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Explicit Formulas for the Nth-Order Wavefunction and Energy in Nondegenerate Rayleigh–Schrödinger Perturbation Theory*

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The wavefunction and energy in nth order of Rayleigh–Schrödinger perturbation theory are shown to be given by

$$E_n=\sum_{\sigma_1,\sigma_2,\cdots,\sigma_n;\ (\sigma_1+2\sigma_2+\cdots+n\sigma_n=n;\ \sigma_i\geq 0, i=1,2,\cdots,n)}(\sigma_1!\sigma_2!\cdots\sigma_n!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\times\langle V(a^{-1}V)^{n-1}\rangle^{\sigma_n},$$

$$\chi_n=(a^{-1}V)^n\,|\,0\rangle+\sum_{j=1}^{n-1}\sum_{(\sigma_1+2\sigma_2+\cdots=n-j;\ \sigma_i\geq 0, i=1,2,\cdots)}(\sigma_1!\sigma_2!\cdots)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\times\langle V(a^{-1}V)^{n-j-1}\rangle^{\sigma_{n-1}}(d/dE_0)(a^{-1}V)^j\,|\,0\rangle.$$

Here $|\,0\rangle$ is the unperturbed eigenfunction of H_0 with energy E_0, V is the perturbation, $\langle V\cdots V\rangle$ denotes $\langle 0\,|\,V\cdots V\,|\,0\rangle$, and a^{-1} is $(1-|\,0\rangle\langle 0\,|)(E_0-H_0)^{-1}(1-|\,0\rangle\langle 0\,|)$. The wavefunction is given in the so-called "intermediate normalization." Partial summations of these formulas give exactly the wavefunction and energy in Brillouin–Wigner perturbation theory.

I. INTRODUCTION

Explicit formulas for the energy and wavefunction in Rayleigh Schrödinger perturbation theory have been known for many years.[1–5] Although elegant, the known formulas[1–5] have redundancies (equal terms occurring more than once) and involve nontrivial bookkeeping. The purpose of this paper is to derive more concise formulas with minimal bookkeeping. In addition, the new formulas are used to express the energy and wavefunction to the nth order of Brillouin–Wigner perturbation theory *explicitly* as partial summations of the Rayleigh–Schrödinger series.

Section II contains a statement of Rayleigh–Schrödinger perturbation theory and a comparison of various explicit formal solutions. The new formulas are derived in Sec. III, and the connection with Brillouin–Wigner perturbation theory is shown in Sec. IV.

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[1] T. Kato, Progr. Theoret. Phys. (Kyoto) **4**, 514 (1949).

[2] C. Bloch, Nucl. Phys. **6**, 329 (1958).

[3] R. Huby, Proc. Phys. Soc. (London) **78**, 529 (1961).

[4] K. A. Brueckner, Phys. Rev. **100**, 36 (1955).

[5] (a) T. T. Holloway and J. E. Kilpatrick, "High Order Nondegenerate Perturbation" (to be published). (b) We note in passing that Eq. (21) can be obtained from Eq. (22) as follows: (1) Take all distinct orders for the $(\Sigma\sigma_i)$ factors and multiply by $\Pi(\sigma_i!)/(\Sigma\sigma_i)!$ (the reciprocal of the number of distinct permutations). (2) Replace each $\cdots V\rangle\langle V\cdots$ by $\cdots V(-S^0)V\cdots$. (3) note that

$$[(\Sigma\sigma_i)!]^{-1}(-d/dE_0)^{\Sigma\sigma_i-1}\cdots a^{-1}\cdots a^{-1}\cdots\cdots a^{-1}\cdots=(\Sigma\sigma_i)^{-1}\sum_{(m_1+m_2+\cdots+m_l=n-1;\ m_i\geq 1, i=1,2,\cdots,l)}\cdots S^{m_1}\cdots\times S^{m_2}\cdots\cdots S^{m_l}\cdots.$$

