Pramāṇa, Vol. 3, No. 6, 1974, pp 363-369. © Printed in India.

On the decaying states and the transition rates

N D SEN GUPTA
Tata Institute of Fundamental Research, Bombay 400005

MS received 13 October 1973; after revision 1 June 1974

Abstract. The object of this paper is to point out that the hypothesis of decaying states, *i.e.*, states with amplitude having a factor $e^{-\gamma t}$ (γ-real) is not compatible with the wave equation with a hermitian hamiltonian. An attempt has been made to obtain the expression for relative population density in general. It is shown that the usual expressions for the transition rates, which are proportional to time, may be obtained for a very restricted interval of time.

Keywords. Decaying states; transition rates.

1. Introduction

Since the early days of quantum mechanics, decaying states have been introduced in an *ad hoc* manner to explain various classes of physical phenomena. In spectroscopy, this is introduced to reproduce the line-shape (the Lorentz factor) both in emission and absorption spectra, so as to bypass the difficulty with vanishing denominators, which appear in the usual perturbation expansions in case of resonance. To be precise, by the introduction of decaying states, the appearance of secular terms in time, *i.e.*, terms which increases indefinitely with time are avoided. Another important physical process which apparently led one to the concept of decaying states, is the spontaneous emission from an excited state to any other admissible states of lower energy. Yet another category of phenomena, which are explained with the help of intermediate decaying states are the nuclear reactions and the resonance reaction in particular.

The concept of decaying states, in wave mechanics was first introduced by Weisskopf and Wigner (1930 *a*, *b*) in their classic papers, to explain the natural width of spectral lines. This was latter adopted suitably to explain various other problems, in particular, the quantum theory of dispersion by Breit (1933), Fermi (1932). Further, Breit and Wigner (1936) explained the observed capture cross-section of slow neutrons with the help of metastable states. The phenomenon of spontaneous emission was readily explained with the help of decaying states by Weisskopf (1933). Perhaps this was the main motivation to introduce the concept of decaying states.

The object of this paper is to examine critically the system of equations pertaining to the physical phenomena. It is shown that the system of equations does not admit solutions which correspond to decaying states, so long as the interaction hamiltonian is hermitian. In fact, in a series of publications, the author (Sen

Gupta 1970 *a*, *b*, *c*, 1972, 1973 *a*, *b*) has been able to present the solution of the Schrödinger equation with time-dependent perturbation, which remains normalized with the evolution of time to any order of the perturbation parameter, provided the hamiltonian is hermitian.

The next section begins with a brief introduction of the general system of equations relevant to the class of physical phenomena. Then, it is followed by investigations on the nature of the solutions and their physical significance. The last section is a general discussion on the decaying states and the results obtained in the paper.

2. The equation for the evolution of state and the solution

2.1. *The equation for the amplitude*

Following Dirac's theory, Weisskopf and Wigner (1930 *a*) wrote the wave equation for the interaction of atoms and radiation in terms of the probability amplitudes as,

$$i\hbar \frac{da}{dt}(q, n_1, n_2, \ldots) = (E_q + h \sum_\rho n_\rho \nu_\rho)\, a(q, n_1, n_2, \ldots) + \sum_\rho \sum_u \omega^\rho_{qu} [\sqrt{n_\rho + 1}\, a(u, n_1, \ldots, n_\rho + 1, \ldots) + \sqrt{n_\rho} a(u, n_1, \ldots, n_\rho - 1, \ldots)] \quad (1)$$

