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Conduction-electron effect in quantum tunneling diffusion of hydrogen on metal surfaces

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The effective-medium theory of electrons by Norskov and Lang suggests that hydrogen adsorbed on transition metals is affected by only one-third of the electron densities when compared with interstitial hydrogen in the metals. As an important consequence, we show that the hydrogen-electron coupling parameter κ (as defined by Kondo) on W and Ni surfaces is close to $\frac{1}{2}$ as opposed to 0.2 for interstitial hydrogen and positive muons in metals. It means that the electron-controlled under-barrier tunneling rate of hydrogen on W and Ni, proportional to $T^{2\kappa-1}$, varies weakly with temperature. Our numerical calculation shows that the over-barrier hopping can directly cross over to electron-controlled tunneling. We thus believe that the conduction-electron mechanism is a strong candidate to explain the weakly temperature-dependent tunneling of hydrogen on W and Ni.

In this paper, we investigate conduction-electron effects on quantum tunneling of hydrogen on metals.[1,2] We intend to show that the hydrogen-electron coupling parameter κ, obtained from the phase shifts of electrons when scattering off an adsorbed hydrogen-induced potential, is close to $\frac{1}{2}$.[3–6] Consequently the electron-controlled tunneling of hydrogen on metals has an inherently weak temperature dependence. As the electron effect can be shown to take over the phonon effect at temperatures as high as $\frac{1}{4}$ of the Debye temperature Θ_D, this result offers a persuasive explanation of nonactivated tunneling of hydrogen on W and Ni.[7–9]

Small-polaron theories and the electron theory of Kondo are rather successful in explaining most experimental observations of the transport of dilute interstitials in solids.[1,10–23] This includes crossovers from classical over-barrier hopping to activated phonon-assisted tunneling and transitions from the latter to electron-controlled tunneling at lower temperatures.

However, quantum tunneling diffusion of hydrogen on metal surfaces remains to be fully understood.[7,8] Using field emission microscopes, Gomer and co-workers found that the diffusion of hydrogen on W and Ni sharply changes from classical over-barrier hopping to under-barrier tunneling near $\Theta_D/4$. The sharpness of the transition is now fairly well understood in the framework of quantum transition-state theory.[16–18] The unexpected result is the near temperature independence of the tunneling diffusion rate $D_{\text{tunnel}}(T)$ over a large temperature range. On W(110) $D_{\text{tunnel}}(T)$ remains unchanged (within a 30% experimental uncertainty) from 27 to 150 K.[7] Such a weak temperature dependence has not been observed for interstitial muons or impurity-trapped hydrogen in metals.[19–23] Recently, Zhu and co-workers have also studied the diffusion of hydrogen on Ni using an independent experimental technique.[9,24] On Ni(111), they found that the diffusion of hydrogen indeed changes from an over-barrier hopping to a weakly temperature-dependent tunneling.[9] Their results confirmed the observation by Lin and Gomer in many aspects.[9,25]

The fact that weakly temperature-dependent impurity tunneling is observed only on metal surfaces suggests clues to possible mechanisms. Auerbach *et al.* attributed the observation by Gomer and co-workers to weak hydrogen-phonon coupling.[26] Using the rate expression for phonon-assisted activated tunneling,[10,11,16,19]

$$D_{\text{tunnel}}(T)\sim(T)^{-1/2}\exp(-E_a/k_BT), \tag{1}$$

the activation energy E_a would have to be less than 0.08 kcal/mol in order to account for the less than 30% variation in $D_{\text{tunnel}}(T)$ when T changes from 27 to 150 K. As we will show numerically later, such a small activation energy would enable the electron effect to become dominant at well above $\Theta_D/4$ and the over-barrier hopping would directly cross over to electron-controlled tunneling.[1] Zhu and Deng explored an extended phonon mechanism that included quadratic hydrogen-phonon coupling.[27] They found that the quadratic coupling, enhanced by the two dimensionality of surface phonons, could also lead to a weakly temperature-dependent tunneling over a fairly large temperature interval at intermediate temperatures. At lower temperatures, however, the phonon effect is still expected to give way to the electron effect as pointed out by Kondo.[28] This occurs for muon in Cu at $T\approx\Theta_D/7$ and for hydrogen in $Nb(OH)_x$ at $T\approx\Theta_D/4$.[20,21] These arguments persuade us to consider the nonadiabatic conduction-electron effect proposed by Kondo.[1] When the electron effect is predominant, an interstitial tunneling transition rate varies as $T^{2\kappa-1}$. It is easily seen that the tunneling diffusion of hydrogen will be weakly temperature dependent if the hydrogen-electron coupling parameter κ approaches $\frac{1}{2}$.

