New Dimension in *Ab Initio* Electronic Structure Theory: Temperature, Pressure, and Chemical Potential

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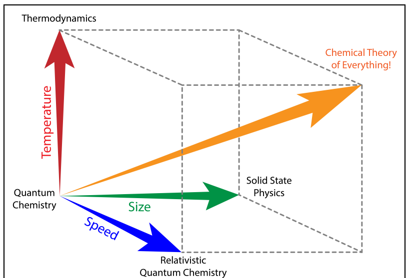
Abstract

Ab initio electronic structure theory has transformed gas-phase molecular science with its predictive ability. In the attempt to bring such predictive ability to macroscopic systems and condensed matter, the theory must integrate quantum mechanics with statistical thermodynamics, so that thermodynamic functions such as free energy, internal energy, entropy, and chemical potentials are computed as functions of temperature in a systematically converging series of approximations. A general, versatile strategy of elevating *ab initio* electronic structure theory to nonzero temperatures is introduced and discussed.

TOC Graphic



Dimensions of quantum many-body theory for chemistry

Quantum many-body theory deals with a system of many interacting particles obeying a quantum-mechanical equation of motion. Although many of its underlying ideas and mathematical tools have originated in nuclear physics and quantum electrodynamics, the most fully developed is *ab initio* electronic structure theory for atoms and molecules.[1] This is partly thanks to the availability of the exact electronic Hamiltonian, negligible non-Born–Oppenheimer effects, and a body of precise experimental data for tens of millions of catalogued molecules. It offers several hierarchies of systematic approximate methods that are convergent towards the exact solution of the electronic Schrödinger equation. These hierarchies, such as configuration-interaction (CI) theory,[2,3] coupled-cluster (CC) theory,[2,4,5] many-body perturbation theory (MBPT),[2,5,6] have complementary strengths and weaknesses, and their applicabilities and cost-accuracy balances are well documented. All conceivable electronic properties have been formulated within their frameworks and are computable with predictive accuracy. It may be said that the predictive abilities of *ab initio* relativistic electronic structure theory helped vet special theory of relativity most rigorously.[7,8]

Size-extensive (or size-consistent)[9] members of these hierarchies can, in principle, achieve the same for macroscopic chemical systems. Such *ab initio* condensed-matter applications are also rapidly becoming a reality by virtue of advances in algorithms and computing technologies.[10–23] For condensed matter, discrete energies are no longer as useful as in atomic or molecular cases; instead, thermodynamic functions such as free energies, internal energy, and entropy are desired as direct observables of experiments; everything exists at a finite temperature, and the default zero-temperature approximation becomes inaccurate or even irrelevant for metallic solids, small-gap semiconductors, nonideal atomic or molecular gases and liquids, etc. A whole new *ab initio* theory is needed that integrates quantum mechanics and statistical thermodynamics for systems containing Avogadro's number of interacting particles.

Today, *ab initio* electronic structure theory faces an exciting prospect of expanding into a new dimension of quantum statistical mechanics by incorporating thermodynamic variables of temperature, pressure, and chemical potential as inputs and by reporting thermodynamic functions as outputs. The existing zero-temperature theories for an isolated atom or molecule would become just a special case of the more general, finite-temperature theories for thermodynamic functions of macroscopic chemical systems (however, see below for a surprise twist!). Not only should the latter be able to describe such fascinating thermal electronic effects as Mott transitions,[24] Peierls distortion,[25] and high-T_c superconductivity,[26] but they may also bridge the gap between *ab initio* electronic structure theory and classical theories of nonideal gases and liquids such as the Ursell–Mayer cumulant expansion,[27–34] which has inspired CC theory, thus coming full circle.

Starting from *ab initio* quantum chemistry for light-element atoms and molecules at zero temperature, we have added a new physics dimension of "size" to reach *ab initio* condensed matter physics.[18] We have also introduced an orthogonal dimension of "speed" to define *ab initio* relativistic quantum chemistry,[7] which can address any molecule made of any elements across the periodic table. The present research program explores another orthogonal dimension of "temperature," elevating the underlying physics from quantum mechanics to quantum statistical thermodynamics. Together, they cover quantum many-body physics of all conceivable chemical systems at equilibrium made of any number of particles interacting through a potential of any mathematical form at any temperature. A finite-temperature extension of *ab initio* electronic structure theory, therefore, has a potential of ultimately evolving into *chemical theory of everything* (Fig. 1).

This *Perspective* documents challenges we have faced in formulating a finite-temperature extension of the MBPT hierarchy, in particular, of *ab initio* electronic structure theory, and our general and versatile strategy of overcoming them.

Quantum Statistical Mechanics

Let us briefly summarize the exact theory of equilibrium thermodynamics of electrons in the grand canonical ensemble.[34–36] It can describe an ideal gas of atoms or molecules that can exchange electrons while maintaining the overall charge neutrality of the gas. It is also applicable to electronic structures of solids and liquids.

The grand partition function Ξ is defined by

$$\Xi \equiv \sum_I e^{-\beta(E_I - \mu N_I)}, \tag{1}$$

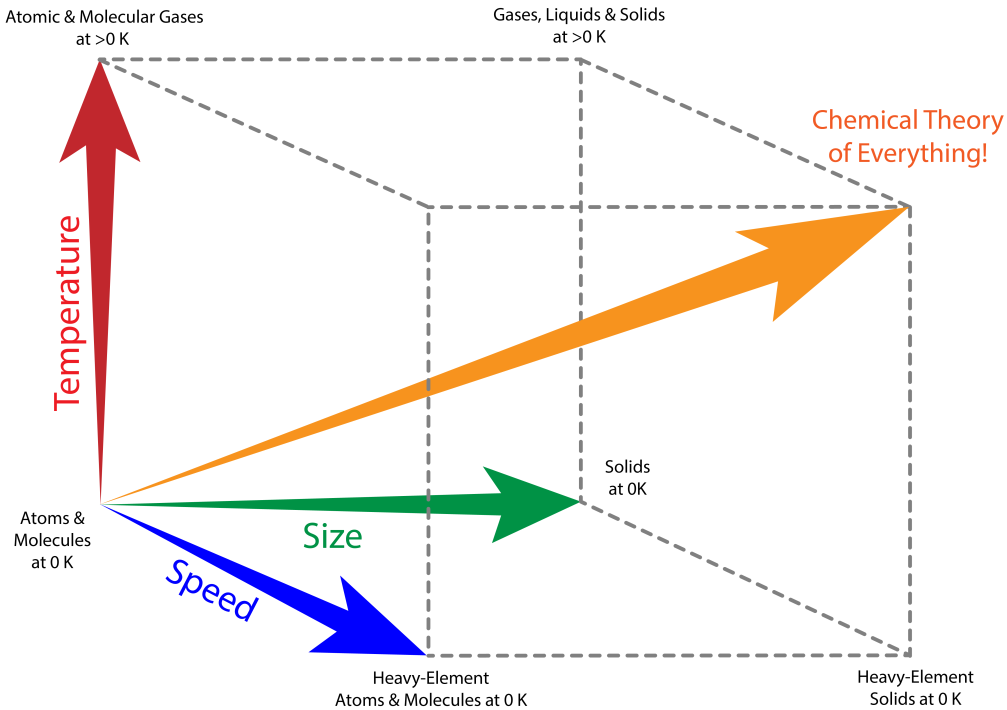


Figure 1: Dimensions of quantum many-body theory for chemistry.

where $\beta = (k_{\mathrm{B}}T)^{-1}$ is the inverse temperature, E_I and N_I are the energy and number of electrons in the Ith state, and the summation is taken over all states with any number of electrons down to zero. The chemical potential μ takes the value that makes the average number of electrons cancel exactly the total nuclear charge. Without this provision, the system would be a massively charged plasma, which no longer obeys equilibrium thermodynamics because the energy is not extensive.[37–40] If the constituent particles are not electrically charged, μ can take an arbitrary value.

Thermodynamic functions are then unambiguously derived from Ξ or, equivalently, defined with the Ith-state thermal population (density-matrix element),

$$\rho_I \equiv \frac{e^{-\beta(E_I-\mu N_I)}}{\Xi}. \tag{2}$$

The grand potential Ω, internal energy U, and entropy S are given by

$$\Omega \equiv -\frac{1}{\beta}\ln\Xi = \sum_I \rho_I(E_I - \mu N_I) + \frac{1}{\beta}\sum_I \rho_I \ln\rho_I, \tag{3}$$

$$U \equiv -\frac{\partial}{\partial\beta}\ln\Xi + \mu\bar{N} = \sum_I \rho_I E_I, \tag{4}$$

$$S \equiv \frac{U - \Omega - \mu\bar{N}}{T} = -k_{\mathrm{B}}\sum_I \rho_I \ln\rho_I, \tag{5}$$

whereas the average number of electrons $\bar{N}$,

$$\bar{N} \equiv \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\Xi = \sum_I \rho_I N_I, \tag{6}$$

must agree with the total nuclear charge, and this condition determines μ. Since $\Omega = -PV$,[34] the pressure P and volume V tacitly enter the formalism.

The two definitions of each thermodynamic function — one based on Ξ and the other on ρ_I — are fully equivalent to each other in this exact theory, but this is not necessarily the case in an approximate theory. The exact theory also satisfies the fundamental thermodynamic relationships such as

$$\Omega = U - \mu\bar{N} - TS, \tag{7}$$

$$\bar{N} = -\frac{\partial\Omega}{\partial\mu}, \tag{8}$$

$$S = -\frac{\partial\Omega}{\partial T}, \tag{9}$$

whose adherence also needs to be checked for an approximate theory.

Thermodynamics of electrons in the canonical ensemble is described by the foregoing formalisms by setting $\mu = 0$ and restricting the summation over I to only charge-neutral states. Note that different ensembles must converge in a sound application of equilibrium thermodynamics[39] (violating cases include a massively charged plasma mentioned above and a celestial mechanical system held together by gravitation, both characterized by long-range forces). For instance, the grand canonical ensemble of an ideal gas of atoms that can exchange electrons should be recovered exactly by the canonical ensemble for an ideal gas of clusters of noninteracting atoms that can exchange electrons, in the limit of an infinite cluster size.

Finite-Temperature Full Configuration Interaction

A unique advantage of *ab initio* electronic structure theory, which may be responsible for its rapid development, is the availability of the full-configuration-interaction (FCI) method[3] that determines an exact, basis-set solution of the electronic Schrödinger equation. It offers benchmark data, with which a whole hierarchy of converging approximations can be verified, calibrated, and assessed.