II. RAYLEIGH–SCHRÖDINGER PERTURBATION THEORY

Consider a Hamiltonian H, which is the sum of an unperturbed Hamiltonian H_0 and a perturbation V,

$$H=H_0+V. \tag{1}$$

Let Ψ denote a nondegenerate eigenfunction of H with energy E,

$$(H-E)\Psi=0. \tag{2}$$

Develop Ψ and E in power series in the strength of V,

$$\Psi=|\,0\rangle+\chi_1+\chi_2+\cdots, \tag{3}$$

$$E=E_0+E_1+E_2+\cdots, \tag{4}$$

where

$$(H_0-E_0)\,|\,0\rangle=0, \tag{5}$$

and where $|\,0\rangle$ and Ψ are normalized according to

$$\langle 0\,|\,0\rangle=1, \tag{6}$$

$$=\langle 0\,|\,\Psi\rangle, \tag{7}$$

$$\langle 0\,|\,\chi_i\rangle=0,\qquad (i=1,2,\cdots). \tag{8}$$

The standard textbook approach[6] to solving Eqs. (2)–(8) is to find E_n and χ_n recursively:

$$\chi_1=a^{-1}V\,|\,0\rangle, \tag{9}$$

$$\chi_n=a^{-1}V\chi_{n-1}-\sum_{k=1}^{n-1}E_ka^{-1}\chi_{n-k}, \tag{10}$$

$$E_1=\langle 0\,|\,V\,|\,0\rangle, \tag{11}$$

$$E_n=\langle 0\,|\,V\,|\,\chi_{n-1}\rangle. \tag{12}$$

[6] See, for example, A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1965), Vol. 2, p. 688.

Here a^{-1} denotes the reduced resolvent,

$$a^{-1}=(1-|0\rangle\langle 0|)(E_0-H_0)^{-1}(1-|0\rangle\langle 0|). \quad (13)$$

A. Various Explicit Formal Solutions

The first explicit formulas for E_n and χ_n, not involving lower-order E_m and χ_m, were derived by Kato.[1] Let S^0 and S^k be defined by

$$S^0=-|0\rangle\langle 0|, \quad (14)$$

$$S^k=a^{-k}, \qquad (k\geq 1). \quad (15)$$

Then Kato's formula[7] is

$$E_n=\sum_{\substack{(k_1+k_2+\cdots+k_{n+1}=n-1;\\ k_i\geq 0, i=1,2,\cdots,n+1)}} \mathrm{Tr}\{S^{k_1}VS^{k_2}V\cdots VS^{k_{n+1}}\}. \quad (16)$$

Bloch[2] obtained similar formulas having fewer terms but requiring more elaborate bookkeeping:

$$E_n=\sum_{\substack{(k_1+k_2+\cdots+k_{n-1}=n-1;\\ k_1+k_2+\cdots+k_p\geq p, p<n-1;\\ k_i\geq 0, i=1,2,\cdots,n-1)}} \langle 0|VS^{k_1}VS^{k_2}V\cdots S^{k_{n-1}}V|0\rangle, \quad (17)$$

$$\chi_{n-1}=\sum_{\substack{[\text{same qualification}\\ \text{as for Eq. (17)}]}} S^{k_1}VS^{k_2}V\cdots S^{k_{n-1}}V|0\rangle. \quad (18)$$

A superficially different set of formulas in a form suggested by Brueckner[4] were derived from Bloch's formulas by Huby[3] (to whose paper the reader is referred for the complete prescription):

$$E_n=\langle V(a^{-1}V)^{n-1}\rangle-\langle Va^{-1}\langle V\rangle(a^{-1}V)^{n-2}\rangle - \langle Va^{-1}Va^{-1}\langle V\rangle(a^{-1}V)^{n-3}\rangle-+\cdots, \quad (19)$$

$$\chi_n=(a^{-1}V)^n|0\rangle-a^{-1}\langle V\rangle(a^{-1}V)^{n-1}|0\rangle - a^{-1}Va^{-1}\langle V\rangle(a^{-1}V)^{n-2}|0\rangle-+\cdots. \quad (20)$$

A formula, similar to Kato's and Bloch's for E_n, has been suggested[5a] (without proof[5b]):

$$E_n=\sum_{(k_1+k_2+\cdots+k_{n-1}=n-1;\, k_i\geq 0, i=1,2,\cdots n-1)} (1+\text{no. of zero } k_i)^{-1}\langle VS^{k_1}VS^{k_2}V\cdots S^{k_{n-1}}V\rangle. \quad (21)$$

In addition, there are two diagrammatic methods, one[8] based on the application of Goldstone[9] diagrammology to a one-particle state, the other[10] being a more heuristic recipe.

