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## Lower and upper bounds for time-smoothed total transition probabilities and their rates

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**Abstract.** A formalism of time-smoothed total transition probabilities and their rates is developed which employs Laplace averages of these quantities. Under conditions pertinent to scattering processes, the Laplace-average formalism is shown to yield results equivalent to those obtained from a stationary-state formalism. Rigorous lower and upper bounds are obtained for the Laplace-averaged quantities which reduce to equalities for two-level systems. The lower bounds appear to be potentially useful for estimating lower bounds for total cross sections of various processes.

### 1. Introduction

Most fundamental theoretical descriptions of physical and chemical systems at the present time involve quantities which, despite their being formally exact, necessitate approximations for their evaluation. In such cases, there is evident merit in having procedures of approximation which can be carried out and which provide some means of assessing the adequacy of the approximated quantities in theoretical terms. Even if a full theoretical assessment of their adequacy is not feasible, approximated quantities that demonstrably serve to put bounds—either lower or upper—on their exact counterparts can be useful.

Several such procedures for estimating some quantum-mechanical properties of systems (Weinhold 1972) and for estimating some of the properties of systems which are in statistical mechanical equilibrium (Girardeau and Mazo 1973, Golden 1974a, b) are now known. No comparable mathematical apparatus for estimating time-dependent properties of systems is yet available, although some progress has been made recently to alleviate this situation (Golden 1973, 1975, Platz and Gordon 1973). With this end in mind, the present paper provides a treatment of time-dependent total transition probabilities and their rates which culminates in providing expressions for both lower and upper bounds to time-smoothed values of these quantities.

The following section provides an introduction to a formalism of time-smoothed total transition probabilities and their rates, which employs Laplace averages (Kohn and Luttinger 1957, Golden 1969) of these quantities, especially relating to their

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equivalent experimental use. The next section establishes an equivalence between the results obtainable from the Laplace-average formalism and those obtainable from a stationary-state formalism pertinent to the description of scattering processes. Several rigorous lower and upper bounds for Laplace-averaged total transition probabilities and their rates are derived in the succeeding section, for conditions not necessarily restricted to those prevailing in scattering processes. In § 5, the bounds are compared to the exact results obtained for a two-state system and some indication is given as to their possible use in other cases.

## 2. Preliminary measurability considerations

We will confine our attention to a Gibbsian ensemble of systems that is originally characterized by a statistical operator  $\rho_0$  corresponding to a pure state

$$\rho_0^\dagger = \rho_0 = \{\rho_0\}^2, \quad (2.1)$$

with (assuming that all traces to be considered exist)

$$\text{Tr } \rho_0 = 1. \quad (2.2)$$

At any later time  $t$ , the evolution of the statistical operator is determined by

$$i\hbar \frac{\partial \rho(t)}{\partial t} = [\mathbf{H}, \rho(t)] \quad (2.3)$$

which is von Neumann's equation of motion (von Neumann 1955).  $\mathbf{H}$  is the (time-independent) Hamiltonian of the system which, with no undue loss of generality, will be supposed to possess a purely discrete spectrum of eigenvalues that is bounded from below, no one of which is a limit-point of the others; the number of eigenvalues in any finite range is presumed to be finite, however large. The formal solution of equation (2.3) is

$$\rho(t) = \mathbf{U}^\dagger(t) \rho_0 \mathbf{U}(t) \quad (2.4)$$

where

$$\mathbf{U}(t) = \exp[it\mathbf{H}/\hbar] \quad (2.5)$$

so that

$$\text{Tr } \rho(t) = \text{Tr } \rho_0 = 1. \quad (2.6)$$

The probability that a system will be found at time  $t$  in the same state which characterized it initially is

$$P(t) = \text{Tr } \rho(t) \rho_0. \quad (2.7)$$

The complementary probability that the system will then be found in some state other than the one which characterized it initially is

$$T(t) = 1 - P(t) = 1 - \text{Tr } \rho(t) \rho_0 \quad (2.8)$$

while, clearly, its time rate-of-change is

$$\dot{T}(t) \equiv \frac{dT(t)}{dt} = -\text{Tr } \frac{\partial \rho(t)}{\partial t} \rho_0. \quad (2.9)$$

$T(t)$  will be referred to as the *total transition probability*, while  $\dot{T}(t)$  represents the *total transition probability rate*. Both are dynamical quantities requiring a detailed knowledge of  $\rho(t)$  so their evaluation is generally a formidable undertaking.

