

# Size-consistent Brillouin-Wigner perturbation theory with an exponentially parametrized wave function: Brillouin-Wigner coupled-cluster theory

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Size consistency of the Brillouin-Wigner perturbation theory is studied using the Lippmann-Schwinger equation and an exponential ansatz for the wave function. Relation of this theory to the coupled-cluster method is studied and a comparison through the effective Hamiltonian method is also provided.

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## I. INTRODUCTION

In up-to-date quantum chemistry the many-body methods, especially many-body Rayleigh-Schrödinger perturbation theory (MB RSPT) and coupled-cluster (CC) methods, play an important role [1-6]. An appealing feature of these methods is the fact that they scale properly with the number of particles and that they obey the linked-cluster theorem. This is possibly the reason why less attention has been paid to the Brillouin-Wigner perturbation theory (BWPT). Besides the size inconsistency, the finite order BWPT has other seemingly inferior features: the perturbation expressions depend on the exact energy and the convergence of BWPT is believed to be slow.

The purpose of this paper is to analyze BWPT through the Lippmann-Schwinger equation and its connection with the effective Hamiltonian method as well as with CC theory. On the basis of this analysis we formulate size-consistent BWPT with an exponential ansatz for the wave function. We believe that making BWPT size consistent can bring more attention to this method. Some features of the size-consistent BWPT with respect to RSPT and CC will also be illuminated.

## II. THEORY

Let us have the Schrödinger equation

$$H \Psi_i = \mathcal{E}_i \Psi_i . \quad (1)$$

We assume that we are able to split the Hamiltonian  $H$  into two parts, namely,

$$H = H_0 + V , \quad (2)$$

where  $H_0$  is the unperturbed Hamiltonian and  $V$  is the perturbation. In this paper we will work with the Moller-Plesset (MP) partitioning, which implies

$$\langle \Phi_0 | V | \Phi_0 \rangle = 0 . \quad (3)$$

Nevertheless, in some equations this term will be used in order not to change the generally accepted structure of these equations. Further, we assume that we know the solution of the unperturbed eigenvalue problem,

$$H_0 \Phi_i = E_i \Phi_i . \quad (4)$$

Let  $|\Phi_i\rangle$  be the configuration state functions constructed from Hartree-Fock (HF) molecular orbitals. According to the BWPT expansion [7] the exact wave function (1) for the ground state is given by

$$|\Psi_0\rangle = (1 + BV + BVBV + \dots) |\Phi_0\rangle \quad (5)$$

and the exact energy for the ground state  $\mathcal{E}_0$  can be written as

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V + VB + VBVB + \dots | \Phi_0 \rangle , \quad (6)$$

where  $B$  is the Brillouin-Wigner (BW) -type resolvent

$$B = \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i|}{\mathcal{E}_0 - E_i} . \quad (7)$$

Let us introduce in formal analogy with scattering theory the operator  $T_B$ ,

$$T_B = V + VB + VBVB + \dots , \quad (8)$$

which we can write also in the form

$$T_B = V + V B T_B . \quad (9)$$

This equation is known in scattering theory as the Lippmann-Schwinger equation [8].

It is interesting to note that this equation was used in many-body theory to generate the high orders of BWPT but was not used for direct infinite order calculations.

In a recent paper [9] we have demonstrated its practical use in direct infinite order calculations and its connection to truncated configuration interaction (CI) calculations. The total ground state energy (6) is given using (9) by the equation

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | T_B | \Phi_0 \rangle \quad (10)$$

or in the equivalent form

$$\begin{aligned} \mathcal{E}_0 = & \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle \\ & + \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | T_B | \Phi_0 \rangle}{\mathcal{E}_0 - E_i} . \end{aligned} \quad (11)$$

The matrix elements of  $T_B$  operator are calculated from Eq. (9) as follows:

$$\langle \Phi_i | T_B | \Phi_0 \rangle = \langle \Phi_i | V | \Phi_0 \rangle + \sum_{j \neq 0} \frac{\langle \Phi_i | V | \Phi_j \rangle \langle \Phi_j | T_B | \Phi_0 \rangle}{\mathcal{E}_0 - E_j} . \quad (12)$$

