also been extensively employed by the author[9,10] in the calculation of the ionic antishielding factors γ_∞ and the atomic shielding or antishielding factors R, both pertaining to the perturbation by the nuclear quadrupole moment Q. It has also been shown that the expression for R_Θ [Eq. (18)] approaches the usual formula for γ_∞ (for a single $n's$ electron), in the limit in which the radial spread of the np-vacancy wave function is very small compared to the radial extent of the $n's$-electron wave function.

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Solution of the Schrödinger Equation with a Periodic Perturbation

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The object of the paper is to obtain a perturbation expansion of the wave function which satisfies arbitrary initial conditions. For periodic perturbations, a method is developed to obtain the solution without any secular terms. It maintains the normalization condition for all times, which assures the unitarity of the transition amplitudes.

I. INTRODUCTION

In recent years, there has been revival of interest in the time-dependent-perturbation theory and, in particular, in the periodic perturbation in quantum mechanics. In the time-dependent-perturbation theory, following the conventional method for obtaining the perturbation expansion, one encounters serious difficulty due to the occurrence of secular terms, i.e., terms of the type $P(t)T(t)$, where $P(t)$ is a polynomial and $T(t)$ is a trigonometric function of time t, in the coefficients of the series. They arise when one takes the perturbation expansion as a Taylor series in the perturbation parameter and integrates successively to obtain the coefficients (see Sommerfeld[1] and Schiff[2]). Following the methods of perturbation theory in celestial mechanics, Kramers[3] suggested a procedure for eliminating the secular terms which arise from the constant term in the perturbation. But even in absence of the constant term in the perturbation, there appear secular terms in the usual perturbation expansion, both in the presence and absence of resonance. This is clearly shown in Sec. IV, Eqs. (50) and (52), for the simplest case of periodic perturbation. As a consequence of this, the unitarity of the transition amplitudes is apparently lost. This has attracted the attention of various authors in recent years. Wallace[4] has been able to bypass this difficulty by developing a method in which the transition amplitudes are directly calculated. But it may not be irrelevant to point out that, so long as the perturbation Hamiltonian and the total Hamiltonian are bounded for all times, the Schrödinger equation should admit of solutions which are bounded for all times. As a matter of fact, Schrödinger[5] noted in his early papers on the time-dependent-perturbation theory that secular terms should not appear in the solutions of the wave equations with periodic coefficients.

Hence it seems that the usual perturbation expansions which are simply Taylor expansions in terms of the perturbation parameter are inadequate. As a matter of fact, the present author[6,7] has been able to obtain a class of solutions which have no secular terms of the Schrödinger equation with a time-dependent-perturbation Hamiltonian by introducing a more general type of expansion in terms of the perturbation parameter. This class of solutions is characteristic of the perturbation Hamiltonian and is not related to the initial-value problem.

The object of this paper is to obtain a perturbation solution without any secular term, which evolves from an arbitrary initial state and remains bounded for all times. For simplicity, we will consider only periodic perturbation—the method can be easily generalized to other cases. In Sec. II the solution is obtained for a system in the absence of resonance. The case of resonance, which needs special attention, is considered in Sec. III. The difference between the perturbation expansion according to the conventional method and that suggested in this paper is shown clearly, with the help of a very common physical problem. Section V is devoted to discussion on the nature of the solutions.

Let the Schrödinger equation be given by

$$i\hbar \frac{\partial \psi}{\partial t} = [H_0 + H'(t)]\psi ; \tag{1}$$

H' is the periodic perturbing part of the Hamiltonian, such that

$$H'(t + 2\pi/\omega) = H'(t) . \tag{2}$$

It can be expressed in terms of a small parameter ϵ and expanded in a Fourier series as

$$H'(t) = \sum_{-\infty}^{\infty} (\epsilon H_1^{(n)} + \epsilon^2 H_2^{(n)} + \cdots)\, e^{in\omega t} . \tag{3}$$

Further let the normalized eigenfunctions and eigenvalues (which are assumed to be discrete) of the unperturbed Hamiltonian H_0 be φ_j and E_j ($j = 1, 2, \ldots,$), i.e.,

$$H_0 \varphi_j = E_j \varphi_j . \tag{4}$$

$\{\varphi_j\}$ are assumed to form a complete set.

