Unitary solution for an evolution operator in quantum mechanics

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The Fredholm method for solving linear integral equations can yield a unitary solution for a Schrödinger equation of an evolution operator. Explicit results are derived in the simple case of an atomic system undergoing transitions towards a continuum of constant density of states after the application of a constant perturbation.

I. INTRODUCTION

As is well known, the usual perturbation series does not lead to a unitary solution for a Schrödinger equation of an evolution operator. Furthermore, the accuracy of the series depends on the relevant interval of time, and its convergence is limited by the magnitude of the applied perturbation. For these reasons, various attempts have been undertaken, during recent years, to improve the classical treatment.[1-3]

In the present paper, an elementary formalism based on the conjugate use of the Laplace transformation and the Fredholm method for solving multidimensional integral equations is developed for the integral Schrödinger equation of an evolution operator (Sec. II). The application will be restricted to a schematic atomic system undergoing transitions from an initial state a towards a continuum of states b, as a result of the application of a Heaviside unit-step perturbation (Sec. III).

II. FREDHOLM-LAPLACE FORMALISM IN A SIMPLE MODEL

In 1900, Fredholm[4] published a famous report in which he developed a general method for solving linear integral equations. The main feature of the Fredholm analysis consisted in regarding the integral equation as the limit of a finite linear system. This is particularly well suited to the discrete nature in quantum mechanics of the spectrum of natural systems. Strictly speaking, the continuous spectrum of a bounded system appears, indeed, as a limit of the highly dense, real discrete spectrum.

Consider a physical system of unperturbed Hamiltonian H_0 exposed, from $t=0$, to an external potential $A(t)$. The complete Hamiltonian is

$$H = H_0 + A(t). \tag{1}$$

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

$$\frac{dU}{dt} = (i\hbar)^{-1}[H_0 + A(t)]U(t),$$

or, in the integral form,

$$U(t) = 1 + (i\hbar)^{-1}\int_0^t [H_0 + A(t')]U(t')dt'. \tag{2}$$

It is convenient to introduce the Laplace transform of $U(t)$:

$$F(\nu) = \int_0^\infty U(t')e^{-\nu t'}dt'.$$

If the perturbation is assumed constant for $t > 0$, $F(\nu)$ is a solution of the equation

$$\nu F(\nu) = 1 + (1/i\hbar)(H_0 + A)F(\nu). \tag{3}$$

Let $\epsilon_k = \hbar\omega_k$ be the eigenvalues of H_0. The matrix elements F_a^b of F, in the basis of the eigenfunctions of H_0, are solutions of the linear system

$$\nu F_a^b = \delta_a^b + \frac{1}{i\hbar}\left(\epsilon_b F_a^b + \sum_k A_k^b F_a^k\right)$$

or

$$(\nu + i\omega_b)F_a^b = \delta_a^b + \sum_k \frac{A_k^b}{i\hbar} F_a^k. \tag{4}$$

δ_a^b is the Kronecker delta. From now on, the summation on repeated state indices k will be omitted and we will put

$$\nu + i\omega_b = d_b.$$

The diagonal matrix elements of A which are not able to induce transitions between the states of H_0 may be equated to zero without loss of generality. It will be assumed, in addition, that transitions can only occur from a definite state a towards a continuum of states $b, c, \ldots, k, l, m, \ldots$. Thus we have

$$A_k^k = 0, \quad A_a^k \neq 0, \quad A_k^l = 0 \text{ if } kl \neq a. \tag{5}$$

Equation (4) can now be written in the simpler form

$$F_a^b = \delta_a^b/d_a + (A_k^b/i\hbar d_b)F_a^k. \tag{6}$$

This linear system is the Schrödinger equation for $F(\nu)$. Note that in the general case, a distinct linear system is obtained for each state a, which behaves like a label. Dropping for the time being the subscript a, we will rewrite Eq. (6) in the compact form

$$F^b + (K_l^b/d_b)F^l = \delta^b/d_b\,, \tag{7}$$

where $K_l^b/d_b = -A_l^b/i\hbar d_b$ is the kernel in which, for clarity in the following, the denominator d_b is separated out. Upon solving (7) by Cramer's theorem, we obtain

$$F^b = N^b/D\,, \tag{8}$$

where D is the determinant of the system and N^b the determinant obtained from D by replacing the coefficients of F^b by δ^b/d_b.

