[1]M. Baranger, Phys. Rev. 112, 855 (1958).
[2]S. Brechot and H. Van Regemorter, Ann. Astrophys. 27, 432 (1964).
[3]J. Davis and D. Roberts, Proc. Phys. Soc. (London) 92, 889 (1967).
[4]S. Brechot, Astron. Astrophys. 1, 91 (1969).
[5]H. Griem (unpublished).
[6]M. Gailitis, Zh. Experim. i Teor. Fiz. 44, 1974 (1963) [English transl.: Soviet Phys. – JETP 17, 1328 (1963)].
[7]O. Bely, D. Moores, and M. Seaton, in Proceedings of the Third International Conference on the Physics of Electronic and Atomic Collisions, London, 1963, edited by M. R. C. McDowell (North-Holland Publishing Co., Inc., Amsterdam, 1964).
[8]M. Seaton, Proc. Phys. Soc. (London) 88, 801, 1963 (1966).
[9]O. Bely and H. Griem (unpublished).
[10]H. Van Regemorter (private communication).
[11]M. Seaton, J. Phys. 2, 5 (1969).
[12]H. Griem, Phys. Rev. 165, 258 (1968).

PHYSICAL REVIEW VOLUME 185, NUMBER 1 5 SEPTEMBER 1969

Multiple-Time-Scale Perturbation Theory and Constant Atomic Transition Rates*

G. L. Brooks, Jr.,† and L. M. Scarfone
Department of Physics, University of Vermont, Burlington, Vermont 05401
(Received 13 May 1969)

A conventional perturbation approach to the problem of induced emission by an atom exposed to electromagnetic radiation is reviewed. The calculation is known to contain a familiar mathematical anomaly requiring a nonphysical restraint on the time range of validity of the derived expression for the atomic transition rate. The problem is then solved again in the formalism of multiple-time-scale perturbation theory. This approach avoids the mathematical difficulty in question, and yields for the transition rate a more general expression. During the restricted time interval, in which the conventionally obtained result is valid, it and the more general expression are identical.

I. INTRODUCTION

It is well known that the application of Dirac's method of variation of constants to certain time-dependent perturbations in quantum-mechanics results in the appearance of secular behavior. Classical-mechanical problems, notably those involving perturbations of celestial orbits, may also exhibit this behavior, and several techniques exist for dealing with it on the classical level.[1] A general method developed by Krylov and Bogolyubov,[2] and Bogolyubov and Mitropolskii,[3] for treating classical-mechanical systems subject to secular behavior has been adapted for use, under the name multiple-time-scale perturbation theory (MTSPT), in other physical situations. Several authors have used MTSPT in the context of nonequilibrium statistical mechanics,[4] and the technique has not only provided useful results but also afforded some physical insights into the processes under examination.[5] In addition, it has been demonstrated that MTSPT can be applied successfully to quantum systems.[6,7] In all the cases alluded to above, the application of ordinary time-dependent perturbation theory results in the appearance of secular terms in the expansion for quantities of interest, whereas MTSPT gives acceptable results. It should be noted, however, that MTSPT is not the only alternative approach to problems in which secular behavior occurs. Sometimes an *ad hoc* nonperturbative approach can be found[8]; for quantum systems, a general approach based on a new variational principle has been proposed as a substitute for the method of variations of constants to avoid secular difficulties.[9]

In this paper, MTSPT will be applied to the case of an atom perturbed by an incident classical electromagnetic radiation field; this is an important example for which ordinary time-dependent perturbation theory fails, in the sense that secular behavior occurs. This example has been chosen for several reasons. First, its solution by MTSPT illustrates well the features of the technique. Second, the example is well known and solved in many texts by the method of variation of constants; the secular terms that consequently appear are taken into account by placing an upper limit on the time interval over which the solution

may be said to be valid. Third, an important result obtained through the usual solution of this example, namely, that radiation-induced atomic transitions proceed at a constant rate is also obtained by applying MTSPT.

II. CONVENTIONAL SOLUTION

An introduction to the technique will be provided through a review of the example of a hydrogenlike atom in a radiation field and its usual solution by the method of variation of constants. Some of the results of this solution will be needed for purposes of comparison later on, and the details of the secular behavior will be used in the formulation of the MTSPT approach to the problem.

The atomic electron is taken to be described by a Hamiltonian H_0, with a set of eigenfunctions $\psi_n^0(\vec{x}, t)$ and their corresponding eigenvalues E_n.[10] When an electromagnetic radiation field is incident on the atom, the total Hamiltonian is

$$H = H_0 + \lambda V(\vec{x}, t), \tag{1}$$

where λV is the operator describing the interaction with the radiation field. The quantity λ is a dimensionless parameter characterizing the strength of the interaction; in this perturbative approach λ is taken to be small. An arbitrary state ψ^0 of the unperturbed atom can be expressed in terms of the stationary eigenstates of H_0 by the following expansion:

$$\psi^0(\vec{x}, t) = \sum_n a_n \psi_n^0(\vec{x}, t), \tag{2}$$

where unit normalization of ψ^0 is assured by requiring that the sum of the squared magnitudes of the (generally complex) constants a_n be unity.