II. SOLUTION IN ABSENCE OF RESONANCE

By the absence of resonance we mean that the difference of none of the pairs of eigenvalues is an integral multiple of $\hbar\omega$. Thus

$$E_j - E_k \neq n\hbar\omega \tag{5}$$

for any j or k, and n is an integer. Obviously, by this we exclude degenerate cases which, according to our method, should be considered as special cases of resonance. We propose to find the solution $\psi(t)$ of Eq. (1) which, at an initial instant t_0, is given by

$$\psi(t_0) = \sum_j b_j \varphi_j , \quad \sum_j |b_j|^2 = 1 . \tag{6}$$

But for the above normalization conditions b_j are arbitrary constants. It is well known that Eq. (1) with subsidiary conditions (2) and (3) has solutions of the form $\Phi(t)e^{i\lambda t}$ where λ is a constant and $\Phi(t)$ is periodic. Hence, we can write the most general solution,

$$\psi(t) = \sum_{j,k} \varphi_j (A_{0,jk}(t) + \epsilon A_{1,jk}(t) + \epsilon^2 A_{2,jk}(t) + \cdots) \times \exp[-i(E_k + \epsilon E_k^{(1)} + \epsilon^2 E_k^{(2)} + \cdots)(t - t_0)/\hbar] . \tag{7}$$

$A_{N,jk}(t)$ are bounded for all times and are periodic with period $2\pi/\omega$:

$$A_{N,jk}(t + 2\pi/\omega) = A_{N,jk}(t) , \qquad A_{N,jk}(t) = \sum_{-\infty}^{\infty} A_{N,jk}^{(n)} e^{in\omega t} . \tag{8}$$

They do not contain any secular term in t. Substituting this expression for $\psi(t)$ in Eq. (1) one obtains

$$\left(E_k - E_j + i\hbar \frac{d}{dt} + \epsilon E_k^{(1)} + \epsilon^2 E_k^{(2)}\right)(A_{0,jk} + \epsilon A_{1,jk} + \epsilon^2 A_{2,jk} + \cdots) = \sum_l (\epsilon H_{1,jl} + \epsilon^2 H_{2,jl} + \cdots)(A_{0,lk} + \epsilon A_{1,lk} + \epsilon^2 A_{1,lk} + \cdots) , \quad H_{N,jl} = (\tilde{\varphi}_j H_N \varphi_l) . \tag{9}$$

In writing this, we have used the following results: If $\lambda_j - \lambda_k \neq n\omega$ (n is any integer) and $P_j(t) = P_j(t + 2\pi/\omega)$, then

$$\sum_j P_j(t)\, e^{i\lambda_j t} = 0 \text{ implies } P_j(t) = 0 . \tag{10}$$

Next, we equate to zero coefficients of same power of ϵ on both sides and integrate to obtain successively higher-order terms. Thus

$$\left(E_k - E_j + i\hbar \frac{d}{dt}\right) A_{0,jk} = 0 , \tag{11}$$

$$\left(E_k - E_j + i\hbar\frac{d}{dt}\right)A_{1,jk} + E_k^{(1)}A_{0,jk} = \sum_l H_{1,jl}A_{0,lk}\ , \tag{12}$$

$$\left(E_k - E_j + i\hbar\frac{d}{dt}\right)A_{2,jk} + E_k^{(1)}A_{1,jk} + E_k^{(2)}A_{0,jk} = \sum_l (H_{1,jl}A_{1,lk} + H_{2,jl}A_{0,lk})\ . \tag{13}$$

