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Unitary determinantal solution of time-dependent Schrödinger equations

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It is shown that the Fredholm-Laplace solution of the Schrödinger integral equation of the evolution operator in the cases of harmonic or constant external perturbations can be put into a physically meaningful determinantal quotient form. The solution exhibits the usual multiple transitions and corresponding linewidth upon expansion. The result lends itself fairly well to the setting up of correct tractable formulas in the important case of continuous spectra capable, for instance, of dealing with resonance phenomena. Furthermore, the determinantal form can be shown to obey the unitary requirement at all times and any order with respect to the applied field or the collision potential. An illustration is given in the simple model of a system submitted to a perturbation of constant matrix elements, in the spectral range of interest assumed of constant density of states.

I. INTRODUCTION

Various attempts have been undertaken in recent years to overcome the difficulties inherent in the approximate methods of solving time-dependent problems in quantum mechanics. The main disadvantage of the usual iterative perturbation expansion, often referred to as the Dirac variation of constants method, lies in the occurrence of "secular" time divergent terms. The latter are responsible for the apparent lack of unitarity of the perturbation expansion. This unitarity should be expected at all times, as a result of the Hermitian nature of the Hamiltonian operator. Langhoff, Epstein, and Karplus[1] have demonstrated, in a general and extensive analysis, that the secular terms can be extracted from the Dirac expansion into an overall phase factor of the eigenfunction, containing the energy-level shift of the system. Methods capable of separating the remaining "regular" part of the wave function are indicated in their paper.

The lack of unitarity of the transition amplitudes inherent in the perturbation series, together with the inability of describing resonance transitions, have also been outlined by Wallace[2] who proposed a numerical means for directly solving the time-dependent equations. The Wallace method which consists of a determinantal procedure for calculating the transition amplitudes is, in a sense, the numerical equivalent of the method presented below, dealing with the same Laplace-transformed functions of time. Improved expansions have also been proposed by Mehrotra and Boggs,[3] Hamman and Fellah.[4] The important case of time periodic perturbations has received particular attention. Shirley[5] has proposed a derivation of the time-evolution operator based on the Floquet theorem. Also derived from the Floquet theorem is the generalized expansion in terms of the perturbation parameter, set down by Sen Gupta[6] for eliminating the secular behavior, as well as the Hermitian operator introduced by Salzman,[7] whose calculation is unfortunately rather difficult. The same purpose was attained, in an alternative way, by Brooks and Scarfone[8] through a "multiple-time-scale" perturbation theory.

Concerning resonance phenomena associated with the matter-radiation interaction, Ziv[9] recently published a generalization of the time-dependent perturbation theory in the framework of a formalism developed in the so-called "effective-system-states basis". This formalism is given as being well suited to quantum-theoretical investigations in spectroscopic problems dealing with complex energies.

Most of the various aforementioned attempts often seem to be of limited practical range, or restricted to particular problems. They do not yield general and reliable expressions for current applications, and the detailed consequences about decay time of occupation probabilities, transition widths due to natural or collisional broadening, etc., are not derived.

The purpose of the present paper is to show, in a quite elementary mathematical scheme that the conjunction of the Laplace transform with the Fredholm method of solving multidimensional integral equations, permits the Laplace image of the evolution operator to be brought into the form of the ratio of two expansions, thoroughly explicited in term of the perturbation Hamiltonian. The result, which displays all physically expected features, is shown to yield no secular contribution in the original time-dependent function which entails in turn, unitarity at all times as it will be shown in a future paper, in connection with the density-matrix problem. Solutions will first be derived in the case of the discrete spectrum which is that of natural systems to a sufficiently fine scale. The way of obtaining formulas in the continuum limit, which is of great practical interest, will be con-

sidered and discussed next.

The major interest of the Laplace transform lies in that the linear differential Schrödinger equation is replaced by a linear system. This interest is still enhanced in many cases where there is no need to calculate the original time-dependent functions to obtain the expected physical responses. In most applications (steady-state problems, for instance) only long-term behavior of the time-dependent observables is customarily considered. The latter can then be obtained by simple application of the elementary properties of the Laplace transform.

Although the method could likely be extended to a large variety of time dependences of the external perturbation, the results will be established, for the sake of simplicity, in the cases usually encountered in current applications (transport phenomena, semiclassical interaction of matter with radiation, etc.), i.e., constant or oscillatory perturbation. Because the perturbation is applied from the initial instant $t=0$, difficulties arising with the currently assumed adiabatic switching on from $t=-\infty$ are avoided.

In Sec. II, the solution will be written first in the initial Fredholm form which will be shown, however, to be unreliable, particularly when working in the continuum limit. An improved determinantal form will be derived in Sec. III, from the Fredholm-Laplace fraction, by means of suitable multipliers. In this so-called "reduced determinantal form," expansions will appear in a remarkably simple recurrence law, revealing both the usual multiple transitions structure and the associated transition width. As an illustration, the typical problem considered in Ref. 10 will be treated again in Sec. IV, but after abandoning the initially adopted simplificative selection rules. Most of the results of the present formalism will be given in a convenient form to facilitate subsequent applications to specific problems in atomic and solid-state physics.

II. FREDHOLM-LAPLACE EXPRESSION OF THE EVOLUTION OPERATOR

A. General formulation

We will take the Hamiltonian of the physical system in the typical form

$$H=H_0+V+Y(t)A(t)\,, \tag{1}$$

H_0 is an unperturbed Hamiltonian. Its eigenstates $|a\rangle, |b\rangle, \ldots, |k\rangle, \ldots$, of eigenvalues $E_a=\hbar\omega_a, \ldots$, are assumed to be known. V is a constant perturbation Hamiltonian, such as a collision potential, and $Y(t)A(t)$ is the time-dependent external perturbation applied from $t=0$ as specified by the Heaviside step function $Y(t)$.

To a sufficiently fine scale the spectrum of natural systems is discrete except for weak degeneracies resulting from symmetry, spin, etc. Very high multiplicity or density of states, appearing in the usual description of the physical properties result from an averaging procedure over the microscopic spectrum. These remarks allow us to start with the discrete spectrum (weak degeneracies could be easily introduced without any change in the essential), and to proceed to approximate averagings, in a further stage, by means of integrations.

The most current forms of $A(t)$ in applications are

(i) $A(t)=A$, const perturbation,

(ii) $A(t)=A\exp(-i\omega t)+A^\dagger\exp(i\omega t)$, harmonic perturbation. Dropping for brevity the Heaviside step function, Eq. (1) will be rewritten in the case of harmonic perturbation as

$$H=H_0+V+A\exp(-i\omega t)+A^\dagger\exp(i\omega t)\,. \tag{2}$$

The resulting Schrödinger equation of the evolution operator $U(t)$ is

$$\frac{dU}{dt}=(i\hbar)^{-1}[H_0+V+A\exp(-i\omega t)+A^\dagger\exp(i\omega t)]\,U(t)\,. \tag{3}$$

Let us introduce the Laplace transform of $U(t)$, defined as

$$F(\nu)=\int_0^t e^{-\nu t}U(t)\,dt\,, \tag{4}$$

or briefly, $F(\nu)\subset U(t)$. We notice that the Laplace transform of $U^\dagger(t)$ is connected with $F(\nu)$ by

$$U^\dagger(t)\supset[F(\nu^*)]^\dagger.$$

We will use the convenient notation

$$[F(\nu^*)]^\dagger=F^\dagger(\nu)\,. \tag{5}$$

Through elementary properties we now have

$$\frac{dU}{dt}\supset\nu F(\nu)-U(0)\,,$$

$$\exp(\pm i\omega t)U(t)\supset F(\nu\mp i\omega)\,,$$

so that Eq. (3) is transformed into

$$\nu F(\nu)=U(0)+(i\hbar)^{-1}\times[(H_0+V)F(\nu)+AF(\nu+i\omega)+A^\dagger F(\nu-i\omega)]\,. \tag{6}$$

The time-evolution operator $U(t)$ satisfies the initial condition $U(0)=1$. Taking Eq. (6) between the bra $\langle b|$ and the ket $|a\rangle$ of the unperturbed Hamiltonian H_0, we obtain

$$\nu F_a^b(\nu) = \delta_a^b - i\omega_a^b F_a^b(\nu) + (i\hbar)^{-1} \sum_k [V_k^b F_a^k(\nu) + A_k^b F_a^k(\nu + i\omega) + A_k^{\dagger b} F_a^k(\nu - i\omega)]. \quad (7)$$

δ is the Kronecker symbol and $F_a^b(\nu) = \langle b | F(\nu) | a \rangle$.