It was demonstrated [9] that when using singly (S) and doubly (D) excited configurations in the resolvent (7) we get the CISD energy. Or generally, the level of truncation in the BW-type resolvent (7) determines the truncated CI energy. The main drawback of the truncated CI method and therefore of the truncated BWPT method is that they do not scale properly with the number of particles. It is therefore very topical to develop the size-consistent BWPT method and to study the size consistency of the truncated CI method. Nowadays in many papers the attention is paid to the development of size-consistent CI methods. Just to mention some recent works, see, e.g., Pople *et al.* [10], Povill *et al.* [11], and Szalay and Bartlett [12]. In doing size-consistent BWPT we show the connection of BWPT with the effective Hamiltonian method as well as CC methods.

The most general approach to the calculation of correlation energy is the method based on the effective Hamiltonian and the Bloch equation [7,13]. The basic idea lies in the introduction of the effective Hamiltonian  $H_{eff}$ , which acts within the  $d$ -dimensional model space and has the property that when diagonalized in this space it gives the part of the spectrum of our exact Hamiltonian. If we separate the complete configurational space into two disjoint subspaces, namely, the model space  $P$  and its orthogonal complement  $Q$ , the projection operators associated with these subspaces will have the form

$$P = \sum_{\alpha \in P} |\Phi_\alpha\rangle \langle \Phi_\alpha| , \quad (13)$$

$$Q = 1 - P = \sum_{\beta \in Q} |\Phi_\beta\rangle \langle \Phi_\beta| .$$

According to Lindgren [7] the construction of  $H_{eff}$  is possible through the wave operator  $\Omega$ ,

$$H_{eff} = PH\Omega P , \quad (14)$$

which is defined through the equation

$$\Psi_i = \Omega (P\Psi_i) , \quad i = 1, 2, \dots, d , \quad (15)$$

and which fulfills the so-called Bloch equation

$$[\Omega, H_0]P = V\Omega P - \Omega PV\Omega P \quad (16)$$

that may be viewed as an equivalent to the Schrödinger equation (1) for wave functions. If we split our Hamiltonian into the unperturbed part  $H_0$  and the perturbation  $V$ , the effective Hamiltonian (14) can be expressed in the form

$$H_{eff} = PH_0P + PV\Omega P \quad (17)$$

which implies that in case of one-dimensional (nondegenerate) model space the ground state energy is given as

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V\Omega | \Phi_0 \rangle . \quad (18)$$

The Bloch equation (16) for the degenerate case may be rewritten in the form [7]

$$(E_0 - H_0)\Omega P = QV\Omega P - \chi PV\Omega P , \quad (19)$$

where  $\chi$  is defined as

$$\Omega = 1 + \chi \quad (20)$$

and for the nondegenerate (one-dimensional) case we have

$$\begin{aligned} \Omega |\Phi_0\rangle = & |\Phi_0\rangle + \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i | V\Omega | \Phi_0 \rangle}{E_0 - H_0} \\ & - \frac{\chi |\Phi_0\rangle \langle \Phi_0 | V\Omega | \Phi_0 \rangle}{E_0 - H_0} . \end{aligned} \quad (21)$$

The realization of the wave operator  $\Omega$  can be done in various ways, e.g., using the expansion

$$\Omega = \sum_{i=0}^{\infty} \Omega^{(i)} \quad (22)$$

and we can obtain the perturbation theory form of the Bloch equation and the perturbation theory formulation for the effective Hamiltonian method. Note that in the Bloch equation (21) we have the Rayleigh-Schrödinger (RS) resolvent

$$R = \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i|}{E_0 - H_0} . \quad (23)$$

