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Exact long-term total transition probability rates and Fermi's 'golden rules'

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Abstract. Fermi's 'golden rule' expressions refer to first- and second-order time-dependent perturbation theory results for transition probability rates involving designated final states which are members of a continuum. By use of a Laplace-average formalism, it is shown that the long-term time-averaged total transition probability rate involving designated initial and final states which are all members of a continuum is *exactly* the sum of the pertinent 'golden rule' expressions. Generalization to higher-order perturbation theory results is suggested.

1. Introduction

Lacking practical solutions to the time-dependent Schrödinger equation which are also exact, one is almost always obliged to deal with the time-dependent properties of real systems in theoretical terms that are approximate. Usage of the relevant approximations in such cases is surely enhanced when they serve as well to put bounds of some sort on the exact quantities to which they pertain, and the peak of such enhancement is undoubtedly attained when the bounds further serve to establish conditions for which an ostensibly practical approximation does become exact. Indeed, as established in the present paper, this is precisely the situation pertaining to *time-dependent total transition probabilities and their rates* and the expressions that are constructed for these quantities from related *time-dependent perturbative approximations* (Dirac 1958) which have been dubbed 'golden rules' by Fermi (Orear *et al* 1950).

A preliminary section shows how certain iterative approximants to the Laplace-averaged statistical operator can be obtained from the equation that determines it, expressed in terms of a suitable representation-diagonal Laplace-averaged statistical operator and a related Feshbach perturbation Hamiltonian of the system (Feshbach 1958, 1962). Some upper and lower bounds for quantities that are closely related to the Laplace-averaged total transition probabilities and their rates (Golden 1976) are obtained in such terms in the following section. The necessary and sufficient conditions for the bounds to become equal are examined in the next section, the sufficiency then being shown to follow when the perturbation Hamiltonian has a square of which the trace becomes vanishingly small as the basis of representation used approaches a continuum. Under these circumstances, it is shown that the long-term time-averaged total transition probability rate becomes rigorously equal to the sum of the pertinent 'golden rule' expressions of Fermi. This constitutes the principal result of the present paper, and how it may be extended is conjectured.

2. Preliminaries

We begin by supposing that the system of interest here is initially characterized by a statistical operator which is a projection, namely,

$$\boldsymbol{\pi}_0^\dagger = \boldsymbol{\pi}_0 = \{\boldsymbol{\pi}_0\}^2, \tag{2.1}$$

and, in representative form, may be expressed as

$$\boldsymbol{\pi}_0 \equiv |\phi_0\rangle\langle\phi_0|, \tag{2.2}$$

so that (assuming that all traces to be considered exist)

$$\mathrm{Tr}\ \boldsymbol{\pi}_0 \equiv \langle\phi_0|\phi_0\rangle = 1. \tag{2.3}$$

At any subsequent time, we suppose that the statistical operator is

$$\boldsymbol{\rho}(t) = \mathrm{e}^{-\mathrm{i}t\boldsymbol{H}/\hbar}\boldsymbol{\pi}_0\mathrm{e}^{+\mathrm{i}t\boldsymbol{H}/\hbar} \tag{2.4}$$

so that it satisfies (von Neumann 1955)

$$\mathrm{i}\hbar\frac{\partial\boldsymbol{\rho}(t)}{\partial t} = [\boldsymbol{H}, \boldsymbol{\rho}(t)], \tag{2.5}$$

where $\boldsymbol{H}$ is the (time-independent) Hamiltonian of the system. (With no undue loss of generality, we suppose the eigenvalue spectrum of the latter to be a purely discrete one, bounded from below and free from any limit points. In view of our ultimate interest in continuous eigenvalue spectra, we shall later allow the eigenvalue spectrum to become essentially dense.)

It turns out to be useful—especially with regard to long-term behaviour—to work with the Laplace-averaged statistical operator (Golden 1976). It is defined as

$$\boldsymbol{R}(\zeta) \equiv \zeta\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-\zeta t}\boldsymbol{\rho}(t), \qquad \zeta > 0, \tag{2.6}$$

and satisfies

$$\mathrm{i}\hbar\zeta\{\boldsymbol{R}(\zeta) - \boldsymbol{\pi}_0\} = [\boldsymbol{H}, \boldsymbol{R}(\zeta)] \tag{2.7}$$

with

$$\mathrm{Tr}\ \boldsymbol{R}(\zeta) = 1. \tag{2.8}$$

(Unless specified otherwise, ζ is assumed to be real.) Our immediate main interest will centre on working with certain tractable approximate solutions to equation (2.7).