For an arbitrary time-dependent perturbation $A(t)$ we would get an integral ν equation. The particular choice of an harmonic perturbation in Eq. (2) permits the simplifying of this integral equation into an equation connecting $F(\nu - i\omega)$, $F(\nu)$, $F(\nu + i\omega)$. Substituting $\nu + in\omega$ (n integer) for ν leads to an infinite set of recursion equations between the $F(\nu + in\omega)$. Let us put for notational simplicity

$$F_k^l(\nu + in\omega) = F_k^{ln}, \quad (8)$$

$$\nu + i\omega_k + in\omega = d_{kn}, \quad (9)$$

we have

$$d_{bn} F_a^{bn} = \delta_a^b 1^n + (i\hbar)^{-1} \sum_k (V_k^b F_a^{kn} + A_k^b F_a^{kn-1} + A_k^{\dagger b} F_a^{kn+1}). \quad (10)$$

The representative space is now to be extended so as to include the n indices. It will be easily realized that this extended Hilbert space, now sustained by the orthonormal set of kets $|bn\rangle$, is the same as that considered by Shirley,[5] as a result of Floquet's theorem. Equations (10) define a linear system equivalent to a matricial equation in that space, F_a^{bn} denotes the bn component of the F column vector, and analogously, $\delta_a^b 1^n$ the bn component of a particular vector which is equal to zero if $b \neq a$ and to 1 if $b = a$ whatever the n integer. 1^n stands for a column vector belonging to the n subspace and all components of which are equal to 1. Notice that a distinct system is obtained for any selected a state.

We will put for simplicity

$$V_k^k = 0, \quad A_k^k = 0. \quad (11)$$

There is no loss of generality in dropping diagonal elements of V which can be incorporated in the definition of H_0. Diagonal elements of A, however, can play a part in "indirect transitions". The corresponding terms (which often add up to zero by parity) can easily be reintroduced in the results.

According to Fredholm's theorem, the linear system (10) tends to an integral equation with respect to the relevant quantum numbers in the continuum limit. Whether the summation be discrete or continuous Eq. (10) can be given a compact form by defining the kernel

$$K_{c_1 n_1}^{c_2 n_2} = i\hbar^{-1}(V_{c_1}^{c_2} \delta_{n_1}^{n_2} + A_{c_1}^{c_2} \delta_{n_1}^{n_2+1} + A_{c_1}^{\dagger c_2} \delta_{n_1}^{n_2-1}), \quad (12)$$

or more simply,

$$K_{c_1}^{c_2} = i\hbar^{-1}(V_{c_1}^{c_2} + A_{c_1}^{c_2}), \quad (13)$$

in the case of static perturbation. It is apparent that $K_{c_1 n_1}^{c_2 n_2}$ is only dependent on $n_2 - n_1$. Note, furthermore, that because of the hermiticity of the interaction Hamiltonian ($K^\dagger = -K$):

$$(K_{c_1 n_1}^{c_2 n_2})^* = -i\hbar^{-1}(V_{c_2}^{c_1} \delta_{n_2}^{n_1} + A^{\dagger c_1}_{c_2} \delta_{n_2+1}^{n_1} + A_{c_2}^{c_1} \delta_{n_2-1}^{n_1}) = -K_{c_2 n_2}^{c_1 n_1}. \quad (14)$$

As shown by Shirley,[5] the consideration of the "Floquet states" $|cn\rangle$ leading to a kernel in the form (12), is equivalent to a quantized-field formalism in the semiclassical limit where the number of quanta is very high. Equation (10) now becomes

$$F_a^{bn} + \frac{K_{kn'}^{bn}}{d_{bn}} F_a^{kn'} = \frac{\delta_a^b}{d_{bn}} 1^n. \quad (15)$$

From now on the summation symbol $\sum$ over repeated indices in products such as KF, KKF, etc., will be omitted.

Equation (15) could be regarded as the Laplace transformed of the Floquet-Schrödinger equation. The oscillatory perturbation case is thus reduced to the static perturbation case by means of an elementary procedure. Since F^{bn} is a column vector, the superscript bn in K_{km}^{bn} is a row index and the subscript km a column index.

The complete solution for the matrix element F_a^{bn} is given by Cramer's theorem. Let $D(\nu)$ be the determinant of the system and $D_{in}^{km}(\nu)$ be the algebraic minor obtained by striking out the ln row and the km column (inversion of the subscript and the superscript significance in the minor notation, relative to the matrix elements of K, is adopted for notational convenience). The general solution of the system (15) can be written as

$$F_a^{bn} = \frac{D_{kn'}^{bn}(\nu)\delta_a^k}{d_{kn'} D(\nu)} 1^{n'} = \frac{D_{an'}^{bn}}{d_{kn'} D} 1^{n'}. \quad (16)$$

In fact, the solution of interest is $F_a^{b0}(\nu) \subset U_a^b(t)$

$$F_a^{b0} = \frac{D_{an}^{b0}}{d_{an} D} 1^n; \quad (17)$$

n indices are missing in the case of static perturbation. It is apparent that F_a^{bn} is simply derived from F_a^{b0} through the substitution $\nu \to \nu + in\omega$.

B. Fredholm expansion of the determinants

We now proceed to give a more explicit form to the above results by expanding the determinants in terms of increasing order of the kernel. This is obtained by applying Cayley's theorem, in current

use in the determinants theory.[11] For systematic calculations it is quite convenient to start with the exponential form given in Appendix A. In the following formulas will be first written, for simplicity, in the case of static perturbation. Since the harmonic perturbation case has been shown to reduce to the static one, formulas pertaining to the former will next be readily obtained as a simple extension of the results to the Floquet bn representation. For the diagonal element we have, to third order,

$$F_a^a=\frac{D_a^a}{d_aD}=\frac{1-\frac{K_l^kK_k^l}{2!d_kd_l}+\frac{2K_l^kK_m^lK_k^m}{3!d_kd_ld_m}+\cdots}{d_a\left(1-\frac{K_l^kK_k^l}{2!d_kd_l}+\frac{2K_l^kK_m^lK_k^m}{3!d_kd_ld_m}+\cdots\right)}\cdot \tag{18}$$

The upper and lower expansions are apparently identical but differ in fact, by the index restriction $k,l,m,\ldots,\neq a$ in the numerator. In addition, in spite of the use of the same notations, the dumming indices $k,l,m,\ldots$, are evidently independent from one another in the different terms. First-order terms are missing because of assumptions (11). Moreover, in each term of a sum such as $K_l^kK_m^lK_k^m/d_kd_ld_m$, all indices are different from one another since terms appearing in the expansion of a determinant cannot have more than one factor belonging to a given row or column. This restriction, however, can be dropped since terms with identical indices in different factors cancel each other. Two identical indices would indeed result from replacing one row (and column) by a row (and column) identical to another one, and thereby from additional determinants of zero value.

For the nondiagonal element $F_a^b(b\neq a)$ the result is as follows:

$$F_a^b=\frac{D_a^b}{d_aD}=\frac{-K_a^b+\frac{K_k^bK_a^k}{d_k}+\frac{K_a^bK_l^kK_k^l}{2d_kd_l}-\frac{K_k^bK_l^kK_a^l}{d_kd_l}+\cdots}{d_bd_a\left(1-\frac{K_l^kK_k^l}{2!d_kd_l}+\frac{2K_l^kK_m^lK_k^m}{3!d_kd_ld_m}+\cdots\right)} \tag{19}$$

($k,l,\ldots,\neq a$ in the numerator). The minor D_a^b can be easily deduced from the complete determinant D by derivation with respect to the element located at the crossing of the a row and the b column,[11] i.e.,

$$D_a^b=\frac{\partial D}{\partial(K_a^b/d_a)}\cdot \tag{20}$$

Use can be made too of the exponential form of the Fredholm determinant [see (A12)].

