Theory of electron-hole pair excitations in unimolecular processes at metal surfaces.
I. X-ray edge effects

J. W. Gadzuk

National Bureau of Standards, Washington, D. C. 20234

H. Metiu*

Department of Chemistry, University of California, Santa Barbara, California 93106
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A theory of the dynamics of molecular processes at solid surfaces must necessarily deal with those aspects of the solid which provide dissipative or irreversible reaction channels, thus giving the particular process a direction in time. While the heat-bath aspects of the solid are often considered from the phonon point of view, there is increasing speculation that the substrate electron-hole pair excitations may be a significant rate-determining factor, at least for metals. This belief is supported by various conclusions which have emerged from theoretical studies of time-dependent perturbations acting on extended Fermi systems, as physically realized in core-level spectroscopies of solids. We present here one phase of a study of surface reaction dynamics, focusing on the irreversible coupling of nuclear motion of an incident beam of atoms or molecules with the substrate electrons. For the cases in which the incident particle undergoes a substrate-induced diabatic transition in its internal electronic state, a sudden localized perturbation on the electrons is turned on. In analogy with the x-ray edge problem, an infrared divergent spectrum of electron-hole pairs is created which could give rise to irreversibility. Specific examples are considered and the ramifications on such observable quantities as sticking coefficients are detailed.

I. INTRODUCTION

The fate of a thermal atomic or molecular beam incident upon a solid surface depends among other things upon the probability of the incident beam transferring its kinetic energy into internal excitations of the substrate. If the first-passage energy transfer is sufficient, the particle may become trapped, whereupon slower processes such as dissociation, complicated chemical reactions, thermal equilibration with the substrate, or subsequent desorption can occur. For a metallic substrate, the relevant excitations (or heat bath) at thermal energies are phonons and electron-hole pairs. Due to the zero-gap pair continuum, a high density of low-lying excited electronic states exists, in qualitative distinction with finite molecular systems. Consequently, the role of electronic excitation in determining the rate of certain dynamic processes at metallic surfaces cannot be ascertained by using traditional gas-phase reaction theories.[1] This calls for some new theoretical approaches.

As it stands now, phonon or lattice theories, if relevant, are most suited for describing the inelastic interaction of a *neutral* rare-gas atom with a substrate via some prescribed sum of pairwise interactions and dissipative stochastic forces.[2] The incident particle has no internal structure, and its properties ideally enter the theory only through their mass value M and pairwise interaction (6–12, or Morse potential, for example).

With regards to electronic excitation, consider-able theoretical work has been carried out for the situation in which a moving ion of fixed charge interacts, via a fluctuating force, with the substrate electrons.[3-5] Dissipative effects due to electronic excitation are included through a friction term in the equation of motion for the incident-particle trajectory. Attempts are under-way[6-8] to formulate models capable of describing the dissipative interaction of an incident particle with a metallic surface in which charge rearrangement (and thus possible chemical reactions) occurs along the trajectory. The purpose of this paper is to present some of the key ideas related to electronic excitation used in one of these studies,[7] demonstrate the relationship which exists with the other works,[6,8] and point out some potential pitfalls to be avoided when mapping treatments of previous time-dependent Fermi-system problems[9-12] onto that of a moving, spatially varying charge distribution outside a metal surface.

II. FOUNDATIONS

The underpinnings of the "pair theories" derive from three related theoretical works:

(i) The Anderson orthogonality theorem which states that the many-body ground state of an infinitely extended Fermi system is orthogonal to the ground state of the same system, within which a localized, stationary scattering potential exists[9];

(ii) The x-ray edge problem which says that due to the long-time transient response of the Fermi system to a localized time-dependent (one-elec-

tron) potential of the core hole, the x-ray absorp-
tion edge displays an integrable infrared diver-
gence of the form $\sim(\omega - \omega_0)^{\alpha-1}$, where ω_0 is the
one-body threshold energy and α is related to the
core-hole scattering potential.[9,10] Such a diver-
gence also shows up as a skewing toward higher
binding energy of x-ray photoemission line shapes,
where the divergence can be regarded as a con-
tinuum of shakeup satellites[13];

(iii) The theory of localized dynamic perturba-
tions in metals, within a boson model, by Müller-
Hartmann, Ramakrishnan, and Toulouse (M-HRT)
in which they display the effects (or lack thereof)
on the edge of various time dependences for the
localized potential. Significantly for this study,
they demonstrate that the probability is *always*
less than unity, that an infinite Fermi system,
subjected to a localized potential which is turned
on and then is turned off, will remain in its ground
system. Excited states are necessarily created.

III. THEORY

A. Abstract model

In this first generation of theories of surface
reaction dynamics, exploratory studies are being
carried out on some variations of the following
theme. An incident particle, at position $\vec{R}$, couples
the jth boson (pair) substrate excitation through
some (to be specified later) interaction $V_j(\vec{R})$. By
placing the particle on a prescribed (and hopefully
meaningful) trajectory $\vec{R}=\vec{R}(t)$, a time dependence
is introduced into the problem through

$$V_j(\vec{R}) = V_j(\vec{R}(t)). \tag{1}$$

Within the boson model, the substrate Hamiltonian
is

$$H = \sum_j \epsilon_j b_j^\dagger b_j + \sum_j [V_j(\vec{R}(t))b_j^\dagger + V_j^*(\vec{R}(t))b_j], \tag{2}$$

where ϵ_j is the pair energy and b_j, $b_j^\dagger$ the boson
operators. At this stage of development, *explicit*
considerations of recoil effects on the incident
particle have not been included. Thus meaningful
trajectories must at least be self-consistent with
any dissipative interactions to the electron gas,
or energy conservation will be violated and other
nonphysical conclusions could follow. To the ex-
tent that Eq. (2) is an adequate first approximation
for our type of problem, then the general mathe-
matical consequences follow immediately from
M-HRT, since Eq. (2) is the Hamiltonian for the
boson excitation spectrum of the many-body Fermi
system driven by a reasonably arbitrary, but pre-
scribed, perturbation supplied by the moving par-
ticle. Our major job consists of picking trajec-
tories or time dependences which simulate some

situations of physical interest.

The simplest trajectory to imagine is that for a
particle elastically scattering from a surface. In
this case the interaction entering Eq. (2) would
be symmetric about $t=0$, defined as the point of
closest approach or the classical turning point,
as shown by the dotted line in Fig. 1. Right away
one must be cautious about the applicability of this
elastic, symmetric trajectory in light of the al-
ready-mentioned theories of Anderson,[9] ND[10]
(Nozieres and DeDominicis), and M-HRT,[11] which
suggest less than unit probability for the purely
elastic trajectory (the no-loss line).