For this purpose, we begin with a suitably chosen orthonormal set $\{|\phi_n\rangle\}_M$, M to be specified later, from which we construct the orthogonal projections

$$\boldsymbol{\pi}_n \equiv |\phi_n\rangle\langle\phi_n|, \tag{2.9}$$

which are each of trace unity, and their union

$$\boldsymbol{P}_M = \sum_{n=0}^{M} \boldsymbol{\pi}_n. \tag{2.10}$$

We suppose that the original set can be augmented to form a complete orthonormal set $\{|\phi_n\rangle\}_\infty \supset \{|\phi_n\rangle\}_M$, from eigenfunctions of

$$\boldsymbol{H}_M \equiv \sum_{n=0}^{M} \boldsymbol{\pi}_n\boldsymbol{H}\boldsymbol{\pi}_n + (\boldsymbol{I} - \boldsymbol{P}_M)\boldsymbol{H}(\boldsymbol{I} - \boldsymbol{P}_M), \tag{2.11}$$

where $\boldsymbol{I}$ is the identity operator. In terms of such a complete set, we construct

$$\boldsymbol{H}_{\mathrm{d}} \equiv \sum_{n=0}^{\infty} \boldsymbol{\pi}_n \boldsymbol{H}_M \boldsymbol{\pi}_n \equiv \sum_{n=0}^{\infty} \boldsymbol{\pi}_n \boldsymbol{H} \boldsymbol{\pi}_n, \tag{2.12}$$

by means of which the original Hamiltonian is evidently expressible as

$$\boldsymbol{H} = \boldsymbol{H}_{\mathrm{d}} + (\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}) \tag{2.13}$$

in terms of which the perturbation Hamiltonian is

$$(\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}) \equiv \sum_{n=0}^{M} \sum_{m=0}^{M} \boldsymbol{\pi}_n \boldsymbol{H} \boldsymbol{\pi}_m (1 - \delta_{nm}) + \sum_{n=0}^{M} [\boldsymbol{\pi}_n \boldsymbol{H}(\boldsymbol{I} - \boldsymbol{P}_M) + (\boldsymbol{I} - \boldsymbol{P}_M)\boldsymbol{H}\boldsymbol{\pi}_n] \tag{2.14}$$

and is a generalization of the one originally introduced by Feshbach for dealing with scattering problems (Feshbach 1958, 1962).

Similar to equation (2.12), we next introduce

$$\boldsymbol{R}_{\mathrm{d}}(\zeta) \equiv \sum_{n=0}^{\infty} \boldsymbol{\pi}_n \boldsymbol{R}(\zeta) \boldsymbol{\pi}_n \tag{2.15}$$

and, after some straightforward manipulations, render equation (2.7) into

$$\begin{aligned} i\hbar\zeta(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta)) &= [\boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta)] + [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}_{\mathrm{d}}(\zeta)] \\ &\quad + \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \boldsymbol{\pi}_n [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta)] \boldsymbol{\pi}_m (1 - \delta_{mn}). \end{aligned} \tag{2.16}$$

We now introduce the quantities $\{\Delta_N \boldsymbol{R}(\zeta)\}$ defined by

$$\begin{aligned} i\hbar\zeta \Delta_{N+1} \boldsymbol{R}(\zeta) &\equiv [\boldsymbol{H}_{\mathrm{d}}, \Delta_{N+1} \boldsymbol{R}(\zeta)] + [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}_{\mathrm{d}}(\zeta)] \\ &\quad + \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \boldsymbol{\pi}_n [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \Delta_N \boldsymbol{R}(\zeta)] \boldsymbol{\pi}_m (1 - \delta_{mn}), \end{aligned} \tag{2.17}$$

where we require that

$$\Delta_N \boldsymbol{R}(\zeta) = \boldsymbol{0}, \qquad N \leqslant 0. \tag{2.18}$$

By combining equations (2.16) and (2.17) we then obtain

$$\begin{aligned} i\hbar\zeta(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1}\boldsymbol{R}(\zeta)) &= [\boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1}\boldsymbol{R}(\zeta)] \\ &\quad + \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \boldsymbol{\pi}_n [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta)] \boldsymbol{\pi}_m (1 - \delta_{mn}), \end{aligned} \tag{2.19}$$

which displays the iterative approximant nature of the $\{\Delta_N \boldsymbol{R}(\zeta)\}$ in relation to $(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))$.