In the calculation of the original of $F(\nu)$ (see below), $|\nu|$ can be taken as larger than any finite given number on the overall contour of integration. By application of Hadamard's theorem the expansions of determinants D, D_a^a, D_a^b can then be shown to converge for any magnitude of the kernel K. Thus expressions (18) and (19) represent the exact solution of the Schrödinger equation (15) and certainly obey the unitary requirement. The latter is a direct consequence of the hermiticity of the operator iK. The verification of this fundamental property, however, is rather difficult since it requires either the complete calculation of the original function $U_a^b(t)$, which is of course, out of the question, or the calculation of the convolution integral

$$F_a^b(\nu)*F_b^{+a}(\nu)\subset|U_a^b(t)|^2, \tag{21}$$

and further summing over b states. This method will be studied in a future paper, in connection with the similar density-matrix formalism. It will be proved that the unitary requirement is not only obeyed for the complete fractions (18) and (19), but still remains at any finite order of both expansions therein.

More detailed expressions can be deduced from Eqs. (18) and (19) by replacing the kernel with (12) or (13). It must be noted that a nonzero answer will be obtained even if $A=0$, i.e., without applied time-dependent perturbation. This is, of course, a consequence of using the basis of the unperturbed Hamiltonian H_0. The initial condition $U(0)=1$ then entails the Kroneker δ_a^b in Eqs. (10) or (15), which is equivalent to assuming the system to be in the a state at $t=0$. It follows that, in the case $A=0$, the preceding treatment gives the subsequent evolution of the system due to the constant V potential alone. In practical applications, the system will be initially assumed to be in a pure eigenstate or in a statistical mixture of eigenstates of H_0+V. On applying the results of Eqs. (18) or (19) with an initial occupation probability function $f(H_0+V)$ similarly expanded with respect to V we will obtain complete cancellation, order by order, of the extra terms not containing the applied perturbation A and, in consequence, a zero response if $A=0$.

Let us now carry out the division of the upper by the lower expansion in Eqs. (18) and (19). We obtain

$$F_a^a=\frac{1}{d_a}\left(1+\frac{K_k^aK_a^k}{d_ad_k}-\frac{K_k^aK_l^kK_a^l}{d_ad_kd_l}+\cdots\right) \tag{22}$$

and

$$F_a^b=\frac{1}{d_a}\left(-\frac{K_a^b}{d_b}+\frac{K_k^bK_a^k}{d_bd_k}-\frac{K_k^bK_l^kK_a^l}{d_bd_kd_l}+\cdots\right) \tag{23}$$

in which index restrictions have vanished. According to Fredholm's theorem this is exactly the

result derived from the iterative procedure, i.e., the Laplace transform of the Dirac perturbative expansion. The right-hand side in Eqs. (22) and (23) represents a geometric series which can be readily summed up, giving

$$\begin{aligned} F_a^a &= d_a^{-1}\langle a|(I+d^{-1}K)^{-1}|a\rangle \\ &= d_a^{-1}\langle a|(I+d^{-1}K)^{-1}d^{-1}d|a\rangle \\ &= d_a^{-1}\langle a|[d(I+d^{-1}K)]^{-1}d|a\rangle \\ &= \langle a|(d+K)^{-1}|a\rangle , \end{aligned} \tag{24}$$

d stands for the operator $d=\nu+i\hbar^{-1}H_0$, and I is the identity operator. Similarly

$$F_a^b = -d_a^{-1}\langle b|d^{-1}K(I+d^{-1}K)^{-1}|a\rangle ,$$

or, since $b\neq a$,

$$\begin{aligned} F_a^b &= d_a^{-1}\langle b|(I+d^{-1}K)^{-1}|a\rangle \\ &= \langle b|(d+K)^{-1}|a\rangle . \end{aligned} \tag{25}$$

Alternative derivations are given in Appendix A [Eqs. (A11) and (A15)].

Thus the expanded form of the matrix elements F_a^a, F_a^b can also be regarded as the matrix elements of the operator $(d+K)^{-1}$. This is not at all surprising for all the equations of the system (15) can be contracted in the following formal expression:

$$(d+K)F=P_a , \tag{26}$$

P_a denoting the projector on the a state. Hence,

$$F=(d+K)^{-1}P_a ,$$

leading to Eqs. (24) and (25).

Fredholm's expressions (18) and (19) are the most direct solution of the linear system (15). However, besides the inadequacies which will be discussed in the next section, they do not lend themselves to the derivation of more tractable results than the iterative expansion does in the important limit of continuous spectrum. In fact, care must be taken to derive from Eq. (18) an expression valid in the continuum limit, since at first sight, as the number of states is increased index restrictions become inconsequential and the limit seems to be $1/d_a$. This is, of course, a physically unacceptable result. To get a correct expression we have first to rewrite the numerator in the form

$$D_a^a = D+\frac{K_k^a K_a^k}{d_a d_k}-\frac{K_k^a K_l^k K_a^l}{d_a d_k d_l}+\cdots ,$$

without index restriction. This leads to

$$F_a^a=\frac{1}{d_a}\left(1+\frac{K_k^a K_a^k}{d_a d_k D}-\frac{K_k^a K_l^k K_a^l}{d_a d_k d_l D}+\cdots\right) .$$

Further division by D in the successive terms again yields the iterative expansion (22) [this can be verified by using the determinant expansion given in (A3) and (A4)], with the above recalled disadvantages as to unitarity at any time.

In the following section, we proceed to show that Fredholm expressions can be given a different but equivalent form much more suited to work in the continuum limit. Heretofore, the above results will be extended to the harmonic perturbation case. The Fredholm form (18) first becomes

$$\begin{aligned} F_a^{a0} &= \frac{D_{an}^{a0}}{d_{an}D}1^n=\frac{D_{a0}^{a0}}{d_{a0}D}+\frac{D_{an}^{a0}}{d_{an}D}1^n \quad (n\neq 0) \\ &= \frac{1-\dfrac{K_{k_2n_2}^{k_1n_1}K_{k_1n_1}^{k_2n_2}}{2!\,d_{k_1n_1}d_{k_2n_2}}+\cdots}{d_{a0}\left(1-\dfrac{K_{k_2n_2}^{k_1n_1}K_{k_1n_1}^{k_2n_2}}{2!\,d_{k_1n_1}d_{k_2n_2}}+\cdots\right)} \\ &\quad +\frac{\dfrac{K_{k_1n_1}^{a0}K_{an}^{k_1n_1}}{d_{k_1n_1}}+\cdots}{d_{an}\left(1-\dfrac{K_{k_2n_2}^{k_1n_1}K_{k_1n_1}^{k_2n_2}}{2!\,d_{k_1n_1}d_{k_2n_2}}+\cdots\right)}1^n(n\neq 0) , \end{aligned} \tag{27}$$

with k_1n_1, $k_2n_2,\ldots,\neq ao$ in the first numerator and $k_1n_1,\ldots,\neq ao$, an, in the following ones. Similarly, Eq. (19) becomes

$$F_a^{b0}=\frac{D_{an}^{b0}}{d_{an}D}1^n=\frac{-K_{an}^{b0}+\dfrac{K_{k_1n_1}^{b0}K_{an}^{k_1n_1}}{d_{k_1n_1}}-\cdots}{d_{an}d_{b0}\left(1-\dfrac{K_{k_2n_2}^{k_1n_1}K_{k_1n_1}^{k_2n_2}}{2!\,d_{k_1n_1}d_{k_2n_2}}+\cdots\right)}1^n , \tag{28}$$

with $k_1n_1,\ldots,\neq bo$, an, in every numerator.

The associated perturbative expansions are derived from

$$(d+K)F=P_{an}1^n , \tag{29}$$

with

$$d=\nu+i\hbar^{-1}H_0+i\omega\sum_n nP_n , \tag{30}$$

where $P_{an}=|an\rangle\langle an|$, $P_n=|n\rangle\langle n|$ stand for the projector on the an and n state, respectively. We thus have

$$F_a^{b0}=\langle b0|(d+K)^{-1}|an\rangle 1^n , \tag{31}$$

giving rise to an evident extension of Eq. (23).