A great simplification in Eq. (21) is achieved by the realization of the linked-cluster theorem [7], which says that in Eq. (21) we calculate only linked connected (LC) diagrams, and therefore, Eq. (21) reads

$$\Omega |\Phi_0\rangle = |\Phi_0\rangle + \left\{ \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i | V\Omega | \Phi_0 \rangle}{E_0 - H_0} \right\}_{LC} . \quad (24)$$

Now, let us introduce the RSPT expansion for the exact energy. Using the linked-cluster theorem we have

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V + V R V + V R V R V + V R V R V R V + \dots | \Phi_0 \rangle_{LC} . \quad (25)$$

If we use the Lippmann-Schwinger equation (9) with the resolvent of RS type (23) we can introduce the operator  $T_R$ ,

$$T_R = V + V R T_R |_{LC} , \quad (26)$$

and the exact energy can be expressed in the form

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | T_R | \Phi_0 \rangle_{LC} , \quad (27)$$

where by  $|_{LC}$  we mean that when calculating matrix elements we consider only contributions from connected diagrams. Comparing Eqs. (10), (18), and (27) we have three different equations for the same energy  $\mathcal{E}_0$ ,

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V \Omega | \Phi_0 \rangle , \quad (28)$$

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | T_R | \Phi_0 \rangle_{LC} , \quad (29)$$

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | T_B | \Phi_0 \rangle . \quad (30)$$

Another possible way to realize the wave operator in Eq. (28) is to use the exponential ansatz [1]

$$\Omega = e^S \quad (31)$$

and up to unitary transformation we have

$$\langle \Phi_0 | T_R | \Phi_0 \rangle_{LC} = \langle \Phi_0 | V e^S | \Phi_0 \rangle_{LC} , \quad (32)$$

$$\langle \Phi_0 | T_B | \Phi_0 \rangle = \langle \Phi_0 | V e^S | \Phi_0 \rangle , \quad (33)$$

or

$$T_R = V e^S |_{LC} , \quad (34)$$

$$T_B = V e^S . \quad (35)$$

Using Eqs. (9), (26), (34), and (35) we have

$$V e^S |_{LC} = V + V R V e^S |_{LC} \quad (36)$$

and

$$V e^S = V + V B V e^S . \quad (37)$$

Note that when substituting Eq. (31) into Eq. (28) we can develop the coupled-cluster method. Instead of doing so we utilize the exponential ansatz (31) to develop the Lippmann-Schwinger equation. Substituting Eqs. (36) and (37) into (29) and (30), we get

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle + \langle \Phi_0 | V R V e^S | \Phi_0 \rangle_{LC} , \quad (38)$$

and

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle + \langle \Phi_0 | V B V e^S | \Phi_0 \rangle . \quad (39)$$

If we substitute for resolvents  $B$  and  $R$  from (7) and (23) we get

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle + \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | V e^S | \Phi_0 \rangle}{E_0 - E_i} \Bigg|_{LC} \quad (40)$$

and

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle + \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | V e^S | \Phi_0 \rangle}{\mathcal{E}_0 - E_i} . \quad (41)$$

Both Eqs. (40) and (41) can be solved iteratively but in both cases we have to know equations for matrix elements  $\langle \Phi_i | V e^S | \Phi_0 \rangle$ . These can be obtained from Eqs. (36) and (37), which can be simplified as

$$e^S |_{LC} = 1 + R V e^S |_{LC} , \quad (42)$$

$$e^S = 1 + B V e^S , \quad (43)$$

or in matrix elements

$$e^S | \Phi_0 \rangle |_{LC} = | \Phi_0 \rangle + \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i | V e^S | \Phi_0 \rangle}{E_0 - E_i} \Bigg|_{LC} , \quad (44)$$

$$e^S | \Phi_0 \rangle = | \Phi_0 \rangle + \sum_{i \neq 0} \frac{|\Phi_i\rangle \langle \Phi_i | V e^S | \Phi_0 \rangle}{\mathcal{E}_0 - E_i} . \quad (45)$$

Equation (44) is identical to the Bloch equation (24) and Eq. (45) is the analog of the Bloch equation (24) with the the BW type of denominator. The Lippmann-Schwinger equation (45) also gives us a new expression, namely, the Bloch equation in BW form. Equations (40), (41) and (44), (45) can be used for practical calculations.

