Physica 93A (1978) 559–573 © North-Holland Publishing Co.

ON ADIABATIC PERTURBATION THEORY FOR THE ENERGY EIGENVALUE PROBLEM

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Received 28 March 1978

The adiabatic perturbation formalism is used to derive several alternative expressions for the effective Hamiltonian of a discrete energy level. It is shown how in the nondegenerate case these expressions may be cast in the form of linked-cluster expansions. The connection between the energy shifts and the scattering matrix is investigated.

1. Introduction

The most customary method to treat quantum-mechanical energy-eigenvalue problems that cannot be solved exactly is the well-known Rayleigh–Schrödinger perturbation theory. Sometimes, however, it turns out to be more convenient to deal with time-independent problems by means of a time-dependent formalism, and particularly so when the Hamiltonian of the system can be expressed in terms of quantized fields. If such is the case a perturbation theory can be formulated that enables one to make use of the techniques of quantum field theory. This approach lends itself naturally to a diagrammatic representation, which has turned out to be extremely useful in the study of nuclei and molecular systems[1]).

Perturbation theory for the degenerate energy-eigenvalue problem can be formulated in terms of an effective Hamiltonian of which the eigenvalues are the energy shifts. Crucial for the applicability of time-dependent methods is the existence of a relation between this Hamiltonian and the time-evolution operator in the interaction picture. Such a relation can be established in the adiabatic limit, i.e. when the interaction is switched on infinitesimally slowly. In the expressions for the effective Hamiltonian that have been used in the literature, the existence of this limit has until recently hardly been investigated[2,3]). In this paper the adiabatic method will be employed to derive several alternative expressions for the effective Hamiltonian of a degenerate energy level; the existence of the adiabatic limits involved will be examined carefully.

The evaluation of the energy shifts by means of field-theoretical methods may be simplified considerably if the effective Hamiltonian can be expressed in terms of the scattering matrix. For nondegenerate energy levels a connection of this type will be proved with the help of linked-cluster expansions. In addition it will be shown how in special cases such a relation can be obtained for degenerate levels as well.

2. The effective Hamiltonian for degenerate states

In the following we shall study a Hamiltonian H that is a sum of an unperturbed Hamiltonian H_0 and a perturbation term H_1; the latter is linear in a coupling constant λ. Both H_0 and H_1 are time-independent Hermitean operators. We consider a degenerate energy level E_0 in the discrete part of the spectrum of H_0; the corresponding eigenstates span a subspace Ω_0 of the Hilbert space. Let the states $|\psi_\alpha\rangle$ be eigenstates of the total Hamiltonian H, with eigenvalues E_α that reduce to E_0 when λ tends to zero; these states span a subspace Ω, which coincides with Ω_0 for $\lambda = 0$. The projectors onto Ω_0 and Ω will be denoted by P_0 and P, respectively. We shall assume that for any nonzero $|\psi\rangle$ in Ω the projection $P_0|\psi\rangle$ onto Ω_0 does not vanish, which is a reasonable assumption if the perturbation is sufficiently small.

The eigenvalue equation for $|\psi_\alpha\rangle$ can be written as:

$$(H - E_0)|\psi_\alpha\rangle = \Delta E_\alpha |\psi_\alpha\rangle, \tag{1}$$

with $\Delta E_\alpha = E_\alpha - E_0$. Projecting both sides onto Ω_0 we obtain:

$$P_0 H_1 |\psi_\alpha\rangle = \Delta E_\alpha P_0 |\psi_\alpha\rangle. \tag{2}$$

This equation can be reduced to an eigenvalue equation within the subspace Ω_0. In fact, by virtue of the assumption made above one can introduce[4]) a linear operator W that transforms the projected state $P_0|\psi_\alpha\rangle$ back into $|\psi_\alpha\rangle$:

$$|\psi_\alpha\rangle = W P_0 |\psi_\alpha\rangle. \tag{3}$$

Substituting (3) into (2) one gets:

$$P_0 H_1 W P_0 |\psi_\alpha\rangle = \Delta E_\alpha P_0 |\psi_\alpha\rangle, \tag{4}$$

which is an eigenvalue equation within Ω_0. The energy shifts ΔE_α are the eigenvalues of the effective Hamiltonian:

$$V = P_0 H_1 W P_0 \tag{5}$$

or, alternatively:

$$V = P_0P(H - E_0)WP_0. \tag{6}$$

The operator V is not necessarily Hermitean since its eigenstates $P_0|\psi_\alpha\rangle$ in general do not form an orthogonal set.