It is straightforward[41] to extend the FCI method to the grand canonical ensemble because its zero-temperature counterpart can define unambiguously and calculate exactly all state energies with any number of electrons. These energies are then summed over to form the grand partition function Ξ. The Ω can be obtained immediately from Ξ. The U and $\bar{N}$ are computed by the density-matrix definitions rather than from Ξ because its partial derivatives with respect to β or μ cannot be easily taken numerically (μ tends to vary with β and vice versa in a finite-difference method). The value of μ that maintains the charge-neutrality can be determined by a bisection method, using the calculated $\bar{N}$. The method can be trivially extended to the canonical ensemble.[41]

The string-based, general-order algorithm[42] is most suitable for computer implementation because it can be readily upgraded to a (zero-temperature) general-order MBPT[43] or general-order CC method.[44] The finite-temperature FCI method is hence an invaluable pilot for the developments of all finite-temperature *ab initio* electronic structure methods and their initial computer programs. Note, however, that it is based on *sum-over-states* formalisms and prohibitively expensive, useful primarily for assisting the developments of more practical methods, which must be expressed by *sum-over-orbitals* formulas.

Fermi–Dirac Theory

Many *ab initio* theories start with a zeroth-order or reference approximation, which is then systematically improved. For electrons, we often rely on Fermi–Dirac theory[41,45–47] as the reference method, which is defined by a one-electron approximation to the Hamiltonian,

$$\hat{H}^{(0)} \equiv \sum_p \epsilon_p \hat{p}^\dagger \hat{p}, \tag{10}$$

where $\hat{p}^\dagger$ and $\hat{p}$ are a creation and annihilation operator of an electron in the pth spin orbital with the orbital energy ϵ_p. With this approximation, each zeroth-order energy $E_I^{(0)}$ of the Ith Slater-determinant state is the sum of occupied orbital energies, leading to a drastic simplification in the zeroth-order grand partition function:

$$\Xi^{(0)} \equiv \sum_I e^{-\beta(E_I^{(0)} - \mu^{(0)} N_I)} = \prod_p \left(1 + e^{-\beta(\epsilon_p - \mu^{(0)})}\right), \tag{11}$$

where the sum is over an exponential (or even factorial) number of all Slater-determinant states, but the product is taken over all spin orbitals only. All thermodynamic functions are also analytically transformed into compact *sum-over-orbitals* expressions, which can be evaluated almost instantly for systems of any size including three-dimensional solids:

$$\begin{aligned} \Omega^{(0)} &= \sum_p \left(\epsilon_p - \mu^{(0)}\right) f_p^- \\ &\quad + \frac{1}{\beta} \sum_p \left(f_p^- \ln f_p^- + f_p^+ \ln f_p^+\right), \end{aligned} \tag{12}$$

$$U^{(0)} = \sum_p \epsilon_p f_p^-, \tag{13}$$

$$S^{(0)} = -k_{\mathrm{B}} \sum_p \left(f_p^- \ln f_p^- + f_p^+ \ln f_p^+\right), \tag{14}$$

as well as

$$\bar{N} = \sum_p f_p^-, \tag{15}$$

which is solved for $\mu^{(0)}$. The $f_p^{\mp}$ are the Fermi–Dirac distribution functions given by

$$f_p^- = \frac{1}{1 + e^{\beta(\epsilon_p - \mu^{(0)})}} \;\; ; \;\; f_p^+ = 1 - f_p^- . \tag{16}$$

The same drastic simplification embodied by Eq. (11) does not transpire in the canonical ensemble. Whether *sum-over-states* formulas simplify into *sum-over-orbitals* formulas largely determines the practical utility of a method, and in this sense, the grand canonical ensemble is useful, while the canonical ensemble is useless. The author could not identify any profound physical reason for this crucial mathematical difference. Since both ensembles are ultimately equivalent and the grand canonical ensemble encompasses the canonical ensemble, we might be fortunate.

Strictly speaking, Fermi–Dirac theory is no longer "*ab initio*" because the Hamiltonian is altered. However, finite-temperature MBPT based on Fermi–Dirac theory as the zeroth-order approximation takes into account the difference $\hat{H} - \hat{H}^{(0)}$ as perturbation and restores the status of *ab initio*.

Finite-Temperature Many-Body Perturbation Theory

A finite-temperature version of MBPT has been extensively developed by Bloch and coworkers,[29,48,49] exploiting the isomorphism of the time-dependent Schrödinger equation and the β-dependent Bloch equation where β plays the role of imaginary time.[45,50–54] However, this time-dependent derivation is even less transparent and less flexible than the same approach sometimes adopted for zero-temperature MBPT in this fundamentally time-independent problem. In it, for instance, the chemical potential, internal energy, and entropy are not expanded in mutually consistent perturbation series, leaving only the grand potential formula with a fixed chemical potential, quickly violating the charge neutrality of the macroscopic electronic structures. Even the first-order corrections to these thermodynamic functions have not been spelled out for a long time.

Then, a more disturbing problem was discovered by Kohn and Luttinger.[55] They showed that the finite-temperature MBPT thus derived may not reduce to the well-established zero-temperature MBPT for a homogeneous electron gas (HEG) as temperature T goes to zero. On this basis, Kohn and Luttinger concluded:[55] "The BG [Brueckner–Goldstone perturbation] series is in general not correct." Although this internal inconsistency between finite- and zero-temperature MBPT — the Kohn–Luttinger nonconvergence problem — was later shown[56] to be circumvented in a HEG, it was predicted to persist for a general degenerate reference. Over the next sixty years, however, this prediction has never been confirmed analytically or numerically, sowing confusions.

The depth of the confusions can be sensed in the following quotations from textbooks for quantum many-body theory, casting doubt on the validity of the very finite-temperature MBPT these textbooks are teaching:

> "... a note of caution is called for whenever we attempt to calculate zero-temperature properties from an expression for the same quantities at nonzero temperatures T by taking the limit $T \to 0$. The physics is not necessarily the same in both cases."[53]

> "In any case it serves as a warning against taking the results of perturbation theory too seriously."[50]

They underscore the existence of a gap in fundamental theoretical physics, awaiting a resolution. The significance and urgency of such a resolution are elevated by the fact that zero-temperature *ab initio* second-order MBPT [MBPT(2)] calculations for one-dimensional solids have been routine since 1990s[10–14,17,22] and extended to MBPT(4)[10,11] and CC with singles and doubles (CCSD)[15,16,19] and to three-dimensional solids[20–23] more recently.

To resolve this issue, we first established a transparent, robust, and general approach to postulating finite-temperature MBPT for all thermodynamic functions at all perturbation orders.[57–59] It consists of two vital elements: First, we base the finite-temperature formulation on an unambiguous definition of the grand partition function, from which all thermodynamic functions can be derived, entirely in a time-independent picture. Second, we return to the canonical definition of any perturbation theory,[5,60] in which the nth-order correction to an observable X is given by

$$X^{(n)} = \frac{1}{n!} \left. \frac{\partial^n X(\lambda)}{\partial \lambda^n} \right|_{\lambda=0}, \tag{17}$$

where $X(\lambda)$ is the exact value of X for a perturbation-scaled Hamiltonian, $\hat{H} = \hat{H}^{(0)} + \lambda\hat{V}$, with λ being the dimensionless perturbation strength. Defined as such, the perturbation series is, by construction, size-extensive and convergent toward exactness.[5] (Conversely, a "perturbation theory" that does not adhere to this canonical definition, such as Brillouin–Wigner perturbation theory, tends to lack size-extensivity.[5]) This approach is in sharp contrast with the previous time-dependent, diagrammatic formulation of zero- and nonzero-temperature MBPT, which exploits the coincidental similarity between the Schrödinger and Bloch equations and tacitly relies on human intuitions when a whole set of diagrams needs to be conjured up exhaustively.[29,45,48–54] Its absence of an unambiguous grand partition function makes it unclear how thermodynamic functions other than the grand potential are expanded in consistent perturbation series and whether the series are convergent.

Our approach, instead, starts with the exact grand partition function of Eq. (1) and differentiating it with respect to λ, leading to a Rayleigh–Schrödinger-like recursion relationship for the perturbation corrections to grand potential $\Omega^{(n)}$ reliably and straightforwardly,[59]

$$\begin{aligned}\Omega^{(n)} &= \langle D^{(n)}\rangle + \frac{(-\beta)}{2!}\sum_{i=1}^{n-1}\left(\langle D^{(i)}D^{(n-i)}\rangle - \Omega^{(i)}\Omega^{(n-i)}\right) \\ &\quad + \frac{(-\beta)^2}{3!}\sum_{i=1}^{n-2}\sum_{j=1}^{n-i-1}\left(\langle D^{(i)}D^{(j)}D^{(n-i-j)}\rangle - \Omega^{(i)}\Omega^{(j)}\Omega^{(n-i-j)}\right) \\ &\quad + \cdots + \frac{(-\beta)^{n-1}}{n!}\left(\langle (D^{(1)})^n\rangle - (\Omega^{(1)})^n\right), \end{aligned} \tag{18}$$

and to similar recursions for the internal energy $U^{(n)}$, entropy $S^{(n)}$, and chemical potential $\mu^{(n)}$. All we have to do is to differentiate the exact definitions of thermodynanmic functions with λ, such as Eqs. (3)–(6), involving no more than some exponentials and logarithms; no complex analysis or top-down diagrammatics are needed. Here, $\langle X\rangle$ means a zeroth-order thermal average,

$$\langle X\rangle = \frac{\sum_I X_I e^{-\beta(E_I^{(0)}-\mu^{(0)}N_I)}}{\sum_I e^{-\beta(E_I^{(0)}-\mu^{(0)}N_I)}}, \tag{19}$$

where X_I is the value of property X for the Ith Slater-determinant state, and $D_I^{(n)} \equiv E_I^{(n)} - \mu^{(n)} N_I$.

The $E_I^{(n)}$, in turn, is the nth-order correction to the Ith Slater-determinant state obtained by a size-extensive, convergent perturbation theory that adheres to the canonical definition of perturbation theory, Eq. (17). Such a perturbation theory, which must accommodate both nondegenerate and degenerate Slater-determinant references, exists under various names[61] including the one fully developed by Hirschfelder and Certain.[62] It defines, in a consistent, uniform, unambiguous approximation, the energies of all states with any number of electrons that enter the grand partition function, ensuring the internal consistency, size-extensivity, and exact convergence of the resulting finite-temperature MBPT at all perturbation orders.[59] (By "exact convergence," we do not mean absolute convergence, but rather that if the perturbation series does converge, it converges at the exact limit, because it does not overlook or incorrectly evaluate any term.)

