BRILLOUIN–WIGNER PERTURBATION THEORY AS A POSSIBLE MORE EFFECTIVE ALTERNATIVE TO MANY-BODY RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY AND COUPLED CLUSTER THEORY

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Brillouin–Wigner perturbation theory is revisited using the Lippmann–Schwinger equation and applied to the H_2O molecule. The results obtained are examined from the view-point of the development of practical computational methods.

In up to date quantum chemistry the many-body methods like many-body Rayleigh–Schrödinger perturbation theory (MB RSPT) and coupled cluster (CC) method play an important role. For nondegenerate systems in which the ground state is well described by a single determinant MB RSPT and particularly CC method are very efficient for the description of correlation energies of atoms and molecules as well as for the calculation of various properties. An appealing feature of these methods is the fact that they scale properly with the number of particles. This is the consequence of application of the linked cluster theorem in these methods. Possibly it is just this reason why less attention has been paid to Brillouin–Wigner perturbation theory (BWPT). Beside 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. Much larger attention was paid to BWPT in older works dealing with the nuclear matter[1,2]. In quantum chemistry BWPT was studied by Löwdin in his monumental series "Studies in Perturbation Theory" in connection with inner projection techniques[3–6]. Related to this problem is the work of Brandas and Bartlett[7,8]. Recently also Cizek and coworkers pointed out the connection of the inner projection and BWPT (refs[9–11]). However we have benefited most directly from papers[12–14] dealing with the CI+B_k method and showing its relationship to BWPT.

The purpose of this paper is twofold. Firstly, we reformulate BWPT on the basis of Lippmann–Schwinger equation and we try to follow the procedure usual in scattering

theory. Our objective is to arrive at very high or infinite orders of BWPT, in contrast to the quoted CI treatments[12–14] focused on excited states and low orders of BWPT. Secondly, we try to demonstrate the utility of this approach in practical calculations. Although the use of BWPT in this context is not new, we want to show that it might be more practical than the corresponding approaches based on MB RSPT/CC theory, particularly in treatments including higher excitations, excited states, and near degeneracy states.

THEORETICAL

As usual in perturbation theory we assume that in Schrödinger equation

$$\hat{H}\Psi_i = E_i\Psi_i \tag{1}$$

we are able to split the Hamiltonian $\hat{H}$ into two parts, namely

$$\hat{H} = \hat{H}^0 + \hat{W} \ , \tag{2}$$

where $\hat{H}^0$ is the unperturbed Hamiltonian and $\hat{W}$ is the perturbation. We will assume Epstein–Nesbet[15] (EN) and Møller–Plesset (MP) partitionings. Further we assume that we know the solution of the unperturbed eigenvalue problem

$$\hat{H}^0 \,|\, \Phi_i \rangle = E_i \,|\, \Phi_i \rangle \tag{3}$$

Let Φ_i be configuration state functions constructed from Hartree–Fock molecular orbitals. Then according to the BWPT expansion[1] the exact wave function (1) for the ground state is given by

$$\Psi = (1 + \hat{Q}_0\hat{W} + \hat{Q}_0\hat{W}\hat{Q}_0\hat{W} + \ldots) \,|\, \Phi_0 \rangle \ , \tag{4}$$

and the exact energy of the ground state is given as

$$E = \langle \Phi_0 \,|\, \hat{H}^0 \,|\, \Phi_0 \rangle + \langle \Phi_0 \,|\, \hat{W} \,|\, \Phi_0 \rangle + \langle \Phi_0 \,|\, \hat{W}\hat{Q}_0\hat{W} \,|\, \Phi_0 \rangle + \ldots \tag{5}$$

or

$$E = \langle \Phi_0 \mid \hat{H}^0 \mid \Phi_0 \rangle + \langle \Phi_0 \mid \hat{W} + \hat{W}\hat{Q}_0\hat{W} + \ldots \mid \Phi_0 \rangle \ . \tag{6}$$

Let us introduce in formal analogy with the scattering theory the operator $\hat{T}$ as

$$\hat{T} = \hat{W} + \hat{W}\hat{Q}_0\hat{W} + \ldots \ , \tag{7}$$

which also may be written in the form

$$\hat{T} = \hat{W} + \hat{W}\hat{Q}_0\hat{T} \ . \tag{8}$$

This equation is known in scattering theory as Lippmann–Schwinger equation[4–16]. It is interesting to note that in many-electron theory this equation was used to generate Brillouin–Wigner perturbation series and it was not used as a recurrent expression which can be brought into matrix form and applied to practical calculations. From Eq. (8) we get for the operator $\hat{T}$ the following relation

$$\hat{T} = (1 - \hat{W}\hat{Q}_0)^{-1}\hat{W} \ . \tag{9}$$

In BWPT the propagator has the form

$$\hat{Q}_0 = \sum_{i \neq 0} \frac{\mid \Phi_i \rangle \langle \Phi_i \mid}{E - E_i} \ . \tag{10}$$

