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Finite-temperature second-order many-body perturbation theory revisited

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ABSTRACT

We present an algebraic, nondiagrammatic derivation of finite-temperature second-order many-body perturbation theory [FT-MBPT(2)], using techniques and concepts accessible to theoretical chemical physicists. We give explicit expressions not just for the grand potential but particularly for the mean energy of an interacting many-electron system. The framework presented is suitable for computing the energy of a finite or infinite system in contact with a heat and particle bath at finite temperature and chemical potential. FT-MBPT(2) may be applied if the system, at zero temperature, may be described using standard (i.e., zero-temperature) second-order many-body perturbation theory [ZT-MBPT(2)] for the energy. We point out that in such a situation, FT-MBPT(2) reproduces, in the zero-temperature limit, the energy computed within ZT-MBPT(2). In other words, the difficulty that has been referred to as the Kohn–Luttinger conundrum, does not occur. We comment, in this context, on a "renormalization" scheme recently proposed by Hirata and He.

1. Introduction

Perturbation theory, particularly the variant due to Rayleigh and Schrödinger [1,2], is one of the most important approaches to finding approximate solutions to quantum–mechanical problems. In essence, one writes the Hamiltonian of interest, $\widehat{H}$, as the sum of an unperturbed part, $\widehat{H}_0$, and a perturbation, $\widehat{H}_1$:

$$\widehat{H} = \widehat{H}_0 + \widehat{H}_1. \tag{1}$$

Then, within time-independent perturbation theory, one constructs approximations to selected eigenstates and eigenenergies of $\widehat{H}$ using the eigenstates and eigenenergies of $\widehat{H}_0$ (which must be known). The key assumption in the version of time-independent perturbation theory that is suitable for nondegenerate states is that the zeroth-order reference state is nondegenerate. When true degeneracies or quasi-degeneracies are present, then $\widehat{H}$ must be prediagonalized within the relevant (quasi-) degenerate subspace of $\widehat{H}_0$ [3–5].

In practice, perturbation theory is most powerful when a low-order expansion suffices. The most widely used post-Hartree–Fock method for the ground-state energy of an interacting many-electron system is second-order Møller–Plesset perturbation theory (MP2) [6–9], which is second-order time-independent perturbation theory for nondegenerate states, employing an $\widehat{H}_0$ that equals the ground-state Fock operator [10] assuming a closed-shell system. MP2 works best when the ground-state Hartree–Fock HOMO–LUMO gap is, in some sense, not too small; MP2 diverges when the HOMO–LUMO gap vanishes [11–13].

MP2 is a special case of standard (i.e., zero-temperature) second-order many-body perturbation theory [10,14–16], in the following referred to as ZT-MBPT(2). In this context, $\widehat{H}$ is assumed to consist of one- and two-body operators [14]. $\widehat{H}$ is then partitioned such that

$$\widehat{H}_0 = \sum_p \varepsilon_p \hat{c}_p^\dagger \hat{c}_p \tag{2}$$

is a one-body operator with known spin–orbital energies ε_p and associated spin orbitals φ_p; $\hat{c}_p^\dagger$ ($\hat{c}_p$) creates (annihilates) an electron in the one-electron state φ_p. Thus, the perturbation

$$\widehat{H}_1 = \sum_{p,q} v_{pq} \hat{c}_p^\dagger \hat{c}_q + \frac{1}{2} \sum_{p,q,r,s} v_{pqrs} \hat{c}_p^\dagger \hat{c}_q^\dagger \hat{c}_s \hat{c}_r \tag{3}$$

generally consists of one- and two-body terms. In Eq. (3), v_{pqrs} is an electron–electron Coulomb repulsion integral. The one-electron

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integral v_{pq} depends on the partitioning scheme selected; for instance, Møller–Plesset partitioning gives $v_{pq} = -\sum_r v_{pr[qr]} n_r$, where we have introduced the notation

$$v_{pr[qr]} = v_{prqr} - v_{prrq}, \tag{4}$$

and n_r is the occupation number of spin orbital φ_r in the Hartree–Fock ground state ($n_r = 0$ or $n_r = 1$).

The ZT-MBPT(2) result for the ground-state energy is [10,16]

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)}, \tag{5}$$

$$E_0^{(0)} = \sum_p \varepsilon_p n_p, \tag{6}$$

$$E_0^{(1)} = \sum_p v_{pp} n_p + \frac{1}{2}\sum_{p,q} v_{pq[pq]} n_p n_q, \tag{7}$$

$$E_0^{(2)} = -\sum_{p,q} \frac{n_q(1-n_p)}{\varepsilon_p - \varepsilon_q} \left| v_{pq} + \sum_r v_{pr[qr]} n_r \right|^2 - \frac{1}{4}\sum_{p,q,r,s} \frac{|v_{pq[rs]}|^2 n_r n_s (1-n_p)(1-n_q)}{\varepsilon_p + \varepsilon_q - \varepsilon_r - \varepsilon_s}. \tag{8}$$

In the zero-temperature formalism, in contrast to the finite-temperature formalism that is in the focus of this paper, the total particle number, $N = \sum_p n_p$, is a well-defined integer.

