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On the generalized golden rule for transition probabilities

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Abstract

We show that the usual expression found in the literature, which tries to generalize the 'Fermi golden rule' beyond second order in perturbation, is (surprisingly) incorrect. After identifying the weak steps of the two usual derivations, we derive a new expression of this generalized golden rule, intrinsically very different from the previous one, even though its form may look similar. We show that this new result already affects the next nonzero term of the transition probability expansion. From a direct comparison of this new result with its exact value—as given by the exact evolution operator—we also show that the usual approaches are inherently quite questionable beyond the second order in perturbation.

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1. Introduction

Everyone has learned that the transition rate per unit time from an initial state $|\varphi_i\rangle$ to a set of final states $|\varphi_f\rangle$ close in energy, due to a coupling V, is given by the 'Fermi golden rule' [1–3]. Its derivation is based on the calculation of

$$U_{fi}(t) = \langle\varphi_f|e^{-iHt/\hbar}|\varphi_i\rangle \tag{1}$$

to lowest order in $V = H - H_0$, the initial and final states being eigenstates of the unperturbed Hamiltonian H_0. The Fermi golden rule follows from $|U_{fi}(t)|^2$ in the large-t limit.

In some advanced textbooks [4–9], higher-order terms in V are calculated. In the large-t limit, their summation is claimed to give [4]

$$U_{fi}(t) \approx e^{-i(\varepsilon_f+\varepsilon_i)\,t/2\hbar}\,[\delta_{fi} - 2\,i\,\pi\,\delta_t(\varepsilon_f - \varepsilon_i)\,\mathcal{T}_{fi}] \tag{2}$$

$$\mathcal{T}_{fi} = \lim_{\eta\to 0^+} \langle\varphi_f|V + V\frac{1}{\varepsilon_i - H + i\eta}V|\varphi_i\rangle \tag{3}$$

$\varepsilon_{\rm i}$ and $\varepsilon_{\rm f}$ being the energies of $|\varphi_{\rm i}\rangle$ and $|\varphi_{\rm f}\rangle$. Although the function $\delta_t(\varepsilon)$, defined by [1,4],

$$\delta_t(\varepsilon) = \frac{\sin(\varepsilon\, t/2\hbar)}{\pi\, \varepsilon} \tag{4}$$

tends to the Dirac distribution when t goes to infinity, one must keep $\delta_t(\varepsilon)$ in $U_{\rm fi}(t)$ in order to possibly calculate $|U_{\rm fi}(t)|^2$ and the transition rate per unit time in a clean way, the square of the Dirac distribution being meaningless.

The purpose of this paper is to show that, although the expressions (2) and (3) for $U_{\rm fi}(t)$ are quite well known, they are, surprisingly enough, incorrect.

The paper is organized as follows.

In a first part, we show why the expression of $\mathcal{T}_{\rm fi}$ given in equation (3) is suspect and we give some hints on what could be a correct expression.

In a second part, we briefly go through the two usual derivations of the generalized Fermi golden rule (i.e. the transition rate summed up to all orders in V) in order to identify possible origins of the problem. In doing so, we will show why, in contradiction to what is usually claimed [3, 4], it is not necessary to impose $\langle\varphi_{\rm i}|V|\varphi_{\rm i}\rangle = 0$ to obtain finite terms in the V expansion of $U_{\rm fi}(t)$.

In a third part, we perform a 'clean' calculation of the V expansion of $U_{\rm fi}(t)$ in the large-t limit and we show that the sum of its dominant terms can be written as equations (2) and (3) with η replaced by η_t defined by

$$\eta_t = 2\hbar/t. \tag{5}$$

This change, which is one of the main results of our paper, is fundamental since it links t to η_t: taking the $\eta_t \to 0$ limit in $\mathcal{T}_{\rm fi}$ then imposes taking it simultaneously in the $\delta_t(\varepsilon_{\rm f} - \varepsilon_{\rm i})$ of $U_{\rm fi}(t)$ as

$$\delta_t(\varepsilon) = \frac{\sin(\varepsilon/\eta_t)}{\pi\, \varepsilon}. \tag{6}$$

In a last part, we discuss some consequences of our new result. Since $U_{\rm fi}(t)$ already differs from the previous one at second order in V, we discuss some possible effects linked to this difference. By comparing our $U_{\rm fi}(t)$ for ${\rm f} = {\rm i}$ to the exact one—given by the true evolution operator—we also show that our new result is just the expansion of the exact term up to second order in $(\varepsilon_{\rm i} - H)/\eta_t$. This thus raises strong doubts on the possibility of obtaining a generalized Fermi golden rule valid beyond second order in V. There is in fact a profound conflict between the 'large-t limit' and 'all orders in V', t and V being closely coupled in the exact $U_{\rm fi}(t)$ through $(\varepsilon_{\rm i} - H)/\eta_t$, i.e. $-V/\eta_t$ when acting on $|\varphi_{\rm i}\rangle$.

Before going through these procedures in detail, let us first make a few comments on some misleading ideas linked to the so-called continuum limit introduced in this problem. While the Fermi golden rule is known to be valid for final states belonging to a continuum, one should not conclude that the final states $|\varphi_{\rm f}\rangle$ are true continuum states. Indeed, the initial and final states being real physical states, they must be square integrable so that, instead of $\langle\varphi_{\rm i}|\varphi_{\rm f}\rangle = \delta({\rm f} - {\rm i})$ as for true continuum states, we have $\langle\varphi_{\rm i}|\varphi_{\rm f}\rangle = \delta_{\rm fi}$ (the $\delta_{\rm fi}$ of equation (2) has exactly this origin). Actually, the introduction of continuum states is just a mathematical trick to allow the replacement of sums by integrals *at the end of the calculation*. By performing this replacement too early in some terms only, one often obtains spurious singularities, which cancel out if the discrete aspect of the problem is considered throughout the calculation. From a physical point of view, one can think of using a continuum limit when the states of interest are close in energy. The problem is then to know the appropriate energy scale for such an approximation to be valid. We will show that the final states do behave as a continuum if their energy differences are small compared with η_t. This parameter η_t, which is the key parameter

of this problem, corresponds to the characteristic energy of the uncertainty principle below which precise energy measurements are meaningless; its appearance as the energy scale for the spectrum of H_0 to look like a continuum is thus quite reasonable. The introduction of a small but finite η_t in the definition of $\delta_t(\varepsilon)$ already allows the calculation of the square of $U_{\rm fi}(t)$ at first order in V. We show here that, in addition, it allows us to take the continuum limit properly. This will be crucial when we will calculate and resum the higher-order terms in V.

The condition 'η_t large compared to the energy difference between eigenstates' is somewhat similar to 't small compared to the Poincaré time' [10]. Indeed, for Hamiltonians having a discrete spectrum—as for finite-size systems—there is a time T_p after which the system returns to, or extremely close to, its initial state: as

$$|\psi(t)\rangle = \mathrm{e}^{-\mathrm{i}\,Ht/\hbar}\,|\psi(0)\rangle = \sum_k \mathrm{e}^{-\mathrm{i}\,E_k t/\hbar}\,|\phi_k\rangle\langle\phi_k|\psi(0)\rangle \tag{7}$$

where $|\phi_k\rangle$ and E_k are the eigenstates and the eigenvalues of H, we see that *if*[1] we can find T_p such that

$$(E_k - E_{k'})\,T_p = 2\,\pi\,\hbar\;N_{kk'} \tag{8}$$

with $N_{kk'}$ integer for any pair (k, k'), then $|\psi(T_p)\rangle$ and $|\psi(0)\rangle$ differ by a phase factor only (when these energy differences decrease, T_p increases so that T_p would be infinite for continuous spectra). The existence of a finite Poincaré time implies that meaningful information on the large-t limit of $U_{\rm fi}(t)$ corresponds to t large but not too large in order to have $t \ll T_p$ if one wants to be in the 'lifetime' part of the system evolution. From equation (8), the condition $t \ll T_p$ also reads

$$\eta_t = \frac{2\,\hbar}{t} \gg \frac{2\,\hbar}{T_p} = \frac{E_k - E_{k'}}{\pi\;N_{kk'}} = \Delta\varepsilon \tag{9}$$

i.e. η_t larger than a characteristic energy difference between two eigenstates. We will see below how such a condition appears in a natural way in this problem.

The validity of the continuum limit being physically linked to η_t, it is clearly of importance to decide whether the large-t limit or the continuum limit has to be taken first. In order to keep this freedom, we will, in this paper, use discrete final states throughout the calculation and, just at the end, look at the physical consequences of our result when each one of the two limits is taken first. Taking them in the wrong order generates inconsistencies such as that responsible for the incorrect result quoted in equation (3). An additional benefit of working with discrete final states is that one can use simple perturbation theory. For true continuum states, one would have to use the analytic dilatation technique [11], which is much heavier and completely hides the physical interplay between the large-t limit and the continuum limit.

A last comment on the difficulty raised by the continuum limit of having non-normalized plane waves for the free Hamiltonian eigenstates: one way to overcome this difficulty, rather traditional, can be to use wavepackets. This procedure is however not very clean as the group of states then has a narrow energy spread, so this wavepacket is not strictly speaking an eigenstate of the free electron Hamiltonian. The simple and clean way to deal with this normalization condition is in fact to put the system in a large box L^3: the box then imposes a momentum quantization in $2\pi/L$, i.e. an energy quantization in $1/L^2$, so that the energy is close to a continuum for large L. It is then easy to follow the L dependences over the whole calculation. Once the quantities of interest have been cleaned up from possible singular terms, one just has to replace discrete sums over momenta by $V/(2\pi)^3$ integrals.

[1] Such a T_p implies that the $(E_k - E_{k'})$ differences are commensurable (as for free electrons in a cubic box). If this is not so, one can show that the probability to return to the initial state is not exactly unity but extremely close to unity. For the sake of simplicity, we restrict here our argument to the 'commensurable case'.