In terms of the foregoing quantities, the *total transition probability* of the system is

$$T(t) = 1 - \operatorname{Tr} \boldsymbol{\rho}(t) \boldsymbol{\pi}_0, \tag{2.20}$$

with an associated *total transition probability rate* of

$$\dot{T}(t) = -\operatorname{Tr} \frac{\partial \boldsymbol{\rho}(t)}{\partial t} \boldsymbol{\pi}_0. \tag{2.21}$$

These quantities have the related Laplace-averaged quantities

$$\bar{T}(\zeta) = 1 - \mathrm{Tr}\, \boldsymbol{R}(\zeta)\boldsymbol{\pi}_0 \tag{2.22}$$

and

$$\check{T}(\zeta) = \zeta \bar{T}(\zeta). \tag{2.23}$$

In alternative forms, we also have from equations (2.3) and (2.7)

$$\bar{T}(\zeta) = \mathrm{Tr}\, (\boldsymbol{R}(\zeta) - \boldsymbol{\pi}_0)^2 \tag{2.24}$$

and from equation (2.15)

$$\bar{T}(\zeta) = \mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))^2 + \mathrm{Tr}(\boldsymbol{R}_{\mathrm{d}}(\zeta) - \boldsymbol{\pi}_0)^2. \tag{2.25}$$

3. Some basic inequalities

We readily obtain from equation (2.7) that

$$\begin{aligned}\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{\pi}_0)^2 &= -\mathrm{Tr}\, \boldsymbol{\pi}_0[\boldsymbol{H}, \boldsymbol{R}(\zeta)]/\mathrm{i}\hbar\zeta = -\mathrm{Tr}\, \boldsymbol{\pi}_0[\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{\pi}_0]/\mathrm{i}\hbar\zeta \\ &\leqslant 4\, \mathrm{Tr}\{\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}\}^2/\hbar^2\zeta^2,\end{aligned} \tag{3.1}$$

where we have made use of the well known Cauchy–Schwarz inequality.

From equations (2.24) and (2.25) we then obtain

$$\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}})^2 \leqslant \mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{\pi}_0)^2 \leqslant \frac{4\, \mathrm{Tr}(\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}})^2}{\hbar^2\zeta^2}. \tag{3.2}$$

We now introduce

$$E_m \equiv \langle\phi_m|\boldsymbol{H}_{\mathrm{d}}|\phi_m\rangle \equiv \langle\phi_m|\boldsymbol{H}_M|\phi_m\rangle \equiv \langle\phi_m|\boldsymbol{H}|\phi_m\rangle \tag{3.3}$$

and

$$R_m \equiv \langle\phi_m|\boldsymbol{R}_{\mathrm{d}}(\zeta)|\phi_m\rangle \equiv \langle\phi_m|\boldsymbol{R}(\zeta)|\phi_m\rangle, \tag{3.4}$$

leaving the ζ dependence of the latter quantities implicit. Then it follows from equation (2.19) that

$$\begin{aligned}&\langle\phi_m|\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1}\boldsymbol{R}(\zeta)|\phi_n\rangle \\ &\quad = \frac{\langle\phi_m|[\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N\boldsymbol{R}(\zeta)]|\phi_n\rangle(1 - \delta_{mn})}{\mathrm{i}\hbar\zeta + (E_n - E_m)}.\end{aligned} \tag{3.5}$$

As a result, we have that

$$\begin{aligned}&\mathrm{Tr}(\Delta_{N+1}\boldsymbol{R}(\zeta))^2 \\ &\quad = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\bigg|\langle\phi_m|\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta)|\phi_n\rangle \\ &\qquad - \frac{\langle\phi_m|[\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N\boldsymbol{R}(\zeta)]|\phi_n\rangle(1 - \delta_{mn})}{\mathrm{i}\hbar\zeta + (E_n - E_m)}\bigg|^2.\end{aligned} \tag{3.6}$$