The method of variation of constants assumes that, when the perturbation is present, an arbitrary state ψ of the perturbed atom may still be expanded in terms of the unperturbed eigenfunctions as in Eq. (2), except that the expansion coefficients a_n become functions of time $a_n(t)$; of course, the sum of their squared magnitudes is still required to be unity for all t. The time dependence of the $a_n(t)$ is found by substituting the expansion for ψ into the perturbed time-dependent Schrödinger equation, and then making use of the orthonormality properties of the eigenfunctions of H_0. The result is

$$i\hbar \frac{da_m(t)}{dt} = \lambda \sum_n V'_{mn}(t) \exp[i(E_m - E_n)t/\hbar] a_n(t), \tag{3}$$

where $\lambda V'_{mn}(t)$ is the (mn) matrix element of the operator $\lambda V(\vec{x}, t)$ with respect to the basis of unperturbed eigenfunctions. If the incoming radiation has angular frequency ω_0, $V'_{mn}(t)$ may be written in Hermitian form

$$V'_{mn}(t) = V_{mn} e^{i\omega_0 t} + V_{mn} e^{-i\omega_0 t}, \tag{4}$$

since $V^*_{mn} = V_{nm}$.

Consider the following situation: An atom, initially in an unperturbed stationary eigenstate s, is exposed to electromagnetic radiation of angular frequency ω_0 at time $t = 0$. It is desired to find the probability that the atom has radiated energy and made a transition to an eigenstate of lower energy by time $t > 0$. In this emission process, the second term on the right-hand side of Eq. (4) is neglected, because it makes a relatively insignificant contribution to the process of interest. Equations (3) and (4) then give

$$i\hbar \frac{da_m(t)}{dt} = \lambda \sum_n V_{mn} \exp[i(E_m - E_n + \hbar\omega_0)t/\hbar] a_n(t); \tag{5}$$

note that the corresponding absorption process would involve the equation

$$i\hbar \frac{da_n(t)}{dt} = \lambda \sum_m V_{nm} \exp[i(E_n - E_m - \hbar\omega_0)t/\hbar] a_m(t). \tag{6}$$

In the problem under consideration, Eq. (5) is solved according to the initial conditions $a_n(t=0) = \delta_{ns}$. The conventional method of solution is to expand the $a_n(t)$ in a power series in λ,

$$a_n(t) = a_n^{(0)}(t) + \lambda a_n^{(1)}(t) + \cdots, \tag{7}$$

substitute into Eq. (5), equate the coefficients of equal powers of λ, and solve the resulting differential equations for the expansion coefficients. The results to first order are, for all m,

$$a_m^{(0)}(t) = \text{const} = \delta_{ms}, \tag{8}$$

$$a_m^{(1)}(t) = \frac{-V_{ms}\{\exp[i(E_m - E_s + \hbar\omega_0)t/\hbar] - 1\}}{(E_m - E_s + \hbar\omega_0)}. \tag{9}$$

In the case of transitions terminating at state $m = R$, where $E_R - (E_s - \hbar\omega_0) = 0$,

$$a_R^{(1)}(t) = -iV_{Rs}t/\hbar. \tag{10}$$

The expression for $a_R^{(1)}(t)$ is an instance of secular behavior in the expansion for $a_R(t)$. From Eqs. (8) and (10), it is seen that the up-to-first-order approximation to $|a_R(t)|^2$, i.e., the prob-

ability of observing the atom in state R at time t, will eventually exceed 1, a physically unacceptable result. Additionally, it is observed from Eq. (9) that, in general, the magnitude oscillates between zero and $|2\lambda V_{ms}/[E_m - E_s + \hbar\omega_0]|$. Thus, for any state r belonging to the set M defined by

$$M \equiv \left\{ r: \frac{\lambda |V_{rs}|}{|E_r - E_s + \hbar\omega_0|} > \frac{1}{2} \right\} , \tag{11}$$

the quantity $|\lambda a_r^{(1)}(t)|$ can at times exceed unity and contribute in a physically unacceptable manner to $|a_r(t)|^2$. By the smallness of $\lambda |V_{rs}|$, M clearly consists of those states in a narrow energy interval about E_R, thus satisfying $E_r - E_s + \hbar\omega_0 \cong 0$. For such states r,

$$a_r^{(1)}(t) \cong -iV_{rs}t/\hbar \tag{12}$$

for suitably small values of t. Equations (10) and (12) suggest that one way to retain the results obtained thus far is to require that $t/\hbar$ be sufficiently small that the expressions for $|\lambda a_r^{(1)}(t)|$, $r \in M$, are physically sensible in magnitude, say $|\lambda a_r^{(1)}(t)| \ll 1$; with this restriction on the time Eq. (9) is acceptable for all m.

