

Phonon-assisted tunneling of adatoms on a solid surface: The influence of quadratic adatom-phonon couplings

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We investigate the influence of quadratic adatom-phonon couplings on the phonon-assisted adatom tunneling on solids based upon the early work of Tonks and Dick. We find that the incoherent tunneling at high temperatures ($T \geq T_D/3$) is not simply thermally activated but described by a rate $\omega_{ij} \approx (\Delta/\hbar)^2 \exp[-E_a/k_B T + E_a^2/(k_B T)^2]$ where Δ is the renormalized tunneling matrix element, E_a is the conventional activation energy caused by linear adatom-phonon couplings, and E_a' is an effective energy arising from the quadratic couplings. We determine the conditions when the activated tunneling behavior is qualitatively altered by the quadratic couplings. As a result of reduced dimensionality, the latter play much more important roles in the tunneling diffusion of hydrogen on metal surfaces than they do in the interstitial tunneling in solids.

I. INTRODUCTION

In this paper, we study the effect of quadratic adatom-phonon couplings upon the phonon-assisted tunneling of an atom on a solid. An initial investigation of the subject was done by Tonks and Dick in their effort to explain the tunneling between different orientations of off-center interstitial Ag^+ in RbCl .¹ Based upon the theoretical work of Tonks and Dicks and a canonical transformation method, we explicitly obtain the incoherent tunneling rate at high temperatures ($T \geq T_D/3$) under the influence of both linear and quadratic couplings and determine the condition when the effect of quadratic couplings becomes dominant over that of conventional linear couplings. The latter have been extensively treated in the literature.²⁻⁷ The present work is an effort to explore possible mechanisms which may lead to the unusual nonactivated tunneling of hydrogen atoms on metals as reported by Gomer and co-workers and Lee *et al.*⁸⁻¹⁰

Conventional theories of phonon-assisted impurity transport in solids start with impurity-phonon interaction energies which vary linearly with displacements of host atoms.²⁻⁷ It is well known that the transport of such an impurity atom is diffusive, and as the temperature decreases, the diffusion rate $D(T)$ transforms from a classical overbarrier hopping to an activated tunneling with a smaller energy barrier which is associated with a lattice relaxation. At still lower temperatures, a bandlike diffusion prevails. The two-phonon scattering processes act to limit the lifetimes of the impurity polaron band states and lead to a tunneling rate varying at an inverse power of T . In metals, onsets of bandlike diffusions are postponed by the conduction-electron effects originally suggested by Kondo.¹¹ There is strong experimental evidence in support of the prescription of the conventional small-polaron theories and the effect of conduction electrons at low temperatures.¹²⁻¹⁸

Recently, Gomer and co-workers reported a series of measurements of diffusion of hydrogen and its isotopes

on tungsten and nickel using a field emission electron microscope.^{8,9} They observed that as the temperature decreases, the diffusion rate $D(T)$ levels off to almost a constant from the overbarrier hopping behavior. This was later confirmed by Lee *et al.* in their study of hydrogen diffusion on $\text{Ni}(111)$ using an optical diffraction technique.¹⁰ The unusual behaviors of hydrogen atoms on metals do not simply fall into the scenarios of the conventional small-polaron theories, and have thus stimulated further theoretical and experimental investigations.^{9,10,19-22} The issue remains to be fully resolved.

The quadratic impurity-phonon couplings, when dominant over the effect of the linear couplings, are capable of causing a nonactivated tunneling as will be explicitly shown. The effect was first considered in the tunneling problem by Dick.²³ Tonks and Dick subsequently developed the theoretical framework of including the quadratic couplings in the calculation of the incoherent tunneling rate in a nonperturbative fashion.¹ In applying the theory to $\text{RbCl}:\text{Ag}^+$, they found that the experimentally determined quadratic coupling parameters produced only small corrections to the activated behavior of the re-orientation tunneling transition at high temperatures. However their conclusion may not be simply generalized to other tunneling systems such as adatoms on metal surfaces. It has been established in recent years that adsorbed atoms can significantly alter surface lattice-vibrational frequencies without inducing sizable lattice relaxation through presumably quadratic adatom-phonon couplings.²⁴⁻²⁹ The effect of the quadratic couplings on quantum tunneling of adatoms along surfaces is enhanced as a result of reduced dimensionality. It is the objective of this paper to explore such a possibility.