The operator W defined by (3), and consequently the operator V(5), can be given in terms of P_0 and P[4,5]). In fact, since W transforms Ω_0 into Ω and has as its inverse the transformation P_0P one can write:

$$W = PP_0(P_0PP_0)^{-1}. \tag{7}$$

Here the inverse $(P_0PP_0)^{-1}$ is defined as an operator inside Ω_0. From (5) or (6) with (7) it follows that a perturbation expansion for the effective Hamiltonian V may be obtained by expressing the projector P as a power series in H_1. This will be achieved in the following section.

3. Adiabatic perturbation theory

In adiabatic perturbation theory the interaction H_1 is switched on by adding a factor $\exp(-\varepsilon|t|)$; if the interaction representation is chosen the total Hamiltonian then reads:

$$H_\varepsilon(t) = H_0 + H_{1\varepsilon}(t) = H_0 + e^{-\varepsilon|t|}\, e^{iH_0t}\, H_1\, e^{-iH_0t}. \tag{8}$$

The time dependence of the states describing the system is determined by the unitary time-evolution operator $U_\varepsilon(t, t')$ defined as:

$$|\psi_\varepsilon(t)\rangle = U_\varepsilon(t, t')|\psi_\varepsilon(t')\rangle. \tag{9}$$

Its properties are discussed in the appendix. According to (9) the operator:

$$U_\varepsilon(0, -\infty)P_0U_\varepsilon(-\infty, 0) \tag{10}$$

is the projector on the space to which the unperturbed space Ω_0 develops in the time interval $(-\infty, 0)$. For finite ε this space will not coincide with the space Ω of eigenstates of the Hamiltonian $H_\varepsilon(0) = H$. However, in the limit $\varepsilon \to 0$ the perturbation is switched on adiabatically and indeed the projector (10) then becomes equal to P, as has been proved recently by Dmitriev[3]). In fact, the formula (A.8) may be employed to write (10) as:

$$U_\varepsilon(0, -\infty)P_0U_\varepsilon(-\infty, 0) = \frac{1}{2\pi i}\oint_C dz\, G_\varepsilon(z) \tag{11}$$

with:

$$G_\varepsilon(z) = \frac{1}{z - H_0} \sum_{n=0}^{\infty} \prod_{k=1}^{n} \left(H_1 \frac{1}{z - H_0 - \mathrm{i}k\varepsilon} \right), \tag{12}$$

while the contour C encircles all poles having $\operatorname{Re} z = E_0$. When the limit $\varepsilon \to 0$ is taken the series (12) can be summed with the result $(z - H)^{-1}$. If in addition the contour C is modified so as to enclose the shifted pole at $z = E$ the limit of the right-hand side of (11) is found to be the projector P:

$$P = \lim_{\varepsilon \to 0} U_\varepsilon(0, -\infty) P_0 U_\varepsilon(-\infty, 0). \tag{13}$$

Likewise one may prove an expression for P with $-\infty$ replaced by ∞. Combining the two and using $P = P^2$ one gets:

$$P = \lim_{\varepsilon \to 0} U_\varepsilon(0, -\infty) P_0 U_\varepsilon(-\infty, \infty) P_0 U_\varepsilon(\infty, 0). \tag{14}$$

A third expression for this projector follows from the identity $P = PP_0(P_0PP_0)^{-1}P_0P$ by substituting (13) and the Hermitean conjugate of (14):

$$P = \lim_{\varepsilon \to 0} U_\varepsilon(0, -\infty) P_0 [P_0 U_\varepsilon(\infty, -\infty) P_0]^{-1} P_0 U_\varepsilon(\infty, 0). \tag{15}$$

The above expressions relate the projector P to the time-evolution operator U_ε and may be employed to derive from (5)–(7) adiabatic formulae for the effective Hamiltonian V and the operator W.

Upon insertion of (13) into (7) one finds:

$$W = \lim_{\varepsilon \to 0} U_\varepsilon(0, -\infty) P_0 [P_0 U_\varepsilon(0, -\infty) P_0]^{-1}. \tag{16}$$

This entails for the operator (5):

$$V = \lim_{\varepsilon \to 0} P_0 H_1 U_\varepsilon(0, -\infty) P_0 [P_0 U_\varepsilon(0, -\infty) P_0]^{-1}. \tag{17}$$

These expressions, which are generalizations to the degenerate case of the so-called "adiabatic formulae" of Gell-Mann and Low[6]), have been given earlier by several authors[2,3,7–10]). To our knowledge the first to prove the existence of the adiabatic limits involved is Bulaevskii; his treatment is less elegant, however, than that of Dmitriev. It should be noted that in ref. 8 the nondegenerate counterpart of (16), as given by Gell-Mann and Low, is assumed to hold in the same form for degenerate states as well; yet by an erroneous reasoning the correct operator (16) is obtained there.