Let us further adopt a simple approximation in the exponential ansatz (31), such that

$$S = S_2 \quad (46)$$

and simultaneously

$$e^{S_2} = 1 + S_2 + \frac{1}{2} S_2^2 . \quad (47)$$

This expansion is complete since the higher order terms do not contribute (as will be seen below). Substituting Eq. (47) into Eqs. (40) and (44), we get

$$\mathcal{E}_0 = \langle \Phi_0 | H_0 | \Phi_0 \rangle + \langle \Phi_0 | V | \Phi_0 \rangle + \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | V | \Phi_0 \rangle}{E_0 - E_i} \Bigg|_{LC} + \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | V S_2 | \Phi_0 \rangle}{E_0 - E_i} \Bigg|_{LC} + \frac{1}{2} \sum_{i \neq 0} \frac{\langle \Phi_0 | V | \Phi_i \rangle \langle \Phi_i | V S_2^2 | \Phi_0 \rangle}{E_0 - E_i} \Bigg|_{LC} \quad (48)$$

and

$$\begin{aligned} \{1 + S_2 + 1/2 S_2^2\}|\Phi_0\rangle|_{LC} = & |\Phi_0\rangle + \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|V|\Phi_0\rangle}{E_0 - E_i} \Big|_{LC} \\ & + \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|VS_2|\Phi_0\rangle}{E_0 - E_i} \Big|_{LC} + \frac{1}{2} \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|VS_2^2|\Phi_0\rangle}{E_0 - E_i} \Big|_{LC} . \end{aligned} \quad (49)$$

Substituting Eq. (47) into Eqs. (41) and (45), we get

$$\begin{aligned} \mathcal{E}_0 = & \langle\Phi_0|H_0|\Phi_0\rangle + \langle\Phi_0|V|\Phi_0\rangle + \sum_{i \neq 0} \frac{\langle\Phi_0|V|\Phi_i\rangle\langle\Phi_i|V|\Phi_0\rangle}{\mathcal{E}_0 - E_i} \\ & + \sum_{i \neq 0} \frac{\langle\Phi_0|V|\Phi_i\rangle\langle\Phi_i|VS_2|\Phi_0\rangle}{\mathcal{E}_0 - E_i} + \frac{1}{2} \sum_{i \neq 0} \frac{\langle\Phi_0|V|\Phi_i\rangle\langle\Phi_i|VS_2^2|\Phi_0\rangle}{\mathcal{E}_0 - E_i} \end{aligned} \quad (50)$$

and

$$\begin{aligned} \{1 + S_2 + 1/2 S_2^2\}|\Phi_0\rangle = & |\Phi_0\rangle + \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|V|\Phi_0\rangle}{\mathcal{E}_0 - E_i} \\ & + \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|VS_2|\Phi_0\rangle}{\mathcal{E}_0 - E_i} + \frac{1}{2} \sum_{i \neq 0} \frac{|\Phi_i\rangle\langle\Phi_i|VS_2^2|\Phi_0\rangle}{\mathcal{E}_0 - E_i} . \end{aligned} \quad (51)$$

The equations for cluster amplitudes can be obtained by projection of Eqs. (49) and (51) onto the corresponding unperturbed state functions.

Detailed analysis of Eqs. (48) and (49) shows that these are coupled clusters with doubles (CCD) equations. The analysis of Eqs. (50) and (51) shows that even these equations are equivalent to CCD equations but they are in the BW form. To distinguish the BW form of CC equations from standard CC equations we will call Eqs. (50) and (51) BWCCD equations. Similarly, when adopting approximation

$$S = S_1 + S_2 \quad (52)$$

we will speak about BWCCSD equations. The results for both sets of Eqs. (48), (49) and (50), (51) are equivalent and therefore Eqs. (50) and (51) are size consistent.

