Remarks Concerning the Adiabatic Theorem and the S-Matrix*

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An improved mathematical formulation and solution of transition rate problems for scattering and reaction problems is given. Difficulties in connecting the time dependent and stationary methods of defining the S-matrix are noted, but not resolved.

I. INTRODUCTION

NEARLY all recent studies[1] in field theory and reaction processes[2] have been based, tacitly or explicitly, on the adiabatic hypothesis. Although the adiabatic hypothesis has been verified by Born[3] for hamiltonians which admit discrete eigenvalues only, a corresponding verification for hamiltonians which have continuous degenerate spectra has not been given. The purpose of the work being reported here is to examine to some extent conditions on the validity of the adiabatic hypothesis and to show that certain important consequences of S-matrix theory do not depend on the adiabatic hypothesis.

II. TIME DEPENDENT PERTURBATION THEORY

In this section we will be concerned with a system described by a hamiltonian

$$H(t)=H_0+Ve^{\alpha t/\hbar}, \tag{1}$$

in which H_0 is the hamiltonian of the non-interacting parts of the system and V is the time independent interaction energy. The factor[4] $e^{\alpha t/\hbar}$ was included to simulate the adiabatic turning off of the interaction as $t\rightarrow-\infty$. For simplicity we suppose that the two operators $H(t)$ and H_0 have exactly the same continuous spectrum of eigenvalues, although not, of course, the same eigenfunctions. The eigenfunctions of H_0 are denoted by ϕ_a and satisfy

$$H_0\phi_a=E_a\phi_a, \tag{2}$$

and

$$\int dN_a(\phi_a,\phi_b)=1 \text{ or } 0, \tag{3}$$

where dN_a is a suitably chosen weighting function of the states ϕ_a, so that the right side of Eq. (3) is 1 if the state ϕ_b is contained in the domain of integration over states ϕ_a, otherwise it is zero.

For the time dependent Schroedinger equation

$$i\hbar\dot{\psi}=H(t)\psi \tag{4}$$

we write a solution in the form

$$\psi=\int dN_aC_a(t)\phi_a\exp(-iE_at/\hbar), \tag{5}$$

from which we obtain, using Eqs. (2), (3), and (4), and taking ϕ_a to be time independent,

$$i\hbar\dot{C}_a(t)=\int dN_b(\phi_a,V\phi_b)C_b(t)\times\exp([i(E_a-E_b)+\alpha]t/\hbar). \tag{6}$$

Integrating Eq. (6), we obtain

$$C_a(t)=C_a{}^0-(i/\hbar)\int_{-\infty}^{t}dt'\int dN_bC_b(t')(\phi_a,V\phi_b)\times\exp([i(E_a-E_b)+\alpha]t'/\hbar), \tag{7}$$

in which $C_a{}^0$ is the initial value of $C_a(t)$ at $t=-\infty$. Iteration of Eq. (7) gives the Liouville-Neumann series solution to Eq. (7)

$$C_a(t)=C_a{}^0+\sum_{n=1}^{\infty}\int dN_bC_b{}^0\times\frac{V_{ab}{}^{(n)}(\alpha)\exp([i(E_a-E_b)+n\alpha]t/\hbar)}{E_b-E_a+in\alpha}, \tag{8}$$

in which

$$V_{ab}{}^{(n)}(\alpha)=\int dN_c\frac{V_{ac}{}^{(1)}V_{cb}{}^{(n-1)}(\alpha)}{E_b-E_c+i(n-1)\alpha}, \quad V_{ab}{}^{(1)}=(\phi_a,V\phi_b). \tag{9}$$

Now, the relative probability that the system will be in the group of states about the state ϕ_a at the time t is $W_a(t)dN_a$ in which

$$W_a(t)=|C_a(t)|^2. \tag{10}$$

The quantity of major interest is the rate of transition to state ϕ_a if the system were initially in state ϕ_b, that is

$$w_{ab}(t)=dW_{ab}(t)/dt, \tag{11}$$

for $C_a{}^0=1_{ab}$, where 1_{ab} is a generalized Dirac δ-function

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[2] The work of Wigner and Eisenbud is the most notable exception to this. E. P. Wigner and L. Eisenbud, Phys. Rev. 72, 22 (1947).
[3] M. Born, Z. Physik 40, 167 (1927).
[4] In the work of Born much more general types of time variations were considered than the simple time variation given by $e^{\alpha t/\hbar}$ which we use.

