Theory of nonadiabatic gas–surface reactions

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A theoretical description of near-resonant charge-exchange processes occurring in gas–surface collisions is presented. The diatomics in molecules method is used for the electronic description of a surface consisting of five atoms. The gas–surface interaction potentials and couplings are obtained with the polyatomics in molecules approach. Trajectories for the "nuclear" variables and transition probabilities are calculated with the common eikonal formalism. Preliminary results are presented for Na scattering from a W(110) surface. The initial kinetic energy of the sodium atom is varied between 5 and 60 eV and its trajectory is restricted to be perpendicular to the surface and striking the center W atom. The results show a noticeable probability (<20%) for electron transfer to the surface.

I. INTRODUCTION

Many surface science experiments that are currently being performed employ as a probe a beam of ions, neutral atoms, electrons, or photons. These experiments give information about the topology and electronic properties of the surface, the amount of impurities present, and the configuration and bonding energies of adsorbed particles. For example, ion scattering spectrometry (ISS) experiments[1] target an energetic beam of ions at the surface and analyze the surviving ions as a function of the beam's incident angle and energy and the crystal orientation. Analyzing the backscattered ions' energy, angular distributions, and intensity gives information about the makeup and topology of the target. Neutralization of the ions that occur by Auger processes result in the production of secondary electrons emitted from the surface. Measuring the electron's energy distribution, as is done in ion neutralization spectrometry (INS) experiments,[2] gives information about the electronic band structure of the surface. In secondary ion mass spectrometry (SIMS) experiments,[3] an energetic beam of ions bombards the surface. The beam transfers energy to the target resulting in secondary collisions that cause the ejection of atoms or molecules from the solid. The energies, angular distributions, and intensities of the sputtered particles provide information about the surface structure and the adsorption sites and configurations of adsorbed particles. Electron stimulated desorption (ESD) experiments[4] use an incident beam of electrons. The difference here is that the electrons transfer electronic, not kinetic energy to the particle that desorbs so that the positions and momenta of the nuclei are initially undisturbed. The angular distributions of the desorbed particles are directly related to their binding geometry and can give information about the importance of surface steps or roughness in surface catalysis.

A common feature in these experiments is the occurrence of reactions at or near the surface that involve transfers of electrons or transitions between electronic states. In ISS or INS, the electron transfer takes place between the incident ion and the target. In SIMS, the transfer is between the sputtered particle and the surface. In ESD, the electron beam induces electronic excitations in the adsorbed particles which causes the desorption of positive or negative ions, neutrals, or metastables. The transfer of more than one electron is possible.

It is clear that, in order to relate the data obtained in these experiments to the fundamental properties of the system being studied, it is necessary to have a basic understanding of the nonadiabatic processes discussed above. Nonadiabatic simply means that more than one electronic state (netural, ionic, excited) is necessary to describe the system. In order to describe the experimental ion intensities, it is necessary to determine the probability of electron transfer. Also, since many experiments show marked azimuthal anisotropies in the intensities, the probability must take into account the structure of the surface. In short, this is a complex problem but its solution is essential to the understanding of the experimental results.

A number of theories have been developed to help interpret these experiments. Generally they concentrate on describing either the motion of the nuclei or the probability of electronic transitions while a few attempt to do both. In order to give a feeling for this subject, the previous work is briefly discussed.

A theoretical method that has been rather useful for describing ISS[5] and SIMS[6] experiments is the classical dynamics approach. Here the emphasis is on following the nuclear motion so that the evolution of the positions and momenta are determined by classical equations of motion. This method has been able to reasonably describe the energy and angular distributions from SIMS experiments.[7] However, this treatment in its pure form is not capable of describing the evolution of the electronic states of the systems.

Changes in the electronic state of the system are caused by a variety of processes. Auger neutralization and de-excitation processes involve more than one electron and have been theoretically described by Hagstrum.[8,9] The formalism is suited for describing low energy ISS or INS experiments. Even though these processes fulfill our nonadiabatic definition they have been called adiabatic processes because there

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is little exchange of energy between the nuclear and electronic motions. An alternative formulation of the processes has been given by Blandin, Nourtier, and Hone and Bloss and Hone,[10] and Brako and Newns[11] where they base their formalism on the time dependent Anderson type Hamiltonian.

