A selfconsistent semiclassical approach to the inelastic scattering of atoms from solid surfaces

D. Kumamoto and R. Silbey

Citation: J. Chem. Phys. 75, 5164 (1981); doi: 10.1063/1.441866
View online: http://dx.doi.org/10.1063/1.441866
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v75/i10
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.
Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors
A self-consistent semiclassical approach to the inelastic scattering of atoms from solid surfaces

D. Kumamoto and R. Silbey

Department of Chemistry and Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 24 July 1981; accepted 4 August 1981)

A self-consistent semiclassical theory of inelastic scattering is developed using a boson Hamiltonian and a time-dependent Hartree solution. The quality of the self-consistent solution is shown to be dependent on the choice of initial state. Two choices of initial state are compared for a simple choice of interaction potential. The results of this analysis are applied to the inelastic scattering of atoms from metal surfaces considering either the electron-hole pair or the phonon models of energy dissipation. The calculation of sticking probabilities is considered.

I. INTRODUCTION

Recently, several experiments have been reported involving the scattering of one or more molecular beams off a metal surface. Janda et al., have performed energy-analyzed scattering of rare gas atoms off tungsten surfaces to examine the dependence of the average energy transferred from the incident atom to the metal surface on the initial beam velocity and the surface temperature. Other groups have been using beam scattering to investigate reaction dynamics. Clearly there is a need for a theoretical description of inelastic scattering from surfaces in the region where the traditional perturbative approaches are not applicable, (i.e., large energy transfer).

Several calculations in this regime have been performed using the classical, generalized Langevin equation (GLE), formalism first adopted for surface scattering problems by Adelman and Doll. In this formulation the coupling between the incident atom and a group of nearest neighbor surface atoms, (the primary zone), is included explicitly, and the coupling of the primary zone to the rest of the lattice, (the bath), is described by a friction kernel and a random force.

In this paper we consider an alternate calculation, one that is able to describe the transfer of energy from the translational motion of the atom to either the phonons or the low-lying electronic excitations of the surface, (the GLE calculation mentioned above considers only the phonon mechanism). This calculation starts with the simple boson Hamiltonian

\[ H = \frac{p^2}{2M} + V_0(x) + \sum_n \eta_\omega_n (a_n^+ a_n + \frac{1}{2}) + \sum_{\eta} B_\eta F(\eta, x)(a_\eta^+ a_\eta) \]  

This Hamiltonian describes a particle with kinetic energy \( \frac{p^2}{2M} \) at a distance \( x \) away from the surface, (\( x \) is measured along a direction normal to the surface). The relevant surface excitations, (phonons or electron-hole pairs), are assumed to be well described as a bath of bosons, and the coupling to each surface mode is linear in the displacement of that mode.

This Hamiltonian has already been applied by several workers to both the phonon and the electron-hole pair models of energy dissipation by a surface. Their calculations are all characterized by a single, semiclassical solution of the Schrödinger equation for the Hamiltonian, Eq. (1). The motivation for the type of solution chosen was that (in a single particle picture) as the atom passes by, the surface will experience a localized, time-dependent perturbation due to its coupling to the atom. Thus, the technique used in the previous calculations was to separate the problem into two parts: that of an atom on a classical trajectory and that of a surface subjected to a localized time-dependent perturbation. Given the atom trajectory, the second part (which is just the problem of a bath of forced harmonic oscillators) is exactly soluble. In the earlier work, the atom trajectory was obtained either by assuming some symmetric form or by solving Hamilton's equations for an atom with the Hamiltonian

\[ H_0 = \frac{p^2}{2M} + V_0(x), \]  

either of which corresponds to elastic scattering. The atom trajectory was then used to obtain a reduced surface Hamiltonian

\[ \hat{H}_s(t) = \sum_\eta \eta \omega_\eta (a_\eta^+ a_\eta + \frac{1}{2}) + \sum_\eta B_\eta F(\eta, x)(a_\eta^+ a_\eta), \]  

where the time dependence is obtained by inserting the trajectory \( x(t) \) calculated above into \( F(\eta, x) \). The reduced Hamiltonian equation (3), is then solved exactly to obtain the probability distribution \( P(\Delta \omega) \) for the surface to gain an amount of energy \( \Delta \omega \).

This solution has two major failings. First and most obviously, it is not self-consistent. In general the energy gained by the surface is not equal to the energy loss in the atom trajectory. Second, the average energy transfer calculated in this fashion is independent of the surface temperature (this is most important for the phonon mechanism since the electron hole pair calculation is a zero temperature calculation).

In this paper, an alternate and self-consistent solution of the Hamiltonian [Eq. (1)] is presented using a time-dependent Hartree (henceforth TDH) approximation. This is our main result. A self-consistent, semiclassical solution is shown to exist and the self-consistent...
equations for such a calculation are derived. The unphysical, temperature independent behavior of the previous phonon mechanism solutions is also corrected. Simply using a self-consistent formulation is not sufficient to correct this behavior. In order to obtain a temperature dependent result, a different initial state must be used. The previous calculations used the eigenstates of the unperturbed surface as their initial states. In this paper, a wave packet initial state is shown to yield improved results. This behavior is observed because the TDH separation is more nearly exact for localized states.7

Our solution of the TDH equations is semiclassical. We calculate an atom trajectory and use it to obtain an effective surface Hamiltonian analogous to Eq. (3). This procedure can be iterated to self-consistency in the average energy transferred [the first moment of P(Δω)].

