracy is partially or fully lifted at the first order of HCPT. The reduced analytical formula of $U^{(1)}$ reads

$$U^{(1)} = \sum_p F_{pp} f_p - \frac{1}{2} \sum_{p,q} \langle pq \rangle \langle pq \rangle f_p f_q - \beta \sum_p F_{pp} e_p f_p f_p^* + \beta \sum_p e_p f_p f_p^*,$$

where $f_p^* = 1 - f_p$ and $F$ is the finite-temperature Fock matrix minus the diagonal zero-temperature Fock matrix,

$$F_{pq} = H_{pq}^{\text{core}} + \sum_r \langle pr \rangle \langle qr \rangle f_r - \delta_{pq} e_p,$$

with $H_{pq}^{\text{core}}$ being the one-electron part of the Fock matrix. The Möller–Plesset partitioning of the Hamiltonian is adopted. The reduced analytical formula of $\mu^{(1)}$ is

$$\mu^{(1)} = \frac{\sum_p F_{pp} f_p f_p^*}{\sum_p f_p f_p^*}.$$
\( F_{pp} = 0 \) at \( T = 0 \) as per its definition [Eq. (40)]. \( E [ \ldots ] \) means the simple average in the zeroth-order degenerate subspace and ‘occ.’ stands for spinorbitals occupied in each of these degenerate Slater determinants.

The penultimate term of Eq. (42) contains

\[
-\beta \sum _{p} \sum _{r} \langle pr | pr \rangle f_r \epsilon _p f_r^\dagger \tag{44}
\]

which is divergent as \( T \to 0 \) and may be viewed as an “anomalous” contribution of Kohn and Luttinger (although the parent term vanishes because \( F_{pp} = 0 \) at \( T = 0 \)). That this is exactly canceled by the corresponding contribution in the last term containing \( \mu^{(1)} \) appears to support the Luttinger–Ward solution even for nonisotropic systems. However, this is not the case and Eq. (43) does not pass the Kohn–Luttinger test [Eq. (25)].

The last expression [Eq. (43)] is identified as the first-order MPPT energy or the thermal HF energy at \( T = 0 \) minus the zeroth-order MPPT energy [12] which generally differs from the first-order HCPT energy [11] if the reference is degenerate. The first-order HCPT energy corrections are the eigenvalues of the perturbation matrix [Eq. (37) of Hirschfelder and Certain [11]] within the zeroth-order degenerate subspace and cannot be expressed in a closed formula such as Eq. (25). The simple average of these eigenvalues can, however, be written in a closed formula [11, 16] which is nothing but Eq. (43), and is usually greater than the eigenvalue for the true (FCI) ground state, which is the correct zero-temperature limit. Therefore, whereas the first-order finite-temperature perturbation theory is not divergent thanks to this cancellation, it still tends to a wrong zero-temperature limit, which is the simple average of the first-order HCPT energy corrections in the zeroth-order degenerate subspace and not the correct limit of the first-order HCPT energy correction for the true ground state. This merely confirms the foregoing conclusion drawn from the SoS formula of \( U^{(1)} \), which is mathematically equivalent to the reduced formula.

According to Table II, the zero-temperature limit of \( U^{(1)} \) in the square-planar \( \text{H}_4 \) is \( -3.3771 \ E_h \) (reached at \( T = 10^2 \) K) and is distinctly higher than the correct zero-temperature limit of \( E^{(1)}_0 = -3.7015 \ E_h \), which is the first-order HCPT energy correction for the neutral triplet ground state, supporting the above conclusion [Eq. (38)] numerically. The comparison furthermore underscores the fact that even if it were not for the degeneracy, \( U^{(1)} \) would not converge at the correct zero-temperature limit of \( E^{(1)}_0 \); rather it would converge at another wrong limit of \( E^{(1)} = -3.6696 \ E_h \), which is the first-order HCPT energy correction for the neutral singlet ground state. This is because the reference wave function in the thermal perturbation calculations in Table II is the finite-temperature HF wave function at \( T = 0 \) for the neutral singlet ground state, which is an overall excited state. Therefore, the nonconvergence in our \( \text{H}_4 \) example originates from the combination of the two causes discussed in Secs. II B and II C, and may be particularly hard to resolve. Figure 6 shows that \( U^{(1)} \) is convergent to a constant at \( T = 0 \), which is distinctly higher than the correct limit of \( E^{(1)}_0 \).

The \( U^{(1)} \) expression in the canonical ensemble [19] is the same as Eq. (35) with every \( F^{(0)}_i \) replaced by \( E^{(0)}_i \) (and also in the definition of the thermal average \( \langle X_i \rangle \) [Eq. (22)]). Therefore, the first-order perturbation theory in the canonical ensemble also fails to converge at the correct zero-temperature limit.