By expanding the right-hand side of this equation, invoking the well known triangle inequality and re-arranging, we can obtain

$$(1 - |X_N|)^2 \leqslant \frac{\mathrm{Tr}(\Delta_{N+1}\boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))^2} \leqslant (1 + |X_N|)^2, \qquad N \geqslant 0, \tag{3.7}$$

where

$$X_N^2 \equiv \left(\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{|\langle \phi_m | [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta)] | \phi_n \rangle (1 - \delta_{mn})|^2}{\hbar^2 \zeta^2 + (E_m - E_n)^2} \right) \times [\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))^2]^{-1}. \tag{3.8}$$

From equation (3.5) we are able to obtain

$$\begin{aligned} &\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1} \boldsymbol{R}(\zeta))^2 \\ &\quad = \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{|\langle \phi_m | [\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta)] | \phi_n \rangle (1 - \delta_{mn})|^2}{\hbar^2 \zeta^2 + (E_m - E_n)^2} \\ &\quad \leqslant -\mathrm{Tr}([\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}}, \boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta)])^2 / \hbar^2 \zeta^2 \\ &\quad \leqslant 4\, \mathrm{Tr}(\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}})^2\, \mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta))^2 / \hbar^2 \zeta^2, \end{aligned} \tag{3.9}$$

where use now has been made of the Cauchy–Schwarz inequality and the one relating the arithmetic and geometric means. Upon re-arranging, we have

$$\frac{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1} \boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_N \boldsymbol{R}(\zeta))^2} \leqslant \frac{4\, \mathrm{Tr}(\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}})^2}{\hbar^2 \zeta^2}. \tag{3.10}$$

Now, it is evident from a comparison of equations (3.8) and (3.9) that

$$X_N^2 \equiv \frac{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta) - \Delta_{N+1} \boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))^2} \tag{3.11}$$

so that, with equation (2.18), it follows that

$$X_{-1}^2 \equiv 1. \tag{3.12}$$

As a result, equation (3.10) yields

$$X_N^2 \leqslant \left(\frac{4\, \mathrm{Tr}(\boldsymbol{H} - \boldsymbol{H}_{\mathrm{d}})^2}{\hbar^2 \zeta^2} \right)^{N+1}, \qquad N \geqslant 0. \tag{3.13}$$

The inequalities of equations (3.2), (3.7), and (3.13) are the basic ones we need for our later purposes.

4. Laplace-averaged total transition probability theorems

It is clear from equation (3.7) that

$$\frac{\mathrm{Tr}(\Delta_{N+1} \boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta) - \boldsymbol{R}_{\mathrm{d}}(\zeta))^2} = 1 \tag{4.1}$$

if and only if

$$X_N^2 = 0. \tag{4.2}$$

However, to suppose that either of these conditions will be rigorously satisfied for some complete orthonormal basis $\{|\phi_n\rangle\}_\infty$ which does *not* consist of eigenfunctions of the Hamiltonian would *seem* incorrect. It is correct, nevertheless, for a broad class of physically relevant bases, a matter we shall establish here.

For this purpose, we take advantage of equation (3.13) and, upon using equation (2.14), proceed to examine

$$\frac{4\,\mathrm{Tr}(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}})^2}{\hbar^2\zeta^2}=\frac{4}{\hbar^2\zeta^2}\left(\sum_{n=0}^{M}\sum_{m=0}^{M}\mathrm{Tr}\;\boldsymbol{\pi}_n\boldsymbol{H}\boldsymbol{\pi}_m\boldsymbol{H}\boldsymbol{\pi}_n(1-\delta_{mn})+2\sum_{n=0}^{M}\mathrm{Tr}\;\boldsymbol{\pi}_n\boldsymbol{H}(\boldsymbol{I}-\boldsymbol{P}_M)\boldsymbol{H}\boldsymbol{\pi}_n\right). \tag{4.3}$$