$|a(q, n_1, n_2, \ldots)|^2$ is the probability that the atom is in qth stationary state, ϕ_q, with energy E_q and radiation consists of n_ρ photons of frequency ν_ρ and

$$\omega^\rho_{qu} = \omega^{\rho *}_{uq} = \sqrt{\frac{\hbar}{\nu_\rho}} \int \frac{e\hbar}{im} \tilde{\phi}_q (A^\rho . \nabla)\, \phi_u d\tau \quad (1')$$

is the matrix element of the interaction hamiltonian between the stationary states ϕ_q and ϕ_u. The solution of eq. (1) is sought for, which satisfies the initial condition

$$\left.\begin{aligned} &a(q, n_1, n_2, \ldots) = 1 \text{ for } q = b \text{ (say)}, \; n_1, = n_2 = \ldots = 0 \\ &a(q, n_1, n_2 \ldots) = 0 \text{ otherwise} \end{aligned}\right\} \quad (2)$$

and further the time dependence of one of them is of the form,

$$a(q, 0, 0, \ldots) = \exp(-2\pi \Gamma t) \quad (3)$$

where Γ is a real constant*.

As a matter of fact, the general mathematical formulation of this class of problems, *e.g.*, dispersion at resonance, spontaneous emission, nuclear reaction, etc. which appeared subsequently may be formulated in the following manner

$$i\hbar \frac{da_N}{dt} = E_N a_N + \epsilon \sum_M W_{NM} a_M \quad (4)$$

($W_{NM} = W^*_{MN}$). The subscripts N, M stand collectively to specify both the state of the atom and radiation. For the initial condition, one of the a's is selected out depending on the particular nature of the problem. It is usually stated as at $t = 0$,

$$|a_N| = 1, \quad a_M = 0, \quad M \neq N \quad (5)$$

---

* See Weisskopf and Wigner (1930 *a*) p. 5 eq. (15 *a*) and p. 64 eq. (18 *a*); (1930 *b*) p. 2 eq. (6 *a*) and p. 23 eq. (12); Breit G (1933) p. 93, eq. (124).

Next, one endeavours to find a solution of eq. (4), with the hypothesis that

$$a_N(t) = \exp(-2\pi\gamma_N t) \tag{6}$$

where γ_N is a (complex) constant and the rest of the calculation is devoted to determine γ_N in terms of the coefficients. It is clear that Weisskopf and Wigner's formulation as stated above is a special case of this.

Here, it may be pointed out that eq. (4) is a first order differential equation in time and it is well known from the theory of differential equations that the initial condition (5) is sufficient to determine uniquely the solution. (Note, a_N are determined but for a constant phase factor which is the same for all a_M). Hence, it should be emphasized that either the hypothesis, namely eqs (3) and (6), is redundant or it is not compatible with the system of equation, eqs (1) and (4), *i.e.*, the system does not, in general, admit solution of the nature as assumed in eqs (3) and (6).

2.2 *The time evolution of the amplitudes*

In order to write the general equation (eq. 4) and the initial condition (5), let us introduce the vector $\boldsymbol{a}(t)$ and the matrix W, given by

$$\boldsymbol{a}(t) = \sum_{E,\xi} a_{E\xi}(t)\, e_{E\xi} \tag{7}$$

$$W_{E\zeta,F\xi} = E\delta_{EF}\delta_{\zeta\xi} + \epsilon V_{E\zeta,F\xi} \tag{8}$$

$e_{E\xi}$ are the unit vectors in the space dual to the Hilbert space of the state vectors of the unperturbed hamiltonian, *i.e.*, of the free atom and the radiation. E, F, stand for the total energy of the state of the atom and radiation. These states are in general degenerate, ζ, ξ, stand collectively for the indices which specify uniquely one of these degenerate states. $a_{E\xi}(t)$ corresponds to a particular $a(E_q, n_1, n_2, \ldots)$ and is the amplitude of the state with energy

$$E = E_q + h \sum n_\rho \nu_\rho \tag{9}$$

The energy states are degenerate as the total energy may be the same but E_q, n_ρ may be different, ξ stands for one of these states. $V_{E\zeta,F\xi}$ is the matrix element of the interaction hamiltonian between these states. ϵ is the parameter which denotes the strength of the interaction. In terms of $\boldsymbol{a}$ and W, the eq. (4) may be written as

$$i\hbar \frac{d\boldsymbol{a}(t)}{dt} = W\boldsymbol{a}(t) \tag{10}$$

Since W is independent of time the unique solution of this equation with the initial $\boldsymbol{a}(t_0)$ at $t = t_0$

$$\boldsymbol{a}(t_0) = \sum_{E,\xi} a_{E\xi}(t_0)\, e_{E\xi} \tag{11}$$

is given by

$$\boldsymbol{a}(t) = \exp\left(-\frac{i}{\hbar} W(t - t_0)\right) \boldsymbol{a}(t_0) \tag{12}$$