This paper is laid out as follows. In Sec. II we present the results of the previous solutions and show the temperature independence of the average energy transferred. In Sec. III we outline the TDH approximation and apply it to the Hamiltonian equation (1). Section IV contains a description of our method and an explicit verification of the self-consistency of our approach. In Sec. V we solve the self-consistent equations for a simple choice of atom-surface interactions and we consider the calculation of sticking probabilities.

II. EARLIER SOLUTIONS

As we have mentioned, the previous semiclassical solutions of the Schrödinger equation for the Hamiltonian equation (1) were constructed by finding an elastic trajectory and using this trajectory to obtain the Hamiltonian equation (3). The interaction picture time development operator for the Hamiltonian equation (3), is

\[ U_I(t,t_0) = e^{-i\mathcal{H}t_0} \exp \left( \frac{i}{\hbar} \sum_n \hat{S}_n a_n^+ \hat{S}_n a_n^0 \right), \]

where

\[ \phi(t) = \frac{1}{\mathcal{N}} \sum_{\ell} B_{\ell} \int_{t_0}^{t} d\tau_{2} \int_{t_0}^{\tau_2} d\tau_{1} \times F(\eta_\ell, \tau_1) F(\eta_\ell, \tau_2) \sin \omega_\ell(\tau_1 - \tau_2) \]

and

\[ \hat{S}_n = \int_{t_0}^{t} d\tau B_n F(\eta, \tau) e^{-i\omega_n \tau}. \]

The probability of an energy change, Δω is given by

\[ P(\Delta \omega) = \sum_n \left| \langle \psi_n \mid U_I(t,t_0) \mid \psi_n \rangle \right|^2 \delta(E_n + E_m - E_m), \]

where \( U_I(t,t_0) \) is the time development operator in the Schrödinger picture, \( m \) is the initial surface state, and \( n \) and \( m \) label the eigenstates of \( H_{so} \), where

\[ H_{so} = \sum_{\ell} \hbar \omega_\ell (a_n^0 a_n^+ + \frac{1}{2}) . \]

Finally, the thermally averaged probability distribution is evaluated in the usual fashion with the result

\[ \langle P(\Delta \omega) \rangle = \int d\tau e^{i\Delta \omega \tau} \langle P(\tau) \rangle , \]

where the double brackets stand for an average over a canonical ensemble, and \( \langle P(\tau) \rangle \) is given by

\[ \langle P(\tau) \rangle = e^{\tau \Gamma} , \]

where

\[ \Gamma(t) = \sum_n \left| \frac{\hat{S}_n}{\hbar} \right|^2 \left\{ [2\eta_n + 1](-1 + \cos \omega_n t) - i \sin \omega_n t \right\} \]

and

\[ n_n = (\hbar \omega_n / \sqrt{\gamma} - 1)^{1/2}. \]

The electron-hole pair result is just the zero temperature limit of this expression.

Consider now the average energy transfer. This is given by the first moment of the distribution \( \langle P(\Delta \omega) \rangle \). We can evaluate this using Eqs. (9), (10), and (11):

\[ \langle \Delta \omega \rangle = \int \frac{1}{\eta} \omega_n \left\langle \hat{I}_n \right\rangle^2 . \]

Note that if \( \hat{I}_n \) is independent of the surface temperature, then the average energy transfer is independent of the surface temperature. This is the case for the switching functions \( F(\eta, \tau) \) used in the previous work, and it will also be the case when we make a TDH separation using eigenstate initial states.

III. THE TIME-DEPENDENT HARTREE APPROXIMATION

We use a time-dependent Hartree formulation to effect a self-consistent separation of the Schrödinger equation for the Hamiltonian equation (1), into an atom part and a surface part. In this section we briefly present the equations of the TDH approximation. The full derivation of the approximation can be found in the paper of McLachlan.8

Consider the Hamiltonian for two systems coupled by a potential

\[ H = H_A + H_B + V . \]

The TDH wave function has the form

\[ \psi(t) = \psi_A(t) \psi_B(t) e^{i\mathcal{H}t}, \]

where \( S(t) \) is a real valued function of the time, \( \psi_A(t) \) and \( \psi_B(t) \) are calculated by self-consistently solving the two Schrödinger equations

\[ i \hbar \frac{\partial \psi_A(t)}{\partial t} = (H_A + \langle \psi_B(t) \mid V \mid \psi_B(t) \rangle) \psi_A(t) \]

and

\[ i \hbar \frac{\partial \psi_B(t)}{\partial t} = (H_B + \langle \psi_A(t) \mid V \mid \psi_A(t) \rangle) \psi_B(t) . \]

\( S(t) \) is given by

\[ S(t) = -\frac{1}{\hbar} \int_{t_0}^{t} d\tau \langle \psi_A(\tau) \psi_B(\tau) \mid V \mid \psi_A(\tau) \psi_B(\tau) \rangle . \]

It is important to keep in mind that the TDH approximation only conserves energy on the average. That is to say, at self-consistency, the expectation value of the
total Hamiltonian with respect to the TDH wave function is a constant of the motion. In the language of Sec. II, at self-consistency, the first moment of $P(\Delta \omega)$ will equal the energy loss in the atom trajectory. This is the criterion we use to evaluate the self-consistency of our semiclassical calculation.