such that $\int 1_{ab}dN_a=1$ if the state ϕ_b is contained in the region of integration over states ϕ_a. Using Eqs. (8), (10), and (11) we obtain

$$w_{ab}(\alpha,t)=\frac{2}{\hbar}1_{ab}\,\mathrm{Im}\sum_{n=1}^{\infty}V_{ab}^{(n)}(\alpha)\exp(n\alpha t/\hbar)+\frac{1}{\hbar}\sum_{n,m=1}^{\infty}\bar{V}_{ab}^{(n)}(\alpha)V_{ab}^{(m)}(\alpha)\times\left(\frac{i}{E_b-E_a+in\alpha}-\frac{i}{E_b-E_a-im\alpha}\right)\times\exp((n+m)\alpha t/\hbar). \quad (12)$$

In the limit as $\alpha\to 0$, Eq. (12) becomes

$$w_{ab}=(2\pi/\hbar)\delta(E_a-E_b)|\mathbf{T}_{ab}|^2+(2/\hbar)1_{ab}\,\mathrm{Im}\mathbf{T}_{ab}; \quad (13)$$

in which

$$\mathbf{T}_{ab}=\lim_{\alpha\to 0}\sum_{n=1}^{\infty}V_{ab}^{(n)}(\alpha). \quad (14)$$

The important result given by Eq. (13) shows that in the adiabatic limit the transition rate from a state ϕ_b at $t=-\infty$ to a state ϕ_a at any finite time t, is independent of the time t, and that transitions take place only between states which conserve energy. The usefulness of the results given above depends on the convergence of the power series in Eq. (14) which defines $\mathbf{T}_{ab}$.

We now note that we may write

$$\mathbf{T}_{ab}=(\phi_a, V\psi_b^+) \quad (15)$$

in which

$$\psi_b^+=\lim_{\epsilon\to 0}\psi_b(\epsilon);\quad \epsilon>0, \quad (16)$$

and

$$\psi_b(\epsilon)=\phi_b+\frac{1}{E_b+i\epsilon-H_0}V\psi_b(\epsilon), \quad (17)$$

with $\epsilon>0$. To see that Eqs. (15) and (16) give the same result for $\mathbf{T}_{ab}$ as Eqs. (9) and (14) do, we solve Eq. (17) for $\psi_b(\epsilon)$ by iteration and substitute into Eq. (15), obtaining a power series of exactly the same form as Eq. (14) except that the imaginary part of the energy denominator, $(n-1)\alpha$, in Eq. (9) is replaced by ϵ. This makes no difference in the limit as α and ϵ approach zero since, in an integral such as Eq. (9), the limit as $\alpha\to 0$ implies that the integral over the energy is to be calculated as a principal value, minus πi multiplied by the residue at the point where energy is conserved. It is, of course, necessary that the limit as $\alpha\to 0$ of the series Eq. (14) converge to the same value as the limit as $\epsilon\to 0$ of the series obtained by iteration of Eq. (17) in Eq. (15) in order that Eqs. (14) and (15) give the same result.

The important Eq. (17) is the basis of the stationary method of solving scattering (Lippman and Schwinger[1]) and reaction problems.

III. THE BEHAVIOR OF WAVE FUNCTIONS ON THE ADIABATIC TURNING ON OF THE INTERACTION

In this section we will show that if one starts a system in the state ϕ_b at $t=-\infty$ under the action of the hamiltonian given by Eq. (1) and in the limit as $\alpha\to 0$ it will be in the state ψ_b^+ at any finite time. To prove[6] this we write the solution to the Schroedinger equation of motion, Eq. (4), in the form

$$\psi(t)=\int dN_a b_a(t)\psi_a^+(\alpha t)\exp(-iE_at/\hbar), \quad (18)$$

in which

$$\psi_a^+(\alpha t)=\lim_{\epsilon\to 0}\psi_a(\alpha t,\epsilon), \quad (19)$$

and

$$\psi_a(\alpha t,\epsilon)=\phi_a+\frac{e^{\alpha t/\hbar}}{E_a+i\epsilon-H_0}V\psi_a(\alpha t,\epsilon). \quad (20)$$