A new richness enters if the particle possesses
some internal degrees of freedom in a narrowly
bounded region in space, due to some other in-
teractions with the substrate. Converting this
proposition into a time description, a form for
$V_j(\vec{R}(t))$ containing the effects of the changes in
the internal degrees of freedom is also shown in
Fig. 1. The discontinuous or steeply changing
region around $t=\pm\tau_c$ corresponds to the change in
internal structure which could lead to a drastic
change in the pair coupling. For this case there
are now at least three different time scales enter-
ing the problem, each with different physical sig-
nificance. Firstly, the width η_1 which sets the
time scale over which the internal transition takes
place on the inward part of the trajectory; sec-
ondly, the width $2\tau_c$ which is a measure of how long
the particle remains in the new internal state on
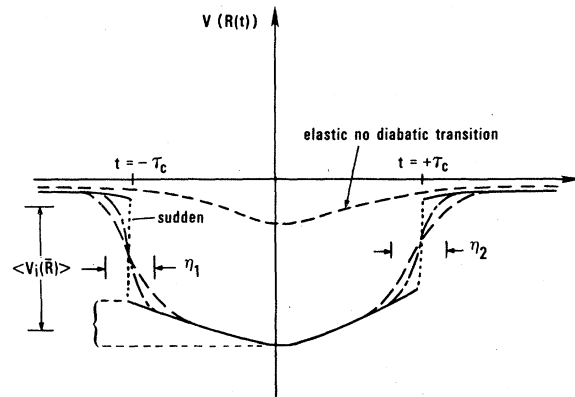the remaining inward and part of the outward tra-

FIG. 1. Time-dependent interaction between moving
incident particle, on a prescribed trajectory, with sub-
strate electron-hole pairs. The gentle and weak poten-
tial, sketched as the dashed curve, corresponds to a
basically elastic process in which no diabatic transitions
occur. The full curves connected by various broken
curves in the vicinity of $t=\pm\tau_c$ correspond to trajector-
ies in which a diabatic transition occurs. The dotted
connection represents a sudden transition. The quantity
$\langle V_i(R)\rangle$ represents some average change in the interac-
tion as a result of the diabatic transition.

jectory; thirdly, the width η_2, which may be different from η_1, the switching rate for restoring the particle to its final internal state.

B. Physical connections

Specific realizations of the above condition have been considered elsewhere by the present authors in quite some detail.[7] For present purposes it is sufficient to note that nuclear motion (or the trajectory) of the multistate incident particle depends upon the particle-surface potential-energy curve, which in turn depends upon the internal state of the incident particle. These are shown schematically as the diabatic potentials[1,7,14] in Fig. 2(a) for a two-state system, initially in state 1 with kinetic energy K_i in region I. At the curve crossing point $z = R_c$, (region II) the surface interaction (not including electron-excitation effects) can induce a diabatic electronic transition[14,15] to state 2 (Franck-Condon factors permitting[7,15]), upon which nuclear motion continues on curve 2 into region III, where (classically) the particle is reflected at $z = R_T$ back toward region II. If throughout this process sufficient energy is irreversibly lost to the substrate, so that the particle energy falls well below the crossing-point energy, then it cannot undergo another diabatic transition in II, taking it to I, and the particle is trapped. Even if the irreversible energy loss is not large enough to bring the system energy below the crossing-point energy, it will still affect the rate of transition back to I, since one expects that at lower energies the Franck-Condon overlap is smaller.

Depending upon the strength of the substrate-induced mixing $V_{12}(R = R_c)$ relative to the "local" kinetic energy $K_i(R_c)$, the diabatic transition may or may not occur. If the transition does occur, the probability is strongly peaked in region II around $z = R_c$. The degree of "suddeness" of the transition thus depends upon the time spent in region II, which in turn depends upon the width of II, as determined by $V_{12}(R)$ and the slopes of $V_1(R_c)$ and $V_2(R_c)$.[1,14] In terms of time scales, one can see that the transit times across II and III are equivalent to η_1 and τ_c discussed previously and shown in Fig. 1. The finite width of region II implies a softer than sudden diabatic transition. We will generally assume a sudden transition, obtain the consequences of this transition, and then soften things at the end. This procedure has algebraic advantages as well as physical insight advantages since singular, but physically correct, behavior is easily kept track of. For instance, any x-ray edge-like phenomenon can readily be retained, whereas perturbative insertions of edge effects into an effective one-electron theory at the end are much more difficult (if not impossible).

Physical examples that are modeled by Fig. 2 might include

(i) Surface ionization of an alkali atom where V_1 and V_2 are the atom and positive-ion curves, respectively;

(ii) Surface-electron attachment to a hydrogen or other electronegative atom;

(iii) Positive-ion neutralization by electron transfer from metal;
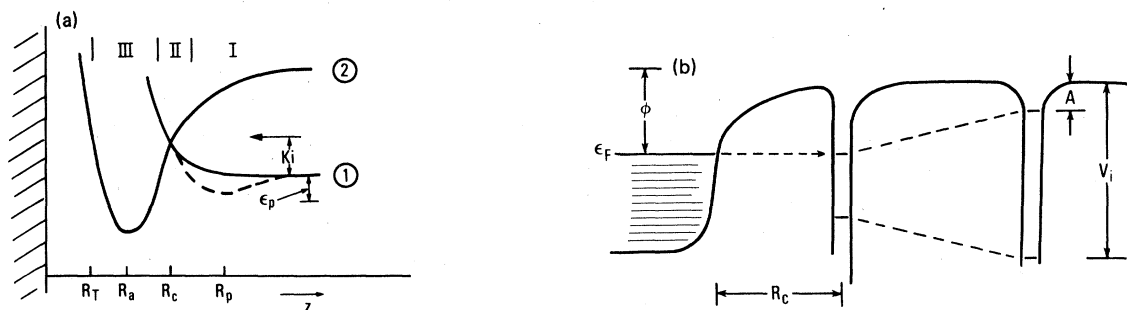
(iv) Quenching of metastables with electron

FIG. 2. (a) Diabatic potential-energy curves as a function of z, the normal distance from the surface, of an incident particle initially in some electronic state 1 and with kinetic energy K_i. The full curve (1) corresponds to an electronic state giving rise to a strictly repulsive surface interaction, whereas the dashed curve represents a state which allows for a weakly physisorbed precursor state with desorption energy ϵ_p and equilibrium separation R_p. Curve 2 corresponds to an electronic state which strongly adsorbs at an equilibrium separation R_a. Within region II, a diabatic electronic transition from curve 1 to curve 2 can occur, with the probability peaked at $z = R_c$, the curve crossing point. Nuclear motion in region III proceeds on curve 2 up to the classical turning point R_T. (b) Specific realization of situation a, as detailed by Nørskov et al., in terms of atomic energy level shifts. The lowering of the affinity level A allows a Fermi-level electron from the substrate to tunnel into the atom, thus creating a negative ion. This possibility is suddenly turned on at a separation R_c where the shifted affinity level coincides with the Fermi level, and this corresponds exactly to R_c in (a), if curve 1 is regarded as an atomic curve and curve 2 as a negative-ion curve.

emission from metal;

(v) Dissociative chemisorption of a diatomic molecule, with V_1 the molecule-surface curve allowing the possibility of a physisorbed precursor and V_2 the atom-surface curve. (This one-dimensional representation is misleading as it cannot represent the relative motion of the two nuclei required for dissociation.)