From Eq. (11) it follows by virtue of Eqs. (6) and (8) and expression (5) that

$$A_{0,jk} = \delta_{jk}b_j\ . \tag{14}$$

In order that $A_{1,jk}$ be periodic [Eq. (12)] for $j=k$, we are obliged to choose

$$E_k^{(1)} = H_{1,kk}^{(0)}\ . \tag{15}$$

Finally, integrating Eq. (12) we get

$$A_{1,jk}^{(m)} = -\frac{H_{1,jk}^{(m)}b_k}{E_j - E_k + m\hbar\omega} \tag{16}$$

for $j\neq k$ and $m\neq 0$. The only nonvanishing constant of integration is

$$A_{1,jj}^{0} = -\sum_k \sum_{-\infty}^{\infty} A_{1,jk}^{(p)} e^{ip\omega t_0}(1-\delta_{kj})\ . \tag{17}$$

It is chosen to satisfy the initial condition (6). We next proceed with the second-order terms in Eq. (13) in exactly the same way. Thus

$$E_k^{(2)} = H_{2,kk}^{(0)} + \sum_l \sum_{-\infty}^{\infty} \frac{|H_{kl}^m|^2(1-\delta_{kl}\delta_{m0})}{E_k - E_l + m\hbar\omega}\ , \tag{18}$$

$$A_{2,jk}^{(m)} = \left(E_k^{(1)}A_{1,jk}^{(m)} - H_{2,jk}^{(m)}b_k - \sum_l \sum_{-\infty}^{\infty} H_{1,jl}^{(m-q)}A_{1,lk}^{(q)}\right)(E_j - E_k + m\omega\hbar)^{-1}\ , \tag{19}$$

for $j\neq k$ and $m\neq 0$. Again, this is the only nonvanishing constant of integration. $A_{2,jj}^{(0)}$ is to be obtained from the initial condition; hence,

$$A_{2,jj}^{(0)} = -\sum_k \sum_{-\infty}^{\infty} A_{2,jk}^{(b)} e^{ib\omega t_0}(1-\delta_{jk})\ . \tag{20}$$

Similarly, one can find higher-order terms.

We do not dwell upon the convergence of the series here. But, noting the fact that $H'(t)$ is bounded and noting the consequent restrictions on its Fourier components, one may expect that it may be possible to establish the convergence of the series. The solution thus obtained remains normalized for all times since it follows from Eq. (1) that

$$|\psi(t)|^2 = \text{const},\quad |\psi(t_0)|^2 = 1\ . \tag{21}$$

This is essentially due to the Hermiticity of the Hamiltonian. The latter property also asserts that $E_j^{(N)}$ for all j and N must be real, which is shown directly in our calculation. As a matter of fact, we write Eq. (7) as

$$\psi(t) = \sum_j b_j(t)\varphi_j,\quad b_j(t_0) = b_j\ , \tag{22}$$

so that

$$\sum_j |b_j(t)|^2 = 1\ , \tag{23}$$

which assures the unitarity of the transition amplitudes for all times. This is tantamount to the statement that the time-dependent perturbation has induced a unitary transformation of the amplitudes $b_j(t)$ from the initial value b_j at $t=t_0$.

III. SOLUTION IN PRESENCE OF RESONANCE

Let us denote the levels which are in resonance by Greek subscripts, so that

$$E_\beta - E_\alpha = n(\beta)\hbar\omega,\quad n(\beta) - n(\gamma) = n(\beta,\gamma) \tag{24}$$

(E_α is any arbitrary fixed reference in the set). n's are integers, and the second equation is only a notation. All other levels not in resonance are denoted by capital latin subscripts. If we try to proceed exactly in the same manner as in Sec. II, we note that we cannot obtain equations like those in (9) for all j, k because of relations (24), but we can still arrive at equations similar to Eq. (9) for the subscripts J corresponding to the nonresonating levels. Hence, we proceed by breaking up the summation in expression (7) in two parts:

$$\psi(t) = \sum_k \varphi_k\left(\sum_\mu (A_{0,k\mu} + \epsilon A_{1,k\mu} + \epsilon^2 A_{2,k\mu} + \cdots) \times \exp[-i(E_\alpha + \epsilon E_\mu^{(1)} + \epsilon^2 E_\mu^{(2)} + \cdots)(t-t_0)/\hbar] + \sum_J (A_{0,kJ} + \epsilon A_{1,kJ} + \epsilon^2 A_{2,kJ} + \cdots) \times \exp[-i(E_J + \epsilon E_J^{(1)} + \epsilon^2 E_J^{(2)} + \cdots)(t-t_0)/\hbar]\right)\ . \tag{25}$$