The main results of our study are that (i) under the influence of both linear and quadratic couplings, the phonon-assisted adatom tunneling at high temperatures is not characterized by a conventional activated behavior but described by a rate $\omega_{ij} \approx (\Delta/\hbar)^2 \exp[-E_a/k_B T + E_a^2/(k_B T)^2]$; (ii) with 10-50% of surface phonon fre-

quency changes, the activated tunneling is qualitatively changed even when the activation energy E_a caused by the linear couplings is a few times $k_B T$; (iii) when the finite coverage effect is taken into account, the main temperature dependence $\exp[-E_a/k_B T + E_a^2/(k_B T)^2]$ remains intact. These results may have significant bearing on the observed nonactivated tunneling of hydrogen on metals.⁸⁻¹⁰

The organization of the paper is as follows. In Sec. II, we define the Hamiltonian which includes quadratic adatom-phonon couplings and give the physical reason why a nonactivated tunneling is generally expected. Starting from the theoretical calculation of Tonks and Dick, we determine the qualitative behavior of the phonon-assisted tunneling rate at high temperatures. The high temperatures here refer to those above $\frac{1}{4}$ to $\frac{1}{3}$ of the Debye temperature T_D . In Sec. III, we evaluate the tunneling rate explicitly by using a canonical transformation method similar to the conventional small-polaron theories.³⁰ In Sec. IV, we derive the general expression of the tunneling rate at high temperatures, which include the effects of both linear couplings and quadratic couplings, and determine the condition when the latter change the activated tunneling behavior. We show that the reduced dimensionality enhances the effect of quadratic couplings on tunneling diffusion of adatoms on surfaces. In Sec. V, we consider the effect of finite coverage. In Sec. VI, we discuss the relevance of the present results to the experimental observations of hydrogen tunneling on metals by Gomer and co-workers and Lee *et al.*⁸⁻¹⁰

II. QUALITATIVE BEHAVIOR

OF THE PHONON-ASSISTED TUNNELING RATE ω_{ij} AT HIGH TEMPERATURES UNDER THE INFLUENCE OF THE QUADRATIC COUPLINGS

Consider a lattice consisting of N heavy atoms with mass m . A light impurity atom (e.g., a hydrogen atom) is allowed to reside atop one of the host atoms. The impurity is separated from the neighboring lattice site by a static barrier E_{static} . Using the notation of Tonks and Dick, the total Hamiltonian of the system can be partitioned into those of unperturbed lattice phonons H_L , the impurity hopping H_D , and the impurity-phonon interaction H_{DL} , which includes both linear $H_{DL}(1)_i$ and quadratic couplings $H_{DL}(2)_i$:¹

$$H = H_L + H_D + H_{DL} , \quad (1)$$

$$H_L = \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}}^{(0)} a_{\mathbf{q}}^+ a_{\mathbf{q}} , \quad (2)$$

$$H_D = \sum_{i,j} \Delta |i\rangle \langle j| , \quad (3)$$

$$H_{DL} = \sum_i [H_{DL}(1)_i + H_{DL}(2)_i] |i\rangle \langle i| . \quad (4)$$

i labels the lattice site at which the impurity resides, j labels the nearest-neighbor sites surrounding i , \mathbf{q} labels the momentum of the unperturbed phonons, $\omega_{\mathbf{q}}^{(0)}$ is the unperturbed phonon frequency, and $a_{\mathbf{q}}^+$ and $a_{\mathbf{q}}$ are the corresponding creation and annihilation operators. To sim-

plify the notation, here we only consider one phonon branch with a polarization $\epsilon_{\mathbf{q}}$. We will include the effect of other branches in the final result as is appropriate. Δ is the renormalized tunneling matrix element as usual. In this section, we examine only the effect of the quadratic couplings $H_{DL}(2)_i$, and the linear couplings $H_{DL}(1)_i$ will be dropped. Specifically, we consider a quadratic interaction energy which varies at the second power of the displacement \mathbf{x}_i of the i th host atom residing at the lattice site \mathbf{R}_i , using the notation of Tonks and Dick,