For the electron mechanism to be operative, one needs to show that (1) κ is justifiably close to $\frac{1}{2}$ on W and Ni while less than 0.2 for interstitial hydrogen and positive muons; (2) an over-barrier hopping can cross over to an electron-controlled tunneling without passing a region of phonon-assisted activated tunneling. The objective of this paper is to address these two issues.

When the transport of an impurity atom in or on a metal is primarily influenced by the interaction with the electrons, Kondo shows that the motion of the atom occurs as a sequence of uncorrelated tunneling transitions from a potential minimum to a neighboring one.[1] The rate $W(T)$ varies with temperature as[1,12,15]

$$W(T)=\frac{\Delta^2}{\hbar D}\frac{\sqrt{\pi}\Gamma(\kappa)}{\Gamma(\kappa+\frac{1}{2})}\left(\frac{\pi K_B T}{D}\right)^{2\kappa-1}\sim T^{2\kappa-1}. \quad (2)$$

Here D is the conduction-electron bandwidth, Δ is the phonon-renormalized tunneling matrix element in units of energy, and κ is the impurity-electron coupling parameter. $\Gamma(\kappa)$ is Euler's gamma function. Kagan and Prokof'ev suggested that D should be the impurity intrawell vibrational frequency ω_0 rather than the Fermi energy ε_F, as those electrons with energies larger than $\hbar\omega_0$ will be able to follow the impurity adiabatically.[29] The tunneling diffusion rate is given by $D_{\text{tunnel}}(T)\approx a^2 W(T)$. a is the separation between two neighboring potential minima (stable sites). Yamada *et al.* showed that κ is a function of phase shifts of conduction electrons at the Fermi surface when scattering off the impurity-induced potential;[2]

$$\kappa=\frac{2}{\pi^2}\left[\tan^{-1}\left(\frac{\sqrt{1-x}\tan\delta_0}{\sqrt{1+x\tan^2\delta_0}}\right)\right]^2, \quad (3)$$

$$x=\frac{\sin^2 k_F a}{k_F^2 a^2}=j_0^2(k_F a). \quad (4)$$

Here only the s-wave phase δ_0 is taken to be nonzero. For small x, κ reaches the maximum value of $\frac{1}{2}$ when δ_0 approaches $\pi/2$.

For positive muon in Cu and Al and for hydrogen in $Nb(OH)_x$, κ was found to be 0.2, 0.15, and 0.055, respectively.[20–22] These values are small compared to 0.5. Richter was among the first to note that the calculation of the Fermi phase shifts by Puska and Nieminen might be used to deduce the approximate values of κ for interstitial hydrogen.[30] We show that the effective-medium theory of hydrogen binding in and on metals by Norskov, Lang, and others combined with the calculation by Puska and Nieminen enables us to deduce κ for both adsorbed and interstitial hydrogen.

In an effort to explain the systematic behaviors of the damping of a vibrating atom on metal surfaces, Puska and Nieminen performed an effective-medium calculation of the Fermi-scattering phase shifts for an atom embedded in a homogeneous electron gas.[3,31] The damping rate of an adsorbed atom through creation and annihilation of electron-hole pairs is related to the same phase shifts that affect the tunneling of the atom on the metal surface.[1–3] For a hydrogen atom with a nucleus charge $Z=1$, Puska and Nieminen tabulated the Fermi phase shifts of electrons for various *local* electron densities $n=3/4\pi r_s^3$. r_s is the density parameter expressed in atomic bohr units. It is noteworthy that for $r_s\geq 2$, only the s wave has a large and nonvanishing phase shift δ_0. For $r_s\geq 2.5$, δ_0 approaches $\pi/2$.

