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Phonon-induced hopping rate enhancement in the Pd–D system

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Abstract

This paper shows that an exact calculation for transition probability can make some systems deviate seriously from Fermi's golden rule. The paper also shows that the corresponding exact calculation of the phonon-induced hopping rate for a deuteron in the Pd–D system plus many-body electron screening, proposed by Ichimaru, can explain experimental factors observed in the Pd–D system. It also predicts that the perfect and low dimensional forms of the Pd lattice are very important factors for the phonon-induced hopping rate enhancement of deuterons in the Pd–D system.

1. Introduction

It must be emphasized that two assumptions were made in calculating the transition probability prior to this paper. Suppose that the Hamiltonian H can be put in the form $H = H^0 + V$, where $V = A\exp(\mathrm{i}\omega t) + A^+\exp(-\mathrm{i}\omega t)$, $|a\rangle$ is a discrete state of H^0, $|b\rangle$ is the state in a continuous spectrum of H^0, B is the domain of $|b\rangle$ and A is 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 probability $P_{a\to B}$ of a transition into one of the states in the domain B at time t through absorbing energy $\hbar\omega$ has been given [1–3] as

$$P_{a\to B} = \int_B P_{a\to b}\rho_b(E_b)\,\mathrm{d}E_b, \tag{1}$$

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

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

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

where $\rho_b(E_b)$ is the density of states at E_b, $E_b = \hbar\omega_b$, $E_a = \hbar\omega_a$, and $A_{ba} = \langle b|A|a\rangle$. Also, $-\epsilon/2 < E_b < \epsilon/2$. The first assumption in calculating the integral in equation (1) in [1–3] is that the width ϵ is sufficiently small such that A_{ba} and ρ_b remain practically constant over the integral, so they can be taken outside the integral sign in equation (1). The second assumption in [1–3] is that t is sufficiently large for ϵ to be much greater than the period of oscillation of the f function in equation (3), i.e. $\epsilon \gg 2\pi\hbar/t$, so that equation (4) is applicable. Under the two assumptions, $P_{a\to B}$ is then [1–3]

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

The probability $P_{a\to B} \propto t$ may then be called Fermi's golden rule [1, 2].

2. Hydrogen ionization

We will take hydrogen ionization as an example for which the two assumptions cannot be used and thus for which Fermi's golden rule will be broken. We can think of the atom as being placed between the plates of a capacitor to which an alternating field $E(t) = 2E_0\sin(\omega t)$ is applied. For the ground state of hydrogen ionization, $E_a = \hbar\omega_a = -13.6$ eV. Schiff [1] then gives

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

where θ and ϕ are the polar angles of wavevector $\boldsymbol{k}$ to the direction of the electric field, $E_b = \hbar^2k^2/2m$, where m is the electron mass, and L^3 is the volume of the box in using box normalization. $|A_{ba}(E_b)|$ is expressed as [1]

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

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

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

Equation (8) now obeys Fermi's golden rule. Note that equation (8) comes from (5), which is obtained in terms of the two assumptions. In the case of boundary ionization, $-\hbar\omega_a = \hbar\omega$, energy conservation tells us that $E_b = \hbar^2k^2/2m = \hbar\omega + \hbar\omega_a = 0$, and thus P_{hydrogen} in equation (8) will be zero. It is obvious that the assumption in equation (8) of zero transition probability for hydrogen boundary ionization is not reasonable.

Let us abandon the two assumptions and make an exact calculation for the integral of equation (1) for the case of hydrogen boundary ionization. Equation (1) will become

$$P_{\text{hydrogen,exact}} = \frac{1}{\hbar^2}\int|A_{ba}|^2\rho_b(E_b)\frac{\sin^2\omega_bt/2}{(\omega_b/2)^2}\,\mathrm{d}E_b. \tag{9}$$

Substituting equations (6) and (7) into (9), completing the integration over θ and ϕ, and noting that $E_b = \hbar\omega_b = \hbar^2k^2/(2m)$, yields