Recursions such as Eq. (18) can be implemented into a general-order algorithm by modifying a string-based, finite-temperature FCI program. It provides benchmark data for $\Omega^{(n)}$, $U^{(n)}$, $S^{(n)}$, and $\mu^{(n)}$ for any arbitrary perturbation order n at a FCI computational cost.[59] Alternatively, Eq. (17) can be evaluated for $X = \Omega$, U, S, or μ by numerically differentiating the corresponding quantities calculated by finite-temperature FCI with a perturbation-scaled Hamiltonian, $\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}$.[63] The latter, which we call the λ-variation method,[60] offers a second route to benchmark data for the several lowest perturbation orders, again at a FCI cost. They agree with each other numerically exactly,[57–59] mutually verifying the recursions and computer programs. They are easily extended to the canonical ensemble.[64]

When applied to an ideal gas of molecules (an ensemble of an infinite number of identical, neutral, nonvibrating, nonrotating molecules that do not interact with each other, but can exchange electrons), our "new" finite-temperature MBPT is convergent[59] toward the finite-temperature FCI (see Fig. 2) unless it is divergent. (Recall that a perturbation series is inevitably occasionally divergent because it has a finite radius of convergence toward FCI; the Kohn–Luttinger nonconvergence problem is fundamentally different from this because it implies the zero radius of convergence toward zero-temperature MBPT under some conditions.) This proves the finite-temperature MBPT is correct and complete in that no term is overlooked and every term is evaluated correctly. All fundamental thermodynamic relationships, such as Eqs. (7)–(9), are obeyed by perturbation corrections on an order-by-order basis (not necessarily by their sums).[59]

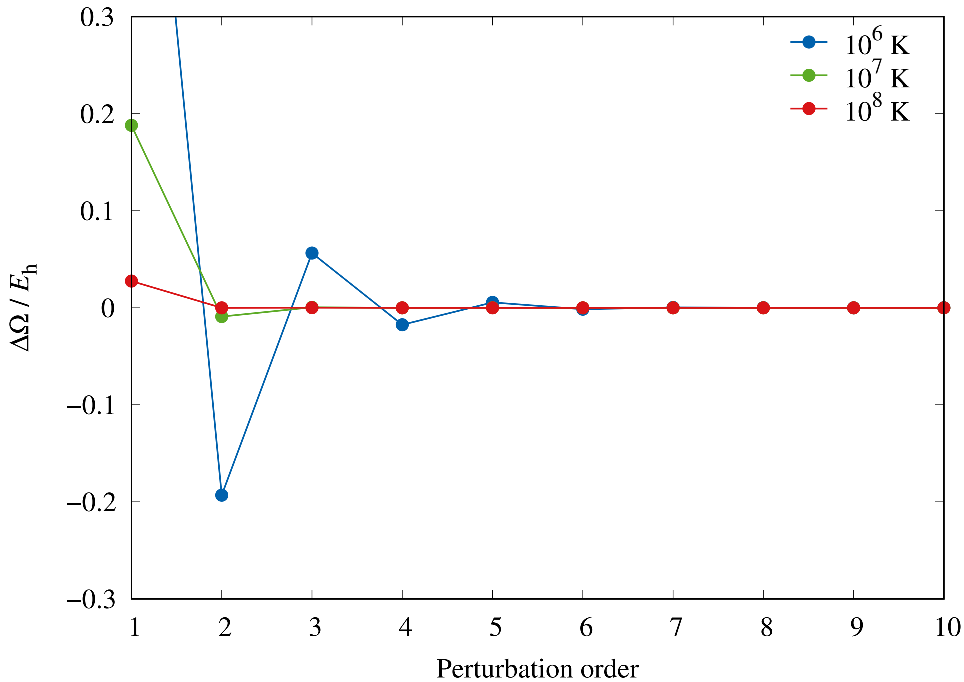


Figure 2: The difference in the grand potential (ΔΩ in E_h) between finite-temperature MBPT(n) and finite-temperature FCI for an ideal gas of the hydrogen fluoride molecules as a function of perturbation order n.[59]

These converging "new" perturbation correction formulas[57–59] differ from the "old" ones[54,65,66] obtained by the time-dependent derivation. Figure 3 plots the first- and second-order perturbation approximations to the grand potential obtained by two different derivation strategies against the exact (finite-temperature FCI) results across a wide range of temperature. While the "new" perturbation approximations systematically approach the exact results as the perturbation order is raised from one to two (to three to four at some temperatures), the "old" perturbation approximations deviate more and more from the exact values with increasing temperature. This is not so much because the "old" formulas are erroneous as because they lack the ability to improve the chemical potential perturbatively; the "old" formulas would be correct if the particles were not electrically charged and the chemical potential could be arbitrarily chosen. For electrons, this is not the case and the chemical potential must also change from the zeroth to first to infinite order to maintain the charge-neutrality at every order; lest the equilibrium thermodynamics break down. The "old" grand potentials in this figure are evaluated with the chemical potentials held fixed at their zeroth-order Fermi–Dirac values at respective temperatures, which differ from the exact chemical potentials considerably, describing a massively charged plasma that does not obey equilibrium thermodynamics. This, in turn, is caused by the fact that the time-dependent derivation starting with the Bloch equation is not flexible enough to provide a clear path to perturbation correction formulas for the chemical potential, internal energy, and entropy. Our alternative, general, and versatile strategy of defining the grand partition function followed by differentiating it with λ repairs this shortcoming.

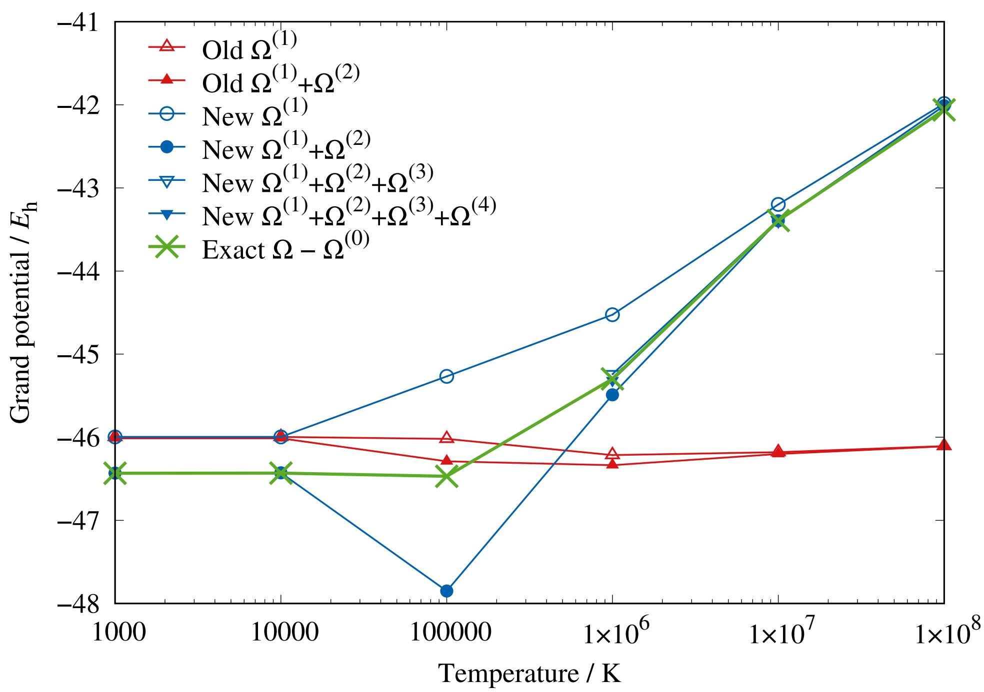


Figure 3: Comparison of the "old" and "new" perturbation approximations to the grand potential (the common zeroth-order grand potential is subtracted for clarity) for the same system as Fig. 2. The exact (finite-temperature FCI) results are superposed.[59,63]

Now that the *sum-over-states* formulas for all thermodynamic functions at all perturbation orders can be reliably obtained in the form of recursions, the next important question is: Do they lend themselves to the same drastic simplification to *sum-over-orbitals* formulas such as in Fermi–Dirac theory? If they did not, the theory would never be useful in practical applications for macroscopic systems because they would cost more than a FCI calculation even at the lowest orders.

At first glance, it appears hopeless that such a simplification takes place because $E^{(n)}$ entering the recursions are the eigenvalues of the following perturbative energy matrix $\boldsymbol{E}^{(n)}$ within a degenerate subspace, and eigenvalues are generally not expressed in a closed form:

$$\boldsymbol{E}^{(n)} = \begin{pmatrix} \langle \Phi_1^{(0)} | \hat{V} | \Phi_1^{(n-1)} \rangle & \dots & \langle \Phi_1^{(0)} | \hat{V} | \Phi_M^{(n-1)} \rangle \\ \vdots & & \vdots \\ \langle \Phi_M^{(0)} | \hat{V} | \Phi_1^{(n-1)} \rangle & \dots & \langle \Phi_M^{(0)} | \hat{V} | \Phi_M^{(n-1)} \rangle \end{pmatrix}, \tag{20}$$

where M is the degree of degeneracy, and Slater-determinant states $\Phi_1^{(0)}$ through $\Phi_M^{(0)}$ share the same zeroth-order energy $E_1^{(0)} = \cdots = E_M^{(0)}$. However, with the aid of a few mathematical tricks, we can indeed simplify the *sum-over-states* formulas into *sum-over-orbitals* expressions exactly, rendering the finite-temperature MBPT efficiently applicable to infinite systems. This can be best explained by examples:

The recursion of Eq. (18) gives a sum-over-states formula for the first-order grand potential,

$$\Omega^{(1)} = \langle D^{(1)} \rangle = \langle E^{(1)} \rangle - \mu^{(1)} \bar{N}. \tag{21}$$

For a nondegenerate reference, $E_I^{(1)} = \sum_i^I h_{ii} + \frac{1}{2} \sum_{i,j}^I \langle ij || ij \rangle - \sum_i^I \epsilon_i$, where $\sum_i^I$ means that i runs over all spin orbitals occupied in the Ith Stater determinant, h_{pq} is a one-electron integral, and $\langle pq || rs \rangle$ is an antisymmetrized two-electron integral. If all states were nondegenerate at the zeroth order, we could reduce this zeroth-order thermal average into a sum-over-orbitals expression as

$$\begin{aligned} \langle E^{(1)} \rangle &= \frac{\sum_I E_I^{(1)} e^{-\beta(E_I^{(0)} - \mu^{(0)} N_I)}}{\sum_I e^{-\beta(E_I^{(0)} - \mu^{(0)} N_I)}} && (22) \\ &= \sum_p h_{pp} f_p^- + \frac{1}{2} \sum_{p,q} \langle pq || pq \rangle f_p^- f_q^- - \sum_p \epsilon_p f_p^-, && (23) \end{aligned}$$

using combinatorial identities listed in Appendix A of Hirata and Jha,[58] which can be worked out relatively easily on demand. Here, $\sum_p$ means that p runs over all spin orbitals, and f_p^- is the Fermi–Dirac distribution function given in Eq. (16). Note that the summations in Eq. (23) are at most the number of orbitals squared in length and can be carried out for solids, while the summations in Eq. (22) are over exponentially (or factorially) many Slater determinants and are hopeless even for a midsize molecule.