The feature that all three mechanisms have in common (as do most significant curve-crossing problems) is that in the localized spatial region around R_c (or temporarily around $-\tau_c \pm \eta^{-1}$ in Fig. 1), a drastic and sudden charge rearrangement occurs on the incident particle, and it is the time-dependent change of potential associated with this charge rearrangement that is responsible for the electron-hole pair excitations, through $V_j(\vec{R}(t))$ in Eq. (2). For ionization or attachment, the monopole changes by one unit, whereas for dissociation, dipole or higher multipoles are involved, obviously with weaker but still nontrivial coupling to electron-hole pairs.

We note in passing that Nørskov and coworkers[6] (NL) have put forth a model for the special case of electron attachment on an atom characterized by an electron valence and affinity level which vary with distance from the substrate, as shown in Fig. 2(b). A central issue in their model is the point in real space where the affinity level becomes degenerate with the substrate Fermi level, since it is at that location that the possibility of electron transfer from metal to incident atom sharply turns on. If instead of single-electron levels, one considers potential-energy curves and diabatic transitions as in Fig. 2(a), then if one identifies V_1 as the atom-surface curve and V_2 as the negative-ion-surface curve, $z = R_c$ is identical with the NL critical point. NL further recognize that if a level shifts, it also broadens,[6] thus smearing out the atom negative-ion transition region. The physical origins of this broadening are the same as those giving a finite width to region II in Fig. 2. Thus *at this stage*, it appears that the physical content of our model, when applied to the specific problem addressed by NL, is identical with that of NL. From this point we may then diverge.

C. M-HRT solution

The limited objective of this paper is to consider certain aspects of the excitation spectrum of a Fermi system subjected to various time-dependent potentials, hopefully chosen to simulate some realistic classes of behavior of a particle incident upon a metallic surface. The time dependence enters through imposed trajectories displaying the generic types of temporal variation

we feel must be included in a complete theory. All considerations are done within the framework of M-HRT,[11] some principal results of which are now quoted.

Knowing the state of the Fermi system at some time t_0, the excitation spectrum of electron-hole pairs, within the boson model specified by Eq. (2), is given by

$$S_t(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega\tau} \exp\left(\sum_j C_j(\tau)\right) d\tau, \qquad (3a)$$

where

$$C_j(\tau) = (e^{-i\epsilon_j\tau} - 1)|f_j(t, t_0)|^2, \qquad (3b)$$

and

$$f_j(t, t_0) = i \int_{t_0}^{t} V_j(\vec{R}(t')) e^{i\epsilon_j t'} dt'. \qquad (3c)$$

The probability of leaving the system in its initial ground state at time t, after $V_j(\vec{R}(t))$ has acted for the time period $t - t_0$, (in other words the strength of the "no-loss line"), is

$$P_G^0(t) = \exp\left(-\sum_j |f_j(t, t_0)|^2\right) \equiv \exp[-\beta(t)]. \qquad (4)$$

The density of states for excitations with energy less than the Fermi energy is well approximated by the linear relation

$$\rho(\epsilon) \approx \rho_{\epsilon_F}^2 \epsilon, \qquad (5)$$

where ρ_{ϵ_F} is the Fermi-level density of states.

Equations (3)–(5) form a closed set which can be evaluated for any prescribed trajectory and potential curve, and which completely specify the problem, within the limitations of the driven boson modeling of the actual physical problem. The results for Eqs. (3) and (4) have been long known.[16] The linear density of states, Eq. (5), is the feature which makes the electron-gas problem different from phonon or other boson problems.[11,17]

D. No-loss line

Brako and Newns (BN) have recently focused attention on some possible relations between the no-loss line intensity, inelastic spectrum, trajectories, and potential switching rates.[8] We now add some additional insights.

A reasonable premise is that the time dependence of the trajectory-derived potential in Eqs. (2) and (3) (Fig. 1) is necessarily characterized by at least two independent time scales, the switching scale through region II and the time duration within which the system propagates under the fully switched-on potential (through region III). For illustrative general purposes, suppose that the potential is piecewise continuous so that

$$V_j(\mathbf{R}(t)) = \begin{cases} 0, & t < -(\tau_c + \delta) \\ V_j^{sw}(R_{II}(t)), & -(\tau_c + \delta) < t < -\tau_c \\ V_j^{on}(R_{III}(t)), & -\tau_c < t < +\tau_c \\ V_j^{sw}(R_{II}(t)), & \tau_c < t < \tau_c + \delta \\ 0, & t > \tau_c + \delta \end{cases} \qquad (6)$$

where δ is the switching time and τ_c the half-transit time. From Eqs. (3c) and (6), the function

$$f_j = i \int_{-(\tau_c + \delta)}^{-\tau_c} V_j^{sw}(t') e^{i\epsilon_j t'} dt' + i \int_{-\tau_c}^{\tau_c} V_j^{on}(t') e^{i\epsilon_j t'} dt'$$
$$+ i \int_{\tau_c}^{\tau_c + \delta} V_j^{sw}(t') e^{i\epsilon_j t'} dt'$$

will, for most reasonable explicit choices, necessarily take the form

$$f_j = F_{sw}\left(e^{-i\epsilon_j(\tau_c + \delta)}, e^{-i\epsilon_j \tau_c}\right) + G_{on}\left(e^{i\epsilon_j \tau_c}\right)$$
$$+ H_{sw}\left(e^{i\epsilon_j(\tau_c + \delta)}, e^{i\epsilon_j \tau_c}\right), \qquad (7)$$

where F, G, and H depend on the specifics of $V(t)$, but are basically oscillatory. The general form of β in Eq. (4), which follows from Eq. (7), is one which includes a sum of terms for each independent step switching on, transit, and then switching off, plus interference terms, between each process. Simplifications arise if one of the time scales is much larger or smaller than the range of integration on ϵ_j in Eq. (4). In both limits, $\beta(t)$, and thus the probability of staying on the no-loss line, become independent of the time scale in question. In the large limit, both the direct and interference terms in $|f_j|^2$ will be rapidly oscillating, causing the $d\epsilon_j$ integral either to go to zero or some average, but time-scale-independent, value.