Consider the application of the TDH approximation to the Hamiltonian equation (1). We seek wave functions of the form

$$\psi_{TDH}(r, q^N, t) = \psi_s(r, t) \psi_q(q^N, t) e^{-i/\hbar H_{TDH}}.$$  (20)

The wave function $\psi_s(r, t)$ obeys the equation

$$i\hbar \frac{\partial}{\partial t} \psi_s(r, t) = \left[ \frac{p^2}{2M} + V_0(z) + \sum_n F(\eta_n, z) B_n(\alpha_n + a^*_n) \right] \psi_s(r, t) = H_0(t) \psi_s(r, t),$$  (21)

where we have defined

$$\langle Q^{TDH}_s | \psi_{TDH}(t) \rangle = \langle Q | \psi_{TDH}(t) \rangle.$$  (21a)

The wave function $\psi_q(q^N)$ obeys the equation

$$i\hbar \frac{\partial}{\partial t} \psi_q(q^N, t) = \left[ \sum_n F(\eta_n, z) B_n(\alpha_n + a^*_n) \right] \psi_q(q^N, t) = H_{so}(t) \psi_q(q^N, t),$$  (22)

where

$$\langle \{ \Omega \}^{TDH}_q | \psi_{TDH}(t) \rangle = \langle \{ \Omega \} | \psi_{TDH}(t) \rangle.$$  (22a)

We have already shown that subject to a choice of $\langle F(\eta_n, z) \rangle_{TDH}^2$, Eq. (23) is exactly soluble. Thus we can write down the surface Hamiltonian wave function:

$$\psi_s(t) = e^{-i\phi(t)} \exp \left[ -i/\hbar \sum_{\eta} \int_{t_0}^t dt' B_{\eta} \langle F(\eta, z) \rangle^2_{TDH} \right] \psi_s(t_0),$$  (24)

where

$$\phi(t) = \frac{1}{\hbar} \sum_{\eta} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' B_{\eta} \langle F(\eta, z) \rangle^2_{TDH} \sin \omega_n(t_1 - t_2).$$  (25)

and

$$I_n(t) = \int_{t_0}^t dt' B_{\eta} \langle F(\eta, z) \rangle^2_{TDH} e^{-i\omega_n(t_1 - t_2)}.$$  (26)

We can now evaluate the surface expectation value in Eq. (21). Expanding the expression for $\langle \psi_s | a^{*}_{\eta} + a_{\eta} | \psi_s \rangle$ as a sum of successively higher order commutators, we find that the first commutator is a $c$-number and therefore all high order commutators are zero. Thus,

$$\langle a^{*}_{\eta} + a_{\eta} \rangle_{TDH} = \langle a^{*}_{\eta} | a^{*}_{\eta} \rangle_0 + \frac{i}{\hbar} \langle I_{\eta}(t) - I_{\eta}(t) \rangle_{TDH},$$  (27)

where

$$\langle a^{*}_{\eta} \rangle_0 = \langle \psi_s(t_0) | \exp \left[ i/\hbar \int_0^t dt F(\eta, z) B_{\eta}(a_{\eta} + a^{*}_{\eta}) \right] \psi_s(t_0) \rangle \langle \psi_s(t_0) | \psi_s(t_0) \rangle.$$  (28)

Finally, we can write down our general form for $H_a(t)$ as

$$H_a(t) = \frac{p^2}{2M} + V_0(z) + \sum_{\eta} \frac{i}{\hbar} \int_{t_0}^t dt' B_{\eta} \langle F(\eta, z) \rangle^2_{TDH} \langle I_{\eta}(t') - I_{\eta}(t') \rangle_{TDH} \langle \psi_s(t) | \psi_s(t) \rangle.$$  (29)

$H_a(t)$ is given by Eq. (23).

IV. SOLUTION OF THE TDH EQUATIONS, CONSIDERATION OF THE INITIAL CONDITIONS

In this section $H_{so}(t)$ and $H_a(t)$ are studied for two sets of initial conditions, then the average energy transfer is examined and a way of calculating this quantity is proposed that is energetically self-consistent throughout the atom trajectory.

The first case we consider is that of the atom initially in an eigenstate of $H_{so}$ and the incident atom initially in a wave packet state. That is to say, we choose

$$\psi_s(t_0) = \exp \left[ -i/\hbar H_{so} t_0 \right] |n_1 \cdots n_N \rangle,$$  (30)

each surface mode in an eigenstate at $t = t_0$. Likewise, the particle initial state is

$$\psi_q(t_0) = \exp \left[ -i/\hbar H_{so} t_0 \right] \int d\kappa A(\kappa) e^{i\kappa \tau}.$$  (31)

We discuss the approximation first within the context of a fully quantum mechanical calculation in order to show that the problems with temperature dependence occur because of the TDH separation and not as a result of a semiclassical solution of the TDH equations. We note in this regard, that the separation of the problem used in the previous calculations is tantamount to assuming a product wave function. Hence their solution can be no better than a TDH solution, since the TDH wave function is derived with a variational principle.