Using Eq. (7) we can now rewrite Eq. (6) as

$$E = \langle \Phi_0 \mid \hat{H}^0 \mid \Phi_0 \rangle + \langle \Phi_0 \mid \hat{T} \mid \Phi_0 \rangle \ , \tag{11}$$

and the wave function as

$$\mid \Psi \rangle = (1 + \hat{Q}_0\hat{T}) \mid \Phi_0 \rangle \ . \tag{12}$$

Our task is to bring Eq. (*11*) to a form suitable for practical calculations. We substitute from Eqs (*8*) and (*10*) into Eq. (*11*),

$$E = \langle \Phi_0 \mid \hat{H}^0 \mid \Phi_0 \rangle + \langle \Phi_0 \mid \hat{W} \mid \Phi_0 \rangle + \sum_{i \neq 0} \frac{\langle \Phi_0 \mid \hat{W} \mid \Phi_i \rangle \langle \Phi_i \mid \hat{T} \mid \Phi_0 \rangle}{E - E_i} \ . \tag{13}$$

Let us now introduce the following notation

$$W_{0i} = \langle \Phi_0 \mid \hat{W} \mid \Phi_i \rangle \ , \tag{14}$$

and

$$T_{i0} = \langle \Phi_i \mid \hat{T} \mid \Phi_0 \rangle \ . \tag{15}$$

Then we may write Eq. (*13*) as

$$E = H_{00}^0 + W_{00} + \sum_{i \neq 0} \frac{W_{0i} T_{i0}}{E - E_i} \ . \tag{16}$$

This equation cannot be used to calculate the energy E because except the energy E we do not know the matrix elements T_{i0}. But using Eq. (*8*) we may write

$$\langle \Phi_i \mid \hat{T} \mid \Phi_0 \rangle = \langle \Phi_i \mid \hat{W} \mid \Phi_0 \rangle + \sum_{j \neq 0} \frac{\langle \Phi_i \mid \hat{W} \mid \Phi_j \rangle \langle \Phi_j \mid \hat{T} \mid \Phi_0 \rangle}{E - E_j} \ , \tag{17}$$

which in the notation of Eqs (*14*) and (*15*) becomes

$$T_{i0} = W_{i0} + \sum_{j \neq 0} \frac{W_{ij} T_{j0}}{E - E_j} \ . \tag{18}$$

If we realize that

$$\langle \Phi_i \mid \hat{T} \mid \Phi_0 \rangle = \langle \Phi_0 \mid \hat{T} \mid \Phi_i \rangle \ , \tag{19}$$

we also have

$$\langle \Phi_i \mid \hat{T} \mid \Phi_0 \rangle = \langle \Phi_0 \mid \hat{W} \mid \Phi_i \rangle + \sum_{j \neq 0} \frac{\langle \Phi_0 \mid \hat{W} \mid \Phi_j \rangle \langle \Phi_j \mid \hat{T} \mid \Phi_i \rangle}{E - E_j} \qquad (20)$$

or

$$T_{i0} = W_{0i} + \sum_{j \neq 0} \frac{W_{0j} T_{ji}}{E - E_j} \ , \qquad (21)$$

where

$$T_{ji} = \langle \Phi_j \mid \hat{T} \mid \Phi_i \rangle \ . \qquad (22)$$

Again using Eq. (*8*) we obtain

$$T_{ji} = \langle \Phi_j \mid \hat{W} \mid \Phi_i \rangle + \sum_{k \neq 0} \frac{\langle \Phi_j \mid \hat{W} \mid \Phi_k \rangle \langle \Phi_k \mid \hat{T} \mid \Phi_i \rangle}{E - E_k} \ , \qquad (23)$$

which can be rewritten also as

$$T_{ji} = W_{ji} + \sum_{k \neq 0} \frac{W_{jk} T_{ki}}{E - E_k} \ , \qquad (24)$$

and in the matrix notation as

$$\boldsymbol{T} = \boldsymbol{W} + \boldsymbol{UT} \ , \qquad (25)$$

where the matrix $\boldsymbol{U}$ is defined as

$$U_{jk} = \frac{W_{jk}}{E - E_k} \ . \qquad (26)$$

From Eq. (*25*) we have

$$\boldsymbol{T} = (1 - \boldsymbol{U})^{-1} \boldsymbol{W} \ . \qquad (27)$$

This equation might be used for the expression of the wave function (*12*). It should be noted that the analogy of Eq. (*27*) with the Lippmann–Schwinger equation expressed by Eq. (*9*) is only formal. In scattering calculation the W matrix, expressed in a Gaussian basis set, has the same size in any order of the BWPT expansion. On contrary, in electron correlation problem the size of W matrix depends on the particular order of the perturbation expansion.

