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Nonperturbative Approach to the Theory of Transition Probabilities

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A nonperturbative approach to the theory of transition probabilities is presented. The results of this theory are employed to investigate the validity of the assumptions inherent in the perturbative approach. For this purpose, the simple examples of absorption of radiation (first-order process) and Raman scattering (second-order process) are used. The method proposed, which is based upon finite-difference techniques, represents an accurate solution of the time-dependent Schrödinger equation in a given representation and has many advantages over methods based upon the perturbation series.

INTRODUCTION

In several recent papers[1,2] attention has been drawn to the conditions which are necessary to define the concept of "transition probability per unit time" within the framework of time-dependent perturbation theory. Since the most important formula of perturbation theory is the widely used "golden rule" for the transition probability per unit time, the validity of the assumptions employed to derive the rule is a matter of some importance. Briefly, the necessary conditions[3-5] are that the time should be sufficiently long that energy conservation can be assured and yet sufficiently short that the total probability of transition is small. At first sight, these conditions appear to be somewhat contradictory, but, in the absence of an accurate expression for the transition probability, there appears to be little possibility of ascertaining the correctness of the assumptions.

Brooks and Scarfone[1] have recently investigated this problem by a modified form of perturbation theory which still employs the idea of an infinite-series expansion, but in which it is comparatively easy to guarantee such necessary properties as the unitarity of transition amplitudes.

In this paper, we shall describe an accurate method by means of which transition amplitudes may be calculated and, therefore, by means of which the aforementioned difficulties may be resolved. Before doing so, however, it will be useful to survey the advantages and disadvantages of the perturbation-series approach to the calculation of transition probabilities.

This approach has an advantage which the alternative we shall propose does not possess: that a formal expression can be written for the transition amplitude. This formal expression, as an infinite series, cannot be employed in practice, it being necessary in general to terminate it at the first relevant nonvanishing term. For certain simple processes this technique appears to be fairly satisfactory, but for many others, such as the amplitude for a low-energy collision, it is certainly inadequate. Furthermore, this approach, since it is an "initial-rate" theory, cannot adequately describe important cases which involve single and multiple resonances. In addition, the calculated transition amplitudes are not ordinarily unitary.

The alternative which we shall propose is not based upon perturbation theory and has none of the disadvantages inherent in such methods. On the other hand, since numerical techniques are involved, analytic expressions cannot be written for the transition amplitudes. In spite of this, the corresponding equations do possess essentially all of the information represented in the corresponding perturbation-series expressions. Thus, for example, energy conservation, selection rules, etc., are easily distinguished.

The organization of the paper is as follows. The theory of the probability of transition to a given state is first discussed by means of perturbation theory and by the alternative finite-difference method. The resulting transition probabilities are compared using an example similar to that of Brooks and Scarfone.[1] Transitions to states within the continuum are then examined, and the concept of a time-independent transiton probability per unit time investigated. Comparative calculations are carried out for a "second-order" process, namely, Raman scattering, to compare the results for first- and second-order processes. Finally, the transition probability for resonance Raman scattering[6] is calculated, illustrating the ease with which resonances can be treated by means of the numerical method.

PROBABILITY OF TRANSITION BETWEEN TWO GIVEN STATES

We shall, first of all, consider transitions from a given initial state $|i\rangle$ of the system to a given final state $|f\rangle$, the problem of transitions to states of the continuum being subsequently discussed.

The conventional perturbation-series approach to the theory of transition probabilities is admirably described in a number of texts.[3-5] Here we shall mention only those formulas relevant to our interest.

Irrespective of how one might define a "transition probability per unit time," it is always possible to define the probability of transition:

$$W_{i\to f}(t) = |\langle f|U(t,t_0)|i\rangle|^2, \tag{1}$$

where $U(t,t_0)$ is the evolution operator defined by the relation

$$|\Psi(t)\rangle = U(t,t_0)|\Psi(t_0)\rangle. \tag{2}$$

The problem of calculating the transition probability reduces to that of calculating the transition amplitude $\langle f|U(t,t_0)|i\rangle$ which, in turn, is equivalent to solving the time-dependent Schrödinger equation in the chosen representation.

