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Departures from the Fermi Golden Rule

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This paper shows that exact calculation for the transition probability in quantum mechanics gives rise to breaking the Fermi golden rule, and energy conservation, and gives two examples.

1. INTRODUCTION

We will emphasize that two assumptions were made in calculating the transition probability before this paper was prepared. Suppose the Hamiltonian H can be put in the form $H = H^{(0)} + V$, $V = A\exp(i\omega t) + A^{+}\exp(-i\omega t)$, $|a\rangle$ is a discrete state of $H^{(0)}$, $|b\rangle$ the state in a continuous spectrum of $H^{(0)}$, B the domain of $|b\rangle$, A a time-independent operator, and that at initial time t_0, which is taken to be zero, the system is in the state $|a\rangle$. The transition probability $W_{a\to B}$ into one of the states in the domain B at time t by absorbing an energy $\hbar\omega$ is (Greiner, 1994; Messiah, 1962; Schiff, 1968)

$$W_{a\to B} = \int_B W_{a\to b}\rho_b(E_b)\,dE_b, \tag{1}$$

$$W_{a\to b} = \frac{1}{\hbar^2}|A_{ba}|^2 f(t, \omega_b - \omega_a - \omega), \tag{2}$$

$$f(t, \omega_b - \omega_a - \omega) = \frac{\sin^2 \frac{(\omega_b - \omega_a - \omega)t}{2}}{\left(\frac{\omega_b - \omega_a - \omega}{2}\right)^2}, \tag{3}$$

$$\lim_{t\to\infty} f(t, \omega_b - \omega_a - \omega) = 2\pi t\delta(\omega_b - \omega_a - \omega), \tag{4}$$

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where $\rho_b(E_b)$ is the density of states at E_b, $E_b = \hbar\omega_b$, $E_a = \hbar\omega_a$, and $A_{ba} = \langle b|A|a\rangle$. Take $-\epsilon/2 < E_b < \epsilon/2$. The first assumption to calculate the integral in Eq. (1) in Greiner (1994), Messiah (1962), and Schiff (1968) is that the width ϵ is sufficiently small that A_{ba} and ρ_b are practically constant over the integral so that they can be taken outside the integral sign in Eq. (1). The second assumption in Greiner (1994), Messiah (1962), and Schiff (1968) is that t is sufficiently large for ϵ to be much greater than the period of oscillation of the f function in Eq. (3), i.e. $\epsilon \gg 2\pi\hbar/t$, so that Eq. (4) can be used. Under the two assumptions $W_{a\to B}$ is (Greiner, 1994; Messiah, 1962; and Schiff, 1968)

$$W_{a\to B} = \frac{2\pi}{\hbar}|A_{ba}(E_b)|^2\rho_b(E_b)t. \tag{5}$$

That the $W_{a\to B} \propto t$ is called the Fermi golden rule (Greiner, 1994; Schiff, 1968). In the transition $a \to B$ the energy is conserved because of Eq. (4) (Greiner, 1994; Messiah, 1962; Schiff, 1968).

This paper points out that in some cases one cannot use the two assumptions, and this leads to breaking the Fermi golden rule and energy conservation in the transition processes. We take the hydrogen ionization as the first example in Section 2, and the relaxation process in complex macroscopic system as the second example in Section 3.

2. HYDROGEN IONIZATION

In case of hydrogen ionization in a ground state, $E_a = \hbar\omega_a = -13.6$ eV. Greiner (1994) gives

$$\rho_b(E_b) = \frac{mL^3k}{8\pi^3\hbar^2}\,\sin\theta\,d\theta\,d\phi, \tag{6}$$

where θ and ϕ are the polar angles of wave vector $\mathbf{k}$ to the direction of electric field, $E_b = \hbar^2k^2/(2m)$, m is the electron mass, and L^3 the volume of the box. The box is a capacitor. The field $E(t) = 2E_0\sin(\omega t)$ is along the direction perpendicular to the capacitor. $|A_{ba}(E_b)|$ is (Schiff, 1968)

$$|A_{ba}(E_b)| = \left|\frac{32eE_0ka_0^5\cos\theta}{\left(\pi a_0^3L^3\right)^{1/2}\left(1+k^2a_0^2\right)^3}\right|, \tag{7}$$

where a_0 is the Bohr radius. Substituting Eqs. (6) and (7) into Eq. (5) and completing the integration over θ and ϕ, $W_{a\to B}$ in Eq. (5) becomes

$$W_{\text{hydrogen}} = \frac{1024me^2E_0^2a_0^7}{3\hbar^3}\frac{k^3}{\left(1+a_0^2k^2\right)^6}t. \tag{8}$$

Equation (8) obeys the Fermi golden rule. In case of boundary ionization $-\hbar\omega_a = \hbar\omega$, the energy conservation tells us $E_b = \hbar^2k^2/(2m) = \hbar\omega + \hbar\omega_a = 0$, and thus

W_{hydrogen} in Eq. (8) is zero. It is obviously not reasonable that the transition probability of hydrogen boundary ionization is zero.

