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# Sticking probability on metal surfaces: Contribution from electron-hole-pair excitations

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We use a recently proposed method to calculate the probability $P(E)$ that an incoming particle loses a given energy $E$ to electron-hole-pair excitations. For the case for which an adsorbate level crosses the Fermi energy, we present a simple analytical calculation of the probability $P(E)$ and the sticking probability. For the case for which no such crossing occurs, we give simple estimates and show results of more detailed numerical calculations. For not too heavy adsorbates with levels in the neighborhood of the Fermi energy, we find that the energy loss due to electron-hole-pair excitations should be important. We show that the relative width of $P(E)$ is of the order 1; i.e., the probability for an energy loss $E$ is not sharply peaked around the average energy loss as tacitly assumed in a friction-coefficient approach to sticking.

## I. INTRODUCTION

The theoretical discussion of the sticking probability, which is defined as the probability that an atom or a molecule approaching a surface will be adsorbed, has in recent years attracted a large interest as a relatively simple example of a dynamical surface process.[1-7] The incoming particle can be adsorbed only if its kinetic energy is dissipated into other degrees of freedom. Two energy-loss mechanisms have been assumed to be responsible: the coupling to the translational motion of the substrate ion cores, i.e., excitation of phonons,[1] and the energy loss to the low-energy particle-hole pairs, when the atom or molecule is adsorbed on a metal surface.[2-7] Because of the complexity of the problem various simplifying assumptions have been introduced in the calculation of the sticking probability.

The first detailed discussion of the electron-hole-pair mechanism has been presented by Suhl *et al.*[2] Their approach is based on the use of a Fokker-Planck equation for the adparticle motion. The dissipative effect of the substrate is described in an average way by a friction coefficient. The limitations of the underlying assumption of this approach will be discussed after the presentation of our results. Nørskov and Lundqvist[4] have emphasized the importance of the possibility that an initially unoccupied adsorbate level moves below the Fermi level and becomes occupied. Because of the finite velocity of the adsorbate there is a nonzero probability that this crossing occurs in a nonadiabatic fashion leading to an energy-loss mechanism. Avoiding a fully quantum-mechanical description they estimate the probability for this to happen. We will present a detailed description of the contribution of this effect to the sticking probability.

Recently, Brako and Newns[5] have presented a discussion of the spectrum of excitations created, when the adparticle is described as an external perturbation to the metal. Their calculation of the spectrum is limited to small perturbations by the use of the approximate method of Müller-Hartmann *et al.*[8] In this method the excitations in the Fermi (electron) system are treated as bosons, which makes the model soluble.

The weak-coupling assumption restricts their discussion of the spectrum to small changes in the adsorbate densities of states during the adsorption process. As we will show, this always is a poor assumption and, e.g., the effect stressed by Nørskov and Lundquist[4] cannot be described. Brako and Newns[5] also use a result by Hamann[9] to calculate the elastic-scattering probability in special cases for strong perturbations. From that they present a discussion of the sticking probability for zero temperature $T_g$ of the gas atoms. However, no results are given for the $T_g \neq 0$ sticking probability.

In an earlier paper[10] (in the following referred to as I), we have developed a strong-coupling boson description for perturbations that vary slowly in time. This provides us with a general expression for the probability $P(E)$ that the adsorbate loses an energy $E$ to the substrate. We shall use this method to obtain some general results for the electron-hole-pair contribution to the sticking probability. A discussion of the other methods mentioned above will then be given. In an appendix we present a rigorous proof of our boson approach in terms of Tomonaga bosons.[11,12]

## II. MODEL

We consider the electronic-loss mechanism for the case of nonactivated adsorption. We assume that the incoming atom or molecule has a velocity $v_i$ far from the surface. When the adsorbate approaches the surface it is first accelerated due to the binding forces and it obtains a velocity $v(t)$ much larger than $v_i$. Closer to the surface it is decelerated by repulsive forces and is bounced off the surface. Because of the large mass of the adsorbate we assume that its nuclear motions can be treated classically. Thus the adsorbate is assumed to describe a trajectory $z(t)$ defined by

$$M\frac{d^2z(t)}{dt^2}=-\frac{dE(z)}{dz}\,, \tag{1}$$

where $M$ is the mass of the adsorbate and $E(z)$ is the ground-state energy of the system with the adsorbate at a distance $z$ from the surface. The interaction between the adsorbate and the substrate is described in the spirit of the Anderson model[13] and we use the Hamiltonian

$$H_t=\sum_k \epsilon_k n_k+\epsilon_a[z(t)]n_a + \sum_k V_{ak}[z(t)]\psi_a^\dagger\psi_k+\text{H.c.}\,, \tag{2}$$

where the substrate levels are described by $\epsilon_k$, the adsorbate level by $\epsilon_a[z(t)]$, and $V_{ak}[z(t)]$ gives the interaction between the two systems. We take into account that the energy of the adsorbate level can depend on the separation to the substrate and that the coupling is reduced with increasing separation. For simplicity we neglect the lateral motion of the adsorbate assuming normal incidence. This is no severe restriction, since for slow incoming particles the adsorbate velocity is almost perpendicular to the surface after it has been accelerated by the surface attraction, even if the incidence is not normal.

From the Hamiltonian (2) we can calculate the energy $E(z)$ as a function of adsorbate position. Since (2) only describes the attractive forces, we add a term

$$E_R(z)=V_R e^{-\lambda_R z} \tag{3}$$

to $E(z)$ to include the repulsion due to the penetration of the adsorbate into the cores of the substrate atoms.