Following the perturbation-series approach, $U(t,t_0)$ is expanded as an infinite series:

$$U(t,t_0) = U_0(t,t_0) + \sum_{n=1}^{\infty} U^{(n)}(t,t_0), \tag{3}$$

where

$$U^{(n)}(t,t_0) = (i\hbar)^{-n}\int d\tau_n, \ldots, d\tau_1\, U_0(t,\tau_n)V(\tau_n)$$

$$\times U_0(\tau_n,\tau_{n-1})\ldots U_0(\tau_1,t_0), \tag{4}$$

$$t > \tau_n > \tau_{n-1}, \ldots, > t_0 .$$

The transition amplitude then becomes

$$\langle f|U(t,t_0)|i\rangle = \sum_n \langle f|U^{(n)}(t,t_0)|i\rangle, \tag{5}$$

where, as usual, we assume that $\langle f|U^{(0)}(t,t_0)|i\rangle$.

As it stands, Eq. (5) is more a formal, rather than an operational, expansion. Since only the first few terms may be retained in practice, the resulting approximate formulas can only be valid for short times. Even if one retains only the first nonvanishing term, the resulting expression is not necessarily simply evaluated, since it may involve (second- and higher-order terms) sums over complete states of operator products. In passing, it is worth noting that much of this difficulty does not occur in the theory to be described in this paper, since sums rather than products of operators are involved. In itself, this represents an enormous advantage over the perturbation-series approach.

To formulate the alternative approach to the calculation of transition amplitudes, we return to the original problem of solving the time-dependent Schrödinger equation in a given representation. Making the usual assumption that $|\Psi(t)\rangle$ may be expanded in terms of some complete set of orthonormal basis functions

$$|\Psi(t)\rangle = \sum_j a_j(t)|\phi_j(t)\rangle, \tag{6}$$

the Schrödinger equation reduces to the following well-known equation for the coefficients $a_j(t)$:

$$i\hbar\frac{da_k}{dt}(t) = \sum_j a_j(t)V_{kj}(t), \tag{7}$$

where

$$V_{kj}(t) = \langle\phi_k(t)|V(t)|\phi_j(t)\rangle . \tag{8}$$

Since

$$a_f(t) = \langle\phi_f(t)|\Psi(t)\rangle$$

$$= \langle\phi_f(t)|U(t,t_0)|\Psi(t_0)\rangle, \tag{9}$$

it is obvious that

$$a_f(t) = \langle\phi_f(t)|U(t,t_0)|\phi_i(t_0)\rangle \tag{10}$$

if the initial state $|i\rangle = |\Psi(t_0)\rangle = |\phi_i(t_0)\rangle$. Evaluation of the time-dependent coefficients, i.e., solution of the set of equations (7), is therefore completely equivalent to calculating the complete transition amplitude.

The method of solving the set of equations (7) which will be employed in this paper is as follows: First, we rewrite (7) in matrix form

$$(i\hbar)\frac{d}{dt}\,\underline{a}(t) = \underline{D}(t)\,\underline{a}(t), \tag{7'}$$

where $\underline{a}(t)$ is a column vector of coefficients and the matrix elements of $\underline{D}(t)$ are given by $D_{kj}(t)$

$= V_{kj}(t)$.

The derivative $d\underline{a}(t)/dt$ may now be expressed to any desired degree of accuracy by a finite-difference formula. Here, for simplicity, we shall use the simplest such formula:

$$\frac{d\underline{a}(t)}{dt} \approx \delta t^{-1}[\underline{a}(t+\delta t) - \underline{a}(t)] \ . \tag{11}$$

Obviously, for this expression to be accurate, δt must be chosen to be sufficiently small. Higher-order approximations may be derived by standard methods.[7] Substitution of (11) into (7′) yields the expression

$$\underline{a}(t+\delta t) = [1 + (i\hbar)^{-1}\,\delta t\,\underline{D}(t)]\,\underline{a}(t) \ , \tag{12}$$

which is the final analytic expression which we shall develop. Equation (12) is in an ideal form for an iterative type of calculation. Given the initial conditions $\underline{a}(t_0)$, knowing $\underline{D}(t)$, and by choosing δt small enough, we may calculate $\underline{a}(t+\delta t)$, which may then be properly normalized to assure unitarity. The resulting expression may be substituted into the right-hand side of Eq. (12) and the procedure repeated indefinitely to obtain $\underline{a}(t)$ for any given time t.