An alternative expression for V is found by starting from (6) instead of (5) and substituting (13) and (16):

$$V = \lim_{\varepsilon \to 0} T_\varepsilon P_0 U_\varepsilon(-\infty, 0)(H - E_0) U_\varepsilon(0, -\infty) P_0 T_\varepsilon^{-1}. \tag{18}$$

Here we introduced the abbreviation:

$$T_\varepsilon = P_0 U_\varepsilon(0, -\infty) P_0. \tag{19}$$

The form (18) shows explicitly that the non-Hermitean effective Hamiltonian can have real eigenvalues only.

The denominator in (16) and (17) is the sum of a zeroth-order term P_0 and a contribution that vanishes for $\lambda \to 0$. Hence the series expansion of the function $(1+x)^{-1}$ in powers of x can be applied to the operator $[P_0 U_\varepsilon(0, -\infty) P_0]^{-1}$. Then V becomes:

$$V = \lim_{\varepsilon \to 0} P_0 H_1 U_\varepsilon(0, -\infty) P_0 \left\{ P_0 + \sum_{k=1}^{\infty} (-1)^k [P_0 U_\varepsilon(0, -\infty) P_0 - P_0]^k \right\}. \tag{20}$$

The important feature of this result is the way in which the effective Hamiltonian may be obtained now as a function of the perturbation H_1. In the factor between square brackets the perturbation occurs only through the operator $U_\varepsilon(0, -\infty)$. According to (A.5) the latter can be expressed by means of time-ordered products of $H_{1\varepsilon}(t)$ as:

$$U_\varepsilon(0, -\infty) = \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{0} \mathrm{d}t_1 \dots \mathrm{d}t_n \, T[H_{1\varepsilon}(t_1) \dots H_{1\varepsilon}(t_n)]. \tag{21}$$

In the remaining part of (20) we may write:

$$H_1 U_\varepsilon(0, -\infty) = \int_{-\infty}^{\infty} \mathrm{d}t_0 \, \delta(t_0) H_{1\varepsilon}(t_0) U_\varepsilon(t_0, -\infty). \tag{22}$$

Upon substituting (A.5) and symmetrizing between t_0 and the other time variables we get:

$$H_1 U_\varepsilon(0, -\infty) = \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{\infty} \mathrm{d}t_1 \dots \mathrm{d}t_n \, \mathrm{i}\delta(t_{\max}) T[H_{1\varepsilon}(t_1) \dots H_{1\varepsilon}(t_n)], \tag{23}$$

with $t_{\max} = \max(t_1, \dots, t_n)$. In this way the first factor of (20) is now also expressed by means of time-ordered products of $H_{1\varepsilon}(t)$ only. As a result the perturbation theory for degenerate energy levels is formulated entirely in terms of time-ordered products of the perturbation. If the Hamiltonian H_0 of the unperturbed system and the perturbation H_1 can be described by quantum field theory the ensuing time-ordered products of field operators may be dealt with in the usual way by applying Wick's theorem. In this way one obtains an expansion for the effective Hamiltonian in terms of Feynman diagrams.

The expression (20) with (21) can be written more concisely as:

$$V = \lim_{\varepsilon\to 0} \sum_{n=0}^{\infty} (-\mathrm{i})^n \int_{-\infty}^{0} \mathrm{d}t_1 \ldots \mathrm{d}t_n\, P_0 H_{1\varepsilon}(0)$$
$$\times \{\theta(-t_1) - P_0\} H_{1\varepsilon}(t_1) \{\theta(t_1 - t_2) - P_0\} \ldots H_{1\varepsilon}(t_n) P_0. \tag{24}$$

Starting from this formula an alternative expansion of V may be found which makes uses of a folded version of Feynman diagrams; this approach is a generalization of the folded-diagram techniques used in many-body theory[7,9,10]) and will be discussed in a subsequent paper[11]). In addition the form (24) of the effective Hamiltonian is particularly suited to establish the connection between the adiabatic and the standard time-independent perturbation theories[4,11,12]).