$$H_{DL}(2)_i = \mathbf{x}_i \cdot \mathbf{B} \cdot \mathbf{x}_i . \quad (5)$$

Before we proceed with any detail calculation, it is helpful to explore what we may expect under the influence of the above Hamiltonian. The impurity tunneling rate at high temperatures can be qualitatively obtained through a physical argument. For this purpose, we consider a one-dimensional linear lattice. For comparison, we first review the conventional linear coupling model where the interaction energy Bx_i^2 is replaced with Ax_i .²⁻⁷ The total energy is lowered by a local lattice relaxation. The relaxation energy, loosely speaking, acts as a barrier which must be overcome by the impurity atom in order to execute the site-site tunneling.² Thus it is responsible for an activated tunneling following the over-barrier hopping. In the case of pure quadratic couplings, the presence of the impurity causes no lattice relaxation except for an overall perturbation of the phonon frequencies. When the temperature increases, the thermal agitations of phonons destroy the alignment of the ground-state energy levels of the impurity at the initial and final sites, and in turn reduce the site-site tunneling transition rate. This is what we found.

Using a moment expansion technique and evaluating the resultant circle and dot diagrams, Tonks and Dick derived a site-site tunneling transition rate ω_{ij} which includes the effects of both linear and quadratic couplings.¹ Dropping the contribution from the linear couplings for the moment and using the Holstein method of steepest descent, the high-temperature limit of ω_{ij} is obtained,

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \left[\frac{\pi}{b_c} \right]^{1/2} \exp \left[- \frac{a_c^2}{4b_c} \right] . \quad (6)$$

b_c and a_c , contributed by the circle diagrams involving quadratic couplings only, are expressed as¹

$$a_c = \frac{B}{2} \sum_{\mathbf{q}} \frac{[x_i^j(\omega_{\mathbf{q}})]^2 - [x_{i+1}^j(\omega_{\mathbf{q}})]^2}{\omega_{\mathbf{q}}} [N(\omega_{\mathbf{q}}) + 1/2] , \quad (7)$$

$$b_c = \frac{B^2}{4} \sum_{\mathbf{q}, \mathbf{q}'} \frac{[x_i^j(\omega_{\mathbf{q}})x_i^j(\omega_{\mathbf{q}'}) - x_{i+1}^j(\omega_{\mathbf{q}})x_{i+1}^j(\omega_{\mathbf{q}'})]^2}{\omega_{\mathbf{q}}\omega_{\mathbf{q}'}} \times [N(\omega_{\mathbf{q}}) + 1/2][N(\omega_{\mathbf{q}'}) + 1/2] , \quad (8)$$

where the effective coupling parameter

$$B \equiv \epsilon_{\mathbf{q}} \cdot \mathbf{B} \cdot \epsilon_{\mathbf{q}'}$$

is taken to be a constant. $x_i^j(\omega_{\mathbf{q}})$ and $x_{i+1}^j(\omega_{\mathbf{q}})$, similarly defined in Ref. 1, are the expansion coefficients for the i th and $(i+1)$ th host atomic displacements in terms of per-

turbed phonon normal modes with the impurity residing at the i th lattice site,

$$x_\beta = \sum_q x_\beta^i(\omega_q) i \left[\frac{\hbar}{2\omega_q} \right]^{1/2} [a_q^i - a_q^{i+}] . \quad (9)$$

$N(\omega_q)$ is the occupying number of the perturbed mode ω_q . By substituting Eqs. (7)–(9) into Eq. (6) and using the approximation of $N(\omega_q) + 1/2 \approx (k_B T / \hbar \omega_q) [1 + (\hbar \omega_q)^2 / 12(k_B T)^2]$ at high temperatures, we arrive at

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \left[\frac{\pi}{\gamma k_B^2 T^2} \right]^{1/2} \exp \left[-\alpha + \frac{E_{a'}^2}{k_B^2 T^2} \right] , \quad (10)$$

where

$$\gamma = \frac{B^2}{4\hbar^2} \sum_{q,q'} \frac{[x_i^i(\omega_q)x_i^i(\omega_{q'}) - x_{i+1}^i(\omega_q)x_{i+1}^i(\omega_{q'})]^2}{\omega_q^2 \omega_{q'}^2} , \quad (11)$$

$$\alpha = \frac{B^2}{16\hbar^2 \gamma} \left\{ \sum_q \frac{[x_i^i(\omega_q)]^2 - [x_{i+1}^i(\omega_q)]^2}{\omega_q^2} \right\}^2 , \quad (12)$$

$$E_{a'}^2 = \frac{\alpha \hbar^2}{12\gamma} \sum_{q,q'} \frac{\omega_q^2 + \omega_{q'}^2}{\omega_q^2 \omega_{q'}^2} [x_i^i(\omega_q)x_i^i(\omega_{q'}) - x_{i+1}^i(\omega_q)x_{i+1}^i(\omega_{q'})]^2 . \quad (13)$$

It is clear that ω_{ij} increases as T decreases. This is very different from the behavior prescribed by the linear couplings.^{2–7} However, it is not unexpected for pure quadratic couplings as we have argued earlier.