We have defined our interaction to be a function only of the distance, $z$ from the surface, so we will only need to consider the $z$ component of the wave function $\psi_s(t)$. Then, since for this initial state $(a^{*}_{\eta}(t) + a_{\eta}(t))_0 = 0$, the TDH Hamiltonian for the incident atom becomes

$$H_a(t) = \frac{p^2}{2M} + V_0(z) - \sum_{\eta} \frac{2}{\hbar} F(\eta, z) B_{\eta}^2 \int_0^t \langle F(\eta, z) \rangle^2_{TDH} \sin \omega_n(t - \tau) d\tau.$$  (32)

Notice that $\langle F(\eta, z) \rangle^2_{TDH}$ was chosen to be real, in which case

$$I_n(t) = I_{n}^2(t) = 2iB_{\eta} \int_0^t d\tau \langle F(\eta, z) \rangle^2_{TDH} \sin \omega_n(t - \tau).$$  (33)

The surface Hamiltonian is still given by Eq. (23). Notice at this point that this atom Hamiltonian is independent of the choice of surface eigenstate. Every initial surface eigenstate, (or more importantly an ensemble of atom-surface systems), produces an atom trajectory that is only a function of the atom initial condition.

Consider next the case where the atom is initially in a wave packet state, and the surface initial state is

$$\psi_s(t_0) = \exp \left[ -i/\hbar H_{so} t_0 \right] [g^{(1)}(y_1) \cdots g^{(1)}(y_N) \cdots g^{(N)}(y_N)],$$  (34)

That is to say, each surface mode is initially in a Glauber wave packet state. In what follows, $j$ labels the initial condition and $\eta$ labels the mode. Glauber states are Gaussian wave packets that have the property

$$\langle a_{\eta} | g^{(N)}(y_\eta) \rangle = \sigma_{\eta j} \langle g^{(N)}(y_\eta) \rangle.$$  (35)
where \( \alpha_n \) is a complex number.

If we define

\[
\alpha_n = \frac{1}{\omega_n} \exp(i \theta_n)
\]

and

\[
Q_n = \frac{e^2}{2} \theta_n \left( g^{(i\omega)}(y) \right) \left[ a_n^\dagger(t) + a_n(t) \right] g^{(i\omega)}(y)
\]

we can rewrite Eq. (29) as

\[
H_n(t) = \frac{p^2}{2m} + V_0(z) + \sum_\eta F(\eta, z) \eta_0 \sin(\omega_n t + Q_n)
\]

and the change in energy is given by the expression

\[
\Delta E_n = \sum_\eta \hbar \omega_n \left( a_n^\dagger a_n \right)_{TDH} - \left( a_n^* a_n \right)_0 .
\]

We can calculate \( \langle a_n^\dagger a_n \rangle_{TDH} \) directly using Eq. (24),

\[
\langle a_n^\dagger a_n \rangle_{TDH} = \langle a_n^* a_n \rangle_0 + \frac{i}{\hbar} \left| \psi_n(t_0) \right| \exp \left[ -(i/\hbar) H_n t_0 \right]
\]

and recalling the definition we used to obtain Eq. (36):

\[
\Delta E_n = \sum_\eta \frac{\omega_n}{\hbar} p^2 \left[ \int_0^t d\tau \left( F(\eta, z) \right)_{TDH} e^{-i\omega_n \tau} \right]^2 ,
\]

which can be compared to our previously derived value [Eq. (14)] to verify our general formula.

The surface energy change with the wave packet initial condition equation (34), can also be calculated. Using Eq. (34) in Eq. (39) we can derive after some algebra and recalling the definition we used to obtain Eq. (36):

\[
\Delta E_n = \sum_\eta \frac{\omega_n}{\hbar} p^2 \left[ \int_0^t d\tau \left( F(\eta, z) \right)_{TDH} e^{-i\omega_n \tau} \right]^2 \left( \frac{8\omega_n^2}{\hbar^2} \right) \int_0^t d\tau \left| \alpha_n \right| \left( \langle F(\eta, z) \rangle_{TDH} \cos(\omega_n t + Q_n) \right) .
\]

It is a formal result of the TDH theory, and we explicitly show\(^{11}\) elsewhere that the solution of Schrödinger's equation for \( H_n(t) \) gives the same average energy change, (though of course, with opposite sign).

We can now make a few observations. If the atom trajectory, (and hence \( \langle F(\eta, z) \rangle_{TDH} \), is independent of the surface initial condition, then the thermally averaged energy transfer will be independent of the surface temperature. This is obvious for the eigenstate formula equation (40). Notice that in the wave packet formula, the thermal average will produce an unweighted sum over \( Q_n \). Thus the last term will vanish. Examination of the eigenstate atom Hamiltonian equation (32), reveals that the atom trajectory will have no surface initial state dependence since the Hamiltonian itself has no dependence on the surface initial state. Thus a fully self-consistent TDH solution using eigenstates as initial states will never give a temperature dependent average energy transfer.