4. Alternative expressions for the effective Hamiltonian

In the preceding section the effective Hamiltonian V for a degenerate energy level has been written in a form that permits the use of field-theoretical methods. We want to present now a number of alternative expressions for V with this same property; some of these are generalizations of formulae given previously in the literature.

Let us start with (A.4). Choosing $(t, t') = (0, \pm\infty)$ so that $H_\varepsilon(t) = H$ and $H_\varepsilon(t') = H_0$ we get the well-known relation of Gell-Mann and Low[6]):

$$HU_\varepsilon(0, \pm\infty) - U_\varepsilon(0, \pm\infty)H_0 = \mp \mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} U_\varepsilon(0, \pm\infty). \tag{25}$$

If it is multiplied on both sides by P_0 the effective Hamiltonian (17) may be cast into the form:

$$V = \lim_{\varepsilon\to 0} \left[\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} P_0 U_\varepsilon(0, -\infty) P_0\right] [P_0 U_\varepsilon(0, -\infty) P_0]^{-1} \tag{26}$$

(cf. refs. 3, 8); in the nondegenerate case it reduces to a formula for ΔE that is generally attributed to Gell-Mann and Low. Analogously one finds from (18) and (25):

$$V = \lim_{\varepsilon\to 0} T_\varepsilon P_0 U_\varepsilon(-\infty, 0) \left[\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} U_\varepsilon(0, -\infty)\right] P_0 T_\varepsilon^{-1}. \tag{27}$$

From this expression it can be shown that the effective Hamiltonian has an alternative series expansion, with retarded commutators instead of chronological products; in fact (A.10) and (A.11) yield immediately:

$$V = \lim_{\varepsilon\to 0} T_\varepsilon P_0 \sum_{n=1}^{\infty} (-\mathrm{i})^{n-1}\varepsilon \int_{-\infty}^{0} \mathrm{d}t_1 \int_{-\infty}^{t_1} \mathrm{d}t_2 \dots \int_{-\infty}^{t_{n-1}} \mathrm{d}t_n$$
$$\times [\dots [H_{1\varepsilon}(t_1), H_{1\varepsilon}(t_2)], \dots H_{1\varepsilon}(t_n)] P_0 T_\varepsilon^{-1}. \tag{28}$$

Expansions of this type have been used before in quantum field theory in order to study the connection between operators in the Heisenberg and in the interaction representation[13]).

The formulae (26) and (27) are asymmetric in the time variables. A more symmetrical result can be obtained by employing the symmetrized form of (25), viz

$$U_\varepsilon(\infty, 0) H U_\varepsilon(0, -\infty) - \tfrac{1}{2}\{U_\varepsilon(\infty, -\infty), H_0\} = \tfrac{1}{2}\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} U_\varepsilon(\infty, -\infty). \tag{29}$$

If (15) and (16) are substituted in (6) an expression for V arises in which the left-hand side of (29) may be recognized. As a consequence we find for the effective Hamiltonian:

$$V = \lim_{\varepsilon\to 0} T_\varepsilon [P_0 U_\varepsilon(\infty, -\infty) P_0]^{-1} \left[\tfrac{1}{2}\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} U_\varepsilon(\infty, -\infty)\right] P_0 T_\varepsilon^{-1}. \tag{30}$$

A related formula, with the inverse of $P_0 U_\varepsilon(\infty, -\infty) P_0$ replaced by its Hermitean conjugate, follows by using (14) instead of (15).

In the special case of a nondegenerate level (30) reduces to the expression for the energy shift ΔE that has been obtained by Sucher along different lines[14]). It may be remarked that his derivation relied upon the interchange of two adiabatic limits; this difficulty has been circumvented in the present treatment.

In the literature the energy shift for a nondegenerate level is sometimes written as an integral of the expectation value of H_1 with respect to the coupling constant λ. Indeed, since $\lambda\, \mathrm{d}H/\mathrm{d}\lambda$ equals H_1, differentiation of the eigenvalue equation gives:

$$\langle\psi|\psi\rangle \lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} \Delta E = \langle\psi|H_1|\psi\rangle \tag{31}$$

and hence:

$$\Delta E = \int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} \frac{\langle\psi|H_1|\psi\rangle}{\langle\psi|\psi\rangle}. \tag{32}$$

