Resolvent operator approach to many-body perturbation theory. I. Closed shells

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In this paper, we develop a time-dependent approach to many-body perturbation theory for closed shells based on the resolvent of the Schrödinger equation. We introduce a quantity $S(t) = i\langle\phi|\exp[-i(H-E_0)t]\psi\rangle / \langle\phi|\psi\rangle$, where ϕ and ψ are, respectively, the unperturbed and exact wave functions for the system and E_0 is the unperturbed energy. The Fourier transform of $S(t)$, $S(\omega) = \langle\phi|(\omega + E_0 - H)^{-1}|\psi\rangle / \langle\phi|\psi\rangle$, is a matrix element of the resolvent containing the exact function ψ and, thus, has a pole at $\omega = (E - E_0)$, the correlation energy. Starting from a time-dependent perturbation expansion of $S(t)$ via the Gellman–Low adiabatic theorem, we have obtained a Dyson-like equation: $S^{-1}(\omega) = S_0^{-1}(\omega) + \Sigma\langle\phi|\psi\rangle$ for $S(\omega)$. Such a derivation requires judicious grouping of terms of the perturbation series for $S(t)$. It has been shown that specific regroupings of the terms of $S(t)$ into appropriate "top" and "bottom" parts and corresponding time-integration procedures yield a Σ which generates the Brillouin–Wigner (BW) or Rayleigh–Schrödinger (RS) energy series. Σ for both the cases are identified as the "top" parts. The characteristic features of the BW series, namely, the appearance of disconnected and ω-dependent diagrams is to be contrasted with that of the RS series, which contains connected and ω-independent diagrams only, and both emerge naturally as a consequence of the dissection procedure into appropriate top and bottom parts.

I. INTRODUCTION

In the literature there currently exist several many-body-perturbation theories (MBPT) for the evaluation of many-Fermion wave functions and energy levels.[1–12] Brueckner[1] and Goldstone[2] pioneered the development of MBPT for closed shells using a time-dependent (TD) formalism, whereas Hugenholtz[3] developed a parallel time-independent (TI) approach. For open-shell systems, several TD[4–6] and TI theories[7–10] have also been developed. All of these perturbation theories (except that of Ref. 6) obtain expressions for the state energies in terms of power series expansions in the perturbation V. In the present paper we approach the development of a perturbation theory through the *resolvent* of the Schrödinger equation (SE) $(H-E)\Psi = 0$. Many-body perturbation theory has long been an active area of research. In July of 1981, the National Resource for Computation in Chemistry sponsored a workshop on this subject. However, there is to this date no concensus of opinion about *which* perturbative approach is to be preferred. Alternative theories which apply to degenerate or nearly degenerate states differ not only in their methods of derivation but also in their order-by-order working equations. Thus, in our opinion, there still remains a need for unification and classification in the perturbative treatment of such systems. We feel that the development given here has several novel aspects. We achieve a fully Hermitian theory which applies to closed-shell (nondegenerate) and open-shell (degenerate or nearly degenerate) problems. We obtain both Brillouin–Wigner and Rayleigh–Schrödinger versions in a single development. Our theory allows us to compute not only state energies but also state-to-state energy differences, including ionization energies. We believe that these developments make substantial contributions toward making perturbation theory a useful tool for the quantum chemist.

Our approach can be succinctly summarized as follows. Instead of obtaining a series for the energy E from the usual transition formula $E = \langle\Phi|H|\Psi\rangle$, where Φ is a zeroth order function, we find E as a pole of a quantity of the form $S(\epsilon) \sim \langle\Phi|(\epsilon - H)^{-1}|\Psi\rangle$ involving the resolvent[13] $(\epsilon - H)^{-1}$. Operationally, $S(\epsilon)$ is cast in a Dyson-like form $S^{-1}(\epsilon) \sim S_0^{-1}(\epsilon) + \Sigma$ in the development given here. Just as in perturbation theories which express the energy as a transition formula, our development involving the resolvent S can, in principle, be approached either in a TD or TI manner. We have chosen the TD approach because we feel that it has distinct advantages. Within our TD formalism, both Rayleigh–Schrödinger (RS) and Brillouin–Wigner (BW) type perturbation series emerge merely as alternative schemes for the time integrations arising in our development. Choices for performing time integrations specific to the RS or BW cases are dictated by our desire to obtain an effective operator Σ which is ϵ-independent or ϵ-dependent, respectively. Such manipulations are found to be rather straightforward in our TD approach, whereas analogous developments would be quite formidable in a TI approach. The relative degrees of complexity of other TI and TD developments can be appreciated by comparing the works of Hugenholtz[3] and Goldstone,[2] respectively, in which a transition formula is used to express E for closed shells. In addition, our resolvent based approach developed within the TD framework allows us to use the *same* methodology to obtain perturbation theories for *both* closed- and open-shell systems in either the RS or BW form.