Summation in k is over all the levels, that in μ is over the resonating levels only, and that in J is over the remaining nonresonating levels. Substituting for $\psi(t)$ from Eq. (25) in Eq. (1), we obtain

$$\left(E_J - E_k + i\hbar\frac{d}{dt} + \epsilon E_J^{(1)} + \epsilon^2 E_J^{(2)} + \cdots\right)(A_{0,kJ} + \epsilon A_{1,kJ} + \epsilon^2 A_{2,kJ} + \cdots)$$

$$= \sum_{l} (\epsilon H_{1,kl} + \epsilon^2 H_{2,kl} \cdots)(A_{0,lJ} + \epsilon A_{1,lJ} + \epsilon^2 A_{2,lJ} + \ldots), \quad (26)$$

for all k, J, and

$$\left(E_\alpha - E_k + i\hbar\frac{d}{dt} + \epsilon E_\mu^{(1)} + \epsilon^2 E_\mu^{(2)} + \ldots\right)(A_{0,k\mu} + \epsilon A_{1,k\mu} + \epsilon^2 A_{2,k\mu} + \ldots)$$

$$= \sum_{l} (\epsilon H_{1,kl} + \epsilon^2 H_{2,kl} \cdots)(A_{0,l\mu} + \epsilon A_{1,l\mu} + \epsilon^2 A_{2,l\mu} + \ldots) \quad (27)$$

for all k and μ. In writing Eq. (27) we assumed that $E_\mu^{(1)}$, which are yet to be determined, are distinct. In case they are not , one has to proceed a little carefully by maintaining suitable linear combinations. From Eq. (26) we can determine $E_J^{(N)}$, $A_{N,kJ}$ working exactly in the same manner as in Sec. II; hence, we do not repeat the calculation. But the method for determining $E_\mu^{(N)}$, $A_{N,k\mu}(t)$ is quite different and reminiscent of those in the time-independent-perturbation theory. For the zeroth order (corresponding to the unperturbed solution)

$$\left(E_\alpha - E_\beta + i\hbar\frac{d}{dt}\right)A_{0,k\mu} = 0 . \quad (28)$$

The most general solution of Eq. (28), subject to the condition (8), is

$$A_{0,\gamma\mu} = a_{\gamma\mu}\, e^{-in(\gamma)\omega t}, \quad A_{0,J\mu} = 0 . \quad (29)$$

$a_{\gamma\mu}$ are constants. They are determined from first-order terms and the initial condition (6), which leads to

$$\sum_{\mu} a_{\gamma\mu}\, e^{-in(\gamma)\omega t_0} = b_\gamma . \quad (30)$$

From Eq. (27) the first-order terms for k belonging to the resonating set are given by

$$\left(E_\alpha - E_\beta + i\hbar\frac{d}{dt}\right)A_{1,\beta\mu} + E_\mu^{(1)} A_{0,\beta\mu} = \sum_{l} H_{1,\beta l} A_{0,l\mu} . \quad (31)$$

The periodicity condition on $A_{1,\beta\mu}$ immediately leads to

$$\sum_{\gamma} (E_\mu^{(1)}\delta_{\beta\gamma} - H_{1,\beta\gamma}^{[n(\gamma,\beta)]})\, a_{\gamma\mu} = 0 . \quad (32)$$