Equations (11)–(13) do not lend themselves to a direct, quantitative analysis since $x_i^i(\omega_q)$ and $x_{i+1}^i(\omega_q)$ involve perturbed phonon normal modes. For a real system, it is possible to numerically diagonalize H in the presence of $H_{DL}(2)_i$ to obtain $x_i^i(\omega_q)$ and $x_{i+1}^i(\omega_q)$ and in turn evaluate the parameters defined in Eqs. (11)–(13).^{1,23} In the next section, we employ a canonical transformation method to obtain these parameters analytically. It is val-

id as long as the approximation of the steepest descents is justified.

III. A CANONICAL TRANSFORMATION CALCULATION OF ω_{ij} AT HIGH TEMPERATURES

From the result obtained by Tonks and Dick, the transition rate can be written in the following form:¹

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \int_{-\infty}^{+\infty} ds \exp[i(E_i - E_j)s/\hbar] \exp[F_c(s)] . \quad (14)$$

$E_i - E_j$ is the ground-state energy misalignment or the bias. The high-temperature limit of ω_{ij} is obtained by expanding $F_c(s)$ around $s \sim 0$ up to s^2 terms and then integrating Eq. (14). The key here is that the procedure is equivalent to keeping the terms up to B^2 in $F_c(s)$. This can be achieved equally well by using a canonical transformation method similar to the tactics used in treating the linear couplings.³⁰ We choose a transformation $\exp(U_i)$ such that $\exp(U_i)H\exp(-U_i)$ in Eq. (1) is diagonalized up to B^2 . The transformation is expressed in terms of the unperturbed phonons by

$$U_\beta = \frac{B\hbar}{2} \sum_{q,q'} \frac{x_\beta(\omega_q^{(0)})x_\beta(\omega_{q'}^{(0)})}{\sqrt{\omega_q^{(0)}\omega_{q'}^{(0)}[\omega_q^{(0)} + \omega_{q'}^{(0)}]}} [a_q^+ a_{q'}^+ - a_q a_{q'}] \\ + \frac{B\hbar}{2} \sum_{q \neq q'} \frac{x_\beta(\omega_q^{(0)})x_\beta(\omega_{q'}^{(0)})}{\sqrt{\omega_q^{(0)}\omega_{q'}^{(0)}[\omega_q^{(0)} - \omega_{q'}^{(0)}]}} [a_q a_{q'}^+ - a_q^+ a_{q'}] , \quad (15)$$

where²

$$x_i(\omega_q^{(0)}) = \left[\frac{2}{mN} \right]^{1/2} \sin \left[\mathbf{q} \cdot \mathbf{R}_i + \frac{\pi}{4} \right] . \quad (16)$$

\mathbf{R}_i is the position vector of the i th lattice atom. The site-site tunneling rate can be written exactly as³⁰

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \int_{-\infty}^{+\infty} ds e^{i(E_i - E_j)s/\hbar} [\langle \Phi_L | e^{-iH_L s/\hbar} e^{U_i} e^{-U_{i+1}} e^{iH_L s/\hbar} e^{U_{i+1}} e^{-U_i} | \Phi_L \rangle - | \langle \Phi_L | e^{U_{i+1}} e^{-U_i} | \Phi_L \rangle |^2] . \quad (17)$$