Because our development is capable of yielding energy *differences* as poles of a quantity (S) which obeys a Dyson-like equation, it bears a seemingly strong relationship to the many-body propagator methods pioneered by Linderberg and Öhrn.[17] There are, however, some differences in the two approaches to these problems.

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In the present MBPT development, the choice of the so-called reference function (see Sec. IIA) dictates the nature of the resultant energy difference. In this first paper, the reference function (Φ) is taken to contain the same number of electrons as the exact function (Ψ) and to be a good zeroth order approximation to Ψ. As a result, the Dyson-like equation yields, through its pole, an energy difference equal to the correlation energy (the difference between the zeroth order energy of Φ and the exact energy of Ψ). In the second paper (II) we choose Φ to be a good zeroth order description of a so-called "core" state which may contain fewer or more electrons than the exact state Ψ. However, the resultant pole of S gives an energy difference equal to the exact energy of Ψ minus the exact (i.e., correlated) energy of that state which Φ describes in zeroth order. For example, if Φ is a zeroth order (e.g., Hartree–Fock) representation of ^1S Li^- and Ψ is the exact wave function for ^2S Li, the pole of S occurs at the fully correlated electron affinity of Li, *not* at the energy difference $E_{\text{exact}}(\text{Li}) - E_{\text{zeroth order}}(\text{Li}^-)$.

Certainly, the propagator methods mentioned above are also capable of giving some of these same energy differences. The electron propagator[18] (EP) yields ionization potentials and electron affinities as poles of an object which obeys a Dyson equation. The EP is formulated in terms of an exact state Ψ and a set of ionization operators which act on Ψ to add or remove one electron from Ψ. The space spanned by the functions resulting from these operators acting on Ψ is then used to describe the system having one electron more or fewer than Ψ. In analogous manner the polarization propagator[19] (PP) yields electronic excitation energies (which conserve electron number). In the development of the PP a set of excitation operators act on an exact reference state Ψ to generate functions which can be combined to give the desired excited-state wave functions.

In summary, both propagator methods and the MBPT techniques developed here are capable of generating excitation energies and ionization energies. Propagators are not commonly employed to evaluate correlation energies (as our MBPT method does in paper I), although contour integration of the electron propagator has been used for this purpose.[17] The most substantial differences between the propagator and MBPT theories lie in the techniques used in their derivation and in generating a systematic hierarchy for approximating the terms occurring in their Dyson-like equations.

The essential characteristics of our theory become particularly transparent when developed for closed-shell systems, which we now undertake to describe. Unlike the closed-shell case, the unperturbed wave function for an open-shell species cannot be characterized by a unique spin–orbital occupancy. This makes the corresponding open-shell theory somewhat more involved. In our next paper, we generalize the present theory to make it applicable to such open-shell problems. In our third paper, we give the results of applying our theory to several test atomic and molecular systems.

II. THEORY

A. General developments

Let Φ and Ψ be the unperturbed (single determinant) and exact wave functions, respectively, in the Heisenberg representation, corresponding to the Hamiltonian H. These functions are assumed to obey

$$H_0\Phi = E_0\Phi \tag{1}$$

and

$$H\Psi = E\Psi \ , \tag{2}$$

with

$$H = H_0 + V \ . \tag{3}$$

We make the conventional choice of H_0 as the Hartree–Fock (HF) operator.[14]

We now introduce a quantity

$$S(t) = i\langle\Phi\,|\exp[-i(H-E_0)t]\,|\Psi\rangle/\langle\Phi\,|\Psi\rangle \ , \tag{4}$$

whose one-sided Fourier transform is given by

$$S(\omega) = \int_{-\infty}^{0} S(t)e^{i\omega t}dt = \langle\Phi\,|\,\frac{1}{\omega + E_0 - H}\,|\Psi\rangle/\langle\Phi\,|\Psi\rangle \ . \tag{5}$$

Clearly, $S(\omega)$ has a pole at $\omega = E - E_0$, *the correlation energy*. Our aim is to derive a perturbation expansion for $S(t)$ about an "unperturbed component" S_0, defined by

$$\begin{aligned} S_0(t) &= i\langle\Phi\,|\exp[-i(H_0-E_0)t]\,|\Phi\rangle/\langle\Phi\,|\Psi\rangle \\ &= i/\langle\Phi\,|\Psi\rangle \ . \end{aligned} \tag{6}$$

Let us note that $S_0(t)$ is independent of t. It will be seen later that the denominator $\langle\Phi\,|\Psi\rangle$ appearing in Eqs. (5) and (6) does not contribute to the position of the *pole* of $S(\omega)$, so that all the information about the poles is contained in the numerators of S and S_0.

As will be shown later, a regrouping of the terms in the perturbation expansion of S leads to a Dyson-like equation of the form

$$S(t) = S_0 - S_0\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2\,\Sigma(t_1 - t_2)S(t_2)\langle\Phi\,|\Psi\rangle \ . \tag{7}$$

Depending upon the procedure used for carrying out the time integrations in Eq. (7), one obtains equations for $S(\omega)$ having either an ω-dependent or ω-independent Σ. The former corresponds to a BW and the latter to a RS perturbation series for $S(\omega)$.