Consider first the expression for D:

$$D = \begin{vmatrix} 1 & K_b^a/d_a & K_c^a/d_a & \cdots \\ K_a^b/d_b & 1 & K_c^b/d_b & \cdots \\ K_a^c/d_c & K_b^c/d_c & 1 & \cdots \\ \cdots & \cdots & \cdots & \end{vmatrix}. \tag{9}$$

In order to obtain an expansion in successive powers of the applied field A, this determinant is expanded with respect to the principal diagonal. The result is

$$D = 1 - \frac{K_l^k K_k^l}{2!d_k d_l} + \frac{2}{3!}\frac{K_l^k K_m^l K_k^m}{d_k d_l d_m} + \cdots . \tag{10}$$

A similar expression can be derived for the determinant N_a^b by replacing the elements of the b column in D with δ_a^b/d_b:

$$N_a^b = \delta_a^b - \frac{K_a^b}{d_b d_a} + \frac{K_k^b K_a^k}{d_b d_k d_a} + \cdots . \tag{11}$$

Hence we obtain for the diagonal and nondiagonal matrix elements of $F(\nu)$,

$$F_a^a = \frac{1}{d_a(1 - K_l^k K_k^l/2d_k d_l + \cdots)}\,,$$

$$F_a^b = \frac{-K_a^b + K_l^b K_a^l/d_l + \cdots}{d_b d_a(1 - K_l^k K_k^l/2d_k d_l + \cdots)}\,. \tag{12}$$

We now return to the explicit form of the kernel K, including the selection rules assumed in (5):

$$F_a^a = (d_a + |A_a^k|^2/\hbar^2 d_k + \cdots)^{-1}$$

$$= [\nu + i\omega_a + |A_a^k|^2/\hbar^2(\nu + i\omega_k) + \cdots]^{-1}, \tag{13}$$

$$F_a^b = \left(\frac{A_a^b}{i\hbar} + \frac{|A_a^k|^2}{\hbar^2 d_k} + \cdots\right)\left[\, d_b\left(d_a + \frac{|A_a^k|^2}{\hbar^2 d_k} + \cdots\right)\right]^{-1}$$

$$= \frac{A_a^b}{i\hbar}\left[(\nu + i\omega_b)\left(\nu + i\omega_a + \frac{|A_a^k|^2}{\hbar^2(\nu + i\omega_k)} + \cdots\right)\right]^{-1}. \tag{14}$$

Equation (14) is restricted to the linear response. The expressions so obtained for the Laplace transform of an evolution operator include in the denominators the quantum broadening up to second order in the applied field. Since the final states k belong to a quasicontinuum, the complex width can be calculated by means of an integration,

$$\Gamma_a(\nu) = \sum_k \frac{|A_a^k|^2}{\hbar^2(\nu + i\omega_k)} = \int_{\omega_1}^{\omega_2} \frac{|A_a^k|^2 \theta(\omega_k)\, d\omega_k}{\hbar^2(\nu + i\omega_k)}\,, \tag{15}$$

where ω_1 and ω_2 denote the bounds of the continuous spectrum, and $\theta(\omega_k)$ the spectral density of states. As far as $\theta(\omega_k)$ is a continuous function in the range (ω_1, ω_2), the integral in (15) is an integral of Cauchy's type which defines an analytic function of ν, outside the cut $(-i\omega_2, -i\omega_1)$ on the imaginary axis.