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

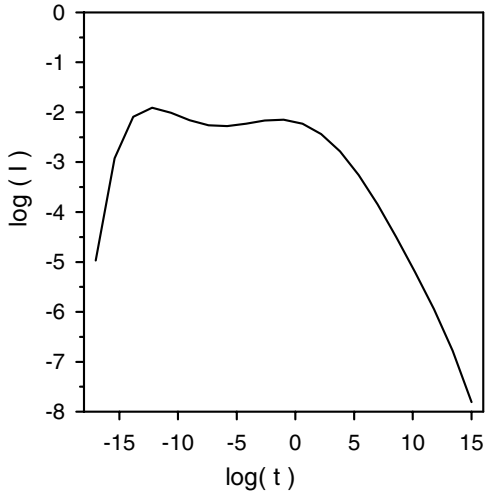

Figure 1. A curve of $\log(I)$ versus $\log(t)$ where, based on equation (10), I is proportional to the transition probability, $P_{\text{hydrogen,exact}}$, of hydrogen boundary ionization. This curve shows that $P_{\text{hydrogen,exact}}$ is nearly equal to a constant over the range $10^{-13} < t < 10^{6}$ (s).

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

where, for convenience, $\omega = \omega_b$. Equation (11) clearly indicates that $|A_{ba}|^2 \rho_b(E_b)$ is strongly energy-dependent. The exact integration for equation (11) is shown in figure 1. This indicates that $P_{\text{hydrogen,exact}}$ is not equal to zero and is nearly time-independent over a wide time interval, from 10^{-13} to 10^{6} s. Therefore, $P_{\text{hydrogen,exact}}$ is not proportional to time. We can say that Fermi's golden rule has not been obeyed.

3. Phonon-induced hopping rate enhancement of deuterons in the Pd–D system

For the Pd–D system the explicit form of the D-phonon interaction Hamiltonian, H_{int}, in the deformation potential approximation is expressed as [4, 5]

$$H_{\text{int}} = \sum_{m,p} c_m^+ a(p) c_m C i \left[\frac{\hbar}{2NM\omega}\right]^{\frac{1}{2}} \boldsymbol{p} \cdot \boldsymbol{e}(p) + \text{h.c.}, \tag{12}$$

where N is number of Pd atoms in the Pd–D system, c_m is the annihilation operator of a deuteron at site m, $a(p)$ is the phonon annihilation operator, M is the mass of a Pd atom, $\boldsymbol{e}(p)$ is the longitudinal polarization unit vector, $\boldsymbol{p} \cdot \boldsymbol{e}(p) = p$ for a longitudinal phonon, p is the wavenumber of the phonon, ω is the phonon frequency, and C is the deformation potential coefficient. For a one-dimensional Pd lattice, the interaction between a Pd^{2+} ion and a deuteron is $\epsilon = 2e^2/(0.5a)$, where $a = 4.0$ Å [6]. From [5], $\delta\epsilon = C\delta(Na)/Na$. Therefore, $C = -14.4$ eV.

Let us assume that the deuteron is at m at $t = 0$. The probability amplitude of finding the deuteron still at $\boldsymbol{m}$ at $t > 0$ is the following Green function of time at finite temperature [4]:

$$G(t) = -\mathrm{i}\langle T c_{\boldsymbol{m}}(t) c_{\boldsymbol{m}}^+(0)\rangle. \tag{13}$$

A waiting-time distribution $Q(t)$ is $Q(t) = |G(t)|^2$ [7]. The lifetime of a deuteron at m, i.e. $\langle t \rangle$, is given as [7]

$$\langle t \rangle = -\int_0^\infty t \, \mathrm{d}Q(t). \tag{14}$$

For an exact derivation, reference [4] gives

$$Q(t) = \mathrm{e}^{-P(t)}. \tag{15}$$

The transition probability of the deuteron $P(t)$ is then expressed as [4]

$$P(t) = \frac{2C^2}{\hbar NM} \sum_p [2n(\boldsymbol{p}) + 1] \frac{p^2}{\omega} \frac{\sin^2 \omega t/2}{\omega^2}, \tag{16}$$

where $n(p)$ is the Bose distribution of the phonon. We will now just consider the zero-point energy term in equation (16). Because the signs of the two terms in equation (16) are the same, $P(t)$ will become larger if we also consider the term with the Bose distribution of the phonon. For the zero-point energy term, equation (16) can be transformed into the integration

$$P(t) = \frac{2C^2}{\hbar NM} \int_0^\infty \mathrm{d}\omega \, \rho(\omega) \frac{p^2}{\omega} \frac{\sin^2 \omega t/2}{\omega^2}, \tag{17}$$

