

On the summation of the Brillouin-Wigner type perturbation series

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Abstract. It is shown that if the 'mean excitation energy' assumption is introduced in the Brillouin-Wigner perturbation series, then the resulting series can be exactly summed. The implications of the result for calculating energy shift and for constructing trial functions are examined with special reference to the ground state of the helium atom.

Keywords. Brillouin-Wigner series; mean excitation energy approximation; correlated trial function; helium atom.

1. Introduction

A widely used device to simplify the second order perturbation expression for energy consists in replacing the excitation energies (Δ_n) of the unperturbed system by a mean excitation energy Δ . This device, sometimes referred to as the closure approximation, enables the second order energy correction to be expressed entirely in terms of the unperturbed ground state wave function. It thus provides a simple recipe for estimation of many properties and there are several examples in the literature (Bethe and Salpeter 1957; Pople *et al* 1959; Atkins 1970) where such an approximation proves useful. A consequence of this approximation is the functional form for the wave function which can be used as a trial function for a variational calculation (Lenard-Jones 1930). Examples of such an approach include calculation of the polarisability of a helium and of Van der Waals' interaction energy between two hydrogen atoms (Pauling and Wilson 1935).

The utility of the closure approximation within the framework of the second-order perturbation theory suggests that it may be profitable to introduce the 'mean excitation energy' assumption in all the orders of the perturbation expansion. The resulting expression should be potentially more accurate for evaluation of the energy shift as well as for construction of trial functions. However, to test this idea it is necessary to first sum the infinite-order perturbation series in a closed form. We outline in this paper a method that has been found useful for summing the Brillouin-Wigner type perturbation series. The implications of the results are then briefly discussed by taking the correlation problem in the ground state of a helium atom as an example.

2. Summation of the approximate Brillouin-Wigner series

Let the Hamiltonian H of a system be written as

$$H = H_0 + V, \quad (1)$$

where H_0 is the unperturbed part and V is the perturbation. The first order energy correction (T_0) has the form

$$T_0 = \langle 0 | V | 0 \rangle \equiv V_{00} \quad (2)$$

where $|0\rangle$ is the ground state of H_0 . The second and higher order corrections (T_n ; $n \neq 0$) according to the Brillouin-Wigner perturbation theory are

$$T_n = \sum'_{i_1, \dots, i_n} \frac{V_{0i_1} V_{i_1 i_2} \dots V_{i_{n-1} i_n} V_{i_n 0}}{(E - E_{i_1}^0) \dots (E - E_{i_n}^0)}, \quad (3)$$

where i_n 's are the complete set of states associated with H_0 with the eigen values $E_{i_n}^0$ and E is the ground state energy of H . The prime over the summations indicates that the state $|0\rangle$ is to be excluded from all the summations. If E_0^0 is the energy of the unperturbed ground state, then

$$E = E_0^0 + \Delta E, \quad (4)$$

where $\Delta E \equiv S = \sum_{n=0}^{\infty} T_n$. (5)

We now equate each of the bracketed terms in the denominator of (3) to a constant Δ . This is the closure approximation. In the context of the Brillouin-Wigner expansion, the assumption means that the differences in energies of the excited states of the unperturbed system are considered to be negligible as compared to their separation from the exact ground state.

Equation (3) now becomes

$$T_n = 1/\Delta^n \sum'_{i_1, \dots, i_n} V_{0i_1} V_{i_1 i_2} \dots V_{i_{n-1} i_n} V_{i_n 0}. \quad (6)$$

Consider first the summation over i_n . If the missing state is added and subtracted, the summation over i_n can be contracted to yield:

$$T_n = 1/\Delta^n \sum'_{i_1, \dots, i_{n-1}} V_{0i_1} \dots (V^2)_{i_{n-1} 0} \dots V_{00} / \Delta T_{n-1}. \quad (7)$$

Contracting the remaining summations in the same manner, we get*

$$T_n = \frac{(V^{n+1})_{00}}{\Delta^n} - \sum_{r=1}^n \frac{(V^r)_{00}}{\Delta^r} T_{n-r}. \quad (8)$$