Consider some special cases. As $\delta \to 0$, the sudden switching limit is reached, in which case $|f_j|^2 = |f_j(e^{i\epsilon_j \tau_c})|^2$ so the strength of the no-loss line depends on the duration or "lifetime" of the switched-on state, as illustrated elsewhere.[18] For $\tau_c \to 0$, $|f_j|^2$ contains not only contributions from switching on and off but interferences between the on and off processes, which may depend upon the switching rate. In a one-parameter potential model, problems of interpretation can arise due to ambiguity as to whether the one parameter is a switching-on and -off rate or a lifetime for a suddenly switched-on potential. This will be discussed shortly. Finally we note that as $\tau_c \to$ large, the switch-on and -off processes do not interfere.

M-HRT[11] and BN[8] have considered various explicit forms of switching potentials with BN particularly emphasizing the one-parameter symmetric form as a model for the particle-surface interaction. As elucidated here, we are interested in modeling physical processes which require at least two time parameters. It is enlightening to examine the exponentially switched-on and -off potential of M-HRT, including a time delay $2\tau_c$ between the completion of the turn on and initiation of turn off, throughout which interval a time-independent potential exists, that is,

$$V_j(t) = V_j[e^{\eta(t + \tau_c)}\Theta(-t - \tau_c) + \Theta(\tau_c + t)$$
$$- \Theta(t - \tau_c) + e^{-\eta(t - \tau_c)}\Theta(t - \tau_c)], \qquad (8)$$

where η has the same significance as δ^{-1}. From Eqs. (3c) and (8)

$$f_j \equiv \lim_{\substack{t_0 \to -\infty \\ t \to +\infty}} f_j(t, t_0)$$
$$= 2iV_j\left(\frac{\sin\omega\tau_c}{\omega} + \frac{1}{\omega^2 + \eta^2}(\eta\cos\omega\tau_c - \omega\sin\omega\tau_c)\right). \qquad (9)$$

Some subtleties arising from the interplay between the various time scales are nicely illustrated by considering Eq. (9) and the resulting no-loss line intensity in a number of limiting cases. As will be stressed, limits are only meaningful when given in relation to other relevant time or energy scales.

(a) Sudden switching limit (sud): In this "step-function" limit, $\eta \to \infty$ relative to both τ_c^{-1} and ω_c which is a measure of the maximum pair-excitation energy. Thus Eq. (9) reduces to

$$f_j^{sud} \simeq 2iV_j(\sin\omega\tau_c)/\omega,$$

and with Eqs. (4) and (5),

$$\beta^{sud} = 4\rho_{\epsilon_F}^2 |\vec{V}|^2 \int_0^{\omega_c} \frac{\sin^2 \omega\tau_c}{\omega} d\omega. \qquad (10)$$

As is common in all problems associated with localized potentials in Fermi systems,[10-12] the energy dependence of the scattering potential has been taken to be a constant for energies less than some cutoff ω_c and zero for energies above. This procedure is related to the assumption that the potential is localized on the order of atomic dimensions, yielding a cutoff of order ~1–10 eV, oftentimes taken equal to the Fermi energy. This step will be examined in more detail later. Equation (10) is quite well behaved. For special cases in which $\tau_c \ll \omega_c^{-1}$, $\sin^2 \omega\tau_c \approx (\omega\tau_c)^2$, and Eq. (10) becomes

$$\beta^{sud} \simeq 2\rho_{\epsilon_F}^2 \vec{V}^2 \omega_c^2 \tau_c^2,$$

so

$$P_G^{sud} = \exp(-\gamma\tau_c^2), \qquad (11)$$

with $\gamma \equiv 2\rho^2 \vec{V}^2 \omega_c^2$. Equation (11) displays the physically satisfying result that the probability after the action of the potential ends for the metal to remain in the ground state decreases as the

duration of the potential increases. For a sudden on and off potential ($\tau_c \to 0$), the overlap $P_G^{\text{sud}}(\tau_c = 0) = 1$, since in this limit, nothing has happened.

(b) Near sudden (ns) limit: Here we evaluate Eqs. (4), (5), and (9), retaining the lowest-order correction to the $\eta^{-1} = 0$ limit, but still requiring $\eta \gg \omega_c$, τ_c^{-1}. Equation (9) becomes

$$f_j^{\text{ns}} \simeq 2iV_j(\omega^{-1}\sin\omega\tau_c + \eta^{-1}\cos\omega\tau_c) . \tag{12}$$

Dropping terms $\sim 1/\eta^2$, Eqs. (4), (5), and (12) give

$$\beta^{\text{ns}} \simeq \frac{\gamma}{\omega_c^2}\left(2\int_0^{\omega_c}\frac{\sin^2\omega\tau_c}{\omega}d\omega \right. $$
$$\left. + \frac{1}{\eta\tau_c}[1-\cos(2\omega_c\tau_c)]\right). \tag{13}$$

Again for the special case in which $\omega_c\tau_c \ll 1$, Eq. (13) easily reduces to

$$\beta^{\text{ns}} \simeq \beta^{\text{sud}}(1 + 2/\eta\tau_c) , \tag{14}$$

which presents the surprising conclusion that the probability that the system remains in the ground state initially decreases as the sudden switching is softened in the direction of adiabaticity. This finding is due in part to pathological behavior of exponential switching and to the previously mentioned ambiguity between softer switching versus increased transit time. In addition, the exponential wings have increased the value of $\int_{-\infty}^{\infty} V(t)dt$ through which the potential acts, and it seems reasonable that this increase should be reflected in a more effective excitation out of the ground state.

(c) Adiabatic limit (ad): We will first obtain the adiabatic probability P_G^a proceeding in a naive way, and then point out the reasons for the inapplicability of the conclusions to the semi-infinite Fermi system. One would like to say that the adiabatic limit occurs as $\eta \to 0$. Equation (9) is then

$$f_j^{\text{ad}} = 2iV_j[\omega^{-1}\sin\omega\tau_c + \omega^{-2}(-\omega\sin\omega\tau_c)] = 0 .$$

Consequently, $P_G^{\text{ad}} = 1$, consistent with the definition of an adiabatic process. The fallacy in this line of logic is the assumption that the limit $\eta \to 0$ exists. In fact, the correct limit is $\eta \ll \omega_{\text{min}}$, where ω_{min} is the minimum excitation energy. For finite Fermi systems, the two conditions can be made equivalent as η becomes arbitrarily close, but not necessarily equal, to zero. On the other hand, for the infinite Fermi system, $\omega_{\text{min}} \to 0$. Thus the true adiabatic condition $\eta \ll \omega_{\text{min}}$ can never be attained while simultaneously still having a process (switching) occur. This is just another statement of the Anderson orthogonality theorem.