This result is believed to be due to Pauli[15]). Within the framework of adiabatic perturbation theory such formulae may also be derived for the effective Hamiltonian V. From the Gell-Mann–Low identity (25) one gets:

$$\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda}[P_0 U_\varepsilon(-\infty, 0)(H - E_0) U_\varepsilon(0, -\infty) P_0] = P_0 U_\varepsilon(-\infty, 0) H_1 U_\varepsilon(0, -\infty) P_0. \tag{33}$$

Integration and insertion into (18) then yields:

$$V = \lim_{\varepsilon \to 0} T_\varepsilon \left[\int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} P_0 U_\varepsilon(-\infty, 0) H_1 U_\varepsilon(0, -\infty) P_0 \right] T_\varepsilon^{-1}. \tag{34}$$

For the nondegenerate case (34) is equivalent to Pauli's formula (32), as follows by using the adiabatic expression (13) for the projector $|\psi\rangle\langle\psi|\psi\rangle^{-1}\langle\psi|$. It should be remarked that in contrast to the generalizations (26) and (30) of the Gell-Mann–Low and Sucher expressions, the present form of V in terms of H_1 does not contain an explicit factor ε, so that the adiabatic limit becomes more manageable.

So far we have studied the full effective Hamiltonian V. If only the average $\overline{\Delta E}$ of the energy shifts for a degenerate level is of interest we may limit ourselves to a discussion of the trace $\mathrm{Tr}\, V = \overline{\Delta E}\, \mathrm{Tr}\, P_0$. In that case the similarity transformations T_ε (19) occurring in some of the above results drop out. In particular (34) then becomes:

$$\mathrm{Tr}\, V = \lim_{\varepsilon \to 0} \int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} \mathrm{Tr}[P_0 U_\varepsilon(-\infty, 0) H_1 U_\varepsilon(0, -\infty) P_0], \tag{35}$$

or, with (13):

$$\mathrm{Tr}\, V = \int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} \mathrm{Tr}(H_1 P). \tag{36}$$

In the latter formula the adiabatic limit no longer occurs; indeed an alternative proof analogous to that of (32) may be given. Once the expression (36) has been established any of the forms (13)–(15) for the projector P can be inserted. With (15) we get for instance:

$$\mathrm{Tr}\, V = \lim_{\varepsilon \to 0} \int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'} \mathrm{Tr}\{[P_0 U_\varepsilon(\infty, -\infty) P_0]^{-1} P_0 U_\varepsilon(\infty, 0) H_1 U_\varepsilon(0, -\infty) P_0\}. \tag{37}$$

If (14) had been used the inverse operator in the integrand would have been replaced by the Hermitean conjugate. The close resemblance of the latter formulae with (35) suggests that these would have straightforward generalizations similar to (34) as well; however, in these cases the adiabatic limit does not exist, as is seen already in third-order perturbation theory.

5. Connected-diagram expansions and the relation with the S matrix

In the previous section general expressions for the effective Hamiltonian V have been derived, which can be developed in terms of time-ordered products of the interaction Hamiltonian H_1. If the latter is a product of field operators Wick's theorem may be used to arrive at an expansion of V in Feynman diagrams.

For the nondegenerate case it is possible to choose the unperturbed state $|\psi_0\rangle$ as the vacuum state and to use it as a starting point for the second-quantization formalism. Then the numerator of (17), with (21) inserted, may be factorized in the familiar way[16]):

$$\langle\psi_0|H_1 U_\varepsilon(0,-\infty)|\psi_0\rangle = \sum_{n=0}^{\infty}\sum_{m=0}^{n}\frac{(-i)^n}{n!}\binom{n}{m}$$
$$\times\int_{-\infty}^{0} dt_1\dots dt_n\,\langle\psi_0|T[H_{1\varepsilon}(0)H_{1\varepsilon}(t_1)\dots H_{1\varepsilon}(t_m)]|\psi_0\rangle_c$$
$$\times\langle\psi_0|T[H_{1\varepsilon}(t_{m+1})\dots H_{1\varepsilon}(t_n)]|\psi_0\rangle. \tag{38}$$

Here the subscript c denotes the part of the matrix element that is represented by the set of all connected Feynman diagrams. By taking m and $n-m$ as summation variables the two sums in (38) may be carried out independently, with the result:

$$\langle\psi_0|H_1 U_\varepsilon(0,-\infty)|\psi_0\rangle = \langle\psi_0|H_1 U_\varepsilon(0,-\infty)|\psi_0\rangle_c\langle\psi_0|U_\varepsilon(0,-\infty)|\psi_0\rangle. \tag{39}$$

As a consequence (17) becomes in the nondegenerate case:

$$\Delta E = \lim_{\varepsilon\to 0}\langle\psi_0|H_1 U_\varepsilon(0,-\infty)|\psi_0\rangle_c, \tag{40}$$

which is an example of a connected-diagram expansion for the energy shift.