The wave packet initial state atom Hamiltonian equation (37), does depend on the surface initial state and therefore the thermally averaged energy transfer will have a temperature dependence. This observation and the comments made in the previous paragraph prompt a further observation. For temperatures above absolute zero, it is inappropriate to calculate energy transfer using this kind of semiclassical solution and a single representative atom trajectory (or switching function). The correct result includes many trajectories in the expression for the average energy transfer.

In summary, we have derived the TDH equations for our Hamiltonian equation (1), and calculated the average energy transfer in terms of \( \langle F(\eta, z) \rangle_{TDH} \). \( \langle F(\eta, z) \rangle_{TDH} \) is the only quantity that we must evaluate in a self-consistent fashion. We have manipulated our equations so that we can determine \( \langle F(\eta, z) \rangle_{TDH} \) by self-consistently solving the Schrödinger equation for \( H_n(t) \), given by either Eq. (32) or Eq. (37), alone. We have chosen our atom initially to be in a wave packet state. It is well known\(^{12}\) that under a set of restrictive assumptions, a wave packet will tend to follow the laws of classical mechanics. We will now show that if we solve Hamilton's equations self-consistently using either form for \( H_n(t) \) and then identify the classically calculated \( \langle F(\eta, z) \rangle_{TDH} \), we will get a trajectory for the incident atom that has the property that the sum of the classical energy of the atom and the expectation value of the energy of the surface perturbed by \( F(\eta, z(t)) \) is constant throughout the trajectory. That is to say, if we use total energy as our criterion, we have a self-consistent solution of the TDH equations.

Consider a classical point particle with Hamiltonian, \( H_n(t) \). Applying Hamilton's equations to Eq. (32) (eigenstate initial conditions) gives

\[
\dot{z}(t) = \frac{p(t)}{M} ,
\]

\[
\dot{p}(t) = \left[ \frac{\partial F(z(t))}{\partial z(t)} - \sum_\eta \frac{2}{\hbar} \frac{\partial F(z(t))}{\partial \omega_n(t)} \right] \int_0^t d\tau F(z(\tau)) \sin \omega_n(t - \tau) .
\]

Take the time derivative of the Hamiltonian \( H_n(t) \), [Eq. (32)]
then insert Eqs. (42) and (43) into Eq. (44) and integrate with respect to time

$$\Delta E_n(t) = -\sum_{r}^{\infty} B_r^2 \omega_n \int_{t_0}^{t} d\tau F(\eta, z(\tau)) e^{-i\omega_n \tau} \right|^2. \quad \text{(45)}$$

Comparing this to Eq. (40) verifies that indeed the requirement of conservation of energy has been satisfied if we identify $F(\eta, z(t))$ with $\langle F(\eta, z) \rangle^{\mathrm{TDN}}$.

A similar derivation goes through in just the same fashion for the wave packet initial state Hamiltonian, Eq. (37). We reiterate that what this shows is that this semiclassical approach makes sense. Energy is conserved not only between initial and final states but also at all times throughout the collision.

Finally, we must solve the classical equations of motion for a point particle with Hamiltonian $H_a(t)$. This corresponds to the self-consistent determination of $F(\eta, z(t))$. We calculate $F(\eta, z(t))$ with a successive approximations scheme.

More explicitly, we label the calculated trajectory $z_1(t)$. Then $z_{1+1}(t)$ is calculated by using (for example in the eigenstate initial state Hamiltonian)

$$H_a(t) = \frac{p^2}{2m} + V_0(z) - \sum_{r}^{\infty} \frac{2}{r} B_r^2 F(\eta, z) e^{-i\omega_n \tau} \int_{t_0}^{t} \int_{t_0}^{t} \left. d\tau F(\eta, z(\tau)) \sin \omega_n (t - \tau) \right| \right|^2. \quad \text{(46)}$$

That is to say, we use $z_1(t)$ in $H_a(t)$, then we calculate $z_{1+1}(t)$ using this assumed $H_a(t)$. If we choose the zeroth-order trajectory to be an elastic trajectory with Hamiltonian $H_a$ [Eq. (2)], we can view the earlier solution (Sec. II) as the zeroth order calculation in a hierarchy of approximations. In the next section the equations for a particularly simple choice of $F(\eta, z)$ and $V_0(z)$ are solved and it is demonstrated that at least for this simple problem the successive approximations scheme converges.

V. SAMPLE CALCULATION

For our sample calculation, we choose

$$V_0(z) = V_{00} \cdot \left[1 - \theta(z) \right], \quad \text{(47)}$$

$$F(\eta, z) = -F_{10} \cdot \left[1 - \theta(z - z_0) \right]. \quad \text{(48)}$$

This corresponds to Gadzuk and Metiu's sudden switching limit.

Consider first the calculation of trajectories with the eigenfunction initial state Hamiltonian. In this case $H_a(t)$ is given by Eq. (32). The zeroth order trajectory corresponds to specular scattering off the hard wall at $z = 0$. The zero of time is defined to be that time when the particle is at the wall, i.e., $z(t = 0) = 0$. Then on the zeroth order trajectory the particle is at $z = z_c$ for $t = \pm \tau_c$. This defines $\tau_c$.