2. Why $\mathcal{T}_{\rm fi}$ cannot be correct

Since

$$V|\varphi_{\rm i}\rangle = (H - H_0)\,|\varphi_{\rm i}\rangle = (H - \varepsilon_{\rm i})\,|\varphi_{\rm i}\rangle \tag{10}$$

the matrix element appearing in equation (3) also reads

$$\langle\varphi_{\rm f}|V\left[1 + \frac{H-\varepsilon_{\rm i}}{\varepsilon_{\rm i} - H + {\rm i}\eta}\right]|\varphi_{\rm i}\rangle = \langle\varphi_{\rm f}|(H-\varepsilon_{\rm f})\,\frac{{\rm i}\eta}{\varepsilon_{\rm i} - H + {\rm i}\eta}|\varphi_{\rm i}\rangle$$
$$= {\rm i}\eta\left[-\langle\varphi_{\rm f}|\varphi_{\rm i}\rangle + (\varepsilon_{\rm i} - \varepsilon_{\rm f} + {\rm i}\eta)\,\langle\varphi_{\rm f}|\frac{1}{\varepsilon_{\rm i} - H + {\rm i}\eta}|\varphi_{\rm i}\rangle\right]. \tag{11}$$

For ${\rm f} = {\rm i}$, the above expression inserted in $\mathcal{T}_{\rm f\,i}$ leads to $\mathcal{T}_{\rm ii} = 0$, the bracket of equation (11) staying finite when η goes to zero: by inserting the closure relation for the eigenstates of H, we can rewrite the second term of this bracket for ${\rm f} = {\rm i}$, as[2]

$$A_{\rm i}(\eta) = {\rm i}\eta\sum_k \frac{\varepsilon_{\rm i} - E_k - {\rm i}\eta}{(\varepsilon_{\rm i} - E_k)^2 + \eta^2}\,|\langle\phi_k|\varphi_{\rm i}\rangle|^2. \tag{12}$$

We then note that $\eta^2/(\varepsilon^2 + \eta^2)$ stays between zero and unity so

$${\rm Re}\ A_{\rm i}(\eta) < \sum_k |\langle\phi_k|\varphi_{\rm i}\rangle|^2 = \langle\varphi_{\rm i}|\varphi_{\rm i}\rangle = 1. \tag{13}$$

Similarly, $0 < |\eta\,\varepsilon|/(\varepsilon^2 + \eta^2) < 1/2$, so $|{\rm Im}\ A_{\rm i}(\eta)| < 1/2$.

It could be objected that if $|\varphi_{\rm i}\rangle$ is a continuum state, $\langle\varphi_{\rm i}|\varphi_{\rm i}\rangle$ is not unity but infinite. However, this $|\varphi_{\rm i}\rangle$ would not be physical, so its time evolution is of no interest.

We thus conclude that the $\eta \to 0^+$ limit cannot be taken for granted in $\mathcal{T}_{\rm fi}$, otherwise $\mathcal{T}_{\rm ii}$ would be equal to zero and $|U_{\rm ii}(t)|$ would be equal to unity, which is clearly incorrect. If η is replaced by η_t as shown below in equation (61), the $\eta_t \to 0$ limit in $\mathcal{T}_{\rm fi}$ and the $t \to \infty$ in $\delta_t(\varepsilon_{\rm f} - \varepsilon_{\rm i})$ have to be taken simultaneously in $U_{\rm f\,i}(t)$. For ${\rm f} = {\rm i}$, the $1/\eta_t$ factor of $\delta_t(0)$ then cancels the η_t factor of $\mathcal{T}_{\rm ii}$ to provide a finite $|U_{\rm ii}(t)|$ different from unity, as expected.

3. Usual derivations of the $U_{\rm fi}(t)$ expansion

There are two standard ways to obtain the V expansion of $U_{\rm fi}(t)$:

3.1. Derivation based on the state evolution

The most usual procedure relies on the resolution of the Schrödinger equation satisfied by

$$|\psi(t)\rangle = {\rm e}^{-{\rm i}Ht/\hbar}\,|\varphi_{\rm i}\rangle. \tag{14}$$

Expanding $|\psi(t)\rangle$ on the eigenstates $|\varphi_k\rangle$ of H_0

$$|\psi(t)\rangle = \sum_k a_k(t)\,{\rm e}^{-{\rm i}\varepsilon_k t/\hbar}\,|\varphi_k\rangle \tag{15}$$

and inserting this expansion into the Schrödinger equation provides a set of differential equations satisfied by the a_k:

$${\rm i}\hbar\,\dot{a}_k(t) = \sum_{k'} V_{kk'}\,{\rm e}^{{\rm i}(\varepsilon_k - \varepsilon_{k'})t/\hbar}\,a_{k'}(t). \tag{16}$$

[2] With a possible integral contribution, if the spectrum of H contains a continuum.

These coupled equations are solved perturbatively by expanding $a_k(t)$ as

$$a_k(t) = \sum_{n=0}^{\infty} a_k^{(n)}(t) \tag{17}$$

with $a_k^{(n)}(t)$ of the order of V^n.

(i) The zeroth-order term is obvious and reads $a_k^{(0)}(t) = \delta_{ki}$. We then deduce the differential equation satisfied by $a_k^{(1)}(t)$

$$\mathrm{i}\hbar\, \dot{a}_k^{(1)}(t) = V_{ki}\, \mathrm{e}^{\mathrm{i}(\varepsilon_k - \varepsilon_i)t/\hbar}. \tag{18}$$

While its resolution has to be performed separately for $\varepsilon_k \neq \varepsilon_i$ and $\varepsilon_k = \varepsilon_i$, its solution can be written using a single expression

$$a_k^{(1)}(t) = -V_{ki}\, \Delta_t(\varepsilon_k - \varepsilon_i) \tag{19}$$

where $\Delta_t(\varepsilon)$ is defined by

$$\Delta_t(\varepsilon) = \frac{\mathrm{e}^{\mathrm{i}\varepsilon t/\hbar} - 1}{\varepsilon} \qquad \text{for} \quad \varepsilon \neq 0 \tag{20}$$

$$= \frac{\mathrm{i}t}{\hbar} \qquad \text{for} \quad \varepsilon = 0. \tag{21}$$

Note that $\varepsilon_k = \varepsilon_i$ includes $k = i$ but also any degenerate states of $|\varphi_i\rangle$. For the sake of simplicity, we will assume in the following that $|\varphi_i\rangle$ is nondegenerate.

(ii) From equations (16) and (19)–(21), we obtain the differential equation satisfied by $a_k^{(2)}(t)$

$$\mathrm{i}\hbar\, \dot{a}_k^{(2)}(t) = -\sum_{k' \neq i} V_{kk'}\, V_{k'i}\, \mathrm{e}^{\mathrm{i}(\varepsilon_k - \varepsilon_{k'})t/\hbar}\, \Delta_t(\varepsilon_{k'} - \varepsilon_i) - \frac{\mathrm{i}t}{\hbar}\, V_{ki}\, V_{ii}\, \mathrm{e}^{\mathrm{i}(\varepsilon_k - \varepsilon_i)t/\hbar}. \tag{22}$$

Here again, we have to calculate contributions from $\varepsilon_k = \varepsilon_i$ and $\varepsilon_{k'} = (\varepsilon_k$ or $\varepsilon_i)$ separately. However, all these contributions can be written using a single expression

$$a_k^{(2)}(t) = -\sum_{k'} V_{kk'}\, V_{k'i}\, \Delta_t(\varepsilon_k - \varepsilon_i, \varepsilon_{k'} - \varepsilon_i) \tag{23}$$

where $\Delta_t(\varepsilon, \varepsilon')$ is defined for $\varepsilon' \neq 0$ as

$$\Delta_t(\varepsilon, \varepsilon') = \frac{\Delta_t(\varepsilon - \varepsilon') - \Delta_t(\varepsilon)}{\varepsilon'} \tag{24}$$

while for $\varepsilon' = 0$ we take the limit of the above expression when ε' goes to zero.

(iii) The same procedure gives the third-order term as

$$a_k^{(3)}(t) = -\sum_{k'k''} V_{kk'}\, V_{k'k''}\, V_{k''i}\, \Delta_t(\varepsilon_k - \varepsilon_i, \varepsilon_{k'} - \varepsilon_i, \varepsilon_{k''} - \varepsilon_i) \tag{25}$$

where $\Delta_t(\varepsilon, \varepsilon', \varepsilon'')$ is defined in terms of $\Delta_t(\varepsilon, \varepsilon')$ as

$$\Delta_t(\varepsilon, \varepsilon', \varepsilon'') = \frac{\Delta_t(\varepsilon - \varepsilon'', \varepsilon' - \varepsilon'') - \Delta_t(\varepsilon, \varepsilon')}{\varepsilon''} \tag{26}$$

for $\varepsilon'' \neq 0$, while for $\varepsilon'' = 0$ we again take the limit of equation (26) when ε'' goes to zero. This, in particular, gives $\Delta_t(0, 0, 0) = (\mathrm{i}t/\hbar)^3/3!$.

(iv) And so on for the higher-order terms, which are found to have a similar form.

Let us stress that all these $a_k^{(n)}$'s are finite even if $V_{ii} \neq 0$, in contradiction with many textbooks, which claim that it is necessary to impose $V_{nn} = 0$ (by including these diagonal terms of V into H_0) in order to have finite contributions to the V expansion of $a_k(t)$.

3.2. Derivation based on the evolution operator

The other derivation is based on the integral representation[3] of the evolution operator

$$e^{-iHt/\hbar} = \int_{-\infty}^{-\infty} \frac{dx}{-2i\pi} \frac{e^{-i(x+i\alpha)t/\hbar}}{x + i\alpha - H} \tag{27}$$

which is valid for $t > 0$ and *any* positive α, the V expansion being obtained from the identity

$$\begin{aligned} \frac{1}{a-H} &= \frac{1}{a-H_0} + \frac{1}{a-H_0} V \frac{1}{a-H} \\ &= \sum_{m=0}^{n} \left(\frac{1}{a-H_0} V \right)^m \frac{1}{a-H_0} + \left(\frac{1}{a-H_0} V \right)^{n+1} \frac{1}{a-H}. \end{aligned} \tag{28}$$

The two derivations lead to the same result

$$U_{fi}(t) = \sum_{n=0}^{\infty} U_{fi}^{(n)}(t) = e^{-i\varepsilon_f t/\hbar} \sum_{n=0}^{\infty} a_f^{(n)}(t) \tag{29}$$

provided that we discard the last term of equation (28) in the large-n limit, which is equivalent to saying that $a_k(t)$ can be expanded in powers of V.