In order to place the following analysis in its proper perspective, suppose that an experimenter is able to select a sub-ensemble consisting of  $N(t)$  systems from the available Gibbsian ensemble of systems. Suppose also that he is capable of instantly measuring the number of systems  $n(t)$  which can be characterized as being in some state other than the original one, and that he is also able to directly measure  $\dot{n}(t)$ , the time rate-of-change of  $n(t)$ . When done under *quasi-closed conditions*, the experimenter arranges that

$$N(t) = N_0 \quad \text{for all } t \quad (2.10)$$

and concludes that

$$(\dot{n}(t))_{\text{closed}} = N_0 \dot{T}(t). \quad (2.11)$$

Alternatively, when done under *quasi-steady state conditions*, the experimenter arranges that

$$\dot{N}(t) = \dot{N}_0 \quad \text{for all } t \quad (2.12)$$

and concludes that

$$(\dot{n}(t))_{\text{steady}} = \dot{N}_0 T(t). \quad (2.13)$$

Both  $T(t)$  and  $\dot{T}(t)$  are dynamical quantities, as noted earlier, whereas  $N_0$  and  $\dot{N}_0$  are not. As a result, the measured  $\dot{n}(t)$  are not intrinsic properties of the system, but usually depend on how the experiments are performed.

Inherent difficulties in evaluating  $T(t)$  or  $\dot{T}(t)$  theoretically can be alleviated to some extent if emphasis is given to the values that they attain for indefinitely large values of  $t$ , although caution is required since the quantities may possess no genuine asymptotic limit as  $t$  become indefinitely large (Golden and Longuet-Higgins 1960, Farquhar 1964). For this reason, it proves useful to work with those *time-smoothed values* which are exemplified by the Laplace averages (Golden 1969) of the quantities. Explicitly, we shall be concerned with

$$\bar{T}(\zeta) \equiv \zeta \int_0^{\infty} dt e^{-\zeta t} T(t) \quad (2.14)$$

and

$$\bar{\dot{T}}(\zeta) \equiv \zeta \int_0^{\infty} dt e^{-\zeta t} \dot{T}(t) \quad (2.15)$$

where, for the present,  $\zeta$  is a real positive quantity.

Instead of dealing with the direct-temporal behaviour of measured  $\dot{n}(t)$ , an experimenter will have no difficulty in working with their Laplace averages

$$\bar{\dot{n}}(\zeta) \equiv \zeta \int_0^{\infty} dt e^{-\zeta t} \dot{n}(t). \quad (2.16)$$

As a result, equations (2.11) and (2.13) yield

$$(\bar{\dot{n}}(\zeta))_{\text{closed}} = N_0 \bar{\dot{T}}(\zeta) \quad (2.17)$$

and

$$(\bar{\dot{n}}(\zeta))_{\text{steady}} = \dot{N}_0 \bar{T}(\zeta). \quad (2.18)$$

In the previous terms, the long-term time-averaged behaviour of the quantities involved is associated with sufficiently small values of  $\zeta$ . Their initial behaviour is to be associated with sufficiently large values of  $\zeta$ .

Because of the difference in the experimental procedures that led to equations (2.17) and (2.18), there is no *a priori* reason to expect that the respective  $\bar{n}(\zeta)$  which are measured will usually be the same. However, because of their non-dynamical character, both  $N_0$  and  $\dot{N}_0$  can be chosen to be functions of  $\zeta$  so that they are equivalent. Thus, if identical long-term time-averaged behaviour is desired, it is only necessary that

$$\lim_{\zeta \rightarrow 0^+} \{(\bar{n}(\zeta))_{\text{closed}}/(\bar{n}(\zeta))_{\text{steady}}\} = 1. \quad (2.19)$$