The expression inside the square brackets should be equated to $\exp[F_c(s)]$.^{1,2} By expanding the expression and evaluating the terms up to B^2 , we arrive at the high-temperature approximation of $F_c(s)$,

$$F_c(s) = - \sum_{q \neq q'} \frac{B^2 \hbar^2}{[(\omega_q^{(0)})^2 - (\omega_{q'}^{(0)})^2]^2} [x_i(\omega_q^{(0)})x_i(\omega_{q'}^{(0)}) - x_{i+1}(\omega_q^{(0)})x_{i+1}(\omega_{q'}^{(0)})]^2 \\ \times \left[\frac{(\omega_q^{(0)})^2 + (\omega_{q'}^{(0)})^2}{2\omega_q^{(0)}\omega_{q'}^{(0)}} [2N(\omega_q^{(0)}) + 1][2N(\omega_{q'}^{(0)}) + 1] - 1 \right] \\ + \frac{B^2 \hbar^2}{2} \sum_{q,q'} \frac{[x_i(\omega_q^{(0)})x_i(\omega_{q'}^{(0)}) - x_{i+1}(\omega_q^{(0)})x_{i+1}(\omega_{q'}^{(0)})]^2}{\omega_q^{(0)}\omega_{q'}^{(0)}[\omega_q^{(0)} + \omega_{q'}^{(0)}]^2} \\ \times \{ [N(\omega_q^{(0)}) + 1][N(\omega_{q'}^{(0)}) + 1] e^{i(\omega_q^{(0)} + \omega_{q'}^{(0)})s} + N(\omega_q^{(0)})N(\omega_{q'}^{(0)}) e^{-i(\omega_q^{(0)} + \omega_{q'}^{(0)})s} \} \\ + \frac{B^2 \hbar^2}{2} \sum_{q,q'} \frac{[x_i(\omega_q^{(0)})x_i(\omega_{q'}^{(0)}) - x_{i+1}(\omega_q^{(0)})x_{i+1}(\omega_{q'}^{(0)})]^2}{\omega_q^{(0)}\omega_{q'}^{(0)}[\omega_q^{(0)} - \omega_{q'}^{(0)}]^2} \\ \times \{ [N(\omega_q^{(0)}) + 1]N(\omega_{q'}^{(0)}) e^{i(\omega_q^{(0)} - \omega_{q'}^{(0)})s} + N(\omega_q^{(0)})[N(\omega_{q'}^{(0)}) + 1] e^{-i(\omega_q^{(0)} - \omega_{q'}^{(0)})s} \} . \quad (18)$$

Expanding $F_c(s)$ up to s^2 , ω_{ij} is easily calculated using the method of steepest descent.^{1,2} It has the same expression as Eq. (10) with³⁰

$$\gamma = \frac{B^2}{2m^2N^2} \sum_{\mathbf{q} \neq \mathbf{q}'} \frac{1 - \cos(\mathbf{q} \cdot \delta) \cos(\mathbf{q}' \cdot \delta)}{[\omega_{\mathbf{q}}^{(0)} \omega_{\mathbf{q}'}^{(0)}]^2}, \quad (19)$$

$$\alpha = \frac{\gamma}{4}, \quad (20)$$

$$E_a^2 = \frac{B^2 \hbar^2}{96m^2N^2} \sum_{\mathbf{q} \neq \mathbf{q}'} \frac{[\omega_{\mathbf{q}}^{(0)}]^2 + [\omega_{\mathbf{q}'}^{(0)}]^2}{[\omega_{\mathbf{q}}^{(0)} \omega_{\mathbf{q}'}^{(0)}]^2} \times [1 - \cos(\mathbf{q} \cdot \delta) \cos(\mathbf{q}' \cdot \delta)]. \quad (21)$$

Now these parameters can be explicitly evaluated in terms of B and the density of states of the unperturbed phonons. One should be careful to separate the surface phonon contributions from those of terminated bulk phonons.

IV. COMPETITION BETWEEN THE EFFECT OF THE QUADRATIC COUPLINGS AND THAT OF THE LINEAR COUPLINGS

We go back to the general expression of ω_{ij} of Tonks and Dick which includes the effects of both the linear and the quadratic couplings,¹

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \left[\frac{\pi}{b_c + b_d} \right]^{1/2} \exp \left[- \frac{(a_c + c)^2}{4(b_c + b_d)} \right]. \quad (22)$$

c and b_d are mainly contributed by the linear couplings,

$$H_{DL}(1)_i = \sum_i \mathbf{A} \cdot \mathbf{x}_i |i\rangle \langle i|. \quad (23)$$

In the absence of the quadratic couplings, $b_d \approx 4k_B T E_a$, $c \approx 4E_a$. E_a is the conventional activation energy due to $H_{DL}(1)_i$.^{2-7,30} From the result of the preceding section, we find $a_c = k_B T \gamma$. Consequently, the condition when the quadratic couplings qualitatively change the activated tunneling behavior may be defined as

$$E_a \approx \frac{k_B T \gamma}{4}. \quad (24)$$

We examine Eq. (24) for tunneling in three-dimensional solids and on two-dimensional surfaces separately as the phonon density of states follows different power laws of the frequency.