Because of the finite velocity of the adsorbate, there is a nonzero probability that some of the kinetic energy of the adsorbate will be transferred to electronic excitations in a nonadiabatic process. We therefore want to calculate

$$P(\epsilon)=\langle\phi(\infty)|\,\delta(\epsilon-(H_\infty-E_\infty^0))\,|\phi(\infty)\rangle\,, \tag{4}$$

where $|\phi(\infty)\rangle$ is the solution of the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}|\phi(t)\rangle=H_t|\phi(t)\rangle \tag{5}$$

for $t\to\infty$ and $E_\infty^0$ is the ground-state energy of the system for large adsorbate-substrate separations. The function $P(\epsilon)$ describes the probability that the system has an excitation with the energy $\epsilon$ when the adsorbate has left the surface. This probability is well defined, since the time-dependent Hamiltonian $H_t$ approaches a limiting value for $t\to\infty$. If the energy lost to electronic excitations is larger than the initial kinetic energy, the adsorbate has insufficient energy to leave the substrate and sticks to the surface.

This model is not fully consistent since the particle trajectory is calculated under the assumption that no energy is lost. In practice, this inconsistency should not be very important, since the strong nonadiabatic effects usually occur at a distance where the velocity $v$ is much larger than the initial velocity $v_i$. Therefore, if the adsorbate has lost an energy of the order $\frac{1}{2}Mv_i^2$, this leads to a small change of $v$, which as we shall see below determines the strength of the nonadiabatic effects. In the stochastic description of sticking by Iche and Nozières[7] the probabilities for an energy loss $E$ in the first round trip are important input parameters. Our distribution $P(E)$ provides a microscopic determination of these probabilities.[14]

In our approach we do not consider the nonadiabatic effects due to the forces described by the repulsive potential $V_R(z)$. This coupling involves the phonon-loss mechanism which has been discussed elsewhere.[1,15]

It is in principle straightforward to calculate $P(E)$ numerically by the methods we have introduced to calculate x-ray photoemission (XPS) spectra of adsorbates.[16] Because the adparticle usually presents a perturbation varying *slowly* on an electronic time scale, this is in practice a difficult numerical problem. We therefore use instead an analytical method presented in I, which is valid in that regime. We sketch here the intuitive derivation given in I, and present the rigorous proof of our bosonization in terms of coherent particle-hole pairs, i.e., Tomonaga bosons[11,12] in the Appendix. The Hamiltonian at $t+dt$ is written as

$$H_{t+dt}=H_t+\dot{H}_t dt+O(dt^2)\,. \tag{6}$$

We replace the change $\dot{H}_t$, which involves fermion operators, by boson operators

$$\dot{H}_t=\sum_\alpha(\dot{H}_t)_\alpha(b_{\alpha,t}+b_{\alpha,t}^\dagger)\,, \tag{7}$$

where $b_{\alpha,t}$ creates a particle-hole excitation of energy $\omega_\alpha=\epsilon_i-\epsilon_j$. The matrix elements are given in terms of the one-particle eigenstates of $H_t$,

$$(\dot{H}_t)_\alpha = \langle \epsilon_i^t | \dot{H}_t | \epsilon_j^t \rangle \tag{8}$$

with

$$H_t | \epsilon_i^t \rangle = \epsilon_i | \epsilon_i^t \rangle .$$

The boson operators $b_{\alpha,t}$ at time $t$ are given, except for a time-dependent shift ($c$ number), by their expression for $t \to -\infty$. It is consistent with our dropping of the diagonal terms of the perturbation to neglect this shift. Integrating (7) over time we obtain the Hamiltonian[10] ($b_\alpha = \lim_{t\to-\infty} b_{\alpha,t}$):

$$H_t = \sum_\alpha \omega_\alpha b_\alpha^\dagger b_\alpha + \sum_\alpha W_\alpha(t)(b_\alpha + b_\alpha^\dagger) \tag{9}$$

with

$$W_\alpha(t) = \int_{-\infty}^{t} (\dot{H}_{t'})_\alpha dt' . \tag{10}$$

The probability $P(\epsilon)$ is given by (see I)

$$P(\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\epsilon t} \exp\left( - \sum_\alpha \left| \frac{\lambda_\alpha}{\omega_\alpha} \right|^2 (1 - e^{-i\omega_\alpha t}) \right), \tag{11}$$

where

$$\lambda_\alpha = \int_{-\infty}^{\infty} (\dot{H}_t)_\alpha e^{i\omega_\alpha t} dt . \tag{12}$$

This probability has a delta function $\delta(\epsilon)$ with the strength

$$P_0 = \exp\left( - \sum_\alpha \left| \frac{\lambda_\alpha}{\omega_\alpha} \right|^2 \right), \tag{13}$$

which describes the probability for elastic scattering. The first moment is given by

$$\mu_1 \equiv \int_0^\infty \epsilon P(\epsilon) d\epsilon = \sum_\alpha | \lambda_\alpha |^2 / \omega_\alpha \tag{14}$$

and for the second moment we have

$$\mu_2 \equiv \int_0^\infty \epsilon^2 P(\epsilon) d\epsilon = \mu_1^2 + \sum_\alpha | \lambda_\alpha |^2 . \tag{15}$$

In I we have shown that for slowly varying perturbations this boson description gives exactly the same results for the moments $\mu_1$ and $\mu_2$ as the direct fermion calculation. For the special cases where a direct fermion calculation for the no-loss peak has been possible[9] our boson approach also gives the exact result.[10] For slowly varying perturbations only excitations involving states close to the Fermi energy are important. Then the matrix element $(\dot{H}_t)_\alpha$ can be evaluated at the Fermi energy and we find[10]

$$\begin{aligned} \lambda_\alpha \equiv \lambda(\omega_\alpha) &= \int_{-\infty}^{\infty} \langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle e^{i\omega_\alpha t} dt \\ &= \int_{-\infty}^{\infty} [\dot{\delta}_{\epsilon_F}(t)/\pi] e^{i\omega_\alpha t} dt , \end{aligned} \tag{16}$$

where in the second equality we have used the identity of $\langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle$ with the time derivative of the generalized instantaneous phase shifts at the Fermi level. The average energy transfer is given by[10]

$$\mu_1 = \pi \int_{-\infty}^{\infty} (\langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle)^2 dt . \tag{17}$$