The equivalence of both approaches mentioned above can also be shown in another way. For practical reasons, below we will use operators in their normal product form (denoted by subscript  $N$ ), e.g.,

$$H_N = H - \langle\Phi_0|H|\Phi_0\rangle . \quad (53)$$

Let us employ the exponential ansatz for the wave operator (31) in the case of the nondegenerate ground state  $|\Phi_0\rangle$ ,

$$|\Psi_0\rangle = e^S|\Phi_0\rangle . \quad (54)$$

Then, in accordance with the Baker-Campbell-Hausdorff formula and the linked-cluster theorem we could develop the standard CC theory; for more details see, e.g., [5]. The expression for the ground state correlation energy  $\Delta\mathcal{E}_0$ ,

$$\Delta\mathcal{E}_0 = \mathcal{E}_0 - E_0 , \quad (55)$$

can be written as

$$\Delta\mathcal{E}_0 = \langle\Phi_0|V_N e^S|\Phi_0\rangle_{LC} \quad (56)$$

and the equations for cluster amplitudes can be derived from the condition

$$\langle\Phi_i|H_N e^S|\Phi_0\rangle_{LC} = 0 , \quad (57)$$

so

$$\langle\Phi_i|e^S|\Phi_0\rangle_{LC} = \frac{1}{E_0 - E_i} \langle\Phi_i|V_N e^S|\Phi_0\rangle_{LC} , \quad (58)$$

where  $|\Phi_i\rangle$  represent excited unperturbed wave functions. From Eqs. (1), (2) and (54) we also have

$$(H_{0N} + V_N) e^S|\Phi_0\rangle = \Delta\mathcal{E}_0 e^S|\Phi_0\rangle . \quad (59)$$

Projecting the previous equation onto the unperturbed state functions  $|\Phi_i\rangle$  we have

$$\langle\Phi_i|V_N e^S|\Phi_0\rangle = \langle\Phi_i|(\Delta\mathcal{E}_0 - H_{0N}) e^S|\Phi_0\rangle \quad (60)$$

and when we exploit Eq. (4) with  $H_0$  in its normal product form,

$$H_{0N}|\Phi_i\rangle = (E_i - E_0)|\Phi_i\rangle , \quad (61)$$

we obtain the final equation for amplitudes,

$$\langle\Phi_i|e^S|\Phi_0\rangle = \frac{\langle\Phi_i|V_N e^S|\Phi_0\rangle}{\Delta\mathcal{E}_0 + E_0 - E_i} = \frac{\langle\Phi_i|V_N e^S|\Phi_0\rangle}{\mathcal{E}_0 - E_i} . \quad (62)$$

Analogously, if we project Eq. (59) onto the ground state wave function  $|\Phi_0\rangle$  with the use of Eq. (61), we obtain the expression for the ground state energy in the form

$$\Delta\mathcal{E}_0 = \langle\Phi_0|V_N e^S|\Phi_0\rangle . \quad (63)$$

Using the resolution of unity we can write

$$\Delta\mathcal{E}_0 = \langle\Phi_0|V_N|\Phi_0\rangle + \sum_{i \neq 0} \langle\Phi_0|V_N|\Phi_i\rangle\langle\Phi_i|e^S|\Phi_0\rangle . \quad (64)$$

If we realize that the first term is zero and if we substitute for  $\langle\Phi_i|e^S|\Phi_0\rangle$  from Eq. (62), we finally get

$$\Delta\mathcal{E}_0 = \sum_{i \neq 0} \frac{\langle \Phi_0 | V_N | \Phi_i \rangle \langle \Phi_i | e^S | \Phi_0 \rangle}{\mathcal{E}_0 - E_i}. \quad (65)$$

It is obvious that Eqs. (56) and (58) are equivalent to Eqs. (48) and (49) and Eqs. (65) and (62) are equivalent to Eqs. (50) and (51) (of course, in appropriate normal product form) when projecting Eqs. (49) and (51) onto the corresponding unperturbed wave functions. Since Eqs. (58) and (56) and Eqs. (62) and (65) represent two different ways of solving the same problem without the use of any approximation, their results have to be equivalent.