In the following it will be shown that the expressions (26), (30) and (37) also lead to connected-diagram expansions in the nondegenerate case. The expectation value of the time-evolution operator can be factorized by means of a similar argument as used above; thus one finds:

$$\langle\psi_0|U_\varepsilon(t,t')|\psi_0\rangle = \exp[\langle\psi_0|U_\varepsilon(t,t')|\psi_0\rangle_c]. \tag{41}$$

With the help of this relation the nondegenerate versions of (26) and (30) become:

$$\Delta E = \lim_{\varepsilon\to 0} \mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_0|U_\varepsilon(0,-\infty)|\psi_0\rangle_c \tag{42}$$

and

$$\Delta E = \lim_{\varepsilon\to 0} \tfrac{1}{2}\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda}\langle\psi_0|U_\varepsilon(\infty,-\infty)|\psi_0\rangle_c, \tag{43}$$

respectively. To factorize the numerator in (37) we first write:

$$\begin{aligned} &U_\varepsilon(\infty,0)H_1U_\varepsilon(0,-\infty) \\ &\quad= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-\mathrm{i})^{m+n}}{m!n!}\binom{m+n}{m}^{-1}\int_{-\infty}^{\infty}\mathrm{d}t_1\ldots\mathrm{d}t_{m+n} \\ &\qquad\times \Theta_{m,n}(t_1,\ldots,t_{m+n})T[H_{1\varepsilon}(0)H_{1\varepsilon}(t_1)\ldots H_{1\varepsilon}(t_{m+n})], \end{aligned} \tag{44}$$

where $\Theta_{m,n}(t_1,\ldots,t_{m+n})$ is the characteristic function for the union of the $\binom{m+n}{m}$ regions in which exactly m variables are positive. If at fixed $m+n$ the summation over m is performed we get:

$$\begin{aligned} &U_\varepsilon(\infty,0)H_1U_\varepsilon(0,-\infty) \\ &\quad= \sum_{n=0}^{\infty}\frac{(-\mathrm{i})^n}{n!}\int_{-\infty}^{\infty}\mathrm{d}t_1\ldots\mathrm{d}t_n\, T[H_{1\varepsilon}(0)H_{1\varepsilon}(t_1)\ldots H_{1\varepsilon}(t_n)]. \end{aligned} \tag{45}$$

Upon taking the expectation value the right-hand side may be brought in the same form as that of (38), albeit with different integration boundaries. Hence we have on a par with (39):

$$\begin{aligned} &\langle\psi_0|U_\varepsilon(\infty,0)H_1U_\varepsilon(0,-\infty)|\psi_0\rangle \\ &\quad= \langle\psi_0|U_\varepsilon(\infty,0)H_1U_\varepsilon(0,-\infty)|\psi_0\rangle_c\langle\psi_0|U_\varepsilon(\infty,-\infty)|\psi_0\rangle \end{aligned} \tag{46}$$

and consequently, from (37):

$$\Delta E = \lim_{\varepsilon\to 0}\int_0^\lambda \frac{\mathrm{d}\lambda'}{\lambda'}\langle\psi_0|U_\varepsilon(\infty,0)H_1U_\varepsilon(0,-\infty)|\psi_0\rangle_c. \tag{47}$$

The connected-diagram expansions obtained here may be recast in a form that relates the energy shift with the connected part of the S matrix. A formula of this kind has been employed sometimes in the literature, in order to take full advantage of the covariant S-matrix methods. It has been used, for instance, to evaluate retarded interatomic interaction energies in the framework of covariant quantum electrodynamics[17,18]).

Rodberg[19]) has suggested a general proof of the relation with the scattering matrix. However, his way of taking the adiabatic limit requires rather complicated contour integrations, in the course of which certain poles (viz those at the origins of the complex planes) are ignored without sufficient justification.