(d) Zero transit time limit: In the extreme in which $\tau_c \to 0$, the particle travels through region III so fast that this part of the potential might just

as well not have existed. For $\tau_c^{-1} \gg \omega_c$, η (i.e., $\tau_c \to 0$), Eq. (9) reduces to

$$f_j^{\tau_c} = 2iV_j\eta/(\omega^2 + \eta^2) . \tag{15}$$

With Eqs. (4), (5), and (15), we readily obtain

$$\beta^{z\tau_c} = 4\rho_{\epsilon_F}^2 \bar{V}^2\eta^2 \int_0^{\omega_c} \frac{\omega\,d\omega}{(\omega^2+\eta^2)^2}$$

$$= \beta_0^{z\tau_c}/(1 + \eta^2/\omega_c^2),$$

with

$$\beta_0^{z\tau_c} \equiv 2\rho_{\epsilon_F}^2\bar{V}^2 . \tag{16}$$

In the limit in which $\eta/\omega_c \to 0$, either by slow switching relative to the band of excitations or by a broadband limit $\omega_c \to \infty$, as discussed by M-HRT,[11] we obtain their result that with the symmetric exponential switching (with zero-transit time) the probability of remaining in the ground state is

$$P_G^{z\tau_c}(\eta/\omega_c \to 0) = \exp(-\beta_0^{z\tau_c}) , \tag{17}$$

and it is *independent* of the switching parameter. The word independent must be treated cautiously as Eq. (17) is valid only under a limiting condition on η, which makes the generality of this result actually quite dependent upon η. In passing we also note that for fast switching ($\eta \gg \omega_c$), Eq. (16) becomes

$$\beta^{z\tau_c}(\eta \gg \omega_c) \to 0,$$

in which case $P_G^{z\tau_c}(\eta \gg \omega_c) = 1$, as it should. A process characterized by a quick switch on and off with no time for the system to sample the new potential is equivalent to nothing happening, in which case the ground state should not be disturbed. The unit overlap probability demonstrates this mathematically.

(e) Sudden on, long transit time: As with case (a), Eqs. (4), (5), and (9) reduce to Eq. (10). In the present case, different approximations on $\sin^2\omega\tau_c$ are required. For $\tau_c \to \infty$, we try replacing this rapidly oscillating (between 0 and 1) function by $\frac{1}{2}$, its average value. Then

$$\beta_{\tau_c}^{\text{sud}} = 2\rho_{\epsilon_F}^2 \bar{V}^2 \int_0^{\omega_c} \frac{d\omega}{\omega} , \tag{18}$$

which shows the logarithmic infrared divergence typical of these types of problems. An appeal to physics helps out. Since the perturbation lasts for a large but still finite time (relative to ω_{min}^{-1} of the Fermi system), the zero lower limit is replaced by $1/\tau_c$, in which case

$$\beta_{\tau_c}^{\text{sud}} = 2\rho_{\epsilon_F}^2\bar{V}^2 \ln(\omega_c\tau_c) \equiv \alpha_0 \ln(\omega_c\tau_c) . \tag{19}$$

Thus the no-loss line decreases as $1/\tau_c^{\alpha_0}$, going to zero for permanent switching. This is yet another manifestation of the Anderson theorem.

Note that the extra factor of 2 in Eq. (19) arises from switching on and then off.

E. Reactions, inelastic processes, and sticking probability

We have so far discussed a model in which it is assumed that the rearrangement of the electronic charge taking place during a chemical reaction occurring at the metal surface is perceived by the metal electrons as a time-dependent, rapidly varying potential. This potential causes electron-hole pair excitations and diminishes the probability that when the reaction is terminated the metal remains in the ground state. The energy needed for these excitations is provided by the reacting system, and thus the process affects the rate of reaction.

In order to understand qualitatively how the metal electron excitation can influence the reaction rate, one must take into account that the electron excitation must be accompanied by a change in molecular state and energy. The molecular system must go from some initial state $|i\rangle$ with energy E_i to some final state $|f\rangle$ with energy E_f. This is a change in the diabatic electronic state, as well as the nuclear state, of the molecular system. In first order, the probability that this happens is the product of the probability P_{if} that the molecular states change multiplied with the probability that the electrons in the metal can absorb the energy $(E_f - E_i) = \hbar\omega$. The latter is proportional to the structure factor $S(\omega)$. The probability P_{if} contains the molecular Franck-Condon factors and the probability of the diabatic transition. The total rate is proportional to the sum of all the terms $P_{if}S(\omega)$ over the initial states compatible with the sample preparation and final states accepted by the detection scheme as products. The details of this process will be discussed in a future paper.[7] Presently, we concentrate on the properties of $S(\omega)$. Qualitatively, large values of $S(\omega)$ mean that the metal is eager to accept the energy $\hbar\omega$. If the molecular system is also eager to release that energy (e.g., P_{if} is large for $E_f - E_i = \hbar\omega$), then the process $|i\rangle \rightarrow |f\rangle$ provides a large contribution to the rate. It is therefore of some interest to compute $S(\omega)$ for the case of the time-dependent potentials specified above.

As seen from Eqs. (3) and (5), this requires evaluation of integrals of the form

$$C(\tau) \equiv \sum_j c_j(\tau)$$

$$= \rho_{\epsilon_F}^2 \int_0^{\epsilon_c} \epsilon(e^{-i\epsilon\tau} - 1)|f_j|^2 d\epsilon, \tag{20}$$

which differ from the quantities calculated in the last section only by the exponential within the integral. The standard procedure for dealing with the long-time behavior of $C(\tau)$ is to approximate the exponential by unity for $\epsilon < 1/\tau$ and by zero above.[10-12] Thus

$$C(\tau) \simeq \rho_{\epsilon_F}^2 \int_{1/\tau}^{\epsilon_c} \epsilon|f_j|^2 d\epsilon, \tag{21}$$

where $|f_j|^2$ has been well discussed. As an example, for a sudden-on potential,

$$|f_j|^2 = \bar{V}^2/\epsilon^2$$

and the spectrum is

$$S_t(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega\tau + C(\tau)} d\tau$$

$$= \frac{1}{2\pi} \int \frac{e^{i\omega\tau}}{(\epsilon_c\tau)^\alpha} d\tau \simeq \left(\frac{\alpha}{\epsilon_c^\alpha}\right)\frac{1}{\omega^{1-\alpha}}. \tag{22}$$

To the extent that the electron-hole contribution to the reaction probability can be equated with the probability for exciting the Fermi system above some critical energy ϵ_s (this happens if the reactive process is such that the molecular system must lose at least the amount of energy ϵ_s), determined by the details of the potential curves and the particle kinetic energy,[19] we have the simple result that

$$P_s(\text{sud}) = \int_{\epsilon_s}^{\epsilon_c} d\omega S_t(\omega) = 1 - \left(\frac{\epsilon_s}{\epsilon_c}\right)^\alpha. \tag{23}$$

For zero-strength interactions $\alpha = 0$, and thus $P_s(\text{sud}) = 0$; likewise, with large energy transfer when $\epsilon_s \sim \epsilon_c$.