We can now perform the integrals in Eq. (32) to obtain the first iteration atom Hamiltonian:

$$H_a(t) = \frac{P^2}{2M} + V_0(z) - \sum_{r}^{\infty} \frac{2}{r} B_r^2 F(\eta, z) \int_{t_0}^{t} \int_{t_0}^{t} \left. d\tau F(\eta, z(\tau)) \sin \omega_n (t - \tau) \right| \right|^2. \quad \text{(49)}$$

This Hamiltonian describes the classical motion of a particle in a square well potential whose depth oscillates up and down. By Newton's second law, the particle may only accelerate when the first derivative of the potential is nonzero. There are only two places where that occurs. The first is at $z = 0$ where an essentially infinite hard wall elastically scatters the particle. The other place is at the entrance to the interaction region ($z = z_c$). Therefore, we can derive the change in kinetic energy of the particle simply by knowing the well depth at the times when the particle is at $z_c$.

Thus, the only important times for the Hamiltonian [Eq. (49)] are odd multiples of $\tau_c$, because these are the times when the particle encounters the edge of the interaction region. Note that at $t = -\tau_c$, the particle enters the interaction region, but the oscillating term in the Hamiltonian is zero:

$$H_a(-\tau_c) = \frac{P^2}{2M} + V_0(z). \quad \text{(50)}$$

Therefore, the particle does not accelerate as it enters the interaction region. The transit time, defined as the time required for the particle to travel from $z = z_c$ to $z = 0$ and back to $z = z_c$ again, is still $2\tau_c$. At time, $t = \tau_c$, the particle either escapes or it bounces back. If the particle bounces back, then in this iteration it is trapped, since

$$H_a(t = \tau_c) = H_a(\tau_c). \quad \text{(52)}$$

If we use our first order trajectories and Eq. (32), it
is easy to see that the escaping trajectories give back Eq. (49) and hence are unchanged throughout any subsequent iteration procedures. Therefore, we will only consider the trapped trajectories.

Using the trapped trajectories we input in Eq. (32) gives

\[ H_e(t) = \frac{P_e^2}{2M} + V_0(z) \]

\[ -2 \sum_n \frac{\epsilon_n^2}{2} F_n(z) \left[ -F_n \right] \frac{1}{\omega_n} \left[ 1 - \cos \omega_n \left( t + \tau_e \right) \right], \quad t \leq -\tau_e. \]

(53)

Again, we get the result that at time \( t = -\tau_e \), the particle enters the interaction region but does not accelerate. Therefore, the only important times are still the odd multiples of \( \tau_e \). After \( N \) bounces off the hard wall, the particle approaches the boundary of the interaction region at \( t = (2N - 1)\tau_e \). At that time, the barrier the particle must surmount to escape is

\[ \Delta E^*_{s} = 2 \sum_n \frac{\epsilon_n^2}{2} F_n(z) \frac{1}{\omega_n} \left[ 1 - \cos 2N\omega_n \tau_e \right]. \]

(54)

So, if the particle escapes after \( N \) bounces, then this result gives the self-consistent change in energy for the trajectory. This includes the one bounce results calculated earlier. Note that recycling an \( N \) bounce, escaping trajectory into Eq. (32) gives a different \( H_e(t) \), but regenerates the same \( N \) bounce, escaping trajectory.

Consider now the sum on states. We can evaluate the sum on states for the electron-hole model of Gadzuk and Metiu, by replacing the sum with an integral over a density of states and (as in Gadzuk and Metiu) making \( B_n \) and \( F_n \) independent of \( \eta \) for \( \omega_n \) less than a cutoff \( \omega_c \).

For the electron-hole pair model the density of states is given by

\[ \rho(\epsilon) \approx \rho_{\text{ph}} \epsilon. \]

(55)

Then evaluating the integral gives

\[ \Delta E^*_{s} = 2B^2 F^2 \rho^2_{\text{ph}} \epsilon_c \left[ \frac{1}{\omega_c} \sin \frac{2N\omega_c \tau_e}{2N\omega_c \tau_c} \right], \]

(56)

where \( \epsilon_c = \hbar \omega_c \).

This formula illustrates the dephasing time for surface excitations. For \( \tau_e \) much greater than \( 1/\omega_c \), the \( \sin \pi/\tau \) term decays away, even for \( N = 1 \), and \( \Delta E^*_{s} \) becomes

\[ \Delta E^*_{s} = 2B^2 F^2 \rho^2_{\text{ph}} \epsilon_c. \]

(57)

We could repeat the iteration process for the wavepacket Hamiltonian and in general, it would require \( M \) interactions to generate an \( M \) bounce self-consistent trajectory. Alternatively, we can write down a Hamiltonian that generates all the self-consistent trajectories.