III. REDUCED DETERMINANTAL FORM OF THE EVOLUTION OPERATOR

A. Improved form of the Fredholm solutions

We first notice that expansions appearing in Eqs. (18) and (19) involve terms which do not seem physically acceptable in describing transitions from a given initial state a into some final state b. In the denominators, terms not containing the a state

can be separated at any order. The second-order terms, for instance, can be written as

$$K_l^k K_k^l/2d_k d_l = K_l^k K_k^l/2d_k d_l + K_m^a K_a^m/d_a d_m ,$$

with $k, l, \ldots, \neq a$ on the right-hand side. k, l may include states which are not at all involved in the transition under consideration. Similar unexpected terms also appear in the numerators, multiplying a- and b-dependent terms, for instance, the third-order term $K_a^b K_l^k K_k^l/2d_k d_l$ in Eq. (19). On the other hand, as mentioned above, Fredholm expressions do not yield a reliable result in the continuum limit. We are going to show that these unexpected features can be eliminated by a transformation of the Fredholm solution.

To work out the desired form of F_a^a, let us expand the determinant D with respect to the elements of the a column. We obtain

$$D = D_a^a + (K_a^l/d_l) D_l^a .$$

The cofactor D_l^a of K_a^l/d_l can, in turn, be expanded with respect to the a row,

$$D = D_a^a + (K_a^l K_k^a/d_l d_a) D_{la}^{ak} ,$$

where D_{la}^{ak} denotes the cofactor of K_k^a/d_a in the determinant D_l^a. Applying the usual rule for obtaining the sign of a given cofactor, it is easy to see that

$$D_{la}^{ak} = - D_{al}^{ak} ,$$

which allows us to write

$$D = D_a^a - (K_a^l K_k^a/d_l d_a) D_{al}^{ak} ,$$

whence

$$F_a^a = 1/[d_a - K_a^l (D_{al}^{ak}/d_l D_a^a) K_k^a] . \tag{32}$$

The quotient of determinants can be further explained by using Eq. (25),

$$D_{al}^{ak}/d_l D_a^a = \langle k | (I + d^{-1}K')^{-1} d^{-1} | l \rangle \quad (k, l, \ldots, \neq a)$$

where the prime in K' means that the a state is omitted (i.e., $K_r^s = 0$ if $r, s = a$). Instead of K' we can introduce the complementary projector $Q_a = I - P_a$ [see Eq. (A8)]. We thus have

$$K_k^a (D_{al}^{ak}/d_l D_a^a) K_a^l = \langle a | K (I + Q_a d^{-1} K)^{-1} Q_a d^{-1} K | a \rangle ,$$

or, since $K_a^a = 0$ it equals

$$- \langle a | K (I + Q_a d^{-1} K)^{-1} | a \rangle . \tag{33}$$

We shall thus write F_a^a in the final form

$$F_a^a = 1/[d_a + \langle a | K (I + Q_a d^{-1} K)^{-1} | a \rangle] . \tag{34}$$

A systematic way of obtaining this result consists in writing F_a^a in the form

$$F_a^a = 1/d_a D(D_a^a)^{-1} , \tag{35}$$

and next performing the division $D(D_a^a)^{-1}$. The equivalence is proven in Eq. (A17).

The nondiagonal element F_a^b, as given by Eq. (19) can be transformed in a quite similar way,

$$F_a^b = \frac{D_a^b (D_a^a)^{-1}}{d_a D (D_a^a)^{-1}} , \tag{36}$$

where the notations $D_a^b (D_a^a)^{-1}$, $D(D_a^a)^{-1}$ mean that the indicated divisions are carried out. To derive a formal expression for $D_a^b (D_a^a)^{-1}$ let us expand D_a^b with respect to the a column

$$D_a^b = (K_a^l/d_l) D_{al}^{ba} = - (K_a^l/d_l) D_{al}^{ab} ,$$

hence, by using Eq. (25)

$$\begin{aligned} D_a^b (D_a^a)^{-1} &= - (K_a^l/d_l) D_{al}^{ab} (D_a^a)^{-1} \\ &= - \langle b | (I + d^{-1}K')^{-1} d^{-1} | l \rangle K_a^l \\ &= - \langle b | (I + Q_a d^{-1} K)^{-1} d^{-1} Q_a K | a \rangle , \end{aligned}$$

or, since $(I + Q_a d^{-1}K)^{-1}$ and $d^{-1} Q_a K$ commute,

$$D_a^b (D_a^a)^{-1} = - \langle b | d^{-1} K (I + Q_a d^{-1} K)^{-1} | a \rangle .$$

We thus arrive at the final expression for $b \neq a$,

$$F_a^b = - \frac{\langle b | d^{-1} K (I + Q_a d^{-1} K)^{-1} | a \rangle}{d_a + \langle a | K (I + Q_a d^{-1} K)^{-1} | a \rangle} . \tag{37}$$

Equations (34) and (37) yield the required new expressions of the F matrix elements, which will be referred to as reduced determinantal forms. Alternative derivations are given in Appendix A. On detailing the expressions of the relevant operators, they can be written in the following explicit form:

$$F_a^a = \frac{1}{d_a - K_k^a K_a^k/d_k + K_k^a K_l^k K_a^l/d_k d_l - \ldots} , \tag{38}$$

$$F_a^b = \frac{-K_a^b + K_k^b K_a^k/d_k - K_k^b K_l^k K_a^l/d_k d_l + \ldots}{d_b (d_a - K_k^a K_a^k/d_k + K_k^a K_l^k K_a^l/d_k d_l - \ldots)} , \tag{39}$$

$(k, l, m, \ldots, \neq a)$. The index restrictions $k, l, m, \ldots, \neq a$ now concern both the upper and lower series.

The expansions are again absolutely convergent along the integration contour in the ν plane since $|\nu|$ can be chosen larger than any given finite number. The convergence quickness, however, is changed relative to the expansions in Eqs. (18) and (19). On performing the division of the numerator by the denominator in Eqs. (38) and (39), we are left once more with the iterative expansions (22) and (23). For instance, in (39) the division strictly has the effect of removing the index restrictions $k, l, \ldots, \neq a$ in the numerator.

Again extension to the harmonic perturbation case is straightforward. Starting from the Fredholm expressions (27) and (28) the related reduced determinantal forms are written as

$$F_a^{a0}=\frac{1}{d_{a0}D(D_{a0}^{a0})^{-1}}+\frac{D_{an}^{a0}(D_{an}^{an})^{-1}}{d_{an}D(D_{an}^{an})^{-1}}1^n$$

$$=\frac{1}{d_{a0}+\langle a0|K(I+Q_{a0}d^{-1}K)^{-1}|a0\rangle}$$

$$-\frac{\langle a0|d^{-1}K(I+Q_{an}d^{-1}K)^{-1}|an\rangle}{d_{an}+\langle an|K(I+Q_{an}d^{-1}K)^{-1}|an\rangle}1^n \quad (n\neq 0) \qquad (40)$$

and

$$F_a^{b0}=\frac{D_{an}^{b0}(D_{an}^{an})^{-1}}{d_{an}D(D_{an}^{an})^{-1}}1^n$$

$$=-\frac{\langle b0|d^{-1}K(I+Q_{an}d^{-1}K)^{-1}|an\rangle}{d_{an}+\langle an|K(I+Q_{an}d^{-1}K)^{-1}|an\rangle}1^n \quad (b\neq a) \qquad (41)$$

with the definition (30) of the operator d.