The traditional approach to extending many-body perturbation theory to finite temperature makes extensive use of techniques adopted from quantum field theory [14,15,17–19]. Particularly, there is an emphasis on diagrammatic techniques, using concepts that are not widely known in the theoretical chemical-physics community. First steps towards introducing finite-temperature second-order many-body perturbation theory [FT-MBPT(2)] to the chemical-physics literature were recently taken by Hirata and co-workers [20,21]. Motivated by the observation by Kohn and Luttinger [22] that, in the zero-temperature limit, the mean energy obtained within FT-MBPT(2) does not, in general, converge to the energy E_0 obtained within ZT-MBPT(2), Hirata and co-workers proposed a "renormalized" version of FT-MBPT(2) [20].

The present paper is an attempt to enhance the accessibility of finite-temperature many-body perturbation theory through an elementary, nondiagrammatic derivation of FT-MBPT(2) equations for the mean energy and mean particle number. These equations may be employed for describing finite or infinite electronic systems that are in contact with a heat and particle bath. This includes investigations of the electronic structure of warm dense matter [23–26].

As we will show, if ZT-MBPT(2) is applicable, i.e., if there is a nonzero (ideally, large) HOMO–LUMO gap in the one-particle energy spectrum of $\widehat{H}_0$, then, as the temperature goes to zero, FT-MBPT(2) connects smoothly to ZT-MBPT(2). In other words, the Kohn–Luttinger conundrum, which motivated the work of Hirata and co-workers [20], does not exist in situations in which the application of second-order many-body perturbation theory is meaningful. Furthermore, we clarify in this paper the meaning of what Hirata and co-workers call "conventional" FT-MBPT(2) [20]. In contrast to what they suggested, they did not, in fact, give an expression for the energy. Finally, we comment on their proposed "renormalized" FT-MBPT(2).

2. Finite-temperature many-body perturbation theory

Finite-temperature many-body perturbation theory (FT-MBPT) [14,15,17–19] is based on the grand-canonical ensemble [27]. The fundamental quantity describing the state of a system in the grand-canonical ensemble, such that the parameters of the theory are the temperature T (or $\beta = 1/T$ in suitable units), the volume V, and the chemical potential μ, is the density operator

$$\hat{\rho} = \frac{e^{-\beta(\widehat{H}-\mu\widehat{N})}}{Z_G}. \tag{9}$$

Here,

$$\widehat{N} = \sum_p \hat{c}_p^\dagger \hat{c}_p \tag{10}$$

is the total particle number operator, and

$$Z_G = \mathrm{Tr}\left\{ e^{-\beta(\widehat{H}-\mu\widehat{N})} \right\} \tag{11}$$

is the grand partition function.

For the noninteracting reference system, the grand-canonical density operator is given by

$$\hat{\rho}_0 = \frac{e^{-\beta(\widehat{H}_0-\mu\widehat{N})}}{Z_G^{(0)}}, \tag{12}$$

where

$$Z_G^{(0)} = \mathrm{Tr}\left\{ e^{-\beta(\widehat{H}_0-\mu\widehat{N})} \right\}. \tag{13}$$

The Fermi–Dirac factor,

$$\bar{n}_p = \frac{1}{e^{\beta(\varepsilon_p-\mu)}+1}, \tag{14}$$

emerges, for the noninteracting reference system, as the ensemble-averaged expectation value of the spin–orbital particle number operator

$$\hat{n}_p = \hat{c}_p^\dagger \hat{c}_p, \tag{15}$$

i.e.,

$$\bar{n}_p = \langle \hat{n}_p \rangle_0 = \mathrm{Tr}\{\hat{\rho}_0 \hat{n}_p\}. \tag{16}$$

As is well known, this is the sole meaning of the Fermi–Dirac factor in Eq. (14). It is not a fundamental quantity of quantum statistical mechanics; it is derived from Eq. (16) using Eqs. (12) and (13).

FT-MBPT is not a perturbation theory directly for the (mean) energy of a given system, but for its grand partition function, Eq. (11). To this end, note that the operator

$$\widehat{U}(\beta) = e^{-\beta(\widehat{H}-\mu\widehat{N})} \tag{17}$$

appearing in Eq. (11) has the structure of a time evolution operator with time argument $-i\beta$ ("imaginary time") and Hamiltonian $\widehat{H} - \mu\widehat{N}$. One can, thus, define a corresponding operator in the interaction picture,

$$\widehat{U}_\mathrm{I}(\beta) = e^{\beta(\widehat{H}_0-\mu\widehat{N})} \widehat{U}(\beta). \tag{18}$$

This satisfies the "equation of motion" (known as Bloch equation)

$$\frac{\partial}{\partial\beta} \widehat{U}_\mathrm{I}(\beta) = -\widehat{H}_1(\beta) \widehat{U}_\mathrm{I}(\beta), \tag{19}$$

where

$$\widehat{H}_1(\beta) = e^{\beta(\widehat{H}_0-\mu\widehat{N})} \widehat{H}_1 e^{-\beta(\widehat{H}_0-\mu\widehat{N})}. \tag{20}$$

At $\beta = 0$, i.e., at infinite temperature, $\widehat{U} = \mathbb{1}$ (the identity operator) and, therefore, $\widehat{U}_\mathrm{I} = \mathbb{1}$. Using this point of reference, Eq. (19) may be integrated and the resulting integral equation may be solved iteratively. Hence, through second order we have

$$\widehat{U}_\mathrm{I}(\beta) = \mathbb{1} - \int_0^\beta du\, \widehat{H}_1(u) + \int_0^\beta du\, \widehat{H}_1(u) \int_0^u du'\, \widehat{H}_1(u'). \tag{21}$$