In writing Eq. (18) as a solution of Eq. (4) it is assumed that the functions $\psi_a^+(\alpha t)$ form a complete set. If we differentiate Eq. (20) with respect to time and take ϕ_a to be time independent we obtain

$$\dot{\psi}_a(\alpha t,\epsilon)=\frac{\alpha e^{\alpha t/\hbar}}{E_a+i\epsilon-H(t)}V\psi_a(\alpha t,\epsilon), \quad (21)$$

a relation which will use later. Applying Eqs. (1) and (4) to Eq. (18) gives

$$i\hbar\dot{b}_a(t)=\int dN_b b_b(t)(\psi_a^+(\alpha t),\dot{\psi}_b^+(\alpha t))\times\exp[i(E_a-E_b)t/\hbar]. \quad (22)$$

In the derivation of Eq. (22) the assumption is made that $(\psi_a^+(\alpha t),\psi_b^+(\alpha t))=1_{ab}$, an assertion which will be proved later provided certain conditions are satisfied. Integrating Eq. (22) with respect to time gives

$$b_a(t)=b_a^0-(i/\hbar)\int_{-\infty}^{t}dt'\int dN_b b_b(t')(\psi_a^+(\alpha t'),\dot{\psi}_b^+(\alpha t'))\times\exp(i(E_a-E_b)t'/\hbar), \quad (23)$$

in which b_a^0 is the initial value of $b_a(t)$ at $t=-\infty$. Using Eq. (21) in Eq. (23) and integrating by parts with respect to time

$$b_a(t)=b_a^0+\lim_{\epsilon\to 0}\int\frac{\alpha dN_b b_b(t)(\psi_a^+(\alpha t),V\psi_b^+(\alpha t))}{[E_b-E_a+i\alpha][E_b-E_a+i\epsilon]}\times\exp\{[i(E_a-E_b)+\alpha]t/\hbar\}-\lim_{\epsilon\to 0}\int\frac{\alpha dN_b}{[E_b-E_a+i\alpha][E_b-E_a+i\epsilon]}\int_{-\infty}^{t}dt'\times\exp\{[i(E_a-E_b)+\alpha]t'/\hbar\}\times\{[(\dot{\psi}_a^+(\alpha t'),V\psi_b^+(\alpha t'))+(\psi_a^+(\alpha t'),V\dot{\psi}_b^+(\alpha t'))]b_b(t')+(\psi_a^+(\alpha t'),V\psi_b^+(\alpha t'))\dot{b}_b(t')\}. \quad (24)$$

[6] If the series solution Eq. (8) of Eq. (7) converges to a solution of Eq. (7) one can then prove the adiabatic hypothesis as stated above.

We now note that the integration over the state ϕ_b in Eq. (24) of both the second and third terms involves an integration over the energy E_b of the form

$$\lim_{\epsilon\to 0}\int \alpha dE f(E,\alpha,\epsilon)/[(E+i\alpha)(E+i\epsilon)]. \qquad (25)$$

In the limit as $\alpha\to 0$ integrals of the form Eq. (25) vanish provided the integral exists for finite α and ϵ and provided $f(E,0,0)$ is regular at $E=0$. For expressions of the form Eq. (25) to vanish in the limit $\alpha\to 0$ and $\epsilon\to 0$ it is necessary that both α and ϵ have the same sign. We thus see that if the time integral in the third term is bounded as a function of α then in the limit as $\alpha\to 0$, $b_a(t)\to b_a^0$. This shows that, subject to the boundedness condition above, as an interaction is turned on adiabatically an initial state ϕ_a at $t=-\infty$ changes in the course of time into the state ψ_a^+ which is a linear combination of the initial state plus outgoing waves.

IV. THE IRRELEVANCE OF THE ADIABATIC HYPOTHESIS

The important and well-known result which is restated in this paper is the transition rate from the state ϕ_b at $t=-\infty$ to the state ϕ_a at a finite time as given by Eq. (13) in terms of the matrix element $\mathbf{T}_{ab}$ as it is determined by Eqs. (15), (16), and (17). The function of the adiabatic hypothesis was to insure that the system would be in the state ψ_b^+ at a finite time if it started in the state ϕ_b at $t=-\infty$. The use of the adiabatic process may, however, be completely circumvented by imposing the appropriate boundary condition at a finite time.