Apart from being a numerically exact solution for the transition amplitude, expression (12) is in many ways much simpler to handle than the perturbation series. This is especially the case for processes which cannot adequately be described by the first few terms of the perturbation series, i.e., processes such as slow collisions, for which the various Born approximations are not appropriate. The simplistic feature of (12) in this context is that products of operators do not appear in (12), whereas they do appear in the perturbation expansion, leading to sums of complicated products of matrix elements.

The distinction between the finite-difference method of solution of Eq. (7′) and the perturbation-series method is clearly seen by considering the perturbation-series approach to the two-level system. In this case, Eq. (7′) becomes

$$\begin{aligned} (i\hbar)\frac{da_1(t)}{dt} &= a_1(t)\,V_{11}(t) + a_2(t)\,V_{12}(t) \ , \\ (i\hbar)\frac{da_2(t)}{dt} &= a_1(t)\,V_{21}(t) + a_2(t)\,V_{22}(t) \ . \end{aligned} \tag{13}$$

The perturbation-series approach follows by successive substitution of equations derived from the initial conditions. Thus, if $a_1(t_0) = 1$, $a_2(t_0) = 0$, then we would have

$$\begin{aligned} (i\hbar)\frac{da_1(t)}{dt} &= V_{11}(t) \ , \\ (i\hbar)\frac{da_2(t)}{dt} &= V_{21}(t) \ , \end{aligned} \tag{14}$$

whence

$$\begin{aligned} a_1(t) &\simeq 1 + (i\hbar)^{-1}\int_{t_0}^{t} V_{11}(\tau)\,d\tau \ , \\ a_2(t) &\simeq (i\hbar)^{-1}\int_{t_0}^{t} V_{21}(\tau)\,d\tau \ . \end{aligned} \tag{15}$$

These results are simply those of first-order perturbation theory. Substitution of (15) into (13) followed by integration would lead to the second-order expression, and so on.

EXAMPLE 1. STIMULATED ABSORPTION IN A TWO-LEVEL SYSTEM

The example considered is similar to that discussed in detail by Brooks and Scarfone.[1] The perturbation may be written in the form

$$V(t) = V e^{i\omega t} \ , \tag{16}$$

where $V = -\vec{E}\cdot\vec{R}$, and where, if $\omega > 0$, the perturbation leads to emission, whereas, if $\omega < 0$, absorption results. According to first-order perturbation theory, the transition probability for the absorption process may be written

$$W^{(1)}_{i\to f}(t) = |V_{fi}|^2 f(t, \omega'), \tag{17}$$

where

$$\omega' = \omega + \omega_{fi} \ , \quad \omega_{fi} = \hbar^{-1}(E_f - E_i) \ , \tag{18}$$

$$f(t, \omega') = 2(1 - \cos\omega' t)/\omega'^2 \ .$$

For large t, the function $f(t, \omega')$ has the property

$$f(t, \omega') \xrightarrow[t\to\infty]{} 2\pi t\,\delta(\omega') \ , \tag{19}$$

and it is tempting, but not quite correct, to insert Eq. (19) into (17). In spite of error incurred, it is not uncommon for this approximation to be made in the literature. The transition probability [(17)] is large only for $\omega + \omega_{fi} \approx 0$, which is the condition necessary for energy conservation. For the purposes of our illustrative calculation, we have chosen $V_{fi} = 0.1$, $\hbar = 1$. Then, at resonance, Eq. (17) becomes

$$W^{(1)}_{i\to f}(t) = \lim_{\omega'\to 0} 0.02 f(t, \omega') \ . \tag{17′}$$

This function, which increases at t, is represented by the dashed curve in Fig. 1. $W^{(1)}_{i\to f}(t)$ is obviously unbounded, corresponding to the fact that the first-order transition amplitude is not unitary.

Proceeding by the finite-difference method based upon Eq. (12), the matrix $\underline{D}$ is given by

$$\underline{\mathrm{D}} = \begin{pmatrix} 0 & V_{if}\exp[it\hbar^{-1}(E_i - E_f + \hbar\omega)] \\ V_{fi}\exp[it\hbar^{-1}(E_f - E_i + \hbar\omega)] & 0 \end{pmatrix} = \begin{pmatrix} 0 & 0.1\exp[it(\omega - \omega_{fi})] \\ 0.1\exp[it(\omega + \omega_{fi})] & 0 \end{pmatrix} . \quad (20)$$