For interstitial tunneling in solids, we consider acoustic phonons (three branches) with a three-dimensional density of states $\rho(\omega) = 9N\omega^2/(\omega_D)^3$. A straightforward evaluation of γ , including all three acoustic-phonon branches, leads to the following condition:

$$E_a \leq \frac{3}{4} k_B T \left[\frac{2B}{m\omega_D^2} \right]^2. \quad (25)$$

If the fractional change of the lattice phonon frequency is 50% so that $2B/m\omega_D^2 \sim 1$, the condition is $E_a \leq 2k_B T = 0.4$ kcal/mol for $T = 100$ K. For a 25% change in phonon frequencies, one requires $E_a \leq 2k_B T = 0.1$ kcal/mol for $T = 100$ K. These some-

what stringent conditions may be the reasons that quadratic couplings have not been found to be significant in muon and hydrogen tunneling in solids.¹²⁻¹⁸ This also explains why Tonks and Dick did not find the quadratic couplings to be qualitatively important in the tunneling of off-center interstitial Ag^+ in RbCl .¹

The situation changes when we consider an adatom tunneling along a surface of a solid. It interacts with surface acoustic phonons with a two-dimensional density of states $\rho_s(\omega) = 6N_s\omega/(\omega_D)^2$, in addition to the terminated bulk phonons. γ is enhanced by a factor of $\ln(\hbar\omega_D/\Delta)$ and Eq. (25) becomes

$$E_a \leq \frac{3}{4} k_B T \left[\frac{2B}{m\omega_D^2} \right]^2 \ln \left[\frac{\hbar\omega_D}{\Delta} \right]. \quad (26)$$

The enhancement factor $\ln(\hbar\omega_D/\Delta)$ comes from the divergence of the integrand when integrating Eq. (19) and the fact that Δ/\hbar acts as a low-frequency cutoff of the integration.⁴ The phonons with frequencies below Δ/\hbar affect the adatom tunneling only by contributing a random distribution of additional biases which we will discuss in Sec. V. Equation (26) turns out to be fairly easily satisfied for adsorbates on metal surfaces. For surface phonon branches whose frequencies are changed by adsorbed atoms by 20–25% [e.g., H on Ni(110), O, C, S, and N on Ni(100)], we find $2B/m\omega_D^2 \sim 0.5$.²⁴⁻²⁹ With $\hbar\omega_D \sim 35$ meV and $\Delta \sim 0.01$ meV, this leads to $E_a \leq 4.5k_B T = 0.9$ kcal/mol with $T \sim 100$ K. For a 50% change of surface phonon frequencies, we find $E_a \leq 3.6$ kcal/mol for $T = 100$ K. These conditions are not difficult to meet from the experimentally measured energy barriers in activated tunneling regions for muons and hydrogen in and on solids.^{12-18,22} It should be noted that activation energies caused by the linear couplings are not subject to the same enhancement since the divergence of the integrand in Eq. (19) near $\omega \sim 0$ does not occur for E_a .^{2-7,30} This analysis indicates that the quadratic couplings play much more important roles when a quantum tunneling system is coupled to phonons with dimensions less than 3.

When Eq. (26) is satisfied, ω_{ij} in Eq. (22) is reduced approximately to

$$\omega_{ij} = \left[\frac{\Delta}{\hbar} \right]^2 \left[\frac{\pi}{4E_a k_B T + \gamma k_B^2 T^2} \right]^{1/2} \times \exp \left[- \frac{\gamma}{4} - \frac{E_a}{k_B T} + \frac{E_a^2}{k_B^2 T^2} \right]. \quad (27)$$

We note that E_a in Eq. (20) is enhanced by the same factor $\ln(\hbar\omega_D/\Delta)$. From Eq. (20), we arrive at an estimate of $E_a \approx \hbar\omega_D/2$ for a 25% surface phonon frequency change or $2B/m\omega_D^2 \sim 0.5$. It is comparable to E_a . Consequently, the site-site tunneling following the overbarrier hopping can either be activated or nonactivated over a fairly large temperature range, or even increase with the decrease of temperature.