The new formulas derived here are

$$E_n=\sum_{(\sigma_1+2\sigma_2+\cdots+n\sigma_n=n;\ \sigma_i\geq 0, i=1,2,\cdots,n)} (\sigma_1!\sigma_2!\cdots\sigma_n!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\langle V(a^{-1}V)^{n-1}\rangle^{\sigma_n}, \quad (22)$$

$$\chi_n=(a^{-1}V)^n|0\rangle+\sum_{j=1}^{n-1}\sum_{(\sigma_1+2\sigma_2+\cdots=n-j;\,\sigma_i\geq 0, i=1,2,\cdots)} (\sigma_1!\sigma_2!\cdots\sigma_{n-j}!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1} \times\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\langle V(a^{-1}V)^{n-j-1}\rangle^{\sigma_{n-j}}(d/dE_0)(a^{-1}V)^j|0\rangle, \qquad (n=1,2,\cdots). \quad (23)$$

Only a^{-1} depends explicitly on E_0, and the (d/dE_0) are evaluated via

$$(d/dE_0)a^{-k}=-ka^{-k-1}. \quad (24)$$

B. Comparison of Explicit Formulas

Note that all the explicit formulas except Eqs. (19) and (20) involve partitioning an integer into a sum of nonnegative integers.

The numbers of terms in Eqs. (16) and (17) have been determined by Bloch[2]. Equation (16) (Kato) has the largest number of terms, $(2n)![n!(n-1)!]^{-1}$. Equation (17) (Bloch) has $(2n-2)![n!(n-1)!]^{-1}$, which is a reduction by a factor of $2n(2n-1)$. [Equation (19) (Huby–Brueckner) has the same number of terms[3] as Eq. (17).] The number of terms in Eq. (21) can be shown to be $(2n-3)![(n-1)!(n-2)!]^{-1}$, which is reduction from Eq. (16) by a factor $4(2n-1)$, but an increase over Eq. (17) by $n/2$. On the other hand, the bookkeeping for Eq. (17) is more complicated than for Eqs. (16) and (21), which have a similar restrictions on the k_i.

The number of terms in Eq. (22) is one less than the number of partitions of n into positive integers (for $n\geq 2$). This number is far less than for any of the other formulas, but is also misleading because the derivatives, when taken explicitly, increase the number of terms. Nevertheless, even allowing for the differentiations, the ordered structure of Eq. (22) must result in the least redundancy. The bookkeeping for the σ_i in Eq. (22) is simpler than for Eqs. (16) and (21), because the partitions of n are ordered.

Similar comments can be made for the χ_n formulas.

[7] Here only the formula for E_n is given. Kato's Ψ is not normalized the same way as ours.
[8] B. H. Brandow, Rev. Mod. Phys. **39**, 771 (1967).
[9] J. Goldstone, Proc. Phys. Soc. (London) **A239**, 267 (1957).
[10] W. R. Salzman, J. Chem. Phys. **49**, 3035 (1968).

III. DERIVATION

Originally we obtained Eqs. (22) and (23) by a diagrammatic method,[8,9] the essence being to sum all diagrams with identical numerators. However, the approach described below, which is based on complex variable theory, is more concise. Briefly, we sum Eqs. (22) and (23) over n and show that the result is E and Ψ.