The diagonal elements are presumed zero, since the perturbation is assumed not to couple a state with itself. The concept of energy conservation is directly seen in the $\underline{\mathrm{D}}$ matrix. A transition will occur only if the oscillatory part of one or other of the off-diagonal matrix elements is small. If the oscillatory part of the term on the bottom left is small, absorption results, corresponding behavior of the term on the top right leading to emission. Proceeding as previously described, we may calculate $a_f(t)$, from which we obtain

$$W_{i\to f}(t) = |a_f(t)|^2 . \quad (21)$$

Accuracy of calculation was assured by choosing δt sufficiently small that the results were invariant to changes in δt. The plot of $W_{i\to f}(t)$ obtained is shown by the solid curve in Fig. 1. The undulations in this curve are of little significance and result from the "numbers" chosen for our calculation, $\omega - \omega_{fi} \approx 0$ $\omega + \omega_{fi} \approx 2$; i.e., the states are more closely coupled than in a typical physical example.

It can clearly be seen from Fig. 1 that the first-order approximation $W^{(1)}_{i\to f}(t)$ is indeed valid only for the initial time range, for which the "long-time" approximation (19) is clearly not applicable. On the other hand, if a sufficiently long time is chosen such that Eq. (19) is a reasonable approximation, then $W^{(1)}_{i\to f}(t)$ is considerably in error. For comparitive purposes, it is useful to define an index of error for the first-order approximation:

$$\epsilon_W(t) = [W^{(1)}_{i\to f}(t) - W_{i\to f}(t)]/W_{i\to f}(t) . \quad (22)$$

With this definition there is about a 15% error in $W^{(1)}_{i\to f}(t)$ for $W_{i\to f}(t) \simeq 0.17$.

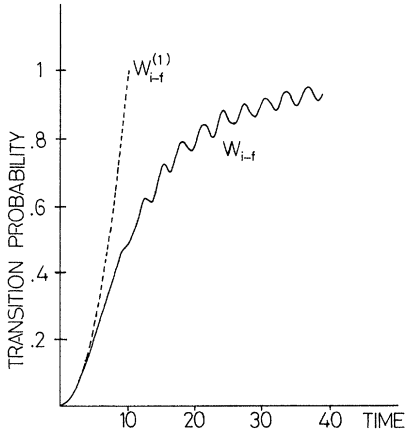

FIG. 1. Comparison of first-order and complete transition probabilities for absorption of radiation.

TRANSITIONS TO CONTINUUM STATES

Since the states of the electromagnetic field and translational states of an atom are both part of a continuous spectrum, it is frequently more meaningful to consider transitions to a continuous group of final states rather than to a given final state. Thus we denote by $W_{i\to F}(t)$ the probability of transitions to a manifold F of final states. $W_{i\to F}(t)$ may be defined[3] in the following manner:

$$W_{i\to F}(t) = \int_{F(E)} W_{i\to f}(t)\,\rho_f(E)\,dE , \quad (23)$$

in which $\rho_f(E)$ represents the density of final states of energy E.

In terms of the perturbation-series approach the first-order approximation is given by

$$W^{(1)}_{i\to F}(t) = \int_{F(E)} W^{(1)}_{i\to f}(t)\,\rho_f(E)\,dE$$
$$= \hbar^{-2}\int_{F(E)} |V_{fi}|^2 \rho_f(E) f(t, \omega + \omega_{fi})\,dE. \quad (24)$$

It is usual to presume that the energy range over which this integral need be evaluated is sufficiently small, that, compared to the energy variation of $f(t, \omega + \omega_{fi})$, the variation with energy of $|V_{fi}|^2$ and $\rho_f(E)$ is sufficiently small that these quantities can be taken out of the integral without appreciable error, leading to

$$W^{(1)}_{i\to F}(t) = \hbar^{-2} |V_{fi}|^2 \rho_f(E_f) \int_{F(E)} f(t, \omega + \omega_{fi})\,dE. \quad (25)$$

Finally, in evaluating the integral, it is presumed that the limits may be extended to infinity, yielding

$$W^{(1)}_{i\to F}(t) = \hbar^{-2} |V_{fi}|^2 \rho_f(E_f) \int_{-\infty}^{+\infty} f(t, \omega + \omega_{fi})\,dE$$
$$= (2\pi/\hbar)\,|V_{fi}|^2 \rho_f(E_f)\,t . \quad (26)$$