Using integration-by-parts, equation (2.15) immediately yields

$$\bar{T}(\zeta) \equiv \zeta \bar{T}'(\zeta) \quad (2.20)$$

so that a knowledge of either  $\bar{T}(\zeta)$  or  $\bar{T}'(\zeta)$  suffices to give the other immediately. Then from equations (2.14) and (2.15) and equations (2.17) and (2.18), equation (2.19) will be fulfilled if

$$\lim_{\zeta \rightarrow 0^+} \{\zeta N_0(\zeta)/\dot{N}_0(\zeta)\} = 1. \quad (2.21)$$

In such cases, there is an evident equivalence resulting from appropriate uses that are made of the limiting values of the Laplace-averaged total transition probabilities or their rates.

Essentially such an equivalence is obtained from the formalism of time-dependent scattering theory, whereby either transition probabilities or their rates are used to determine demonstrably identical cross sections of processes of interest (Goldberger and Watson 1964). Indeed, with appropriate choices of  $N_0(\zeta)$ ,  $\dot{N}_0(\zeta)$  and  $\zeta$ , the Laplace-average formalism considered here gives the aforementioned cross section equivalence in detail—though we will present no proof of it. For our purposes, the relationship expressed by equation (2.20) is central to this equivalence and any approximation that may be made later to either one of  $\bar{T}(\zeta)$  or  $\bar{T}'(\zeta)$  will preserve it.

### 3. Equivalence between Laplace-average and stationary-state formalisms

Before exploiting the Laplace-average formalism to produce expressions that bound  $\bar{T}(\zeta)$  and  $\bar{T}'(\zeta)$  of equations (2.14) and (2.15), we digress to establish an important connection with versions of transition probability theory which make use of a stationary-state formalism (Mott and Massey 1965, Wu and Ohmura 1962).

For this purpose, we first evaluate the Laplace average of equation (2.3), obtaining

$$i\hbar\zeta\{\mathbf{R}(\zeta) - \rho_0\} = [\mathbf{H}, \mathbf{R}(\zeta)] \quad (3.1)$$

where

$$\mathbf{R}(\zeta) = \zeta \int_0^\infty dt e^{-\zeta t} \boldsymbol{\rho}(t). \quad (3.2)$$

We next evaluate equation (2.14), making use of equation (2.8), to obtain

$$\bar{T}(\zeta) = 1 - \text{Tr } \rho_0 \mathbf{R}(\zeta). \quad (3.3)$$

Upon evaluating  $\mathbf{R}(\zeta)$  in a complete orthonormal basis  $\{|\psi_m\rangle\}$ , of eigenfunctions of  $H$  (which however need not be unique) with associated energy eigenvalues  $\{E_m\}$ , we obtain

$$\langle\psi_m|\mathbf{R}(\zeta)|\psi_n\rangle = \frac{i\hbar\zeta\langle\psi_m|\rho_0|\psi_n\rangle}{i\hbar\zeta - (E_m - E_n)} \quad (3.4)$$

whereupon

$$\begin{aligned} \bar{T}(\zeta) &= 1 - \sum_m \sum_n \frac{i\hbar\zeta|\langle\psi_m|\rho_0|\psi_n\rangle|^2}{i\hbar\zeta - (E_m - E_n)} \\ &= 1 - \sum_m \sum_n \frac{\hbar^2\zeta^2|\langle\psi_m|\rho_0|\psi_n\rangle|^2}{\hbar^2\zeta^2 + (E_m - E_n)^2}. \end{aligned} \quad (3.5)$$

This last expression results from the fact that  $\bar{T}(\zeta)$  is real. We now express  $\rho_0$  in representative form, namely

$$\rho_0 \equiv |\phi_0\rangle\langle\phi_0| \quad (3.6)$$

and, without loss of generality, choose the  $H$ -eigenfunction basis to be one which also satisfies

$$\langle\psi_m|\phi_0\rangle\langle\phi_0|\psi_n\rangle\delta_{E_m E_n} = \langle\psi_M|\phi_0\rangle\langle\phi_0|\psi_M\rangle\delta_{mn}\delta_{mM}. \quad (3.7)$$

This is always possible when the energy eigenvalue spectrum has degeneracies and is automatically fulfilled otherwise. Consequently equation (3.5) yields

$$\bar{T}(\zeta) = 1 - \sum_M \sum_N \frac{\hbar^2\zeta^2|\langle\psi_M|\phi_0\rangle|^2|\langle\psi_N|\phi_0\rangle|^2}{\hbar^2\zeta^2 + (E_M - E_N)^2}, \quad (3.8)$$

each summation now involving only a single eigenstate for each energy eigenvalue.