The density parameter r_s is computed from the averaged local electron density $\bar{n}_0$ around a hydrogen atom. Norskov and co-workers studied the binding energies of hydrogen atoms in and on a number of metals within the framework of effective-medium theory.[4–6] They found that the major part of the binding energy comes from a term $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$ that is only the function of the averaged electron density $\bar{n}_0$. The binding sites are determined by the minima of $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0)$. For a series of metals including transition, trivalent, and noble metals, Norskov found that $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0^{\text{bulk}})$ for interstitial hydrogen reaches minimum values when $\bar{n}_0^{\text{bulk}}$ is in the range of 0.025–$0.05 a_B^{-3}$ or $r_s=1.7$–2.1.[5] On the surfaces of Ni(111), Ni(100), W(110), and W(100), however, Nordlander *et al.* found that $\Delta E_{\text{eff}}^{\text{hom}}(\bar{n}_0^{\text{surf}})$ is minimized outside the outermost ionic plane at a position with an averaged electron density $\bar{n}_0^{\text{surf}}\sim 0.009 a_B^{-3}$ or $r_s\sim 3$.[6] The predicted vertical locations of adsorbed hydrogen above Ni(111) and Ni(100) agree well with the findings of the low-energy electron-diffraction measurement and the He diffraction measurement.[32,33] The large difference in the average electron densities at interstitial sites and surface-adsorption sites leads to significantly different Fermi phase shifts.

We first examine positive muon in Cu.[21] The muons move between octahedral sites. At these sites, $\bar{n}_0^{\text{bulk}}\approx 0.021 a_B^{-3}$. Using the results of Puska and Nieminen, we find $\delta_0\approx 0.7\pi/2$. The distance between two neighboring octahedral sites is $a=4.8 a_B$ and therefore we obtain $x\approx 0.040$ from Eq. (4). Inserting δ_0 and x into Eq. (3), we arrive at $\kappa_{\text{calc}}^{\text{Cu}}\approx 0.23$. This value compares fairly well with the experimental value of $\kappa_{\text{expt}}^{\text{Cu}}\approx 0.20$.[21] Muons in Al is another extensively studied system.[22] Positive muons move between octahedral sites with a separation $a=5.4 a_B$. As noted by Richter, the interstitial electron density is higher so that the Fermi phase shift is reduced to $\delta_0\approx 0.65\pi/2$. Again from Eqs. (3) and (4), we obtain $x\approx 0.029$ and in turn $\kappa_{\text{calc}}^{\text{Al}}\approx 0.20$. This result also compares well with the experimental observation of $\kappa_{\text{expt}}^{\text{Al}}\approx 0.17$.[22] Hydrogen in $Nb(OH)_x$ is the third system that has been thoroughly investigated experimentally over a wide temperature range.[20] In the experiment of Steinbinder *et al.*, hydrogen atoms are trapped at tetrahedral sites by OH^- impurities residing at octahedral sites. The two neighboring tetrahedral sites are separated by $a=2.2 a_B$. We did not find the effective-medium calculation of $\bar{n}_0^{\text{bulk}}$ at the tetrahedral sites in Nb. We thus use the value of $\bar{n}_0^{\text{bulk}}\approx 0.028 a_B^{-3}$ at the tetrahedral sites in vanadium as vanadium is also a bcc metal and has the same number of valence electrons as Nb.[5] Using Eqs. (3) and (4), we obtain $\kappa_{\text{calc}}^{\text{Nb}}\approx 0.18$, which should be compared with the experimental value $\kappa_{\text{expt}}^{\text{Nb}}\approx 0.055$ for hydrogen in $Nb(OH)_x$. Given the limitation of the effective-medium theory the predicted hydrogen-electron coupling parameters without adjustable parameters agree with the experimental observations surprisingly well. The good performance of the effective-medium calculation gives us confidence to extend it to adsorbed hydrogen on metals.

Using $\bar{n}_0^{\text{surf}}\approx 0.009 a_0^{-3}$, we obtain an s-wave phase shift $\delta_0\approx 0.9\pi/2$ on both W(110) and Ni(111).[3] On W(110), hydrogen moves between twofold-hollow sites with a separation $a\approx 5.2 a_0$. From Eqs. (3) and (4), we find $x\approx 0.0034$ and $\kappa_{\text{calc}}^{\text{W(110)}}\approx 0.4$. Thus the electron-controlled tunneling rate on W(110) is expected to vary as $W(T)\sim T^{-0.2}$. When T changes by a factor of 5, $W(T)$ is not expected to change by more than 30%. This result is consistent with the experimental observation.[7] Hydrogen on W(111) is the second system on which the diffusion measurement was performed by Gomer and co-workers down to 27 K.[7] They found that the tunneling rate changed only by 20–70 % when T was varied from 27 to 120 K. If we assume that hydrogen atoms move

between the equivalent threefold-hollow sites that have second-layer tungsten atoms directly underneath, the site separation is again $a \approx 5.2a_0$ and we find $\kappa_{\rm calc}^{\rm W(111)} \approx 0.4$ as well.[7,34] The resultant temperature dependence of the tunneling rate also agrees with the experimental observation.[7] For hydrogen on W(211), the observed tunneling diffusion rate from 80 to 160 K can be equally well explained by the electron-controlled tunneling with a calculated $\kappa_{\rm calc}^{\rm W(211)} \approx 0.4$.[7]