A perturbation expansion of $S(t)$ is obtained by introducing the time evolution operator $U_I(0, -\infty)$, expressed in the interaction representation[15]:

$$U_I(t_1, t_2) = \exp(iH_0t_1)\exp[iH(t_1 - t_2)]\exp(-iH_0t_2) \ . \tag{8}$$

As a result, we obtain

$$\begin{aligned} S(t) &= \frac{i\langle\Phi\,|\exp(-iH_0t)\exp(iH_0t)\exp[-i(H-E_0)t]\,|\Psi\rangle}{\langle\Phi\,|\Psi\rangle} \\ &= \frac{i\langle\Phi\,|U_I(t,0)\,|\Psi\rangle}{\langle\Phi\,|\Psi\rangle} \\ &= \frac{i\langle\Phi\,|U_I(t,0)U_I(0,-\infty)\,|\Phi\rangle}{\langle\Phi\,|U_I(0,-\infty)\,|\Phi\rangle} \end{aligned}$$

$$= \frac{i\langle\Phi | U_I(t, -\infty) | \Phi\rangle}{\langle\Phi | U_I(0, -\infty) | \Phi\rangle}$$

$$\equiv N(t)/D \ , \tag{9}$$

where the last two equalities have been obtained using the Gellman–Low adiabatic theorem[15]

$$\frac{|\Psi\rangle}{\langle\Phi|\Psi\rangle} = \frac{U_I(0, -\infty)|\Phi\rangle}{\langle\Phi | U_I(0, -\infty)|\Phi\rangle} \tag{10}$$

and the distributive property of $U_I(t_1, t_2)$.

Let us now begin to analyze the structure of $S(t)$ of Eq. (9) in greater detail. Since the denominator D of $S(t)$ is a time-independent constant, it does not contribute to the pole structure of $S(\omega)$ and need not be considered explicitly. Using the perturbation expansion[15] for $U_I(t, -\infty)$ we have for the numerator N

$$N(t) = i\langle\Phi | U_I(t, -\infty) | \Phi\rangle$$
$$= i\sum_{n=0}^{\infty} \frac{(-i)^n}{n!} \int_{-\infty}^{t} dt_1$$
$$\times \int_{-\infty}^{t} dt_2 \cdots \langle\Phi | T[V_I(t_1)V_I(t_2)\cdots V_I(t_n)] | \Phi\rangle \ . \tag{11}$$

The expectation value $\langle\Phi | \cdots | \Phi\rangle$ occurring in Eq. (11), as calculated using Wick's theorem[15] with Φ taken to define the vacuum, would contain only completely contracted terms (i.e., numbers). In a diagrammatic language such terms correspond to closed diagrams.

B. Resolvent theory: BW form

To facilitate our development of a BW theory, it is useful to write the expression in Eq. (11) in a form in which the time arguments $t_1 \cdots t_n$ appear in descending order:

$$N(t) = i + i\sum_{n=1}^{\infty} (-i)^n \int_{-\infty}^{t} dt_1$$
$$\times \int_{-\infty}^{t_1} dt_2 \cdots \langle\Phi | T[V_I(t_1)V_I(t_2)\cdots] | \Phi\rangle_{cc} \ , \tag{12}$$

where the subscript cc refers to the completely contracted terms.

Our objective is to regroup the completely contracted terms in such a way that we can identify them as a *factored product* of which one term has the form of the numerator N itself and the other we call Σ. Such a factorization is rather easy to visualize if we represent the contracted terms in Eq. (12) diagrammatically. The $N(t)$ in Eq. (12) then corresponds to an infinite series, each term of which can be represented as a diagram

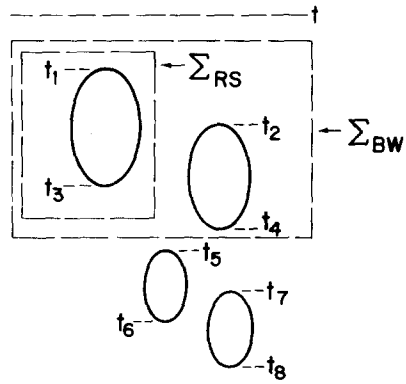

FIG. 1. Diagrammatic representation of a typical term of the expansion of $N(t)$ [Eq. (12)]. The part of the diagram surrounded by a box marked with discontinuous lines and labeled Σ_{BW} refers to the "top" part of the diagram in the BW theory. The rest of the diagram is the "bottom" part. The collection of all the possible top parts constitute the Σ_{BW} of BW theory. The part of the diagram surrounded by a box labeled Σ_{RS} corresponds to the "top" part of the RS theory. The rest of the diagram is the analogous "bottom" part. The collection of all possible top parts again constitutes the corresponding Σ_{RS} of the RS theory.

consisting of *disconnected closed parts* placed with respect to each other in all possible ways (i.e., time orders). The highest attainable limit of time for all of the vertices is t. Figure 1 shows a typical diagram which we have chosen to use in all of our subsequent developments. This diagram is one term of Eq. (12) corresponding to $n = 8$.