It is, however, more a rule than an exception that many zeroth-order Slater-determinant states are degenerate. The $E_I^{(1)}$s for those degenerate states are the eigenvalues of the nondiagonal matrix of Eq. (20), whose elements are given variously as

$$E_{IJ}^{(1)} = \sum_i^I h_{ii} + \frac{1}{2}\sum_{i,j}^I \langle ij||ij\rangle - \sum_i^I \epsilon_i, \quad \text{for } \Phi_J = \Phi_I; \tag{24}$$

$$E_{IJ}^{(1)} = h_{ia} + \sum_j^I \langle ij||aj\rangle, \quad \text{for } \Phi_J = (\Phi_I)_i^a; \tag{25}$$

$$E_{IJ}^{(1)} = \langle ij||ab\rangle, \quad \text{for } \Phi_J = (\Phi_I)_{ij}^{ab}; \tag{26}$$

and are zero otherwise. Eigenvalues of such a matrix (or of any matrix larger than 4×4) cannot be expressed in a closed form, making any further simplification appear unlikely. Nevertheless, we can indeed simplify $\langle E^{(1)}\rangle$ for mixed degenerate and nondegenerate references into the same sum-over-orbitals expression of Eq. (23). This is because the eigenvalues in a degenerate subspace are summed over with an equal weight of $e^{-\beta(E_I^{(0)}-\mu^{(0)}N_I)}$, and, therefore, we do not need to know the *individual* eigenvalues to carry out this summation correctly; we only need the *sum* of the eigenvalues in each degenerate subspace, and this sum is equal to the trace, i.e., the sum over Eq. (24), leading to the same sum-over-orbitals formula of Eq. (23).

Together, we find[57–59]

$$\Omega^{(1)} = \sum_p F_{pp} f_p^- - \frac{1}{2}\sum_{p,q} \langle pq||pq\rangle f_p^- f_q^- - \mu^{(1)}\bar{N}, \tag{27}$$

where $F_{pq} = \epsilon_{pq}^{\text{HF}} - \delta_{pq}\epsilon_p$ with $\epsilon_{pq}^{\text{HF}} = h_{pq} + \sum_r \langle pr||qr\rangle f_r^-$ being the finite-temperature Fock matrix that defines thermal Hartree–Fock (HF) theory.[46,47] Combining with $\Omega^{(0)}$ of Fermi–Dirac theory, Eq. (12), we obtain

$$\Omega^{(0)} + \Omega^{(1)} = \sum_p \left(h_{pp} - \mu^{(0)} - \mu^{(1)}\right) f_p^- + \frac{1}{2}\sum_{p,q} \langle pq||pq\rangle f_p^- f_q^- + \frac{1}{\beta}\sum_p \left(f_p^- \ln f_p^- + f_p^+ \ln f_p^+\right), \quad (28)$$

which closely mirrors the grand potential of thermal HF theory,[46,47] but not exactly, with an important difference[59] (see below).

The second order becomes more instructive.[58,59] The sum-over-states formula of $\Omega^{(2)}$ is obtained from the recursion, Eq. (18), as

$$\begin{aligned}
\Omega^{(2)} &= \langle D^{(2)}\rangle - \frac{\beta}{2}\left(\langle D^{(1)}D^{(1)}\rangle - \langle D^{(1)}\rangle\langle D^{(1)}\rangle\right) \\
&= \langle E^{(2)}\rangle - \frac{\beta}{2}\left(\langle E^{(1)}E^{(1)}\rangle - \langle E^{(1)}\rangle\langle E^{(1)}\rangle\right) \\
&\quad -\mu^{(2)}\bar{N} + \beta\mu^{(1)}\left(\langle E^{(1)}N\rangle - \langle E^{(1)}\rangle\langle N\rangle\right) \\
&\quad -\frac{\beta}{2}\left(\mu^{(1)}\right)^2\left(\langle NN\rangle - \langle N\rangle\langle N\rangle\right). \quad (29)
\end{aligned}$$

The first term, $\langle E^{(2)}\rangle$, can be reduced as before by using the fact that the sum of the eigenvalues of a matrix is equal to the sum of its diagonal elements. For either a degenerate or nondegenerate reference, the diagonal element can be written in the same, closed form of

$$E_{II}^{(2)} = \sum_{i,a}^{\text{denom.}\neq 0} \frac{|h_{ia} + \sum_j \langle ij||aj\rangle|^2}{\epsilon_i - \epsilon_a} + \frac{1}{4}\sum_{i,j,a,b}^{\text{denom.}\neq 0} \frac{|\langle ij||ab\rangle|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (30)$$

where i, j (a, b) run over spin orbitals occupied (unoccupied) in the Ith Slater determinant and "denom.$\neq$ 0" means that the summations are restricted to nonzero denominators ($\epsilon_i - \epsilon_a \neq 0$ or $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b \neq 0$). Using combinatorial identities listed in Appendix A of Hirata and Jha,[58] we can take its zeroth-order thermal average to obtain

$$\langle E^{(2)}\rangle = \sum_{p,q}^{\text{denom.}\neq 0} \frac{|F_{pq}|^2 f_p^- f_q^+}{\epsilon_p - \epsilon_q} + \frac{1}{4}\sum_{p,q,r,s}^{\text{denom.}\neq 0} \frac{|\langle pq||rs\rangle|^2 f_p^- f_q^- f_r^+ f_s^+}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s}, \quad (31)$$

where $F_{pq} = \epsilon_{pq}^{\text{HF}} - \delta_{pq}\epsilon_p$, and p, q, r, s run over all spin orbitals excluding zero-denominator cases.

Going from Eq. (30) to (31) is far more tedious than their apparent similarities may suggest, but what is important is the fact that the derivation logic is linear and every step of it involves no more than elementary combinatorial arithmetic.

The foregoing derivation may give a false impression that the off-diagonal elements of the perturbative energy matrix, Eq. (20), are irrelevant; they are indeed essential in the second term, $\langle E^{(1)}E^{(1)}\rangle - \langle E^{(1)}\rangle\langle E^{(1)}\rangle$, of Eq. (29). For a nondegenerate state, the corresponding summands of $\langle E^{(1)}E^{(1)}\rangle$ and $\langle E^{(1)}\rangle\langle E^{(1)}\rangle$ cancel out exactly, which is desirable and expected because individually they are nonsize-extensive. In a degenerate subspace, $\langle E^{(1)}E^{(1)}\rangle$ is the zeroth-order thermal average of the squares of the eigenvalues of $\boldsymbol{E}^{(1)}$. Owing to the trace invariance of a cyclic matrix product, the sum of the eigenvalues squared is equal to the sum of the diagonal elements of the matrix squared, $(\boldsymbol{E}^{(1)})^2$. Furthermore, a diagonal element of the squared matrix can be broken down into components:

$$
\begin{aligned}
(\boldsymbol{E}^{(1)})^2_{II} &= \langle \Phi_I|\hat{V}|\Phi_I\rangle\langle \Phi_I|\hat{V}|\Phi_I\rangle + \sum_{i,a}^{\text{denom.}=0} \langle \Phi_I|\hat{V}|(\Phi_I)_i^a\rangle\langle (\Phi_I)_i^a|\hat{V}|\Phi_I\rangle \\
&\quad + \sum_{i,j,a,b}^{\text{denom.}=0} \langle \Phi_I|\hat{V}|(\Phi_I)_{ij}^{ab}\rangle\langle (\Phi_I)_{ij}^{ab}|\hat{V}|\Phi_I\rangle
\end{aligned}
\tag{32}
$$

where i, j (a, b) run over spin orbitals occupied (unoccupied) in the Ith Slater determinant, “denom.= 0” means that summations are restricted to only those $(\Phi_I)_i^a$ and $(\Phi_I)_{ij}^{ab}$ that are degenerate with Φ_I (or whose fictitious denominators, $\epsilon_i - \epsilon_a$ or $\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b$, are zero). The thermal average of the first term (nonsize-extensive, diagonal product) no longer cancels out exactly the corresponding summand in $\langle E^{(1)}\rangle\langle E^{(1)}\rangle$, leaving a nonzero residual that must not be overlooked.[58]

Using the sum-over-orbitals formulas of these off-diagonal elements of $\boldsymbol{E}^{(1)}$ in Eqs. (25) and (26) in conjunction with combinatorial identities,[58] after an extremely tedious, yet straightforward arithmetic, we obtain

$$
\langle E^{(1)}E^{(1)}\rangle - \langle E^{(1)}\rangle\langle E^{(1)}\rangle = \sum_{p,q}^{\text{denom.}=0} |F_{pq}|^2 f_p^- f_q^+ + \frac{1}{4}\sum_{p,q,r,s}^{\text{denom.}=0} |\langle pq||rs\rangle|^2 f_p^- f_q^- f_r^+ f_s^+, \tag{33}
$$

where the meaning of "denom.= 0" has already been mentioned. Repeating the same process for every term, we finally get a sum-over-orbitals formula,[58,59]

$$\begin{aligned}\Omega^{(2)} &= \sum_{p,q}^{\text{denom.}\neq 0} \frac{|F_{pq}|^2 f_p^- f_q^+}{\epsilon_p - \epsilon_q} + \frac{1}{4} \sum_{p,q,r,s}^{\text{denom.}\neq 0} \frac{|\langle pq||rs\rangle|^2 f_p^- f_q^- f_r^+ f_s^+}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} \\ &\quad -\frac{\beta}{2} \sum_{p,q}^{\text{denom.}=0} |F_{pq}|^2 f_p^- f_q^+ - \frac{\beta}{8} \sum_{p,q,r,s}^{\text{denom.}=0} |\langle pq||rs\rangle|^2 f_p^- f_q^- f_r^+ f_s^+ \\ &\quad -\mu^{(2)}\bar{N} + \beta\mu^{(1)} \sum_p F_{pp} f_p^- f_p^+ - \frac{\beta}{2}\left(\mu^{(1)}\right)^2 \sum_p f_p^- f_p^+, \end{aligned} \tag{34}$$

which differs from the "old" formula[54,65,66] by the last three terms all involving perturbation corrections to the chemical potential. This expression should be efficiently evaluable for solids.