B. Secular behavior and unitarity

The major improvement gained over the Fredholm or the Dirac iterative forms can be appreciated by considering the related original functions. The Fredholm as well as the reduced determinantal forms can be regarded as rational functions of the ν variable, in which the degree of the denominator is higher than that of the numerator. The original of such a rational fraction is known to be given by a series of exponential functions of time whose arguments are given by the poles of the fraction. Multiple poles give rises to polynominial dependence in time, i.e., secular behavior. The important point is that *neither the Fredholm expressions, nor the reduced determinantal forms (38) and (39) have poles of order higher than one.*

Let us remove for the time being the denominators $d_k d_l, \ldots,$ in the expressions of D, D_a^a, D_a^b, and put

$$\Delta=\Big(\prod_k d_k\Big)D, \quad \Delta_a^a=\Big(\prod_{k\neq a} d_k\Big)D_a^a,$$

$$\Delta_a^b=\Big(\prod_{k\neq a,b} d_k\Big)D_a^b.$$

The roots of the determinant Δ are the purely imaginary numbers $-i\Omega_M$, where Ω_M denote the eigenvalues of the complete Hamiltonian $H_0+i\hbar^{-1}K$. If m is the order of the root $-i\Omega_M$ we thus have

$$\Delta=\prod_M(\nu+i\Omega_M)^m. \qquad (42)$$

Then, by using the following elementary expression[11] of a minor, such as Δ_a^a or Δ_a^b,

$$\Delta_a^a=\frac{\partial\Delta}{\partial i\omega_a}, \quad \Delta_a^b=\frac{\partial\Delta}{\partial K_b^a}. \qquad (43)$$

If ω_a is the energy of a degenerate level, the a index relates to a definite pure substate of the degenerate set. We obtain

$$F_a^a=\Delta_a^a/\Delta=\sum_N\Big(\prod_{M\neq N}(\nu+i\Omega_M)^m\Big)\,n(\nu+i\Omega_N)^{n-1}\frac{\partial i\Omega_N}{\partial i\omega_a}\Big/\prod_M(\nu+i\Omega_M)^m=\sum_N\frac{n}{\nu+i\Omega_N}\frac{\partial\Omega_N}{\partial\omega_a}, \qquad (44)$$

$$F_a^b=\Delta_a^b/\Delta=\sum_N\Big(\prod_{M\neq N}(\nu+i\Omega_M)^m\Big)\,n(\nu+i\Omega_N)^{n-1}\frac{\partial i\Omega_N}{\partial K_b^a}\Big/\prod_M(\nu+i\Omega_M)^m=\sum_N\frac{n}{\nu+i\Omega_N}\frac{\partial i\Omega_N}{\partial K_b^a}. \qquad (45)$$

It is quite apparent in expressions (44) and (45) that $F_a^a(\nu)$ and $F_a^b(\nu)$ have only simple poles. An alternative proof is given in Appendix B in the case of multiple roots resulting from invariance of the complete Hamiltonian $H_0-i\hbar K$. It is shown at once that the relevant roots are in fact those of a definite set pertaining to the irreducible representation sustained by a basis including the a and b states. From Eqs. (44) and (45) the original functions of time can readily be written as

$$U_a^a(t)=\sum_N n\frac{\partial\Omega_N}{\partial\omega_a}\exp(-i\Omega_N t), \qquad (46)$$

$$U_a^b(t)=\sum_N in\frac{\partial\Omega_N}{\partial K_b^a}\exp(-i\Omega_N t), \qquad (47)$$

where summations run over distinct poles only, so that there is not secular contribution. It will be now easily realized that Eqs. (46) and (47), which are derived from the Fredholm form, hold for the reduced form as well, since by the action of the multipliers the poles remain unchanged. Only their detailed expression as expanded in powers of the kernel should change.

Let us now compare expressions (46) and (47) with the original of the iterative expansions (22) and (23). It is apparent that the latter will be expressed in terms of integer powers of t, giving rise to secular contributions, multiplying exponential functions of time whose arguments involve the "unperturbed" roots $-i\omega_a$, $-i\omega_b$, $-i\omega_k$, etc., of D. We may thus expect that the original of the iterative form can be derived from Eqs. (46) and (47) by expanding, with respect to time, the contributions to the exponentials resulting from the frequency shift due to the kernel. If, for example, Ω_k is written as $\omega_k+\Delta\Omega_k$, we will have

$$\exp(-i\Omega_k t)=\exp(-i\omega_k t)(1-i\Delta\Omega_k t+\ldots).$$

This remark provides us with an understanding of the secular terms in complete accordance with the analysis by Langhoff *et al.*[1]

The improvement which is gained with expressions (46) and (47) over the original of (22) and (23) is now cleared up. In practice both types of formulas are confined to a definite order of the kernel K, but because of the secular terms, the iterative forms involve a further approximation only valid at small time and responsible, in addition, for the lost of unitarity. To illustrate this we can say that Eqs. (46) and (47) would be capable of yielding an exact (second-order) result if once the system has undergone two transitions, some selection rule would prevent it from undergoing a third one. On the other hand, the perturbative expansions (22) and (23), in the same conditions would only yield the small-time behavior of the system.

Restricting expansions to a definite order in K does not change the degree of denominators in Eqs. (38) and (39) and thereby the number of exponential terms in Eqs. (46) and (47). This will change, instead, the values of the roots and the coefficients which will turn out to be defined to within the same order. The question then arises as to what extent these approximate results satisfy the unitary requirement. The answer again implies the calculation of the convolution integral (21) in which F matrix elements are given by Eqs. (38) and (39). This amounts to calculating the diagonal matrix element of the related density matrix. It will be shown later that the unitary requirement is still fulfilled at any order of both the upper and lower series of Eqs. (38) and (39).

C. Original in the continuum limit

Instead of the Fredholm form (18) and (19), determinantal expressions (38) and (39) lend themselves fairly well to the derivation of reliable formulas in the continuum limit by substituting integrations for the different summations over dummy indices. Provided the kernel is a continuous function of the quantum numbers, this procedure transforms expressions (38) and (39) into analytic functions. Index restrictions then have no bearing on the value of the result.

Since singularities in the ν plane consist in a definite set of single poles $-i\Omega_k$ lying along the imaginary axis, the originals of $F_a^a(\nu)$ and $F_a^b(\nu)$ are given by the residue theorem. As the number of states is increased, the poles array tends to a cut extending throughout the part of the spectrum of the system belonging to the relevant irreducible representation (Fig. 1) defined in Appendix B. Thus, in the continuum limit the calculation of the evolution operator amount to an integration around a cut belonging to the system spectrum, lying along the imaginary axis.

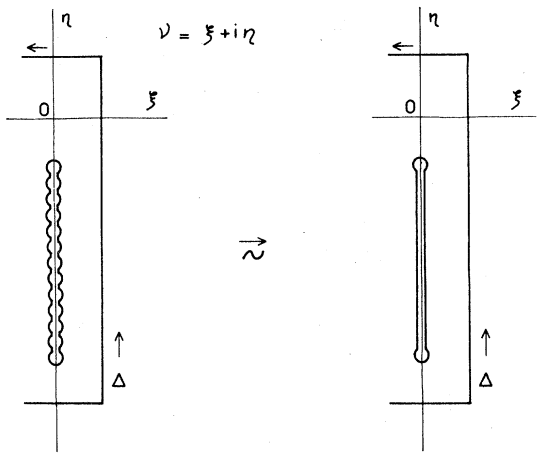

FIG. 1. Evolution of the integration path inside the complex $\nu(\xi,\eta)$ plane as the spectral density of the system is increased towards a continuum.

It is worth noticing that the continuum limit of perturbation expansions, Eqs. (22) and (23), can be obtained as well by performing the division in the continuum limit of expressions (38) and (39). In Eq. (39), for instance, this division simply yields additional terms which remove the index restrictions in the numerator as mentioned above. In the present limit these additional terms which involve at least one integration less than terms of the same order in the numerator, are completely negligible, consistent with the vanishing of index restrictions. A similar behavior holds for Eq. (38). Finally, the forms (34) and (37) or (40) and (41) of the evolution operator matrix elements are quite important. They exhibit all expected properties in applications. The numerator in Eq. (39) is very close to the usual expansion in successive orders of the transition matrix, whereas the denominator can be regarded as the transition width expansion because of its obvious significance.