As we scan this particular diagram from t_1 to t_n (top to bottom), we encounter pairs of successive time vertices t_i, t_{i+1} between which a horizontal line would cut no contracted line. Let t_m be the highest among such t_i's. It is, of course, possible to have diagrams for which $t_m = t_n$, the lowest time. For the diagram shown in Fig. 1 the time t_4 is t_m. A line drawn at t_m separates the given diagram into top and bottom parts. The top part, in general, consists of a set of mutually overlapping closed parts (a special case of the top part may be just one connected diagram). The bottom part, on the other hand, looks like a typical member of $N(t)$ (with $t = t_m$) because it is a diagram having closed parts placed with respect to each other in an arbitrary fashion. For any fixed top part the collection of *all* possible bottom parts (corresponding to all possible contractions involving vertices t_{m+1} to t_n for all t_n) yields $N(t_m)$. Considering now all possible top parts, $N(t)$ can be written as

$$N(t) = i + \sum_{m=1}^{\infty} (-i)^m \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{m-1}} dt_m \langle\Phi | V_I(t_1)\cdots V_I(t_m) | \Phi\rangle_{cc,\,top}$$
$$\times \left[i + i\sum_{k=1}^{\infty} (-i)^k \int_{-\infty}^{t_m} dt_{m+1} \int_{-\infty}^{t_{m+1}} dt_{m+2} \cdots \langle\Phi | V_I(t_{m+1})\cdots V_I(t_{m+k})\Phi\rangle_{cc} \right] \ , \tag{13}$$

where the quantity inside the square brackets [ ] is just $N(t_m)$.

The terms $\langle\Phi | \cdots | \Phi\rangle_{cc,\,top}$ correspond to the top parts of the original diagrams and have mutually overlapping closed parts. Toward obtaining a Dyson-like equation for $N(t)$, we define a quantity Σ'_{BW} through the collection of all the terms $\langle\Phi | \cdots | \Phi\rangle_{cc,\,top}$:

$$\int \Sigma'_{\mathrm{BW}}(t_1, t_m) N(t_m) dt_m \equiv \sum_{m=1}^{\infty} (-i)^m \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{m-1}} dt_m \langle \Phi | V_I(t_1) \cdots V_I(t_m) | \Phi \rangle_{\mathrm{cc,\,top}} \ . \tag{14}$$

Our objective now is to construct a quantity $\Sigma_{\mathrm{BW}}(t_1, t_m)$ in which the intermediate times $t_2 \cdots t_{m-1}$ have been explicitly integrated out. We achieve this by making the time limits of t_m as $-\infty \le t_m \le t_1$ (i.e., independent of the intermediate time t_{m-1}) with consequent changes in the intermediate time variables as $t_m \le t_{m-1} \le t_1, \ldots, t_3 \le t_2 \le t_1$. We then have

$$\begin{aligned}\int \Sigma'_{\mathrm{BW}}(t_1, t_m) N(t_m) dt_m &= -i \frac{1}{-i} \sum_{m=1}^{\infty} (-i)^m \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_m \int_{t_3}^{t_1} dt_2 \int_{t_4}^{t_1} dt_3 \cdots \int_{t_m}^{t_1} dt_{m-1} \langle \Phi | \cdots | \Phi \rangle_{\mathrm{cc,\,top}} N(t_m) \\ &= -i \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_m \Sigma_{\mathrm{BW}}(t_1, t_m) N(t_m) \ ,\end{aligned}$$

where

$$\Sigma_{\mathrm{BW}}(t_1, t_m) \equiv \sum_{m=1}^{\infty} (-i)^{m-1} \int_{t_3}^{t_1} dt_2 \int_{t_4}^{t_1} dt_3 \cdots \int_{t_m}^{t_1} dt_{m-1} \langle \Phi | V_I(t_1) \cdots V_I(t_m) | \Phi \rangle_{\mathrm{cc,\,top}} \ . \tag{15}$$

The terms in Σ_{BW} can be calculated using the conventional Goldstone prescription.[15] Strictly speaking, $\Sigma_{\mathrm{BW}}(t_1, t_m)$ implicitly contains a factor $\delta(t_1 - t_m)$ for its first term (the $m = 1$ term of Σ'). Moreover, it can be easily shown that $\Sigma(t_1, t_m) \equiv \Sigma(t_1 - t_m)$, i.e., Σ_{BW} is a function of its time difference.