After further manipulations, re-arrangements and making use of equation (2.10), we get

$$\mathrm{Tr}(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}})^2=2\sum_{n=0}^{M}(\mathrm{Tr}\;\boldsymbol{\pi}_n\boldsymbol{H}^2-\mathrm{Tr}\;\boldsymbol{\pi}_n\boldsymbol{H}\boldsymbol{\pi}_n\boldsymbol{H}\boldsymbol{\pi}_n)-\sum_{n=0}^{M}\mathrm{Tr}\;\boldsymbol{\pi}_n\boldsymbol{H}(\boldsymbol{P}_M-\boldsymbol{\pi}_n)\boldsymbol{H}\boldsymbol{\pi}_n. \tag{4.4}$$

Because the last series is evidently positive, we obtain

$$\mathrm{Tr}(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}})^2\leqslant 2\sum_{n=0}^{M}\langle\phi_n|(\boldsymbol{H}-E_n)^2|\phi_n\rangle, \tag{4.5}$$

where use has been made of equation (3.3). We note that the quantities to be evaluated in the right-hand side of equation (4.5) involve only the originally chosen $\{|\phi_n\rangle\}_M$ basis.

Each term of equation (4.5) can be recognized as the uncertainty in the energy to be associated with the relevant state that is to be identified with a member of the $\{|\phi_n\rangle\}_M$ basis. When each of the latter is taken in a well defined limiting sense to be described presently, pertinent to the description of scattering processes, to comprise a member of a *continuum*, the associated energy uncertainty becomes arbitrarily small (Jordan 1962). With such a choice of the individual $|\phi_n\rangle$, we may also stipulate that M may increase without limit in such a way that

$$\left(\sum_{n=0}^{M}\langle\phi_n|(\boldsymbol{H}-E_n)^2|\phi_n\rangle\right)\to 0 \tag{4.6}$$

as

$$\langle\phi_n|(\boldsymbol{H}-E_n)^2|\phi_n\rangle\to 0,\qquad \text{all}\quad 0\leqslant n\leqslant M. \tag{4.7}$$

The limiting process implicit in equations (4.6) and (4.7) is the following. The original $\{|\phi_n\rangle\}_M$ basis is presumed to consist of non-localized functions which are nevertheless confined to large finite regions of configuration space; the limiting process here involved is one that extends these regions indefinitely (for a more detailed example, see Golden 1976). At every finite stage of the extension, each $|\phi_n\rangle$ remains normalized to unity; at every finite stage of the extension, M is finite but with a value that does not decrease with increasing extension. When M does become indefinitely large, it is *not required* that $\lim_{M\to\infty}\{|\phi_n\rangle\}_M$ constitute a complete orthonormal basis. In spite of the fact that the several $|\phi_n\rangle$ are not eigenfunctions of $\boldsymbol{H}$, the condition expressed by equation (4.7) implies the existence of energy eigenfunctions with energy eigenvalues which are arbitrarily close in value to the corresponding E_n (Temple 1928, Weinstein 1932a, b, Kato 1949).

Under the circumstances described, equation (4.5) enables the conditions expressed by equations (4.6) and (4.7) to be compactly summarized by

$$\mathrm{Tr}(\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}})^2\to 0,\qquad \boldsymbol{H}\neq\boldsymbol{H}_{\mathrm{d}}. \tag{4.8}$$

Now, from equation (3.13),

$$X_N^2\to 0,\qquad N\geqslant 0, \tag{4.9}$$

so that, by equation (3.7),

$$\frac{\mathrm{Tr}(\Delta_N \boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta)-\boldsymbol{R}_\mathrm{d}(\zeta))^2} \to 1, \qquad N \geqslant 0. \tag{4.10}$$

Equations (4.8)–(4.10) comprise a primary version of the fundamental theorem of this paper.

However, some additional results are obtainable from equation (3.2). When equation (4.8) holds we must also have

$$\mathrm{Tr}\ \boldsymbol{\pi}_0\boldsymbol{R}(\zeta) - \mathrm{Tr}\ \boldsymbol{R}_\mathrm{d}^2(\zeta) \to 1 - \mathrm{Tr}\ \boldsymbol{\pi}_0\boldsymbol{R}(\zeta) \to 0, \tag{4.11}$$

where used has been made of equations (2.7) and (2.24). As a result, we obtain that