Consider the Hamiltonian generated by a trajectory with any atom initial condition (which determines \( \tau_e \)) but artificially constrained to be a trapped trajectory. This Hamiltonian is

\[ H_e(t) = \frac{P_e^2}{2M} + V_0(z) + 2 \sum_n F(\eta, z) B_n \left[ \sigma_j n \right] \left[ \sin \omega_n t + Q_n \right], \]

\[ -2 \sum_n \frac{\epsilon_n^2}{2} F_n(z) \left[ -F_n \right] \frac{1}{\omega_n} \left[ 1 - \cos \omega_n (t + \tau_e) \right], \quad t > -\tau_e. \]

(58)

The incident atom enters the interaction region at \( t = -\tau_e \) and the last term in Eq. (58) is zero, as before. However, the presence of the second term in \( H_e(t) \) means that the atom will experience a force as it enters the region. Thus the transit time will now be \( \tau_e + \frac{\omega_e}{\omega_c} \). After \( M \) bounces off the hard wall at zero, the atom will arrive at \( \tau_e \) at time, \( t = M\tau_e + (M - 1)\tau_e \). At that time it will see a barrier to escape which height is

\[ \Delta E^*_{s} = 2 \sum_n F_n B_n \left[ \sigma_j n \right] \left[ \sin \omega_n (M\tau_e + (M - 1)\tau_e) + Q_n \right] \]

\[ + 2 \sum_n \frac{\epsilon_n^2}{2} F_n(z) \frac{1}{\omega_n} \left[ 1 - \cos \omega_n (M\tau_e + \tau_e) \right]. \]

(59)

Thus if the particle initial energy plus the energy change upon entering the interaction region is greater than \( \Delta E^*_{s} \), the particle will escape and lose an amount of energy \( \Delta E^*_{s} \). The total energy change for an \( M \) bounce, escaping trajectory is

\[ \Delta E_e = 2 \sum_n F_n B_n \left[ \sigma_j n \right] \left[ \sin \omega_n (M\tau_e + (M - 1)\tau_e) + Q_n \right] \]

\[ - \sin \omega_n (M\tau_e + (M - 1)\tau_e) + Q_n \]

\[ - 2 \sum_n \frac{\epsilon_n^2}{2} F_n(z) \frac{1}{\omega_n} \left[ 1 - \cos \omega_n (M\tau_e + \tau_e) \right]. \]

(60)

This is the main result for the wavepacket initial state Hamiltonian. \( M \) is determined, as before, by finding the smallest \( M \) such that the incident energy, \( \epsilon_i \), is greater than \( \Delta E(M) \).

It is clear that recycling these trajectories will yield a different \( H_e(t) \), but solving the new \( H_e(t) \) will give back the same trajectory again. Notice that even after the second term has decayed away, there is still a possibility for escape if we have included the possibility of thermal desorption as well. This behavior is not present in the eigenstate initial state Hamiltonian.

Finally, consider the application of these results to the calculation of sticking probabilities. There are two main issues to be addressed here. The first is how to define the sticking probability itself. The second issue is to determine how many times the particle must bounce in the well before the energy in the surface dephases and we can view the particle as bound.

In the previous semiclassical calculations, the sticking probability was defined as the integral of \( \langle P(\Delta \omega) \rangle \) from \( \epsilon_i \), the incident atom's initial energy to infinity

\[ P_s(\epsilon_i) = \int_{\epsilon_i}^{\infty} d\Delta \omega \langle P(\Delta \omega) \rangle. \]

(61)

We use an alternate, quasiclassical definition that is more consistent with our emphasis on the atom's trajectory and averaged quantities. We define the sticking probability to be the ratio of the number of trajectories that are trapped to the total number of trajectories.

Now consider the second issue put forward above. This requires the comparison of two time scales: (1) the time required for the energy in the surface to dephase, and (2) the transit time. The characteristic time scales for dephasing of the surface excitations are given by the quantities, \( \omega_e \) and \( \omega_c \), (the electron-hole pair cutoff and the Debye frequency). A typical value for \( \hbar \omega_c \)
is 3–7 eV. This implies a dephasing time of $10^{-18}–10^{-16}$ s. A typical value for $\omega_p$ is $4 \times 10^{14}$ Hz, \(1\), (i.e., Pt), which corresponds to a dephasing time of around $10^{-15}$ s. A 300 K particle of mass number 40 has a velocity of $3 \times 10^{12}$ A/s.

Thus, we see that for $x_e < 1$ Å, the electron-hole sticking probability ($T = 0$) is given by the probability of the particle bouncing back once. We then get a simple result for the sticking probability as a function of the particle’s initial energy. The sticking trajectories are all those trajectories for which the initial energy $E_i$ obeys the following inequality:

$$E_i < 2B^2F^2\rho_i^2\epsilon_e = E_{\text{crit}}. \quad (62)$$

Those trajectories for which

$$E_i > 2B^2F^2\rho_i^2\epsilon_e = E_{\text{crit}}, \quad (63)$$

are escaping trajectories.

Gadzuk and Metiu have estimate the magnitude of the quantity $2\rho_i^2B^2F^2$ for a curve crossing model. This quantity is their singularity exponent $\sigma$. They estimate $\sigma$ to be approximately $0.025 – 0.15$. This corresponds to a value of $E_{\text{crit}}$ between 500 and 12 000 K, (for $\epsilon_e$ between $3–7$ eV).