Equations (*16*) and (*18*) can be used to calculate the energy E. We may rewrite them into the form

$$\sum_{j \neq 0} (\delta_{ij} - U_{ij}) T_{j0} = W_{i0} \ , \tag{28}$$

which is a system of linear equations for T_{j0} elements. This system of equations and Eq. (*16*) in the following form

$$E = H_{00}^0 + W_{00} + \sum_{i \neq 0} U_{0i} T_{i0} \tag{29}$$

represent a system of coupled equations for E which can be solved iteratively in the following way: set $E = H_{00}$, get the U matrix from Eq. (*26*), solve the system of linear equations (*28*) for T_{j0} and calculate new E from Eq. (*29*). This procedure is repeated till selfconsistency. It is of course profitable to use a more educated guess to E, for example the CI-SD energy.

Subtract the SCF energy of the ground state $\langle \Phi_0 | \hat{H} | \Phi_0 \rangle$ from all diagonal H matrix elements so that E becomes the correlation energy. Then for the Epstein–Nesbet[15] partitioning of the Hamiltonian the H^0 and W matrix elements are given as

$$\langle \Phi_i | \hat{H}^0 | \Phi_j \rangle = 0 \ , \ i \neq j \ , \tag{30}$$

and

$$\langle \Phi_i | \hat{W} | \Phi_j \rangle = (1 - \delta_{ij}) \langle \Phi_i | \hat{H} | \Phi_j \rangle \ . \tag{31}$$

Energy E_i in the propagator (*10*) and in the U matrix elements (*26*) has the meaning of the SCF excitation energy

$$E_i = \langle \Phi_i | \hat{H} | \Phi_i \rangle - \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \ . \tag{32}$$

For the Møller–Plesset partitioning of the Hamiltonian we have

$$\langle \Phi_i \mid \hat{H}^0 \mid \Phi_j \rangle = \delta_{ij} \langle \Phi_i \mid \hat{F} \mid \Phi_j \rangle \ , \tag{33}$$

where $\hat{F}$ is the Hartree–Fock operator,

$$\langle \Phi_i \mid \hat{W} \mid \Phi_j \rangle = \langle \Phi_i \mid \hat{H} \mid \Phi_j \rangle - \delta_{ij} \langle \Phi_i \mid \hat{F} \mid \Phi_j \rangle \ , \tag{34}$$

and

$$E_i = \langle \Phi_i \mid \hat{F} \mid \Phi_i \rangle \ . \tag{35}$$

Upon substitution of Eqs (30)–(35) in Eqs (28) and (29) the EN and MP partitionings of the Hamiltonian give equivalent systems of equations, which in turn give the same result in any iteration. Distinguishing between the two Hamiltonian partitionings is therefore irrelevant in context of Eqs (28) and (29). When the direct BWPT expansion (5) is used, the EN and MP partitionings of the Hamiltonian give only the same energies at the infinite order.

Our Eq. (18) is the same as those of the linearized CC approaches, except that the correlation energy is absorbed in the energy denominator. Also, the approach represented by Eqs (28) and (29) is equivalent to CI calculation for the particular level of excitation. For example if we restrict the W matrix to single, double, triple and quadruple excitations, we get the CI-SDTQ energies. This of course does not bring any advantage. We believe, however, that the method so formulated is open for introducing various approximations which could reduce computational effort and only cause a small loss in accuracy. We present such an approach in which we neglect triple–triple, triple–quadruple and quadruple–quadruple off-diagonal W_{ij} elements for configuration state functions i and j that differ in their orbital part. This resembles the CI-B$_k$ method but the difference is that in application of the B$_k$ approximation to CI-SD all off-diagonal W_{ij} elements were disregarded[12–14]. We will show in a later paper that our way of using the B$_k$ approximation has a firmer theoretical basis. Hereafter we will refer to this approximation as to LS-B$_k$, indicating that it combines the merits of the Lippmann–Schwinger and the CI-B$_k$ approach. The W matrix in the LS-B$_k$ approximation has a quasi-diagonal form in the block of triples and quadruples. Instead of using the iterative scheme represented by Eqs (28) and (29), we considered it therefore more practical to use a modified GUGA CI procedure, in which we eliminated the loops for neglected W_{ij} elements.

RESULTS

For testing the LS-B$_k$ approximation we selected the water molecule because of a popular benchmark by Saxe et al.[17]. Since we need the CI-SDTQ energies as a standard, we quote the erratum[18] to this benchmark. Also we quote the later papers[19,20] which provide CI, MB RSPT and CC energies for geometries with the stretched O–H bond at $R = 1.5R_e$ and $2.0R_e$. Our LS-B$_k$ data are compared with the literature data obtained by other methods in Table I and Fig. 1.