Defining the numerator of S_0, given in Eq. (6), as $N_0 \equiv i\langle \Phi | \exp[-i(H_0 - E_0)t] | \Phi \rangle = i$, we can write the factored Eq. (13) as follows:

$$N(t) = N_0 - N_0 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_m \Sigma_{\mathrm{BW}}(t_1, t_m) N(t_m) \tag{16}$$

or, equivalently, using Eq. (9),

$$S(t) = S_0 - S_0 \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_m \Sigma_{\mathrm{BW}}(t_1, t_m) S(t_m) D \ . \tag{17}$$

Equations (16) and (17) are the desired Dyson-like equations for $N(t)$ and $S(t)$, respectively.

The next step in the development is to perform the one-sided Fourier transform of Eq. (16) or (17) to obtain $N(\omega)$ or $S(\omega)$, needed for the calculation of the correlation energy:

$$\begin{aligned}N(\omega) &= \int_{-\infty}^{0} dt\, N(t)\, e^{i\omega t} = \frac{1}{\omega} + (-i) \int_{-\infty}^{0} dt\, e^{i\omega t} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_m \Sigma_{\mathrm{BW}}(t_1, t_m) N(t_m) \\ &= \frac{1}{\omega} + (-i) \int_0^{\infty} d(t - t_1)\, e^{i\omega(t - t_1)} \int_0^{\infty} d(t_1 - t_m)\, e^{i\omega(t_1 - t_m)} \Sigma_{\mathrm{BW}}(t_1 - t_m) \int_{-\infty}^{0} dt_m\, e^{i\omega t_m} N(t_m) = \frac{1}{\omega} + \frac{1}{\omega} \Sigma_{\mathrm{BW}}(\omega) N(\omega) \ .\end{aligned} \tag{18}$$

Here, appropriate damping factors have been introduced during integration to damp out the contributions at $\pm\infty$.

Since $S(t) = N(t)/D$, we have

$$S(\omega) = \frac{1}{\omega D} + \frac{1}{\omega D} \Sigma_{\mathrm{BW}}(\omega) S(\omega) D \ . \tag{19}$$

Rewriting Eq. (19) as

$$S^{-1}(\omega) = \omega D - \Sigma_{\mathrm{BW}}(\omega) D \ , \tag{20}$$

we note that the poles of $S(\omega)$ occur where

$$\omega - \Sigma_{\mathrm{BW}}(\omega) = 0 \tag{21}$$

(for $D \neq 0$), and we recall that the value of ω at the pole is ΔE, the correlation energy.

In order to show that the structure of $\Sigma_{\mathrm{BW}}(\omega)$ defined in Eq. (15) corresponds to the BW series for the correlation energy, we again consider a particular term of Eq. (15) and then generalize from it. For example, a term in Σ_{BW}, which is fourth order in V, corresponding to the diagram of Fig. 2, has the value

$$\begin{aligned}\Sigma^{(4)}_{\mathrm{BW}}(\omega) = &\sum_{\alpha\beta\gamma\delta pqrs} (-i)^3 \frac{1}{2^4} \langle \alpha\beta | pq \rangle_a \langle \gamma\delta | rs \rangle_a \langle pq | \alpha\beta \rangle_a \langle rs | \gamma\delta \rangle_a \int_0^{\infty} d(t_1 - t_m) \exp[i\omega(t_1 - t_4)] \int_{t_3}^{t_1} dt_2 \int_{t_4}^{t_1} dt_3 \\ &\times \exp[i(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(t_1 - t_2)] \exp[i(\epsilon_\alpha + \epsilon_\beta + \epsilon_\gamma + \epsilon_\delta - \epsilon_p - \epsilon_q - \epsilon_r - \epsilon_s)(t_2 - t_3)] \exp[i(\epsilon_\gamma + \epsilon_\delta - \epsilon_r - \epsilon_s)(t_3 - t_4)] \\ = &\sum_{\alpha\beta\gamma\delta pqrs} (-i)^3 \frac{1}{2^4} \langle \alpha\beta | pq \rangle_a \langle \gamma\delta | rs \rangle_a \langle pq | \alpha\beta \rangle_a \langle rs | \gamma\delta \rangle_a \int_0^{\infty} d(t_1 - t_2) \exp[i(\omega + \epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(t_1 - t_2)]\end{aligned}$$

$$\times \int_0^\infty d(t_2-t_3)\exp[i(\omega+\epsilon_\alpha+\epsilon_\beta+\epsilon_\gamma+\epsilon_\delta-\epsilon_p-\epsilon_q-\epsilon_r-\epsilon_s)(t_2-t_3)]\int_0^\infty d(t_3-t_4)\exp[i(\omega+\epsilon_\gamma+\epsilon_\delta-\epsilon_r-\epsilon_s)(t_3-t_4)]$$

$$=\sum_{\alpha\beta\gamma\delta pqrs}\frac{1}{2^4}\frac{\langle\alpha\beta|pq\rangle_a\langle\gamma\delta|rs\rangle_a\langle pq|\alpha\beta\rangle_a\langle rs|\gamma\delta\rangle_a}{(\omega+\epsilon_\alpha+\epsilon_\beta-\epsilon_p-\epsilon_q)(\omega+\epsilon_\alpha+\epsilon_\beta+\epsilon_\gamma+\epsilon_\delta-\epsilon_p-\epsilon_q-\epsilon_r-\epsilon_s)(\omega+\epsilon_\gamma+\epsilon_\delta-\epsilon_r-\epsilon_s)}\,. \tag{22}$$