The probability $P_s(t)$ that the atom has made a transition out of state s by time $t > 0$ is given, up to first order, by

$$P_s(t) = \sum_{m \neq s} |a_m^{(0)}(t) + \lambda a_m^{(1)}(t)|^2 , \tag{13}$$

or, when Eqs. (8) and (9) are used, by

$$P_s(t) = \sum_{m \neq s} \frac{4|\lambda V_{ms}|^2}{(E_m - E_s + \hbar\omega_0)^2} \times \sin^2[(E_m - E_s + \hbar\omega_0)t/2\hbar] . \tag{14}$$

Applying the formula

$$\lim_{\alpha \to \infty} (\sin^2\alpha x)/\pi\alpha x^2 = \delta(x) , \tag{15}$$

Eq. (14) can be written in the following asymptotic form for large $t/2\hbar$:

$$P_s(t) = 2\pi |\lambda V_{sR}|^2 (t/\hbar)\delta(E_R - E_s + \hbar\omega_0) , \tag{16}$$

from which the rate of transition is

$$dP_s/dt = 2\pi |\lambda V_{sR}|^2 \hbar^{-1}\delta(E_R - E_s + \hbar\omega_0) . \tag{17}$$

Equation (17) has been obtained under a set of conditions which will now be reviewed. First, in regard to writing Eq. (14) in the form of Eq. (16), it has been necessary to assume that $t/2\hbar$ is "large." Second, and in contrast, $t/\hbar$ has earlier been required to be "small" in order that Eqs. (10) and (12) be physically meaningful. The seeming contradiction in the time restrictions can be resolved by assuming that the coupling constant λ is so small that the quantity $|\lambda a_r^{(1)}(t)|$, $r \in M$, will be $\ll 1$ even for moderately large values of $t/\hbar$, i.e., values of $t/\hbar$ large enough to make Eq. (16) a valid approximation. Thus, Eq. (17) is valid over a time interval whose lower bound is large enough to make Eq. (16) valid, and whose upper bound is small enough to make Eqs. (10) and (12) physically acceptable. The lower bound can be understood physically as the time at which the system has completed its initial reaction to the sudden application of the perturbation at $t = 0$, and has settled into the constant transition-rate behavior. On the other hand, the upper bound exists merely to account for a mathematical anomaly appearing in the solution process. It is just this anomaly that is to be avoided by the application of MTSPT.

III. SOLUTION BY MTSPT

To set up the MTSPT formalism, Eqs. (5) and (6) are considered. In these equations, the transformation

$$a_m(t) \to a_m(\tau), \quad \text{for all } m \tag{18}$$

is made, where τ stands for an infinite set of time variables $(\tau_0, \tau_1, \tau_2, \ldots)$. Based on the observation that the first-order correction $\lambda a_R^{(1)}(t)$ grows in magnitude linearly with λt, the following perturbation expansions are assumed[11]:

$$a_m(\tau) = a_m^{(0)}(\tau) + \lambda a_m^{(1)}(\tau) + \lambda^2 a_m^{(2)}(\tau) + \cdots , \quad \text{for all } m \tag{19}$$

$$\frac{d}{dt} = \frac{\partial}{\partial\tau_0} + \lambda\frac{\partial}{\partial\tau_1} + \lambda^2\frac{\partial}{\partial\tau_2} + \cdots . \tag{20}$$

Associated with the above expansions is the following set of correspondences:

$$\tau_0 = t, \quad \tau_1 = \lambda t, \quad \tau_2 = \lambda^2 t, \quad \ldots \tag{21}$$

Briefly, the method consists of substituting Eqs. (18)–(21) into Eqs. (5) and (6), and solving the resulting equations, according to the appropriate initial conditions, to various orders. In the course of carrying out the solution, the $\tau_0, \tau_1, \ldots$, are to be considered as independent variables, and otherwise unspecified functional dependence on $\tau_0, \tau_1, \ldots$, can be chosen arbitrarily for convenience. When the solutions are obtained, in terms of $\tau_0, \tau_1, \ldots$, they are converted to expressions in terms of the physical time t by Eq. (21), which defines what is called the "physical line."

After substitution of Eqs. (18)–(21), Eqs. (5) and (6) become

$$i\hbar\left[\frac{\partial}{\partial\tau_0}+\lambda\frac{\partial}{\partial\tau_1}+\cdots\right][a_m^{(0)}(\tau)+\lambda a_m^{(1)}(\tau)+\cdots]=\lambda\sum_n V_{mn}\times\exp[i(E_m-E_n+\hbar\omega_0)\tau_0/\hbar]\times[a_n^{(0)}(\tau)+\lambda a_n^{(1)}(\tau)+\cdots], \tag{22}$$

$$i\hbar\left[\frac{\partial}{\partial\tau_0}+\lambda\frac{\partial}{\partial\tau_1}+\cdots\right][a_n^{(0)}(\tau)+\lambda a_n^{(1)}(\tau)+\cdots]=\lambda\sum_m V_{nm}\exp[i(E_n-E_m-\hbar\omega_0)\tau_0/\hbar]\times[a_m^{(0)}(\tau)+\lambda a_m^{(1)}(\tau)+\cdots]. \tag{23}$$