This is an eigenvalue problem. Since the matrix $H_{1,\beta\gamma}^{[n(\gamma,\beta)]}$ is Hermitian the eigenvalues $E_\mu^{(1)}$ are real and there are as many eigenvectors as the number of resonating levels. Let the orthonormal eigenvector of the secular equation (32), corresponding to the eigenvalue be $E_\mu^{(1)}$, be v_μ; so that

$$a_{\gamma\mu} \propto v_\gamma^\mu . \quad (33)$$

Equations (30) and (33) determine $a_{\gamma\mu}$ completely:

$$a_{\gamma\mu} = \sum_{\beta} b_\beta\, \tilde{v}_\beta^\mu v_\gamma^\mu\, e^{in(\beta)\omega t_0} . \quad (34)$$

Finally, integrating Eq. (31) one gets

$$A_{1,\beta\mu} = -\sum_{\gamma}\sum_{-\infty}^{\infty} \frac{H_{1,\beta\gamma}^{(m)} a_{\gamma\mu}}{[m + n(\beta,\gamma)]\hbar\omega}\, e^{i[m-n(\gamma)]\omega t} \times (1 - \delta_{mn(\gamma\beta)}) + g_{\beta\mu}\, e^{-in(\beta)\omega t} . \quad (35)$$

$g_{\beta\mu}$ are constants of integration. They are to be determined from second-order terms and the initial condition. The remaining quantities, namely $A_{1,J\mu}$, can be determined directly from Eq. (27) without any difficulty. Proceeding similarly we can obtain higher-order terms. Since they do not need any new method and are very involved, we do not continue further. On the other hand, it is to be noted that once the secular equation (32) is solved the rest of the work is simple computation. In order to emphasize this point we will show here how to obtain $E_\mu^{(2)}$ and $g_{\beta\mu}$. From Eq. (27) it is easy to write the equation for second-order terms. Now, in order that $A_{2,\gamma\mu}$ be periodic we are obliged to choose $E_\mu^{(2)}$, $g_{\gamma\mu}$ such that

$$\sum_{\gamma} F_{\beta\gamma} a_{\gamma\mu} - E_\mu^{(1)} a_{\beta\mu} = \sum_{\gamma} (E_\mu^{(1)}\delta_{\beta\gamma} - H_{1,\beta\gamma}^{[n(\gamma,\beta)]}) g_{\gamma\mu} , \quad (36)$$

where

$$F_{\beta\gamma} = H_{2,\beta\gamma}^{[n(\gamma,\beta)]} - \sum_{J}\sum_{-\infty}^{\infty} \frac{H_{1,\beta J}^{[n(\gamma,\beta)-m]} H_{1,J\gamma}^{(m)}}{E_J - E_\gamma + m\hbar\omega} - \sum_{\theta}\sum_{-\infty}^{\infty} \frac{H_{1,\beta\theta}^{[n(\theta,\beta)-m]} H_{1,\theta\gamma}^{(m)}}{[m + n(\theta,\gamma)]\hbar\omega}(1 - \delta_{mn(\gamma,\theta)}) . \quad (37)$$

Let

$$g_{\gamma\mu} = \sum_{\theta} G_{\mu\theta} v_\gamma^\theta , \quad (38)$$

so that Eq. (36), with the help of Eqs. (32) and (34), takes the form

$$\left(\sum_{\gamma} F_{\beta\gamma} v_\gamma^\mu - E_\mu^{(2)} v_\beta^\mu\right)\left(\sum_{\theta} \tilde{v}_\theta^\mu b_\theta\, e^{in(\theta)\omega t_0}\right) = \sum_{\theta} (E_\mu^{(1)} - E_\theta^{(1)}) G_{\mu\theta} v_\beta^\theta . \quad (39)$$