When we assume a time dependence of the coupling terms in the Hamiltonian (2) of the form $V_{ak}(t) = V(t) A_k$ with the $A_k$ independent of time we obtain

$$\langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle = \{ \dot{\epsilon}_a(t) + 2[\epsilon_F - \epsilon_a(t)][\dot{V}(t)/V(t)] \} \rho_a^t(\epsilon_F) \tag{18}$$

with

$$V(t) = \left( \sum_k | V_{ak}(t) |^2 \right)^{1/2} . \tag{19}$$

The adsorbate density of states is given by (13)

$$\rho_a^t(\epsilon_F) = \frac{1}{\pi} \times \frac{\mathrm{Im}\Gamma(z(t), \epsilon_F)}{[\epsilon_F - \epsilon_a(t) - \mathrm{Re}\Gamma(z(t), \epsilon_F)]^2 + [\mathrm{Im}\Gamma(z(t), \epsilon_F)]^2} , \tag{20}$$

where

$$\Gamma(z(t), \epsilon_F) = \sum_k \frac{| V_{ak}(z(t)) |^2}{\epsilon_F - i0 - \epsilon_k} . \tag{21}$$

The coupling to the substrate enters the effective adsorbate level position $\tilde{\epsilon}_a(t)$ via the real part of $\Gamma$:

$$\tilde{\epsilon}_a(t) = \epsilon_a(z(t)) + \mathrm{Re}\Gamma(z(t), \epsilon_F) . \tag{22}$$

Using the abbreviation $\Gamma(t) = \mathrm{Im}\Gamma(z(t), \epsilon_F)$ we can rewrite (19) as

$$\langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle = \frac{1}{\pi} \frac{d}{dt} \arctan\left( \frac{\Gamma(t)}{\epsilon_F - \tilde{\epsilon}_a(t)} \right) \tag{23}$$

which shows explictly the general relation between the matrix element and the time derivative of the phase shift (16).

## III. GENERAL RESULTS

In this section we apply the model of Sec. II to various possibilities of the time behavior of the adsorbate density of states $\rho_a^t(\epsilon_F)$. In particular we distinguish between the cases when an adsorbate level crosses the Fermi level during its flight towards the surface and when such a crossing does not take place.

Let us first discuss the case when the crossing occurs. From Eqs. (18), and (20) or Eq. (23) one can see that the matrix element of $\dot{H}$ is large at the time $t=t_0$ when the adsorbate level crosses the Fermi energy, because the phase shift varies rapidly by an amount $\lesssim\pi$. If we neglect for a moment the variation of the resonance width $\Gamma(t_0)$ during the crossing we obtain for the crossing time $\Delta t = 2\Gamma(t_0)/\dot{\tilde{\epsilon}}_a(t_0)$. During the time $\Delta t$ the matrix element is of the order $\dot{\tilde{\epsilon}}_a(t_0)/\Gamma(t_0)$ and the contribution to the average energy transfer $\mu_1$ [Eq. (17)] is $\sim\Delta t[\dot{\tilde{\epsilon}}_a(t_0)/\Gamma(t_0)]^2\sim\dot{\tilde{\epsilon}}_a(t_0)/\Gamma(t_0)$. Thus the contribution is large if the crossing of the Fermi level takes place far outside the surface where $\Gamma(t_0)$ is small. This is the situation that has been emphasized by Nørskov and Lundqvist.[4] We now discuss this case in more detail. Around the level-crossing time $t_0$ the time derivative of the phase shift shows a pronounced maximum with a falloff time determined by $\Delta t$.
The function of time which describes this behavior around $t_0$ we denote by $f(t)$. The second time which is important is given by the round-trip time $T$ between the downward crossing and the upward crossing of the level at time $t_0+T$. As discussed above we use trajectories which are symmetrical in time with respect to the turning point. Therefore the upward crossing is described by the same functional form. At time $t_0+\frac{1}{2}T$ the matrix element of $\dot{H}_t$ has to vanish. All these requirements are fulfilled, if we choose

$$\langle\epsilon_F^t|\dot{H}_t|\epsilon_F^t\rangle = f(t) - f(t+T)\,. \tag{24}$$

For $\lambda(\omega)$ we obtain

$$\lambda(\omega) = f(\omega)(1-e^{i\omega T})\,. \tag{25}$$

The value of the Fourier transform $f(\omega)$ for $\omega=0$ is determined by the change in phase shift when the Fermi level is crossed:

$$|f(\omega=0)|\approx|[\delta_{\epsilon_F}(t_0+\tfrac{1}{2}T)-\delta_{\epsilon_F}(-\infty)]/\pi|\lesssim 1\,.$$

We can obtain an explicit form for $f(t)$ when we linearize the inverse of the argument of the arctan in (23) at $t=t_0$. With the crossing time $\Delta t$ this leads to

$$f(t) = -\frac{1}{\pi}\,\frac{\Delta t/2}{(t-t_0)^2+(\Delta t/2)^2}\,. \tag{26}$$