The problem is, as before, to find the probability that an atom in state s at time $t=0$ will have made a downward transition (emission process) at time $t>0$, in response to perturbing electromagnetic radiation incident upon it beginning at $t=0$. The initial conditions for this problem are

$$a_m(\tau=0)=\delta_{ms}, \tag{24}$$

where $\tau=0$ means $\tau_0=0$, $\tau_1=0$, ... The equations generated by comparing coefficients of equal powers of λ are now considered. From the coefficients of λ^0 the equation

$$i\hbar\frac{\partial}{\partial\tau_0}a_m^{(0)}(\tau)=0, \quad \text{for all } m \tag{25}$$

is obtained, meaning that $a_m^{(0)}$ has no τ_0 dependence, i.e.,

$$a_m^{(0)}=a_m^{(0)}(\tau_1,\tau_2,\ldots). \tag{26}$$

In accord with initial conditions, the behavior of the $a_m^{(0)}$ is further specified to be

$$\begin{aligned} &a_s^{(0)}(\tau_1,\tau_2,\ldots)\neq 0,\\ &a_r^{(0)}(\tau_1,\tau_2,\ldots)\neq 0, \text{ for } r\in M;\\ &a_k^{(0)}(\tau_1,\tau_2,\ldots)=0, \text{ for } k\notin M,\ k\neq s \end{aligned} \tag{27}$$

by the following argument: The application of ordinary time-dependent perturbation theory shows, from Eqs. (10) and (12), that probability tends to flow from state s into states $r\in M$, predominantly. For states k, $k\neq s$, and $k\notin M$, Eq. (9) shows that $|\lambda a_k^{(1)}(t)|\ll 1$, for all $t>0$, and, thus, that $|a_k(t)|\ll 1$. The acceptance of these predictions of ordinary time-dependent perturbation theory as qualitatively valid is here used to assert that, for $k\notin M$ and $k\neq s$,

$$a_k(\tau)=0+\lambda a_k^{(1)}(\tau)+\cdots,$$

that is, that $a_k(\tau)$ is never larger than $0(\lambda)$ in magnitude.

Making use of Eqs. (27), and noting that the process under consideration is an emission process beginning with state s, the following equations are found from the coefficients of λ^1 in Eqs. (22) and (23): for $m=s$, the initial state,

$$i\hbar\left[\frac{\partial}{\partial\tau_0}a_s^{(1)}(\tau)+\frac{\partial}{\partial\tau_1}a_s^{(0)}(\tau_1,\tau_2,\ldots)\right]=\sum_{r\in M}V_{sr}\exp[i(E_s-E_r-\hbar\omega)\tau_0/\hbar]a_r^{(0)}\times(\tau_1,\tau_2,\ldots)+V_{ss}\exp(-i\omega\tau_0)a_s^{(0)}(\tau_1,\tau_2,\ldots); \tag{28}$$

for $m=r\in M$

$$i\hbar\left[\frac{\partial}{\partial\tau_0}a_r^{(1)}(\tau)+\frac{\partial}{\partial\tau_1}a_r^{(0)}(\tau_1,\tau_2,\ldots)\right]=\sum_{r'\in M}V_{rr'}\exp[i(E_r-E_{r'}+\hbar\omega)\tau_0/\hbar]a_{r'}^{(0)}\times(\tau_1,\tau_2,\ldots)+V_{rs}\exp[i(E_r-E_s+\hbar\omega)\tau_0/\hbar]a_s^{(0)}(\tau_1,\tau_2,\ldots); \tag{29}$$

for $m=k$, $(k\neq s,\ k\notin M)$

$$i\hbar\frac{\partial}{\partial\tau_0}a_k^{(1)}(\tau)=\sum_{r\in M}V_{kr}\exp[i(E_k-E_r+\hbar\omega)\tau_0/\hbar]a_r^{(0)}(\tau_1,\tau_2,\ldots)+V_{ks}\exp[i(E_k-E_s+\hbar\omega)\tau_0/\hbar]a_s^{(0)}(\tau_1,\tau_2,\ldots). \tag{30}$$

Before proceeding with the solution of these equations, the problem under consideration must be described in more detail. For a nearly monochromatic classical light source, the electromagnetic radia-

tion contains a distribution of frequencies $f(\omega)$, with some frequency, say ω_0, corresponding to the peak of the distribution. In the discussion above, ω_0 satisfies the relation $E_R-(E_S-\hbar\omega_0)=0$; it is now assumed that the frequency distribution is so narrow that, for any ω for which $f(\omega)=0$, $E_m-(E_S-\hbar\omega)\neq 0$ for all m, unless $m=R$ *and* $\omega=\omega_0$. This means that the width of the energy distribution of the incident radiation (calculated by $E=\hbar\omega$) is less than the distance between E_R and its neighboring energy levels. For generality, Eqs. (28)–(30) have been written in terms of ω [those values for which $f(\omega)\neq 0$] rather than ω_0.