We will suppose that the system is in the state $\psi_b(\epsilon)$ at $t=0$ with $\psi_b(\epsilon)$ given by Eq. (17) and calculate the transition rate to the state ϕ_a at any finite time in the limit as $\epsilon\to 0$. We now drop the time dependent factor $\exp(\alpha t/\hbar)$ from the hamiltonian Eq. (1). If the system is in the state $\psi_b(\epsilon)$ at $t=0$, then at other time t, it will be in the state

$$\psi_b(\epsilon,t)=e^{-iHt/\hbar}\psi_b(\epsilon). \qquad (26)$$

The rate of transition from the state $\psi_b(\epsilon,t)$ to the state ϕ_a is

$$\begin{aligned} w_{ab}(\epsilon,t)&=\frac{d}{dt}|(\phi_a, e^{-iHt/\hbar}\psi_b(\epsilon))|^2\\ &=-(i/\hbar)(\phi_a,\psi_b(\epsilon,t))^*\\ &\qquad\times(\phi_a, H_b\psi_b(\epsilon,t))+\text{c.c.}, \end{aligned} \qquad (27)$$

in which

$$H_b=H-E_b. \qquad (28)$$

We will now show that

$$\lim_{\epsilon\to 0} w_{ab}(\epsilon,t)=w_{ab}, \qquad (29)$$

with w_{ab} given by Eq. (13). According to Eq. (17)

$$H_b\psi_b(\epsilon)=i\epsilon(\psi_b(\epsilon)-\phi_b). \qquad (30)$$

Define

$$f_b(\epsilon,t)=\exp(iE_bt/\hbar)\psi_b(\epsilon,t)=\exp(-iH_bt/\hbar)\psi_b(\epsilon). \qquad (31)$$

Differentiating Eq. (31) with respect to time and using Eq. (30) one obtains

$$\begin{aligned} \dot{f}_b(\epsilon,t)&=-(i/\hbar)\exp(-iH_bt/\hbar)H_b\psi_b(\epsilon)\\ &=(\epsilon/\hbar)f_b(\epsilon,t)-(\epsilon/\hbar)\exp(-iH_bt/\hbar)\phi_b. \end{aligned} \qquad (32)$$

The solution of differential Eq. (32) subject to the boundary condition $f_b(\epsilon,0)=\psi_b(\epsilon)$ gives

$$f_b(\epsilon,t)=e^{\epsilon t/\hbar}\left\{\psi_b(\epsilon)+i\epsilon\frac{[1-\exp(-i(H_b-i\epsilon)t/\hbar)]}{H_b-i\epsilon}\phi_b\right\}. \qquad (33)$$

Substituting the relation given in Eq. (33) into Eq. (27) and using Eqs. (30) and (17) one obtains

$$\begin{aligned} w_{ab}(\epsilon,t)&=e^{2\epsilon t/\hbar}\Bigg\{\bigg(\phi_a,\phi_b+\frac{1}{E_b-E_a+i\epsilon}V\psi_b(\epsilon)\\ &\quad+i\epsilon\frac{[1-\exp(-i[H_b-i\epsilon]t/\hbar)]}{H_b-i\epsilon}\phi_b\bigg)^*\\ &\quad\times\bigg(\phi_a,\frac{1}{E_b-E_a+i\epsilon}V\psi_b(\epsilon)\\ &\quad+\frac{[1-\exp(-i[H_b-i\epsilon]t/\hbar)]}{H_b-i\epsilon}H_b\phi_b\bigg)+\text{c.c.}\Bigg\}\\ &=e^{2\epsilon t/\hbar}\Bigg\{i1_{ab}[(\phi_a,V\psi_b(\epsilon))^*(\phi_a,V\psi_b(\epsilon))]\\ &\quad+\frac{2\epsilon}{(E_b-E_a)^2+\epsilon^2}|(\phi_a,V\psi_b(\epsilon))|^2\\ &\quad+\bigg[\epsilon\bigg(1_{ab}+\frac{(\phi_a,V\psi_b(\epsilon))^*}{E_b-E_a-i\epsilon}\\ &\quad-i\epsilon\bigg(\phi_a,\frac{1-\exp(-i(H_b-i\epsilon)t/\hbar)}{H_b-i\epsilon}\phi_b\bigg)^*\bigg)\\ &\quad\times(\phi_a,[1-\exp(-i(H_b-i\epsilon)t/\hbar)][H_b/(H_b-i\epsilon)]\phi_b)\\ &\quad-i\epsilon^2\bigg(\phi_a,\frac{[1-\exp(-i(H_b-i\epsilon)t/\hbar)]}{H_b-i\epsilon}\phi_b\bigg)^*\\ &\qquad\times\bigg(\phi_a,\frac{1}{E_b-E_a+i\epsilon}V\psi_b(\epsilon)\bigg)+\text{c.c.}\bigg]\Bigg\}(1/\hbar). \end{aligned} \qquad (34)$$