Now let us abandon the two assumptions made in Section 1, and make an exact calculation for the integral of Eq. (1) for the case of hydrogen boundary ionization. In case of hydrogen boundary ionization Eq. (1) becomes

$$W_{\text{hydrogen, exact}} = \frac{1}{\hbar^2} \int |A_{ba}|^2 \rho_b(E_b) \frac{\sin^2 \frac{\omega_b t}{2}}{\left(\frac{\omega_b}{2}\right)^2} dE_b, \tag{9}$$

Substituting Eqs. (6) and (7) into Eq. (9) and completing the integration over θ and ϕ yield

$$W_{\text{hydrogen, exact}} = \frac{4096\sqrt{2}m^{5/2}e^2E_0^2a_0^7}{3\pi\hbar^{9/2}} I, \tag{10}$$

$$I = \int \frac{\sin^2 \frac{\omega t}{2}}{\sqrt{\omega}(1 + 4.85 \times 10^{-17}\omega)^6} \, d\omega, \tag{11}$$

where $\omega = \omega_b$ for convenience. Equation (11) clearly shows that $|A_{ba}|^2 \rho_b(E_b)$ is strongly energy-dependent. The exact integration for Eq. (11) is shown in Fig. 1. Figure 1 tells us that $W_{\text{hydrogen, exact}}$ is not equal to zero, and is nearly time-independent in a wide time interval. Therefore, we can say that the Fermi golden rule has not been obeyed. Because $E_b = \hbar\omega_b$ can be nonzero in the hydrogen boundary ionization, the energy is not conservative in this process. To understand the origin of the nonenergy conservation let us see Fig. 2. Figure 2 clearly indicates that the maximum transition probability is not at $\omega_b = 0$, and the second peak is not too low.

3. KWW FORM OF RELAXATION FUNCTION

In complex macroscopic systems, such as the fast ionic conductor, the Kohlrausch–Williams–Watts (KWW) form of relaxation, i.e. $\exp[-(t/\tau^*)^\beta]$ ($\beta < 1$), was observed and mentioned in many papers (William and Watts, 1970; León *et al.*, 1997; Ngai and León, 1999). If $\beta = 1$, then KWW form becomes Debye form. Several models, such as the coupling model (Ngai *et al.*, 1984), the diffusion-controlled model (Elliot and Owens, 1991), and the jump relaxation model (Callaway, 1991), have been proposed to explain the KWW form. This paper proposes a phonon model, and makes an exact calculation for the related transition probability of the relaxing particle without using the two assumptions in Section 1. The relaxing particle–phonon system can be described by

$$H = \sum_i c_i^+ c_i \left[\epsilon + \sum_{\mathbf{q}} M_{\mathbf{q}}(a_{\mathbf{q}}^+ + a_{\mathbf{q}}) \right] + \sum_{\mathbf{q}} \omega_{\mathbf{q}} a_{\mathbf{q}}^+ a_{\mathbf{q}}, \tag{12}$$