As a result, the calculation of the original of (13) or (14) can be reduced to an integration along this cut (Fig. 1). In addition, the main contribution comes from the vicinity of the initial energy ω_a. In this region ($\nu = i\eta \pm \epsilon$, with $\epsilon \to +0$ and $\eta \sim -\omega_a$) the value of Γ_a is[5]

$$\Gamma_a(i\eta \pm \epsilon) = -i\beta_a \pm \gamma_a = -\frac{i}{\hbar^2}\int_{\omega_1}^{\omega_2} \frac{|A_a^k|^2 \theta(\omega_k)\, d\omega_k}{\eta + \omega_k}$$

$$\pm \frac{\pi}{\hbar^2}\left[\, |A_a^k|^2 \theta(-\eta)\right]_{\eta = -\omega_a}\,, \tag{16}$$

where β_a is the frequency shift and γ_a the transition width; the sign is "+" or "−" according to whether the cut is approached from the right- or

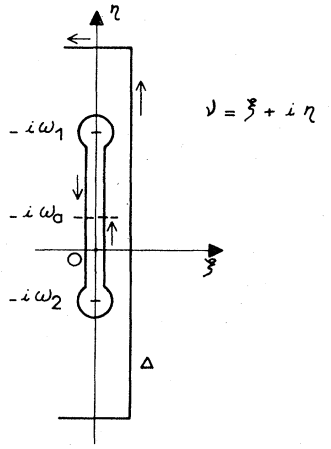

FIG. 1. Contour used for calculating the original Laplace transform of the evolution operator in the complex ν (ξ, η) plane.

left-hand side.

An explicit calculation for a somewhat simplified case is given in Sec. III.

III. COMPLEX TRANSITION WIDTH AND EVOLUTION OPERATOR FOR CONSTANT MATRIX ELEMENTS AND DENSITY OF STATES

Since transitions occur toward states b of the continuum with energy $\omega_b \sim \omega_a$, it is permissible to assume constant matrix elements A_a^k and constant spectral density θ in the range of interest. This will soon become evident. With these assumptions the complex transition width Γ_a can be explicitly calculated as follows:

$$\Gamma_a = \sum_k \frac{|A_a^k|^2}{\hbar^2(\nu + i\omega_k)} \simeq -i\frac{|A|^2\theta}{\hbar^2} \ln\frac{\nu + i\omega_2}{\nu + i\omega_1}, \quad (17)$$

i.e., on each side of the cut ($\nu = i\eta \pm \epsilon$),

$$\Gamma_a(i\eta \pm \epsilon) = -i\beta_a \pm \gamma_a = -i\frac{\gamma_a}{\pi} \ln\left|\frac{\eta + \omega_2}{\eta + \omega_1}\right| \pm \gamma_a, \quad (18)$$

where $\gamma_a = \pi|A|^2\theta/\hbar^2$.

Owing to expression (17), one gets for the original F_a^b, given by Eq. (14),

$$U_a^b(t) = \frac{A_a^b}{i\hbar}\frac{1}{2\pi i}\int_\Delta e^{\nu t}\, d\nu \Big/ (\nu + i\omega_b)\left(\nu + i\omega_a - \frac{i\gamma_a}{\pi}\ln\frac{\nu + i\omega_2}{\nu + i\omega_1}\right)$$

$$= \frac{A_a^b}{i\hbar} e^{-i\omega_b t}\int_0^t e^{i\omega_b t'}\frac{dt'}{2\pi i}\int_\Delta e^{\nu t'} d\nu \Big/ \left(\nu + i\omega_a - \frac{i\gamma_a}{\pi}\ln\frac{\nu + i\omega_2}{\nu + i\omega_1}\right). \quad (19)$$

Δ is any vertical axis on the right-hand side of the singularities of the integrand. Here, these singularities reduce to the logarithmic cut, so that the integral on the right-hand side in (19) can be written

$$\frac{1}{2\pi i}\int_\Delta e^{\nu t'} d\nu \Big/ \left(\nu + i\omega_a - \frac{i\gamma_a}{\pi}\ln\frac{\nu + i\omega_2}{\nu + i\omega_1}\right) = \frac{1}{2\pi i}\left[\int_{-\omega_2}^{-\omega_1} e^{i\eta t'} i\, d\eta \Big/ \left(i\eta + i\omega_a - \frac{i\gamma_a}{\pi}\ln\left|\frac{\eta + \omega_2}{\eta + \omega_1}\right| + \gamma_a\right)\right.$$

$$\left. - \int_{-\omega_2}^{-\omega_1} e^{i\eta t'} i\, d\eta \Big/ \left(i\eta + i\omega_a - \frac{i\gamma_a}{\pi}\ln\left|\frac{\eta + \omega_2}{\eta + \omega_1}\right| - \gamma_a\right)\right]. \quad (20)$$