In the limit as $\epsilon\to 0$, Eq. (34) gives

$$w_{ab}=(2\pi/\hbar)\delta(E_a-E_b)|(\phi_a, V\psi_b{}^+)|^2 +(2/\hbar)1_{ab}\,\mathrm{Im}(\phi_a, V\psi_b{}^+), \quad (35)$$

provided the matrix elements $(\phi_a, V\psi_b{}^+)=\mathbf{T}_{ab}$ are continuous functions of the states ϕ_a and ϕ_b, and provided the matrix elements

$$(\phi_a, ([1-\exp(-i[H_b-i\epsilon]t/\hbar)]/[H_b-i\epsilon])\phi_b)$$
and
$$(\phi_a, [1-\exp(-i[H_b-i\epsilon]t/\hbar)]\phi_b), \quad (36)$$

are bounded as $\epsilon\to 0$. The matrix elements in Eq. (36) will, in fact, be bounded unless the operator H is pathological since the first of these is the time integral of unitary operator and second is the difference of two unitary operators. Thus, the validity of Eq. (29) is proven. The valuable relations

$$\int dN_a w_{ab}(\epsilon, t)=\frac{d}{dt}(\psi_b(\epsilon, t), \psi_b(\epsilon, t))=0$$
$$\int dN_a w_{ab}=0 \quad (37)$$

are here the immediate consequence of the fact that $\phi_b(\epsilon, t)$ satisfies the Schroedinger equation of motion [Eq. (4)].

We now give an independent derivation of the second of the relations given in Eq. (37). Defining the operator $T(\epsilon)$ by the equation

$$T(\epsilon)\phi_a=V\psi_a(\epsilon), \quad (38)$$

we may write Eq. (17) in the form,

$$\psi_a(\epsilon)=\phi_a+\frac{1}{E_a+i\epsilon-H_0}T(\epsilon)\phi_a. \quad (39)$$

From Eq. (30) we see that $\psi_a{}^+$ is a solution of the hermitian eigenvalue problem

$$H\psi_a{}^+=E_a\psi_a{}^+, \quad (40)$$

from which we may infer that

$$\lim_{\epsilon\to 0}(\psi_a(\epsilon), \psi_b(\epsilon))=0;\quad E_a\neq E_b. \quad (41)$$

Calculating $(\psi_a(\epsilon), \psi_b(\epsilon))$ by Eq. (39) we obtain

$$(\psi_a(\epsilon), \psi_b(\epsilon))=1_{ab}+\frac{1}{E_b-E_a+i\epsilon}[\mathbf{T}_{ab}(\epsilon)-\mathbf{T}_{ba}{}^*(\epsilon)] +\frac{1}{E_b-E_a+2i\epsilon}\int dN_c\mathbf{T}_{ca}{}^*(\epsilon)\mathbf{T}_{cb}(\epsilon) \times\left[\frac{1}{E_c-E_b-i\epsilon}-\frac{1}{E_c-E_a+i\epsilon}\right]. \quad (42)$$

In the limit as $\epsilon\to\infty$, Eq. (42) yields

$$(\psi_a{}^\dagger, \psi_b{}^\dagger)=1_{ab}+\left\{P\frac{1}{E_p-E_a}-\pi i\delta(E_a-E_b)\right\} \times\left\{\mathbf{T}_{ab}-\mathbf{T}_{ba}{}^*+\mathrm{P}\int dN_c\mathbf{T}_{ca}{}^*\mathbf{T}_{cb} \times\left(\frac{1}{E_c-E_b}-\frac{1}{E_c-E_a}\right)+\pi i\int dN_c\mathbf{T}_{ca}{}^*\mathbf{T}_{cb} \times[\delta(E_c-E_b)+\delta(E_c-E_a)]\right\}. \quad (43)$$