It follows that:

$$\sum_{n=1}^{\infty} T_n = \sum_{n=1}^{\infty} \frac{(V^{n+1})_{00}}{\Delta^n} - \sum_{n=1}^{\infty} \sum_{r=1}^n \frac{(V^r)_{00}}{\Delta^r} T_{n-r}. \quad (9)$$

The double sum in (9) can be decoupled by interchanging the summations over n and r . The result, utilising the definition (5), is:

$$\sum_{n=1}^{\infty} T_n = \sum_{n=1}^{\infty} \frac{(V^{n+1})_{00}}{\Delta^n} - S \sum_{r=1}^{\infty} \frac{(V^r)_{00}}{\Delta^r}. \quad (10)$$

Adding T_0 to both the sides yields:

$$\begin{aligned} \sum_{n=0}^{\infty} T_n = S = \Delta \sum_{n=0}^{\infty} \langle 0 | V^{n+1} / \Delta^{n+1} | 0 \rangle \\ - S \sum_{r=1}^{\infty} \langle 0 | V^r / \Delta^r | 0 \rangle, \end{aligned} \quad (11)$$

$$\text{or} \quad S = \Delta E = \frac{\Delta \sum_{n=0}^{\infty} \langle 0 | V^{n+1} / \Delta^{n+1} | 0 \rangle}{\sum_{r=0}^{\infty} \langle 0 | V^r / \Delta^r | 0 \rangle}. \quad (12)$$

Interchanging** the order of summation and integration in the numerator and the denominator of (12) enables the summation of the geometric series leading to the expression***

$$\Delta E = \frac{\langle 0 | \frac{V}{[1 - (V/\Delta)]} | 0 \rangle}{\langle 0 | \frac{1}{[1 - (V/\Delta)]} | 0 \rangle}. \quad (13)$$

*For a wide class of perturbations, the matrix elements of $(V)^r$ for arbitrary r may become divergent; for the coulomb potential, for example, all integrals with $r \geq 3$ are infinite. The formal expressions of the type $(V^r)_{nm}$ are therefore to be understood in a regularised form, viz.

$$\int_{\epsilon}^{\infty} \int \phi_n^* V^r \phi_m \rho^2 d\rho d\Omega$$

where ϵ is a small positive quantity. This regularisation is reminiscent of the 'ultraviolet cut-off' in higher order perturbations in quantum electrodynamics. Since we are interested in only the sum of the perturbation series, we can define all such integrals with a cut-off ϵ , perform the sum, and then let $\epsilon \rightarrow 0$.

**Such interchanges are assumed to be permissible since all the integrals are defined with a cut-off.

***In equation (13), isolated singularities exist in the integrand at $V = \Delta$. Some of these singularities fall on the path of integration for 'attractive' perturbations since Δ is negative. However, the integrals in (13) can always be defined by a suitable analytic continuation in the variable Δ .

The perturbation series for the wave function can be handled in exactly the same manner. It yields for (unnormalised) the result*

$$|\psi\rangle = \frac{1}{[1 - (V/\Delta)]} |0\rangle. \quad (14)$$

3. Discussion

We briefly discuss now the implications of formulae (13) and (14) taking the ground state of helium-like atoms as an example. If H_0 and V are defined as

$$H_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \quad (15)$$

$$V = 1/r_{12}, \quad (16)$$

then the energy shift ΔE according to (13) becomes

$$\Delta E = \frac{\langle 0 | \frac{1}{r_{12} + a} | 0 \rangle}{\langle 0 | \frac{r_{12}}{r_{12} + a} | 0 \rangle}, \quad (17)$$

where $a = -1/\Delta$; \mathbf{a} , by definition, being a negative quantity. The interesting feature of the above equation is that it expresses the energy shift entirely in terms of the ground state wave function provided the coulomb repulsion $1/r_{12}$ is replaced by an effective interaction $1/(r_{12} + a)$. Since ΔE is not bounded, the parameter a cannot be obtained variationally; it has to be chosen to fit the data. Preliminary calculations (Jolly *et al* 1979) show that it is possible to achieve a satisfactory agreement for the energy shift values for ten members of the helium isoelectronic sequence in terms of a single free parameter. The question whether a break-up of the helium Hamiltonian different from that employed in (15) and (16) is more convenient or not as well as the question whether the form for the effective interaction can be retained even in three- and more electron system, needs further investigation.