IV. APPLICATION TO A SIMPLE MODEL

As an illustration of the results of Sec. III, we now return to the typical problem initially considered in Ref. 10 but dropping, however, the selection rules which permitted in that reference a rather simplified derivation of the transition amplitudes. The physical system is thus assumed to be acted upon, from $t=0$, by a constant perturbation A which induces transitions from an initial state a toward states $b, c, \ldots$, be-

longing to a continuum, in which final energies are close to that of the a state. The Hamiltonian of the system is

$$H=H_0+AY(t)\,, \tag{48}$$

when, from Eq. (13),

$$K=i\hbar^{-1}A\,.$$

The second-order approximation in the probabilities of presence is obtained by rewriting expressions (38) and (39) in the form

$$F_a^a(\nu)=\frac{1}{\nu+i\omega_a+\hbar^{-2}\int_{\omega_1}^{\omega_2}|A_a^k|^2\theta(\omega_k)d\omega_k/(\nu+i\omega_k)}\,, \tag{49}$$

$$F_a^b(\nu)=\frac{i\hbar^{-1}A_a^b}{(\nu+i\omega_b)\left[\nu+i\omega_a+\hbar^{-2}\int_{\omega_1}^{\omega_2}|A_a^k|^2\theta(\omega_k)d\omega_k/(\nu+i\omega_k)\right]}, \tag{50}$$

ω_1, ω_2 are spectrum ends of the system, and $\theta(\omega_k)$ is the spectral density of states. These expressions are formally the same as in Eqs. (13) and (14) of Ref. 10 and lead to the definition of the complex transition width

$$\Gamma(i\eta\pm\epsilon)=-i\hbar^{-2}\int_{\omega_1}^{\omega_2}|A_a^k|^2\theta(\omega_k)d\omega_k/(\eta+\omega_k)\pm\pi\hbar^{-2}|A_a^k|^2\theta(-\eta_k)=-i\beta(\eta)\pm\gamma(\eta)\,. \tag{51}$$

The sign is + or − according to whether ν approaches the right- or the left-hand side of the cut.

In the simplified model where A_a^k and $\theta(\omega_k)$ can be taken as constant over the spectral range of interest

$$\Gamma=-i\frac{A^2\theta}{\hbar^2}\left(\ln\frac{\nu+i\omega_2}{\nu+i\omega_1}\right)_{\nu=i\eta\pm\epsilon}=-i\beta\pm\gamma\,, \tag{52}$$

ϵ real and positive infinitely small number, and

$$\beta=\frac{\gamma}{\pi}\ln\left|\frac{\eta+\omega_2}{\eta+\omega_1}\right|\,,\quad \gamma=\frac{\pi A^2\theta}{\hbar^2}\,. \tag{53}$$

Calculation of the original of $F(\nu)$ is straightforward if we ignore the η dependance of β. The result which is given in Eqs. (21) and (22) of Ref. 10 is in complete accordance with the unitary requirement.

In fact, in the present simple model, an explicit result to all orders can be set up. Since the matrix elements of the kernel $K=i\hbar^{-1}A$ are constant, the series appearing in (38) and (39) are easily summed up, yielding the result

$$F_a^a(\nu)=\frac{1}{\nu+i\omega_a-\dfrac{iA^2\theta}{\hbar^2}\ln\dfrac{\nu+i\omega_2}{\nu+i\omega_1}\left(1+\dfrac{A\theta}{\hbar}\ln\dfrac{\nu+i\omega_2}{\nu+i\omega_1}\right)^{-1}}\,, \tag{54}$$

$$F_a^b(\nu)=\frac{\dfrac{A}{i\hbar}\left(1+\dfrac{A\theta}{\hbar}\ln\dfrac{\nu+i\omega_2}{\nu+i\omega_1}\right)^{-1}}{(\nu+i\omega_b)\left[\nu+i\omega_a-\dfrac{iA^2\theta}{\hbar^2}\ln\dfrac{\nu+i\omega_2}{\nu+i\omega_1}\left(1+\dfrac{A\theta}{\hbar}\ln\dfrac{\nu+i\omega_2}{\nu+i\omega_1}\right)^{-1}\right]}\,. \tag{55}$$

Using the simplified notations (53)

$$F_a^a(\nu)=\frac{1}{\nu+i\omega_a-(i\beta\mp\gamma)[1-(i\hbar/A)(i\beta\mp\gamma)]^{-1}}\,,$$

$$F_a^b(\nu)=\frac{(A/i\hbar)[1-(i\hbar/A)(i\beta\mp\gamma)]^{-1}}{(\gamma+i\omega_b)\{\nu+i\omega_a-(i\beta\mp\gamma)[1-(i\hbar/A)(i\beta\mp\gamma)]^{-1}\}}\,.$$

We are led to define the complex transition width

$$-iB\pm\Gamma=\frac{-i\beta\pm\gamma}{1\mp(i\hbar/A)(i\beta\mp\gamma)}$$

$$=\frac{-i[\beta+\hbar(\beta^2+\gamma^2)/A]\pm\gamma}{(1+\hbar\beta/A)^2+\hbar^2\gamma^2/A^2}\,, \tag{56}$$

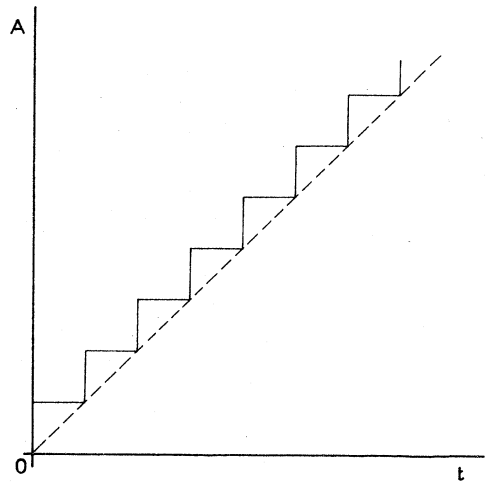

FIG. 2. Steps sequence tending towards a perturbation linearly increasing with time.

which permits us to rewrite Eqs. (54) and (55)

$$F_a^a(\nu)=\frac{1}{\nu+i\omega_a-iB\pm\Gamma}, \tag{57}$$

$$F_a^b(\nu)=\frac{(A/i\hbar)[1-(i\hbar/A)(i\beta-\gamma)]^{-1}}{(\nu+i\omega_b)(\nu+i\omega_a-iB\pm\Gamma)}. \tag{58}$$

This is again the same result as in Ref. 10 except for the new components of the complex width. The related original functions of time are

$$U_a^a(t)=\exp[-i(\omega_a-B)t-\Gamma t], \tag{59}$$

$$U_a^b(t)=\frac{A}{i\hbar}\,\frac{\exp(-i\omega_b t)}{1-(i\hbar/A)(i\beta-\gamma)}\,\frac{\exp[i(\omega_{ba}+B)t-\Gamma t]-1}{i(\omega_{ba}+B)-\Gamma}. \tag{60}$$

Hence, the total occupation probability on taking into account the definition (56) of Γ,

$$\sum_a |U_a^a(t)|^2+\sum_{b\neq a}|U_a^b(t)|^2=e^{-2\Gamma t}+\frac{\Gamma}{\pi}\int_{-\infty}^{+\infty}\frac{e^{-2\Gamma t}-2e^{-\Gamma t}\cos(\omega_{ba}+B)t+1}{(\omega_{ba}+B)^2+\Gamma^2}\,d\omega_b=1, \tag{61}$$

according to Eq. (25) of Ref. 10.

Of particular interest is often in applications the long-term behavior of the transition amplitudes. In the present problem this behavior can, of course, be directly derived from Eqs. (59) and (60) giving the result at any time, within the above approximation which consists of ignoring variations of the logarithm in Eqs. (54) and (55) throughout the transition width along the cut. It must be noticed, however, that the long-term limit could be obtained here in a more rigorous way without the calculation of the original functions (59) and (60).