Equations (41) and (43) give

$$\mathbf{T}_{ab}-\mathbf{T}_{ba}{}^*+\mathrm{P}\int dN_c\mathbf{T}_{ca}\delta\mathbf{T}_{cb}\left(\frac{1}{E_c-E_b}-\frac{1}{E_c-E_a}\right) +\pi i\int dN_c\mathbf{T}_{ca}{}^*\mathbf{T}_{cb}[\delta(E_c-E_b)+\delta(E_c-E_a)]=0 \quad (44)$$

for $E_a\neq E_b$. If, however, $\mathbf{T}_{ab}$ is a continuous function of the states ϕ_a and ϕ_b, then Eq. (44) must also hold for $E_a=E_b$. Thus, Eq. (44) gives, for $a=b$,

$$(2\pi/\hbar)\int dN_c\delta(E_c-E_a)|\mathbf{T}_{ca}|^2+(2/\hbar)\,\mathrm{Im}\mathbf{T}_{aa}=0, \quad (45)$$

which is the explicit expression for the second of Eq. (47).

Substitution of Eq. (44) in Eq. (43) gives the relationship

$$(\psi_a{}^+, \psi_b{}^+)=1_{ab}, \quad (46)$$

which was assumed in the derivation of Eq. (22).

V. CONNECTION WITH THE S-MATRIX

The results given in this paper are related to the more conventional forms[1] of the Heisenberg S-matrix theory in accordance with the following definitions:

$$T_{ab}=-2\pi i\delta(E_a-E_b)\mathbf{T}_{ab} \quad (47)$$

and

$$S=1+T. \quad (48)$$

The S-matrix defined by the relations given in Eqs. (47) and (48) can be shown to be left unitary by using Eq. (44) as follows:

$$\begin{aligned}(S^\dagger S)_{ab}&=1_{ab}+T_{ab}+T_{ab}{}^\dagger+(T^\dagger T)_{ab}\\ &=1_{ab}-2\pi i\delta(E_a-E_b)(\mathbf{T}_{ab}-\mathbf{T}_{ba}{}^*)\\ &\quad+4\pi^2\int dN_c\mathbf{T}_{ca}{}^*\mathbf{T}_{cb}\delta(E_a-E_c)\delta(E_b-E_c)\\ &=1_{ab}+2\pi\delta(E_a-E_b)\left\{[\mathbf{T}_{ab}-\mathbf{T}_{ba}{}^*]/i +2\pi\int dN_c\mathbf{T}_{ca}{}^*\mathbf{T}_{cb}\delta(E_c-E_a)\right\}\\ &=1_{ab}.\end{aligned} \quad (49)$$

The proof that $SS^\dagger=1$ required additional relations which will be developed now. If we calculate

$$\mathbf{T}_{ab}(\epsilon)-\mathbf{T}_{ba}^*(\epsilon) = -\left\{\left(\mathbf{T}(\epsilon)\phi_a\left[\frac{1}{E_a-i\epsilon-H_0}-\frac{1}{E_p+i\epsilon-H_0}\right]\mathbf{T}(\epsilon)\phi_b\right)\right\}$$

or (50)

$$\mathbf{T}_{ab}(\epsilon)-\mathbf{T}_{ba}^*(\epsilon)+\int dN_c\mathbf{T}_{ca}^*(\epsilon)\mathbf{T}_{cb}(\epsilon) \times\left\{\frac{1}{E_c-E_b-i\epsilon}-\frac{1}{E_c-E_a+i\epsilon}\right\}=0.$$

We first note that in the limit as $\epsilon\rightarrow 0$, Eq. (50) reduces to Eq. (44) and thus gives an independent proof of Eq. (44). We further note that Eq. (50) is also valid for negative ϵ, from which we get, for $\epsilon>0$,

$$\mathbf{T}_{ab}(-\epsilon)-\mathbf{T}_{ba}^*(-\epsilon)+\int dN_c\mathbf{T}_{ca}^*(-\epsilon)\mathbf{T}_{cb}(-\epsilon) \times\left\{\frac{1}{E_c-E_b+i\epsilon}-\frac{1}{E_c-E_a-i\epsilon}\right\}=0. \quad (51)$$