3. \( U^{(2)} \)

The zero-temperature limit of the SoS analytical formula for \( U^{(2)} \) [Eq. (21)] is

\[
\lim _{T \to 0} U^{(2)} = \bar{E} \left[ F^{(2)}_i \right] = -\beta \text{cov} \left( F^{(1)}_i, F^{(1)}_i \right) \tag{45}
\]

where the simple average and covariance are taken over all zeroth-order degenerate states. The second equality follows from the fact that \( \text{cov}(F^{(0)}_i, X_i) = 0 \) for any \( X_i \) because \( F^{(0)}_i \) has zero variance in the degenerate subspace. In contrast, \( F^{(1)}_i \) generally has a lower degree of degeneracy than \( F^{(0)}_i \) and, if so, has a nonzero variance, making the last term divergent as \( T \to 0 (\beta \to \infty) \). Therefore, the zero-temperature limit of \( U^{(2)} \) is divergent for a degenerate reference, and disagrees with the correct limit of the second-order HCPT energy correction \( E^{(2)}_0 \) for the true (FCI) ground state, which is always finite. The foregoing discussion on \( U^{(1)} \) implies that even if it were not for the divergent covariance term, \( U^{(2)} \) would still reach a wrong zero-temperature limit because \( \bar{E} \left[ F^{(2)}_i \right] \) differs from \( E^{(0)}_0 \). Worse still, even if it were not for degeneracy in the reference, \( U^{(2)} \) may not converge at the correct zero-temperature limit, if the reference fails to connect to the true (FCI) ground state as \( \lambda \to 1 \). Hence, we conclude

\[
\lim _{T \to 0} U^{(2)} \neq E^{(2)}_0 \tag{47}
\]

for a degenerate reference.

The reduced analytical formula of \( U^{(2)} \) reads [16].
\[ U^{(2)} = \sum_{p,q} \frac{|F_{pq}|^2 f_p^+ f_q^+}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)|^2 f_p f_q f_r f_s^+}{\epsilon_p + \epsilon_q + \epsilon_r - \epsilon_s} - \beta \sum_{p,q} \frac{|F_{pq}|^2 f_p^+ f_q^+ - \beta}{4} \sum_{p,q,r,s} \frac{|(pq)(rs)|^2 f_p f_q f_r f_s^+}{\epsilon_p + \epsilon_q + \epsilon_r - \epsilon_s} \]

where the average is taken over all degenerate reference Slater determinants and \(i, j (a, b)\) run over all occupied (unoccupied) spinorbitals in each of these determinants excluding degenerate HOMO and LUMO (i.e., \(\epsilon_i < \epsilon_{\text{f}}\) and \(\epsilon_a > \epsilon_{\text{f}}\)), whereas \(\epsilon_p = \epsilon_a\) means that \(p\) runs over all spinorbitals that are degenerate with HOMO.

The sum of the first two terms, which resembles the usual second-order MPPT energy correction, is the simple average \(E[E^{(2)}]\) of the second-order HCPT energy corrections over the degenerate reference Slater determinants. It differs from the second-order HCPT energy correction \(E_{\text{HCPT}}^{(2)}\) for the true (FCI) ground state. The latter is an eigenvalue of some perturbation matrix [Eq. (57) of Hirschfielder and Certain] and thus cannot be written as a closed formula. Hence, even if it were not for the remaining four terms that all contain divergent \(\beta\), \(U^{(2)}\) would not converge at the correct zero-temperature limit.

The third term contains the anomalous contribution as its diagonal summands,

\[ -\beta \sum_p f_p^+ f_p \left( \sum_{r} \langle pr|pr\rangle f_r^+ \right)^2 \]

which may be compared with the anomalous contribution labeled “\(\Omega_{\text{A}}\)” [Eq. (22) of Ref. 1] by Kohn and Luttinger. This divergent term (at \(T = 0\)) is shown to be canceled by a term containing \((\mu^{(1)})^2\) [Eq. (18) of Ref. 1] for a HEG. This is borne out in Eq. (49) in a more general context since

\[ -\beta \sum_p f_p^+ f_p + \beta (\mu^{(1)})^2 \sum_p f_p^+ \]

is shown to be canceled by the fifth term, although \(\Omega_{\text{A}}\) is also \(-\infty\) (so is in a HEG), but this calculation merely constitutes a misuse of the non-degenerate perturbation theory for a degenerate reference and

\[ = 0, \]