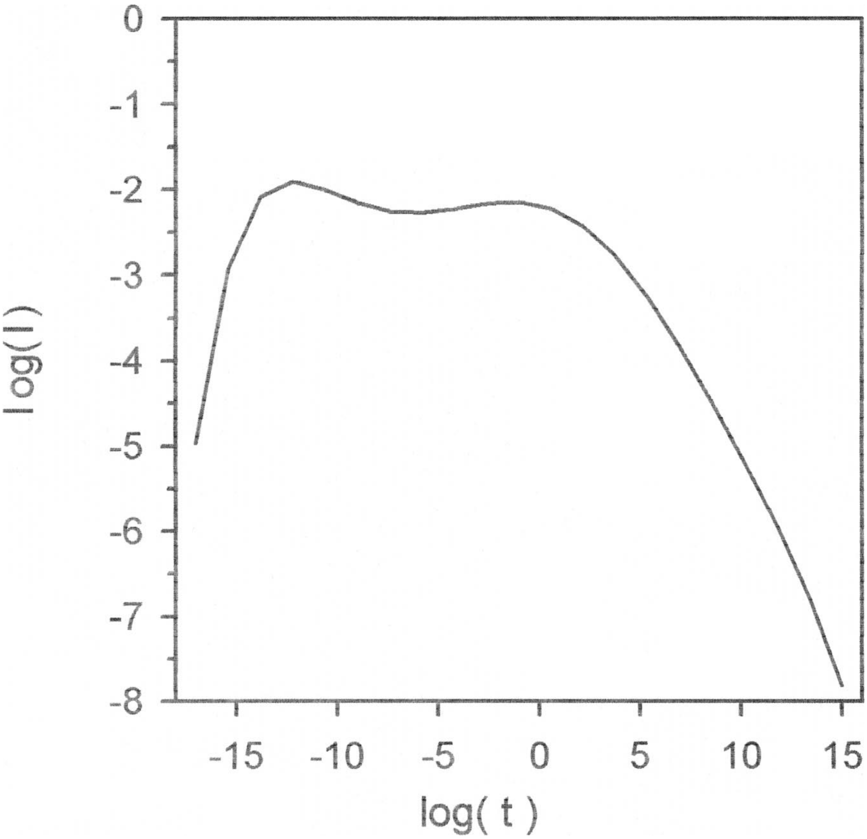

Fig. 1. The curve of $\log(I)$ vs. $\log(t)$. I is proportional to the transition probability, $W_{\text{hydrogen,exact}}$, of the hydrogen boundary ionization (see Eq. (10)). This curve shows that $W_{\text{hydrogen,exact}}$ is nearly equal to a constant over the range $10^{-13} < t < 10^{6}$ (seconds).

where c_i^{+} and $a_{\mathbf{q}}^{+}$ are the creation operators of the relaxing particle at site i and phonon with wave vector $\mathbf{q}$, respectively. $M_{\mathbf{q}}$ is (Callaway, 1991)

$$M_{\mathbf{q}} = C_i \left(\frac{\hbar}{2NM\omega_{\mathbf{q}}} \right)^{0.5} |\mathbf{q}|, \tag{13}$$

where N is the number density of atoms, C the coefficient of the deformation potential, and M the mass of the atom. The probability amplitude of finding the relaxing particle still at site i at time $t > 0$ was given by Mahan (1981) as $G(t)$. $G(t)$ is