It is possible to rewrite these $U_{fi}^{(n)}(t)$ in terms of $\delta_t(\varepsilon)$ by noting that

$$e^{-i\varepsilon_f t/\hbar} \Delta_t(\varepsilon) = 2i\pi\, e^{-i(\varepsilon_f+\varepsilon_i)t/2\hbar}\, e^{+i(\varepsilon+\varepsilon_i-\varepsilon_f)t/2\hbar}\, \delta_t(\varepsilon) \tag{30}$$

with $\delta_t(\varepsilon)$ defined as in equation (4) for $\varepsilon \neq 0$ while for $\varepsilon = 0$ we take $\delta_t(0) = 1/\pi\eta_t$, i.e. its limit when $\varepsilon \to 0$. For $n \geqslant 1$, this leads to

$$U_{fi}^{(n)}(t) = -2i\pi\, e^{-i(\varepsilon_f+\varepsilon_i)t/2\hbar}\, \sigma_{fi}^{(n)}(t) \tag{31}$$

where, in view of equations (19), (23) and (25),

$$\sigma_{fi}^{(1)}(t) = V_{fi}\, \delta_t(\varepsilon_f - \varepsilon_i) \tag{32}$$

$$\sigma_{fi}^{(2)}(t) = \sum_{k'} V_{fk'} V_{k'i}\, \delta_t(\varepsilon_f - \varepsilon_i, \varepsilon_{k'} - \varepsilon_i) \tag{33}$$

$$\sigma_{fi}^{(3)}(t) = \sum_{k'k''} V_{fk'} V_{k'k''} V_{k''i}\, \delta_t(\varepsilon_f - \varepsilon_i, \varepsilon_{k'} - \varepsilon_i, \varepsilon_{k''} - \varepsilon_i) \tag{34}$$

etc. The $\delta_t(\varepsilon)$, $\delta_t(\varepsilon, \varepsilon')$, $\delta_t(\varepsilon, \varepsilon', \varepsilon'')$, ... functions are related to each other through

$$\delta_t(\varepsilon, \varepsilon') = \frac{e^{-i\varepsilon'/\eta_t}\, \delta_t(\varepsilon - \varepsilon') - \delta_t(\varepsilon)}{\varepsilon'} \tag{35}$$

$$\delta_t(\varepsilon, \varepsilon', \varepsilon'') = \frac{e^{-i\varepsilon''/\eta_t}\, \delta_t(\varepsilon - \varepsilon'', \varepsilon' - \varepsilon'') - \delta_t(\varepsilon, \varepsilon')}{\varepsilon''} \tag{36}$$

etc. The above definition of $\delta_t(\varepsilon, \varepsilon')$ is valid for $\varepsilon' \neq 0$ while for $\varepsilon' = 0$ we take its limit when $\varepsilon' \to 0$. We use similar definitions for the other functions $\delta_t(\varepsilon, \varepsilon', \ldots)$. The above $\sigma_{fi}^{(n)}(t)$ are exact. In the next section, we will extract from their large-t limit a dominant term with a form suitable for the summation over n. However, in order to know what 'large t' precisely means, let us reconsider its connection with the Poincaré time.

[3] Equation (27) can be quickly checked by inserting the closure relation of the H eigenstates. The right-hand side is then calculated by using an integration contour C which contains the real axis and the lowest half circle (see figure 1). For $t > 0$, the contribution of the half circle gives zero while for any positive α all the poles $E_k - i\alpha$ are in the lowest half plane, so their contributions do generate all the terms of the left-hand side of equation (27).

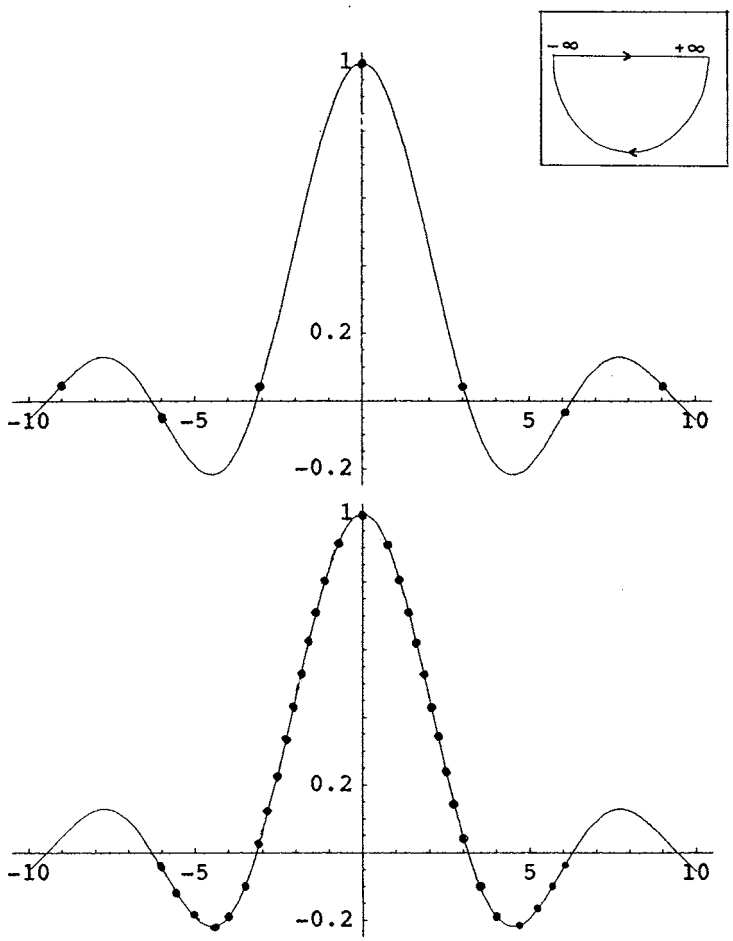

Figure 1. The dots show the possible $\delta_t(\varepsilon_k - \varepsilon_i)/\delta_t(0)$ for two values of t. The upper curve corresponds to the largest t (i.e. the smallest η_t). When t increases, the amount of ε_k which gives a sizeable $\delta_t(\varepsilon_k - \varepsilon_i)/\delta_t(0)$ decreases. Inset: the integration contour C.

3.3. Connection between 'large t' and the Poincaré time

We will restrict ourselves here to f = i since it allows us to pick up the point very simply. Since $\delta_t(0) = 1/\pi\eta_t$, equation (32) gives

$$\sigma_{ii}^{(1)}(t) = V_{ii}/\pi\eta_t \tag{37}$$

for arbitrary t. From equations (33) and (35), we obtain the second-order term of $\sigma_{ii}(t)$ as

$$\sigma_{ii}^{(2)}(t) = -\frac{i}{\pi\eta_t^2}\,V_{ii} + \sum_{k'\neq i}|V_{k'i}|^2\,\frac{e^{-i(\varepsilon_{k'}-\varepsilon_i)/\eta_t}\,\delta_t(\varepsilon_{k'}-\varepsilon_i) - 1/\pi\eta_t}{\varepsilon_{k'}-\varepsilon_i} \tag{38}$$

in which we have used the specific value of $\delta_t(\varepsilon, \varepsilon')$ for $\varepsilon = 0$. When t is equal to the Poincaré time T_{0p} of the Hamiltonian H_0—which is of the order of the Poincaré time of H—all the $(\varepsilon_{k'} - \varepsilon_i)/\pi\eta_{T_{0p}}$ are integers, so $\delta_{T_{0p}}(\varepsilon_{k'} - \varepsilon_i) = 0$ for all $\varepsilon_{k'} \neq \varepsilon_i$. This leads to

$$\sigma_{ii}^{(2)}(T_{0p}) = -\frac{i}{\pi\eta_{T_{0p}}^2}\,V_{ii} + \frac{1}{\pi\eta_{T_{0p}}}\sum_{k'\neq i}\frac{|V_{k'i}|^2}{\varepsilon_i - \varepsilon_{k'}}. \tag{39}$$

From these first two terms, we obtain the expansion of $U_{\rm ii}(T_{0p})$ as

$$U_{\rm ii}(T_{0p}) = {\rm e}^{-{\rm i}\varepsilon_{\rm i}T_{0p}/\hbar}\left[1 - {\rm i}\frac{T_{0p}}{\hbar}\left(V_{\rm ii} + \sum_{k'\neq {\rm i}}\frac{|V_{k'{\rm i}}|^2}{\varepsilon_{\rm i}-\varepsilon_{k'}}\right) + \frac{1}{2}\left(-{\rm i}\frac{V_{\rm ii}\,T_{0p}}{\hbar}\right)^2 + \cdots\right] \tag{40}$$

which is nothing but the expansion of ${\rm e}^{-{\rm i}\tilde{\varepsilon}_{\rm i}T_{0p}}$ where $\tilde{\varepsilon}_{\rm i}$ is the energy which tends to $\varepsilon_{\rm i}$ when V goes to zero, as obtained from perturbation theory

$$\tilde{\varepsilon}_{\rm i} = \varepsilon_{\rm i} + V_{\rm ii} + \sum_{k'\neq {\rm i}}\frac{|V_{k'{\rm i}}|^2}{\varepsilon_{\rm i}-\varepsilon_{k'}} + \cdots. \tag{41}$$

Consequently, $|U_{\rm ii}(T_{0p})|^2 = 1$, as expected for $t = T_{0p}$.

For such a t, the situation is quite drastic since all the contributions from the $\delta_t(\varepsilon_{k'} - \varepsilon_{\rm i})$ of equation (38) give exactly zero. In the general case, i.e. for $t \neq T_{0p}$, we can identify two different regimes for these δ_t terms, depending on the value of η_t compared with the possible values of $\varepsilon_{k'} - \varepsilon_{\rm i}$. If η_t is much smaller than all these differences (see figure 1(a)), all the δ_t terms of equation (38) are negligible with respect to $1/\pi\eta_t$. $\sigma^{(2)}_{\rm ii}(t)$ and $U_{\rm ii}(t)$ are then given by equations similar to equations (39) and (40) with $\eta_{T_{0p}}$ replaced by η_t. For such a small η_t, we have $|U_{\rm ii}(t)|^2 \approx 1$: there is no lifetime associated with the probability of staying in the $|\varphi_{\rm i}\rangle$ state. In contrast, if there are $\varepsilon_{k'} - \varepsilon_{\rm i}$ differences smaller than η_t, the corresponding δ_t are as large as $1/\pi\eta_t$ (see figure 1(b)). Because of their exponential prefactor in equation (38), these δ_t terms generate a complex contribution to $\sigma^{(2)}_{\rm ii}(t)$. The real part tends to decrease the 'energy' change of the $|\varphi_{\rm i}\rangle$ state as given by second-order perturbation theory, equation (41), while the imaginary part generates an imaginary contribution to this 'energy', i.e. a lifetime. We can say that when η_t increases, i.e. when t decreases from T_{0p}, ever more $|\varphi_{k'}\rangle$ states go 'inside' the sizeable part of the $\delta_t(\varepsilon_{k'} - \varepsilon_{\rm i})$ curve. By doing so, they leave the sum giving the energy shift, to join the states contributing to the lifetime.