In contrast to the sudden-on case, the excitation spectrum generated by an exponentially switched-on potential is

$$S_\eta(\omega) = \left(\frac{1}{\Gamma(\alpha)\eta^\alpha}\right)\frac{\exp(-\omega/\eta)}{\omega^{1-\alpha}}, \tag{24}$$

which redistributes weight from the high-energy tail (where $\omega > \eta$) back towards this no-loss position. Essentially this form of spectrum guarantees that there can be no Fermi-system response until the perturbation is acting. As a consequence of Eq. (24), the "reaction probability" is reduced from the sudden-limit value to

$$P_s(\eta) = \int_{\epsilon_s}^{\infty} S_\eta(\omega) d\omega = \frac{\Gamma(\alpha, \epsilon_s/\eta)}{\Gamma(\alpha)}, \tag{25}$$

where now the upper limit ϵ_c can be taken at ∞, since the exponential in $S_\eta(\omega)$ ensures convergence. Here $\Gamma(\alpha, \epsilon_s/\eta)$ is the incomplete gamma function.

From these few examples, one can see how the effects of electron-hole pairs, as excited via the phenomenological time-dependent potentials de-

signed to stimulate the dynamic interaction of the reacting incident system with electrons in the metal, may lead to contributions to the reaction probability. To go further, specific coupling models must be constructed in order that numerical values for the all-important exponent α can be ascertained.

F. Singularity exponent

At this point, some prescription must be offered for converting the discussed perturbation $V(\mathbf{R}(t))$ into a singularity index α. First we assume that the perturbation is "semiseparable" in the sense that

$$V(\vec{\mathbf{R}}(t)) \simeq \sum_i \langle V_i(\overline{R}) \rangle F_i(t) . \tag{26}$$

Basically, the function $F_i(t)$ is the switching function, causing a more or less localized perturbation in time (and thus in a defined spatial region). A much more gentle time dependence results from motion along the smooth potentials between violent curve crossings. We assume some average constant value, call it $\langle V_i(\overline{R}) \rangle$, to account for this aspect of the time dependence. The switching function allows for sharp transitions between smooth curves, as with our diabatic transitions or NL's affinity level hitting the Fermi level.

At the curve crossing point, as shown in Fig. 2(a), the perturbation on the Fermi system (substrate electron gas) is

$$V(R(t \approx -\tau_c)) \approx \sum_{\vec{q}} \Delta V_{\vec{q}} \rho_{\vec{q}} F(t \approx -\tau_c) , \tag{27}$$

where $\Delta V_{\vec{q}}$ is the qth Fourier component of the change of interaction potential in going from the internal electronic state of curve 1 to that of curve 2 at $R = R_c$, and $\rho_{\vec{q}}$ is the qth Fourier component of the conduction electron density which includes the induced density. For the case of surface interactions, $\vec{q}$ is a two-dimensional wave vector parallel to the surface. Adapting some x-ray edge results of Langreth[20] to the present problem, the $C(\tau)$ function, for interactions of the form of Eq. (27), is

$$C(\tau) = -\sum_{\vec{q}_{\shortparallel}} |\Delta V_{\vec{q}_{\shortparallel}}|^2$$
$$\times \int_0^\infty d\omega' S(\vec{q}_{\shortparallel}, \omega') |F(\omega')|^2 (e^{-i\omega'\tau} - 1) , \tag{28}$$

where $S(\vec{q}_{\shortparallel}, \omega')$ is the two-dimensional dynamic form factor for the electron gas surface, and $F(\omega')$ is the Fourier transform of the switching function $(= 1/\omega'^2$ for sudden switching). Note that any static relaxation shifts have not been included, as they just change the energy zero in a way which

can be incorporated into the definition of ϵ_s, as in Eq. (25). For a perturbation due to a *change* in a charge distribution equal to $\delta\rho_0(\vec{\mathbf{r}})$ totally outside the surface, it has been shown within a separable image charge model[21] that

$$|\Delta V_{\vec{q}_{\shortparallel}}|^2 = V(q_{\shortparallel})|\delta\rho(\vec{q}_{\shortparallel})|^2 , \tag{29a}$$

with

$$\delta\rho(\vec{q}_{\shortparallel}) = \int_0^\infty dz \, e^{-q_{\shortparallel} z} \delta\rho_0(\vec{q}_{\shortparallel}, z) , \tag{29b}$$

$$\delta\rho_0(\vec{q}_{\shortparallel}, z) = \int d^2 r_{\shortparallel} e^{i\vec{q}_{\shortparallel} \cdot \vec{r}_{\shortparallel}} \delta\rho_0(\vec{\mathbf{r}}) , \tag{29c}$$

and

$$V(q_{\shortparallel}) = 2\pi e^2/q_{\shortparallel} \tag{29d}$$

defined with respect to an origin at the image plane.