Defining the transition probability per unit time by the relation

$$w_{i\to F} = dW_{i\to F}(t)/dt \quad (27)$$

we see that

$$w^{(1)}_{i\to F} = (2\pi/\hbar)\,|V_{fi}|^2 \rho_f(E_f) , \quad (28)$$

which is the well-known "golden rule" and which represents a time-independent rate of transition. In the case of the absorption of radiation example, the quantity $W^{(1)}_{i\to F}(t)$ is plotted in Fig. 2 (dashed curve). The gradient of this function corresponds

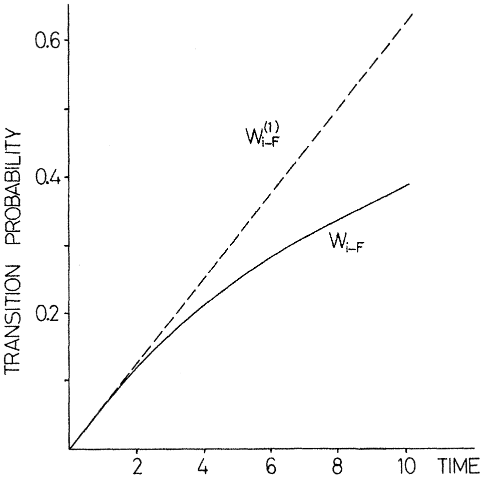

FIG. 2. Probability of transition to a manifold F of final states.

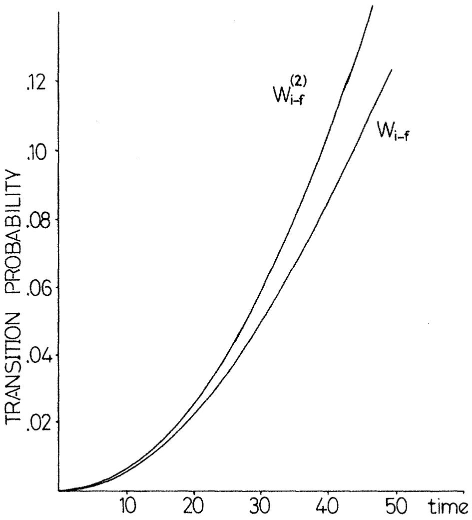

FIG. 4. Transition probabilities for ordinary Raman scattering.

to $w^{(1)}_{i\to F}$.

By making the same basic assumptions as those contained in Eqs. (23)–(27), i.e., putting

$$W_{i\to F}(t)=\rho_f(E_f)\int_{-\infty}^{+\infty}W_{i\to f}(t)\,dE\ , \qquad (29)$$

it is possible to calculate $W_{i\to F}(t)$ by the finite-difference technique. This may simply be done by calculation of $W_{i\to f}(t)$ as a function of ω, then by numerically integrating the resulting expressions at any given time t with respect to ω. The results of such a calculation are plotted in Fig. 2 (solid curve). Again it can be seen that the first-order approximation is valid only in the initial time region. Moreover, the correct transition probability per unit time, given by the gradient of $W_{i\to F}(t)$, is seen to be time dependent, as one would in fact expect.

EXAMPLE 2. RAMAN AND RESONANCE RAMAN SCATTERING

Within the framework of perturbation theory, the transition probability for Raman scattering may be represented by the following second-order expression[8, 9]:

$$W^{(2)}_{i\to f}(t)$$
$$=\hbar^{-4}\left|\sum_v\left\{\frac{V_{fv}(\omega_2)V_{vi}(\omega_1)}{\omega_2+\omega_{vi}}+\frac{V_{fv}(\omega_1)V_{vi}(\omega_2)}{\omega_1+\omega_{vi}}\right\}\right|f(t,\omega')\ , \qquad (30a)$$

where in this case $\omega'=\omega_{fi}+\omega_1+\omega_2$. For the purposes of a comparitive calculation we shall consider the case in which only one term is retained in the summation over intermediate states. Diagrammatically, the process to be described might be represented as in Fig. 3, the energy levels shown in the figure being chosen for convenience. Putting $V_{fv}=V_{vi}=\beta$, $\hbar=1$, then we have

$$W^{(2)}_{i\to f}(t)=\beta^4\left|\frac{1}{200+\omega_2}+\frac{1}{200+\omega_1}\right|^2 f(t,\omega')\ . \qquad (30b)$$

Choosing $\omega_1=-195$, $\omega_2=145$, which satisfies energy conservation for the scattering process, and choos-

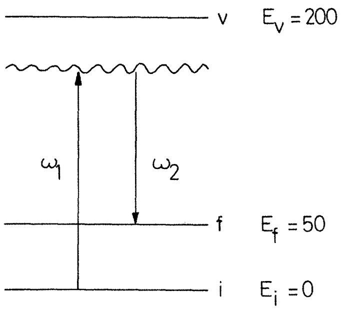

FIG. 3. Energy levels involved in Raman scattering.