The two integrals on the right-hand side cancel at large distances. As expected, the calculation is thus localized in the vicinity of the frequency ω_a along the cut. It follows that the limits of integration can be taken as $\pm\infty$ without appreciable error, and the natural logarithm can be regarded as constant, with the value

$$\frac{i\gamma_a}{\pi}\ln\left|\frac{\eta + \omega_2}{\eta + \omega_1}\right| \simeq -\frac{i\gamma_a}{\pi}\ln\left|\frac{-\omega_a + \omega_2}{-\omega_a + \omega_1}\right| = -i\beta_a.$$

Finally, the integration in Eq. (20) can be readily performed, and yields

$$\frac{1}{2\pi i}\int_\Delta e^{\nu t} d\nu \Big/ \left(\nu + i\omega_a - i\gamma_a \ln\frac{\nu + i\omega_2}{\nu + i\omega_1}\right)$$

$$= \frac{1}{2\pi i}\left(\int_{-\infty}^{+\infty} \frac{e^{i\eta t} i\, d\eta}{i\eta + i\omega_a - i\beta_a + \gamma_a} - \int_{-\infty}^{+\infty} \frac{e^{i\eta t} i\, d\eta}{i\eta + i\omega_a - i\beta_a - \gamma_a}\right)$$

$$= \exp[-i(\omega_a - \beta_a)t - \gamma_a t].$$

Hence, from (19) we obtain

$$U_a^b(t) = \frac{A_a^b}{\hbar} e^{-i\omega_b t}\frac{\exp[i(\omega_{ba} + \beta_a)t - \gamma_a t] - 1}{i(\omega_{ba} + \beta_a) - \gamma_a}. \quad (21)$$

Similarly, for the diagonal element (13) we get

$$U_a^a(t) = \exp[-i(\omega_a - \beta_a)t - \gamma_a t]. \quad (22)$$

Expressions (21) and (22) are classical results which can be obtained by particular approximation methods.[6] The verification of the unitarity is straightforward. The probability for the system to be in state a or any state b at time t are given by

$$|U_a^a(t)|^2 = e^{-2\gamma_a t}, \quad (23)$$

$$|U_a^b(t)|^2 = \frac{|A_a^b|^2}{\hbar^2}\frac{e^{-2\gamma_a t} - 2e^{-\gamma_a t}\cos(\omega_{ba} + \beta_a)t + 1}{(\omega_{ba} + \beta_a)^2 + \gamma_a^2}, \quad (24)$$

respectively. After summing and using the above simplifying assumptions, we obtain

$$
\begin{aligned}
&|U_a^a(t)|^2 + \sum_b |U_a^b(t)|^2 \\
&= e^{-2\gamma_a t} + \int_{-\infty}^{+\infty} \frac{|A_a^b|^2}{\hbar^2} \\
&\qquad \times \frac{e^{-2\gamma_a t} - 2e^{-\gamma_a t}\cos(\omega_{ba}+\beta_a)t + 1}{(\omega_{ba}+\beta_a)^2 + \gamma_a^2}\theta\, d\omega_b \\
&= e^{-2\gamma_a t} + \frac{\gamma_a}{\pi}\left(e^{-2\gamma_a t}\frac{\pi}{\gamma_a} - 2e^{-\gamma_a t}\frac{\pi}{\gamma_a}e^{-\gamma_a t} + \frac{\pi}{\gamma_a}\right) = 1.
\end{aligned}
\tag{25}
$$

IV. CONCLUSION

The general method discovered by Fredholm for solving a linear multidimensional integral equation has been applied to the integral Schrödinger equation in quantum mechanics, and leads to correct expressions for the diagonal and nondiagonal matrix elements of an evolution operator.

The illustration of the method is restricted here to the transition of an atomic system, exposed to a constant perturbation, toward a continuum of constant density of states.

Dropping the above simplifying assumptions, the method can be pushed further in various physical situations. However, a mathematical transformation is then required, in the general case, to eliminate spurious terms with no physical significance that appear in expansions (10) and (11) of the determinants. This will be studied in forthcoming publications in connection with more specific problems.

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