### III. IMPLEMENTATION

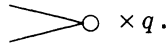
In this part we want to show that the computational effort required for one iteration in BWCCSD theory is practically the same as that for the standard CCSD method. We do not want to deal with extra details since the implementation of new parts in the BWCCSD approach is not complex, at all.

Let us first deal with the equations for amplitudes (51) or (62). In order to obtain the  $S_1$  and  $S_2$  amplitudes we can employ the equation

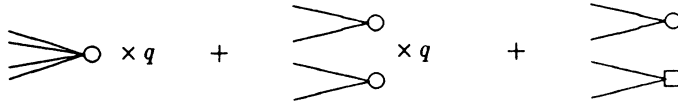
$$\langle \Phi_i | e^{(S_1+S_2)} | \Phi_0 \rangle = \frac{\langle \Phi_i | V_N e^{(S_1+S_2)} | \Phi_0 \rangle}{\Delta\mathcal{E}_0 + E_0 - E_i}, \quad (66)$$

which can be simplified to

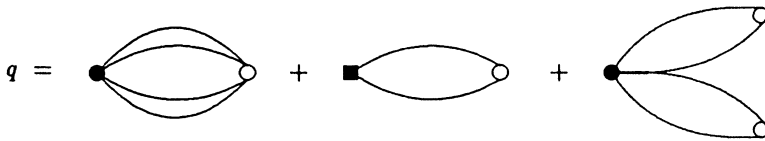
For single excitations



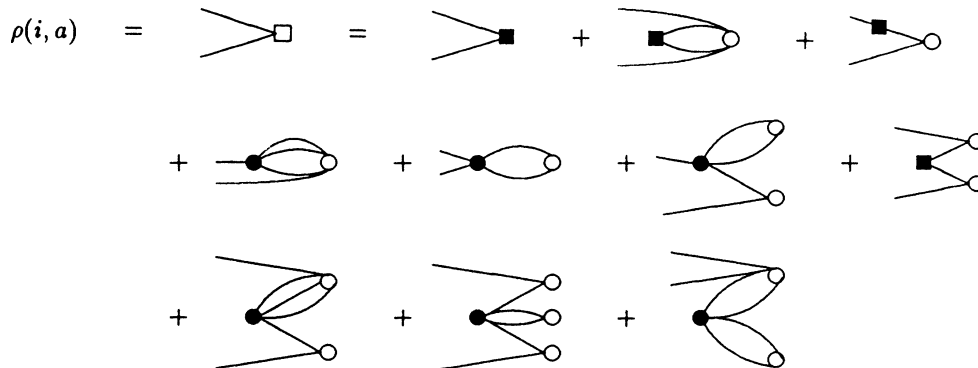
For double excitations



where  $q$  is defined as



and where the intermediate  $\rho(i, a)$  is defined as



$$\langle \Phi_i | S_i | \Phi_0 \rangle = \frac{\langle \Phi_i | V_N e^{(S_1+S_2)} | \Phi_0 \rangle}{\Delta\mathcal{E}_0 + E_0 - E_i} - \langle \Phi_i | e^{(S_1+S_2)} | \Phi_0 \rangle_{DC}, \quad (67)$$

where the subscript DC stands for disconnected diagrams (in the case of monoexcitations this term does not contribute and in the case of double excitations it is equal to  $\frac{1}{2} \langle \Phi_i | S_1 S_1 | \Phi_0 \rangle$ ). As we can see, there are some basic differences between BWCCSD and CCSD in obtaining amplitudes, namely, (i) in the CCSD method the denominators contain only differences of corresponding orbital energies (i.e., diagonal Hartree-Fock matrix elements), while in BWCCSD the denominators contain also the correlation energy, i.e.,

$$\mathcal{E}_0 - E_i = \Delta\mathcal{E}_0 + E_0 - E_i, \quad (68)$$

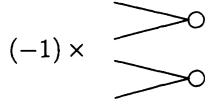
and (ii) there are some disconnected contributions in BWCCSD, while in CCSD we work only with connected contributions.