In the following, we will be interested in the lifetime regime of $U_{\rm ii}(t)$, i.e. in t large but not too large, in order to have an $\varepsilon_{k'} - \varepsilon_{\rm i}$ energy distribution similar to the lower curve of figure 1.

4. The large-time limit

4.1. Second-order term

Using equation (4), $\delta_t(\varepsilon, \varepsilon')$ given in equation (35) also reads

$$\delta_t(\varepsilon, \varepsilon') = \frac{\cos(\varepsilon'/\eta_t)\,\delta_t(\varepsilon - \varepsilon') - \delta_t(\varepsilon)}{\varepsilon'} - {\rm i}\pi\,\delta_t(\varepsilon')\,\delta_t(\varepsilon - \varepsilon'). \tag{42}$$

For η_t small, $\delta_t(\varepsilon)$ is strongly localized around $\varepsilon = 0$, so the imaginary part of $\delta_t(\varepsilon, \varepsilon')$ looks like $-{\rm i}\pi\,\delta_t(\varepsilon')\,\delta_t(\varepsilon)$. Its real part looks like $(-1/\varepsilon')\,\delta_t(\varepsilon)$ for ε' large, while for ε' small we expect this $1/\varepsilon'$ singular behaviour to be cut at a few η_t from zero since $\delta_t(\varepsilon, \varepsilon')$ remains finite when $\varepsilon' \to 0$. Consequently, we guess that the large-t limit of $\delta_t(\varepsilon, \varepsilon')$ should be

$$\frac{1}{-\varepsilon' + {\rm i}\eta_t}\,\delta_t(\varepsilon) = -\left[\hat{\mathcal{P}}_t\left(\frac{1}{\varepsilon'}\right) + {\rm i}\,\pi\,\hat{\delta}_t(\varepsilon')\right]\hat{\delta}_t(\varepsilon) \tag{43}$$

where we have set

$$\hat{\mathcal{P}}_t\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon}{\varepsilon^2 + \eta_t^2} \tag{44}$$

$$\pi\,\hat{\delta}_t(\varepsilon) = \frac{\eta_t}{\varepsilon^2 + \eta_t^2}. \tag{45}$$

$\hat{\delta}_t(\varepsilon)$, like $\delta_t(\varepsilon)$, is a function of width η_t which tends to the Dirac distribution in the small-η_t limit. In order to prove that this guess is correct, and to estimate the correction accurately, we rewrite $\delta_t(\varepsilon, \varepsilon')$ as

$$\delta_t(\varepsilon, \varepsilon') = \delta_t(\varepsilon) \left[\frac{1}{-\varepsilon' + \mathrm{i}\eta_t} + \frac{1}{\eta_t} d_t \left(\frac{\varepsilon}{\eta_t}, \frac{\varepsilon'}{\eta_t} \right) \right] \tag{46}$$

which serves as a definition for $d_t(x, x')$. Using equation (35), we find

$$d_t(x, x') = \frac{1}{x' - \mathrm{i}} + \frac{1}{D(x)} \frac{D(x - x') - D(x)}{x'} \tag{47}$$

with $D(x) = (\mathrm{e}^{2\,\mathrm{i}\,x} - 1)/x$. By inserting equation (46) into equation (33) we obtain

$$\sigma_{\mathrm{fi}}^{(2)}(t) = \delta_t(\varepsilon_\mathrm{f} - \varepsilon_\mathrm{i}) \left[\sum_{k'} \frac{V_{fk'} V_{k'\mathrm{i}}}{\varepsilon_\mathrm{i} - \varepsilon_{k'} + \mathrm{i}\,\eta_t} + W_{\mathrm{fi}}^{(2)}(\eta_t) \right]. \tag{48}$$

The sum is simply the matrix element

$$\langle \varphi_\mathrm{f} | V \frac{1}{\varepsilon_\mathrm{i} - H_0 + \mathrm{i}\,\eta_t} V | \varphi_\mathrm{i} \rangle \tag{49}$$

while the second term is defined as

$$W_{\mathrm{fi}}^{(2)}(\eta_t) = \frac{1}{\eta_t} \sum_{k'} V_{fk'} V_{k'\mathrm{i}}\, d_t \left(\frac{\varepsilon_\mathrm{f} - \varepsilon_\mathrm{i}}{\eta_t}, \frac{\varepsilon_{k'} - \varepsilon_\mathrm{i}}{\eta_t} \right). \tag{50}$$

Since $d_t(0, x' \gg 1) = \mathrm{i}/2x'^2 + \mathrm{O}(1/x'^3)$ while $d_t(0, x' \ll 1) = x'/3 + \mathrm{O}(x'^2)$, the main contributions to $W_{\mathrm{ii}}^{(2)}(\eta_t)$ in the $\eta_t \to 0$ limit originate from $\varepsilon_{k'}$ lying within a few η_t from ε_i. Here again, we find two different regimes:

(i) η_t is small enough for all the possible $\varepsilon_{k'} - \varepsilon_\mathrm{i}$ to be much larger than η_t. We then have $W_{\mathrm{ii}}^{(2)}(\eta_t) \approx 0$

(ii) η_t is large enough for a large number of $\varepsilon_{k'}$ to lie within a few η_t of ε_i. Since $\varepsilon_{k'}$ appears in d_t through $x_{k'} = (\varepsilon_{k'} - \varepsilon_\mathrm{i})/\eta_t$, this reduced variable is then close to a continuous variable. We can replace the sum over k' by an integral over $x_{k'}$, so that for $\mathrm{f} = \mathrm{i}$

$$W_{\mathrm{ii}}^{(2)}(\eta_t) \approx \int_{(\varepsilon_0 - \varepsilon_\mathrm{i})/\eta_t}^{+\infty} \mathrm{d}x_{k'}\, \overline{V}(\varepsilon_\mathrm{i} + \eta_t\, x_{k'})\, d_t(0, x_{k'}) \tag{51}$$

where ε_0 is the ground state energy of H_0 and $\overline{V}(\varepsilon_{k'})$ the result of the summation of $|V_{k'\mathrm{i}}|^2$ over all variables but $\varepsilon_{k'}$. Because $\varepsilon_0 < \varepsilon_\mathrm{i}$, the lower boundary of the integral tends to $-\infty$ when η_t goes to zero. When this lower boundary is exactly $-\infty$, the integration contour of figure 1 shows that the integral is zero, the bracket of equation (51) having a single pole $x_{k'} = \mathrm{i}$ in the upper half-plane. For η_t small, the $d_t(0, x' \gg 1)$ limit used in the evaluation of the integral between $-\infty$ and $(\varepsilon_0 - \varepsilon_\mathrm{i})/\eta_t$ leads to

$$W_{\mathrm{ii}}^{(2)}(\eta_t \to 0) \approx \mathrm{i}\,\eta_t \frac{\overline{V}}{2\,(\varepsilon_\mathrm{i} - \varepsilon_0)} + \mathrm{O}(\eta_t^2) \tag{52}$$

in which $\overline{V}(\varepsilon_{k'})$ has been replaced by a constant $\overline{V}$ for evaluation purposes.

We thus conclude that, since the correction to the matrix element equation (49) appearing in $\sigma_{\mathrm{fi}}^{(2)}(t)$ tends to zero as η_t when η_t goes to zero, we can retain this matrix element only in the large-t limit of $\sigma_{\mathrm{fi}}(t)$ at second order in V.

4.2. Third-order term

If we turn to the third-order term of $\sigma_{\rm fi}(t)$ we find, using equation (35), that $\delta_t(\varepsilon,\varepsilon',\varepsilon'')$ given in equation (36) also reads

$$\delta_t(\varepsilon,\varepsilon',\varepsilon'')=\frac{1}{\varepsilon'-\varepsilon''}\left[\frac{{\rm e}^{-{\rm i}\varepsilon'/\eta_t}}{\varepsilon'}\,\delta_t(\varepsilon-\varepsilon')-\frac{{\rm e}^{-{\rm i}\varepsilon''/\eta_t}}{\varepsilon''}\,\delta_t(\varepsilon-\varepsilon'')\right]+\frac{\delta_t(\varepsilon)}{\varepsilon'\,\varepsilon''}. \tag{53}$$

Its imaginary part, equal to

$${\rm Im}\ \delta_t(\varepsilon,\varepsilon',\varepsilon'')=-{\rm i}\,\pi\ \frac{\delta_t(\varepsilon')\,\delta_t(\varepsilon-\varepsilon')-\delta_t(\varepsilon'')\,\delta_t(\varepsilon-\varepsilon'')}{\varepsilon'-\varepsilon''} \tag{54}$$

looks like

$$-{\rm i}\,\pi\ \left[\frac{\delta_t(\varepsilon')}{-\varepsilon''}+\frac{\delta_t(\varepsilon'')}{-\varepsilon'}\right]\delta_t(\varepsilon) \tag{55}$$

for ε' and ε'' large compared to η_t while the real part of $\delta_t(\varepsilon,\varepsilon',\varepsilon'')$ looks like $\delta_t(\varepsilon)/\varepsilon'\varepsilon''$ in the same limit. However, because $\delta_t(\varepsilon,\varepsilon',\varepsilon'')$ stays finite for ε' or $\varepsilon''\to 0$, we expect the above singularities in $1/\varepsilon'$ and $1/\varepsilon''$ to be cut at a few η_t from zero. This leads us to guess that the large-t limit of $\delta_t(\varepsilon,\varepsilon',\varepsilon'')$ should be

$$\frac{1}{(-\varepsilon'+{\rm i}\,\eta_t)\,(-\varepsilon''+{\rm i}\,\eta_t)}\,\delta_t(\varepsilon) \tag{56}$$

for large t. In order to verify this guess and to estimate the correction precisely, we rewrite $\delta_t(\varepsilon,\varepsilon',\varepsilon'')$ as

$$\delta_t(\varepsilon,\varepsilon',\varepsilon'')=\delta_t(\varepsilon)\left[\frac{1}{(-\varepsilon'+{\rm i}\,\eta_t)\,(-\varepsilon''+{\rm i}\,\eta_t)}+\frac{1}{\eta_t^2}\,d_t(\varepsilon/\eta_t,\varepsilon'/\eta_t,\varepsilon''/\eta_t)\right] \tag{57}$$

which serves as definition for $d_t(x,x',x'')$. By inserting this equation into the definition of $\sigma_{\rm fi}^{(3)}(t)$, we find

$$\sigma_{\rm fi}^{(3)}(t)=\delta_t(\varepsilon_{\rm f}-\varepsilon_{\rm i})\left[\sum_{k'k''}\frac{V_{fk'}\,V_{k'k''}\,V_{k''{\rm i}}}{(\varepsilon_{\rm i}-\varepsilon_{k'}+{\rm i}\,\eta_t)\,(\varepsilon_{\rm i}-\varepsilon_{k''}+{\rm i}\,\eta_t)}+W_{\rm fi}^{(3)}(\eta_t)\right]. \tag{58}$$