The perturbation corrections to μ, U, and S are obtained completely analogously:[58,59] Step one, differentiate the exact definitions of these thermodynamic functions, Eq. (4)–(6), with respect to λ to arrive at recursions; Step two, obtain order-by-order sum-over-states formulas for the perturbation corrections from the recursions; Step three, reduce each zeroth-order thermal average in the sum-over-states formulas by combining the degenerate perturbation energy expressions, trace invariance of cyclic matrix products to avoid eigenvalues, and combinatorial identities to arrive at compact sum-over-orbitals formulas. (The last step, especially the discoveries of combinatorial identities, seems only possible in the grand canonical ensemble, but not in the canonical ensemble.) Thus, both sum-over-states and sum-over-orbitals expressions for $\Omega^{(n)}$, $\mu^{(n)}$, $U^{(n)}$, and $S^{(n)}$ for $1 \leq n \leq 3$ have been established for the first time.[57–59] For instance,

$$\mu^{(1)} = \frac{\sum_p F_{pp} f_p^- f_p^+}{\sum_p f_p^- f_p^+}, \tag{35}$$

and

$$U^{(1)} = \sum_p F_{pp} f_p^- - \frac{1}{2}\sum_{p,q} \langle pq||pq\rangle f_p^- f_q^- - \beta \sum_p \left(F_{pp} - \mu^{(1)}\right) \epsilon_p f_p^- f_p^+, \tag{36}$$

$$U^{(0)} + U^{(1)} = \sum_p h_{pp} f_p^- + \frac{1}{2}\sum_{p,q} \langle pq||pq\rangle f_p^- f_q^- - \beta \sum_p \left(F_{pp} - \mu^{(1)}\right) \epsilon_p f_p^- f_p^+. \tag{37}$$

The last expression is close, but not equal to the internal energy of thermal HF theory[46,47,59] (see below). See the original papers[58,59] for other higher-order formulas.

Just as in the historical development of zero-temperature Møller–Plesset perturbation theory for atomic and molecular applications,[2,5,6,43] in the finite-temperature MBPT also, the recursions and subsequent algebraic reductions can be first established,[57–59] upon which more expedient quantum-field-theoretical techniques of normal-ordered second quantization and Feynman diagrams at finite temperature[59] can be built bottom up. On this basis, the linked-diagram theorem (thus size-extensivity) at finite temperature can be rigorously proven,[59] although this is implied by the adherence to the canonical definition of perturbation theory, Eq. (17). Unusual diagrams such as the anomalous[55] and renormalization[59] diagrams are shown to manifest only at nonzero temperature, which are also anticipated by the aforementioned, straightforward (if tedious) algebraic derivations.[59] The anomalous diagrams, such as the third and fourth terms of $\Omega^{(2)}$ in Eq. (34) carrying a factor of β, have been implicated in the Kohn–Luttinger nonconvergence problem,[55] which we now discuss.

Kohn–Luttinger Nonconvergence Problem

The internal energy — the thermal average of all state energies — must reduce to the energy of the lowest-lying states that are solely populated as $T \to 0$. In the exact theory, therefore,

$$\lim_{T\to 0} U = \lim_{T\to 0} \frac{\sum_I E_I e^{-\beta(E_I-\mu N_I)}}{\sum_I e^{-\beta(E_I-\mu N_I)}} = E_0. \tag{38}$$

Since this statement appears so self-evident, Kohn and Luttinger's prediction[55] that this may not be the case with perturbation approximations for a degenerate reference is highly counterintuitive, and it has been dismissed by some researchers.[54,66] According to Kohn and Luttinger,[55] the deviation of the zero-temperature limit of $U^{(n)}$ from $E_0^{(n)}$ could be infinity because some terms in $U^{(n)}$ carry a divergent factor of $\beta = (k_\mathrm{B}T)^{-1}$ [see, e.g., Eq. (36)].

With the converging finite-temperature MBPT formulas for all thermodynamic functions and their general-order implementation fully established as described above,[59] we are in a unique position to prove or disprove Kohn and Luttinger's prediction both analytically and numerically. The question is whether the following equality holds or not for a general degenerate reference:

$$\lim_{T\to 0} U^{(n)} \stackrel{?}{=} E_0^{(n)}, \tag{39}$$

where $E_0^{(n)}$ is the nth-order degenerate perturbation correction[62] to the ground-state energy.

Let us first examine the numerical results of a general-order finite-temperature MBPT calculation for an ideal gas of the square planar H_4 molecule with a degenerate HF reference.[67] Figure 4 shows that only $U^{(0)}$ of Fermi–Dirac theory reduces correctly to $E_0^{(0)}$, but as soon as the perturbation is turned on, the internal energies approach wrong zero-temperature limits: $U^{(1)}$ converges at a finite value as $T \to 0$, but it differs from $E_0^{(1)}$ of degenerate perturbation theory; at the second and all higher orders, $U^{(n)}$ is divergent as $T \to 0$, while the corresponding $E_0^{(n)}$ is always finite (not shown to avoid clutter), displaying an infinite error at $T = 0$. This figure, therefore, unequivocally confirms the existence of the Kohn–Luttinger nonconvergence problem.[67,68]

These numerical results can be rationalized analytically.[67] The recursion[59] for $U^{(n)}$ gives the following sum-over-states formulas[67] for $n = 0$, 1, and 2:

$$U^{(0)} = \langle E^{(0)} \rangle, \tag{40}$$

$$U^{(1)} = \langle E^{(1)} \rangle - \beta \operatorname{cov}\left[D^{(0)}, D^{(1)}\right], \tag{41}$$

$$\begin{aligned} U^{(2)} = {} & \langle E^{(2)} \rangle - \beta \operatorname{cov}\left[D^{(1)}, D^{(1)}\right] - \beta \operatorname{cov}\left[D^{(0)}, D^{(2)}\right] \\ & + \frac{\beta^2}{2} \operatorname{cov}\left[D^{(0)}, (D^{(1)})^2\right] - \beta^2 \operatorname{cov}\left[D^{(0)}, D^{(1)}\right] \langle D^{(1)} \rangle, \end{aligned} \tag{42}$$

where $\operatorname{cov}[X, Y] \equiv \langle XY \rangle - \langle X \rangle \langle Y \rangle$ and $D_I^{(n)} \equiv E_I^{(n)} - \mu^{(n)} N_I$ with $E_I^{(n)}$ being the Ith eigenvalue of the nth-order perturbation energy matrix of Eq. (20).

If the reference is nondegenerate, each zeroth-order thermal average $\langle \ldots \rangle$ is dominated by the

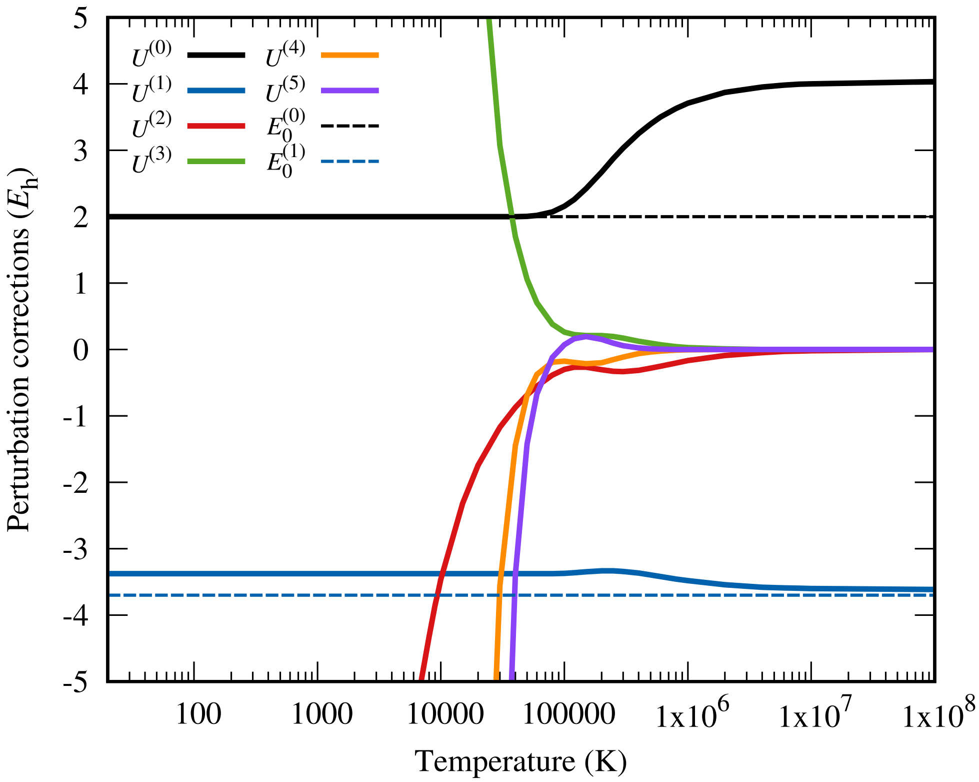


Figure 4: Perturbation corrections to the internal energy ($U^{(n)}; 0 \leq n \leq 5$) as a function of temperature for an ideal gas of the square-planar H_4 molecules with a degenerate reference. Perturbation corrections to the ground-state energy ($E_0^{(n)}; 0 \leq n \leq 1$) from degenerate perturbation theory (as the correct zero-temperature limits) are shown as dashed lines. $E_0^{(n)}$ for $n \geq 2$ are not shown to avoid clutter, but they are close to zero. Reproduced from Hirata[68] with permission from Elsevier.

single lowest zeroth-order energy state, and $\lim_{T\to 0}\langle E^{(n)}\rangle = E_0^{(n)}$ and $\lim_{T\to 0}\mathrm{cov}[\ldots] = 0$, implying

$$\lim_{T\to 0} U^{(n)} = E_0^{(n)} \text{ for a nondegenerate reference.} \tag{43}$$

There is no Kohn–Luttinger nonconvergence problem in this case.