$$\mathrm{Tr}\ \boldsymbol{\pi}_0\boldsymbol{R}(\zeta) \to 1. \tag{4.12}$$

The consequence of equations (4.10) and (4.11) is that

$$\frac{\mathrm{Tr}(\Delta_N \boldsymbol{R}(\zeta))^2}{\mathrm{Tr}(\boldsymbol{R}(\zeta)-\boldsymbol{\pi}_0)^2} \to 1, \qquad N \geqslant 0, \tag{4.13}$$

enabling *any* of the approximants to serve in giving an *exact* expression for the Laplace-averaged total transition probability. The essence of equation (4.11) is that

$$R_n \to \delta_{n0}, \qquad \text{all} \quad \zeta, \tag{4.14}$$

which enables an important simplification to be made later of the $\{\Delta_N \boldsymbol{R}(\zeta)\}$ matrix elements and facilitates their evaluation. (In scattering processes characterized by a finite cross section, the equivalent of equation (4.14) is well known (Heitler 1953).) Equations (4.8), (4.13) and (4.14) comprise a secondary version of the fundamental theorem of this paper.

4.1. *Fermi's 'golden rule' theorems*

In order to exploit equation (4.13), we must provide a calculable expression for $\{\Delta_N \boldsymbol{R}(\zeta)\}$. For purposes of being explicit, we proceed to obtain matrix elements for $\Delta_1\boldsymbol{R}(\zeta)$ and $\Delta_2\boldsymbol{R}(\zeta)$, obtainable from equations (2.17) and (2.18) and under conditions corresponding to equations (4.8) and (4.14). After some manipulation, we find that

$$\langle\phi_m|\Delta_1\boldsymbol{R}(\zeta)|\phi_n\rangle \to \left(\frac{\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_0\rangle\delta_{n0}}{\mathrm{i}\hbar\zeta+(E_0-E_m)} - \frac{\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_n\rangle\delta_{m0}}{\mathrm{i}\hbar\zeta+(E_n-E_0)}\right). \tag{4.15}$$

After somewhat more manipulations, we find that (maintaining a discrete basis formalism despite the continuum implicit in the condition of equation (4.8))

$$\begin{aligned}
&\langle\phi_m|\Delta_2\boldsymbol{R}(\zeta)|\phi_n\rangle \\
&\to \Bigg[\left(\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_0\rangle + \sum_l \frac{\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_l\rangle\langle\phi_l|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_0\rangle}{\mathrm{i}\hbar\zeta+(E_0-E_l)}\right)\delta_{n0}[\mathrm{i}\hbar\zeta+(E_0-E_m)]^{-1} \\
&\quad - \left(\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_n\rangle - \sum_l \frac{\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_l\rangle\langle\phi_l|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_n\rangle}{\mathrm{i}\hbar\zeta+(E_l-E_0)}\right)\delta_{m0}[\mathrm{i}\hbar\zeta+(E_n-E_0)]^{-1} \\
&\quad - \frac{\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_0\rangle\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_n\rangle[2\mathrm{i}\hbar\zeta+(E_n-E_m)]}{[\mathrm{i}\hbar\zeta+(E_n-E_0)][\mathrm{i}\hbar\zeta+(E_0-E_m)][\mathrm{i}\hbar\zeta+(E_n-E_m)]}\Bigg].
\end{aligned} \tag{4.16}$$

Instead of working directly with equation (4.13), we make use of equations (2.23) and (2.24) to obtain

$$\frac{\zeta\,\mathrm{Tr}(\Delta_N \boldsymbol{R}(\zeta))^2}{\dot{T}(\zeta)} \to 1, \qquad N \geqslant 0. \tag{4.17}$$

Upon setting $N=1$ and substituting equation (4.15), we get

$$\left(\frac{2}{\hbar}\sum_{m=0}^{\infty}\frac{\hbar\zeta|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_m\rangle|^2}{\hbar^2\zeta^2+(E_0-E_m)^2}\right)(\dot{T}(\zeta))^{-1} \to 1. \tag{4.18}$$