Schematically every fourth-order term of Σ_{BW} will be of the form

$$\frac{V_4}{(\omega+x_1)(\omega+x_2)(\omega+x_3)}$$

and, hence, the series for $\Sigma_{BW}(\omega)$ can be expressed compactly as

$$\Sigma_{BW}(\omega)=\sum_{m=1}^{\infty}\frac{V_m}{(\omega+x_1)\cdots(\omega+x_{m-1})}\,. \tag{23}$$

Here, x_i stands for orbital energy differences ($\Sigma_\alpha\epsilon_\alpha-\Sigma_p\epsilon_p$) in which α and p are, respectively, the hole and particle lines contained between the time vertices t_i and t_{i+1} and V_m denotes the product of m antisymmetrized two-electron integrals. The desired pole of $S(\omega)$ as computed from Eq. (21) [$\omega=\Delta E=\Sigma_{BW}(\Delta E)$] thus generates, through Eq. (23), precisely the BW series for energy.

It is clear from the mode of construction of $\Sigma_{BW}(\omega)$ that it consists of all closed diagrams having mutually overlapping closed parts. The diagrams having more than one closed part are thus *disconnected*. Since, in general, t_1 and t_m in Σ_{BW} of Eq. (15) are unequal times, $\Sigma_{BW}(\omega)$ will explicitly depend on ω. This implies that the computation of the correlation energy from Eq. (21) has to be performed in an iterative manner. These characteristic features of the BW series are in important contrast with the RS series, which we undertake to derive now.

C. Resolvent theory: RS form

In order to construct the RS perturbation series from the same general expression [Eq. (12)] for $N(t)$, we have to choose the time variables in such a way that the one-sided Fourier transform of Eq. (16) yields an *ω-independent* Σ_{RS}. The result analogous to Eq. (21), giving $\omega=\Delta E=\Sigma_{RS}$, can then be solved directly as a power series in V.

To demonstrate the appropriate time integration procedure for the RS case, we again analyze the same typical diagram shown in Fig. 1. Consider the closed part of the diagram which contains t_1, the highest time vertex. In contrast to the BW case, this closed part of the diagram would be defined as the top part for the RS case. Thus, any top part of a diagram for the RS case is always a connected closed diagram. For the specific case shown in Fig. 1, the top part is the one containing vertices t_1 and t_3. The rest of the diagram is called the bottom part, the highest vertex (t_2 in Fig. 1) of which can be anywhere below t_1; thus the top and bottom parts can be overlapping. For any given top part, the bottom part is a typical member of $N(t_1)$ because the upper limit of time for all of the vertices of the bottom part is t_1. Clearly, all such possible bottom parts constitute $N(t_1)$.

For a general diagram, we can relabel the time vertices of the top and bottom parts as follows: the time vertices in the top part are denoted in descending order successively as $t_1, t_2, \ldots, t_l$ and, similarly, the bottom part vertices as $t_{l+1}, \ldots, t_n$. $N(t)$ can now be written as

$$N(t)=i+\sum_{l=1}^{\infty}(-1)^l\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_{l-1}}dt_l\,\langle\Phi|V_I(t_1)\cdots V_I(t_l)|\Phi\rangle_{cc,top}$$
$$\times\left[i+i\sum_{k=1}^{\infty}(-i)^k\int_{-\infty}^{t_1}dt_{l+1}\int_{-\infty}^{t_{l+1}}dt_{l+2}\cdots\langle\Phi|V_I(t_{l+1})\cdots V_I(t_{l+k})|\Phi\rangle_{cc}\right], \tag{24}$$

where the quantity inside the square brackets is $N(t_1)$. In analogy with the BW development, we use the quantity in Eq. (24) containing $\langle\Phi|\cdots|\Phi\rangle_{cc,top}$ to define Σ_{RS} as

$$\int\Sigma_{RS}(t_1)N(t_1)dt_1=i+\sum_{l=1}^{\infty}(-1)^l\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_{l-1}}dt_l\,\langle\Phi|V_I(t_1)\cdots V_I(t_l)|\Phi\rangle_{cc,top}N(t_1)$$
$$=i-i\int_{-\infty}^{t}dt_1\,\Sigma_{RS}(t_1)N(t_1)dt_1\,,$$

where

$$\Sigma_{RS}(t_1)=\sum_{l=1}^{\infty}(-i)^{l-1}\int_{-\infty}^{t_1}dt_2\int_{-\infty}^{t_2}dt_3\cdots\int_{-\infty}^{t_{l-1}}dt_l\,\langle\Phi|V_I(t_1)\cdots V_I(t_l)|\Phi\rangle_{cc,top}\,. \tag{25}$$