If instead the reference is M-fold degenerate ($E_0^{(0)} = E_1^{(0)} = \cdots = E_{M-1}^{(0)}$), each zeroth-order thermal average $\langle \ldots \rangle$ is now dominated evenly by the M states in this degenerate subspace. Therefore, $\lim_{T\to 0}\langle E^{(n)}\rangle = E[E^{(n)}]$, where the right-hand side is the average of the eigenvalues of $\boldsymbol{E}^{(n)}$ within the degenerate subspace. The zero-temperature limit of $\mathrm{cov}[D^{(i)}, D^{(j)}]$ is then the covariance of the two distributions $\{D^{(i)}\}$ and $\{D^{(j)}\}$ within the same degenerate subspace. It is zero if one or both of the two distributions has zero variance, such as when $i = 0$ and/or $j = 0$; otherwise it is nonzero. Therefore, for a degenerate reference,

$$\lim_{T\to 0} U^{(0)} = E\left[E^{(0)}\right] = E_0^{(0)}, \tag{44}$$

$$\lim_{T\to 0} U^{(1)} = E\left[E^{(1)}\right] \begin{cases} = E_0^{(1)}, & \text{if } E_0^{(1)} = \cdots = E_{M-1}^{(1)}; \\ \neq E_0^{(1)}, & \text{otherwise,} \end{cases} \tag{45}$$

$$\lim_{T\to 0} U^{(2)} = E\left[E^{(2)}\right] - \beta\,\mathrm{cov}\left[D^{(1)}, D^{(1)}\right] \begin{cases} = E\left[E_0^{(2)}\right], & \text{if } E_0^{(1)} = \cdots = E_{M-1}^{(1)}; \\ = -\infty, & \text{otherwise.} \end{cases} \tag{46}$$

The zero-temperature limit of Fermi–Dirac theory ($U^{(0)}$) is always correct, regardless of whether the reference is degenerate or nondegenerate. The $U^{(1)}$ converges at a finite value as $T \to 0$, and it agrees with $E_0^{(1)}$ of degenerate perturbation theory if and only if the degeneracy is not lifted at the first order. If the degeneracy is lifted, instead, the zero-temperature limit of $U^{(1)}$ is the average of $E_0^{(1)}, \ldots, E_{M-1}^{(1)}$, which is no longer equal to $E_0^{(1)}$; there is a finite deviation in the zero-temperature limit of $U^{(1)}$ from the correct limit of $E^{(1)}$. In the latter case, furthermore, $\mathrm{cov}[D^{(1)}, D^{(1)}]$ is nonzero, causing $U^{(2)}$ to be divergent as $T \to 0$ ($\beta \to \infty$), while $E_0^{(2)}$ is always finite. Hence, there is an infinite deviation in the zero-temperature limit of $U^{(2)}$ from the correct limit of $E^{(2)}$. (When $E_0^{(1)} = \cdots = E_{M-1}^{(1)}$, but the degeneracy is lifted at the second order, the zero-temperature limit of

$U^{(2)}$ is the average of $E_I^{(2)}$s within the degenerate subspace, and is not equal to $E_0^{(2)}$.) These explain Fig. 4 and confirm Kohn and Luttinger's prediction analytically:[67] Finite-temperature MBPT has a wrong zero-temperature limit if the reference is degenerate and this degeneracy is partially or fully lifted at some perturbation order. The deviation can be infinite at second and higher orders, which must not be confused with the well-known infrared divergence of MBPT(n) ($n \geq 2$) in a metal.[45,52]

If we took the zero-temperature limit of the exact U first [Eq. (38)] and then expanded this limit E_0 in a perturbation series next, we would always arrive at the correct zero-temperature limit $E_0^{(n)}$ at any perturbation order regardless of the reference. However, this is not the order of actions we take; we first expand U in a perturbation series, followed by taking the zero-temperature limit, and this limit is always incorrect under certain conditions. What is the root cause of this nonconvergence?

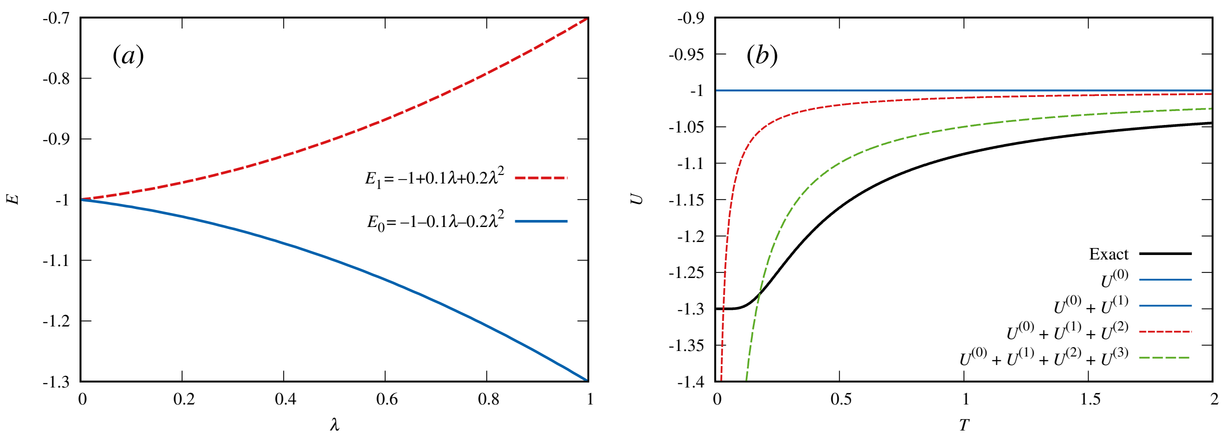


Figure 5: (a) State energies of a two-state model as a function of perturbation strength λ. (b) Internal energy U of the two-state model and its Taylor-series expansions in λ as a function of temperature T. Reproduced from Hirata[67] with permission from American Physical Society.

The nonconvergence can be reproduced by a simple model internal energy $U(T)$ of a two-state system:[67]

$$U(T) = \left. \frac{E_0(\lambda)e^{-E_0(\lambda)/T} + E_1(\lambda)e^{-E_1(\lambda)/T}}{e^{-E_0(\lambda)/T} + e^{-E_1(\lambda)/T}} \right|_{\lambda=1}, \tag{47}$$

where $E_0(\lambda)$ and $E_1(\lambda)$ are the energies of the two states, each of which lends itself to a Taylor-series expansion in perturbation strength λ ($\lambda = 1$ corresponds to the physical state). Consider the case where $E_0 = -1 - 0.1\lambda - 0.2\lambda^2$ and $E_1 = -1 + 0.1\lambda + 0.2\lambda^2$ (the left panel of Fig. 5). The E_0

and E_1 are degenerate at the zeroth order ($\lambda = 0$) and this degeneracy is lifted as the perturbation (such as correlation) is turned on ($\lambda > 0$) and remains lifted in the exact limit ($\lambda = 1$). The corresponding $U(T)$ as a function of T is drawn as a thick black curve in the right panel of Fig. 5, which is smooth and convergent at the energy of the lowest-lying state $E_0(\lambda = 1) = -1.3$ as $T \to 0$. While the first-order Taylor-series approximation $U^{(0)} + U^{(1)}$ is finite and constant, the second- and all higher-order Taylor-series approximations are divergent at $T = 0$. Therefore, the perturbation (Taylor) series of $U(T)$ in λ is not convergent at exact $U(T = 0) = E_0(\lambda = 1)$, even though E_0 and E_1 are described exactly by second-order perturbation theory. This model, therefore, reproduces the Kohn–Luttinger nonconvergence occurring when the degeneracy of the reference is lifted at the first order.

Physically, it may be unsurprising or even expected that a perturbation theory fails if the reference and exact descriptions are qualitatively different, e.g., when the ground state is degenerate at the zeroth order, but becomes nondegenerate in the exact limit. However, this expectation alone does not fully explain the Kohn–Luttinger nonconvergence because zero-temperature MBPT is always convergent at the correct limit (unless divergent) regardless of the degeneracy of the ground state and whether it is partially or fully lifted upon inclusion of correlation. The root cause must be mathematical.

Indeed, the nonconvergence is traced to the fact that the exact $U(T)$ [Eq. (4) or (47)] is nonanalytic at $T = 0$ (recall that the Boltzmann factor $e^{-\beta(E-\mu N)}$ is also nonanalytic at $T = 0$).[67] A nonanalytic function refers to a smooth function that is infinitely differentiable, but whose Taylor series has zero radius of convergence in some domains. Finite-temperature MBPT is, therefore, an example of *nonanalytic physics*, wherein perturbation theory tends to fail. Another example is superconductivity, whose gap formula,[69,70] $2\delta\, e^{-1/\rho V}$, is nonanalytic at zero electron-phonon coupling V. This is why "perturbation theory would not be easy to apply"[53] to the problem of superconductivity even though V is small (recall that the Bardeen–Cooper–Schrieffer theory[69,70] is variational). Yet another example is the Feynman–Dyson perturbation expansion of many-body Green's functions (MBGF),[71] whose exact definitions, $(\omega - {}^{N}E_0 + {}^{N-1}E_I)^{-1}$ and $(\omega - {}^{N+1}E_I + {}^{N}E_0)^{-1}$, are nonanalytic in many domains of ω. Even though the Feynman–Dyson diagrammatic perturbation expansion is the mathematical basis of quantum field theory,[72] it is found to be largely nonconvergent.

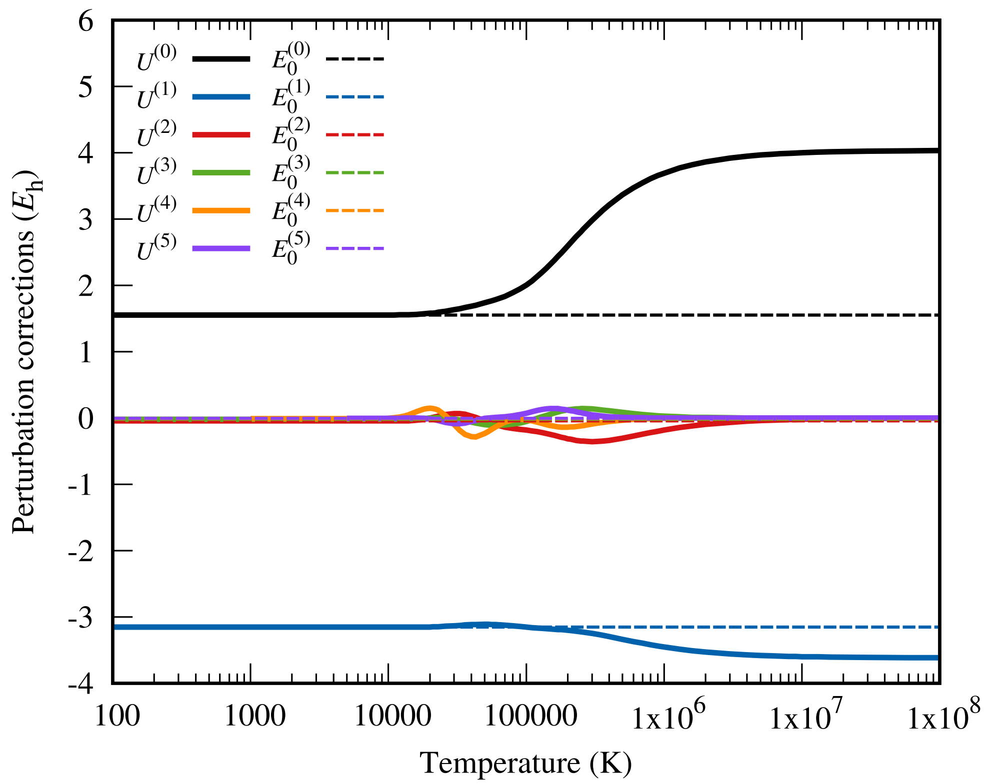


Figure 6: Same as Fig. 4, but with a symmetry-broken nondegenerate reference. Reproduced from Hirata[68] with permission from Elsevier.