When  $\zeta$  becomes vanishingly small, we obtain

$$\bar{T}(0+) \equiv \lim_{\zeta \rightarrow 0+} \bar{T}(\zeta) = 1 - \sum_M |\langle\psi_M|\phi_0\rangle|^4. \quad (3.9)$$

In terms of a complete, orthonormal (but not necessarily unique) basis  $\{|\phi_k\rangle\}$  which includes the original  $|\phi_0\rangle$ , we may evidently write

$$\bar{T}(0+) = \sum_M |\langle\psi_M|\phi_0\rangle|^2 \sum_{k \neq 0} |\langle\phi_k|\psi_M\rangle|^2. \quad (3.10)$$

By construction, the *probability distribution in energy* associated with the original state is given by the set  $\{|\langle\psi_M|\phi_0\rangle|^2\}$ , so that the fraction of energy eigenvalues not exceeding  $E$  to be associated with the original distribution is

$$f_0(E) \equiv \sum_M \theta(E - E_M) |\langle\psi_M|\phi_0\rangle|^2 \quad (3.11)$$

where  $\theta(x)$  is the Heaviside unit-function of its argument. By rewriting

$$\sum_{k \neq 0} |\langle\phi_k|\psi_M\rangle|^2 \equiv \sum_{k \neq 0} |\langle\phi_k|\psi_{E_M}\rangle|^2 \quad (3.12)$$

we can then express equation (3.10) as a Stieltjes integral:

$$\bar{T}(0+) = \int_{-\infty}^{+\infty} df_0(E) \sum_{k \neq 0} |\langle\phi_k|\psi_E\rangle|^2. \quad (3.13)$$

In circumstances where the energy eigenvalue spectrum is sufficiently dense for the quantities in equation (3.13) to be adequately represented by continuous functions of  $E$ , an application of the mean-value theorem then gives

$$\bar{T}(0+) \equiv \sum_{k \neq 0} |\langle \phi_k | \psi_{E^0} \rangle|^2 \quad (3.14)$$

where  $|\psi_{E^0}\rangle$  is an appropriate energy eigenstate, with eigenvalue  $E^0$ . (The asymptotic designation of the equality here merely calls attention to the condition of spectral density that has been invoked.)

A typical term in the sum of equation (3.14) can be recognized immediately as the probability of finding a system in an appropriate state (Dirac 1958) different from (and orthogonal to) the initial state  $|\phi_0\rangle$  if it were known to be in the stationary state  $|\psi_{E^0}\rangle$ . As a consequence, and despite the rather small likelihood of generally finding a system truly to be in an eigenstate of the energy, the long-term time-averaged total transition probability can always be expressed in a form that is entirely equivalent to that expected from a stationary-state formulation whenever the relatively innocuous condition of denseness of the eigenvalue spectrum that has been invoked in obtaining equation (3.14) does prevail.

Just such an equivalence is well-known (Jordan 1962, Wu and Ohmura 1962) for the conditions pertinent to a description of scattering processes which, however, are more stringent than those invoked here (Jordan 1962). In such cases, the mean energy of the system is presumed to be known with an arbitrarily small uncertainty, namely

$$\Delta_0 \equiv \langle \phi_0 | (\mathbf{H} - \langle \phi_0 | \mathbf{H} | \phi_0 \rangle)^2 | \phi_0 \rangle \ll \delta^2 \quad (3.15)$$

where  $\delta$  is arbitrarily small, but positive. By invoking equation (3.7), introducing

$$\langle \phi_0 | \mathbf{H} | \phi_0 \rangle \equiv E^0 \quad (3.16)$$

and suitably rearranging the results of substitution into equation (3.15), we get

$$1 \gg \sum_M \left( \frac{E_M - E^0}{\delta} \right)^2 |\langle \phi_0 | \psi_M \rangle|^2 \geq \min \left( \frac{E_M - E^0}{\delta} \right)^2. \quad (3.17)$$