When Eq. (28) is integrated with respect to τ_0, the term

$$i\hbar\frac{\partial}{\partial\tau_1}a_S^{(0)}(\tau_1,\tau_2,\ldots),$$

which is clearly independent of τ_0, makes a contribution that is proportional to τ_0 to the expression for $a_S^{(1)}$. To avoid this difficulty, it is permissible to set

$$\frac{\partial}{\partial\tau_1}a_S^{(0)}(\tau_1,\tau_2,\ldots)=0, \tag{31}$$

so that $a_S^{(0)}=a_S^{(0)}(\tau_2,\ldots)$. The remaining portion of Eq. (28) can be integrated with respect to τ_0 to give

$$a_S^{(1)}(\tau_0,\tau_1,\ldots)=\sum_{r\in M}\{-iV_{Sr}\int_0^{\tau_0/\hbar}d\zeta\exp[i(E_S-E_r-\hbar\omega)\zeta]\}$$
$$\times a_r^{(0)}(\tau_1,\tau_2,\ldots)-iV_{SS}\int_0^{\tau_0/\hbar}d\zeta\exp(-i\hbar\omega\zeta)a_S^{(0)}(\tau_2,\ldots). \tag{32}$$

Considering Eq. (29), it is observed that to avoid secular blowup with τ_0 in $a_r^{(1)}(\tau)$, it is necessary to set

$$\frac{\partial}{\partial\tau_1}a_r^{(0)}(\tau_1,\tau_2,\ldots)=0 \quad\text{or}\quad a_r^{(0)}=a_r^{(0)}(\tau_2,\ldots). \tag{33}$$

Noting that Eq. (33) holds for all $r\in M$, integration of the remaining portion of Eq. (29) with respect to τ_0, yields

$$a_r^{(1)}(\tau_0,\tau_1,\ldots)=\sum_{r'\in M}[-V_{rr'}/(E_r-E_{r'}+\hbar\omega)]\{\exp[i(E_r-E_{r'}+\hbar\omega)\tau_0/\hbar]-1\}$$
$$\times a_{r'}^{(0)}(\tau_2,\ldots)-iV_{rS}\int_0^{\tau_0/\hbar}d\zeta\exp[i(E_r-E_S+\hbar\omega)\zeta]a_S^{(0)}(\tau_2,\ldots). \tag{34}$$

Finally, Eq. (30), containing no terms independent of τ_0, is integrated at once to give

$$a_k^{(1)}(\tau_0,\tau_1,\ldots)=\sum_{r\in M}[-V_{kr}/(E_k-E_r+\hbar\omega)]\{\exp[i(E_k-E_r+\hbar\omega)\tau_0/\hbar]-1\}$$
$$\times a_r^{(0)}(\tau_2,\ldots)-\frac{V_{ks}}{E_k-E_S+\hbar\omega}\{\exp[i(E_k-E_S+\hbar\omega)\tau_0/\hbar]-1\}a_S^{(0)}(\tau_2,\ldots). \tag{35}$$

Next, the coefficients of λ^2 in Eq. (23) give the following equation for $a_S^{(2)}(\tau)$:

$$i\hbar\left[\frac{\partial}{\partial\tau_0}a_S^{(2)}(\tau)+\frac{\partial}{\partial\tau_1}a_S^{(1)}(\tau)+\frac{\partial}{\partial\tau_2}a_S^{(0)}(\tau_2,\ldots)\right]=\sum_n V_{Sn}\exp[i(E_S-E_n-\hbar\omega)\tau_0/\hbar]a_n^{(1)}(\tau)$$
$$=\sum_{r\in M}V_{Sr}\exp[i(E_S-E_r-\hbar\omega)\tau_0/\hbar]\,a_r^{(1)}(\tau)+\sum_{k\notin M,k\neq S}V_{Sk}\exp[i(E_S-E_k-\hbar\omega)\tau_0/\hbar]a_k^{(1)}(\tau)$$
$$+V_{SS}\exp(-i\omega\tau_0)a_S^{(1)}(\tau). \tag{36}$$

Now, in the above equation the term $V_{SS}e^{-i\omega\tau_0}a_S^{(1)}(\tau)$, which describes the transition from state s to state s through the influence of the perturbation, must be omitted. It is clear that the states corresponding to $a_n^{(1)}(\tau)$ on the right-hand side of the first equality in Eq. (36) are to be regarded as the initial states in an absorption process terminating at state s, i.e., the reverse of the emission process under consideration. Since the states $a_r^{(1)}(\tau)$ and $a_k^{(1)}(\tau)$ have previously been calculated as final states in an emission process beginning with s, they are acceptable for use here. On the other hand, $a_S^{(1)}(\tau)$ was, of

course, calculated as the initial state in such a process, and cannot consistently be one of the $a_n{}^{(1)}(\tau)$ in Eq. (36). The resolution of this difficulty is easily accomplished by allowing $k = s$ in the term

$$\sum_{k \notin M,\, k \neq s} V_{sk} \exp[i(E_s - E_k - \hbar\omega)\tau_0/\hbar] a_k{}^{(1)}(\tau).$$