Hence, the Kohn–Luttinger nonconvergence problem does exist, but its impact on the theory's applications should be limited because it can be avoided easily.[68] Figure 6 plots the temperature dependence of $U^{(n)}$ ($0 \leq n \leq 5$) for the same system as in Fig. 4 obtained with a symmetry-broken HF solution as the reference, which is no longer degenerate. All of $U^{(n)}$s thus obtained rapidly converge at the correct limits of $E^{(n)}$ as $T \to 0$. Switching from a degenerate to nondegenerate reference is also straightforward; a HF program tends to spontaneously converge towards a lower-energy, symmetry-broken, nondegenerate root rather than towards a higher-energy, symmetric, degenerate root. Locating the latter is usually computationally much harder, requiring symmetry constraints to be imposed.

Finite-temperature MBPT is efficient, size-extensive, and converging towards exactness, and its predicted nonconvergence behavior can be avoided easily in practice. It is, therefore, expected to be a workhorse for insulating or semiconducting solids at nonzero temperature, if not for metals. It has also been extended to anharmonic vibrations,[73] which have a more complex Hamiltonian and obey Bose–Einstein quantum statistics.

Thermal Hartree–Fock Theory

In zero-temperature HF theory,[2] the expectation value $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$ of the exact Hamiltonian $\hat{H}$ in a single Slater-determinant wave function Φ_0 is adopted as an approximate total energy. This energy is minimized by varying orbitals in Φ_0 with the constraints that the orbitals be orthonormal. It leads to the Brillouin condition, $\epsilon_{ia} = h_{ia} + \sum_j^{\text{occ.}} \langle ij || aj \rangle = 0$, where i and a are an occupied and virtual orbital, respectively, and $\boldsymbol{\epsilon}$ is the zero-temperature Fock matrix, originally introduced as the matrix of Lagrange's undetermined multipliers for the orthonormality constraints. The Brillouin condition can be replaced by a stronger condition that the Fock matrix $\boldsymbol{\epsilon}$ be diagonal, which is justified by the invariance of the HF wave function and energy with respect to unitary transformations among occupied orbitals or among virtual orbitals. The eigenvalues of the Fock matrix ("HF orbital energies") then have the compelling physical meaning as approximate electron binding energies as per Koopmans' theorem.

The finite-temperature generalization of HF theory, known as thermal HF theory,[46,47] is postulated completely differently, even though it reduces correctly to zero-temperature HF theory as $T \to 0$. There are two Hamiltonians involved: the exact Hamiltonian $\hat{H}$ and an auxiliary one-electron Hamiltonian $\hat{H}_0 \equiv \sum \epsilon_p^{\text{HF}} \hat{p}^\dagger \hat{p}$, where ϵ_p^{HF} is a variational parameter. The state energies (denoted by E_I^{HF1}) entering the Boltzmann factor are defined with $\hat{H}_0$, i.e.,

$$E_I^{\text{HF1}} \equiv \langle \Phi_I | \hat{H}_0 | \Phi_I \rangle = \sum_i^{\text{occ.}} \epsilon_i^{\text{HF}}. \tag{48}$$

The thermal population (density matrix) is then of the one-electron type:

$$\rho_I^{\mathrm{HF1}} \equiv \frac{e^{-\beta(E_I^{\mathrm{HF1}}-\mu^{\mathrm{HF}}N_I)}}{\sum_I e^{-\beta(E_I^{\mathrm{HF1}}-\mu^{\mathrm{HF}}N_I)}} = \frac{\prod_i^{\mathrm{occ.}} e^{-\beta(\epsilon_i^{\mathrm{HF}}-\mu^{\mathrm{HF}})}}{\prod_p^{\mathrm{all}}\left(1+e^{-\beta(\epsilon_p^{\mathrm{HF}}-\mu^{\mathrm{HF}})}\right)}, \tag{49}$$

On the other hand, the Ith state energy (denoted by E_I^{HF2}) entering the density-matrix definition of the grand potential [Eq. (3)] is the expectation value of the exact $\hat{H}$ in the Ith Slater determinant, i.e.,

$$E_I^{\mathrm{HF2}} \equiv \langle \Phi_I|\hat{H}|\Phi_I\rangle = \sum_i^I h_{ii} + \frac{1}{2}\sum_{i,j}^I \langle ij||ij\rangle. \tag{50}$$

The grand potential of thermal HF theory, therefore, makes a hybrid use of these two Hamiltonians or two definitions of state energies:

$$\Omega^{\mathrm{HF}} \equiv \sum_I \rho_I^{\mathrm{HF1}}\left(E_I^{\mathrm{HF2}}-\mu^{\mathrm{HF}}N_I\right)+\frac{1}{\beta}\sum_I \rho_I^{\mathrm{HF1}}\ln\rho_I^{\mathrm{HF1}} \tag{51}$$

$$= \sum_p \left(h_{pp}-\mu^{\mathrm{HF}}\right)f_p^- + \frac{1}{2}\sum_{p,q}\langle pq||pq\rangle f_p^- f_q^- + \frac{1}{\beta}\left(f_p^-\ln f_p^- + f_p^+\ln f_p^+\right), \tag{52}$$

where

$$f_p^- = \frac{1}{1+e^{\beta(\epsilon_p^{\mathrm{HF}}-\mu^{\mathrm{HF}})}} \;\; ; \;\; f_p^+ = 1-f_p^-. \tag{53}$$

The minimization of Ω^{HF} by varying ϵ_p^{HF} with no constraints then leads to

$$\epsilon_p^{\mathrm{HF}} = h_{pp} + \sum_q \langle pq||pq\rangle f_q^-. \tag{54}$$

The corresponding formula for the internal energy is written as

$$U^{\mathrm{HF}} = \sum_p h_{pp} f_p^- + \frac{1}{2}\sum_{p,q}\langle pq||pq\rangle f_p^- f_q^-, \tag{55}$$

which is identified as the zeroth-order thermal average $\langle E^{(0)}\rangle + \langle E^{(1)}\rangle$.

No equivalent of the Brillouin condition emerges at finite temperature (whose occupied/virtual distinction of orbitals is incongruent with nonzero temperature in the first place). No single grand partition function seems identifiable, either, from which all thermodynamic functions can be derived; a grand partition function summing over $\langle\Phi_I|\hat{H}|\Phi_I\rangle$ or E_I^{HF2} of Eq. (50) leads to a different method known as the thermal single-determinant approximation of Kaplan and Argyres[74] with severely limited practical utility. No physical meaning is known for "orbital energies" or ϵ_p^{HF} of thermal HF theory,[75] which are temperature dependent (cf. quantized energies are constant of temperature) and have sometimes been invoked to simulate metal-insulator phase transitions somewhat unquestioningly.[76]

It has also been revealed[59] that Ω^{HF} and U^{HF} disagree with $\Omega^{(0)} + \Omega^{(1)}$ [Eq. (28)] or $U^{(0)} + U^{(1)}$ [Eq. (37)], respectively. This is unlike the zero-temperature HF theory, whose energy expression is that of the first-order Møller–Plesset perturbation theory ($E^{(0)} + E^{(1)}$).[2] This indicates that thermal HF theory treats different contributions in Ω or U at different levels of perturbation approximation: It treats energy at the first order, but chemical potential and entropy at the zeroth order. The differences can thus be identified as

$$\Omega^{(0)} + \Omega^{(1)} - \Omega^{\text{HF}} = -\mu^{(1)}\bar{N}, \tag{56}$$

$$U^{(0)} + U^{(1)} - U^{\text{HF}} = TS^{(1)}, \tag{57}$$

which are generally nonzero. Only when a thermal HF solution is adopted as the reference (whereupon $\mu^{(1)} = S^{(1)} = 0$), does the first-order finite-temperature MBPT agree with thermal HF theory.[47] Nevertheless, all fundamental thermodynamic relationships, Eqs. (7)–(9), are still satisfied by thermal HF theory,[47,77] and its zero-temperature limit is correctly HF theory ($\lim_{T\to 0} U^{\text{HF}} = E^{\text{HF}}$).

Hence, despite its nonlinear derivation logic and inconsistent treatments of different contributions to Ω^{HF} or U^{HF}, thermal HF theory (and its closely related thermal density-functional theory[78]) is remarkably robust and broadly applicable to insulating, semiconducting, and metallic solids as well as their temperature-dependent energy bands (whose physical meaning is proposed in the following section). The emergence[59] of its total-energy and Fock-matrix expressions in the finite-temperature MBPT formulas and normal-ordered second-quantized Hamiltonian at nonzero temperature also underscores the fundamental significance of thermal HF theory.

Thermal Quasiparticle Theory

The immense success of thermal HF theory inspires a thermal *quasiparticle* theory[79] that includes the effects of electron correlation while keeping to its quasi-one-electron framework. For instance, an *n*th-order quasiparticle theory can be postulated by its grand potential of the form,

$$\Omega^{\mathrm{QP}(n)} \equiv \sum_{i=0}^{n} \langle E^{(i)} \rangle - \mu^{\mathrm{QP}(n)} \bar{N} + \frac{1}{\beta} \sum_{p} \left(f_p^- \ln f_p^- + f_p^+ \ln f_p^+ \right) \tag{58}$$

with

$$f_p^- = \frac{1}{1 + e^{\beta\left(\epsilon_p^{\mathrm{QP}(n)} - \mu^{\mathrm{QP}(n)}\right)}} \;\; ; \;\; f_p^+ = 1 - f_p^-, \tag{59}$$

where $\epsilon_p^{\mathrm{QP}(n)}$s are variational parameters. In line with thermal HF theory, only the energy contribution is described at the corresponding perturbation order, while the chemical potential and entropy terms are unchanged from the Fermi–Dirac (zeroth-order) formulas. This $\Omega^{\mathrm{QP}(n)}$ is then minimized by varying $\epsilon_p^{\mathrm{QP}(n)}$, leading to

$$\epsilon_p^{\mathrm{QP}(n)} = \sum_{i=0}^{n} \frac{\partial \langle E^{(i)} \rangle}{\partial f_p^-}. \tag{60}$$

The zeroth-order thermal quasiparticle theory is identified as Fermi–Dirac theory ($\Omega^{\mathrm{QP}(0)} = \Omega^{(0)}$, etc.), whereas the first-order instance is thermal HF theory ($\Omega^{\mathrm{QP}(1)} = \Omega^{\mathrm{HF}}$, etc.). At any order, the theory obeys all fundamental thermodynamic relationships [Eqs. (7)–(9)]. However, not only are higher-order perturbation corrections to the chemical potential and entropy neglected, but the anomalous-diagram contributions [e.g., some of the β-multiplied terms in Eq. (34)] to the energy are also missing in $\Omega^{\mathrm{QP}(n)}$. Clearly, this series cannot be convergent towards exactness, but it is curious to know its performance at lower orders.

