General solution to the Kohn–Luttinger nonconvergence problem

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Abstract

A simple, but general solution is proposed for the Kohn–Luttinger problem, i.e., the nonconvergence of the finite-temperature many-body perturbation theory with its zero-temperature counterpart as temperature is lowered to zero under some circumstances. How this nonconvergence can be avoided by altering the reference wave function is illustrated numerically by using up to the fifth order of the perturbation theory.
The Kohn–Luttinger problem\footnote{1–3} refers to the eponymous authors’ prediction that the finite-temperature many-body perturbation theory for electrons\footnote{1, 2, 4–8} does not always reduce to the zero-temperature counterpart as temperature goes to zero. On this basis, they concluded that “BG [Brueckner–Goldstone perturbation] series is therefore in general not correct”\footnote{1}. In this light, contemporary textbooks contain a qualification about the validity of the very finite-temperature perturbation theory they teach. March, Young, and Sampanthar\footnote{9} wrote, “a note of caution is called for whenever we attempt to calculate zero-temperature properties from an expression for the same quantities at non-zero temperature $T$ by taking the limit $T \to 0$. The physics is not necessarily the same in both cases.” Thouless\footnote{10} was more blunt, writing, “In any case it serves as a warning against taking the results of perturbation theory too seriously.” For over 60 years since the Kohn–Luttinger paper\footnote{1}, however, it has been unclear whether the predicted inconsistency actually exists\footnote{8} and if it does, what causes it.

Last year, having established\footnote{11–14} the finite-temperature perturbation theory for the grand potential ($\Omega$), chemical potential ($\mu$), and internal energy ($U$), we showed\footnote{3} that the first- and second-order perturbation corrections to $U$ indeed disagree with the corresponding corrections to the ground-state energy as $T \to 0$ when the reference wave function differs qualitatively from the exact one. In particular, when the degeneracy of the reference wave function is partially or fully lifted at the first-order degenerate Hirschfelder–Certain perturbation theory\footnote{15}, the second-order corrections to $\Omega$ and $U$ are divergent\footnote{3}. The cause of this nonconvergence or divergence is traced to the fact that the definitions of $\Omega$ and $U$ are nonanalytic at $T = 0$ and cannot be expanded in a converging power series. Therefore, the Kohn–Luttinger problem does exist, and may be defined more broadly: The finite-temperature many-body perturbation theory has zero radius of convergence at $T = 0$ for a qualitatively wrong reference\footnote{3}.

In this Letter, we first show that the divergence due to a degenerate reference occurs at higher order of the finite-temperature perturbation theory, and verify it numerically using its general-order algorithm\footnote{14}. We then demonstrate how this divergence can be avoided by simply changing the reference to a nondegenerate one. Since the singlet and triplet instability theorems\footnote{16} guarantee that for any given degenerate Hartree–Fock (HF) wave function there is always a lower-lying nondegenerate wave function, the proposed solution is general. We shall consider the perturbation corrections to $U$ in the grand canonical ensemble\footnote{14}, but what follows applies equally to $\Omega$ and to the canonical ensemble\footnote{17}.

The general-order algorithm implements the recursion relation\footnote{14} that defines the $n$th-order
correction to the grand potential $\Omega^{(n)}$ in terms of lower-order corrections, which reads

$$
\Omega^{(n)} = \langle D^{(n)} \rangle + \frac{(-\beta)}{2!} \sum_{i=1}^{n-1} \left( \langle D^{(i)} D^{(n-i)} \rangle - \Omega^{(i)} \Omega^{(n-i)} \right)
$$

$$
+ \frac{(-\beta)^2}{3!} \sum_{i=1}^{n-2} \sum_{j=1}^{n-i-1} \left( \langle D^{(i)} D^{(j)} D^{(n-i-j)} \rangle - \Omega^{(i)} \Omega^{(j)} \Omega^{(n-i-j)} \right)
$$

$$
+ \cdots + \frac{(-\beta)^{n-1}}{n!} \left[ \langle (D^{(1)})^n \rangle - (\Omega^{(1)})^n \right],
$$

(1)

where $\beta = 1/k_B T$ and $\langle \ldots \rangle$ denotes the zeroth-order thermal average, i.e.,

$$
\langle X \rangle = \frac{\sum_{I} X_{I} e^{-\beta \frac{n}{2} D_{I}^{(0)}}}{\sum_{I} e^{-\beta \frac{n}{2} D_{I}^{(0)}}},
$$