To establish the desired relation with the S matrix we shall choose as a starting point the formulae (40) and (47); these expressions for ΔE do not contain an explicit factor ε, so that the adiabatic limit can be taken immediately. Then (40), with (23) inserted, gets the form:

$$\Delta E = \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \mathrm{i}\delta(t_{\max}) \langle \psi_0 | T[H_1(t_1) \ldots H_1(t_n)] | \psi_0 \rangle_c. \tag{48}$$

Similarly (47) with (45) yields[20,21])

$$\Delta E = \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \mathrm{i}\delta(t_1) \langle \psi_0 | T[H_1(t_1) \ldots H_1(t_n)] | \psi_0 \rangle_c. \tag{49}$$

The right-hand sides of the above two formulae have the same appearance as the Dyson series (A.5) for the connected part of the S matrix, the only difference being the delta functions in the integrands. In particular (49) shows that the energy ΔE can be evaluated by writing out the connected diagrams of the scattering matrix and suppressing, apart from a factor i, one of the time integrations.

The connection with the S matrix can be presented in a more concise way[18]). We make the formal step of replacing the bra and ket vectors $\langle \psi_0 |$ and $| \psi_0 \rangle$ in (48) by final and initial states $\langle \psi_f |$ and $| \psi_i \rangle$, respectively; when the time variables t are replaced by $t + \tau$ the expression (48) gets the form:

$$\Delta E = \mathrm{e}^{\mathrm{i}(E_f - E_i)\tau} \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{-\infty}^{\infty} \mathrm{d}t_1 \ldots \mathrm{d}t_n \, \mathrm{i}\delta(t_{\max} + \tau)$$
$$\times \langle \psi_f | T[H_1(t_1) \ldots H_1(t_n)] | \psi_i \rangle_c. \tag{50}$$

Here E_f and E_i are the energies associated with the final and initial states. Upon bringing the exponential in front to the left-hand side and integrating from $\tau = -\infty$ to $\tau = \infty$ the right-hand side becomes the Dyson series for the S matrix. Hence we finally arrive at the result:

$$S_{fi,c} = -2\pi \mathrm{i} \delta(E_f - E_i) \Delta E, \tag{51}$$

which could equally well be proved from (49); it is in fact the relation assumed in the literature. In view of (41) we may write it in the suggestive form:

$$S_{fi} = \exp[-2\pi \mathrm{i} \delta(E_f - E_i) \Delta E], \tag{52}$$

which of course has strictly speaking no mathematical significance, in view of the fact that (41) has no adiabatic limit.

In the present section we have confined ourselves to the case of a nondegenerate unperturbed energy level, for which connected-diagram expansions can be established. These expansions were crucial in the derivation of the above S-matrix formulae. The connected-diagram expansions given here do no longer hold for degenerate levels since the second quantization as introduced above would have led then to a degenerate vacuum; to circumvent this problem the introduction of folded diagrams is essential[7,9,10]).

In special cases a formula analogous to (51) can be derived even for degenerate levels. In fact, if in the effective Hamiltonian (17) the inverse operator need not be considered, for instance in lowest-order perturbation theory, a similar reasoning as given above may be applied. As a result one finds

$$S_{\mathrm{fi}} = \delta_{\mathrm{fi}} - 2\pi \mathrm{i}\delta(E_{\mathrm{f}} - E_{\mathrm{i}})V, \tag{53}$$

which shows that the effective Hamiltonian reduces in this particular case to the transition matrix.

Appendix

Some properties of the time-evolution operator

The time-evolution operator $U_\varepsilon(t, t')$ in the interaction picture satisfies the differential equation:

$$\mathrm{i}(\partial/\partial t)U_\varepsilon(t, t') = H_{1\varepsilon}(t)U_\varepsilon(t, t') \tag{A.1}$$

and the initial condition $U_\varepsilon(t, t) = 1$. The adiabatic interaction Hamiltonian is given by:

$$H_{1\varepsilon}(t) = \mathrm{e}^{-\varepsilon|t|}\,\mathrm{e}^{\mathrm{i}H_0 t}\,H_1\,\mathrm{e}^{-\mathrm{i}H_0 t}. \tag{A.2}$$

Here H_1 is the time-independent perturbation Hamiltonian in the Schrödinger picture; it is linear in the coupling constant λ.