The probability of finding the system in any state denoted by the subscripts

E and ξ at any subsequent instant of time t, is given by

$$| a_{E\xi}(t) |^2 = | e_{E\xi} . a(t) |^2 \tag{13}$$

In order to express this directly in terms of $a_{E\xi}(t_0)$ we pass from the vectors $\{e_{E\xi}\}$ which are associated with the state vector of the non-interacting system ($\epsilon = 0$) to the eigen vectors $\{e'_{E(\xi)}\}$ of W. They are defined by

$$We'_{E(\xi)} = E(\xi)\, e'_{E(\xi)} \tag{14}$$

$E(\xi)$ are the eigenvalues which tend to E as $\epsilon \to 0$, the degeneracy may be partially or completely removed. The transformations from $\{e_{E\xi}\}$ to $\{e'_{E(\xi)}\}$ and *vice versa* are unitary, and may be written as

$$\left.\begin{aligned} e'_{E(\xi)} &= \sum U^{F\eta}_{E(\xi)} e_{F\eta} \\ e_{E\xi} &= \sum U^{F(\zeta)}_{E(\xi)} e'_{F(\zeta)} \end{aligned}\right\} \tag{15}$$

so that

$$\sum_{F,\eta} U^{F\eta *}_{E(\xi)}\, U^{G(\theta)}_{F\eta} = \delta_{EG}\delta_{\xi\theta} \tag{16}$$

Let us now express $a(t_0)$ in terms of $e'_{E(\xi)}$

$$\left.\begin{aligned} a(t_0) &= \sum_{E,\xi} c_{E(\xi)} e'_{E(\xi)} \\ \text{with} \quad & \\ c_{E(\xi)} &= \sum_{F,\eta} a_{F\eta}(t_0)\, U^{E(\xi)}_{F\eta} \end{aligned}\right\} \tag{16}$$

Hence, from eqs (12) and (14)

$$a(t) = \sum_{E,\xi} \left[\exp -\frac{i}{\hbar} E(\xi)(t - t_0)\right] c_{E(\xi)} e'_{E(\xi)} \tag{17}$$

The most important point which needs to be emphasized here is that the factors depending on time in the above expression are all unimodular [$E(\xi)$ are all real] and it is easy to check up

$$| a(t) |^2 = | a(t_0) |^2 \tag{18}$$

Hence, if the initial state is normalized it will remain so subsequently. This is a direct consequence of the hermiticity of the hamiltonian. Secular terms in time appear only because one usually expands the exponential operator in eq. (12) in powers of interaction parameter ϵ, while working in the characteristic space of the hamiltonian in absence of interaction. The basic reason for passing to this space of W, the operator which induces the transition, is that the unitary operator exp [$-$ (i/$\hbar$) $W(t - t_0)$] reduces to unimodular factors exp [$-$ (i/$\hbar$) $E(\xi)$ $(t - t_0)$.