(2)

where $I$ runs over all states, $D_{I}^{(n)} = E_{I}^{(n)} - \mu_{I}^{(n)} N_{I}$, $E_{I}^{(n)}$ is the $n$th-order Hirschfelder–Certain degenerate perturbation correction [15] to the $I$th-state energy, $\mu_{I}^{(n)}$ is the $n$th-order perturbation correction to the chemical potential, and $N_{I}$ is the number of electrons in the $I$th state. Starting with $\Omega^{(0)}$ and $\mu^{(0)}$ furnished by the Fermi–Dirac theory, arbitrarily high orders of $\Omega^{(n)}$ can be generated. It is important to base our theory on the Hirschfelder–Certain degenerate perturbation theory [15] because the latter is the proper Rayleigh–Schrödinger perturbation theory for degenerate and non-degenerate references. While unimportant in this study, in deriving reduced analytical formulas, $E_{I}^{(n)}$ can be replaced by the corresponding diagonal element of the effective Hamiltonian matrix of the degenerate perturbation theory [12–14], which can be expressed in a closed form by the Slater–Condon rules.

The recursion for $U^{(n)}$ is given [14] by

$$
U^{(n)} = \langle E^{(n)} \rangle + (-\beta) \sum_{i=1}^{n} \langle D^{(i)} D^{(n-i)} \rangle
$$

$$
- (-\beta) \sum_{i=1}^{n} \Omega^{(i)} (U^{(n-i)} - \mu^{(n-i)} N)
$$

$$
+ \frac{(-\beta)^2}{2!} \sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \langle D^{(i)} D^{(j)} D^{(n-i-j)} \rangle
$$

$$
- \frac{(-\beta)^2}{2!} \sum_{i=1}^{n-1} \sum_{j=1}^{n-i} \Omega^{(i)} \Omega^{(j)} (U^{(n-i-j)} - \mu^{(n-i-j)} N)
$$

$$
+ \cdots + \frac{(-\beta)^{n}}{n!} \langle (D^{(1)})^n \rangle
$$

$$
- \frac{(-\beta)^{n}}{n!} \langle (\Omega^{(1)})^n \rangle (U^{(0)} - \mu^{(0)} N),
$$

(3)
FIG. 1. $U^{(n)}$ ($0 \leq n \leq 5$) as a function of temperature with a degenerate Hartree–Fock reference of the square-planar $H_4$.

where $\bar{N}$ is the average number of electrons that keeps the system electrically neutral. Note that $\Omega^{(1)} = \langle D^{(1)} \rangle$ and $U^{(0)} - \mu^{(0)} \bar{N} = \langle D^{(0)} \rangle$. Similar recursions exist for $\mu^{(n)}$ and $S^{(n)}$ [14].

Figure 1 shows $U^{(n)}$ ($0 \leq n \leq 5$) as a function of $T$ for an ideal gas of square-planar $H_4$ (0.8 Å in the STO-3G basis set) with a degenerate HF reference. The ideal gas is an ensemble of an infinite number of rigid and nonrotating $H_4$ molecules that do not interact with one another except to export or import electrons. Our previous paper [3] included the same data for $0 \leq n \leq 2$ using sum-over-orbital formulas, and this study extends the calculation to the fifth-order perturbation theory with the general-order algorithm [14]. The dashed lines indicate the correct zero-temperature limits of $U^{(0)}$ and $U^{(1)}$, which are determined by the zero-temperature Hirschfelder–Certain degenerate perturbation theory [15] and are denoted by $E^{(0)}$ and $E^{(1)}$, respectively.

As shown before [3], $U^{(0)}$, i.e., the Fermi–Dirac theory converges correctly at $E^{(0)}$ as $T \to 0$, whereas $U^{(1)}$ approaches a finite, but incorrect zero-temperature limit, which differs from the correct limit of $E^{(1)}$. Worse yet, $U^{(2)}$ is divergent, while the correct limit $E^{(2)}$ is finite. In this study, it is shown that $U^{(3)}$ through $U^{(5)}$ as well as all higher-order corrections diverge and thus have a wrong zero-temperature limit.

From an analytical viewpoint, $\Omega^{(n)}$ and $U^{(n)}$ contain $\beta \text{ cov}(D^{(i)}, D^{(n-i)})$ (where ‘cov’ stands for the covariance within a degenerate subspace) [3, 14], which is responsible for the divergence at $\beta = \infty$ in the event that both $D^{(i)}$ and $D^{(n-i)}$ have a distribution within the degenerate subspace of the reference state. When the degeneracy of the reference is partially or fully lifted for the first time at the $n$th order of the Hirschfelder–Certain degenerate perturbation theory [15], giving $D^{(n)}$ a
FIG. 2. $U^{(n)}$ ($0 \leq n \leq 5$) as a function of temperature with a nondegenerate Hartree–Fock reference of the square-planar $H_4$.