With this alteration, and using Eqs. (34) and (35) for $a_r{}^{(1)}(\tau)$ and $a_k{}^{(1)}(\tau)$, Eq. (36) yields

$$\begin{aligned}
i\hbar\left[\frac{\partial}{\partial\tau_0} a_s{}^{(2)}(\tau) + \frac{\partial}{\partial\tau_2} a_s{}^{(0)}(\tau_2, \ldots)\right] &= \sum_{r \in M} \sum_{r' \in M} \frac{-V_{rr'} V_{sr}}{E_r - E_{r'} - \hbar\omega} \{\exp[i(E_s - E_{r'})\tau_0/\hbar] \\
&- \exp[i(E_s - E_{r'} + \hbar\omega)\tau_0/\hbar]\} a_{r'}{}^{(0)}(\tau_2, \ldots) + \sum_{r \in M} |V_{rs}|^2 a_s{}^{(0)}(\tau_2, \ldots) \\
&\times \{-i \int_0^{\tau_0/\hbar} d\zeta \exp[i(E_r - E_s + \hbar\omega)(\zeta - \tau_0/\hbar)]\} + \sum_{k \notin M,\, k \neq s} \sum_{r \in M} [-V_{sk} V_{kr}/(E_k - E_r + \hbar\omega)] \\
&\times \{\exp[i(E_s - E_r)\tau_0/\hbar] - \exp[i(E_s - E_r - \hbar\omega)\tau_0/\hbar]\} a_r{}^{(0)}(\tau_2, \ldots) + \sum_{k \notin M,\, k \neq s} \frac{|V_{ks}|^2}{E_k - E_s + \hbar\omega} \\
&\times \exp[i(E_s - E_k - \hbar\omega)\tau_0/\hbar] a_s{}^{(0)}(\tau_2, \ldots) + \sum_{k \notin M,\, k \neq s} [-|V_{ks}|^2/(E_k - E_s + \hbar\omega)] a_s{}^{(0)}(\tau_2, \ldots) \\
&+ \sum_{r \in M} \frac{-V_{ss} V_{sr}}{E_s - E_r + \hbar\omega} \{\exp[i(E_s - E_r)\tau_0/\hbar] - \exp(-i\omega\tau_0)\} a_r{}^{(0)}(\tau_2, \ldots) \\
&+ \frac{|V_{ss}|^2}{\hbar\omega} [\exp(-i\omega\tau_0) - 1] a_s{}^{(0)}(\tau_2, \ldots).
\end{aligned} \tag{37}$$

A certain asymptotic form of Eq. (37) will now be developed. The integral appearing in Eq. (37) can be rewritten as follows:

$$-i \int_0^{\tau_0/\hbar} d\zeta \exp[i(E_r - E_s + \hbar\omega)(\zeta - \tau_0/\hbar)] = -i \int_0^{\tau_0/\hbar} d\gamma \exp[i(E_s - E_r - \hbar\omega)\gamma]. \tag{38}$$

The relation

$$-i \int_0^{\infty} d\gamma \exp(ix\gamma) = \frac{\mathcal{P}}{x} - i\pi\delta(x), \tag{39}$$

gives

$$\lim_{(\tau_0/\hbar) \to \infty} -i \int_0^{\tau_0/\hbar} d\gamma \exp[i(E_s - E_r - \hbar\omega)\gamma] = \frac{\mathcal{P}}{E_s - E_r - \hbar\omega} - i\pi\delta(E_s - E_r - \hbar\omega). \tag{40}$$

The equation resulting from substitution of expression (40) for the integral (38) is the asymptotic form of Eq. (37) for $\tau_0/\hbar$ very large. Several terms independent of τ_0, and thus, capable of causing secular blow-up in the expression for $a_s{}^{(2)}(\tau)$, occur in the resulting equation; they are eliminated by specifying the τ_2 dependence of $a_s{}^{(0)}(\tau_2, \ldots)$ in the following way:

$$\begin{aligned}
\frac{\partial}{\partial\tau_2} a_s{}^{(0)}(\tau_2, \ldots) = \Bigg(&\sum_{r \in M} |V_{rs}|^2 \{i[\mathcal{P}/\hbar(E_s - E_r - \hbar\omega)] - \frac{\pi}{\hbar}\delta(E_s - E_r - \hbar\omega)\} \\
&+ \sum_{k \notin M,\, k \neq s} [i|V_{ks}|^2/\hbar(E_k - E_s + \hbar\omega)] + i|V_{ss}|^2/\hbar^2\omega \Bigg) a_s{}^{(0)}(\tau_2, \ldots).
\end{aligned} \tag{41}$$