The most complex and time-consuming part represents connected contributions of the first term on the right hand side of Eq. (67) and they can be calculated in the same way as is done in the standard CCSD method. For practical calculations we use the spin-orbital formulation of Stanton *et al.* [14] and the computer code for CCSD method [25].

Disconnected contributions of the first term on the right hand side of Eq. (67) can be diagrammatically represented as follows.

In previous graphs we used the symbols  $\cdot$  for one-particle perturbation,  $\bullet$  for two-particle perturbation, and  $\circ$  for cluster amplitudes.

We can see that the structure of the intermediate  $\rho(i, a)$  is the same as that for connected contributions to  $t_1$  amplitudes in the CCSD method. Therefore we can get the  $\rho(i, a)$  intermediate without any additional work. Considering these expressions for unlinked contributions of the first term on the left hand side of Eq. (67) it is obvious that the consumption of computational time of all these processes in comparison to the CCSD method is proportional at most to  $N^4$  with respect to the number of basis functions. For the second term on the left hand side of Eq. (67), which can be diagrammatically represented (for double excitations) as



the situation is analogous; it is proportional to  $N^4$ .

Let us briefly mention the calculation of correlation energy. When we use Eqs. (50), (65), and (68) the expression for the correlation energy  $\Delta\mathcal{E}_0$  can be written as

$$\Delta\mathcal{E}_0 = \sum_{i \neq 0} \frac{\langle \Phi_0 | V_N | \Phi_i \rangle \langle \Phi_i | V_N e^{(S_1 + S_2)} | \Phi_0 \rangle}{\Delta\mathcal{E}_0 + E_0 - E_i}. \quad (69)$$

As the matrix elements

$$\omega_i = \langle \Phi_i | V_N e^{(S_1 + S_2)} | \Phi_0 \rangle$$

are already calculated, see the first term on the left hand side of eq. (67); we get the expression for correlation energy in the form

$$\Delta\mathcal{E}_0 = \sum_{i \neq 0} \frac{\langle \Phi_0 | V_N | \Phi_i \rangle}{\Delta\mathcal{E}_0 + E_0 - E_i} \omega_i. \quad (70)$$

Because the index  $i$  runs over single and double excitations the calculation of the correlation energy (70) contains at most  $N^4$  processes.

Since the most time-consuming processes in one iteration step of the CCSD method depends on the number of basis function as  $N^6$ , it is evident that the additional consumption of computational time required for the realization of the one-iteration BWCCSD method is obviously negligible. From the given scheme we can also see that for higher versions of the CC method (which is not the subject of this work, e.g., CCSDT) the situation is analogous.

#### IV. NUMERICAL RESULTS

In this section we give some numerical results to illustrate the methods introduced in this work. We calculate BWCCD and BWCCSD energies for three small closed shell systems, namely, Be, H<sub>2</sub>O, and F<sup>-</sup>; and we also present some single-reference open-shell BWCCSD results for two doublet states (Na and CN) and one triplet state (O<sub>2</sub>). The corresponding results are listed in Table I. As a reference wave function we have used the restricted HF (RHF) solution for closed-shell systems and restricted open shell HF (ROHF) solution according to Roothaan [15] for open-shell systems. It is worth noting that the BWCCD method for open-shell systems is not very suitable due to the much more important role of single excitations.

As we can see from Table I, the results for the BWCCD and BWCCSD methods are actually identical to those for the CCD and CCSD methods in all cases, so one can conclude that the numerical equivalence of CC and BWCC has been confirmed. In order to prove the size consistency of the BWCCD and BWCCSD methods we have chosen a simple example with two Be atoms in quasi-infinite distance (1000 a.u.). In this sense it is not surprising that the BWCCD and BWCCSD energies for the 2Be super-

TABLE I. Self-consistent field (SCF) and various correlation energies for some small closed-shell and open-shell systems (in  $-E/E_H$ )