We review the experimental evidence of large surface phonon frequency changes. Using electron-energy-loss and helium energy-loss spectrometers, Ibach and co-

workers, Toennies and co-workers, and others observed that adsorbates on metals usually induce large changes in surface phonon frequencies without necessarily causing significant lattice relaxation.²⁴⁻²⁹ The relative frequency changes are in the range from 10% to 50%. They are attributed to the charge rearrangement in the surface region as a result of adsorbate-metal interactions at the bonding site.²⁵ In part, they can also be the result of the quadratic response of an adsorbate to the displacements of substrate atoms. This is unfortunately a lesser studied aspect of surface dynamics and yet can be significantly responsible for the phonon-assisted tunneling on solids.

Depending upon the symmetry and the polarization of a lattice-vibrational mode, the adatom-phonon interaction may vary either linearly or *nonlinearly* with the displacements characterizing the mode.³¹ A predominantly quadratic coupling prevails when an adsorbate interacts with substrate atoms through radial forces and the relative position vectors of the host atoms are perpendicular to the displacements of the mode. In this case, the ground-state energy of the adsorbate varies at the second power of the displacements.¹⁴ The coupling to the A_2 mode (S_1) of an atomic adsorbate at fourfold hollow sites on Ni(100) represents such an example.^{25,26} The same is true for a short-bridge bonded adatom on Ni(110) to the S_1 phonons.²⁸ On Ni(111) or W(111), terminally bonded as well as threefold bonded adsorbates may primarily interact with shear modes through quadratic couplings as well.³¹

V. EFFECT OF FINITE COVERAGE

We now explore the effect of finite densities or coverage in the case of tunneling on a surface. This is necessary since all adatom tunneling measurements are done at finite coverage and thus we must understand the possible effect of adatom-adatom interactions on the temperature dependence of tunneling rates. The experimentally measured rate is an ensemble average of all possible biases $E_i - E_j$ caused by hydrogen-hydrogen interactions [see Eq. (16)]. The transition rates for hydrogen on metals ($\sim 10^4 \text{ sec}^{-1}$) are much lower than the hydrogen well frequency or the inverse of the transit time (10^{13} sec^{-1}).^{8-10,20} Consequently, each tunneling is executed by an adatom, with the positions of other adatoms, within the range of the adatom-adatom interaction, remaining unchanged. Unlike noninteracting particles such as dilute muons or hydrogen atoms in solids, the interaction between adatoms at finite coverage leads to a distribution of biases whose occupations do not follow the Boltzmann-Maxwell distribution.³² The occupation of a site with a given energy E_i is only a function of the coverage and is essentially temperature independent. If we model the effect of finite coverages by a Gaussian distribution of biases, $\rho(E_i - E_j) = [1/\pi^{1/2}\sigma(\theta)] \exp[-(E_i - E_j)^2/\sigma(\theta)^2]$, when the width $\sigma(\theta) \gg k_B T$, the ensemble average of ω_{ij} [Eq. (17)] leads to^{11,32}

$$\omega_{ij,av} = \left(\frac{\Delta}{\hbar} \right)^2 \frac{2\sqrt{\pi}}{\sigma(\theta)} \exp \left\{ -\frac{\gamma}{4} - \frac{E_a}{k_B T} + \frac{E_a^2}{k_B^2 T^2} \right\}. \quad (28)$$

It means that when the biases spread over a range larger than the thermal energy $k_B T$, the fluctuation contribution to the tunneling rate is dominated by the spread of the biases. Most importantly, however, the main temperature dependence $\exp[-E_a/k_B T + E_a^2/(k_B T)^2]$ remains intact.

In cases of tunneling of hydrogen on metals, the direct dipole-dipole coupling strength, obtained from the workfunction change $\Delta\Phi(\theta)$, is usually of lesser significance. Take $\Delta\Phi(\theta)$ ($=0.1 \text{ eV}$) at $\theta=0.3$ on Ni(111).³³ The effective dipole moment of each hydrogen is roughly $p = \Delta\Phi/4\pi N_s \theta = 0.02ea_B \sim 4.8 \times 10^{-20} \text{ esu}$. This gives an averaged dipole-dipole interaction energy $\delta E \sim 6p^2(N_s \theta)^{3/2} \sim 10^{-4} \text{ eV}$. It is small compared to the thermal energy $k_B T \sim 10^{-2} \text{ eV}$. The indirect coupling can be deduced from the change of the thermal-desorption energy $E_{\text{des}}(\theta)$ and turns out to be fairly large. At $\theta \sim 0.3$ to 0.4 , $E_{\text{des}}(\theta)$ changes from $E_{\text{des}}(0)$ by more than 1 kcal/mol or 0.05 eV/atom for H on Ni(111).³³ One-half of this energy, $2.5 \times 10^{-2} \text{ eV}$, is associated with one hydrogen atom. It is large compared to $k_B T$. We should note at this juncture that the random biases caused by phonons of frequencies below Δ/\hbar are also small compared to $\sigma(\theta)$ and thus can be neglected.⁴