We will make use of the following property of the Laplace transformation:

$$\lim_{t\to\infty}U(t)=\lim_{\nu\to+\infty}[\nu F(\nu)]. \tag{62}$$

If the transformed function is of the form $F(\nu)=f(\nu)/(\nu+i\omega)$, Eq. (62) will be more conveniently written as

$$\lim_{t\to\infty}U(t)=\exp(-i\omega t)\lim_{\nu\to+0}[\nu F(\nu-i\omega)]. \tag{63}$$

On applying this property to Eqs. (57) and (58), we obtain

$$U_a^a(t\to\infty)=0, \tag{64}$$

$$U_a^b(t\to\infty)=\frac{A}{i\hbar}\,\frac{1}{1-(i\hbar/A)(i\beta-\gamma)}\,\frac{\exp(-i\omega_b t)}{i(\omega_{ab}-B)+\Gamma}. \tag{65}$$

with the same definition of γ, as before, and the following more accurate definition of β:

$$\beta=\frac{A^2\theta}{\hbar^2}\ln\frac{\omega_2-\omega_a}{\omega_1-\omega_a}.$$

This is, therefore, the best choice for the constant value of β as time is increased. The limiting values (64) and (65) are identical to those deduced from Eqs. (59) and (60).

It may look surprising that the essential of the result is finally the same as in Ref. 10 in spite of the dropping of the selection rules which now allows the external field A to induce successive transitions in the system. The reason for this lies in the constant value of A which entails energy conservation. If we imagine that the system was submitted to successive steps, resulting in an overall finite value of the mean derivative dA/dt (Fig. 2), the occupation probability distribution would be getting further spread out from one step to the next one, and the final distribution in increasing time would, of course, extend uniformly throughout the allowed spectrum.

V. CONCLUSION

The general solution of the time-dependent Schrödinger equation for a constant or harmonic external applied field has been put into a so-called reduced determinantal form derived from the Fredholm-Laplace solution. This new form of the solution, which only requires a quite elementary mathematical apparatus, is capable of yielding approximate expressions of the evolution operator to definite order with respect to the collision potential and the applied external field, which both

bring out the physically expected multiple transitions structure and the associated transition width resulting from natural and collisional broadening. Particularly emphasized is the absence of secular contributions which is the reason why the expected unitarity of the transition amplitudes is guaranteed at any time, unlike that which occurs in usual perturbation series which is only an "initial-rate" approach. A similar formalism can be worked out in the density-matrix formalism and will be published in a forthcoming paper.

APPENDIX A: EXPONENTIAL EXPRESSIONS OF FREDHOLM DETERMINANTS

In this appendix convenient methods of performing calculations on determinant expansions are set up and applied to specific cases encountered in the text. The methods will also prove useful in further developments of the theory.

Let us write the explicit expression of the Fredholm determinant D. It is always permissible to assume the first row (and column) is that of the a state and the second one that of the b state.

$$D=\begin{vmatrix} 1+K_a^a/d_a & K_b^a/d_a & K_c^a/d_a\cdots \\ K_a^b/d_b & 1+K_b^b/d_b & K_c^b/d_b \\ K_a^c/d_c & K_b^c/d_c & 1+K_c^c/d_c \\ \vdots & & \end{vmatrix} . \tag{A1}$$

Introduce the n-times iterated kernel as

$$S_n=\frac{K_l^k K_m^l K^m\cdots K_k^r}{d_k d_l d_m\cdots d_r}, \tag{A2}$$

with implicit summations over the n indices k, l, $m,\ldots,r$ and without any index restriction. D can be put into the form[12]

$$D=\exp\left(\frac{S_1}{1}-\frac{S_2}{2}+\frac{S_3}{3}-\cdots+(-)^{n+1}\frac{S_n}{n}+\cdots\right) . \tag{A3}$$

This equation can be used for finite as well as for infinite order. For instance, on expanding the exponential, we obtain the following expression of a 4×4 determinant:

$$D_4=1+\frac{S_1}{1}+\frac{S_1^2-S_2}{2}+\left(\frac{S_1^3}{6}-\frac{S_1S_2}{2}+\frac{S_3}{3}\right)+\left(\frac{S_1^4}{24}-\frac{S_1^2S_2}{4}+\frac{S_2^2}{8}+\frac{S_1S_3}{3}-\frac{S_4}{4}\right) . \tag{A4}$$

The successive bracketed terms represent the determinants of order $0,1,\ldots,4$, which are obtained in the ordinary Cayley expansion. S_1 vanishes if the diagonal elements K_j^j are zero. As pointed out in the text, the absence of the index restrictions $k\neq l\neq m\neq,\ldots,$ which normally appears in the direct development of (A1), is irrelevant.

Of course the fifth- and higher-order determinants could also be written in Eq. (A4). However, because the order of the iterated kernel would then be larger than the number of states, index repetition could never be avoided so that these additional contributions would correspond to determinants with, at least, two identical rows and columns and therefore of zero value.

With the help of the operator $d=\nu+i\hbar^{-1}H_0$, S_n can be written as

$$S_n=\mathrm{Tr}(d^{-1}K)^n . \tag{A5}$$

It is then readily recognized that the exponential form (A3) can be given the formal expression

$$D=\det(I+d^{-1}K)=\exp\mathrm{Tr}\ln(I+d^{-1}K) , \tag{A6}$$

which is made use of in the text. I is the identity operator. We note the property

$$\det(I+AB)=\det(I+BA) , \tag{A7}$$

which results from permutations under the trace. Similar expressions can be written for the minors D_a^a, D_a^b. Let P_a be the projector on the a state and Q_a the projector on the complementary space, with the obvious properties

$$P_a+Q_a=I,\quad P_aQ_a=Q_aP_a=0 .$$

Elimination of the a row and the a column, in D_a^a, is equivalent to replace the kernel K with Q_aKQ_a,

$$D_a^a=\det(I+d^{-1}Q_aKQ_a) ,$$

or using Eq. (A7)

$$D_a^a=\det(I+Q_ad^{-1}K)=\det(I+d^{-1}KQ_a) . \tag{A8}$$

From Eqs. (A6) and (A8) an operational expression of the expanded iterative form of $F_a^a=D_a^a/d_aD$ can easily be derived. We have

$$D_a^a/D=\det[(I+Q_ad^{-1}K)(I+d^{-1}K)^{-1}] ,$$

writing $Q_aK=K-P_aK$, rearranging and using Eq. (A6)

$$D_a^a/D=\exp\mathrm{Tr}\ln[I-P_ad^{-1}K(I+d^{-1}K)^{-1}] . \tag{A9}$$

It is straightforward to verify that for any operator A

$$\mathrm{Tr}\ln(I+P_aA)=\ln(1+\langle a|A|a\rangle) , \tag{A10}$$

whence

$$F_a^a=D_a^a/d_aD=d_a^{-1}[1-\langle a|d^{-1}K(I+d^{-1}K)^{-1}|a\rangle]=d_a^{-1}\langle a|(I+d^{-1}K)^{-1}|a\rangle=\langle a|(d+K)^{-1}|a\rangle , \tag{A11}$$

which is the result (24).

As to the minor D_a^b $(b\neq a)$ we will start with the expression (A1) of D (with $K_a^a=K_b^b=\cdots=0$). Making use of the elementary properties of determinants, the structure of D_a^b can be written as

$$D_a^b = \begin{vmatrix} 0 & 1 & 0 & 0 \\ K & 0 & K & K \\ K & 0 & 1 & K \\ K & 0 & K & 1 \end{vmatrix} = \begin{vmatrix} 1 & 1 & 0 & 0 \\ K & 1 & K & K \\ K & 0 & 1 & K \\ K & 0 & K & 1 \end{vmatrix} + \begin{vmatrix} -1 & 1 & 0 & 0 \\ 0 & 1 & K & K \\ 0 & 0 & 1 & K \\ 0 & 0 & K & 1 \end{vmatrix} + \begin{vmatrix} 0 & 0 & 0 & 0 \\ K & -1 & K & K \\ K & 0 & 1 & K \\ K & 0 & K & 1 \end{vmatrix}$$

(d^{-1} factors are omitted). The third determinant on the right is zero. We thus obtain

$$D_a^b = \det(I + Q_a d^{-1} K Q_b + |a\rangle\langle b|) - \det(I + Q_a d^{-1} K Q_b); \tag{A12}$$