On Ni(111), hydrogen atoms occupy threefold-hollow sites. There are two types of hollow sites: *b-ABC* and *c-ABC*.[32] There is one second-layer Ni atom directly underneath each *b-ABC* site, while there are no such second-layer Ni atoms underneath *c-ABC* sites. A density-functional calculation of hydrogen on Ni(111) by Wang predicted that the most stable sites are *b-ABC* sites and the *c-ABC* sites are less favored by 0.02 eV or 0.5 kcal/mol.[32,35] This is consistent with the low-energy electron-diffraction measurement.[32] Such a small energy difference [compared to the heat of desorption $E_{\rm des} \sim 23$ kcal/mol (Ref. 32)] is difficult to distinguish in thermal-desorption mass measurements. It is also small compared to the static diffusion barrier ($E_{\rm diff} \sim 4$ kcal/mol) and usually within the experimental uncertainties of $E_{\rm diff}$.[8,9] Thus, at high temperatures the over-barrier hopping occurs among both *b-ABC* and *c-ABC* sites without distinction. However, this binding-energy difference (20 meV) is much larger than the bare tunneling matrix element on Ni(111), ~4 meV.[36] Consequently, the electron-controlled tunneling should take place only between the nearest "equivalent" threefold-hollow sites with $a \approx 4.7a_0$. Using this result and $\tilde{n}_0^{\rm surf} \approx 0.009 a_0^{-3}$, we obtain $x \approx 1 \times 10^{-5}$. From Eq. (3), we once again get $\kappa_{\rm calc}^{\rm Ni(111)} \approx 0.4$. When T changes by a factor of 2 from 160 to 80 K, $W(T)$ changes by no more than 15%, in excellent agreement with the experimental results of Lin and Gomer and Lee *et al.*[8,9]

We now address the second issue. To use the conduction-electron mechanism to explain the experimental observation, one also needs to demonstrate that over-barrier hopping can cross over directly to electron-controlled tunneling on metals. As shown by Gillan and others, the classical quantum crossover occurs in a very short temperature interval and the overall transition rate is not a simple sum of a classical over-barrier hopping rate and an under-barrier tunneling rate as one might have expected.[16–18] We thus only need to show numerically that with reasonably weak hydrogen-phonon coupling the electron effect can take over the phonon effect at or above the experimentally observed crossover temperatures $\Theta_D/3 \sim \Theta_D/4$.[7–9]

We start with the expression for an under-barrier incoherent tunneling rate employed by Kondo,[1,28]

$$W(T) = \frac{\Delta_0^2}{\hbar^2} \int_{-\infty}^{+\infty} dt\, \Phi_p(t) \Phi_e(t), \tag{5}$$

where the phonon factor

$$\Phi_p(t) = \exp\left\{ -\lambda \int_0^{\omega_D} \frac{J(\omega)}{\omega^2} \{(1-\cos\omega t)[2n(\omega)+1] + i \sin\omega t\} d\omega \right\} \tag{6}$$

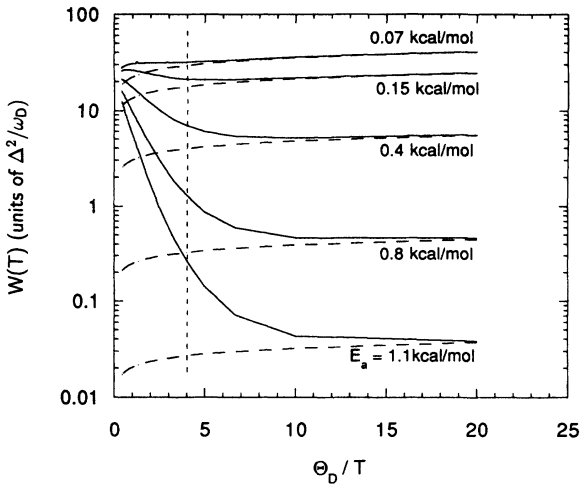

FIG. 1. Calculated under-barrier tunneling rates vs Θ_D/T [see Eqs. (5)–(7)]. Solid lines: including both the phonon effect and the conduction-electron effect. Dotted lines: including only the conduction-electron effect. The vertical dotted line indicates the crossover temperatures observed for hydrogen on W and Ni.