When the level crossing occurs far outside the surface the variation of $\Gamma(t)$ can be neglected during the crossing and we have $\Delta t = 2\Gamma(t_0)/\dot{\tilde{\epsilon}}_a(t_0)$ as mentioned earlier. This yields for $\lambda(\omega)$

$$|\lambda(\omega)|^2 = 2(1-\cos\omega T)e^{-\omega\Delta t}\,. \tag{27}$$

We note that $|\lambda(\omega)|^2\leq 2$ *independent* of $\Delta t$ and $T$. The approximation (16) of evaluating the matrix elements with states at the Fermi energy is correct only for adsorbate densities of states at the Fermi energy that vary *slowly* in time, i.e., the following discussion of the spectral function is restricted to $1/\Delta t \ll 2\Gamma(t_0)$. From Eq. (27) we find

$$\int_0^\infty \frac{d\omega}{\omega}|\lambda(\omega)|^2(1-e^{-i\omega t}) = -\ln\frac{T^2+\Delta t^2}{\Delta t^2} + \ln\frac{T+(\Delta t+it)^2}{(\Delta t+it)^2}\,. \tag{28}$$

From Eq. (11) we obtain the probability ($\sum_\alpha \to \int\omega\,d\omega$):

$$P(\epsilon) = \frac{\Delta t^2}{\Delta t^2+T^2}\,\delta(\epsilon) + \frac{\Delta t^2T^2}{\Delta t^2+T^2}\,\epsilon e^{-\epsilon\Delta t}\,. \tag{29}$$

For large $T$ the weight of the no-loss peak is

$$P_0 = (\Delta t/T)^2\,. \tag{30}$$

This result that the probability for elastic scattering is given by the square of the ratio of the crossing time and the time between the crossings is independent of our special form (26) for $f(t)$. This follows from (25) and the general properties of $f(t)$ discussed above. If the Fermi-level crossing takes place fairly far outside the surface, we have $P_0 \ll 1$ and

$$P(\epsilon) = \Delta t^2\epsilon e^{-\epsilon\Delta t}\,. \tag{31}$$

This result gives us the average energy transfer

$$\mu_1 = 2/\Delta t \tag{32}$$

and the relative width

$$\Delta \equiv [(\mu_2-\mu_1^2)/\mu_1^2]^{1/2} = 1/\sqrt{2}\,. \tag{33}$$

Thus the width of the distributionis of the same order as the average energy transfer. This result is independent of $\Delta t$ and follows from $|\lambda(\omega)|\leq 2$.

From Eq. (29) we can calculate the sticking coefficient. We assume that the incoming particles have a Boltzmann distribution with the temperature $T_g$, and calculate the probability that an atom with the initial kinetic energy $\epsilon$ loses an energy $\epsilon' > \epsilon$.

$$s_{T_g} = \int_0^\infty d\epsilon\,\frac{e^{-\epsilon/kT_g}}{kT_g}\int_\epsilon^\infty P(\epsilon')d\epsilon' = \frac{T^2}{\Delta t^2+T^2}\,\frac{1+2\Delta tkT_g}{(1+\Delta tkT_g)^2} \tag{34}$$

We have assumed that $\Delta t$ is independent of the initial energy $\epsilon$, since at the time when the energy loss takes place the particle has normally been accelerated so that its velocity is fairly independent of the initial velocity. For $\Delta t \ll T$ the low-temperature ($kT_g \ll 1/\Delta t$) sticking coefficient is very *close to one*. We should mention that due to our classical description of the adparticle our discussion does *not* include the possible low-temperature anomalies of the sticking coefficient resulting from a quantum-mechanical description of the adparticle.[17]

In many cases the adsorbate resonance does not cross the Fermi energy. To obtain an estimate of the function $\lambda(\omega)$ we use

$$|\lambda(\omega)| \leqslant \frac{1}{\pi} \int_{-\infty}^{\infty} \left| \frac{d}{dt} \arctan\left(\frac{\Gamma(t)}{\epsilon_F - \tilde{\epsilon}_a(t)}\right) \right| dt . \quad (35)$$

We assume that $|\Gamma(t)/[\epsilon_F - \tilde{\epsilon}_a(t)]|$ grows continuously before the adsorbate has reached its turning point and decreases continuously afterwards. This is, for instance, normally the case if $\epsilon_a(t)$ is constant. Then

$$|\lambda(\omega)| \leqslant \frac{2}{\pi} \max_t \left| \arctan\left(\frac{\Gamma(t)}{\epsilon_F - \tilde{\epsilon}_a(t)}\right) \right| \equiv \lambda_{\max} \leqslant 1 . \quad (36)$$

For small values of $\omega$, $\lambda(\omega)$ is linear in $\omega$, which can be seen by performing a partial integration of Eq. (16). The function $\lambda(\omega)$ is also small for $\omega \gg \omega_c = 1/\Delta\tau$, where $\Delta\tau$ is the time over which the integrand in Eq. (16) varies substantially. Then we expect $\lambda(\omega)$ to have roughly the shape

$$|\lambda(\omega)| = (\omega/\omega_c)\, e^{-\omega/\omega_c}\, \lambda_{\max} \quad (37)$$

which gives the average energy transfer

$$\mu_1 = \tfrac{1}{4} \lambda_{\max}^2 \omega_c \quad (38)$$

and the relative width

$$\Delta = \left(\frac{\mu_2 - \mu_1^2}{\mu_1^2}\right)^{1/2} = \frac{\sqrt{3/2}}{\lambda_{\max}} > \sqrt{3/2} . \quad (39)$$

As a crude estimate for $\omega_c$ we can use

$$\omega_c \sim \alpha v_{\max} , \quad (40)$$

where $v_{\max}$ is the maximum velocity of the adsorbate and $\alpha = [d\Gamma(z)/dz]/\Gamma(z)$ is the corresponding logarithmic derivative of $\Gamma(z)$.