We now modify the formal expressions to more readily accommodate any continuum. For this purpose, we represent the sum in equation (4.18) as a Stieltjes integral, namely,

$$\sum_{m=0}^{\infty}\frac{\hbar\zeta|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_m\rangle|^2}{\hbar^2\zeta^2+(E_0-E_m)^2} = \int_{-\infty}^{+\infty}\mathrm{d}n_E\,\frac{\hbar\zeta\,\Sigma_k\,|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_k(E)\rangle|^2}{\hbar^2\zeta^2+(E_0-E)^2}, \tag{4.19}$$

where n_E is the number of distinct eigenvalues of $\boldsymbol{H}_M$ not exceeding E and k is a discrete label identifying a degenerate eigenstate of $\boldsymbol{H}_M$. Now, when n_E is adequately represented by a continuous function of E, we may write

$$\sum_{m=0}^{\infty}\frac{\hbar\zeta|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_m\rangle|^2}{\hbar^2\zeta^2+(E_0-E_m)^2} = \int_{-\infty}^{+\infty}\mathrm{d}E\,\rho_E\,\frac{\hbar\zeta\,\Sigma_k\,|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_k(E)\rangle|^2}{\hbar^2\zeta^2+(E_0-E)^2}, \tag{4.20}$$

where

$$\rho_E \equiv \mathrm{d}n_E/\mathrm{d}E. \tag{4.21}$$

Finally, we suppose that $\zeta \to 0+$, thereby giving emphasis to the long-term time-averaged properties under examination. As a result of the Cauchy singular integral relation (Titchmarsh 1948) we may take

$$\pi\delta(E_0-E) \equiv \lim_{\hbar\zeta\to 0+}\frac{\hbar\zeta}{\hbar^2\zeta^2+(E_0-E)^2}, \tag{4.22}$$

the Dirac δ function, so that we obtain

$$\frac{(2\pi/\hbar)\int_{-\infty}^{+\infty}\mathrm{d}E\,\rho_E\delta(E_0-E)\,\Sigma_k\,|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_k(E)\rangle|^2}{\dot{T}(0+)}$$
$$= \frac{(2\pi/\hbar)\,\Sigma_k\,|\langle\phi_0|\boldsymbol{H}-\boldsymbol{H}_\mathrm{d}|\phi_k(E_0)\rangle|^2\rho_{E_0}}{\dot{T}(0+)} \to 1. \tag{4.23}$$

The numerator is recognizable as the first-order time-dependent perturbation theory result (Dirac 1958). The individual terms are the 'golden rule number 2' expressions of Fermi (Orear *et al* 1950). The importance of the theorem expressed by equation (4.23) is that the 'golden rule' expressions sum *exactly* to yield the long-term time-averaged total transition probability rate.

We now set $N=2$ in equation (4.17) and substitute equation (4.16) and obtain

$$\left(\frac{2}{\hbar}\sum_{m=0}^{\infty}\frac{\hbar\zeta|\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle+\Sigma_l\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_l\rangle\langle\phi_l|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle/[\mathrm{i}\hbar\zeta+(E_0-E_l)]|^2}{\hbar^2\zeta^2+(E_0-E_m)^2}\right)$$
$$\times(\bar{T}(\zeta))^{-1}$$
$$+\left(\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{|\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle|^2|\langle\phi_n|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle|^2[4\hbar^2\zeta^2+(E_n-E_m)^2]}{[\hbar^2\zeta^2+(E_n-E_0)^2][\hbar^2\zeta^2+(E_m-E_0)^2][\hbar^2\zeta^2+(E_n-E_m)^2]}\right)(\bar{T}(\zeta))^{-1}\to 1, \quad (4.24)$$

where the last term has made use of equation (2.23). Under the conditions expressed by equation (4.8), this term vanishes as we now show. Since

$$\frac{4\hbar^2\zeta^2+(E_n-E_m)^2}{\hbar^2\zeta^2+(E_n-E_m)^2}\leqslant 4, \quad (4.25)$$

we can see that, after some straightforward manipulation,

$$\left(\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{|\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle|^2|\langle\phi_n|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle|^2[4\hbar^2\zeta^2+(E_n-E_m)^2]}{[\hbar^2\zeta^2+(E_n-E_0)^2][\hbar^2\zeta^2+(E_m-E_0)^2][\hbar^2\zeta^2+(E_n-E_m)^2]}\right)(\bar{T}(\zeta))^{-1}$$
$$\leqslant\left(\frac{2/\hbar\,\Sigma_{m=0}^{\infty}\hbar\zeta|\langle\phi_m|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle|^2/[\hbar^2\zeta^2+(E_m-E_0)^2]}{\bar{T}(\zeta)}\right)^2\bar{T}(\zeta). \quad (4.26)$$

In view of equations (4.11) and (4.18) the last term of the left-hand side of equation (4.24) vanishes, as asserted.