System	SCF	CCD	CCSD	BWCCD	BWCCSD
Be <sup>a</sup>	14.572 984	0.051 871	0.052 486	0.051 871	0.052 486
2 Be <sup>a,b</sup>	29.145 969	0.103 743	0.104 972	0.103 743	0.104 972
H <sub>2</sub> O <sup>c,d</sup>	76.064 564	0.245 442	0.247 283	0.245 442	0.247 283
F <sup>-a</sup>	99.459 102	0.306 461	0.308 943	0.306 461	0.308 943
CN ( <sup>2</sup> Σ <sup>+</sup> ) <sup>e,f,g</sup>	92.208 831		0.321 720		0.321 720
Na ( <sup>2</sup> S) <sup>g,h</sup>	161.846 414		0.083 908		0.083 908
O <sub>2</sub> ( <sup>3</sup> Σ <sub>g</sub> <sup>-</sup> ) <sup>e,g,i</sup>	149.650 063		0.403 366		0.403 366

<sup>a</sup>ANO (5.4.3.2) spherical basis set [20].

<sup>b</sup> $r=1000.0$  a.u. (quasi-infinite distance).

<sup>c</sup>ANO (5.3.2;3.2) spherical basis set [20].

<sup>d</sup> $r=1.790$  a.u.,  $\phi=105.5$  [21].

<sup>e</sup>POL (5.3.2) Cartesian basis set [22].

<sup>f</sup> $r=2.2144$  a.u. [23].

<sup>g</sup>Corresponding SCF and CCSD values were taken from Ref. [25].

<sup>h</sup>POL (7.5.2) Cartesian basis set [24].

<sup>i</sup> $r=2.207$  a.u. [21].

system are exactly two times larger than those for the single Be atom (see Table I) even though it is clear that this feature directly follows from the equivalence with corresponding CC results.

## V. DISCUSSION

The exact energy dependence of individual orders of the BWPT expansion and the size inconsistency of the method were the reasons why this method was not further studied and used for practical calculations. The many-body formulation of BWPT was done by Brandow [13,16,17]. He used BWPT to develop quasidegenerate RSPT introducing the concept of folded diagrams [13]. However, the size inconsistency of BWPT was not studied in detail. In this article, analyzing the connection of BWPT and the Lippmann-Schwinger equation with the size-consistent effective Hamiltonian method and CC theory and using the exponential ansatz for the exact nondegenerate wave function, we developed BWCC theory.

The connection of RSPT with CC theory is well known; see, e.g., [18]. We can see that the fully analogous relation is also between BWPT and BWCC theory. While in the RSPT case the individual orders of perturbation expansion as well as the individual iterations of the CC procedure are size consistent, in the BWPT and BWCC cases they are not. However, as was shown in this work, converged BWCC results are not only size consistent but also identical to corresponding CC results. It can be said that the cluster expansion forms of both different perturbational approaches are identical. It is therefore interesting to note that the complete expansion in both BWPT and RSPT methods is not the only common result of both approaches, but as presented in this paper, also the limited versions like BWCCD and (BWCCSD) are com-

mon. It is worth noting that the BWCCD (BWCCSD) theory contains disconnected diagrams. The practical implementation and the numerical complexity is approximately the same as that for CCD (CCSD) theory.

One could ask, what is the reason for developing the size-consistent BWPT theory? We note that such a theory may play an important role in the development of size-consistent CI theories. Another problem is that the present stage of developing multireference (MR) RSPT and MR CC theories is still far from being satisfactory. One of the crucial problems in existing MR RSPT and MR CC methods is the presence of so-called intruder states. Intruder states may cause the divergence problem, which is due to the vanishing denominators in the RS-type propagators. The formulation of MR BWPT or MR BWCC theories is much simpler than that of MR RSPT and MR CC theories. Moreover, the presence of the BW-type propagators can avoid the intruder state problem. In this article we give only the proof of the equivalence of BWCC and CC approaches. The detail analysis of the cancellation of size-inconsistent contributions in BWCC theory will be the subject of a future paper [19].

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