where the reduced formula for \(\mu^{(1)}\) [Eq. (41)] was used in the first equality. However, these systematic cancellations, shown to eliminate all anomalous contributions at any perturbation order for isotropic systems \(E_{\text{HCPT}}^{(2)}\) fall short of resolving the divergence of \(U^{(2)}\) for more general, nonisotropic systems: The off-diagonal summands of the third term of Eq. (49) are not compensated for by the fifth term, although \(F_{pq} = 0\) for \(p \neq q\) in the canonical HF reference. More importantly, the fourth and sixth terms seem to bear no simple relationship and do not cancel each other, making the zero-temperature limit of \(U^{(2)}\) divergent [reaffirming Eq. (47)].
does not give the correct zero-temperature limit. Even if all \( \beta \)-dependent terms were erased in the SoS or reduced formulas of \( U^{(2)} \), the resulting formulas would not reach the correct zero-temperature limit of \(-0.0187\, E_h \), but instead converge at a wrong limit, which is the second-order HCPT energy correction for the neutral, singlet ground state \((-0.0534\, E_h \) because the reference chosen was the singlet.

Since \( U^{(2)} \) in the canonical ensemble\(^\text{19}\) is isomorphic to Eq. \((21)\) except that each \( F_i^{(0)} \) is replaced by \( E_i^{(0)} \), it also suffers from divergence at \( T = 0 \). While the divergence may possibly (though highly improbably) be systematically removed by a clever choice of \( \mu \), the resulting finite zero-temperature limit of \( U^{(2)} \) would still not converge at the correct value for the true (FCI) ground state because one cannot know whether the reference corresponds to the true ground state without actually performing a FCI calculation. Therefore, the Kohn–Luttinger conundrum cannot be resolved by some alternative treatment of \( \mu \), contrary to Luttinger and Ward\(^\text{14}\) or Balian \textit{et al} \(^\text{26}\) because \( \mu \) does not even enter the thermodynamics in the canonical ensemble.

To summarize, when the reference wave function is qualitatively different from the true (FCI) ground-state wave function (in the sense that the degrees of degeneracy differ between the zeroth and infinite orders and/or the ordering of the ground state changes with \( \lambda \)), \( U^{(1)} \) and \( U^{(2)} \) do not converge at the respective correct zero-temperature limits. Since this nonconvergence persists regardless of the perturbation strength, the finite-temperature perturbation theories in the grand canonical and canonical ensembles are said to have zero radius of convergence at \( T = 0 \). This is not caused by an improper treatment of \( \mu \) (since the canonical ensemble does not involve \( \mu \)), but rather ultimately by the nonanalytic nature of the Boltzmann factor \( e^{-E^{(0)} / k_B T} \) at \( T = 0 \).

### IV. ZERO-TEMPERATURE LIMIT OF \( \mu \)

The chemical potential \( \mu \) is determined by solving the electroneutrality condition\(^\text{15,17}\)

\[
\bar{N} = \langle N \rangle \equiv \frac{\sum_i N_i e^{-\beta F_i}}{\sum_i e^{-\beta F_i}},
\]

where \( \bar{N} \) is the average number of electrons that keeps the system electrically neutral. As \( T \to 0 \), the thermal average is increasingly dominated by the term with the most negative \( F_i \), where the \( i \)th state is usually the neutral (degenerate or nondegenerate) ground state (i.e., \( I = 0 \)). However, if we kept only this greatest summand in the numerator, we could not determine \( \mu \) at \( T = 0 \) because the equation holds for any value of \( \mu \) since \( N_0 = \bar{N} \). What actually determines \( \mu \) at \( T = 0 \) is the most dominant summands for ionized and electron-attached states with \( N_I \neq \bar{N} \). Assuming the most common scenario in which the most negative \( F_i \) for ionized and electron-attached states occur for \( N_I = \bar{N} \pm 1 \), we see that the above equation is satisfied at \( T = 0 \) if the contributions to the right-hand side from the cation and anion ground states cancel with each other exactly, whereupon we have

\[
N_{\text{deg. cation}}^{\text{deg.}} e^{-\beta E_{\text{cation}} + \beta \mu (N - 1)} = N_{\text{deg. anion}}^{\text{deg.}} e^{-\beta E_{\text{anion}} + \beta \mu (N + 1)},
\]

where \( E_{\text{cation}} \) and \( N_{\text{deg. cation}}^{\text{deg.}} \) are the energy and degeneracy of the cation ground state (and the anion counterparts similarly defined). This can be solved for \( \mu \) as

\[
\mu = \frac{E_{\text{anion}} - E_{\text{cation}}}{2} + \frac{1}{2\beta} \ln \frac{N_{\text{deg. cation}}}{N_{\text{deg. anion}}},
\]

which implies

\[
\lim_{T \to 0} \mu = \frac{E_{\text{anion}} - E_{\text{cation}}}{2}.
\]