$|a\rangle\langle b|$ stands for the element 1 in the first row of the second column. For the derivation of the iterative form of $F_a^b = D_a^b / d_a D$, we first substitute $Q_a = I - P_a$, $Q_b = I - P_b$ in Eq. (A12), which gives

$$D_a^b = \det(I + d^{-1}K - P_a d^{-1}K - d^{-1}KP_b + P_a d^{-1}KP_b + |a\rangle\langle b|) - \det(I + d^{-1}K - P_a d^{-1}K - d^{-1}KP_b + P_a d^{-1}KP_b),$$

whence from Eq. (A6),

$$D_a^b D^{-1} = \det[I - (P_a d^{-1}K + d^{-1}KP_b - P_a d^{-1}KP_b - |a\rangle\langle b|)(I + d^{-1}K)^{-1}]$$
$$- \det[I - (P_a d^{-1}K + d^{-1}KP_b - P_a d^{-1}KP_b - |a\rangle\langle b|)(I + d^{-1}K)^{-1}]. \tag{A13}$$

The first determinant on the right-hand side is of the form $\det(I + S + P_a T)$. $P_a T$ is a matrix involving nonzero elements in the a row only. By separating out the elements of the same row pertaining to $I + S$, we have

$$\det(I + S + P_a T) = \det(I + S) + \det(I + Q_a S + P_a T) - \det(I + Q_a S). \tag{A14}$$

Let us now apply the latter identity to the first determinant in Eq. (A13). We readily obtain after simplification and arrangement

$$D_a^b D^{-1} = \exp \mathrm{Tr} \ln[I - (I + d^{-1}K)^{-1}(Q_a d^{-1}KP_b - |a\rangle\langle b|)] - \exp \mathrm{Tr} \ln[I - (I + d^{-1}K)^{-1} Q_a d^{-1}KP_b],$$

using then the property (A10):

$$D_a^b D^{-1} = 1 - \langle b|(I + d^{-1}K)^{-1} Q_a d^{-1}K|b\rangle + \langle b|(I + d^{-1}K)^{-1}|a\rangle - 1 + \langle b|(I + d^{-1}K)^{-1} Q_a d^{-1}K|b\rangle.$$

whence

$$F_a^b = d_a^{-1}\langle b|(I + d^{-1}K)^{-1}|a\rangle. \tag{A15}$$

The reduced determinantal forms of F_a^a and F_a^b [Eqs. (34) and (37)] can also be easily derived by using Eqs. (A6), (A7), and (A12). Writing $d^{-1}K = P_a d^{-1}K + Q_a d^{-1}K$ in (A6) and proceeding as in (A9), we have

$$D(D_a^a)^{-1} = \det[(I + Q_a d^{-1}K + P_a d^{-1}K)(I + Q_a d^{-1}K)^{-1}] = \exp \mathrm{Tr} \ln[I + P_a d^{-1}K(I + Q_a d^{-1}K)^{-1}],$$

using then, the property (A10),

$$D(D_a^a)^{-1} = 1 + d_a^{-1}\langle a|K(I + Q_a d^{-1}K)^{-1}|a\rangle, \tag{A16}$$

whence

$$F_a^a = 1/d_a D(D_a^a)^{-1} = 1/[d_a + \langle a|K(I + Q_a d^{-1}K)^{-1}|a\rangle]. \tag{A17}$$

For calculating F_a^b, we first substitutes $Q_b = I - P_b$ in (A12):

$$D_a^b = \det(I + Q_a d^{-1}K - Q_a d^{-1}KP_b + |a\rangle\langle b|) - \det(I + Q_a d^{-1}K - Q_a d^{-1}KP_b),$$

whence

$$D_a^b (D_a^a)^{-1} = \exp \mathrm{Tr} \ln[I - (I + Q_a d^{-1}K)^{-1}(Q_a d^{-1}KP_b - |a\rangle\langle b|)] - \exp \mathrm{Tr} \ln[I - (I + Q_a d^{-1}K) Q_a d^{-1}KP_b] = \langle b|(I + Q_a d^{-1}K)^{-1}|a\rangle, \tag{A18}$$

and

$$F_a^b = \frac{D_a^b (D_a^a)^{-1}}{d_a D (D_a^a)^{-1}} = \frac{\langle b|(I + Q_a d^{-1}K)^{-1}|a\rangle}{d_a + \langle a|K(I + Q_a d^{-1}K)^{-1}|a\rangle} = -\frac{\langle b|d^{-1}K(I + Q_a d^{-1}K)^{-1}|a\rangle}{d_a + \langle a|K(I + Q_a d^{-1}K)^{-1}|a\rangle}. \tag{A19}$$

APPENDIX B: FACTORIZATION OF FREDHOLM DETERMINANT D

We develop in this appendix a group theoretical argument to show that the calculation of the original of $F_a^a(\nu)$, $F_a^b(\nu)$ only involves a definite set of single poles which is defined by the selection rules of the transition under consideration.

The determinant D can be factorized out into determinants of lower order, in connection with the completely reduced representation of the symmetry group of the complete Hamiltonian $H_0 - i\hbar K$ (Fig. 3). Multiple roots refer to degenerate eigenvalues, which, in turn correspond to multidimensional irreducible representations. The determinant pertaining to such a representation is then blocked out into a number of independent and identical blocks equal to the multiplicity of the degenerate level. The order of each block is the number of times the relevant irreducible representation appears in the completely reduced representation. Since H_0 is invariant in the symmetry group of $H_0 - i\hbar K$, this decomposition can be written on the basis of the eigenstates of H_0. In Fig. 3, β and β' (which refer to a twofold level) have equal elements in corresponding positions.

Let us now consider the quotients D_a^a/d_aD, D_a^b/d_aD. Of course, the a row and the a column cross inside a definite block, say β in Fig. 3, but the same is true for the crossing point of the b row and the a column relative to an a-b transition. Indeed if the crossing point (a,b) would fall outside all of the blocks, no transition could ever occur, at any order, between a and b states. As a result, the quotients D_a^a/d_aD and D_a^b/d_aD simplify into the quotient of only the minor and the determinant pertaining to the relevant block β. In a more precise way Eqs. (18) and (19) and (38) and (39) can also be regarded as expanded form of the following:

$$F_a^a = D_a^{a(\beta)}/d_aD^{(\beta)} = 1/d_aD^{(\beta)}(D_a^{a(\beta)})^{-1}, \tag{B1}$$

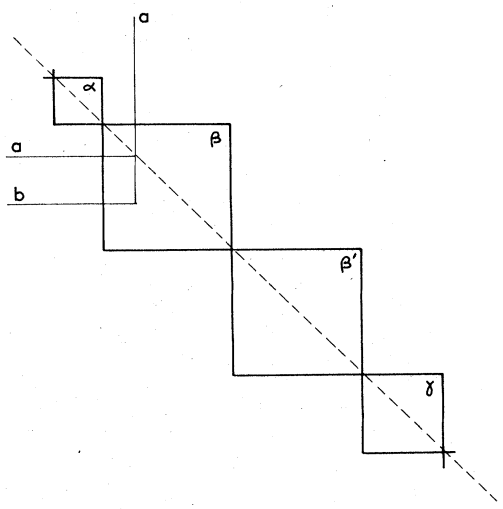

FIG. 3. Schematic structure of the Fredholm determinant on a symmetric states basis. β and β' are equal blocks referring to a two-dimensional irreducible representation of the symmetry group.

$$F_a^b = D_a^{b(\beta)}/d_aD^{(\beta)} = D_a^{b(\beta)}(D_a^{a(\beta)})^{-1}/d_aD^{(\beta)}(D_a^{a(\beta)})^{-1}, \tag{B2}$$

so that the energy of a degenerate level cannot appear more than once as a pole of F_a^a or F_a^b. The effect of accidental degeneracies is removed the same was as in Eqs. (46) and (47). The originals can be written in the form similar to Eqs. (46) and (47)

$$U_a^a(t) = \sum_N n \frac{\partial \Omega_N^{(\beta)}}{\partial \omega_a} \exp(-i\Omega_N^{(\beta)}t), \tag{B3}$$

$$F_a^b(t) = \sum_N in \frac{\partial \Omega_N^{(\beta)}}{\partial K_b^a} \exp(-i\Omega_N^{(\beta)}t), \tag{B4}$$

where summations are now restricted to the irreducible representation β.

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