We can now compare the contributions to $\mu_1$ from Eq. (32) and Eq. (38). For chemisorption we can obtain a $\lambda_{\max}$ in Eq. (37) which is of the order unity. The parameter $\alpha$ depends on how rapidly the substrate wave functions decay outside the surface and it may be of the order 1.0 a.u. Then we have

$$(\mu_1)_{\text{surface}} \sim \tfrac{1}{2} v_{\max} . \quad (41)$$

For the case when the adsorbate level crosses the Fermi energy we have

$$(\mu_1)_{\text{cross}} \sim \frac{v_0}{\Gamma(t_0)} \frac{d\tilde{\epsilon}_a}{dz} , \quad (42)$$

where $v_0$ is the velocity when the adsorbate resonance crosses the Fermi energy. Normally $v_0$ is much smaller than $v_{\max}$. On the other hand $d\tilde{\epsilon}_a/dz$ can be much larger than $\Gamma(t_0)$. Thus the relative magnitude of $(\mu_1)_{\text{surface}}$ and $(\mu_1)_{\text{cross}}$ depends on the system.

We now give some numerical examples of the two situations discussed. We assume that the coupling constants $V_{ak}(z)$ can be described by $(|\epsilon| \leqslant B)$:

$$\sum_k |V_{ak}(z)|^2 \delta(\epsilon - \epsilon_k) = \frac{2}{\pi B^2} [V(z)]^2 (B^2 - \epsilon^2)^{1/2} , \quad (43)$$

where $2B$ is the band width and

$$V(z) = V_0 \frac{(e^{-\alpha z} - e^{-\alpha z_{\max}})}{e^{-\alpha z} + 1} . \quad (44)$$

We have assumed that $V(z) = 0$ for $z$ larger than $z_{\max}$. The parameter $\alpha$ describes the decay of the wave functions outisde the surface and we assume $\alpha = \sqrt{\Phi}$, where $\Phi$ is the work function. Far inside the surface, i.e., for negative $z$, $V(z)$ in (44) saturates at the value $V_0$. In the following we use the parameters $2B = 4$ eV, $z_{\max} = 3.5\, a_0$, and $\Phi = 5$ eV. For the parameters in Eq. (3) we use $V_R = 1$ eV and $\lambda_R = 4\, a_0^{-1}$. For the initial adsorbate energy we use $\epsilon = \frac{1}{2} M v^2 = 0.025$ eV and $M = 2$ proton masses, which corresponds to a hydrogen molecule.

We first consider the case when the adsorbate resonance crosses the Fermi energy and assume

$$\epsilon_a(z) = 2(z - 2) , \quad (45)$$

in units of eV. In Fig. 1 we show results for the

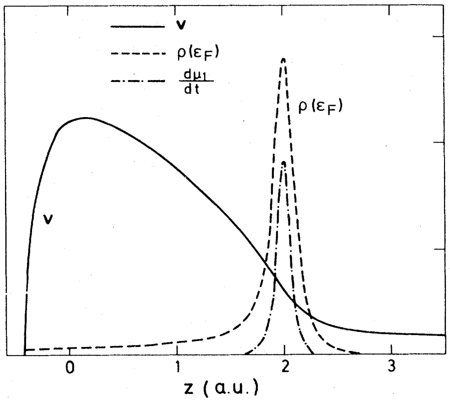

FIG. 1. The velocity $v$, the density of states at the Fermi energy $\rho_a(\epsilon_F)$, and the average energy transfer per time unit $d\mu_1/dt$ as a function of distance. The adsorbate level position varies linearly with distance and $V_0 = 3.5$ eV. The scale of the figure is arbitrary and the real maximum values of the curves are $0.23 a_0$ eV ($v$), 1.39 eV$^{-1}$ [$\rho_a(\epsilon_F)$], and 0.091 eV$^2$ ($d\mu_1/dt$).

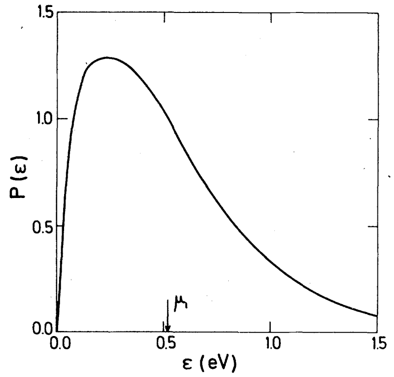

FIG. 2. The probability distribution $P(\epsilon)$ for the parameters in Fig. 1.

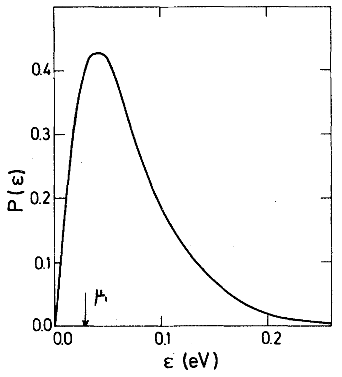

FIG. 4. The probability distribution $P(\epsilon)$ for the parameters in Fig. 3.

adsorbate velocity. At $z=2$ the kinetic energy is about 9 times higher than the initial energy $\epsilon$ provided that the particle has lost no energy. If the particle has lost the energy $\epsilon$ its velocity at this point is reduced by a factor $\sqrt{8/9}\approx 0.94$. Since we are interested in the probability that the energy loss is smaller than $\epsilon$, it is reasonable to calculate the trajectory $z(t)$ under the assumption of no energy loss. In Fig. 1 we also show how the density of states at the Fermi energy, $\rho_a(z,\epsilon_F)$, varies with distance and how the average energy transfer per time unit

$$\frac{d\mu_1}{dt}=\pi(\langle\epsilon_F^t|\dot{H}_t|\epsilon_F^t\rangle)^2 \qquad (46)$$

depends on the distance. The friction coefficient[2,3] is given by dividing $d\mu_1/dt$ by the velocity squared. Since $d\mu_1/dt$ is proportional to the square of $\rho_a(z_1\epsilon_F)$ it is very localized to the region where the resonance goes through the Fermi level. In Fig. 2 we show the probability $P(\epsilon)$. This distribution has an almost negligible delta function with the weight $P_0=0.018$. This agrees fairly well with the predictions of Eq. (30) which gives $P_0=0.014$. We find an average energy transfer $\mu_1=0.52$ eV compared with $\mu_1=0.53$ eV from Eq. (32) and a relative width $\Delta=0.74$ compared with $\Delta=0.71$ according to Eq. (33). These fairly small deviations are due to the more realistic $f(t)$.