Finally, one obtains from this

$$E_\mu^{(2)} = \sum_{\beta,\gamma} \tilde{v}_\beta^\mu F_{\beta\gamma} v_\gamma^\mu , \quad (40)$$

$$G_{\mu\nu}(E_\mu^{(1)} - E_\nu^{(1)}) = \sum_{\beta,\gamma} \tilde{v}_\beta^\nu F_{\beta\gamma} v_\gamma^\mu \left(\sum_{\theta} \tilde{v}_\theta^\mu b_\theta\, e^{in(\theta)\omega t_0}\right) , \quad (41)$$

for $\mu \neq \nu$. $G_{\mu\mu}$ is to be determined from the initial condition

$$\sum_\gamma A_{1,\mu\gamma}(t_0) = 0 . \qquad (42)$$

It can be easily checked that $E_\mu^{(2)}$ are real (due to the Hermiticity of the Hamiltonian). Further, $E_\mu^{(2)}$ are independent of initial conditions. They are the characteristics of the perturbation and are determined by the perturbation Hamiltonian.

IV. SPECIAL CASE

In order to show the basic differences between perturbation expansions according to the conventional time-dependent-perturbation theory and that following the method suggested above, we take up in this section the simplest example of periodic perturbation, such that

$$H'(t) = \epsilon H \cos\omega t . \qquad (43)$$

This encompasses a wide class of physical phenomena, e.g., the action of a monochromatic beam of radiation on atomic or molecular systems. Following the conventional method, let us expand the wave function in the form

$$\psi(t) = \sum_j \left(A_j^{(0)}(t) + \epsilon A_j^{(1)}(t) + \epsilon^2 A_j^{(2)}(t) + \cdots\right)\varphi_j . \qquad (44)$$

Substituting this in Eq. (1) with the expression (43) for $H'(t)$, we get

$$i\hbar \frac{dA_j^{(0)}}{dt} - E_j A_j^{(0)} = 0 , \qquad (45)$$

$$i\hbar \frac{dA_j^{(N)}}{dt} - E_j A_j^{(N)} = \sum_k H_{jk} A_k^{(N-1)} \cos\omega t \quad (N \geq 1) . \qquad (46)$$

We solve these equations with the initial condition given by Eq. (6) so that

$$A_j^{(0)}(t) = b_j \exp[-iE_j(t-t_0)/\hbar] . \qquad (47)$$

The nature of the coefficients for higher-order terms is quite different in the absence and in presence of resonance.

A. Absence of Resonance

$$A_j^{(1)} = \sum \frac{H_{jk} b_k \exp[-iE_k(t-t_0)/\hbar]}{\hbar^2\omega^2 - (E_j - E_k)^2} \times [(E_j - E_k) C_{jk}(1, t) - i\hbar\omega S_{jk}(1, t)] , \qquad (48)$$

where

$$\begin{aligned} C_{jk}(n, t) &= \cos n\omega t - \cos n\omega t_0 \exp[i(E_k - E_j)(t-t_0)/\hbar] , \\ S_{jk}(n, t) &= \sin n\omega t - \sin n\omega t_0 \exp[i(E_k - E_j)(t-t_0)/\hbar] \end{aligned} \qquad (49)$$

In this case the first-order coefficients are the same as in Sec. III, due to the particular choice of the perturbation as $H_{jj}^{(0)} = 0$. It has been noted in Sec. II [Eq.(15)] that the only difference is due to $H_{jj}^{(0)}$. However, even with this choice (i.e., $H_{jj}^{(0)}$) the difference manifests itself in the second-order terms. For $n = 2$, from Eqs. (46), (48), and (49)

$$\begin{aligned} A_j^{(2)} = \sum_{kl} \frac{H_{jk} H_{kl} b_l \exp[-iE_l(t-t_0)/\hbar]}{2[\hbar^2\omega^2 (E_j - E_k)^2]} &\{ i\delta_{lj} (E_k - E_j)(t-t_0)/\hbar \\ &+ (\delta_{lj} - 1)(E_k - E_l)(E_j - E_l)^{-1}(1 - \exp[i(E_l - E_j)(t-t_0)/\hbar]) + [4\hbar^2\omega^2 - (E_j - E_k)^2]^{-1} \\ &\times [((E_k - E_l)(E_j - E_l) + 2\hbar^2\omega^2) C_{jl}(2, t) - i\hbar\omega (E_j + E_l - 2E_k) S_{jl}(2, t)] \\ &+ 2[(E_j - E_k)^2 - \hbar^2\omega^2]^{-1} \exp[i(E_l - E_k)(t-t_0)/\hbar][(E_k - E_l)\cos\omega t_0 \\ &- i\hbar\omega \sin\omega t_0][(E_j - E_k) C_{jk}(1, t) - i\hbar\omega S_{jk}(1, t)] \} . \end{aligned} \qquad (50)$$