The sum is simply

$$\langle\varphi_{\rm f}|V\,\frac{1}{\varepsilon_{\rm i}-H_0+{\rm i}\,\eta_t}\,V\,\frac{1}{\varepsilon_{\rm i}-H_0+{\rm i}\,\eta_t}\,V|\varphi_{\rm i}\rangle \tag{59}$$

while the second term is given by

$$W_{\rm fi}^{(3)}(\eta_t)=\frac{1}{\eta_t^2}\sum_{kk'}V_{fk'}\,V_{k'k''}\,V_{k''{\rm i}}\,d_t\left(\frac{\varepsilon_{\rm f}-\varepsilon_{\rm i}}{\eta_t},\frac{\varepsilon_{k'}-\varepsilon_{\rm i}}{\eta_t},\frac{\varepsilon_{k''}-\varepsilon_{\rm i}}{\eta_t}\right). \tag{60}$$

We show in the appendix that $W_{\rm fi}^{(3)}(\eta_t)$ goes to zero when $\eta_t\to 0$.

4.3. Large-t limit of $U_{\rm fi}(t)$

Calculations similar to the above lead to higher-order $\sigma_{\rm fi}^{(n)}(t)$ having the same form, so that, for $n\to\infty$, we can sum up all these terms, using equation (28), as

$$U_{\rm fi}(t)={\rm e}^{-{\rm i}(\varepsilon_{\rm f}+\varepsilon_{\rm i})\,t/2\hbar}\ \left\{\delta_{\rm fi}-2{\rm i}\pi\,\delta_t(\varepsilon_{\rm f}-\varepsilon_{\rm i})\left[\langle\varphi_{\rm f}|V+V\,\frac{1}{\varepsilon_{\rm i}-H+{\rm i}\,\eta_t}\,V|\varphi_{\rm i}\rangle+{\rm O}(\eta_t)\right]\right\} \tag{61}$$

the correction ${\rm O}(\eta_t)$ originating from the sum of all the corrections $W_{\rm fi}^{(n)}(\eta_t)$. However, since $\delta_t(0)=1/\pi\eta_t$, this correction for ${\rm f}={\rm i}$ has to go to zero faster than η_t in order to give a

negligible contribution to the large-t limit of $U_{\rm ii}(t)$. Let us forget this correction $\mathrm{O}(\eta_t)$ for a while and see what we obtain from the other terms of $U_{\rm fi}(t)$, called $\hat{U}_{\rm fi}(t)$. They are quite similar to the result usually quoted for the generalized Fermi golden rule (equations (2) and (3)), except that η is replaced by η_t. By performing the same manipulation as in equations (10) and (11), we now obtain

$$\langle\varphi_{\rm f}|V + V\,\frac{1}{\varepsilon_{\rm i} - H + {\rm i}\,\eta_t}\,V|\varphi_{\rm i}\rangle = {\rm i}\,\eta_t\left[-\langle\varphi_{\rm f}|\varphi_{\rm i}\rangle + \langle\varphi_{\rm f}|\frac{\varepsilon_{\rm i} - \varepsilon_{\rm f} + {\rm i}\,\eta_t}{\varepsilon_{\rm i} - H + {\rm i}\,\eta_t}\,V|\varphi_{\rm i}\rangle\right] \tag{62}$$

so that for f = i equations (61) and (62) lead to

$$\begin{aligned}\hat{U}_{\rm ii}(t) &= {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\left\{1 - 2{\rm i}\pi\,\frac{1}{\pi\,\eta_t}\,{\rm i}\,\eta_t\,\left[-1 + \langle\varphi_{\rm i}|\frac{{\rm i}\,\eta_t}{\varepsilon_{\rm i} - H + {\rm i}\,\eta_t}\,V|\varphi_{\rm i}\rangle\right]\right\}\\ &= {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\langle\varphi_{\rm i}|\frac{{\rm i}\,\eta_t - (\varepsilon_{\rm i} - H)}{{\rm i}\,\eta_t + (\varepsilon_{\rm i} - H)}|\varphi_{\rm i}\rangle.\end{aligned} \tag{63}$$

Equations (61) and (63), which follows directly from it, are the key results of our paper. The reader may be surprised by this new expression of $\hat{U}_{\rm ii}(t)$. To reassure him or her, we can already check that it does give the expected result up to second order in V. Indeed, equation (63) also reads

$$\hat{U}_{\rm ii}(t) = {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\langle\varphi_{\rm i}|1 - 2\,\frac{\varepsilon_{\rm i} - H}{{\rm i}\,\eta_t + \varepsilon_{\rm i} - H}|\varphi_{\rm i}\rangle. \tag{64}$$

Using equations (10) and (28), its lowest-order terms are

$$\begin{aligned}\hat{U}_{\rm ii}(t) &\approx {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\left[1 + 2\,\langle\varphi_{\rm i}|\left(\frac{1}{{\rm i}\,\eta_t + \varepsilon_{\rm i} - H_0} + \frac{1}{{\rm i}\,\eta_t + \varepsilon_{\rm i} - H_0}\,V\,\frac{1}{{\rm i}\,\eta_t + \varepsilon_{\rm i} - H_0} + \cdots\right)V|\varphi_{\rm i}\rangle\right]\\ &\approx {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\left[1 + \frac{2}{{\rm i}\,\eta_t}\,\langle\varphi_{\rm i}|\left(1 + V\,\frac{1}{{\rm i}\,\eta_t + \varepsilon_{\rm i} - H_0} + \cdots\right)V|\varphi_{\rm i}\rangle\right].\end{aligned} \tag{65}$$

The V^2 matrix element being

$$\frac{V_{\rm ii}^2}{{\rm i}\,\eta_t} + \sum_{k\neq{\rm i}}\,\frac{|V_{k{\rm i}}|^2}{\varepsilon_{\rm i} - \varepsilon_k + {\rm i}\,\eta_t} \tag{66}$$

while $2/{\rm i}\,\eta_t = -{\rm i}t/\hbar$, we thus find

$$\hat{U}_{\rm ii}(t) = {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\left[1 - \frac{{\rm i}t\,V_{\rm ii}}{\hbar} + \frac{1}{2}\left(\frac{-{\rm i}t\,V_{\rm ii}}{\hbar}\right)^2 - \frac{{\rm i}t}{\hbar}\sum_{k\neq{\rm i}}\,\frac{|V_{k{\rm i}}|^2}{\varepsilon_{\rm i} - \varepsilon_k + {\rm i}\,\eta_t} + \mathrm{O}(V^3)\right] \tag{67}$$

which is exactly what we want:

(i) If η_t is much smaller than all possible $\varepsilon_k - \varepsilon_{\rm i}$, we can discard it from the last term. We then find

$$\hat{U}_{\rm ii}(t) = {\rm e}^{-{\rm i}\tilde{\varepsilon}_{\rm i}\,t/\hbar} \tag{68}$$

where $\tilde{\varepsilon}_{\rm i}$ is obtained from second-order perturbation theory, as in equation (41). For such η_t, we find $|\hat{U}_{\rm ii}(t)|^2 \approx 1$, so the system is not in its 'lifetime' regime.

(ii) If η_t is larger than many $\varepsilon_k - \varepsilon_{\rm i}$, the sum of equation (67) may be expressed as

$$\sum_{k\neq{\rm i}}\,|V_{k{\rm i}}|^2\left[\hat{\mathcal{P}}_t\left(\frac{1}{\varepsilon_{\rm i} - \varepsilon_k}\right) - {\rm i}\,\pi\,\hat{\delta}_t(\varepsilon_{\rm i} - \varepsilon_k)\right] \tag{69}$$

using the definitions of equations (44) and (45). Equation (67) then gives

$$\begin{aligned}\hat{U}_{\rm ii}(t) &\approx {\rm e}^{-{\rm i}\varepsilon_{\rm i}\,t/\hbar}\,\left\{1 - \frac{{\rm i}t}{\hbar}\left[V_{\rm ii} + \sum_{k\neq{\rm i}}\,|V_{k{\rm i}}|^2\,\hat{\mathcal{P}}_t\left(\frac{1}{\varepsilon_{\rm i} - \varepsilon_k}\right)\right] + \frac{1}{2}\left(\frac{-{\rm i}t\,V_{\rm ii}}{\hbar}\right)^2 - t\,\frac{\Gamma(t)}{2}\right\}\\ &\approx {\rm e}^{-{\rm i}\tilde{\varepsilon}_{\rm i}(t)\,t/\hbar}\,{\rm e}^{-t\,\Gamma(t)/2}\end{aligned} \tag{70}$$

with $\Gamma(t)$ defined as

$$\Gamma(t) = \frac{2\pi}{\hbar} \sum_{k\neq \mathrm{i}} |V_{k\mathrm{i}}|^2 \, \hat{\delta}_t(\varepsilon_k - \varepsilon_\mathrm{i}). \tag{71}$$

When t increases, $\Gamma(t)$ tends to the lifetime of the usual Fermi golden rule, provided that many ε_k are still under the sizeable part of the $\hat{\delta}_t(\varepsilon)$ curve, i.e., η_t is still large enough for the spectrum of H_0 to look like a continuum on the η_t scale. The phase part of $\hat{U}_{\mathrm{ii}}(t)$ is now related to a 'time-dependent energy' $\tilde{\varepsilon}_\mathrm{i}(t)$ given by

$$\tilde{\varepsilon}_\mathrm{i}(t) = \varepsilon_\mathrm{i} + V_{\mathrm{ii}} + \sum_{k\neq \mathrm{i}} |V_{k\mathrm{i}}|^2 \, \hat{\mathcal{P}}_t \left(\frac{1}{\varepsilon_\mathrm{i} - \varepsilon_k} \right) \tag{72}$$

which tends to the energy of the second-order perturbation theory when η_t goes to zero.