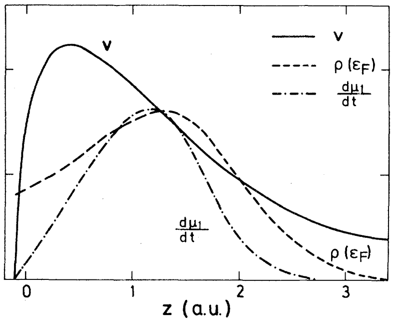

FIG. 3. The same quantities as in Fig. 1 but for a constant $\epsilon_a=2$ eV and with $V_0=6$ eV. The maximum values of the curves are $0.11a_0$ eV ($v$), $0.08\,\mathrm{eV}^{-1}$ [$\rho_a(\epsilon_F)$], and $0.000\,81\ \mathrm{eV}^2$ ($d\mu_1/dt$).

In Fig. 3 we show results for the case when the adsorbate level does not cross the Fermi energy but is assumed to remain constant. We notice that $\rho_a(z,\epsilon_F)$ becomes large when $\mathrm{Im}\Gamma(z,\epsilon_F)\sim|\epsilon_F-\tilde{\epsilon}_a|$ which happens for $z\sim 1.3$. Closer to the surface $\mathrm{Im}\Gamma$ becomes so large that $\rho_a(z,\epsilon_F)$ is reduced again. The quantity $d\mu_1/dt$ behaves in a similar way although the large values of $v(z)$ for small $z$ shifts the maximum towards smaller $z$. The probability $P(\epsilon)$ is shown in Fig. 4. In this case there is a strong $\delta$ function at $\epsilon=0$ with weight $P_0=0.61$. The average energy transfer is $\mu_1=0.028$ eV and the relative width is 1.64. These results are in good agreement with the qualitative arguments presented before. In Table I we show some more results for other values of $V_0$ and $\epsilon_a$. When the coupling is increased, i.e., $V_0$ is increased or $|\epsilon_F-\epsilon_a|$ is reduced, the relative width is reduced in agreement with Eqs. (36) and (39).

In our discussion we have completely neglected the spin of the electrons. For the case when a

TABLE I. Results obtained using a $z$-independent $\epsilon_a$. The binding energy of the adsorbate to the surface is given by $E_B$.

| $\epsilon_a$ (eV) | $V_0$ (eV) | $E_B$ (eV) | $\Delta$ | $P_0$ | $\mu_1$ (eV) |
|---|---|---|---|---|---|
| 5 | 4 | 0.10 | 5.45 | 0.95 | 0.0023 |
| 5 | 6 | 0.34 | 2.54 | 0.80 | 0.0132 |
| 5 | 8 | 0.77 | 1.84 | 0.66 | 0.026 |
| 2 | 6 | 0.81 | 1.64 | 0.61 | 0.028 |
| 2 | 8 | 1.5 | 1.42 | 0.52 | 0.037 |
| 2 | 10 | 2.2 | 1.33 | 0.48 | 0.044 |

level crossing occurs far away from the surface, neglecting the spin is in the spirit of the *unrestricted* Hartree-Fock picture. In the other case we have discussed, the energy transfer occurs close to the metal surface, where the *restricted* Hartree-Fock picture is appropriate. Then the distribution $P(\epsilon)$ including spin is simply obtained by the self-convolution of our result for $P(\epsilon)$.

## IV. CONCLUDING REMARKS

We have calculated the sticking probability in a model that includes the electron-hole-pair loss mechanism. We have considered the cases when an adsorbate resonance crosses the Fermi energy during the adsorption process and when such a crossing does not take place. In the former case there can be a large contribution to the average energy transfer far from the surface, while in the latter case the main contribution arises close to the surface. For not-too-heavy atoms, reasonable parameters give energy losses that are important on the scale of thermal energies.

From the results obtained we can discuss the validity of the underlying assumptions in the use of the Fokker-Planck equation for the adparticle for calculating the sticking probability. As in our boson model, the adatom is treated classically and it is assumed to exert a slow perturbation on the substrate electrons. In addiiton it is assumed that the dissipation of energy to the substrate can be described in an average way by a friction coefficient. This assumption is justified if the probability $P(E)$ for losing the energy $E$ is strongly peaked around the average energy transfer, i.e., if the relative width $\Delta$ of $P(E)$ is small. For the case when an adsorbate level crosses the Fermi energy we found $\Delta \approx 1/\sqrt{2}$. If no such crossing takes place the width decreases with increasing coupling, but has a lower bound $\Delta \gtrsim 1$. These results were obtained under fairly general conditions and the proof of Eq. (35) shows that $\Delta \ll 1$ is impossible, when we consider a single round trip of the incoming particle. This result is very different from the result for $P(E)$ due to the coupling to phonons, which is also given by an expression like (11), but with the $\lambda_\alpha$ having a different meaning.[15] In the phonon case the coupling constant is not bounded and in the classical limit (many phonons) one obtains a $P(E)$ sharply peaked around the average energy loss.[15] It is the occurrence of the phase shifts in our exact calculation of $P(E)$ which makes $\Delta \ll 1$ impossible for the slowly varying perturbation presented by the incoming particle *even* if the perturbation is *strong* and cannot be described in the weak-coupling approximation.[5] We therefore prove the conjecture made by Brako and Newns[5] from their weak-coupling calculation for $P(E)$.