The first term in the above expression increases linearly with time. This is an undeserving feature, in the conventional perturbation theory. If the process is continued to further higher orders, terms with increasingly higher powers of time t will appear. But each term in the perturbation expansion as developed above [Eqs. (16) and (19)] remains bounded for all times. This is also expected from the theory of differential equations of the type we are discussing, namely, Eqs. (1) and (2).

B. Presence of Resonance

In order to avoid unnecessary complications, we consider that only two levels, φ_1 and φ_2, are resonating. In this case, if one proceeds with the perturbation expansion according to the conventional method, secular terms appear even in the first-order coefficients. Let the resonance condition be expressed by

$$E_2 - E_1 = \hbar\omega . \qquad (51)$$

As noted above, the expression for $A_j^{(0)}(t)$ is the same as before [Eq. (47)]. Again, the expressions for $A_j^{(1)}$ ($j > 2$) are the same as in the previous case [Eq. (48)]. But the expression for A_s ($s = 1, 2$) is found to be

$$A_s^{(1)} = -i(\hbar\omega)^{-1} H_{ss'} b_s \exp[-iE_{s'}(t-t_0)/\hbar]\,\{\omega(t-t_0)\exp[i(s'-s)\omega t] + \exp[i(s-s')\omega t_0]\sin\omega(t-t_0)\} + \sum_k{}' [\hbar^2\omega^2 - (E_j - E_k)^2]^{-1} \times H_{sk} b_k \exp[-iE_k(t-t_0)/\hbar]\,[(E_s - E_k)C_{sk}(1,t) - i\hbar\omega S_{sk}(1,t)]\,. \quad (52)$$

The prime in the summation means that $k=s$ is to be excluded, and $s'=2$ or 1 when $s=1$ or 2. In this case the secular terms which increase linearly with time appear even in the first-order coefficients, so that they become unbounded with time. This severely restricts the application of the expansion by the conventional method. But the perturbation expansions developed in this paper are free from this shortcoming.

V. DISCUSSION

The most important point of difference of the solution obtained in this paper and the solution obtained from the conventional perturbation theory is that the indices of the exponential coefficients in expressions (7) and (25) are power series in ϵ. Hence, if one expands them directly then each term increases indefinitely with time, which leads to secular terms in the usual perturbation theory, as shown in Eqs. (50) and (52). These indices are related to the mass renormalization in quantum electrodynamics. Eberly and Frank[8] and Eberly and Reiss[9,10] have obtained them in some special cases by summing exactly Feynman–Dyson perturbation series. These indices do not contribute when one is confined to first-order terms, as in many physical problems $H_{kk}^0 = 0$, but they manifest themselves in second- and higher-order terms in the perturbation parameters. The other point of interest to be noted is that in the case of resonance the solution $\psi(t)$ in Eqs. (25) and (29) does not coincide with any of the $\varphi_s \exp(-iE_s t/\hbar)$ ($s=1, 2$) as $\epsilon \to 0$ for all times; they may be made to do so only at some suitable instants, as has been noted in Sec. IV. The appearance of secular terms owing to the vanishing of denominators, in the usual perturbation theory in case of resonance, is due to the tacit assumption that $\psi(t)$ as $\epsilon \to 0$ tends to $\varphi_j \times \exp(iE_j t/\hbar)$ for some j. Finally, the solutions obtained here remain normalized for all times if the initial solution is normalized; hence the unitarity of the transition amplitudes is assured at each instant, as noted before.

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