Equation (41) has the solution

$$a_s{}^{(0)}(\tau_2, \ldots) = a_s{}^{(0)}(\tau_2 = 0, \tau_3, \ldots) \exp\left\{\sum_n \left[i\left(\frac{\mathcal{P}}{E_s - E_n - \hbar\omega}\right)|V_{ns}|^2 \frac{\tau_2}{\hbar} - \pi|V_{ns}|^2 \delta(E_s - E_n - \hbar\omega)\tau_2/\hbar\right]\right\}, \tag{42}$$

where the summation is over all the unperturbed eigenstates of the atom. This expression for $a_S^{(0)}(\tau_2, \ldots)$ contains an exponential decay factor, so that Eq. (34) for $a_\gamma^{(1)}(\tau)$ is bounded in magnitude. In a similar fashion, an expression for $a_\gamma^{(0)}(\tau_2, \ldots)$ can be calculated, and shown to be such that $a_S^{(1)}(\tau)$ is also bounded in magnitude. Equation (35) for $a_k^{(1)}(\tau)$, is also, as a consequence, bounded in magnitude, but does not contain any potentially secular terms to begin with.

The physical quantity of interest is the probability $|a_S(t)|^2$ that state s is occupied at time $t > 0$. An approximation to this probability can be obtained from Eq. (42). First, $a_S^{(0)}(\tau_2, \ldots)$ is expressed on the physical line by applying prescription (21)

$$a_S^{(0)}(\lambda^2 t, \ldots) = a_S^{(0)}(\lambda^2 t = 0, \ldots) \exp\left\{\sum_n \left[i\left(\frac{\mathcal{P}}{E_S - E_n - \hbar\omega}\right)|\lambda V_{nS}|^2 \frac{t}{\hbar} - \pi|\lambda V_{nS}|^2 \delta(E_S - E_n - \hbar\omega)t/\hbar \right]\right\}. \tag{43}$$

Ignoring the higher-order ($\lambda^3 t$, etc.) time scales, the squared magnitude of $a_S^{(0)}(\lambda^2 t, \ldots)$ is

$$|a_S^{(0)}(t)|^2 = |a_S^{(0)}(t=0)|^2 \exp\{-[\textstyle\sum_n 2\pi|\lambda V_{nS}|^2 \delta(E_S - E_n - \hbar\omega)]t/\hbar\}. \tag{44}$$

Since the distribution of frequencies in the light incident on the atom is such that only ω_0 has the property that $\hbar\omega_0$ exactly equals the energy difference between E_S and a lower-energy eigenvalue (in fact, $\hbar\omega_0 = E_S - E_R$), the behavior of $|a_S^{(0)}(t)|^2$ when contributions from all frequencies in $f(\omega)$ are superposed will be the same as

$$|a_S^{(0)}(t)|^2 = |a_S^{(0)}(t=0)|^2 \exp[-(2\pi/\hbar)|\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0)t]. \tag{45}$$

Finally, consistency, to this order, with the initial conditions of the problem requires

$$|a_S^{(0)}(t=0)| = 1, \tag{46}$$

so that

$$|a_S(t)|^2 \cong |a_S^{(0)}(t)|^2 = \exp[-(2\pi/\hbar)|\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0)t]. \tag{47}$$

This result has been obtained from the asymptotic form of Eq. (37) as $\tau_0/\hbar \to$ very large; on the physical line, this condition is $t/\hbar$ very large. More specifically, Eq. (47) is valid for times large enough that

$$-i\int_0^{t/\hbar} d\gamma e^{ix\gamma} \cong \frac{\mathcal{P}}{x} - i\pi\delta(x). \tag{48}$$

IV. DISCUSSION OF RESULTS

The transition rate $(d/dt)P_S(t)$ can be calculated at once from Eq. (47):

$$\begin{aligned}\frac{d}{dt}P_S(t) &= -\frac{d}{dt}|a_S^{(0)}(t)|^2 = (2\pi/\hbar) \\ &\times |\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0)\exp[-(2\pi/\hbar) \\ &\times |\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0)t] \\ &= (2\pi/\hbar)|\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0)|a_S^{(0)}(t)|^2.\end{aligned} \tag{49}$$

The transition rate is proportional to the probability of occupation of state s at time t. In Eq. (49), if $|\lambda V_{RS}|^2 t/\hbar$ is sufficiently small, the exponential may be approximated by the zero-order term in its expansion, so that

$$\frac{d}{dt}P_S(t) \cong (2\pi/\hbar)|\lambda V_{RS}|^2 \delta(E_S - E_R - \hbar\omega_0). \tag{50}$$