It is important to note that Σ_{RS} is completely time independent as can be seen in the following analysis. The expectation value $\langle\,\rangle_{cc,top}$ part of Eq. (25) can always be written as a product of functions of $(t_1-t_2), (t_2-t_3), \ldots, (t_{l-1}-t_l)$. With these changes of time variables $\Sigma_{RS}(t_1)$ can be written as

$$\Sigma_{RS}(t_1)=\sum_{l=1}^{\infty}(-i)^{l-1}\int_0^\infty d(t_1-t_2)\int_0^\infty d(t_2-t_3)\cdots\int_0^\infty d(t_{l-1}-t_l)\langle\text{function of }(t_1-t_2),(t_2-t_3)\cdots(t_{l-1}-t_l)\rangle_{cc,top}\,, \tag{26}$$

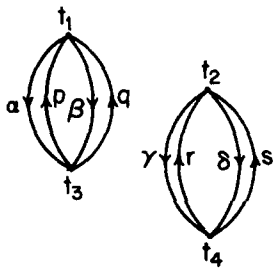

FIG. 2. A typical fourth-order diagram of Σ_{BW}.

which is independent of t_1. Hence Σ_{RS} is a time-independent constant for the RS case, and therefore Eq. (24) for $N(t)$ can be rewritten as

$$N(t) = N_0 - N_0 \Sigma_{RS} \int_{-\infty}^{t} dt_1 N(t_1) , \tag{27}$$

and, similarly,

$$S(t) = S_0 - S_0 \Sigma_{RS} \int_{-\infty}^{t} dt_1 N(t_1) D . \tag{28}$$

Equations (27) and (28) are the corresponding Dyson-like equations for $N(t)$ and $S(t)$, respectively, for the RS case.

The one-sided Fourier transformation of Eq. (27) gives

$$\begin{aligned} N(\omega) &= \int_{-\infty}^{0} dt \exp(i\omega t) N(t) \\ &= \frac{1}{\omega} - i\Sigma_{RS} \int_{-\infty}^{0} dt \exp(i\omega t) \int_{-\infty}^{t} dt_1 N(t_1) \\ &= \frac{1}{\omega} - i\Sigma_{RS} \int_{0}^{\infty} d(t - t_1) \exp[i\omega(t - t_1)] \\ &\quad \times \int_{-\infty}^{0} dt_1 \exp(i\omega t_1) N(t_1) , \end{aligned}$$

or

$$N(\omega) = \frac{1}{\omega} + \frac{1}{\omega} \Sigma_{RS} N(\omega) \tag{29}$$

and, similarly,

$$S(\omega) = \frac{1}{\omega D} + \frac{1}{\omega D} \Sigma_{RS} S(\omega) D \tag{30}$$

or

$$S^{-1}(\omega) = \omega D - \Sigma_{RS} D . \tag{31}$$

We note that the pole of $S(\omega)$ occurs where $\omega - \Sigma_{RS} = 0$ for $D \neq 0$. Also, as in the BW case, we can show that the Σ_{RS} of Eqs. (25) or (26) yields the well-known RS energy series.[2] Figure 3 shows a typical second-order term of Σ_{RS} which corresponds to the expression

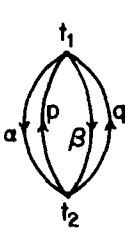

FIG. 3. A typical second-order diagram of Σ_{RS}.

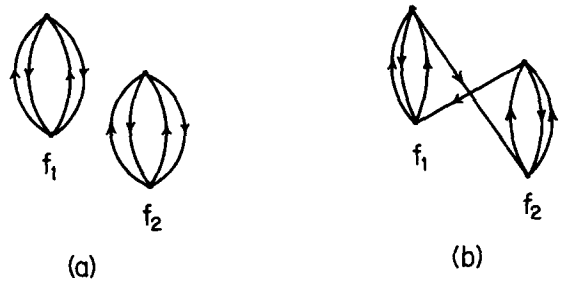

FIG. 4. (a) A typical fourth-order diagram of Σ_{BW} violating size-consistency (SC) requirement in BW theory. The physically disconnected parts of the diagram marked f_1 and f_2 involve orbitals corresponding to the respective fragments. The diagram therefore gives a nonvanishing contribution at infinite interfragment separation. (b) The corresponding diagram of Σ_{RS} in RS theory. Due to the physically connected nature of the diagram, it is impossible to have an expression containing integrals belonging exclusively to one or the other fragment. As integrals containing orbitals from both the fragments vanish at infinite interfragment separation, such terms vanish, rendering the RS theory size-consistent.

$$\begin{aligned} \Sigma_{RS}^{(2)} &= (-i) \sum_{\alpha p \beta q} \frac{1}{2^2} \langle \alpha\beta | pq \rangle_a \langle pq | \alpha\beta \rangle_a \\ &\quad \times \int_{0}^{\infty} d(t_1 - t_2) \exp[i(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)(t_1 - t_2)] \\ &= \frac{1}{2^2} \sum_{pq\alpha\beta} \frac{\langle \alpha\beta | pq \rangle_a \langle pq | \alpha\beta \rangle_a}{(\epsilon_\alpha + \epsilon_\beta - \epsilon_p - \epsilon_q)} , \end{aligned}$$

which is, indeed, a second-order term of the RS correlation energy.