The probability for elastic scattering can be large for the case when the adsorbate level does not cross the Fermi energy. However, for the situation considered by Nørskov and Lundqvist[4] when the level crosses the Fermi energy we find small values for $P_0$ and their neglect of elastic scattering should be justified.

## APPENDIX

In this appendix we present a rigorous derivation of our result Eqs. (11) and (16) for the excitation probability $P(E)$ for slowly varying perturbations. This exact solution is obtained by the use of coherent particle-hole excitations, which rigorously obey boson commutation relations, when one works in a subspace of states with no holes deep in the Fermi sea and no electrons high above the Fermilevel.[11,12] This is the relevant subspace for the problem we are considering: A perturbation varying on a time scale $T$ only produces excitations with respect to the *instantaneous* Hamiltonian in a range $\pm 1/T$ around the Fermi level. In contrast to Tomonaga's original analysis we can therefore choose the subspace as small as we want, simply by increasing $T$. This allows us to obtain the exact solution for $P(\epsilon)$ in terms of the instantaneous phase shifts at the Fermi level, i.e., we are not restricted to small perturbations like Schotte and Schotte[11] in their discussion of x-ray spectra.

As in I we consider a system of spinless $s$-type electrons, i.e., the eigenstates $|\epsilon^t\rangle$ of the Hamiltonian $H_t$ are labeled by the energy *only*. If we introduce creation and annihilation operators $\psi^\dagger_{\epsilon,t}$ $(\psi_{\epsilon,t})$ of these eigenstates we can write the Hamiltonian as

$$H_t = \int_0^B \epsilon \psi^\dagger_{\epsilon,t} \psi_{\epsilon,t} d\epsilon , \tag{A1}$$

where the energy zero is taken at the bottom of the band, $B$ is the band width, and the $\psi_{\epsilon,t}, \psi^\dagger_{\epsilon',t}$ obey fermion anticommutation relations

$$\{\psi_{\epsilon,t}, \psi^\dagger_{\epsilon',t}\} = \delta(\epsilon - \epsilon') , \tag{A2}$$

etc. To make closer contact to the formulation of Tomonaga,[11] we first work with a fictitious finite system and take the limit of infinite volume in the end of the calculation. We discretize the energy variable

$$\epsilon_n = nB/N = n\Delta\epsilon \quad (n = 0, 1 \ldots , N) \tag{A3}$$

and later take the limit $N \to \infty$. The Hamiltonian and the anticommutation relations are then replaced by

$$H_t = \Delta\epsilon \sum_{n=0}^{N} n \psi^\dagger_{n,t} \psi_{n,t} \tag{A4}$$

and

$$\{\psi_{n,t}, \psi^\dagger_{n',t}\} = \delta_{n,n'} , \tag{A5}$$

etc. Now following Tomonaga[11] and Schotte and Schotte[12] we introduce coherent particle-hole excitation operators $(n > 0)$;

$$b_{n,t} = \frac{1}{\sqrt{n}} \sum_{m=0}^{N-n} \psi^\dagger_{m,t} \psi_{m+n,t} . \tag{A6}$$

Using the fermion anticommutation relations (A5) it is straightforward to derive the commutation relations for the $b_{n,t}$ $(n, n' > 0)$,

$$[b_{n,t}, b_{n',t}] = [b^\dagger_{n,t}, b^\dagger_{n',t}] = 0 \tag{A7}$$

and

$$[b_{n,t}, b^\dagger_{n',t}] = \delta_{n,n'} . \tag{A8}$$

The commutation relations (A8) hold exactly if one restricts the physical relevant states to the subspace $S$ of states with no hole below $\epsilon_F - \epsilon_0$ and no electron above $\epsilon_F + \epsilon_0$. A careful discussion of how large $\epsilon_0$ can be chosen is given by Tomonaga[11]. As mentioned above, in our discussion of slowly varying perturbations we do not have to worry about the largest possible value of $\epsilon_0$, because we can choose the relevant subspace as small as we want by increasing $T$.

The commutator of $b_{n,t}$ with $H_t$ can easily be calculated:

$$[b_{n,t}, H_t] = \Delta\epsilon\, n b_{n,t} . \tag{A9}$$

This indicates that except for a constant, $H_t$ can be expressed in terms of the boson operators in the form

$$H_t = \sum_{n=1}^{N} \Delta\epsilon\, n b^\dagger_{n,t} b_{n,t} + E^t_0 . \tag{A10}$$

An explicit proof of this relationship has been given by Tomonaga.[11] Like in the Luttinger model[18] with our definition of the boson operators (A6) we even do not have to introduce the linearization used in Tomonaga's proof. The constant in (A10) is given by the ground-state energy $E^t_0$. In the limit $N \to \infty$ we can replace (A6), (A8), and (A10) by

$$b_{\epsilon,t} = \frac{1}{\sqrt{\epsilon}} \int_0^{B-\epsilon} \psi^\dagger_{\epsilon',t} \psi_{\epsilon'+\epsilon,t}\, d\epsilon' , \tag{A11}$$

$$[b_{\epsilon,t}, b^\dagger_{\epsilon',t}] = \delta(\epsilon - \epsilon') , \tag{A12}$$

and

$$H_t = \int_0^B \epsilon b^\dagger_{\epsilon,t} b_{\epsilon,t}\, d\epsilon + E^t_0 . \tag{A13}$$

This *exact* representation of $H_t$ (in the subspace $S$) is the starting point for our derivation of Eqs. (11) and (16).