Another needed relation follows from

$$(\psi_a(-\epsilon),\, V\psi_b(\epsilon)) =\mathbf{T}_{ba}^\dagger(-\epsilon)+\left(\mathbf{T}(-\epsilon)\phi_a,\,\frac{1}{E_b+i\epsilon-H_0}\mathbf{T}(\epsilon)\phi_b\right) \quad (52)$$
$$=\mathbf{T}_{ab}(\epsilon)+\left(\mathbf{T}(-\epsilon)\phi_b,\,\frac{1}{E_a+i\epsilon-H_0}\mathbf{T}(\epsilon)\phi_b\right),$$

from which one sees that

$$\mathbf{T}_{ab}(\epsilon)=\mathbf{T}_{ba}^*(-\epsilon), \quad (53)$$

if $E_a=E_b$. We now calculate $(SS^\dagger)_{ab}$ using Eqs. (47), (48), (51), and (53);

$$(SS^\dagger)_{ab}=1_{ab}-2\pi i\delta(E_a-E_b)(\mathbf{T}_{ab}-\mathbf{T}_{ba}^*) +4\pi^2\int dN_c\mathbf{T}_{ac}\mathbf{T}_{bc}^*\delta(E_a-E_c)\delta(E_b-E_c)$$
$$=1_{ab}+2\pi\delta(E_a-E_b)\lim_{\epsilon\rightarrow 0}\left\{[\mathbf{T}_{ba}^*(-\epsilon)-\mathbf{T}_{ab}(-\epsilon)]/i \right. \quad (54)$$
$$\left. -\pi\int dN_c\mathbf{T}_{ca}^*(-\epsilon)\mathbf{T}_{cb}(-\epsilon) \times\left\{\frac{1}{E_c-E_b+i\epsilon}-\frac{1}{E_c-E_a-i\epsilon}\right\}\right\}$$
$$=1_{ab}.$$

In deriving the above relationship we use the fact that, for all relevant matrix elements of $T_{ab}(\epsilon)$ and $T_{ba}^*(-\epsilon)$, $E_a=E_b$, hence Eq. (53) holds, and the principal parts in the integral contained in Eq. (54) vanish.

VI. REMARKS

Although these results appear generally valid, severe restrictions must be placed on the interaction energy, V, for some of the conclusions to hold. One of the most limiting of these assumptions, that the functions ψ_a^+ constitute a complete set, was utilized in proving the adiabatic theorem. For example, the functions ψ_a^+ will not form a complete set when the operator H_0 has only a continuous spectrum, and $H(t)$ has the same continuous spectrum as H_0 plus additional discrete eigenvalues.

We will show that completeness here is a necessary condition for the adiabatic hypothesis to hold. If the system starts in the state ϕ_b at $t=-\infty$, then under the action of the hamiltonian, Eq. (1), at time t, it will be in the state

$$\psi_b(t,\alpha)=U(t,\alpha)\phi_b, \quad (55)$$

in which $U(t,\alpha)$ is a unitary operator (i.e., $U^\dagger U$ $UU^\dagger=1$). Since $U(t,\alpha)$ is a unitary operator, the set of states $\psi_b(t,\alpha)$ is complete. Thus we see that in the limit as $\alpha\rightarrow 0$ the set of states $\phi_b(t,\alpha)$ (if they approach a limit) will approach a complete set and, therefore, cannot approach the set of states ψ_b^+, if the set of states ψ_b^+ is not complete. The same argument leads us to conclude that in the limit as $\alpha\rightarrow 0$ the states $\psi_b(t,\alpha)$ will not approach stationary states[6] unless the set of states ψ_b^+ is complete.

The fact that the limit as $\alpha\rightarrow 0$ of $\psi_b(t,\alpha)$ differs from ψ_b^+ does not prove that a transition rate calculated by

$$w_{ab}=\lim_{\alpha\rightarrow 0}\frac{d}{dt}|(\phi_a,\,\psi_b(t,\alpha))|^2, \quad (56)$$

will differ from the transition rate as given by

$$w_{ab}-\lim_{\epsilon\rightarrow 0}\frac{d}{dt}|(\phi_a,\,e^{-iHt/\hbar}\psi_b(\epsilon))|^2. \quad (57)$$

We have, however, not succeeded in obtaining a proof of the equivalence of Eqs. (56) and (57) except when expression (12) approaches Eq. (13) in the limit $\alpha\rightarrow 0$ and the series of Eq. (14) has the limiting value $(\phi_a,\,V\psi_b^+)$, nor have we proven that Eqs. (56) and (57) will not give the same result if the functions ψ_b^+ do not constitute a complete set. We have merely noted that if one could show that

$$\lim_{\alpha\rightarrow 0}\psi_b(t,\alpha)=\exp(-iE_bt/\hbar)\psi_b^+ +\sum_n C_n\phi_n\exp(-iE_nt/\hbar), \quad (58)$$

in which ϕ_n are the discrete eigenfunctions of H and the

[6] In the paper of Lippmann and Schwinger, an essential step in the development of the transition rate formula [Eq. (1.72)] was an assumption equivalent to the requirement that the states $\psi_b(t,\alpha)$ approach stationary states in the limit as $\alpha\rightarrow 0$, and consequently that the states ψ_b^+ form a complete set.