VI. RELEVANCE TO THE HYDROGEN TUNNELING ON METALS

The reports of nonactivated diffusion of hydrogen on tungsten surfaces by Gomer and co-workers have stimulated theoretical interests to understand possible mechanism responsible for temperature-independent tunneling.¹⁹ Since the experimental observations of the hydrogen tunneling diffusion are made in the temperature range from 30 to 120 K, it is difficult to abandon lattice phonons and conduction electrons as major factors which affect the hydrogen tunneling. For phonon-assisted processes, conventional linear adatom-phonon coupling models always lead to a well-known activated tunneling or a bandlike tunneling.²⁻⁷ Both exhibit large temperature dependence. Although possible, it seems unlikely that for hydrogen on all single-crystal surfaces of tungsten and nickel (five different surfaces), activation energies are much smaller than those found for hydrogen and muon in metals.^{8,9} Another possible explanation is to assume that the hydrogen tunneling on metals is predominantly assisted by the conduction electrons.^{11,15-18} In this case, the incoherent tunneling rate for an isolated adatom would vary as $T^{2\kappa-1}$. κ is the Kondo electron-adatom coupling constant. After taking into account the effect of finite coverage, the fluctuation part of the tunneling rate T^{-1} is replaced by $1/\sigma(\theta)$. This mechanism is appealing since with small enough κ (less than 0.1), the ensemble-averaged tunneling rate ($\sim T^{2\kappa}$) appears only weakly temperature dependent. The difficulty with the conduction-electron mechanism is that it becomes dominant over the phonon effect only at temperatures below $0.1T_D \approx 40 \text{ K}$ even with E_a as small as 0.2 kcal/mol and $\kappa \approx 0.1$. Thus it is yet to be justified for hydrogen on W and Ni.³²

The nonlinear adatom-phonon coupling model present-

ed in this paper offers another possible explanation. The important point is that the effect of quadratic couplings is substantially enhanced in the case of tunneling transport along the surface of a solid. If we use the comparable parameters as in Sec. IV, i.e., $E_a \approx 0.5$ kcal/mol or $E_a/k_B = 240$ K, $E_a'/k_B = 110$ K, we find that the tunneling rate given by Eq. (28) changes by no more than 25% from 70 to 160 K, which is the temperature range investigated by Lin and Gomer and Lee *et al.* for hydrogen on Ni surfaces.^{9,10} A similar result has also been obtained recently by Mattsson, Engberg, and Wahnström using a path-integral centroid calculation where they found that by including quadratic coupling terms, the tunneling rate changes from a classical Arrhenius form to a nonactivated behavior as given by Eq. (28).³⁴ We believe that the present work has clearly offered a physical picture of the result of Mattsson, Engberg, and Wahnström. We note that the tunneling rate will level off instead of taking off at low temperatures for two reasons: (i) the quadratic couplings becomes less important when Eq. (26) is no longer satisfied, and when that happens, (ii) the conduction-electron effect becomes more dominant. With the limited experimental evidence (quantum tunnel-

ing diffusions of hydrogen have only been studied experimentally on W and Ni) and surface dynamics information, it is difficult to state definitively whether or on which metal surface the quadratic coupling effect is the cause of the nonactivated tunneling. Unless the conduction-electron effect takes over at unusually high temperatures for reasons yet to be explored, the quadratic coupling effect is clearly an important mechanism which has to be considered in adatom tunneling along surfaces, particularly at temperatures as high as $\frac{1}{3}$ to $\frac{1}{4}$ of Debye temperatures. We hope that the present work will stimulate reliable *ab initio* calculation of both linear and quadratic adatom-phonon couplings for at least hydrogen on W and Ni. This will certainly help to further clarify this issue.

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