From (A.1) one can derive a differential equation for U_ε in terms of λ by using time-translation arguments. If in (A.1) the time variables t, t' are replaced by $t+\tau$, $t'+\tau$ (with t, t' and τ of equal sign) an equation of the same form may be recovered in which a modified coupling constant $\lambda' = \lambda \exp[-(\operatorname{sgn} t)\varepsilon\tau]$ shows up. Since the solution of the differential equation (A.1) is uniquely determined by the initial condition one arrives at the relation:

$$U_\varepsilon(t, t' \mid \lambda) = e^{-iH_0\tau}\, U_\varepsilon(t+\tau, t'+\tau \mid \lambda\, e^{(\operatorname{sgn} t)\varepsilon\tau})\, e^{iH_0\tau}. \tag{A.3}$$

Upon differentiating with respect to τ and putting $\tau = 0$ one gets:

$$H_\varepsilon(t)U_\varepsilon(t, t' \mid \lambda) - U_\varepsilon(t, t' \mid \lambda)H_\varepsilon(t') + (\operatorname{sgn} t)\mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda} U_\varepsilon(t, t' \mid \lambda) = 0, \tag{A.4}$$

valid for $\operatorname{sgn} t = \operatorname{sgn} t'$; this is a generalization of the identity of Gell-Mann and Low[6]).

Both (A.1) and (A.4) can be solved iteratively in the form of a perturbation expansion. In particular, the time differential equation (A.1) yields the Dyson series containing time-ordered products of the perturbation:

$$U_\varepsilon(t, t') = \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{t'}^{t} \mathrm{d}t_1 \ldots \mathrm{d}t_n\, T[H_{1\varepsilon}(t_1) \ldots H_{1\varepsilon}(t_n)]. \tag{A.5}$$

The time integration may in principle be carried out straightforwardly with the help of (A.2). A particularly simple expression is obtained in the special case that the integration extends to infinity. It may be derived alternatively from the coupling-constant differential equation (A.4) as will be shown now. To that end $U_\varepsilon(t, \pm\infty)$ is written in the spectral form:

$$U_\varepsilon(t, \pm\infty) = \int_{-\infty}^{\infty} \mathrm{d}z\, \tilde{U}_\varepsilon(t, \pm\infty; z)\delta(z - H_0), \tag{A.6}$$

which gives after insertion in (A.4):

$$\left[z - H_0 \mp \mathrm{i}\varepsilon\lambda \frac{\mathrm{d}}{\mathrm{d}\lambda}\right]\tilde{U}_\varepsilon(t, \pm\infty; z) = H_{1\varepsilon}(t)\tilde{U}_\varepsilon(t, \pm\infty; z). \tag{A.7}$$

If this equation is solved in successive orders of λ we get immediately:

$$U_\varepsilon(t, \pm\infty) = \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}z\, e^{-\mathrm{i}(z - H_0 \mp \mathrm{i}n\varepsilon)t} \frac{1}{z - H_0 \mp \mathrm{i}n\varepsilon} H_1 \ldots \frac{1}{z - H_0 \mp \mathrm{i}\varepsilon} H_1 \delta(z - H_0), \tag{A.8}$$

which is the desired result.

The similarity transform of an arbitrary operator $A(t)$ with respect to $U_\varepsilon(t, t')$ may be expanded in a series analogous to (A.5). This can be proved from the equation of motion:

$$\mathrm{i}\frac{\partial}{\partial t'}[U_\varepsilon(t', t)A(t)U_\varepsilon(t, t')] = [H_{1\varepsilon}(t'), U_\varepsilon(t', t)A(t)U_\varepsilon(t, t')], \tag{A.9}$$

which is an immediate consequence of (A.1). After integration and iterative solution one gets an expansion involving retarded commutators instead of time-ordered products:

$$U_\varepsilon(t',t)A(t)U_\varepsilon(t,t')$$
$$=\sum_{n=0}^{\infty}(-\mathrm{i})^n\int_{t'}^{t}\mathrm{d}t_1\int_{t'}^{t_1}\mathrm{d}t_2\ldots[\ldots[A(t),H_{1\varepsilon}(t_1)],\ldots,H_{1\varepsilon}(t_n)]. \tag{A.10}$$

To employ this retarded-commutator expansion in the main text the following auxiliary relation is required:

$$U_\varepsilon(t',t)\mathrm{i}\lambda\frac{\mathrm{d}}{\mathrm{d}\lambda}U_\varepsilon(t,t')=\int_{t'}^{t}\mathrm{d}t''\;U_\varepsilon(t',t'')H_{1\varepsilon}(t'')U_\varepsilon(t'',t'); \tag{A.11}$$

it relates the λ and t dependence of the time-evolution operator and may be proved by differentiating with respect to t and using $\lambda\;\mathrm{d}H_{1\varepsilon}/\mathrm{d}\lambda=H_{1\varepsilon}$.

Acknowledgements

This investigation is part of the research programme of the "Stichting voor Fundamenteel Onderzoek der Materie (FOM)", which is financially supported by the "Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek (ZWO)".

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