where $\rho(\omega)$ corresponds to the density of states. We know from equation (4.6) of [8] that, for a completely random lattice, p^2 in equation (17) represents $|\boldsymbol{k} - \boldsymbol{k}'|^2$, where $\boldsymbol{k}$ and $\boldsymbol{k}'$ are the wavevectors of a particle before and after absorption of a phonon, respectively. The $|\boldsymbol{k} - \boldsymbol{k}'|^2$ does not depend on energy for a completely random lattice [8]. We take the average value of $|\boldsymbol{k} - \boldsymbol{k}'|$ in the Brillouin zone, i.e. $|\boldsymbol{k} - \boldsymbol{k}'| = \bar{p} = \pi/2a$. For a perfect lattice, $|\boldsymbol{k} - \boldsymbol{k}'| = p = \omega/v$, where v is the sound velocity. We then take

$$p = \left(\frac{\omega}{v}\right)^{1-\beta'} \bar{p}^{\beta'}, \tag{18}$$

where $\bar{p} = \pi/2a$ and $0 \leqslant \beta' \leqslant 1$. For a perfect lattice $\beta' = 0$; for a completely random lattice $\beta' = 1$. The case of $0 < \beta' < 1$ in equation (18) is our assumption. Let us first consider the one-dimensional case. The formula of the density of states (equation (23.34) in [9]) can be used in the one-dimensional case, and $\rho_1(\omega) = L/(2\pi v_1)$ for a one-dimensional Pd–D system, where L is the length of the Pd–D system, v_1 is the longitudinal sound velocity [9], and the subscript 1 represents the one-dimensional system. The value of v_1 can be obtained from the Bohm–Staver formula [10], $v = \sqrt{2ZE_\mathrm{F}/3M}$, where E_F is the Fermi energy of the Pd–D lattice. Since $E_\mathrm{F} = 2.33$ eV, $Z = 2$ and $M = 106 \times 1.67 \times 10^{-24}$ g, therefore $v_1 = 1.68 \times 10^5$ cm s^{-1}. Letting $\beta = 1 - 2\beta'$ and $A = C^2\pi^{2\beta'}L/[\pi\hbar NMv^{3-2\beta'}(2a)^{2\beta'}]$, (17) then becomes [11]

$$P_1(t) = \left(\frac{t}{\tau_1}\right)^{1-\beta}, \tag{19}$$

$$\tau_1 = \left[\frac{A\pi}{4\Gamma(2-\beta)\sin[\pi(1-\beta)/2]}\right]^{-\frac{1}{1-\beta}}, \tag{20}$$

where Γ is the gamma function. If the one-dimensional Pd–D system now approaches a perfect lattice ($\beta = 1$), then the transition probability of the deuteron under the action of the phonons now deviates seriously from Fermi's golden rule (see equation (19)). Substitution of equation (19) into (14) and (15) yields

$$\langle t \rangle_1 = \tau_1 \Gamma\left(1 + \frac{1}{1-\beta}\right). \tag{21}$$

The physical meaning of $\langle t\rangle_1$ is the lifetime of a deuteron at a site m. Therefore, the hopping rate of a deuteron at a site under the action of phonon interaction is $w_1 = 1/\langle t\rangle_1$. Numerical calculations give the following results: for $\beta = 0.8$, $\tau_1 = 3.37\times10^{-35}$ s, $\langle t\rangle_1 = 4.0\times10^{-33}$ s, and $w_1 = 2.5\times10^{32}$ s^{-1}; for $\beta = 0.9$, $\tau_1 = 1.15\times10^{-69}$ s, $\langle t\rangle_1 = 4.17\times10^{-63}$ s, and $w_1 = 2.4\times10^{62}$ s^{-1}.

In the above calculations, we assumed that the limit of the phonon frequency is infinite. In the case of an upper limit $\omega_D = 10^{13}$ Hz, equation (17) becomes

$$P_{\text{finite},1}(t) = A\int_0^{\omega_D t} \mathrm{d}(\omega t)\,\frac{\sin^2\omega t/2}{(\omega t)^{2-\beta}}t^{1-\beta}. \tag{22}$$

$P_{\text{finite},1}(t)$ can also be written in the form of equation (19):

$$P_{\text{finite},1}(t) = \left(\frac{t}{\tau_{\text{finite},1}}\right)^{1-\beta}, \tag{23}$$

$$\langle t\rangle_{\text{finite},1} = \tau_{\text{finite},1}\Gamma\left(1+\frac{1}{1-\beta}\right), \tag{24}$$

where the definition of $\tau_{\text{finite},1}$ can be obtained from equations (22) and (23).