FIG. 3. The same as Fig. 2 with a different range.

distribution, $\Omega^{(2n)}$ and $U^{(2n)}$ become divergent at $T = 0$. When the reference state is nondegenerate, $D_0^{(i)}$ and $D_0^{(n-i)}$ (subscript 0 standing for the reference) are just single numbers and cannot have a distribution, making all terms carrying a factor of $\beta$ vanish as $T \to 0$. Then, $\Omega^{(n)}$ or $U^{(n)}$ are no longer divergent.

Since one is normally interested in $\Omega$ and $U$ at lower temperatures first, the theory is rather useless when the reference is degenerate. It may be said that the pathological behavior of the perturbation theory is amplified by finite temperature, considering the fact that the zero-temperature Hirschfelder–Certain degenerate perturbation theory \cite{15} is rapidly convergent for the same degenerate reference.

One can, however, easily avoid this nonconvergence or divergence by altering the reference.
With no symmetry restriction, the HF calculation naturally converges to a symmetry-broken non-degenerate wave function with an energy of $-1.6017\ E_h$. The latter is much lower than the energy of $-1.3791\ E_h$ of the degenerate reference used in Fig. 1. See Ref. [3] for more details about the degenerate reference. Starting from the nondegenerate reference, the finite-temperature perturbation theory for $U^{(n)}$ converges at the correct zero-temperature limit of $E^{(n)}$ provided by the nondegenerate (Møller–Plesset) perturbation theory [18] for all $0 \leq n \leq 5$ considered. This is shown in Figs. 2 and 3. (The oscillations of $U^{(n)}$ seen in the middle of the graph are due to the temperature reaching the lowest excitation energy for the first time, causing the perturbation series to converge more slowly.)

It may be emphasized that this simple solution to the Kohn–Luttinger problem is not specific to the square-planar $H_4$, but is generally applicable to any finite, degenerate system. This is because the singlet and triplet instability theorems [16] state that for any given HF solution with degenerate (or form-degenerate) highest occupied and lowest unoccupied molecular orbitals, there exists a lower-lying, symmetry-broken solution with the degeneracy lifted. The degenerate solution is only metastable, and it is actually easier to find a nondegenerate HF solution with a lower energy. If “strong correlation” is characterized by the extent to which a perturbation theory fails to converge, the Kohn–Luttinger problem may be viewed as a particularly severe case of strong-correlation problems. Our general solution, however, suggests that this is a manufactured problem caused by a metastable degenerate reference, and is best addressed at the level of mean-field theories. For a homogeneous electron gas, in which Kohn and Luttinger [1] originally considered the potential issue of nonconvergence, the Overhauser theorems [19, 20] also guarantee a lower-energy nondegenerate HF solution.

Finally, Fig. 4 verifies the convergence of the perturbation series of $\Omega$ and $U$ at the exact limits set by the thermal full configuration interaction [21] at a given temperature. The temperature of $10^6\ K$ was chosen only because the finite-temperature perturbation theory happens to be nondivergent there. The latter method evaluates the grand partition function with the exact energies of all states with any number of electrons (made available by the zero-temperature full-configuration-interaction method) and derives thermodynamic functions from it [21]. That the series reach the same numerically exact values at the tenth order either from the degenerate or nondegenerate reference underscores the correctness of the finite-temperature perturbation theory introduced by us [12–14], not overlooking any diagrammatic contribution such as anomalous and renormalization diagrams.
FIG. 4. Convergence of the perturbation approximations to $\Omega$ and $U$ in comparison with the thermal full-configuration-interaction values of the square-planar $H_4$ at $T = 10^6$ K.

It is important to distinguish two types of convergence discussed in this Letter: The convergence of the finite-temperature perturbation theory towards the zero-temperature perturbation theory as $T \to 0$, which is the focus of this study; the convergence of the finite-temperature perturbation theory towards the exact (thermal-full-configuration-interaction) limit at a given temperature, which is illustrated in Fig. 4. The former is not expected for a qualitatively wrong reference [3], but restored by changing the reference. This has been argued mathematically on the basis of the recursion, and verified numerically for up to the fifth order. The latter convergence towards the exact limit is guaranteed (unless the perturbation series diverges [22]) because the finite-temperature perturbation theory [12–14] is correct.

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