An approximation scheme for the dynamic form factor due to Gumhalter and Newns[22] (GN) will be used here. GN show that within the RPA response picture, the long-wavelength, low-frequency surface form factor is well represented by

$$\lim_{q_{\shortparallel} \ll \kappa_{\rm FT}, \omega \ll \omega_p} S_0(q_{\shortparallel}, \omega) = \frac{2}{\pi\sqrt{3}} \left(\frac{\omega}{\omega_p}\right)\left(\frac{q_{\shortparallel}}{\kappa_{\rm FT}}\right)\left(\ln\frac{2\kappa_{\rm FT}}{q_{\shortparallel}} - \frac{1}{2}\right)$$
$$- \frac{2}{3\pi}\left(\frac{\omega}{\omega_p}\right)^2 + \cdots , \tag{30}$$

with $\kappa_{\rm FT}$ the Fermi-Thomas screening parameter equal to $2.95/r_s^{1/2}$ Å^{-1}, and $\omega_p = 47/r_s^{3/2}$ eV, the plasmon energy. Next, GN introduce an ansatz for the frequency cutoff by setting

$$S(q_{\shortparallel}, \omega) \simeq \frac{dS_0(q_{\shortparallel}, \omega)}{d\omega}\bigg|_{\omega=0} \omega e^{-\omega/q_{\shortparallel} v_F} , \tag{31}$$

with v_F the Fermi velocity. The line $\omega = q_{\shortparallel} v_F$ is the maximum pair energy for given $q_{\shortparallel}$. Also note from Eq. (30) that $S_0'(q_{\shortparallel}, \omega)$ is frequency independent for $\omega \ll \omega_p$. Collecting Eqs. (28)–(31), the pair excitation function is thus

$$C(\tau) \simeq \sum_{\vec{q}_{\shortparallel}} \alpha(\vec{q}_{\shortparallel}) \int_0^\infty d\omega' \omega' e^{-\omega'/\omega_c} |F(\omega')|^2 (e^{-i\omega'\tau} - 1) , \tag{32a}$$

with

$$\alpha(\vec{q}_{\shortparallel}) \equiv V(q_{\shortparallel})|\delta\rho(\vec{q}_{\shortparallel})|^2 S_0(q_{\shortparallel}, \omega' = 0) , \tag{32b}$$

and

$$\omega_c \equiv q_{\shortparallel} v_F . \tag{33c}$$

By introducing the exponential cutoff, the upper limit on the ω' integration can be taken to infinity with no spurious ultraviolet divergences. This has the advantage that the integrals, for reasonable switching functions $F(\omega')$, can be performed analytically. Alternatively, the cutoff exponential can be set equal to unity, and the upper limit on

ω' put equal to ω_c.

As an example, consider sudden switching, in which case

$$|F(\omega')|^2 = (1/\omega')^2 ,$$

and the ω' integral is then identical in structure to the standard pair-excitation integral, as in Eq. (20). Treating the oscillatory term in the same way as was done in Eq. (21), Eq. (32) becomes

$$C_0(\tau) \simeq \sum_{\vec{q}_{\|}} \alpha(q_{\|}) \ln[\omega_c(q_{\|})\tau] . \tag{33}$$

The final simplification of GN is to decouple α and the ln terms in Eq. (33) by setting $\omega_c(q_{\|})$ $= \omega_c(R_c^{-1})$, a constant whose value is determined by R_c, the distance from the surface where the perturbation is turned on.[23] Then with

$$\alpha_s \equiv \sum_{\vec{q}_{\|}} \alpha(\vec{q}_{\|}) , \tag{34}$$

the excitation spectrum, in analogy with Eq. (22), is immediately obtained as

$$S_s^c(\omega) \simeq \left(\frac{\alpha_s}{\omega_c^{\alpha_s}}\right) \frac{1}{\omega^{1-\alpha_s}} , \tag{35}$$

where superscript c signifies cutoff. The other procedure is to retain the cutoff exponential, in which case, for sudden switching, the integral in Eq. (32a) can be performed analytically, yielding

$$S_s^x(\omega) = \left(\frac{1}{\Gamma(\alpha_s)\omega_c^{\alpha_s}}\right) \frac{\exp(-\omega/\omega_c)}{\omega^{1-\alpha_s}} \tag{36}$$

valid for all ω. Depending upon which form is used for the excitation spectrum, the pair contribution to the sticking probability is completely specified by either Eqs. (23) and (35), or by (24) and (36) together with Eqs. (30), (32b), and (34) for a given physical process characterized by ϵ_s, $\delta\rho(q_{\|})$ [Eqs. (29b), (29c)] and ω_c.

To illustrate via a specific example, consider the case of a suddenly created point charge at $z = R_c$. With

$$\delta\rho_0(\vec{r}) = \delta^2(r)\delta(z - R_c) ,$$

Eqs. (29b), (29c) yield $\delta\rho(\vec{q}_{\|}) = e^{-q_{\|}R_c}$. Equations (29d), (32b), and (34) yield

$$\alpha_s = e^2 \int_0^\infty dq_{\|} e^{-2q_{\|}R_c} S_0'(q_{\|}, \omega = 0) . \tag{37}$$

Noting that $S_0' \propto q_{\|}(\ln q_{\|}/2\kappa_{FT} + \tfrac{1}{2})$, Eq. (37) integrates to

$$\alpha_s = \frac{0.367}{\kappa_{FT}R_c} \left(\frac{e^2}{4R_c} \frac{1}{\hbar\omega_p}\right) [\ln(4\kappa_{FT}R_c) - 0.923] , \tag{38}$$

which is our final result for the singularity exponent, corresponding to the sudden appearance or disappearance of a point charge a distance R_c

from the surface. In terms of real processes, this is a model for the pair excitation which accompanies a diabatic transition from an atomic to an ionic curve[7] at $z = R_c$ (Fig. 2a), or alternatively for the tunneling transition from substrate to adparticle which turns on at the distance $z = R_c$, where the affinity level drops to the Fermi level. To get a feel for the quantitative significance of this effect, α_s is plotted as a function of R_c, treating the substrate electron density (r_s) parametrically in Fig. 3. These results display all the qualitatively correct features expected in the singularity index, such as

(i) Decreasing value as R_c increases, and thus the interaction strength decreases;

(ii) Larger value for less dense substrate electron gas (larger r_s), at fixed R_c, since α is roughly proportional to some monotonic function of the ratio of the interaction potential divided by a characteristic substrate electronic energy (Fermi, plasmon, etc.). The decrease in substrate energy with increasing r_s leads to the larger values of α_s with r_s;

(iii) Correct order of magnitude and limiting values of α_s with R_c. For a point hole embedded in an electron gas, $\alpha \approx (\delta_l/\pi)^2$, where δ_l is the hole potential phase shift. As an example, for s-wave scattering only, $\delta_l = \pi/2$ and $\alpha = 0.25$, which sets an upper limit to the meaningful values of α_s. As seen in Fig. 3, the results from Eq. (38) are satisfyingly in accord with this limit.