alone gives the usual small-polaron result.[1,10,11] The electron factor

$$\Phi_e(t) = \exp\left\{ -2\kappa \ln\left[\frac{\sinh(\pi k_B T t/\hbar)}{(\pi k_B T t/\hbar)} \sqrt{1+(Dt/\hbar)^2} \right] - i2\kappa \tan^{-1}\left(\frac{Dt}{\hbar}\right) \right\} \tag{7}$$

alone gives the result of Eq. (2).[1] Δ_0 here is the bare tunneling matrix element. We assume that the spectral density for the phonon part is given by $J(\omega) = \lambda \omega^3$ for $0 \leq \omega \leq \omega_D$, and $J(\omega) = 0$ for $\omega_D < \omega$.[1,12] The strength of the hydrogen-phonon coupling is then characterized by the dimensionless parameter $\eta \equiv \lambda \omega_D^2$. At temperatures above $\Theta_D/2$, the phonon-dominated tunneling is activated with an activation energy $E_a = \eta \hbar \omega_D/12$. In the case of Ni, which has a Debye temperature $\Theta_D = 450$ K, a value of $\eta = 13.3$ gives $E_a = 1$ kcal/mol and $\eta = 1$ corresponds to $E_a = 0.08$ kcal/mol. Using $\kappa = 0.4$ and $D = 100\omega_D$, we have calculated $W(T)$ for a series of η values by numerically integrating Eqs. (5)–(7). The results are shown in Fig. 1. For comparison, we have also displayed the tunneling rates by the conduction-electron effect alone, which are calculated by setting $\Phi_p(t) = \exp\{-\lambda \int_0^{\omega_D} d\omega J(\omega)/\omega^2\}$ in Eq. (6). The residual phonon effect only renormalizes the magnitudes of the rates. We see that even when E_a is as large as 0.4–0.5 kcal/mol, the electron-controlled tunneling already becomes dominant at or above $T = \Theta_D/4$. This conclusion did not change when we replaced $D = 100\omega_D$ in our calculation with the hydrogen intrawell vibrational frequency $D = \omega_{\rm H} \approx 2\omega_D$ as suggested by Kagan and Prokof'ev.[29] The activation energies of 0.4–0.5 kcal/mol correspond to lattice relaxation energies of 0.1 eV/atom. These values are certainly reasonable and realistic for adsorbed hydrogen on metals as discussed by Lee *et al.*[24] We specially note that $E_a = 0.08$ kcal/mol is the estimate that we obtained earlier to explain the tunneling rate of hydrogen

on W(110) in terms of pure phonon effect.[26] Our numerical calculation clearly suggests that the electron effect already dominates over the phonon effect at temperatures as high as Θ_D.

In conclusion, the unusually weak temperature dependence of tunneling diffusion rates for hydrogen on W and Ni has been a standing issue in quantum transport phenomena. We have shown here that the observed tunneling diffusion of hydrogen on these two metals can be attributed to an electron-controlled tunneling with the hydrogen-electron coupling parameter $\kappa \approx 0.4$. The large coupling parameter $\kappa \approx 0.4$ on transition metals can be deduced from the effective-medium theory and is a general result of reduced conduction-electron densities at hydrogen-adsorption sites. For interstitial hydrogen and positive muons in metals, the same theory produces hydrogen-electron coupling parameters $\kappa_{\text{calc}} \sim 0.2$ that agree well with the experimental observations. We have also shown numerically that with realistically weak hydrogen-phonon couplings, the electron-controlled tunneling may immediately follow the classical over-barrier hopping. We hope that this work will stimulate more refined theoretical calculations of hydrogen-electron coupling parameters. It is also desirable that the electron mechanism be further tested, either on suitably chosen metals with hydrogen-electron coupling parameters significantly less than 0.5, or in the temperature range where the conduction-electron density at the Fermi surface can be altered as a result of phase transitions, for example, from normal state to superconducting state.[37,38]

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