This enables us to conclude that an energy eigenfunction  $|\psi_{E^0}\rangle$  exists for the present circumstances such that (Kato 1949, Temple 1928, Weinstein 1932a, b)

$$\langle \varphi_0 | \mathbf{H} | \varphi_0 \rangle - \delta \leq \langle \psi_{E^0} | \mathbf{H} | \psi_{E^0} \rangle \leq \langle \varphi_0 | \mathbf{H} | \varphi_0 \rangle + \delta \quad (3.18)$$

and it has an associated energy eigenvalue arbitrarily close in value to the original mean energy. In this case,  $|\psi_{E^0}\rangle$  of equation (3.14) will be the stationary state of the system that 'best' approximates the time-dependent function evolving from the given  $|\phi_0\rangle$ . (Despite the language, however, we do not here require that such an asymptotic limit should actually exist in order to obtain the equivalence.)

#### 4. Lower and upper bounds for Laplace-averaged total transition probabilities and their rates

Assured by the analysis of the preceding sections that the Laplace-average formalism does produce results able to be obtained with other formalisms that are known to be exact—under conditions that are pertinent to their being obtained—we now proceed to determine some rigorous lower and upper bounds for  $\bar{T}(\zeta)$  and  $\bar{T}(\zeta)$ .

For this purpose, we first rearrange equation (3.8) to yield

$$\bar{T}(\zeta) = \sum_M \sum_N \frac{(E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2}{\hbar^2 \zeta^2 + (E_M - E_N)^2}. \quad (4.1)$$

In an alternative form, making use of equation (3.9), we further obtain

$$\bar{T}(\zeta) = \bar{T}(0+) - \hbar^2 \zeta^2 \sum_M \sum_N \frac{(1 - \delta_{MN}) |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2}{\hbar^2 \zeta^2 + (E_M - E_N)^2}. \quad (4.2)$$

We now express the two preceding equations as follows:

$$\bar{T}(\zeta) = \int_0^\infty dx e^{-x\hbar^2 \zeta^2} \sum_M \sum_N (E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 e^{-x(E_M - E_N)^2} \quad (4.3)$$

and

$$\bar{T}(\zeta) = \bar{T}(0+) - \hbar^2 \zeta^2 \int_0^\infty dx e^{-x\hbar^2 \zeta^2} \sum_M \sum_N (1 - \delta_{MN}) |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 e^{-x(E_M - E_N)^2}. \quad (4.4)$$

Any procedure which is capable of producing upper or lower bounds to the *integrands* which are involved will yield appropriate bounds to  $\bar{T}(\zeta)$ , as we now show.

#### 4.1. A lower bound for $\bar{T}(\zeta)$

A lower bound to the sum in equation (4.3) can be obtained from the well-known inequality (Hardy *et al* 1934)

$$\sum_k x_k e^{-y_k} \geq e^{-\sum_k x_k y_k} \quad (4.5)$$

where

$$\sum_k x_k = 1, \quad x_k, y_k \geq 0. \quad (4.6)$$

We rearrange the terms in equation (4.3) to be in agreement with equation (4.6) and obtain

$$\begin{aligned} & \sum_M \sum_N (E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 e^{-x(E_M - E_N)^2} \\ & \geq \sum_M \sum_N (E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 \\ & \quad \times \exp \left\{ \frac{-x \sum_{MN} (E_M - E_N)^4 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2}{\sum_{MN} (E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2} \right\}. \end{aligned} \quad (4.7)$$