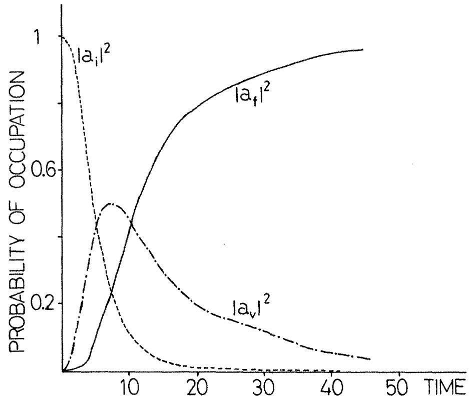

FIG. 5. Time dependence of occupation probabilities for states involved in resonance Raman scattering.

ing $\beta = 0.2$, then one may verify that

$$W^{(2)}_{i\to f}(t) = 0.000066t^2 . \qquad (30c)$$

This function is plotted in Fig. 4 (dashed curve). Since the perturbation $V(t)$ may be written as a sum:

$$V(t) = V^{\alpha}\exp[i\omega_1 t] + V^{\beta}\exp[i\omega_2 t] , \qquad (31)$$

the D matrix in the finite-difference approach may be expressed as a sum of two matrices, one for each perturbation. Making the usual assumption, which is also inherent in the perturbation treatment, that the initial and final states are not directly coupled by the perturbation, the D matrix may be written:

$$\underline{D} = \begin{pmatrix} 0 & 0 & V^{\alpha}_{iv}\exp[i(\omega_1 - \omega_{vi})t] \\ 0 & 0 & V^{\alpha}_{fv}\exp[i(\omega_1 - \omega_{vf})t] \\ V^{\alpha}_{vi}\exp[i(\omega_{vi} + \omega_1)t] & V^{\alpha}_{vf}\exp[i(\omega_{vf} + \omega_1)t] & 0 \end{pmatrix}$$

$$+ \begin{pmatrix} 0 & 0 & V^{\beta}_{iv}\exp[i(\omega_2 - \omega_{vi})t] \\ 0 & 0 & V^{\beta}_{fv}\exp[i(\omega_2 - \omega_{vf})t] \\ V^{\beta}_{vi}\exp[i(\omega_{vi} + \omega_2)t] & V^{\beta}_{vf}\exp[i(\omega_{vf} + \omega_2)t] & 0 \end{pmatrix} , \qquad (32)$$

where, as before, we have assumed that $\hbar = 1$, etc. Using the same values of the energy levels, matrix elements, etc., as in the perturbation treatment, the transition probability for the scattering process

$$W_{i\to f}(t) = |a_f(t)|^2 \qquad (33)$$

was calculated by the finite-difference method as previously described. The results of the calculation are shown for the initial time region by the solid curve in Fig. 4. Although the general behavior of these curves is similar to that for the first-order absorption process, we see in this case that a 15% error, as defined by analogy with Eq. (22), is incurred for $W_{i\to f}(t) \approx 0.03$, which is a much smaller total probability of transition than for the first-order process. In other words it would appear that the higher the order of the process, the shorter the "time interval" for which the lowest-order approximation will be reasonably correct. This would seem to be a fairly reasonable finding.

RESONANCE RAMAN SCATTERING

Resonance Raman scattering[6] occurs if $\omega_1 + \omega_{vi} \approx 0$. In that case, expression (30) is not at all applicable without modification to include the lifetime of the intermediate state $| v \rangle$. On the other hand, the existence of an intermediate-state resonance presents absolutely no problem for the finite-difference method, even in the case of a "sharp" intermediate state. The probability of occupation of each of the three levels involved in resonance scattering is illustrated in Fig. 5, the transition probability for scattering being once again given by Eq. (33). Although the calculation is not reported in this paper, it is simple to include the effects of state lifetimes within the finite-difference approach.

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