At the zeroth order, the above equation leads to\(^\text{18}\)

\[
\lim_{T \to 0} \mu^{(0)} = \frac{E^{(0)}_{\text{anion}} - E^{(0)}_{\text{cation}}}{2} = \frac{\epsilon_H + \epsilon_L}{2},
\]

where \( \epsilon_H \) and \( \epsilon_L \) are the HOMO and LUMO energies, respectively, and Eq. \((31)\) was used in the second equality. The reduced analytical formula of \( \mu^{(0)} \) is\(^\text{15}\)

\[
\bar{N} = \sum_p f_p^-,
\]

which becomes indeterminate at \( T = 0 \) since it is satisfied by any \( \mu^{(0)} \) in the domain \( \epsilon_H < \mu^{(0)} < \epsilon_L \). At \( T = 0 \), the sum is dominated by the contributions from the HOMO and LUMO, and hence,

\[
N_{\text{deg.}}^{\text{H}} f_H^+ = N_{\text{deg.}}^{\text{L}} f_L^-,
\]

where \( N_{\text{deg.}}^{\text{H}} \) and \( N_{\text{deg.}}^{\text{L}} \) are the degrees of degeneracy of the HOMO and LUMO, respectively. For a nondegenerate reference, this can be solved for \( \mu^{(0)} \) to give

\[
\mu^{(0)} = \frac{\epsilon_H + \epsilon_L}{2} + \frac{1}{2\beta} \ln \frac{N_{\text{deg.}}^{\text{H}}}{N_{\text{deg.}}^{\text{L}}},
\]

which means

\[
\lim_{T \to 0} \mu^{(0)} = \frac{\epsilon_H + \epsilon_L}{2}.
\]

For a degenerate reference, \( \mu^{(0)} = \epsilon_H = \epsilon_L \) at \( T = 0 \), where Eq. \((53)\) holds.

At the first order, we can similarly write

\[
\lim_{T \to 0} \mu^{(1)} = \frac{E^{(1)}_{\text{anion}} - E^{(1)}_{\text{cation}}}{2},
\]

where \( E^{(1)}_{\text{cation}} \) and \( E^{(1)}_{\text{anion}} \) are the first-order HCPT energy corrections of the cation and anion ground states, respectively. If they are degenerate at the zeroth order and the degeneracy is partially or fully lifted at the first order, these energy corrections are the eigenvalues of the perturbation matrix [Eq. \((37)\) of Ref. \cite{11}] and cannot be simplified any further. However, if the degrees of degeneracy are unchanged, they are expressed
by the first-order MPPT formula and obey Koopmans’ theorem, reducing the right-hand side to
\[
\lim_{T \to 0} \mu^{(1)} = 0,
\]
(62)
in the canonical HF reference. The reduced analytical formula of \(\mu^{(1)}\) is given by Eq. (41) and reproduced here for the reader’s convenience:
\[
\mu^{(1)} = \frac{\sum P F_{pp} f^+_p f^-_p}{\sum P f^+_p f^-_p}.
\]
(63)
The right-hand side has the same zero-temperature limit as Eq. (62) for degenerate and nondegenerate references because \(F_{pp} = 0\) at \(T = 0\).
Likewise, the zero-temperature limit of \(\mu^{(2)}\) is
\[
\lim_{T \to 0} \mu^{(2)} = \frac{E^{(2)}_{\text{anion}} - E^{(2)}_{\text{cation}}}{2},
\]
(64)where \(E^{(2)}_{\text{anion}}\) and \(E^{(2)}_{\text{cation}}\) are the second-order HCPT energy corrections. When the degeneracy is partially or fully lifted at the second order, they are the eigenvalues of the perturbation matrix [Eq. (57) of Ref. 11] and the right-hand side of the above equation does not simplify any further. If this is not the case and the neutral reference is nondegenerate, the right-hand side is identified as the average of the \(\Delta \text{MP2}^\ast\) energy.

If we assume a canonical, nondegenerate HF reference with the same degrees of degeneracy for the HOMO and LUMO, then \(F_{pp} = 0\) and \(\mu^{(1)} = 0\) at \(T = 0\) and the above formula reproduces Eqs. (65) and (66).
Table II lists \(\mu^{(0)}\), \(\mu^{(1)}\), and \(\mu^{(2)}\) of the square-planar \(H_4\) as a function of temperature with the zero-temperature limits [Eqs. (56), (61), and (64)]. They all come within 0.1 m\(E_h\) of the respective limits at \(T \leq 10^4\) K, which are finite even for this degenerate reference.