By straightforward manipulation, we can then obtain

$$\sum_M \sum_N (E_M - E_N)^2 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 = 2 \langle \phi_0 | (\mathbf{H} - E^0)^2 | \phi_0 \rangle \quad (4.8)$$

and

$$\sum_M \sum_N (E_M - E_N)^4 |\langle \psi_M | \phi_0 \rangle|^2 |\langle \psi_N | \phi_0 \rangle|^2 = 2 \langle \phi_0 | (\mathbf{H} - E^0)^4 | \phi_0 \rangle + 6 \{ \langle \phi_0 | (\mathbf{H} - E^0)^2 | \phi_0 \rangle \}^2 \quad (4.9)$$

where we have introduced equation (3.16). Upon introducing the definition of equation



(3.15), namely

$$\Delta_0 \equiv \langle \phi_0 | (\mathbf{H} - E^0)^2 | \phi_0 \rangle \quad (4.10)$$

and the quantity

$$\Gamma_0 \equiv \langle \phi_0 | (\mathbf{H} - E^0)^4 | \phi_0 \rangle + 3(\Delta_0)^2, \quad (4.11)$$

incorporating them into equation (4.7) and carrying out the integration called for in equation (4.3), we obtain

$$\bar{T}(\zeta) \geq \frac{2\Delta_0}{\hbar^2 \zeta^2 + \Gamma_0 / \Delta_0}. \quad (4.12)$$

We note, in passing, that despite the lower-bound nature of this expression, it gives the exact limiting asymptotic ( $\zeta \rightarrow \infty$ ) behaviour expected for  $\bar{T}(\zeta)$ :

$$\lim_{\zeta \rightarrow \infty} \hbar^2 \zeta^2 \bar{T}(\zeta) = 2\Delta_0. \quad (4.13)$$

This can be established from equations (4.1), (4.8) and (4.10).

#### 4.2. An upper bound for $T(\zeta)$

A procedure completely analogous to that described can be applied to the sum in equation (4.4). Omitting the details, for the sake of brevity, we can obtain

$$\bar{T}(\zeta) \leq \frac{2\Delta_0}{\hbar^2 \zeta^2 + 2\Delta_0 / \bar{T}(0+)}. \quad (4.14)$$

Here again, the exact limiting asymptotic ( $\zeta \rightarrow \infty$ ) behaviour expected for  $\bar{T}(\zeta)$  is obtained. By contrast with the lower-bound expression, however, the exact limiting asymptotic ( $\zeta \rightarrow 0+$ ) behaviour expected for  $\bar{T}(\zeta)$ —in this case, an identity—is also obtained.

#### 4.3. A lower bound for $\{\bar{T}(\zeta)\}_{\max}$

From the form exhibited in equation (4.1), it is evident that  $\bar{T}(\zeta)$  is a monotonic decreasing function of  $\zeta^2$ . Consequently, we can anticipate that, by equation (2.20)

$$\bar{T}(\zeta) = \zeta \bar{T}(\zeta) \quad (4.15)$$

the Laplace-averaged total transition probability rate will reach a maximum value  $\{\bar{T}(\zeta)\}_{\max}$  at an appropriate value of  $\zeta$ .

Because of equation (4.15), any lower bound for  $\bar{T}(\zeta)$  will immediately yield a lower bound for  $\bar{T}(\zeta)$ . Because of the sense of the inequality, it then follows that any maximum value for the lower bound cannot exceed  $\{\bar{T}(\zeta)\}_{\max}$ . Upon substituting equation (4.12) into equation (4.15) and determining the value of  $\zeta$  which maximizes the result, we will obtain

$$\{\bar{T}(\zeta)\}_{\max} \geq \Delta_0 / \hbar(\Gamma_0 / \Delta_0)^{1/2}. \quad (4.16)$$

#### 4.4. An upper bound for $\{\bar{T}(\zeta)\}_{\max}$

The same kind of argument which has been used to get equation (4.16) can be used with

equation (4.14) to obtain

$$\{\bar{T}(\zeta)\}_{\max} \leq (\Delta_0 \bar{T}(0+))^{1/2} / \sqrt{2} \hbar. \quad (4.17)$$

## 5. Some possible uses of the bounds

The essential simplicity of the lower and upper bounds which have been obtained for the Laplace-averaged total transition probabilities and their rates suggest that their utilization may be effected without the need for making excessively elaborate computations. The present section will illustrate some of the questions they may be useful in answering.