Now let us assume that at $t = 0$ we have a deuteron at site m with energy E_m and a phonon with frequency ω_D, and at $t > 0$ we have just a deuteron at site m. For this physical system the uncertainty relation for energy, equation (44.1) of [12], gives $\omega_D t = 1$ for any value of t. Numerical calculations give the following results: for $\beta = 0.8$, $\tau_{\text{finite},1} = 3.8\times10^6\tau_1$, $\langle t\rangle_{\text{finite},1} = 1.54\times10^{-26}$ s, and $w_{\text{finite},1} = 6.5\times10^{25}$ s^{-1}; for $\beta = 0.9$, $\tau_{\text{finite},1} = 1.6\times10^{16}\tau_1$, $\langle t\rangle_{\text{finite},1} = 6.72\times10^{-47}$ s, and $w_{\text{finite},1} = 1.48\times10^{46}$ s^{-1}.

Considering that a deuteron with radius 10^{-13} cm under the action of a phonon has the possibility to hop in all directions, the probability for a deuteron to hop in a specific deuteron is $P = \pi(10^{-13})^2/(4\pi a^2) = 1.56\times10^{-12}$, where a (= 4.0 Å) is approximately the distance between the two deuterons. According to an estimation of Ichimaru for many-body screening effects in the Pd–D system, the collision rate of a deuteron pair is $R_{\text{Ichimaru}} = 7.3\times10^{-31}$ s^{-1} [6]. Considering the hopping rate enhancement of deuterons due to phonons, R_{Ichimaru} generally becomes $R_{\text{Liu}} = R_{\text{Ichimaru}}\,w\text{s}P$. For $\beta = 0.8$ and 0.9, $R_{\text{Liu,finite},1} = 7.4\times10^{-17}$ and 1.69×10^4 s^{-1}, respectively.

If the Pd–D systems are three- or two-dimensional systems, then a similar method gives

$$\tau_{\text{finite},3} = \tau_{\text{finite},1}\left[\frac{v_3^{4+\beta}}{v_1^{2+\beta}}\frac{\pi}{a^2(0.574\times10^{13})^2}\right]^{\frac{1}{1-\beta}}, \tag{25}$$

$$\tau_{\text{finite},2} = \tau_{\text{finite},1}\left[\frac{v_2^{3+\beta}}{v_1^{2+\beta}}\frac{1}{a(0.5\times10^{13})}\right]^{\frac{1}{1-\beta}}, \tag{26}$$

and the forms of equations (23) and (24) do not change. The Bohm–Staver formula gives $v_3 = 3.3\times10^5$ cm s^{-1} and $v_2 = 2.66\times10^5$ cm s^{-1}, where $a = 4.0$ Å. For a three-dimensional system with $\beta = 0.8$ and 0.9, $w_{\text{finite},3} = 4.3\times10^{17}$ and 3.33×10^{29} s^{-1} and $R_{\text{Liu,finite},3} = 4.9\times10^{-25}$ and 3.8×10^{-13} s^{-1}, respectively. The value of $R_{\text{Liu,finite},3}$ for $\beta = 0.9$ is nearly equal to the observed value of 10^{-11} s^{-1} in a three-dimensional Pd–D system [13]. For a two-dimensional system with $\beta = 0.8$ and 0.9, $w_{\text{finite},2} = 2.56\times10^{22}$ and 1.32×10^{39} s^{-1} and $R_{\text{Liu,finite},2} = 2.92\times10^{-20}$ and 1.5×10^{-3} s^{-1}, respectively. Based on values of $R_{\text{Liu,finite},x}$ with $x = 1, 2, 3$, our theory predicts that the perfect and the low dimensional forms of the Pd lattice are very important factors for phonon-induced hopping rate enhancement. It should be noted that, for an ordinary Pd crystal, the lattice cannot be completely perfect. For very a small deviation from perfection, for example $\beta' = 0.15$, then

$w_{\text{finite},3} \approx 10^9\ \text{s}^{-1}$, which is the ordinary transition rate. This is the reason why the collision of a deuteron pair cannot be observed easily in a three-dimensional Pd–D system [14].

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