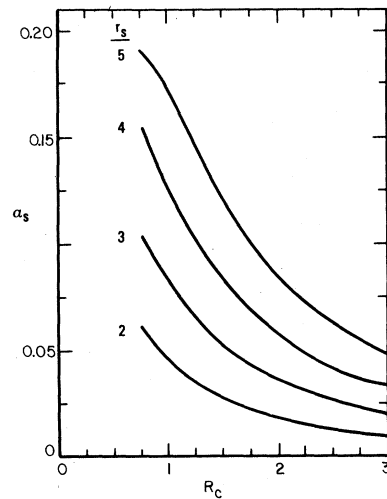Next, in a manner identical to that producing Eqs. (23) and (25), the pair sticking probability

FIG. 3. Singularity index α_s, from Eq. (38), as a function of R_c, the distance from the surface where the diabatic transition from an atomic to ionic state occurs. The substrate electron-density factor r_s is treated parametrically.

is given by

$$P_s^c = 1 - (\epsilon_s/\omega_c)^{\alpha_s}, \qquad (39a)$$

or

$$P_s^x = \Gamma(\alpha_s, \epsilon_s/\omega_c)/\Gamma(\alpha_s). \qquad (39b)$$

The sticking probabilities obtained from Eqs. (39a), (39b) are drawn as a function of ϵ_s/ω_c, treating α_s parametrically in Fig. 4. The values obtained with P_s^x (dashed curves) are slightly smaller than with P_s^c (full curves) due to the exponential cutoff of excitations, even for $\omega < \omega_c$. Since this is a mathematical artifact, the small differences between the two curves have no physical significance. Consequently, Eq. (39a) is the preferred expression due to its algebraic simplicity.

To use these results a prescription must be given for relating physical quantities to x values. Going back to Fig. 2(a), one obtains the following picture. The incident particle, with kinetic energy K_i, may undergo the diabatic transition (sudden switching) at the point R_c, where $V_1(R_c) = V_2(R_c)$. If now the strongly bonding curve $V_2(R)$ is regarded as properly renormalized to include static electron-hole pair effects, then $\epsilon_s = K_i - V_2(R_c)$, where $V_2(R)$ is given with respect to a zero defined by $V_1(R \to \infty)$. The GN cutoff energy is

$$\omega_c \simeq v_F/2R_c = 13.8/r_s \text{ eV},$$

which is in the ~3–7 eV range for real metals. Since the situations of concern in this study relate
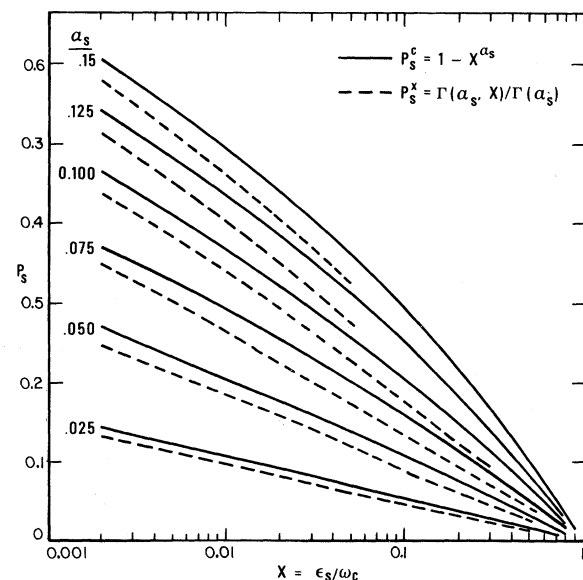

FIG. 4. Electron-hole pair contribution to the sticking probability as a function of one dimensional, renormalized kinetic energy $x = \epsilon_s/\omega_c$. The full curve was obtained from Eq. (39a), whereas the dashed curve is from Eq. (39b).

to incident beams with $K_i \lesssim 0.01$ eV (thermal beams) and with $V_2(R_c)$ near zero, the range of x values will usually be substantially less than 0.1. Furthermore, R_c is likely to fall in the ~1–1.5 Å range, in which case $\alpha_s \sim 0.1$, and from Fig. 4, $P_s \gtrsim 40\%$, due to electron-hole pair contributions alone.

Finally, some comments are due on the reasons for presuming $V_2(R_c) \simeq 0$. Of course this assertion cannot be made without some independent knowledge of $V_1(\vec{R})$ and $V_2(\vec{R})$, either from quantum chemical-like calculations or some spectroscopic type of experiment.[24] In either case, such determinations are of static ground-state properties, for specified nuclear coordinates and internal electronic states, and as such can be regarded as starting input for dynamic theories. Furthermore, only cases in which $V_2(R_c) \simeq 0$ are germane to the present study for the following reason. First consider the "precursor" curve $V_1(R)$ in which a weakly physisorbed species might exist at an equilibrium location R_p. The well depth for such a physisorbed object is less than ~0.1–0.2 eV. For a diabatic transition from state 1 to 2 to be meaningful, a clear separation between these states requires that

$$V_2(R_c) = V_1(R_c) > V_1(R_p),$$

which places a lower limit of ~-0.1 eV on $V_2(R_c)$.

At the other extreme, $V_2(R_c)$ cannot be too much greater than K_i if the diabatic transition is to occur, as Franck-Condon factors[7,15] will be unfavorable. Note that $V_2(R_c) \gtrsim 0$ is the condition for so-called activated chemisorption.[23] The ideas presented in this study should in fact be most relevant to the dynamics of the first passage sticking probability in activated processes.

IV. DISCUSSION

The first phase of an extensive study into the role of substrate electron-hole pairs in the dynamics of molecular processes at metallic surfaces has been presented. We have focused attention on those processes in which the static substrate-particle interaction induces an electronic (diabatic) transition on the incident particle within a limited spatial region outside the surface. By placing the incident particle on a prescribed but self-consistent trajectory, a time dependence is introduced into the problem. The change in charge distribution of the incident particle is seen as a sudden potential change by the substrate pair excitations. In analogy with the x-ray edge problem, this sudden perturbation leaves the electron gas in an excited state, and it is this possibility which gives rise to irreversibility in the total process.

The degree of excitation is incorporated through a singularity index α_s which is a measure of the distribution of excited pair states. A prescription for obtaining α_s in terms of the substrate dynamic form factor and the electronic charge associated with the diabatic transition has been given.

The sudden-limit sticking probability accompanying a surface ionization event was calculated as an example. For reasonable parameter values and dynamic range, pair excitation alone could account for sticking probabilities of the order of at least 50%. It would be premature to attempt any comparison with experimental data, as special considerations must be given to the problem of separating lattice from electronic contributions. At present there does not seem to be any obvious way to make a unique and convincing partitioning. Nonetheless, the present study has demonstrated that the electronic behavior can be at least as important a heat bath as the lattice. In order to assess the ultimate importance of the electronic mechanism in real situations (as opposed to the

model situations considered here), the role of: (i) Franck-Condon factors and quantized trajectories, (ii) "chemical viscosity," (iii) softer-than-sudden diabatic transitions, and (iv) the union of the x-ray edge effect with items (i)–(iv) must be dealt with. Each of these topics is the subject of forthcoming publications.[7]

*This work was carried out at NBS in the Surface Science Division.

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