V. ZERO-TEMPERATURE LIMIT OF \(\Omega\)

The grand potential and internal energy bear the relationship:
\[
\Omega = U - TS - \mu \bar{N},
\]
(68)
where \(S\) in the entropy. As \(T \to 0\), we therefore have
\[
\lim_{T \to 0} \Omega = \lim_{T \to 0} U - \lim_{T \to 0} \mu \bar{N},
\]
(69)
which should also hold at each perturbation order:
\[
\lim_{T \to 0} \Omega (n) = \lim_{T \to 0} U (n) - \lim_{T \to 0} \mu (n) \bar{N}.
\]
(70)
It was the right-hand side that Kohn and Luttinger compared with the energy corrections from diagrammatic Berg perturbation theory. This comparison is unnecessarily complicated by the presence of nonzero \(\mu (n)\). Nevertheless, given that \(\mu (n)\) has a well-defined, finite limit at \(T = 0\), \(\Omega (n)\) should exhibit the same (non)convergence behavior as \(U (n)\), the latter having been established in Sec. III.

For a nondegenerate, correct reference, we can immediately infer from the conclusions in the preceding sections,
\[
\lim_{T \to 0} \Omega (0) = E^{(0)}_{\text{cation}} - E^{(0)}_{\text{anion}} \bar{N},
\]
(71)
\[
\lim_{T \to 0} \Omega (1) = E^{(1)}_{\text{cation}} - E^{(1)}_{\text{anion}} \bar{N},
\]
(72)
\[
\lim_{T \to 0} \Omega (2) = E^{(2)}_{\text{cation}} - E^{(2)}_{\text{anion}} \bar{N},
\]
(73)
TABLE II. Comparison of the zeroth-, first-, and second-order corrections to chemical potential ($\mu^{(n)}$, $0 \leq n \leq 2$) as a function of temperature ($T$) for the square-planar H$_4$ molecule (0.8 Å) with the STO-3G basis set. The HOMO and LUMO energies are 0.05235 $E_h$.

| $T$ / K | $\mu^{(0)}/E_h$ | $\mu^{(1)}/E_h$ | $\mu^{(2)}/E_h$ |
|---------|-----------------|----------------|-----------------|
| $0^\circ$ | 0.05235 | 0.00000 | 0.00086 |
| 10$^2$ | 0.05235 | 0.00000 | 0.00086 |
| 10$^3$ | 0.05235 | 0.00000 | 0.00086 |
| 10$^4$ | 0.05235 | 0.00000 | 0.00086 |
| 10$^5$ | 0.06832 | -0.00227 | 0.02292 |
| 10$^6$ | 0.11259 | 0.00740 | 0.00013 |

* Equations 50, 61, and 63.

The right-hand sides of which are the correct zero-temperature limits. Therefore, there is no Kohn–Luttinger conundrum for a nondegenerate, correct reference. However, it should be reminded that one cannot know whether the reference is correct (i.e., whether the degeneracy is lifted at a higher perturbation order and/or there is no reordering of the ground state) until a FCI calculation is carried out. Furthermore, whereas $E^{(0)}$ are written in the usual closed (diagrammatic) formulas for a nondegenerate reference, $E^{(0)\text{ion}}$ and $E^{(0)\text{cunc}}$ are generally not written as such, but necessitate a complicated procedure outlined by Hirschfelder and Certain to be performed.

For a degenerate reference, we instead obtain

$$\lim_{T \to 0} \Omega^{(0)} = E^{(0)} - \frac{\epsilon_1 + \epsilon_1}{2} \tilde{N},$$  
$$\lim_{T \to 0} \Omega^{(1)} = E\left[E^{(1)}\right] - \frac{E^{(1)\text{ion}} - E^{(1)\text{cunc}}}{2} \tilde{N},$$  
$$\lim_{T \to 0} \Omega^{(2)} = E\left[E^{(2)}\right] - \beta \text{cov}\left(E^{(1)}, F^{(1)}\right) - \frac{E^{(2)\text{ion}} - E^{(2)\text{cunc}}}{2} \tilde{N},$$

where $\epsilon_1 = \epsilon_1$, and $\epsilon_1$, again, reproducing Eq. (71). Therefore, the reduced formula for $\Omega^{(0)}$ converges at the correct zero-temperature limit for both degenerate and nondegenerate references.

The reduced formula of $\Omega^{(1)}$ reads

$$\Omega^{(1)} = \sum_p F_{pp} f_p - \frac{1}{2} \sum_{p,q} \sum_{q,r,s} (pq||pq)f_p f_q f_q - \mu^{(1)} \tilde{N},$$

where $\mu^{(1)}$ should be understood to be its reduced formula [Eq. (81)], which has the zero-temperature behavior given by Eq. (62) for both degenerate and nondegenerate references.