### 5.1. Two-level systems

One primary question relates to the quantitative adequacy of the bounds which have been obtained. The answer to this question generally must be expected to depend upon the system to which the bounds are applied—with one exception. This exception arises when the energy eigenvalue spectrum consists of only two values (each of which may however be degenerate), in which case the bounds we have obtained become *equal*.

To show this, we note that the sum in equation (4.1) will reduce to just a single term when there are only two energy eigenvalues:

$$\bar{T}(\zeta; \text{II}) = 2 \frac{(E_1 - E_2)^2 |\langle \psi_1 | \phi_0 \rangle|^2 |\langle \psi_2 | \phi_0 \rangle|^2}{\hbar^2 \zeta^2 + (E_1 - E_2)^2} \quad (5.1)$$

where the label (II) denotes the two-level nature of the system being considered. By transcribing equations (4.8)–(4.11), we can verify for the present case that

$$\Delta_0(\text{II}) = (E_1 - E_2)^2 |\langle \psi_1 | \phi_0 \rangle|^2 |\langle \psi_2 | \phi_0 \rangle|^2 \quad (5.2)$$

and

$$\Gamma_0(\text{II}) = (E_1 - E_2)^4 |\langle \psi_1 | \phi_0 \rangle|^2 |\langle \psi_2 | \phi_0 \rangle|^2 \quad (5.3)$$

so that

$$\Gamma_0(\text{II}) / \Delta_0(\text{II}) = (E_1 - E_2)^2. \quad (5.4)$$

It follows from equation (5.1) that

$$\bar{T}(0+; \text{II}) = 2 |\langle \psi_1 | \phi_0 \rangle|^2 |\langle \psi_2 | \phi_0 \rangle|^2. \quad (5.5)$$

In these terms, equation (5.1) can be written as

$$\bar{T}(\zeta; \text{II}) = \frac{2\Delta_0(\text{II})}{\hbar^2 \zeta^2 + \Gamma_0(\text{II}) / \Delta_0(\text{II})} \quad (5.6)$$

which is identical to the equality expressed by equation (4.12). It may also be written as

$$\bar{T}(\zeta; \text{II}) = \frac{2\Delta_0(\text{II})}{\hbar^2 \zeta^2 + 2\Delta_0(\text{II}) / T(0+; \text{II})} \quad (5.7)$$

which is identical to the equality expressed by equation (4.14).

In the sense that the bounds obtained in equations (4.12) and (4.14) become equal for two-level systems, the essence of the inequality which has led to them is to ascribe a 'pseudo-two-level' character to the Laplace-averaged total transition probability for a general system. From this viewpoint, inequalities which attempt to ascribe a 'pseudo- $N$ -level' character to the quantities of interest may merit examination.

### 5.2. Bounds to total cross sections

Although it has been assumed that the system of interest possesses a purely discrete energy eigenvalue spectrum, the Laplace-average formalism we have considered may nevertheless cope with situations in which there is a *continuum* present. Formally, this merely requires an appropriate transcription of the expressions which have been obtained.

This can be accomplished by regarding the Hamiltonian of a system which does possess a continuum of energy eigenvalues as the limit of a class of others which do not. Thus, by working with such Hamiltonians which confine the system to large, finite regions of space, we may suppose that their energy eigenvalue spectra are purely discrete. Then, by suitably extending the regions indefinitely, with an appropriate implicit modification of the pertinent Hamiltonians, the actual energy eigenvalue spectrum of the system—including any continua—may presumably be attained. At any intermediate stage, the bounds we have obtained apply without modification and their limiting values may be taken to be the bounds for systems which support continuous energy eigenvalue spectra.