$$G(t) = i\, e^{-it(\epsilon-\Delta)}\, e^{-\Phi(t)}, \tag{14}$$

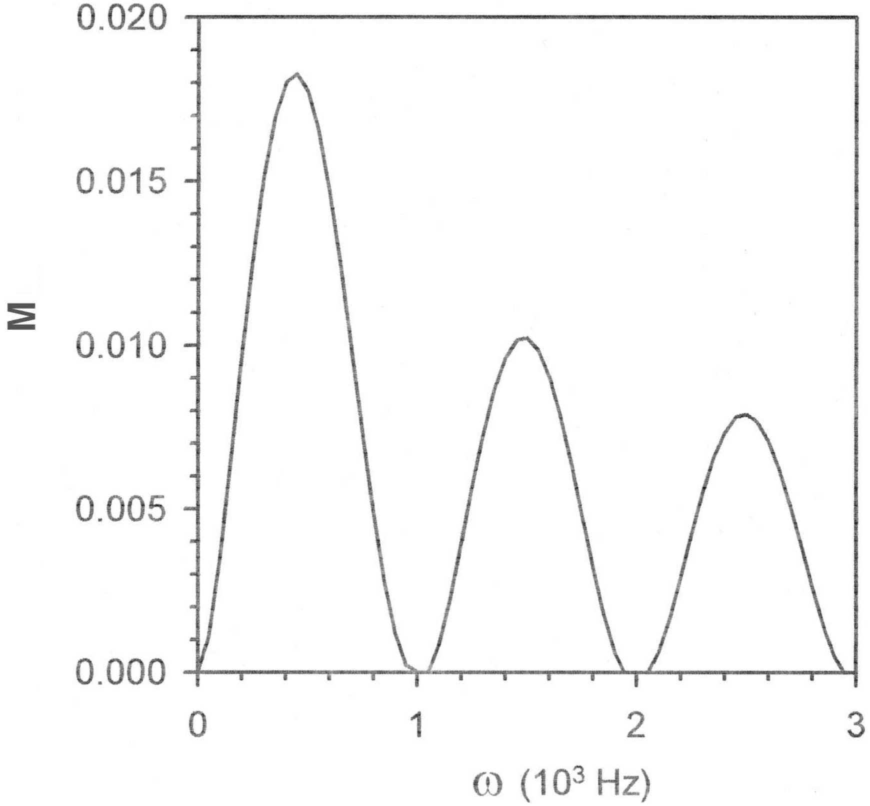

Fig. 2. The curve of $M(=\sin^2(\omega t/2)/[\sqrt{\omega}(1+4.85\times 10^{-17}\omega)^6])$ vs. ω. $t = 10^{-3}$ s. The transition probability at $\omega \to d\omega$ in the hydrogen boundary ionization is proportional to M. If the energy is conservative in the hydrogen boundary ionization, then the maximum value of M should be at $\omega = 0$, and the second peak should be very low.

$$\Delta = \sum_{\mathbf{q}} \frac{|M_{\mathbf{q}}|^2}{\hbar\omega_{\mathbf{q}}}, \tag{15}$$

$$\Phi(t) = \frac{1}{\hbar^2}\sum_{\mathbf{q}}(M_{\mathbf{q}})^2\left(\frac{2N_{\mathbf{q}}+1}{2}\right)\frac{\sin^2\frac{\omega_{\mathbf{q}}t}{2}}{\left(\frac{\omega_{\mathbf{q}}}{2}\right)^2}, \tag{16}$$

$$N_{\mathbf{q}} = \frac{1}{e^{\frac{\hbar\omega_{\mathbf{q}}}{KT}}-1}, \tag{17}$$

The relaxation function $Q(t)$ is

$$Q(t) = |G(t)|^2. \tag{18}$$

Ross showed that

$$Q(t) = e^{-P(t)}, \tag{19}$$

where $P(t)$ is the transition probability of the relaxing particle at site i at $t = 0$ and still at site i at t. Substituting Eqs. (14), (16), and (18) into Eq. (19) yields

$$P(t) = \frac{1}{\hbar^2} \sum_{\mathbf{q}} (M_{\mathbf{q}})^2 \, (2N_{\mathbf{q}} + 1) \, \frac{\sin^2 \frac{\omega_{\mathbf{q}} t}{2}}{\left(\frac{\omega_{\mathbf{q}}}{2}\right)^2}. \tag{20}$$

We do not use the two assumptions in Section 1 for calculation of Eq. (20). From the deformation potential theory the longitudinal acoustic phonon is important (Callaway, 1991). The density of states of the longitudinal acoustic phonon is (Ashcrift and Mermin, 1976)

$$\rho(\omega) = \frac{3\omega^2}{2\pi^2 v^3}, \tag{21}$$

where v is the acoustic velocity. We take $\omega_{\mathbf{q}} = \omega$ in Eq. (21) and in the following for convenience. The relation between ω and $\mathbf{q}$ in Eq. (13) is complex. From complete disorder to perfect order of the lattice the relation between $\mathbf{q}$ and ω is transformed from $q \propto \omega^0$ to $q \propto \omega^1$ (Bergman, 1971). For a real complex system we take that

$$q = \left(\frac{\omega}{v}\right)^{1-n} \bar{q}^n, \tag{22}$$

where $\bar{q}$ is the average value of the phonon wave number (Bergman, 1971). Substituting Eqs. (13), (21), and (22) into (20) and considering that the low frequency phonon is important in the integral yield

$$P(t) = \frac{6C^2 \bar{q}^{2n} KT}{\pi^2 N M v^{5-2n}} \int \frac{\sin^2 \frac{\omega t}{2}}{\omega^{1+\beta}} \, d\omega, \tag{23}$$

where $2n = 1 + \beta$. $\beta = 1$ and $\beta < 1$ correspond to complete and incomplete disorders, respectively. Completing the integration in Eq. (23) yields

$$P(t) = \left(\frac{t}{\tau^*}\right)^{\beta}, \tag{24}$$

$$\tau^* = \left(\frac{2\pi^2 N M v^{4-\beta} \Gamma(1+\beta) \, \sin(\pi\beta/2)}{3C^2 K T \pi \bar{q}^{1+\beta}}\right)^{\frac{1}{\beta}} \tag{25}$$

Substituting Eq. (24) into Eq. (19) yields the KWW form of relaxation function. However, if we use the two assumptions in Section 1, then we will obtain the Fermi golden rule $P(t) \propto t^1$ from Eq. (20), and thus cannot obtain the KWW form.

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