We thus conclude that, although rather surprising at first, the above equation (63) for $U_{\mathrm{ii}}(t)$ is correct at least up to second order in V.

5. Discussion

From a careful study of the expansion of $U_{\mathrm{fi}}(t)$ in the large-t limit, we have generated a dominant term $\hat{U}_{\mathrm{f\,i}}(t)$ similar to the usual expression given in equations (2) and (3), except that $\eta = 0^+$ is replaced by η_t. This change is crucial since it links t and η. It of course affects $U_{\mathrm{ii}}(t)$, which is no longer equal to unity—as discussed in section 2—but is now given by equation (63). It also affects $U_{\mathrm{f}\neq\mathrm{i}}(t)$ at second order in V. We now comment on the consequences of this change for both quantities.

5.1. *Consequence of our new $\hat{U}_{\mathrm{fi}}(t)$ at second order in V*

From equation (61), we find that $\mathcal{T}_{\mathrm{fi}}$ has to be replaced by

$$\mathcal{T}_{\mathrm{fi}}(t) = \langle \varphi_\mathrm{f} | V + V \frac{1}{\varepsilon_\mathrm{i} - H + \mathrm{i}\eta_t} V | \varphi_\mathrm{i} \rangle \tag{73}$$

which depends on t through η_t. Up to second order in V, it reads

$$\mathcal{T}_{\mathrm{fi}}(t) = V_{\mathrm{fi}} + \sum_n V_{fn} \, V_{n\mathrm{i}} \left[\hat{\mathcal{P}}_t \left(\frac{1}{\varepsilon_\mathrm{i} - \varepsilon_n} \right) - \mathrm{i}\pi \, \hat{\delta}_t(\varepsilon_\mathrm{i} - \varepsilon_n) \right] + \mathrm{O}(V^3) \tag{74}$$

while, at the same order in V, $\mathcal{T}_{\mathrm{fi}}$, defined in equation (3), is

$$\mathcal{T}_{\mathrm{fi}} = V_{\mathrm{fi}} + \sum_n \frac{V_{fn} \, V_{n\mathrm{i}}}{\varepsilon_\mathrm{i} - \varepsilon_n} + \mathrm{O}(V^3) \tag{75}$$

if we impose $V_{\mathrm{ii}} = 0$ (by assuming this diagonal term has been included in H_0) in order to avoid the divergence of the sum. Note that, by setting $V_{\mathrm{ii}} = 0$, one also eliminates a term, $-\mathrm{i}\pi \, V_{\mathrm{fi}} \, V_{\mathrm{ii}}$, that equation (3) would otherwise generate.

The first-order term of $\mathcal{T}_{\mathrm{fi}}(t)$ or $\mathcal{T}_{\mathrm{f\,i}}$ may be viewed as a direct transition between $|\varphi_\mathrm{i}\rangle$ and $|\varphi_\mathrm{f}\rangle$ while the second-order term corresponds to a set of two-step processes with virtual transitions toward intermediate states $|\varphi_n\rangle$. We see from equation (74) that the intermediate states appearing in the real part of $\mathcal{T}_{\mathrm{fi}}(t)$ can have an energy quite different from ε_i, while those appearing in the imaginary part must be separated in energy by at most a few η_t from ε_i.

(i) Let us first consider systems in which direct transitions are possible between $|\varphi_\mathrm{i}\rangle$ and a set of states $|\varphi_\mathrm{f}\rangle$ close in energy. Such a system has states with $V_{\mathrm{fi}} \neq 0$ lying within

$\eta_{2t} = \eta_t/2$ from ε_i: indeed, the direct transition probability toward these states changes with time as

$$\frac{\mathrm{d}}{\mathrm{d}t}\sum_\mathrm{f}|U_\mathrm{fi}(t)|^2 \simeq \sum_\mathrm{f} 4\pi^2\,|V_\mathrm{fi}|^2\,\frac{\mathrm{d}}{\mathrm{d}t}\,\delta_t^2(\varepsilon_\mathrm{f}-\varepsilon_\mathrm{i}) \simeq \frac{2\pi}{\hbar}\sum_\mathrm{f}|V_\mathrm{fi}|^2\,\delta_{2t}(\varepsilon_\mathrm{f}-\varepsilon_\mathrm{i}) \tag{76}$$

so that, $\delta_{2t}(\varepsilon)$ being a function of witdh $\eta_t/2$, this direct transition rate is governed by the $|\varphi_\mathrm{f}\rangle$ states lying at $\eta_t/2$ from ε_i. These $|\varphi_\mathrm{f}\rangle$ states (with some others since $\hat{\delta}_t(\varepsilon)$ is a broader function of width η_t) enter the imaginary part of $\mathcal{T}_\mathrm{fi}(t)$ and are excluded from the real part at second order in V. Consequently, for systems with large couplings in which this second-order term is not negligible with respect to the first one, the change from $\mathcal{T}_\mathrm{fi}(t)$ to $\mathcal{T}_\mathrm{fi}$ in which *all* the coupled $|\varphi_\mathrm{f}\rangle$ enter the real part at second order in V must be accessible to experiments. Moreover, in systems such as mesoscopic systems in which the discreteness of the energy spectrum is appreciable, it should also be possible to differentiate states at $\eta_t/2$ from ε_i, such as those appearing in the first-order transition rate, from states at η_t from ε_i, such as as those appearing in the second-order term of $\mathcal{T}_\mathrm{fi}(t)$.

(ii) For systems in which direct transitions to $|\varphi_\mathrm{f}\rangle$ states close in energy to ε_i are impossible, the corresponding V_fi being zero, the $\hat{\delta}_t$ term of equation (74), which selects such states, gives zero. Similarly, the $|\varphi_n\rangle$ which are excluded by $\hat{\mathcal{P}}_t\big(\frac{1}{\varepsilon_\mathrm{i}-\varepsilon_n}\big)$ do not contribute to the sum of $\mathcal{T}_\mathrm{fi}$, their $V_{n\mathrm{i}}$ being zero, so the sums of $\mathcal{T}_\mathrm{fi}(t)$ and $\mathcal{T}_\mathrm{fi}$ are essentially equal (with a possible exception for mesoscopic systems in which states with $V_\mathrm{fi} \neq 0$ would exist at η_t from ε_i but not at $\eta_t/2$).

We conclude that the replacement of η_t by 0^+ in $\mathcal{T}_\mathrm{fi}(t)$ is valid for the lowest nonzero term of $\mathcal{T}_\mathrm{fi}(t)$ (which is first order if direct transitions are possible and second order if not). However, this replacement modifies the next nonzero term, so that if the couplings are large enough for this next-order term to give a sizeable contribution the difference between our new result equation (61) and the previous one equations (2), (3) should be accessible to experiments, mesoscopic systems being most probably the best candidates.

5.2. On the validity of the overall procedures

The expression of $\mathcal{T}_\mathrm{fi}$ given in equation (3) with $\eta = 0^+$ instead of η_t originates basically from a limit $t \to \infty$ taken too early in some of the terms of $U_\mathrm{fi}(t)$. Beside this problem, there is no reason to suspect any other difficulty with the procedures themselves, when handled with care. We will now show why our $\hat{U}_\mathrm{ii}(t)$ leads us to think that these procedures have indeed to be questioned.

(i) It is actually quite easy to compare $\hat{U}_\mathrm{ii}(t)$ to the exact $U_\mathrm{ii}(t)$, since we can rewrite equation (63) as

$$\hat{U}_\mathrm{ii}(t) = \mathrm{e}^{-\mathrm{i}\varepsilon_\mathrm{i}t/\hbar}\,\langle\varphi_\mathrm{i}|\frac{1+\mathrm{i}\,(\varepsilon_\mathrm{i}-H)/\eta_t}{1-\mathrm{i}\,(\varepsilon_\mathrm{i}-H)/\eta_t}|\varphi_\mathrm{i}\rangle \tag{77}$$

and the exact $U_\mathrm{fi}(t)$, equation (1), for $\mathrm{f} = \mathrm{i}$

$$U_\mathrm{ii}(t) = \mathrm{e}^{-\mathrm{i}\varepsilon_\mathrm{i}t/\hbar}\,\langle\varphi_\mathrm{i}|\mathrm{e}^{2\,\mathrm{i}\,(\varepsilon_\mathrm{i}-H)/\eta_t}|\varphi_\mathrm{i}\rangle \tag{78}$$

since $t/\hbar = 2/\eta_t$. By inserting the closure relation for the eigenstates of H in front of $|\varphi_\mathrm{i}\rangle$, these two matrix elements correspond to

$$\sum_k |\langle\phi_k|\varphi_\mathrm{i}\rangle|^2\,A\left(\frac{\varepsilon_\mathrm{i}-E_k}{\eta_t}\right) \tag{79}$$