To make this clear, and for the sake of simplicity, let  $|\phi_0\rangle$  represent a non-localized initial state of a single particle which is nevertheless confined to a large finite region of space, of volume  $V$ , and impinges on a *fixed* scattering centre having an interaction energy of finite range. For distances sufficiently remote from the scattering centre, we suppose that  $|\phi_0\rangle$  represents the particle as having a fixed value of its momentum  $\mathbf{p}$ . In addition, we suppose that the initial state of the system is associated with a flux  $F$  of the particle incident on the scattering centre, defined by

$$F \equiv \mathbf{p}/mV. \quad (5.8)$$

The Hamiltonian of the system may be represented by

$$\mathbf{H} = \frac{\mathbf{p}^2}{2m} + \mathbf{V}(\mathbf{r}), \quad \mathbf{r} \text{ within } V, \quad (5.9)$$

$m$  being the mass of the particle, and  $\mathbf{r}$  being its position;  $\mathbf{V}(\mathbf{r})$  is the interaction of the particle with the scattering centre. The initial state may be represented by

$$|\phi_0\rangle = |\chi_p\rangle/V^{1/2} \quad (5.10)$$

where

$$\mathbf{H}|\chi_p\rangle \sim \frac{\mathbf{p}^2}{2m}|\chi_p\rangle \quad (5.11)$$

as  $r$  becomes sufficiently large, and

$$\langle \chi_p | \chi_p \rangle = V. \quad (5.12)$$

In the foregoing terms, a *time-smoothed total cross section* that is associated with the

transition undergone by the system from its initial state is defined by

$$\bar{\sigma}(\zeta) \equiv \lim_{V \rightarrow \infty} \{\bar{T}(\zeta)/F\}. \quad (5.13)$$

By equations (4.16) and (4.17), the cross section has a maximum value which is bounded from both above and below:

$$\lim_{V \rightarrow \infty} \{(\Delta_0 \bar{T}(0+))^{1/2}/\sqrt{2\hbar F}\} \geq \{\bar{\sigma}(\zeta)\}_{\max} \geq \lim_{V \rightarrow \infty} \{\Delta_0/\hbar(\Gamma_0/\Delta_0)^{1/2}F\}. \quad (5.14)$$

We now suppose that the choice of  $|\phi_0\rangle$  and  $\mathbf{H}$  is taken so that

$$\begin{aligned} \lim_{V \rightarrow \infty} V\Delta_0 &= \langle \chi_p | (\mathbf{H} - E^0)^2 | \chi_p \rangle < \infty \\ \lim_{V \rightarrow \infty} V\Gamma_0 &= \langle \chi_p | (\mathbf{H} - E^0)^4 | \chi_p \rangle < \infty \end{aligned} \quad (5.15)$$

$$\lim_{V \rightarrow \infty} V\bar{T}(0+) \equiv T_0 < \infty$$

whereupon equation (5.14) yields

$$\begin{aligned} \left\{ \frac{mT_0}{\sqrt{2\hbar p}} \right\}^{1/2} [\langle \chi_p | (\mathbf{H} - E^0)^2 | \chi_p \rangle]^{1/2} \\ \geq \{\bar{\sigma}(\zeta)\}_{\max} \geq \left\{ \frac{m\langle \chi_p | (\mathbf{H} - E^0)^2 | \chi_p \rangle}{\hbar p [\langle \chi_p | (\mathbf{H} - E^0)^4 | \chi_p \rangle]^{1/2}} \right\} [\langle \chi_p | (\mathbf{H} - E^0)^2 | \chi_p \rangle]^{1/2}. \end{aligned} \quad (5.16)$$

With simple choices for  $V(\mathbf{r})$  and  $|\chi_p\rangle$ , it should not be difficult to evaluate the right-hand side of equation (5.16). The presence of  $T_0$  in the left-hand side makes evaluation of the upper bound impractical. With somewhat greater computational effort being entailed, the foregoing quantities may be chosen so as to discriminate between various kinds of scattering processes, e.g., elastic against inelastic, and to obtain lower bounds for the (time-smoothed) total cross sections of these processes.

## 6. Conclusions

Rigorous lower and upper bounds have been obtained for the Laplace averages of time-dependent total transition probabilities and their rates, the essence of which is to impose a 'pseudo-two-level' character upon these quantities. The lower bounds appear to have some potential utility in estimating total cross sections of processes without excessive computational effort.

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