This result is to be compared with the expression for dP_S/dt given by Eq. (17). The conditions under which the two results are valid are comparable. In both cases, a lower bound for the time is established by the desire to consider the asymptotic forms of similar expressions appearing in the calculations leading to each result. The condition is that $t/\hbar$ be large enough to ensure the applicability of formula (15) in the one case and formula (40) in the other. In addition, an upper bound for the time is imposed in the two cases. As previously noted, to avoid a mathematical difficulty arising in the course of obtaining Eq. (17), it is necessary to take $|\lambda V_{SR}|t/\hbar$ "small" – certainly less than unity. Application of the same condition to Eq. (49) leads to the approximation (50). Thus, results (49) and (17) are equivalent,

when the same time restrictions are applied; in each case, the compatibility of these restrictions is accomplished by assuming $\lambda \ll 1$. Further, by comparing the two forms of the right-hand side of Eq. (49), it is seen that the effect of the upper limit on the time is to approximate $a_S^{(0)}(t)$ by 1 in the expression for the transition rate; this corresponds to the choice $a_S^{(0)}(t) = 1$ made in the earlier approach. Mathematically speaking, however, no upper limit for the time is required to ensure the validity of the results obtained by MTSPT. From a physical point of view, though, the results cannot be considered true for arbitrarily long times, for the equations to be solved were explicitly restricted to deal with a particular induced emission process.

The imaginary part of the exponential in expression (43) for $a_S^{(0)}(t)$ corresponds to an energy correction. Taking into account the frequency distribution of the perturbing radiation, this energy correction is[12]

$$\sum_n \int_0^\infty d\omega \left| \lambda V_{nS}(\omega) \right|^2 \frac{\mathcal{P}}{E_S - E_n - \hbar\omega} ; \qquad (51)$$

since $V_{nS}(\omega)$ includes the distribution function $f(\omega)$, only those values of ω for which $f(\omega) \neq 0$ contribute to the integral. If a slightly different problem, namely, that in which the perturbing radiation is the electromagnetic field of the atomic electron itself, is considered, the energy correction becomes

$$\Delta E = \sum_{\text{photon}} \sum_n \left| \lambda V_{nS}(\omega) \right|^2 \frac{\mathcal{P}}{E_S - E_n - \hbar\omega} , \qquad (52)$$

where $\sum_{\text{photon}}$ stands for summation over all possible momenta of electromagnetic radiation; in this integral all angular frequencies ω are equally weighted. When Eq. (52) is explicitly computed for hydrogen using the dipole approximation for the perturbation interaction, a nonrelativistic value for the Lamb shift is obtained.[13]

ACKNOWLEDGMENTS

The formalism of MTSPT, and the possibility of its application to the problem discussed in this paper, were first presented to the authors by Dr. David Montgomery at the 1966 Summer Institute for Theoretical Physics at the University of Colorado. Also to be acknowledged, are several helpful conversations with Dr. Montgomery at that time. In the course of the preparation of this paper, Dr. Peter G. Thurnauer offered many productive criticisms for which the authors are grateful. Lastly, one of us (GLB) wishes to acknowledge the support of a NASA Predoctoral Traineeship for much of the period over which the research associated with this paper was performed.

---

*Based on a Ph. D. thesis submitted to the University of Vermont by G. L. Brooks, Jr.

†Present address: Hartford Branch, University of Connecticut, 1280 Asylum Avenue, Hartford, Conn. 06105.

[1]D. Brouwer and G. M. Clemence, Methods of Celestial Mechanics (Academic Press Inc., New York, 1961), Chap. XVI.

[2]N. Krylov and N. Bogolyubov, Introduction to Nonlinear Mechanics (Princeton University Press, Princeton, New Jersey, 1947), translated by S. Lefshetz.

[3]N. Bogolyubov and Y. A. Mitropolskii, Asymptotic Methods in the Theory of Nonlinear Oscillations (Gordon and Breach, Science Publishers, Inc., New York, 1961).

[4]The principal references in this category, and also the primary sources for the formulation of MTSPT used in this article, are E. A. Frieman, J. Math. Phys. 4, 410 (1963); G. Sandri, Ann. Phys. (N. Y.) 24, 332 (1963).

[5]A. H. Kritz and G. Sandri, Phys. Today 19, 57 (1966).

[6]E. Boldt and G. Sandri, Phys. Rev. 135, B1086 (1964).

[7]D. Montgomery and Th. W. Ruijgrok, Am. J. Phys. 33, 946 (1965).

[8]See discussion in Ref. 7.

[9]J. Heinrichs, Phys. Rev. 172, 1315 (1968).

[10]Only the discrete part of the spectrum is considered.

[11]G. Sandri, Ann. Phys. (N. Y.) 24, 332 (1963).

[12]It is assumed that the phases of the different frequency components of the incident radiation are randomly distributed; the separate contributions of the individual frequencies may then be linearly superposed as in Eq. (51).

[13]J. J. Sakurai, Advanced Quantum Mechanics (Addison-Wesley Publishing Co., Reading, Mass., 1967), Secs. 2–8.