In what follows, we use the Taylor series,

$$\sum_{j=1}^{\infty} x^j = x(1-x)^{-1}, \tag{25}$$

$$\sum_{j=1}^{\infty} j^{-1}x^j = -\log(1-x), \tag{26}$$

and the residue theorem, especially in the context

$$[(m-1)!]^{-1}(d/dE_0)^{m-1}F(E_0) = (2\pi i)^{-1}\oint^{(0+)} dz\, z^{-m}F(z+E_0). \tag{27}$$

We also use

$$(x_1+x_2+\cdots)^m = \sum_{\sigma_1\geq 0,\sigma_2\geq 0,\cdots;\ (\sigma_1+\sigma_2+\cdots=m)} m!\prod(\sigma_i!)^{-1}x_1^{\sigma_1}x_2^{\sigma_2}\cdots, \tag{28}$$

and define

$$a_z^{-1} = (1-|0\rangle\langle 0|)(E_0+z-H_0)^{-1}(1-|0\rangle\langle 0|). \tag{29}$$

We take Eqs. (22) and (23), sum over n ($=1, 2, \cdots, \infty$), and use Eqs. (25)–(29) to obtain

$$\text{“}E-E_0\text{”} \equiv \sum_{n=1}^{\infty} E_n[\text{Eq. (22)}],$$

$$= \sum_{\sigma_1\geq 0,\sigma_2\geq 0,\cdots;\ (\sigma_1+\sigma_2+\cdots\geq 1)} \prod(\sigma_i!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots, \tag{30}$$

$$= -(2\pi i)^{-1}\oint_\Gamma dz\log[1-z^{-1}\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle], \tag{31}$$

$$\text{“}\Psi-|0\rangle\text{”} \equiv \sum_{n=1}^{\infty}\chi_n\,[\text{Eq. (23)}],$$

$$= (2\pi i)^{-1}\oint^{(0+)} dz\, z^{-1}(1-a_z^{-1}V)^{-1}a_z^{-1}V|0\rangle \tag{32}$$

$$-(2\pi i)^{-1}\oint_\Gamma dz\log[1-z^{-1}\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle](d/dz)(1-a_z^{-1}V)^{-1}a_z^{-1}V|0\rangle. \tag{33}$$

We must prove that the quantities placed in quotes have their usual meanings. Much could be said about the legality of the above maneuvers, but a full justification is related to the convergence of the perturbation series, which is indeed a difficult problem. Since we are interested only in a formal result, it suffices to assume that there exists a contour Γ encircling the origin such that

$$z-\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle \tag{34}$$

has only one zero inside Γ, say at y,

$$y-\sum_{n=0}^{\infty}\langle V(a_y^{-1}V)^n\rangle = 0, \tag{35}$$

such that (34) has no singularities inside Γ, and such that

$$|z^{-1}|\sum_{n=0}^{\infty}|\langle V(a_z^{-1}V)^n\rangle| < 1$$

on Γ. Then for the integrands in Eqs. (31) and (33), Γ encloses a logarithmic branch cut running from $z=0$ to $z=y$ (see Fig. 1).

To evaluate Eq. (31), write

$$\text{“}E-E_0\text{”} = -(2\pi i)^{-1}\oint_\Gamma dz\log(1-z^{-1}y)$$

$$-(2\pi i)^{-1}\oint_\Gamma dz$$

$$\times\log\{[z-\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle](z-y)^{-1}\}. \tag{36}$$

The second integral has no singularity inside Γ provided (another assumption!) that

$$\lim_{z\to y}(d/dz)\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle \neq 1. \tag{37}$$

The value of the first integral is just y,

$$\text{“}E-E_0\text{”}=y. \tag{38}$$

But examination reveals that Eq. (35) is the Brillouin–Wigner formula for the energy shift,[11] so that $y=E-E_0$, which with Eqs. (38) and (4) proves the correctness of Eq. (22).

To evaluate "$\Psi-|0\rangle$," we integrate the second term in Eq. (33) by parts, note that one differentiated term cancels the first term in Eq. (33), and obtain

$$\text{“}\Psi-|0\rangle\text{”}=(2\pi i)^{-1}\oint_\Gamma dz\Big[z-\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle\Big]^{-1}\times\Big[1-(d/dz)\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle\Big](1-a_z^{-1}V)^{-1}a_z^{-1}V|0\rangle. \tag{39}$$