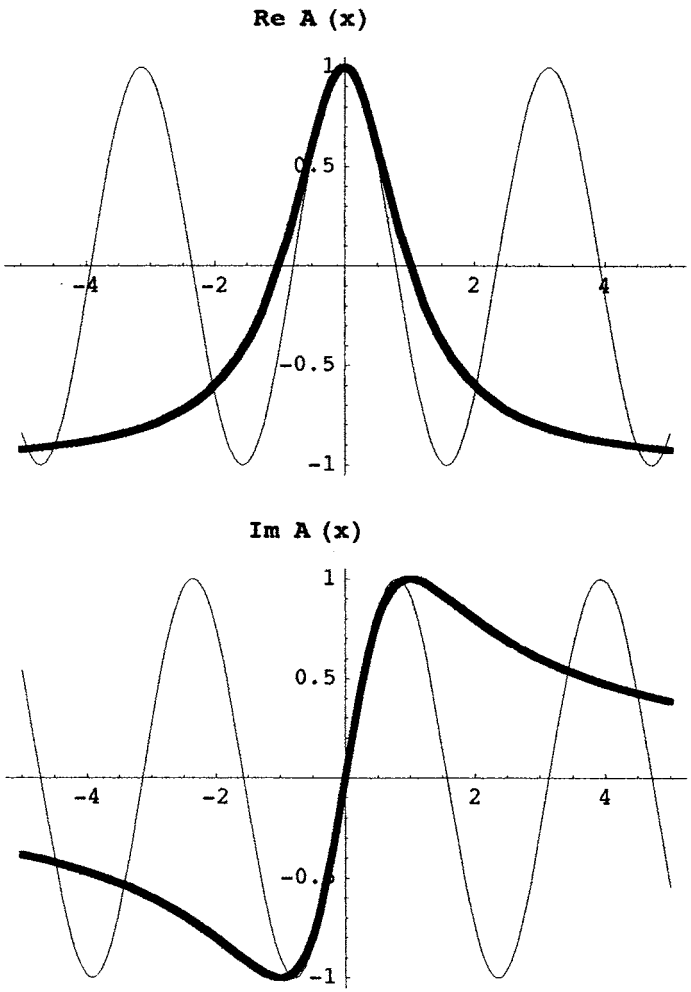

Figure 2. The real and imaginary parts of the $A(x)$ functions associated with the exact evolution operator (thin curve) and the approximate evolution operator (thick curve) as obtained from the standard perturbative procedure.

with $A(x) = \mathrm{e}^{2\,\mathrm{i}\,x}$ for $U_{\mathrm{ii}}(t)$, and $A(x) = (1+\mathrm{i}\,x)/(1-\mathrm{i}\,x)$ for $\hat{U}_{\mathrm{ii}}(t)$, respectively. The real and imaginary parts of these two A are shown in figure 2. They are close to each other for x small only so that $\hat{U}_{\mathrm{ii}}(t)$ is close to $U_{\mathrm{ii}}(t)$ when the $|\phi_k\rangle$ which give nonvanishing $|\langle\phi_k|\varphi_{\mathrm{i}}\rangle|^2$ are such that the corresponding $(\varepsilon_{\mathrm{i}} - E_k)/\eta_t$ are small. Even so, since the two $A(x)$ differ at third order in x, $\hat{U}_{\mathrm{ii}}(t)$ cannot provide a reliable estimate of $U_{\mathrm{ii}}(t)$ beyond second order in $(\varepsilon_{\mathrm{i}} - E_k)/\eta_t$.

(ii) If we now compare equation (77) to (78), we see that $\hat{U}_{\mathrm{ii}}(t)$ is just obtained by rewriting the exact evolution operator as

$$\mathrm{e}^{2\,\mathrm{i}\,(\varepsilon_{\mathrm{i}}-H)/\eta_t} = \frac{\mathrm{e}^{\mathrm{i}\,(\varepsilon_{\mathrm{i}}-H)/\eta_t}}{\mathrm{e}^{-\mathrm{i}\,(\varepsilon_{\mathrm{i}}-H)/\eta_t}} \tag{80}$$

and by replacing the numerator and denominator by their first-order terms, namely

$$\frac{1+\mathrm{i}\,(\varepsilon_\mathrm{i}-H)/\eta_t}{1-\mathrm{i}\,(\varepsilon_\mathrm{i}-H)/\eta_t}. \tag{81}$$

We can note that these *first*-order terms already provide an expansion of the ratio valid up to *second* order, so that the second-order terms of the numerator and denominator in equation (80) would not help to increase the validity of $\hat{U}_{\mathrm{ii}}(t)$. It is important to stress that this nontrivial approximation procedure generates an evolution operator which is still unitary while a naive expansion of the left-hand side of equation (80) up to second order loses this important property. This naive expansion would give an expectation value

$$\langle\varphi_\mathrm{i}|1+2\,\mathrm{i}\,\frac{\varepsilon_\mathrm{i}-H}{\eta_t}+\frac{1}{2}\left(2\,\mathrm{i}\,\frac{\varepsilon_\mathrm{i}-H}{\eta_t}\right)^2+\cdots|\varphi_\mathrm{i}\rangle = 1-\frac{\mathrm{i}t}{\hbar}\,V_{\mathrm{ii}}+\frac{1}{2}\sum_k\left(-\frac{\mathrm{i}t}{\hbar}\,V_{k\mathrm{i}}\right)^2+\cdots \tag{82}$$

rather different from that obtained in equation (67), when using equation (81). As could be expected, the unitarity of the approximate evolution operator plays a crucial role in obtaining the correct (second-order) Fermi golden rule.

(iii) Although $(H-\varepsilon_\mathrm{i})$ is V only when acting on $|\varphi_\mathrm{i}\rangle$, it is reasonable to doubt the possibility for an approximate evolution operator valid up to second order in $(\varepsilon_\mathrm{i}-H)/\eta_t$ to give an expectation value valid beyond second order in V. We have already shown in section 4.3 that $\hat{U}_{\mathrm{ii}}(t)$ is indeed correct up to V^2. Let us now compare the third-order term of $\hat{U}_{\mathrm{ii}}(t)$ with the expansion of $\mathrm{e}^{-\mathrm{i}\tilde{\varepsilon}_\mathrm{i}t/\hbar}$. From equations (64) and (65), this third-order term reads

$$\begin{aligned}\frac{-\mathrm{i}t}{\hbar}\sum_{mn}\frac{V_{\mathrm{i}n}\,V_{nm}\,V_{m\mathrm{i}}}{(\varepsilon_\mathrm{i}-\varepsilon_n+\mathrm{i}\,\eta_t)\,(\varepsilon_\mathrm{i}-\varepsilon_m+\mathrm{i}\,\eta_t)} &= \frac{1}{4}\left(\frac{-\mathrm{i}t\,V_{\mathrm{ii}}}{\hbar}\right)^3\\ &+\left(\frac{-\mathrm{i}t}{\hbar}\right)^2 V_{\mathrm{ii}}\sum_{n\neq\mathrm{i}}\frac{|V_{\mathrm{i}n}|^2}{\varepsilon_\mathrm{i}-\varepsilon_n+\mathrm{i}\,\eta_t}\\ &+\left(\frac{-\mathrm{i}t}{\hbar}\right)\sum_{\substack{n\neq\mathrm{i}\\ m\neq\mathrm{i}}}\frac{V_{\mathrm{i}n}\,V_{nm}\,V_{m\mathrm{i}}}{(\varepsilon_\mathrm{i}-\varepsilon_n+\mathrm{i}\,\eta_t)\,(\varepsilon_\mathrm{i}-\varepsilon_m+\mathrm{i}\,\eta_t)}\end{aligned} \tag{83}$$

while the third-order term of the energy $\tilde{\varepsilon}_\mathrm{i}$ can be obtained from the exact Brillouin–Wigner equation it verifies, namely

$$\tilde{\varepsilon}_\mathrm{i}=\varepsilon_\mathrm{i}+\langle\varphi_\mathrm{i}|V+V\,P_\perp\frac{1}{\tilde{\varepsilon}_\mathrm{i}-H}\,P_\perp\,V|\varphi_\mathrm{i}\rangle \tag{84}$$

where $P_\perp$ is the projection operator on the $|\varphi_{n\neq\mathrm{i}}\rangle$ subspace. Equation (84) leads to

$$\tilde{\varepsilon}_\mathrm{i}=\varepsilon_\mathrm{i}+V_{\mathrm{ii}}+\langle\varphi_\mathrm{i}|V\,P_\perp\frac{1}{\varepsilon_\mathrm{i}+V_{\mathrm{ii}}-H_0-V}\,P_\perp\,V|\varphi_\mathrm{i}\rangle+\mathrm{O}(V^4) \tag{85}$$

so that, from

$$\frac{1}{\varepsilon_\mathrm{i}+V_{\mathrm{ii}}-H_0-V}=\frac{1}{\varepsilon_\mathrm{i}-H_0}+\frac{1}{\varepsilon_\mathrm{i}-H}\,(V-V_{\mathrm{ii}})\,\frac{1}{\varepsilon_\mathrm{i}-H_0}+\mathrm{O}(V^2) \tag{86}$$

the third-order term of $\tilde{\varepsilon}_\mathrm{i}$ is given by

$$\sum_{\substack{n\neq\mathrm{i}\\ m\neq\mathrm{i}}}\frac{V_{\mathrm{i}n}\,V_{nm}\,V_{m\mathrm{i}}}{(\varepsilon_\mathrm{i}-\varepsilon_n)\,(\varepsilon_\mathrm{i}-\varepsilon_m)}-V_{\mathrm{ii}}\sum_{n\neq\mathrm{i}}\frac{|V_{\mathrm{i}n}|^2}{(\varepsilon_\mathrm{i}-\varepsilon_n)^2}. \tag{87}$$

Using this result along with the first two terms of $\tilde{\varepsilon}_\mathrm{i}$ already given in equation (41), we can easily check that the third-order term of the expansion of $\mathrm{e}^{-\mathrm{i}\tilde{\varepsilon}_\mathrm{i}t/\hbar}$ differs from equation (83)

by a prefactor $1/3!$ instead of $1/4$ in front of $V_{\rm ii}^3$, and by the absence of a term equivalent to the last term of equation (87). This proves that $\hat{U}_{\rm ii}(t)$ is incorrect at third order in V already.

(iv) It is rather disappointing to conclude that, even though $\hat{U}_{\rm ii}(t)$ contains higher-order terms in V, its validity does not go beyond that of the *second-order* golden rule. This *a posteriori* shows that the sum of the remainders of $\sigma_{\rm fi}^{(m)}(t)$, discarded when simplifying $U_{\rm fi}(t)$ into $\hat{U}_{\rm fi}(t)$, most probably gives a contribution as large as the sum of the higher-order leading terms of $\sigma_{\rm fi}(t)$. Actually, the expression (78) of the exact evolution operator shows in a transparent way that η_t and $\varepsilon_{\rm i} - H$, i.e. V when acting on $|\varphi_{\rm i}\rangle$, are strongly coupled since they appear through $(\varepsilon_{\rm i} - H)/\eta_t$ only. Therefore, there is *a priori* no hope of producing an approximate evolution operator valid for small η_t, i.e. for large t, which is not also some kind of expansion in V.