It is now possible to carry out the same kind of analysis that led to equation (4.23). We omit the details in the interest of brevity, however. The result is that we can ultimately obtain

$$\left(\frac{2\pi}{\hbar}\sum_k\left|\langle\phi_k(E_0)|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle\right.\right.$$
$$\left.\left.+\sum_l\int_{-\infty}^{+\infty}\mathrm{d}n_E\frac{\langle\phi_k(E_0)|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_l(E)\rangle\langle\phi_l(E)|\boldsymbol{H}-\boldsymbol{H}_{\mathrm{d}}|\phi_0\rangle}{(E_0-E)+\mathrm{i}0}\right|^2\rho_{E_0}\right)(\bar{T}(0+))^{-1}\to 1. \quad (4.27)$$

Again, the numerator is recognizable: apart from minor differences in notation, it corresponds to the second-order time-dependent perturbation theory result (Dirac 1958). The individual terms correspond to Fermi's 'golden rule number 1' expression when the first-order result vanishes (Orear *et al* 1950). As previously, the importance of the theorem expressed by equation (4.27) is the 'golden rule' expressions sum *exactly* to yield the long-term time-averaged total transition probability rate.

We note that, apart from the conditions implicit in and derivable from equation (4.8), the $\{|\phi_n\rangle\}_M$ basis and the $\{|\phi_n\rangle\}_\infty$ basis are arbitrary.

4.2. *Extended 'golden rule' expressions*

An essential point to be made regarding the theorems of equations (4.23) and (4.27) is that they establish that *perturbation theory approximations to first and second orders each sum to the same exact quantity.* From equation (4.13), which is basic to the results obtained here, it is apparent that many more expressions that are equal to the exact

$\bar{T}(0+)$ can be forthcoming. The only question that remains is whether the limiting expressions for $\Delta_N \boldsymbol{R}(\zeta)$, $N>2$, will correspond precisely to the related order of time-dependent perturbation theory.

From the results obtained for $N = 1, 2$, we may reasonably anticipate that the same will be the case for $N > 2$. In such a case, we would have the following extended 'golden rule' theorem: the *perturbation theory approximation to any (finite) order for long-term transition probability rates sum to give the related exact total quantity*, under the conditions summarized by equations (4.8)–(4.14). Until actually demonstrated however, this anticipation must remain a conjecture to be considered at some future time.

5. Conclusions and comments

The time-dependent perturbation theory results for transition probability rates known as Fermi's 'golden rule' expressions are shown here to sum to the exact long-term time-averaged total transition probability rate. This result obtains whenever the basis of representation used to describe the system of interest involves an attainable continuum in terms of which the related Feshbach perturbation Hamiltonian (Feshbach 1958, 1962) has a square the trace of which becomes vanishingly small. The extension of the 'golden rule' expressions to *all* orders of perturbation theory results is conjectured.

A significant matter in the analysis which has been used here is the process formally introduced first in equations (4.6) and (4.7) and extended later throughout the preceding section. As such, it imposes a limiting continuum character upon the basis of description that is accorded the system *prior* to examining the long-term behaviour of the latter. In technical terms, the continuum is imposed at each value of ζ, following which the limiting values of the expressions as $\zeta \to 0+$ is obtained. It is well known (Golden and Longuet-Higgins 1960) that the limit so obtained does depend upon the order in which the limiting processes are applied.

For this reason, no analogue of the 'golden rule' expressions is to be anticipated for systems which overwhelmingly involve states that are purely discrete, e.g., those bases in which the designated *initial state* is so maintained. It is relatively simple to show, but we shall omit doing so, that the total transition probability rate then becomes vanishingly small as $\zeta \to 0+$ in all such cases. Furthermore, a major feature of the 'golden rule' expressions is their emphasis of those transitions which occur between designated states of essentially the same energy. Since non-continuum states of large uncertainty in their energy are readily imaginable, energy conservation in such cases then is to be expected only in an average sense and some transitions are expected to be between designated states that differ appreciably in their energy. For such circumstances, the inequalities which have been obtained may be applicable even though the equalities are not.

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