The only singularity inside Γ in Eq. (39) is a pole at $z=y$ [again, provided Eq. (37) is satisfied], and since

$$\Big[z-\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle\Big]^{-1}\Big[1-(d/dz)\sum_{n=0}^{\infty}\langle V(a_z^{-1}V)^n\rangle\Big]\sim(z-y)^{-1}\quad\text{as}\quad z\to y, \tag{40}$$

we obtain

$$\text{“}\Psi-|0\rangle\text{”}=(1-a_y^{-1}V)^{-1}a_y^{-1}V|0\rangle. \tag{41}$$

But since y is the solution of Eq. (35), i.e., the energy shift, Eq. (41) is just the Brillouin–Wigner formula for $\Psi-|0\rangle$[11]:

$$\text{“}\Psi-|0\rangle\text{”}=\Psi-|0\rangle, \tag{42}$$

and Eq. (23) for χ_n is thus proved.

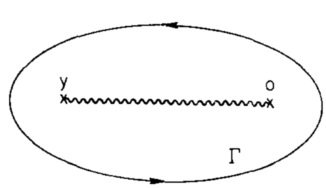

FIG. 1. The contour Γ.

[11] See, for example, N. H. March, W. H. Young, and S. Sampanthar, *The Many-Body Problem in Quantum Mechanics* (Cambridge University Press, London, 1967), p. 18.

IV. CONNECTION BETWEEN RAYLEIGH–SCHRÖDINGER BRILLOUIN–WIGNER EXPANSIONS

The energy shift through Nth-order in Brillouin–Wigner perturbation theory ($\Delta E_{\mathrm{BW}}^{(N)}$) is the root of

$$y=\sum_{n=0}^{N-1}\langle V(a_y^{-1}V)^n\rangle \tag{43}$$

$$=\Delta E_{\mathrm{BW}}^{(N)}, \tag{44}$$

and the corresponding wavefunction is

$$\Psi_{\mathrm{BW}}^{(N)}=|0\rangle+\sum_{n=1}^{N}(a_y^{-1}V)^n|0\rangle,\qquad(y=\Delta E_{\mathrm{BW}}^{(N)}). \tag{45}$$

By only a slight modification of the preceding section [replace

$$\sum_{n=1}^{\infty}\langle V(a_z^{-1}V)^n\rangle\quad\text{and}\quad\sum_{n=1}^{\infty}(a_z^{-1}V)^n|0\rangle$$

by

$$\sum_{n=1}^{N-1}\langle V(a_z^{-1}V)^n\rangle\quad\text{and}\quad\sum_{n=1}^{N}(a_z^{-1}V)^n|0\rangle,$$

respectively], one immediately obtains

$$\Delta E_{\mathrm{BW}}^{(N)}=\sum_{\substack{\sigma_1=0\\(\sigma_1+\sigma_2+\cdots+\sigma_N\geq1)}}^{\infty}\sum_{\sigma_2=0}^{\infty}\cdots\sum_{\sigma_N=0}^{\infty}\prod_{i=1}^{N}(\sigma_i!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\times\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\langle V(a^{-1}V)^{N-1}\rangle^{\sigma_N} \tag{46}$$

and

$$\Psi_{\mathrm{BW}}^{(N)}=|0\rangle+\sum_{j=1}^{N}(a^{-1}V)^j|0\rangle+\sum_{j=1}^{N}\sum_{\substack{\sigma_1=0\\(\sigma_1+\sigma_2+\cdots+\sigma_N\geq1)}}^{\infty}\sum_{\sigma_2=0}^{\infty}\cdots\sum_{\sigma_N=0}^{\infty}\times\prod_{i=1}^{N}(\sigma_i!)^{-1}(d/dE_0)^{\Sigma\sigma_i-1}\langle V\rangle^{\sigma_1}\langle Va^{-1}V\rangle^{\sigma_2}\cdots\times\langle V(a^{-1}V)^{N-1}\rangle^{\sigma_N}(d/dE_0)(a^{-1}V)^j|0\rangle. \tag{47}$$

That is, the Brillouin–Wigner energy and wavefunction to Nth order are obtained from the (infinite) Rayleigh–Schrödinger series [Eqs. (3), (4), (22), and (23)] by omitting all terms with factors $\langle V(a^{-1}V)^{n-1}\rangle$ and $(a^{-1}V)^n|0\rangle$ having $n>N$.

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