The experiments by Erickson and Smith[12] which showed an oscillatory behavior in the He^+ intensity scattered off Pb, Ge, Bi, and In surfaces suggested another mechanism for charge exchange. This behavior as a function of the initial kinetic energy of the ion is similar to that noted in gas phase ion–molecule scattering[13] and has been termed near-resonant charge-exchange processes. This has been observed in ion–surface scattering when the ionization energy of the ion lies within a few electron volts of the d band of the surface. Tully[14] has given a unified treatment that includes both the adiabatic processes (Auger and resonant neuturalization) and nonadiabatic processes (near-resonant charge-exchange). Of interest is his characterization of the initial electronic state as either continuous or discrete in nature. The initial state of an ion scattering from a surface belongs to the continuum whereas the initial state corresponding to an atom scattering from a surface can be thought of as a discrete state embedded in a continuum. This is not difficult to understand if one considers a proton vs a hydrogen atom scattering from the surface. The initial state of the proton surface would simply be the initial electronic state of the surface since there are no electrons on the proton. The surface electrons have energies that belong to energy bands so that its eigenfunctions are members of a continuum. The hydrogen atom however does have an electron that has a discrete eigenvalue. Therefore, the electronic state of the hydrogen-surface system can be considered to be a discrete state that is embedded in a continuum. We will return to this point later.

Nonadiabatic processes also occur in the sputtering of particles from a surface (SIMS experiments). There have been a number of theoretical treatments of this including the work by Norskov and Lundqvist,[15] Sroubek,[16] and Lang.[17] The developments by Sroubek and Lang are based on the Anderson type Hamiltonian and a study of the variation of the parameters needed in this formalism has recently been done.[18]

The above discussion is not meant to be either detailed or complete. Rather it is intended to provide a feeling for the types of mechanisms and experiments involving nonadiabatic processes. A much more detailed discussion can be found in Ref. 19. The developments here will focus on systems exhibiting near-resonant charge-exchange and it is assumed that charge exchange caused by Auger transitions can be neglected. In particular, the low energy scattering of sodium atoms from a W(110) surface is treated. This system has been experimentally studied by Overbosh et al.[20] Since the ionization energy of sodium is close to the work function of tungsten, it is expected that charge transfer should be dominated by near-resonant charge-exchange processes.

There are three main problems that are inherent in the treatments mentioned above that will be addressed. The first involves the electronic representation. Although some of the treatments (Tully, Sroubek) have been formally done in the molecular orbital (MO) representation, there has not been much advancement made in obtaining these orbitals. It will be demonstrated that it is possible to construct these orbitals which also leads to well defined gas–surface interaction potentials. The second problem involves the construction of the coupling matrix element or hopping integral. These, in most treatments, are assumed to have a certain form (exponential, Gaussian, etc.) whose parameters are chosen rather arbitrarily. Since in the treatment presented here the MO's are well defined, so also are the couplings between the MO's, so that a variety of assumptions need not be made. These first two problems will be the subject of Sec. II. The third problem focuses on the nuclear trajectories. In the approaches described above one must assume what the nuclear trajectories are. Whether they are assumed to follow straight lines or obey classical equations of motion via certain forces, the transition amplitudes will depend on what these assumptions are. Instead, a procedure developed by Micha[21] and applied to ion–molecule reactions[22] that is based on using a common eikonal will be used. The advantage in this approach is that both the nuclear "variables" and transition amplitudes are obtained self-consistently so that assumptions about the nuclear trajectory are not needed. This is treated in Sec. III. Section IV presents some preliminary results and the paper closes with a discussion in Sec. V.

II. SURFACE CHARACTERIZATION, INTERACTION POTENTIALS AND COUPLINGS

The system that is considered here is a sodium atom scattering from a W(110) surface. The tungsten surface is represented by a cluster of five tungsten atoms as in shown in Fig. 1. The trajectory of the sodium atom is chosen to be perpendicular to the surface and to collide with the center tungsten atom (see Fig. 1). The restriction on the sodium trajectory allows one to use the symmetry of the system to simplify the problem. This ultimately results in a two electronic state problem but the results should give insight into what to expect in more general cases. This choice of the sodium trajectory is not a limitation of the method presented
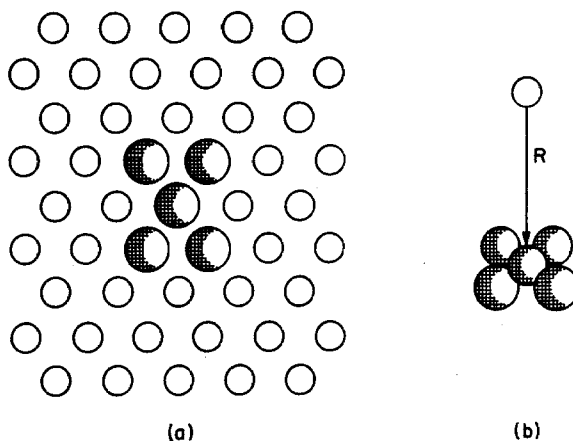