We next turn to the matter of functional form of the trial function for the ground state. Equations (14) to (16) yield

$$\psi = \frac{r_{12}}{r_{12} + a} \exp[-Z(r_1 + r_2)], \quad (18)$$

*We note in passing that if one starts with the original Brillouin-Wigner series (i.e. the series without the mean excitation energy assumption) for the n th order perturbed wave function $|\phi^n\rangle$ in the form

$$|\phi^n\rangle = (XPV)^n |0\rangle,$$

where

$$X = 1/E - H_0; \quad P = \sum_{m \neq 0} |m\rangle \langle m| = 1 - Q = 1 - |0\rangle \langle 0|,$$

then

$$|\phi^n\rangle = (XPV)^{n-1} XV |0\rangle - \phi^{n-1} \langle 0 | XV | 0 \rangle,$$

where the commutability of Q and X has been utilised. Following steps similar to those given above, one obtains the Lippmann-Schwinger equation in place of (14).

where a and Z are the variational parameters. It is interesting to compare the above form with the best two-parameter function (Hylleraas 1928) for helium namely

$$\psi = (1 + br_{12}) \exp [-Z(r_1 + r_2)]. \quad (19)$$

It is obvious that a properly correlated wave function should become independent of r_{12} as $r_{12} \rightarrow \infty$, to ensure the progressive decoupling of electrons as the inter-electron separation increases. Equation (18) satisfies this requirement nicely but the Hylleraas function fails to do so. However, (18) is an exceedingly poor function for small r_{12} . For example, the cusp condition (Roothan and Weiss 1960) which is an important restriction on a helium wave function, is badly violated by (18) but comparatively well satisfied by the Hylleraas function for which $b=0.364$, at the energy minimum. Thus, in spite of its proper form for large r_{12} , (18) is a poorer wave function than (19) in its overall behaviour.

It is reasonable to attribute the inadequacies of (18) to the crudeness of the closure approximation. To overcome the shortcomings of this approximation, we now take recourse to some empiricism. The crucial requirement for the summation procedure to be valid—and hence equation (14) to hold good—is the assumption that Δ is independent of the quantum numbers defining the unperturbed states. However, a constant Δ is not the only way to meet this requirement. All the steps leading to (14) remain valid if Δ is postulated to be some function of the variables r_1 , r_2 and r_{12} . Such an approximation may be termed as the ‘local energy gap’ approximation. To begin with we ignore the dependence on r_1 and r_2 and invoke only the dependence on r_{12} . The fact that (18) based on constant Δ is satisfactory for large r_{12} suggests inverse relationship between Δ and r_{12}^n . The simplest possibility of this type is to assume that

$$\Delta = \alpha + \beta/r_{12}, \quad (20)$$

where α and β are constants. Introducing (20) into (14) yields:

$$\psi = \frac{1 + a_1 r_{12}}{1 + a_2 r_{12}} \exp [(-Z)(r_1 + r_2)]. \quad (21)$$

The cusp condition imposes a restriction on the relative values of a_1 and a_2 and therefore, (21) is effectively a two-parameter function. This function has a satisfactory behaviour for both small and large r_{12} in contrast to the Hylleraas function which is satisfactory only for small r_{12} .

The pre-exponential factor in (21) can be recognised as a [1, 1] Padé type (Baker 1965) function in the variable r_{12} . In view of the known superiority of Padé approximants over the power series expansion as a representation for a function of a single variable, the incorporation of rational functions of the Padé type in trial functions is a promising possibility which is being explored at present.

To summarise, the primary purpose of this work was to investigate the infinite-order perturbation theory based on the mean excitation energy approximation. A secondary purpose was to qualitatively evaluate the expressions obtained for the energy shift and the trial function. Variational calculations using the wave functions suggested by this work are in progress and their results will be reported in due course.

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