For a nondegenerate reference, using $F_{pp} = 0$ at $T = 0$, we obtain

$$\lim_{T \to 0} \Omega^{(1)} = -\frac{1}{2} \sum_{i,j} (i||j) - \lim_{T \to 0} \mu^{(1)} \tilde{N},$$

where the average is taken over all degenerate reference Slater determinants and $i$ and $j$ run over all spinorbitals occupied in the reference Slater determinant. This is the correct zero-temperature limit if the reference Slater determinant connects to the true (FCI) ground state wave function as $A = 0 \to 1$ (setting aside the question of whether the reduced formula of $\mu^{(1)}$ converges at the correct limit).

For a degenerate reference, we have

$$\lim_{T \to 0} \Omega^{(1)} = -\frac{1}{2} \sum_{i,j} (i||j) - \lim_{T \to 0} \mu^{(1)} \tilde{N},$$

where $\mu^{(1)}$ is given by Eq. (67). For a nondegenerate reference, we have

$$\lim_{T \to 0} \Omega^{(2)} = \sum_{i,a} |F_{ia}|^2 f_i f_a + \frac{1}{4} \sum_{p,q,r,s} (pq||rs)f_p f_q f_r f_s - \frac{\beta}{2} \sum_{p,q} |F_{pq}|^2 f_p f_q - \frac{\beta}{8} \sum_{p,q,r,s} (pq||rs)f_p f_q f_r f_s + \frac{\beta}{2} (\mu^{(1)})^2 \sum_p f_p f_p - \mu^{(2)} \tilde{N},$$

where $\mu^{(2)}$ is given by Eq. (84). For a degenerate reference, we have

$$\lim_{T \to 0} \Omega^{(2)} = \sum_{i,a} |F_{ia}|^2 e_i + \frac{1}{4} \sum_{i,j,a,b} (a||b)(i||j)e_i e_j - \frac{\beta}{2} (\mu^{(1)})^2 \tilde{N},$$

where $\mu^{(1)}$ is given by Eq. (71). For a nondegenerate reference, we have

$$\lim_{T \to 0} \Omega^{(2)} = \sum_{i,a} |F_{ia}|^2 e_i - \frac{1}{4} \sum_{i,j,a,b} (a||b)(i||j)e_i e_j - \frac{\beta}{2} (\mu^{(1)})^2 \tilde{N},$$

where $\mu^{(1)}$ is given by Eq. (71).
where $i$ and $j$ ($a$ and $b$) run over spinorbitals occupied (unoccupied) in the reference Slater determinant. The first two terms are identified as the second-order MPPT energy correction.\textsuperscript{10,12,13} If this reference morphs into the true (FCI) ground state as $\lambda \to 1$, the right-hand side equals to the correct zero-temperature limit (provided that the reduced formula of $\mu^{(2)}$ does the same).

For a degenerate reference, we instead find

\[
\lim_{T \to 0} \Omega^{(2)} = E \left[ \sum_{i,a} \frac{|F_{0i}|^2}{\epsilon_i - \epsilon_a} \right] + E \left[ \frac{1}{4} \sum_{i,j,a,b} \frac{|(ij)|ab|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right]
\]

\[
\frac{\beta}{2} \sum_{p<q} |F_{pq}|^2 f_p f_q^* + \frac{\beta}{8} \sum_{p,q,r,s} |(pq)|(rs)|^2 f_p f_q f_r^* f_s^* - \lim_{T \to 0} \mu^{(2)} N, \tag{88}
\]

where the average is taken over all degenerate reference Slater determinants and $i$ and $j$ ($a$ and $b$) run over all occupied (unoccupied) spinorbitals in each of these determinants excluding the HOMO (LUMO). The third term contains the “$\Omega_{2\alpha}$” anomalous contribution,

\[
-\frac{\beta}{2} \sum_p f_p f_p^* \left[ \sum_r \langle pr | pr \rangle f_r^* \right]^2, \tag{86}
\]

which is nearly identical to Eq. (22) of Kohn and Luttinger\textsuperscript{14} and is divergent. As pointed out by these authors, this divergence is canceled exactly by a term involving $(\mu^{(1)})^2$ [Eq. (18) of Ref. 1] in an isotropic system. In our formalism for more general systems, the whole diagonal sum in the third term is canceled exactly by the penultimate term involving $(\mu^{(1)})^2$, namely,

\[
-\frac{\beta}{2} \sum_{p<q} |F_{pq}|^2 f_p f_q^* + \frac{\beta}{2} \left( \sum_{p<q} |F_{pq}|^2 f_p f_q^* \right)^2 - \lim_{T \to 0} \mu^{(2)} N = 0. \tag{87}
\]