(a)   (b)

FIG. 1. (a) W(110) surface. The five shaded atoms in the middle are used to approximate the surface. The lattice constant is 3.16 Å. (b) Trajectory of the sodium atom. It approaches perpendicular to the five atom surface and collides with the central W atom. R is the distance between the sodium atom and the central W atom.

here. It does, however, provide a convenient starting point for this preliminary study.

As mentioned previously, several formalisms of the ionization or neutralization process have employed a MO description for the electronic part of the problem.[14,16] Here the electronic problem is also treated within a MO framework. In a previous paper[23] a simplified treatment of the diatomics in molecules (DIM) procedure was presented that made it especially applicable for the description of surfaces. This procedure is used here for obtaining eigenvalues and eigenfunctions of the neutral and ionic W(110) surface. These are then used in a polyatomic in molecules (PIM)[24] scheme to obtain the sodium-surface interaction potentials and coupling.

In what follows, several approximations are made. Perhaps the most crucial is the definition of the surface. The W(110) surface is approximated by a system consisting of five W atoms as shown in Fig. 1. Since the duration of the scattering event is very short (10^{-15}–10^{-13} s), it is assumed that the interaction of the sodium atom with the surface is very localized so that the revelant part of the electronic problem consists of only a few number of surface atoms. There are a number of advantages in making this assumption. The first and probably most important one is that it allows one to represent the electronic problem with a discrete set of eigenfunctions and eigenvalues. As Tully[14] pointed out, this fits nicely into the initial conditions of the problem. The second advantage is that it allows one to construct these eigenvalues and eigenfunctions in a systematic way using well known techniques. A possible disadvantage is that the magnitudes of the eigenvalues may not be correct. However, since the same approximation is used for both the neutral and ionic surface the relative difference between the ionic and neutral eigenvalues, which is of concern here, should be reasonable.

The second assumption deals with the interactions between the W atoms. In all likelihood all of the valence electrons would contribute to the W_2 bond which is needed in the DIM procedure. It is assumed however that the bonding between the W nuclei is due to one s-like orbital that is either singly or doubly occupied. This assumption could be avoided if either experimental or theoretical values for the multiple bond energies were available. Since these are not available, incorporating a better electronic description offers no advantage.

A formal treatment of the five nuclei system with both five and six electrons is given in Ref. 23. It was shown there how to construct the basis functions and how typical Hamiltonian matrix elements needed in the secular equation are obtained. In the interest of saving space, only the diatomic potentials used in the DIM procedure and the final results will be presented here.

For the five electron case, considering covalent configurations only, the ground ($^1\Sigma$) and first excited state ($^3\Sigma$) potentials for W_2 are needed. The ground state potential is chosen to have the form of a Morse potential,

$$V(r) = D\,(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}). \tag{1}$$

Unfortunately, there is considerable uncertainty as to what the values of D, "a", and r_0 are. Theoretical estimates of D
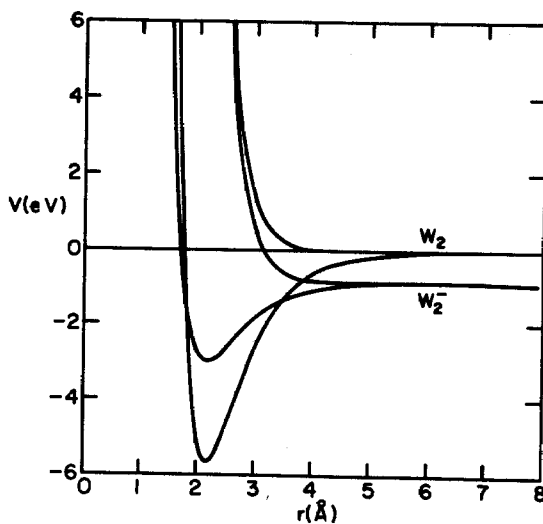