As in I, we now express the Hamiltonian at time $t+dt$ in terms of the boson operators $b_{n,t}$ (or $b_{\epsilon,t}$):

$$H_{t+dt} = H_t + \dot{H}_t\, dt + O(dt)^2 . \tag{A14}$$

In terms of the Fermion operator $\dot{H}_t$ can be written as

$$\dot{H}_t = \sum_{m,m'=0}^{N} (\dot{H}_t)_{mm'} \psi^\dagger_{m,t} \psi_{m',t} \tag{A15}$$

with

$$(\dot{H}_t)_{m,m'} = \langle \epsilon^t_m | \dot{H}_t | \epsilon^t_{m'} \rangle .$$

Let us first discuss the diagonal part $m = m'$. As we can restrict the subspace in the limit $T \to \infty$ to excitations arbitrarily close to $\epsilon_F$ we can replace the matrix element in this neighborhood of the Fermi energy by its value $\epsilon_F$. Then in this region $(\dot{H}_t)^d$ is a constant times the particle-number operator in that region, which is a constant of motion. We therefore have

$$\dot{H}_t = \sum_{m \neq m'} (\dot{H}_t)_{mm'} \psi^\dagger_{m,t} \psi_{m',t} + \langle E^t_0 | \dot{H}_t | E^t_0 \rangle . \tag{A16}$$

In that *immediate neighborhood of the Fermi energy* the off-diagonal part can be *exactly* expressed in terms of the $b_{n,t}$, because we again can replace the matrix element by its value at the Fermi energy

$$\dot{H}_t = \langle \epsilon^t_F | \dot{H}_t | \epsilon^t_F \rangle \sum_{n>0} \sqrt{n}\, (b_{n,t} + b^\dagger_{n,t}) + \dot{E}^t_0 , \tag{A17}$$

where we also have used the Hellmann-Feynman theorem. In the limit $N \to \infty$ we obtain

$$\begin{aligned} H_{t+dt} = & \int_0^B \epsilon b^\dagger_{\epsilon,t} b_{\epsilon,t}\, d\epsilon \\ & + \langle \epsilon^t_F | \dot{H}_t | \epsilon^t_F \rangle \int_0^B \sqrt{\epsilon}\, (b_{\epsilon,t} + b^\dagger_{\epsilon,t}) d\epsilon\, dt \\ & + E_0^{t+dt} + O(dt^2) \end{aligned} \tag{A18}$$

On the other hand, we can express $H_{t+dt}$ directly in terms of boson operators $b_{\epsilon,t+dt}$ (A13):

$$H_{t+dt} = \int_0^B \epsilon b^\dagger_{\epsilon,t+dt} b_{\epsilon,t+dt}\, d\epsilon + E_0^{t+dt} . \tag{A19}$$

A comparison with (A18) leads to the relation between $b_{\epsilon,t}$ and $b_{\epsilon,t+dt}$:

$$b_{\epsilon,t+dt} = b_{\epsilon,t} + \langle \epsilon^t_F | \dot{H}_t | \epsilon^t_F \rangle / \sqrt{\epsilon}\, dt . \tag{A20}$$

Integrating this differential equation we obtain

$$b_{\epsilon,t} = b_\epsilon + \int_{-\infty}^{t} \frac{\langle \epsilon^{t'}_F | \dot{H}_{t'} | \epsilon^{t'}_F \rangle dt'}{\sqrt{\epsilon}} , \tag{A21}$$

where $b_\epsilon$ is the boson operator before the perturbation has been switched on. Now we can use the $N \to \infty$ version of (A17) to express $H_t$ in terms of the $b_\epsilon$:

$$H_t - E_0^t = \int_0^B \epsilon b_\epsilon^\dagger b_\epsilon d\epsilon + [\delta_{\epsilon_F}(t)/\pi] \int_0^B \sqrt{\epsilon}\,(b_\epsilon + b_\epsilon^\dagger) d\epsilon + [\delta_{\epsilon_F}(t)/\pi]^2 \int_0^B d\epsilon \,. \tag{A22}$$

Here we have introduced the instantaneous generalized phase shifts at the Fermi level

$$\delta_{\epsilon_F}(t) = \mathrm{Im}\ln\{\det[1-(\epsilon_F - H_{-\infty} - i0)^{-1}(H_t - H_{-\infty})]\} \tag{A23}$$

and have used the relation (see I)

$$\dot{\delta}_{\epsilon_F}(t) = \pi \langle \epsilon_F^t | \dot{H}_t | \epsilon_F^t \rangle \,. \tag{A24}$$

In (A22) we have expressed the Hamiltonian $H_t$ *rigorously* in terms of boson operators in the subspace of states relevant for slowly varying perturbations. Calculating the distribution $P(E)$ is then a straightforward exercise in boson algebra and leads to Eqs. (11) and (16) where in (11) $\sum_\alpha$ is replaced by $\int \omega\, d\omega$. This proof confirms a long-standing conjecture concerning how the results of the conventional boson description have to be generalized in terms of phase shifts.[8] With our approach one can avoid the more complicated mathematics, which was necessary at this point to obtain partial information on $P(E)$ exactly, as in the weight of the no-loss peak for separable forms of the perturbation.[9]

Our proof also provides the exact solution to the problem of the threshold singularity in x-ray photoemission (XPS). As the threshold behavior is usually calculated by suddenly switching on the perturbation,[19] it might look surprising that we obtain the exact result for the exponent of the power-law singularity working in the opposite limit of a slowly switched-on perturbation. But as the threshold singularity reflects the long-time behavior of the response, the spectrum at threshold can be obtained by our approach as discussed in I, and is just a manifestation of the Anderson orthogonality catastrophe.[20]

In Sec. II we have described a "derivation" for $P(E)$ in terms of the *individual* particle-hole pairs, and the result coincides with the one of the rigorous derivation of this appendix for slowly varying perturbations. As the result (11) *without* the further approximation (16) is also valid for *small* perturbations which may vary rapidly in time,[8] the expression (11) for $P(E)$ has a wider range of applicability than the result following from (A22).

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