However, this falls short of resolving the Kohn–Luttinger conundrum because the off-diagonal sum as well as the whole fourth term still remain and they both carry a factor of $\beta$, which goes to infinity at $T = 0$. Therefore,

\[
\lim_{T \to 0} \Omega^{(2)} = E \left[ \sum_{i,a} \frac{|F_{0i}|^2}{\epsilon_i - \epsilon_a} \right] + E \left[ \frac{1}{4} \sum_{i,j,a,b} \frac{|(ij)|ab|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \right]
\]

\[
\frac{\beta}{2} \sum_{p<q} |F_{pq}|^2 f_p f_q^* + \frac{\beta}{8} \sum_{p,q,r,s} |(pq)|(rs)|^2 f_p f_q f_r^* f_s^* - \lim_{T \to 0} \mu^{(2)} N, \tag{88}
\]

which equals to negative infinity in the likely case where the degeneracy is partially or fully lifted at the first order, and otherwise still disagrees with the correct zero-temperature limit. The latter involves the second-order HCP energy correction for the true ground state, which is an eigenvalue of the perturbation matrix and thus cannot be written in a closed form such as the above.

Table III confirms these conclusions numerically for the square-planar $\text{H}_4$. The correct zero-temperature limits are given in the first row of the table. $\Omega^{(0)}$ approaches $\Omega_{0H}^{(0)} = 1.7886 \, E_{\text{h}}$ as $T \to 0$, although the convergence is much slower than $U^{(0)}$, which must be due to the entropy term in the former. $\Omega^{(1)}$ converges at the wrong zero-temperature limit of $-3.3771 \, E_{\text{h}}$, which is higher than the correct limit of $-3.7015 \, E_{\text{h}}$. $\Omega^{(2)}$ shows a clear sign of divergence as $T \to 0$.

Since the Helmholtz energy and internal energy in the canonical ensemble are equal to each other at $T = 0$, the perturbation corrections to the Helmholtz energy display the same zero-temperature behavior as those of the grand potential.

### VI. CONCLUSIONS

Our findings are summarized as follows:

1. The first-order perturbation corrections to the internal energy ($U$) and grand potential ($\Omega$) according to the finite-temperature perturbation theory in the grand canonical ensemble approach wrong limits as $T \to 0$ and, therefore, become increasingly inaccurate at low temperatures when the reference is degenerate and/or incorrect. The reference is considered incorrect if its degree of degeneracy differs from the one in the true (FCI) ground state or it does not smoothly con-

| $T / K$ | $\Omega^{(0)}/E_{\text{h}}$ | $\Omega^{(1)}/E_{\text{h}}$ | $\Omega^{(2)}/E_{\text{h}}$ |
|--------|-----------------|-----------------|-----------------|
| 0 (HCPT) | 1.7886 | -3.7015 | -0.0222 |
| 0 (HCPT) | 1.7886 | -3.6696 | -0.0569 |
| 0 (MPPT) | 1.7886 | -3.5818 | $-$∞ |
| 0 (HCPT) | 1.7886 | -3.3771 | $\ldots$ |
| 10² | 1.7877 | -3.3771 | -171.9935 |
| 10³ | 1.7798 | -3.3771 | -17.2245 |
| 10⁴ | 1.7008 | -3.3771 | -1.7476 |
| 10⁵ | 0.7938 | -3.3698 | -0.3573 |
| 10⁶ | -14.1403 | -3.5757 | -0.0881 |

\textsuperscript{a} The correct zero-temperature limit. $\Delta U_{0H} = \Omega_{0H}^{(0)}$ at $T = 0$ according to the Hirschfelder–Certain degenerate perturbation theory\textsuperscript{1} for the singlet ground state. See the corresponding footnote of Table II.

\textsuperscript{b} $\Delta U_{0H} = \Omega_{0H}^{(1)}$ at $T = 0$ according to the Hirschfelder–Certain degenerate perturbation theory\textsuperscript{1} for the singlet ground state. See the corresponding footnote of Table II.

\textsuperscript{c} $\Delta U_{0H} = \Omega_{0H}^{(2)}$ at $T = 0$ according to the Möller–Plesset perturbation theory\textsuperscript{10} See the corresponding footnote of Table II.

\textsuperscript{d} The zero-temperature limit of the finite-temperature Hartree–Fock theory. See the corresponding footnote of Table II.
nect to the true ground-state wave function as the perturbation strength ($\lambda$) is raised from zero to unity.

(2) The second-order perturbation corrections to $U$ and $\Omega$ in the grand canonical ensemble are divergent if the degeneracy of the reference wave function is lifted at the first order of the HCPT, and otherwise they converge at finite, but still wrong zero-temperature limits if the reference is degenerate and/or incorrect.