C_n are appropriate constants, then one could demonstrate the equivalence of Eqs. (56) and (57).

Another difficulty is demonstrating rigorously the equivalence between the S-matrix as it is defined by Eqs. (47) and (48) of the stationary method, and its definition as a unitary matrix describing the state of the system at $t=\infty$ in terms of the state at $t=-\infty$; i.e., $\psi(\infty)=S\psi(-\infty)$. Actually, the important conclusions of this paper do not depend on a demonstration of the equivalence of these two definitions of the S-matrices. However, many recent works in field theory have, in effect, depended on the assumption of the equivalence of these two definitions and it would be worthwhile to find a mathematically satisfactory demonstration of the equivalence.

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Imprisonment of Resonance Radiation in Gases. II

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This paper is a continuation of an earlier paper which treated the decay of resonance radiation in optically excited gases for the case of doppler-broadened radiation in plane-parallel enclosures. The treatment is here extended to a second type of enclosure geometry—infinite cylinders—and to a variety of spectral line shapes.

1. INTRODUCTION

THE phenomenon of imprisonment of resonance radiation in gases owes its existence to the selective absorbability of resonance lines by normal atoms of the emitting gas. Over a wide range of gas density this absorbability is so high that a resonance quantum emitted in the interior of a gas-filled enclosure has but a small chance of reaching the walls; hence, the eventual escape of a unit of atomic excitation energy from the enclosure generally takes place only after a large number of repeated emissions and absorptions. Under these conditions the radiation is said to be "imprisoned."

Perhaps the most direct way in which imprisonment manifests itself is in decay experiments with optically excited gases. In this type of experiment an enclosure of gas is irradiated with a beam of resonance radiation, which serves to excite some of the gas atoms to a given resonance state. The incident beam is then abruptly cut off, and the intensity of diffuse radiation, which is proportional to the concentration of atoms in the resonance state, is measured as a function of time. One observes essentially an exponential decay of the form $e^{-\gamma g t}$, where $1/\gamma$ is the radiative lifetime of an isolated atom and g, the "escape factor," is a dimensionless quantity characteristic of the imprisonment process. The quantity g may be regarded as the reciprocal of the number of emission and absorptions of an individual unit of atomic excitation prior to its escape from the enclosure.

In an experiment on the decay of the 6^3P_1 mercury resonance state, which combines optically with the ground state to emit the 2537A resonance line, Zemansky[1] observed values of g as low as 10^{-3}. The quantity g was also found to depend both on vapor density and enclosure geometry.

A theoretical study[2] of the decay problem was recently carried out by the author of the present paper. It was shown that g depends not only upon vapor density and enclosure geometry but also upon the shape of the resonance line. In particular, for an enclosure of the form of an infinite slab of thickness L and for a doppler-broadened resonance line, the following expression for g was obtained:

$$g=1.875/[k_0L(\pi \log\tfrac{1}{2}k_0L)^{\frac{1}{2}}], \tag{1.1}$$

where k_0 is the absorption coefficient at the center of the resonance line. k_0, itself, is specified[3] in terms of the parameters of the system: gas density, gas temperature, wavelength of the line, and lifetime of the resonance state.

More recently,[4] measurements of the imprisonment of resonance radiation in mercury vapor over a wide range of vapor density were carried out at the Westinghouse Research Laboratories. In the region of density for which g had been evaluated—the doppler-broadening region—the agreement between theory and experiment was quite satisfactory.

[1] M. W. Zemansky, Phys. Rev. **29**, 513 (1927).
[2] T. Holstein, Phys. Rev. **72**, 1212 (1947), to be referred to hereafter as "I."
[3] A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (The Macmillan Company, New York, 1934) (to be referred to hereafter as "MZ") Chapter III, pp. 99–100 and Eq. (35).
[4] Alpert, McCoubrey, and Holstein, Phys. Rev. **76**, 1257 (1949).