The full series for Σ_{RS} can be written schematically in the form

$$\Sigma_{RS} = \sum_{m=1}^{\infty} \frac{V_m}{x_1 x_2 \cdots x_{m-1}} , \tag{32}$$

where, as in Eq. (23), x_i stands for the orbital energy difference $(\Sigma_\alpha \epsilon_\alpha - \Sigma_p \epsilon_p)$. Equation (32) is precisely the RS perturbation series for energy in the Bruckner–Goldstone form.[1,2] We emphasize that the particular choices of the time bases and the consequent division of a diagram for the RS case into the "top" and "bottom" parts leading to Eq. (24) ensures that the series for Σ_{RS} consists of terms which correspond to completely connected diagrams (linked diagrams for closed-shell systems). Moreover, as the top and bottom parts are overlapping for the RS case, the time argument for N in the bottom part is t_1, in contrast to a different time t_m in the BW case. As a consequence, the expression for Σ_{RS} does not explicitly contain the unknown energy ω.

Before closing this section, we demonstrate one noteworthy physical implication of the fact that *only connected diagrams* occur in the RS theory, which renders it size-consistent (SC).[16] As the molecular system dissociates to a given set of noninteracting fragment systems, a theory should have the built-in feature that it yields the total energy as a sum of the fragment state energies obtained by applying the theory to each separate fragment (and the total energy should be of a uniform precision at all geometries of the molecule). One can

show that the BW theory does not possess this feature, whereas the RS theory does because in the BW theory the interfragment interaction energy at infinite separation remains nonzero. To see this, consider the typical fourth-order BW diagram shown in Fig. 4(a) in which the two physically disconnected parts labeled f_1 and f_2 involve orbitals corresponding to the respective fragments f_1 and f_2 only. The correlation energy contribution of this BW diagram is of the form

$$E^{(4)} \sim \frac{V(f_1)V(f_1)V(f_2)V(f_2)}{(\omega+x_1)(\omega+x_2)(\omega+x_3)},$$

which remains nonvanishing at infinite separation (i.e., for noninteracting fragments) since it does not involve any integral containing orbitals on *both* fragments. On the other hand, a corresponding diagram of the RS theory shown in Fig. 4(b) involves integrals in its energy expression of the form $V(f_1,f_2)$ which contains orbitals of both fragments. Thus the RS interaction energy goes to zero at infinite separation. In addition, those RS diagrams which involve orbitals of only one fragment f_1 or f_2 give total energy contributions involving a sum of fragment energies at infinite separation. This last conclusion for the RS terms is possible since the denominator of a given term is ω-independent and the energy denominators for the composite and fragments are the same at infinite separation.

III. CONCLUDING REMARKS

The principal results obtained in this paper for closed shells can be summarized as follows. Starting from a perturbation expansion for $N(t)=i\langle\Phi|\exp[-i(H-E_0)t]|\Phi\rangle$ we have obtained a Dyson-like equation $N^{-1}(\omega)=N_0^{-1}(\omega)+\Sigma$ for the one-sided Fourier transform $N(\omega)=\langle\Phi|(\omega+E_0-H)^{-1}|\Psi\rangle$. $N(\omega)$ is, by construction, a matrix element of the resolvent containing the exact function Ψ and thus has a pole at $\omega=(E-E_0)$, the correlation energy. It has been shown that specific regroupings of the terms of $N(t)$ into appropriate top and bottom parts, in which the top parts constitute terms of Σ and the bottom parts those of N, yield both the BW and the RS series for Σ. These two series are generated via suitable choices of time integration schemes. As shown in Fig. 1, a dissection of each term of $N(t)$ by the topmost horizontal line which cuts no internal lines of the diagram generates Σ_{BW}. On the other hand, choosing the top part as the topmost connected part of the diagram generates Σ_{RS}. The latter dissection is dictated by our desire to have Σ_{RS} independent of ω. Although the application of our resolvent MBPT to closed-shell systems does not result in any new final expression (after all there is only one BWPT or RSPT for closed shells), there are novel aspects of our mode of derivation. Moreover, this same method is capable of yielding valuable new results for degenerate and nondegenerate open-shell systems, as shown in the following paper. In the third paper, we also derive explicit formulas for ionization potentials, electron affinities, and transition energies of closed-shell ground states. The third paper also contains our initial results obtained by applying this resolvent-based MBPT to several test systems.

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