It may not be irrelevant to mention that our result up to this stage is exact and no approximation has yet been effected. One is obliged to introduce suitable approximations in determining the eigenvalues $E(\xi)$ and eigenvectors $e'_{E(\xi)}$ of W, eq. (14). The problem is exactly the same, when ϵ is considered as a small parameter, as that of the determination of the energy eigenvalues and the corresponding stationary states in the time-independent perturbation theory. The expressions are well known. Before quoting the results it needs to be mentioned that the

choice of the unit vectors $e_{E\xi}$ for a fixed E, *i.e.*, in the subspace of the eigenvalue E of the unperturbed hamiltonian is quite arbitrary. The time-independent perturbation theory states that the zeroth order of eigenvectors should also be the eigenvector of the interacting hamiltoinian. [It may be noted that we have taken only a linear term in ϵ, eq. (8)]. It is convenient to define (for a fixed E) the eigenvectors of the restriction of the interaction hamiltonian in this subspace, *i.e.*,

$$V_{E\zeta, E\xi} = \delta_{\zeta\xi} V_{E\xi, E\xi} \tag{19}$$

With this choice one can write in the usual manner $E(\xi)$ and $U^{F\eta}_{E(\xi)}$ in powers of ϵ.

2.3. *The transition probabilities*

From eqs (16 and 17), it follows that

$$a_{E\xi}(t) = \sum_{Q, F, \theta, \eta} \exp\left[-\frac{i}{\hbar} Q(\theta)(t - t_0)\right] U^{Q(\theta)}_{F\eta} U^{E\xi}_{Q(\theta)} a_{F\eta}(t_0) \tag{20}$$

Hence, the population density of the state corresponding to the unit vector $e_{E\xi}$ at any instant of time is given by

$$|a_{E\xi}(t)|^2 = \sum_{Q, Q', \theta\theta'} \exp\left[\frac{i}{\hbar}\{Q(\theta) - Q'(\theta')\}(t - t_0)\right] \times A^*_{E\xi}(Q, \theta) A_{E\xi}(Q', \theta') \tag{21}$$

where

$$A_{E\xi}(Q, \theta) = \sum_{F, \eta} U^{E\xi}_{Q(\theta)} U^{Q(\theta)}_{F\eta} a_{F\eta}(t_0) \tag{21'}$$

The terms for which $Q \neq Q'$ are highly oscillatory. Since the period of observations are a few orders higher than the period $h/\{Q(\theta) - Q'(\theta')\}$ corresponding to atomic oscillations, the average contribution to these terms may be neglected. But for the terms for which $Q = Q'$, the frequencies of the oscillating part is

$$\frac{1}{\hbar}\{Q(\theta) - Q(\theta')\} = \frac{\epsilon}{\hbar}(V_{Q\theta, Q\theta} - V_{Q\theta', Q\theta'}) + O(\epsilon^2) \tag{22}$$

The periods associated with these terms are no longer small, because of the factor ϵ. If we neglect the variation, with time, of these terms during the period of observations, which is a few orders less than the period associated with these terms, one can easily write the average population density. The expression reduces to a simple form, in the special case when the initial state is an eigen state of energy E_0 say, *i.e.*,

$$a_{E\xi}(t_0) = \delta_{EE_0} b_\xi, \quad \sum_\xi |b_\xi|^2 = 1 \tag{23}$$

so that,

$$|a_{E_0\lambda}(t)|^2 = |b_\lambda|^2 + \epsilon \sum_\theta \left\{\exp\left[\frac{i}{\hbar}(E_0(\lambda) - E_0(\theta))(t - t_0)\right] \times b^*_\lambda b_\theta \overset{(1)}{U}{}^{E_0\lambda}_{E_0(\theta)} + \text{c.c.}\right\} \tag{24}$$

(retaining only first order terms). Thus the amplitudes [eq. (20)] or the average

amplitudes [eq. (24)] do not contain any secular term which increases indefinitely with time. The energy conservation is satisfied in virtue of the fact that the effective contributions are from the terms for the same Q.