TABLE I
Energies of H_2O (in a.u.) obtained with the double-zeta basis set by different methods at three different OH bond lengths

Method	R_e	$1.5R_e$	$2.0R_e$
SCF	–76.009838	–75.803529	–75.595180
CI-SD[a]	–76.150015	–75.992140	–75.844817
LS-B$_k$	–76.158669	–76.016617	–75.907824
CI-SDTQ[a]	–76.157626	–76.013418	–75.900896
MBPT(4)-SDTQ[b]	–76.156876	–76.008395	–75.888867
CC-SD[b]	–76.156076	–76.008931	–75.895913
CC-SDT-1[c]	–76.157414	–76.013067	–75.910821
FCI[a]	–76.157866	–76.014521	–75.905247

[a] Taken from refs[17,18] for R_e and from ref.[19] for $1.5R_e$ and $2.0R_e$; [b] ref.[20]; [c] ref.[21].
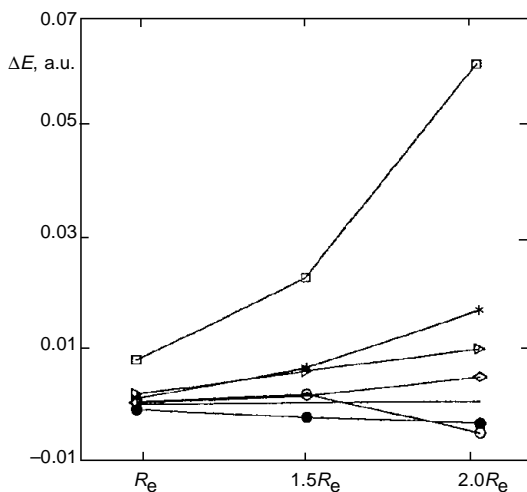

Fig 1.
Energies of H_2O relative to the full-CI energy. The calculations were performed at three different OH bond lengths, using the DZ basis set and the following methods: □ CI-SD (refs[17,19]), * MBPT(4)-SDTQ (ref.[20]), Δ CC-SD (ref.[20]), ○ CC-SDT-1 (ref.[21]), ◇ CI-SDTQ (refs[18,19]), ● LS-B$_k$

DISCUSSION

As we have said at the very beginning the purpose of this paper was to revise the BWPT and to bring it for use in practical calculations. This was done using the Lippmann–Schwinger equation (9). Bringing the Lippmann–Schwinger equation into the matrix form we got the system of equations for T matrix elements (18), which can be solved iteratively by means of Eqs (28) and (29). This approach is more efficient than a direct BWPT expansion (5). Computationally, the crucial step of this procedure is the evaluation of the W matrix elements. As follows from their definition in Eq. (31) they represent the matrix elements for the two-particle operator of the Hamiltonian (2). It is therefore natural to use existing CI programs for their evaluation. This implies that we use spin adapted configuration state functions, in contrast to traditional MB RSPT and CC. Efficient use of the LS-B_k approximation of course requires a rewriting the CI code for skipping the evaluation of T–T, T–Q and Q–Q Hamiltonian matrix elements, or efficient construction of any part of the Hamiltonian matrix as it is required by the particular approximation assumed. Only then it will be possible to decide if LS-B_k or other BWPT variants are liable to become more profitable than the CC methods.

In all other respects the results are promising. As Table I and Fig. 1 show LS-B_k compares favorably with CI-SDTQ and full CI. In contrast to the iterative scheme with the full W matrix, LS-B_k does not furnish the upper bound of the energy. As it is seen in Table I, our LS-B_k energies for H_2O are below the full CI energies. However the respective difference is small, and what is more important, it remains almost constant as the OH bonds are stretched (Fig. 1). Size-inconsistency of the finite order BWPT was a matter of concern. We believe, however, that the presence of D–Q W matrix elements should cancel a major part of the size-consistency error of the CI-SD approach. This will be tested in our later paper. So far we have shown[22] that the size-inconsistency may be eliminated rigorously by introducing wave operator and Bloch equation in Brillouin–Wigner form.

Finally some other merits of LS-B_k should be noted. We mean those that are not so easily met in the CC theory. A close relation of LS-B_k to CI provides a direct way to the wave function and the properties. Also extension to open shell systems, multireference formulation and excited states is straightforward. A problem of intruder states in quasidegenerate multireference case seems to be avoided. The gradient of energy should not be more difficult to obtain than with the CI wave function. Finally we would like to emphasize the clarity and simplicity of the formulation of the theory. It permits easy implementation of various approximations leading to variants of BWPT that are close by its value to different MB RSPT/CC methods.

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