In the phonon model $1/\omega_p$ and $\tau_e$ are of the same order of magnitude. We must therefore calculate trajectories and evaluate $M$ (the number of bounces), as a function of $\alpha$, $Q$, and $\tau_e$. If we assume that the surface temperature is low enough so that once the last term in Eq. (59) has decayed away the particle is bound, we can calculate a sticking probability as

$$P_s(T, \tau_e) = \frac{\langle \theta(M(\alpha, Q, \tau_e) - M_0) \rangle}{\langle \theta(M(\alpha, Q, \tau_e)) \rangle}, \quad (64)$$

where $T$ is the temperature, $M_0$ is some suitably large integer and $\theta$ is a step function. Using this same notation of a cutoff for $M(\alpha, Q, \tau_e)$, we can calculate the average energy of the scattered particles as

$$\langle E_s \rangle = \frac{\langle (E_i + \Delta E_s)(1 - \theta(M - M_0)) \rangle}{\langle \theta(M(\alpha, Q, \tau_e)) \rangle}, \quad (65)$$

where $\Delta E_s$ is given by Eq. (60). The cutoff in $M$ is used to prevent divergences due to the presence of trapped trajectories.

VI. SUMMARY AND DISCUSSION

In summary, we have shown that a self-consistent semiclassical calculation can be performed for the boson Hamiltonian of Eq. (1). The general equations for such a procedure were derived, and then solved for a very simple model.

Our result for the sudden switching, electron-hole pair model is that the zero temperature sticking probability is essentially unity. We note however, that the values of all the parameters used were only approximate and if the net error was an order of magnitude, we could obtain an $E_{\text{crit}}$ between 60 and 1200 K.

Another effect will also reduce $E_{\text{crit}}$. If the interaction potential is not a square well but instead has a tail, then the particle will accelerate as it enters the interaction region at $t = -\tau_e$. If the tail is not too long, the transit time will still be of the order of $\tau_e$, thus the barrier height will still be given by Eq. (57) and the new $E_{\text{crit}}$ will be

$$E_{\text{crit}} = \Delta E_s - \Delta E_{1s}, \quad (66)$$

where $\Delta E_{1s}$ is the energy the particle gained entering the well. In the near sudden regime this effect will be of order $(\tau_{\text{switch}}/\tau_{\text{transit}})$ (the ratio of the switching time to the transit time). $\tau_{\text{switch}}$ is defined as the time the particle spends in a region where the gradient of the potential is nonzero.

For temperatures greater than absolute zero (i.e., for a phonon model), the semiclassical procedure works best with a wave packet initial state. The TDH atom Hamiltonian for such an initial state is given by Eq. (37). It is clear that our self-consistent semiclassical calculation does not supplant the classical GLE calculations mentioned earlier. The calculation of a trajectory using this form for $H_s(t)$ contains all the difficulties of a completely classical solution of the equations of motion for the full Hamiltonian, Eq. (1).

Our results for the zero temperature, sudden limit sticking probabilities compare directly with the calculation of Gadzuk and Metiu, \(a\) and are in good agreement with their results. The following trends are observed: (1) as $\rho_i^2B^2F^2$ increases, the integrated sticking probability increases; in fact, our integrated sticking probability has the same value as theirs to leading order in $\alpha = 2\rho_i^2B^2F^2$:

$$\int_0^{\infty} P_s(E_i) dE_i = 2\rho_i^2B^2F^2\epsilon_e, \quad (67)$$

where $P_s(E_i)$ is the sticking probability for an incident atom with initial energy $E_i$; (2) as $E_i$ becomes large, the sticking probability goes to zero, and (3) as $E_i$ goes to zero, the sticking probability goes to one.

The main qualitative disagreement between our results and those of Gadzuk and Metiu is in the shape of $P_s(E_i)$, and in particular in the existence of a step discontinuity in our function, which is not present in theirs. This is clearly a result of the quasiclassical nature of our definition of sticking probability and would not be present in a fully quantum mechanical solution of the TDH equations. We chose a quasiclassical definition because it only required knowledge of the self-consistent quantity, the average energy transfer.

The purpose of these zero temperature, electron-hole pair calculations is to determine whether or not there are circumstances where the zero gap continuum of electronic excitations will play an important role in the dissipation of the translational energy of the incident atom, that is to say, whether $P_s(E_i)$ is between 0.1 and 1.0 or whether it is much less than 0.1. With regard to this point our calculation is in complete agreement with that of Gadzuk and Metiu. We find that the electronic excitations can play an important role, and that the decisive factor is what Gadzuk and Metiu call the singularity exponent, $\alpha = 2\rho_i^2B^2F^2$.

To conclude, the work that has been presented here is complementary to the previous studies of atom-surface scattering that used the Hamiltonian equation (1). The
previous studies concentrated on obtaining a surface quantity $P(\Delta \omega)$. We have concentrated on properties of the incident atom as described by the self-consistent trajectories. These self-consistent trajectories can also be used to obtain improved distribution functions $P(\Delta \omega)$.

6(a) J. W. Gadzuk and H. Metiu, Phys. Rev. B 22, 2603 (1980);
8A. Messiah, Quantum Mechanics (North Holland, Amsterdam, 1961), Vol. I.