Finally, in the special case with initial condition eq. (23) one can justifiably speak of time-proportional transition rates, only during the interval for which $|\{E_0(\theta) - E_0(\theta')\}(t - t_0)| \ll \hbar$ in order that

$$\sin \frac{1}{\hbar}\{E_0(\theta) - E_0(\theta')\}(t - t_0) \simeq \frac{\epsilon}{\hbar}\{E_1(\theta) - E_1(\theta')\}(t - t_0) \tag{25}$$

where $E_1(\theta)$ is the coefficient of ϵ in the expression for $E_0(\theta)$, so that

$$\{|a_{E_0\lambda}(t)|^2 - |a_{E_0\lambda}(t_0)|^2\} \propto \epsilon^2 (t - t_0) \tag{26}$$

This agrees in form with the usual expression as the first effective contribution is proportional to ϵ^2. But its range of validity is extremely limited since $(t - t_0)$ should be a few orders greater than the periods of atomics oscillations, but it should not be large enough to violate the approximation in eq. (25).

3. Discussion

From the above, it is quite clear that the wave equation does not admit a solution which corresponds to decaying with factors $\exp(-\gamma_n t)$ where γ_n are real. The usual hypothesis [eqs (3) and (6)] for the solution is really not compatible with the wave equation. It should be emphasized that this is valid so long as the total hamiltonian is hermitian. It is this property which immediately forces us to conclude that all the time dependent factors in the amplitudes are unimodular. In this connection it may not be irrelevant to mention that apart from the particular hamiltonian we have considered in the wave equation, any time-dependent hamiltonian which is bounded and closed for all time will always lead to the evolution of normalized states from normalized states.

The *ad hoc* introduction of the decaying factor was motivated from the classical theory, *e.g.*, Drude-Lorentz theory of dispersion. The classical equation being a second order inhomogeneous one, a damping force saves one from the difficulties of the vanishing denominator. But in quantum mechanics the wave equation being linear homogeneous, no such difficulty should arise even in case of resonance. This point was emphasized by Schrödinger (1926; *see* Sen Gupta 1973 *b*), in one of his early papers on the time-dependent perturbation theory. The author has been able to present such solutions in case of resonance (Sen Gupta 1972, 1973 *a*).

The other important reason to introduce the decay factor is to obtain a ready explanation of spontaneous emission. But with the quantization of the radiation field the qualitative difference between spontaneous and induced emission is eliminated and the difference is only of a quantitative nature. Hence, it does not need the introduction of decaying states since induced emission does not need such concepts.

Next, the damping in analogy to the classical theory may arise when the collision terms or terms of similar physical nature are introduced in the hamiltonian at the beginning in which case the hamiltonian is no longer hermitian. In the above investigations we have restricted ourselves to discrete spectra of the non-

interacting hamiltonian, but with due restriction on the hamiltonian which ensures convergence, the discussions may be extended for continuous spectra.

Decaying factors appear occasionally due to the method of approximation which spoils the hermitian property of the total hamiltonian and the imposition of inconsistant initial restrictions or conditions. In fact the problem as stated above with the prescribed intial conditions is a well-posed mathematical problem and the solution is unique. Neither such an hypothesis [eqs (3), (6)] is necessary nor can it be justified (Halany 1966).

References

Breit G 1933 *Mod. Phys.* **5** 91
Breit G and Wigner E 1936 *Phys Rev.* **49** 519.
Fermi E 1932 *Rev. Mod. Phys.* **4** 87
Halany A 1966 *Differential Equations* (*Rumanian*), *English Translation* (New York and London, Academic Press)
Schrödinger E 1926 *Ann. d. Physik* (Sr. 4) **81** 112
Sen Gupta N D 1970 *a Rev. Roum. Phys.* **15** 1003
Sen Gupta N D 1970 *b Rev. Roum. Phys.* **15** 1151
Sen Gupta N D 1970 *c J. Phys. A* (*Gen. Phys.*) **3** 618
Sen Gupta N D 1972 *J. Phys. A* (*Gen Phys.*) **5** 401
Sen Gupta N D 1973 *a Phys. Rev. A* **7** 891
Sen Gupta N D 1973 *b* **1** 165
Weisskopf V and Wigner E 1930 *a Zeit. f. Physik* **63** 54
Weisskopf V and Wigner *F* 1930 *b Zeit. f. Physik* **65** 10
Weisskopf V 1933 *Zeir. f. Physik* **85** 451