(3) The zeroth-order (Fermi–Dirac) theory in the grand canonical ensemble is much more robust and is correct in most (but not all) cases. The zeroth-, first-, and second-order perturbation corrections to the chemical potential ($\mu$) also exhibit convergence at the correct finite zero-temperature limits in most (but not all) cases.

(4) Conclusions (1) through (3) have been numerically verified for the square-planar $\text{H}_4$ that has a degenerate and incorrect reference wave function.

(5) The first- and second-order perturbation corrections to the internal energy and Helmholtz energy according to the finite-temperature perturbation theory in the canonical ensemble display the same nonconvergence behaviors as the counterparts in the grand canonical ensemble as $T \to 0$.

(6) Taken together, the finite-temperature perturbation theories in the grand canonical and canonical ensembles have zero radius of convergence at $T = 0$ and are increasingly useless or even misleading as $T \to 0$ when the reference is degenerate and/or incorrect. Since this occurs in the canonical ensemble, this problem (the Kohn–Luttinger conundrum) cannot be resolved by a clever choice of $\mu$ contrary to the propositions by some authors.\textsuperscript{13,14} Rather, it originates ultimately from the nonanalyticity of the Boltzmann factor at $T = 0$, preventing the energy expression from being expanded in a converging power series. Worse still, one cannot know without carrying out a FCI calculation whether the degree of degeneracy is the same between the reference and FCI and whether the reference corresponds to the true ground state in the FCI solution. Therefore, this conundrum exposes the fundamental flaw of quantum field theory for thermodynamics, which cannot be easily resolved within the framework of perturbation theory.

VII. DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article.

ACKNOWLEDGMENTS

This work was supported by the Center for Scalable, Predictive methods for Excitation and Correlated phenomena (SPEC), which is funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division, as a part of the Computational Chemical Sciences Program and also by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Grant No. de-sc0006028.
In our previous study, we argued that the physically correct way of taking the thermal average of $E_{1}^{(1)}$ at $T = 0$ is to give 100% weight to the lowest $E_{1}^{(1)}$, so that $U^{(1)}$ tends to the lowest $E_{1}^{(1)}$ as $T \to 0$, allowing the SoS formula for $U^{(1)}$ to pass the Kohn–Luttinger test. This argument is not acceptable for two reasons. First, at infinitesimal temperature ($T = 0^+$), the weight is constant across all degenerate states, making $U^{(1)}$ jumps from the simple average of $E_{1}^{(1)}$ in the degenerate subspace to its lowest value as $T = 0^+ \to 0$, which is both nonphysical (qualitatively different from an experimental observation) and nonmathematical (not meeting the mathematical condition of a limit). Second, the lowest $E_{1}^{(1)}$ may not correspond to the true ground state of FCI, i.e., when the case study discussed in Sec. II B applies, as in our $H_4$ example, where the lowest $E_{1}^{(1)}$ is still not the correct zero-temperature limit, $E_{0}^{(1)}$.

The two values of the first-order HCPT energy corrections are the two distinct eigenvalues of the perturbation matrix [Eq. (37) of Hischfelder and Certain(11)] within the degenerate subspace, corresponding to the triplet and singlet neutral ground states. On the other hand, the first-order MPPT energy correction is obtained by evaluating the well-known formula [Eq. (B1) of Ref. (16)] for the single Slater determinant for the singlet neutral ground state. In the zero-temperature limit, the finite-temperature HF theory imparts equal weights (via the density matrix) to the two Slater determinants for the singlet neutral ground state that are symmetrically and energetically equivalent. Its energy minus the zeroth-order energy [Eq. (35)] is listed as the first-order correction according to the finite-temperature HF theory at $T = 0$. The last method generated the molecular orbitals (with degenerate HOMO and LUMO) that made up the single Slater determinant, which was used as a reference for the subsequent MPPT and HCPT as well as the finite-temperature perturbation theory calculations; the usual single-determinant HF theory does not easily produce degenerate HOMO and LUMO owing to the wave function instabilities. Figures 4 and 5 also plot these four values for the square-planar $H_4$. 

S. Hirata and X. He, “On the Kohn–Luttinger conundrum,” J. Chem. Phys. 138, 204112 (2013).
M. R. Pederson and K. A. Jackson, “Pseudoenergies for simulations on metallic systems,” Phys. Rev. B 43, 7312–7315 (1991).
S. Hirata, M. R. Hermes, J. Simons, and J. V. Ortiz, “General-order many-body Green’s function method,” J. Chem. Theory Comput. 11, 1595–1606 (2015).
S. Hirata, A. E. Doran, P. J. Knowles, and J. V. Ortiz, “One-particle many-body Green’s function theory: Algebraic recursive definitions, linked-diagram theorem, irreducible-diagram theorem, and general-order algorithms,” J. Chem. Phys. 147, 044108 (2017).