(v) In relation with the link between $\hat{U}_{\rm ii}(t)$ and the exact $U_{\rm ii}(t)$, we may also note that

$$\mathrm{e}^{2\,\mathrm{i}\,(\varepsilon_{\rm i}-H)/\eta_t} = \left(\frac{\mathrm{e}^{\mathrm{i}\,(\varepsilon_{\rm i}-H)/n\eta_t}}{\mathrm{e}^{-\mathrm{i}\,(\varepsilon_{\rm i}-H)/n\eta_t}}\right)^n = \lim_{n\to\infty}\left(\frac{1+\mathrm{i}(\varepsilon_{\rm i}-H)/\eta_{t/n}}{1-\mathrm{i}(\varepsilon_{\rm i}-H)/\eta_{t/n}}\right)^n \tag{88}$$

so that the approximate evolution operator appearing in $\hat{U}_{\rm ii}(t)$ corresponds to taking $n = 1$ instead of the limit $n \to \infty$. The validity of such a replacement is clearly questionable, as in the large-t limit, $\eta_{t/n}$ is small for $n = 1$, but infinite for $n \to \infty$. When n increases, ever more states of energies close to $\varepsilon_{\rm i}$ play a role in the calculation of the corresponding expectation value (their $(\varepsilon_{\rm i} - H)/\eta_{t/n}$ becoming small), whereas these states would play no role if $n = 1$.

5.3. On the connection with scattering theory

Let us make a last comment in relation to some misleading ideas associated with the expression of $\mathcal{T}_{\rm fi}$. It is often said that the generalized Fermi golden rule given in equations (2) and (3) has to be related to scattering theory and can be derived from a Green function approach [2, 4, 9]. Such a connection is in fact inappropriate since the two problems are different[4].

The problem addressed in this paper corresponds to taking a system in an initial state $|\varphi_{\rm i}\rangle$, an eigenstate of H_0, and to calculating its time evolution in the large-t limit when the system Hamiltonian is a (strictly) *time-independent* Hamiltonian $H = H_0 + V$. In this problem, there is only one small parameter homogeneous to an energy: η_t.

In the derivation of scattering theory using a Green function approach, one basically considers that the particle feels a time-dependent interaction which is introduced *adiabatically*. There is then another small parameter η, originating from the adiabatic approach. Being time independent, it can dominate η_t in the large-t limit. It is then necessary to state which of the two small parameters, η or η_t, goes to zero first. The answer depends on the nature of the physical problem under consideration.

It is important to notice that in the work presented here, relaxation, i.e. the occurrence of a lifetime, is intrinsic, being induced by a small but finite η_t on the eigenenergy scale. In contrast, in scattering theory, relaxation is somewhat extrinsic, as it originates from enforced adiabaticity.

6. Conclusion

We have studied the time evolution of an initial state $|\varphi_{\rm i}\rangle$, an eigenstate of H_0, when the system has a time-independent Hamiltonian H, and we have looked for a Fermi golden rule beyond

[4] It is striking enough to note that in [12] the transition rate is given up to second order in V only when the perturbation is time independent. In contrast, when the perturbation is assumed to be introduced adiabatically, in $\mathrm{e}^{\lambda t}$ with $\lambda \to 0^-$, higher-order terms in V of this transition rate are given.

second order in $V = H - H_0$.

We have first shown that the result previously quoted in the literature for this generalized golden rule is meaningless because of the presence of a spurious $\eta \to 0^+$ limit, which cannot be taken strictly as written.

In order to proceed in a safe way, we have considered Hamiltonians with discrete spectrum only, and we have shown that this discrete spectrum can be considered as a continuum if t is such that the possible eigenenergy differences around the initial-state energy ε_i are small compared to $\eta_t = 2\hbar/t$. This parameter, which turns out to be the key parameter of the problem, is just the energy scale of the uncertainty principle.

We have performed a V expansion of the time evolution of $|\varphi_\mathrm{i}\rangle$. From a careful study of the first few terms of this V expansion, we have identified the form of the dominant contributions in the small-η_t limit. Their summation generates a result similar to the previous one, except for the replacement of η by η_t. This crucial change restores a meaningful result, which now reads

$$\langle\varphi_\mathrm{i}|\mathrm{e}^{-\mathrm{i}\,H t/\hbar}|\varphi_\mathrm{i}\rangle \approx \mathrm{e}^{-\mathrm{i}\,\varepsilon_\mathrm{i}\,t/\hbar}\ \langle\varphi_\mathrm{i}|\frac{\mathrm{i}\,\eta_t - (\varepsilon_\mathrm{i} - H)}{\mathrm{i}\,\eta_t + (\varepsilon_\mathrm{i} - H)}|\varphi_\mathrm{i}\rangle. \tag{89}$$

When calculated up to second order in V, we have checked that this new generalized golden rule agrees with the usual one. However, if we rewrite the left-hand side of the above equation in terms of η_t, we see that its right-hand side simply results from an appropriate expansion in $(\varepsilon_\mathrm{i} - H)/\eta_t$, which preserves unitarity but which is valid up to second order only. This leads us to conclude that, although the new generalized golden rule originates from a summation of V^n dominant terms, up to infinity, it is not valid beyond second order in V. The reason for this disappointing conclusion is quite profound. As $H - \varepsilon_\mathrm{i}$ is nothing but V when acting on $|\varphi_\mathrm{i}\rangle$ while $\varepsilon_\mathrm{i} - H$ and η_t appear only through $(\varepsilon_\mathrm{i} - H)/\eta_t$ in the exact evolution operator, there is no way to produce an approximate expression of this evolution operator that is valid in the large-t limit and not restricted to small V only.

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Appendix. Estimation of $W_\mathrm{fi}^{(3)}(\eta_t)$ in the small η_t limit

From equations (34) and (57), we obtain $d_t(x, x', x'')$ as

$$d_t(x, x', x'') = \frac{-1}{(x' - \mathrm{i})\,(x'' - \mathrm{i})} + \frac{1}{x''\,D(x)} \times \left(\frac{D(x - x') - D(x - x'')}{x' - x''} - \frac{D(x - x') - D(x)}{x'}\right). \tag{A.1}$$

Because $d_t(x, x', x'')$ is large for small x' and x'' only, the ε_k and $\varepsilon_{k'}$ contributing to $W_\mathrm{fi}^{(3)}(\eta_t)$ given in equation (60) lie within a few η_t from ε_i, so that if, for such ε_k and $\varepsilon_{k'}$, the spectrum of H_0 looks like a continuum on the η_t scale, we can replace the sums over ε_k and $\varepsilon_{k'}$ by integrals over x_k and $x_{k'}$. We then obtain for $\mathrm{f} = \mathrm{i}$

$$W_\mathrm{ii}^{(3)}(\eta_t) = \int\!\!\int_{(\varepsilon_0 - \varepsilon_\mathrm{i})/\eta_t}^{\infty} \mathrm{d}x_{k'}\,\mathrm{d}x_{k''}\,\overline{V}(\varepsilon_\mathrm{i} + \eta_t\,x_{k'}, \varepsilon_\mathrm{i} + \eta_t\,x_{k''})\,d_t(x_\mathrm{f}, x_{k'}, x_{k''}) \tag{A.2}$$

where $\overline{V}(\varepsilon_{k'}, \varepsilon_{k''})$ is the result of the summation of $V_{ik'} V_{k'k''} V_{k''i}$ over all variables but energies. Let us rewrite $d_t(x, x', x'')$ as

$$d_t(x, x', x'') = \frac{1}{D(x)}\big[g(x, x', x'') + \tilde{g}(x, x', x'')\big] \tag{A.3}$$

where $g(x, x', x'')$ and $\tilde{g}(x, x', x'')$ are given by

$$g(x, x', x'') = \frac{\mathrm{i}}{(x' - \mathrm{i})\,(x'' - \mathrm{i})}\left[\frac{(1 + \mathrm{i}\,x')\,D(x - x') - D(x)}{x'}\right] \tag{A.4}$$

$$\tilde{g}(x, x', x'') = \frac{1}{x''}\left[\frac{D(x - x') - D(x - x'')}{x' - x''} + \frac{\mathrm{i}}{x'' - \mathrm{i}}\,\frac{D(x - x') - D(x)}{x'}\right]. \tag{A.5}$$

In order to show that $W_{ii}^{(3)}(0) = 0$, we use again the integration contour of figure 1. When $\eta_t = 0$, $\overline{V}$ is a constant. If we consider the first term of $d_t(x, x', x'')$, we find that the integration of $g(x, x', x'')$ over x' gives zero on the lower half circle while $g(x, x', x'')$ has only one pole at $x' = \mathrm{i}$, so that

$$\int_{-\infty}^{+\infty} \mathrm{d}x'\, g(x, x', x'') = 0. \tag{A.6}$$

We are left with the integration over x'', which unfortunately diverges logarithmically when $x'' \to \infty$. Actually, this divergence is spurious since it originates from the brutal replacement of η_t by zero in $\overline{V}$, which makes $\overline{V}(\varepsilon_{k'}, \varepsilon_{k''})$ constant. If we keep η_t finite and invoke the natural convergence of $\overline{V}(\varepsilon_{k'}, \varepsilon_{k''})$ at large $\varepsilon_{k'}$, which can be mimicked by a cut-off ε_m, the integral over x'' reads

$$\overline{V} \int_{(\varepsilon_0 - \varepsilon_i)/\eta_t}^{(\varepsilon_m - \varepsilon_i)/\eta_t} \mathrm{d}x''\, \frac{\mathrm{i}}{x'' - \mathrm{i}} \tag{A.7}$$

which remains finite when η_t goes to zero. Similarly, the integration of $\tilde{g}(x, x', x'')$ over x'' gives zero over the lower half circle while $\tilde{g}(x, x', x'')$ has only one pole at $x'' = \mathrm{i}$, so the integration of $\tilde{g}(x, x', x'')$ over x'' gives zero for $\eta_t = 0$. A similar logarithmic divergence in the integration over x' can be dealt with in the same way as above. Therefore, $W_{ii}^{(3)}(0)$ is indeed zero. It is possible to show that $W_{ii}^{(3)}(\eta_t)$ has a regular behaviour and tends to zero as $W_{ii}^{(2)}(\eta_t)$, when η_t goes to zero.

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