The $\langle E^{(2)} \rangle$ is evaluated in Eq. (31). Substituting it into Eq. (60), we get

$$\epsilon_p^{\mathrm{QP}(2)} = \epsilon_p^{\mathrm{HF}} + \Sigma_{pp}^{(2)} \tag{61}$$

with

$$\begin{aligned}
\Sigma_{pp}^{(2)} \;=\; & \sum_{q}^{\text{denom.}\neq 0} \frac{|F_{pq}|^2}{\epsilon_p - \epsilon_q} f_q^+ - \sum_{q}^{\text{denom.}\neq 0} \frac{|F_{pq}|^2}{\epsilon_q - \epsilon_p} f_q^- \\
& + \sum_{q,r}^{\text{denom.}\neq 0} \frac{\langle qp||rp\rangle F_{rq} + F_{qr}\langle rp||qp\rangle}{\epsilon_r - \epsilon_q} f_r^- f_q^+ \\
& + \frac{1}{2} \sum_{q,r,s}^{\text{denom.}\neq 0} \frac{|\langle pq||rs\rangle|^2}{\epsilon_p + \epsilon_q - \epsilon_r - \epsilon_s} f_q^- f_r^+ f_s^+ \\
& - \frac{1}{2} \sum_{q,r,s}^{\text{denom.}\neq 0} \frac{|\langle pq||rs\rangle|^2}{\epsilon_r + \epsilon_s - \epsilon_p - \epsilon_q} f_q^+ f_r^- f_s^- ,
\end{aligned} \tag{62}$$

defining the second-order thermal quasiparticle theory. This $\Sigma_{pp}^{(2)}$ is a finite-temperature generalization of the second-order self-energy of MBGF theory.[2,60] As $T \to 0$, it reduces to the usual second-order self-energy formula,[2,60] accounting for the leading electron-correlation effects on electron binding energies or energy bands in solids. Hence, Eq. (60) offers an immediate physical meaning of "orbital energies" of thermal quasiparticle theory including thermal HF theory: ϵ_p^{QP} is the increase in the internal energy upon infusion of an infinitesimal fraction of an electron in the pth spin orbital — Janak's theorem generalized to finite temperature.[80,81]

Had the definition of $\Omega^{\mathrm{QP}(n)}$ contained the anomalous-diagram terms (responsible for the Kohn–Luttinger nonconvergence problem), the corresponding $\Sigma_{pp}^{(2)}$ would be divergent for most any system as $T \to 0$ (not just when the neutral, ground-state reference is degenerate). Therefore, as it turns out, the neglect of anomalous-diagram terms is essential for the validity of thermal quasiparticle theory. Whether such a provision is justified formally is an open question, but it may provide crucial information about the valid ansätze of finite-temperature MBGF.[56,82,83]

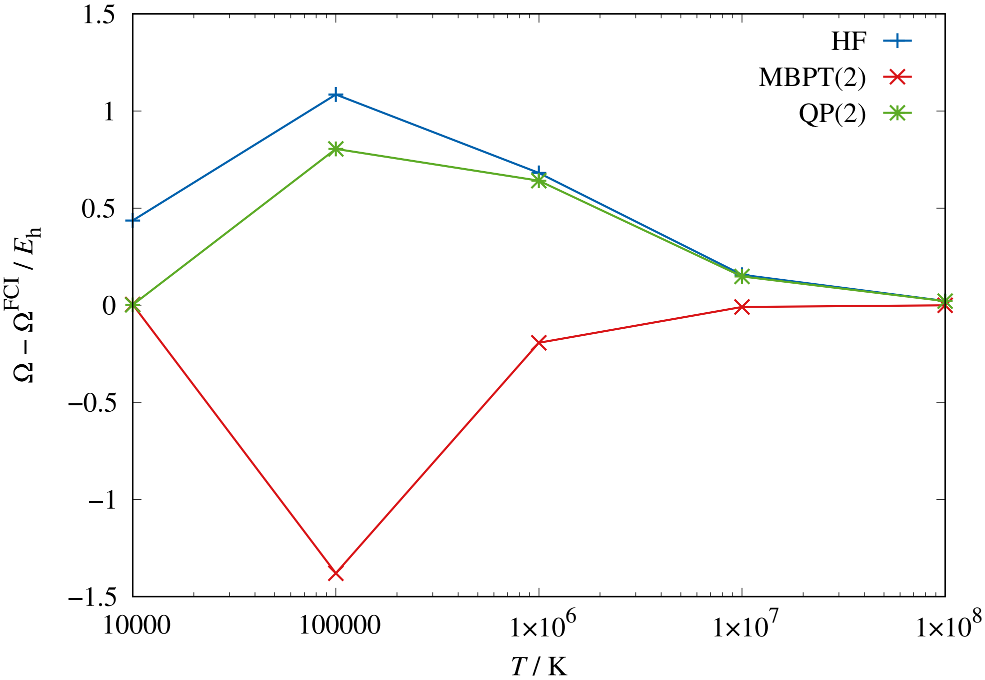


Figure 7: Deviation from the exact (finite-temperature FCI) values in the grand potential obtained by thermal HF theory ("HF"), second-order thermal quasiparticle theory ("QP(2)"), and second-order finite-temperature MBPT ("MBPT(2)") as a function of temperature (T) for the same system as Fig. 2. Reproduced from Hirata[79] with permission from AIP Publishing.

The second-order thermal quasiparticle [QP(2)] theory can, therefore, be viewed as a leading-order electron-correlated generalization of the highly successful thermal HF theory. It is similar to finite-temperature MBPT(2) and will have the same computational cost. However, unlike finite-temperature MBPT(2), QP(2) theory neglects the correlation corrections to the chemical potential and entropy, but instead includes correlation effects on orbital energies and, therefore, on the Fermi–Dirac distribution functions. Figure 7 examines the comparative performance of these three methods. At low temperatures ($T \leq 10000\,\mathrm{K}$), the correlation effect on grand potential Ω is dominated by that on the ground-state energy E_0, and both QP(2) theory and finite-temperature MBPT(2) yield equally accurate results, nearly completely erasing the error in thermal HF theory. At higher temperatures ($T \geq 100000\,\mathrm{K}$), QP(2) theory begins to trail thermal HF theory, displaying somewhat poorer performance than finite-temperature MBPT(2), but is superior to thermal HF theory. At lower temperatures, QP(2) theory seems to be overall best performer for this and another tiny example (not shown),[79] and will be a promising method for electron-correlated energy bands in a solid.

Outlook

The entire *ab initio* electronic structure theory awaits finite-temperature generalizations. Among them, size-extensive theories that can handle solids are prime targets. They include MBPT and CC theory.[5] Finite-temperature CC theory was first explored by Mukherjee and coworkers,[84–86] adopting the time-dependent derivation strategy of Bloch and coworkers.[29,48,49] Their ansatz was implemented by White and Chan[66] in an algorithm that performs explicit time integration. Finite-temperature CC theory based on thermofield theory — also a time-dependent approach — has been proposed by Harsha *et al.*[87–89] Both approaches have been explored by Nooijen and Bao.[90,91] Our time-independent derivation strategy described above can be applied to finite-temperature CC theory, clearly and precisely delineating its grand partition function and various approximations involved. It should be consistent with infinite partial summations of finite-temperature MBPT diagrams, the latter being fully established.[59] They should lead to time-independent, sum-over-orbitals expressions — complementary (or equivalent) to the time-dependent approaches — which will be applicable to insulating, semiconducting, and metallic solids. They will also admit a general-order algorithm, proving or disproving its convergence to exactness.

CC theory gives an accurate correlation energy for a metal, which MBPT(n) at any order $n \geq 2$ fails by the infrared divergence.[45,52] Since it is metallic solids where the thermal excitations of electrons are most prominent, the appeal of finite-temperature MBPT is significantly diminished by its inability to treat them, rendering finite-temperature CC theory all the more important. It avoids the infrared divergence by renormalizing the Coulomb repulsions between electrons, which would otherwise "pile up" towards infinity.[45,52] In fact, this remarkable ability of CC theory to renormalize or temper particle-particle interactions does not stop at (or start from) electronic structure. CC theory was introduced, initially as an infinite partial resummation of ring diagrams of MBPT, for the specific purpose of tempering hardcore repulsive potentials between nucleons in computational nuclear physics.[92,93] Its $e^{\hat{T}}$ operator can excise the portion of a reference wave function penetrating the hardcore region, which would otherwise blow up the energy. This is mathematically equivalent to modifying the nonintegrable potential into one without the hardcore region.[94] For this reason, the crudest approximation for finite nuclei and nuclear matter is Brueckner–Hartree–Fock theory, which (despite its name) is a type of CC theory.

Such hardcore potentials are ubiquitous in chemistry. An nonideal gas or liquid of atoms can be accurately described by inter-atomic interactions of the Lennard-Jones or Buckingham type, which are hardcore-like and nonintegrable. The Ursell–Mayer cumulant expansion[27–34] can temper these potentials, leading to a progressively more accurate equation of state that describes its gas phase, liquid phase, and the transition between them as well as the existence of a critical point where the two phases merge. It is well recognized that the Ursell–Mayer theory is a classical-mechanical version of quantum-mechanical CC theory.[93] Hence, finite-temperature CC theory has a potential of becoming *chemical theory for everything* encompassing electrons in insulating, semiconducting, and metallic solids and nonideal gases and liquids of atoms, as a start, and all the rest ultimately. This exciting prospect of the unification may be achieved by fully establishing the whole hierarchy of converging finite-temperature CC theory series, developing a general algorithm to determine tempered potentials, and elucidating the precise relationships between finite-temperature CC and Ursell–Mayer theory and how quantum effects are systematically incorporated in the latter. The general, versatile derivation strategy for finite-temperature MBPT described herein will be crucial for this development.

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