FIG. 2. Diatomic potentials for W_2 and W_2^-.

ranging from 4 to 7 eV have been made.[25] Here D is rather arbitrarily chosen to be 5.60 eV. The value of a is set to 1.61 Å^{-1}, which is slightly larger than the one used for describing the pair potentials of a W solid.[26] The value of r_0 is selected to be somewhat larger than the theoretical equilibrium distance of Mo_2 made by Wood et al. (p. 167 of Ref. 25). The value used here is 2.20 Å. The excited state is represented by a Born–Mayer potential,

$$V(r) = Ae^{-Br}. \tag{2}$$

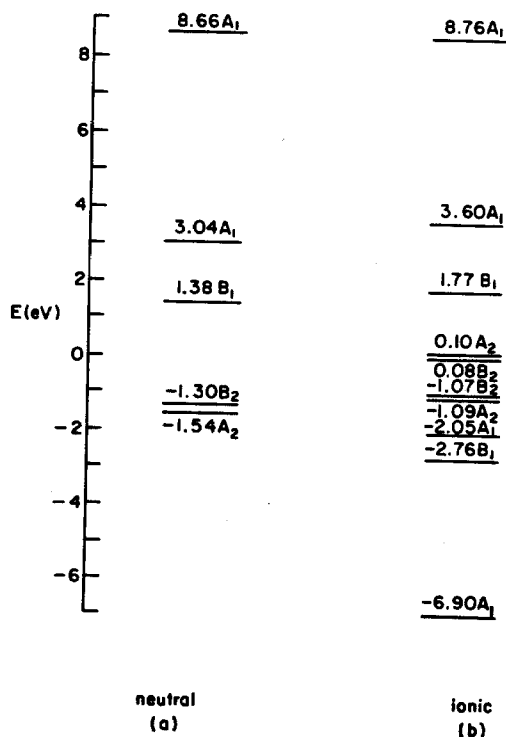The values for A and B are 54 200 eV and 3.50 Å^{-1}.[27] These potentials are shown in Fig. 2.

FIG. 3. Eigenvalues (in eV) and symmetry designations for the five atom surface: (a) neutral surface ($5e^-$); (b) ionic surface ($6e^-$). A C_{2v} symmetry designation is used because in the discussion presented in the text the Na atom approaches directly above the center atom of Fig. 1.

Using the above potentials and carrying out the procedure to determine the Hamiltonian matrix for the five electron case results in a 5×5 secular equation.[23] It is convenient for later purposes to label the eigenvalues and eigenfunctions according to their irreducible representation of the C_{2v} symmetry group. The eigenvalues and the irreducible representation to which they belong are shown in Fig. 3. In what follows, the initial state of our system corresponds to the B_1 state whose eigenvalue is 1.38 eV. As discussed before, the magnitude of this eigenvalue is not important. The interactions of the MO from this state with MO's from the ionic surface is what is of concern here.

For the ionic surface, not only are the potentials introduced above needed but the potentials for W_2^- are required as well. At present, we are aware of no theoretical or experimental work done on this diatomic. Rather than just make an outright guess, the following procedure is used. The bonding of the W_2^- is assumed to be due to the extra electron. This makes it formally equivalent to the H_2^+ molecule. The only difference between the two is the value of the effective nuclear charge. The effective nuclear charge is determined from the eigenvalue equation $(n = 1)$ of the hydrogen atom, i.e.,

$$Z_{eff} = \sqrt{\frac{E_{W^-}}{E_H}}. \tag{3}$$

E_{W^-} is the electron affinity of W which is 0.816 eV[28] and E_H is 13.6 eV. Using these values, Z_{eff} for W is $0.244e^-$. Using this value of Z_{eff} in a generalized form of the H_2^+ problem[29] leads to a well depth for W_2^- of 2.13 eV relative to a W and W^- infinitely far apart and at rest. The attractive potential is then given by

$$V(r) = D(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}) - 0.816 \text{ eV}, \tag{4}$$

where $D = 2.13$ eV and a and r_0 are chosen to be the same as for W_2. The repulsive potential is the same as for W_2 relative to the electron affinity of W. These potentials are also shown in Fig. 2.

Using these potentials in the procedure given in Ref. 23 for the six electron case leads to a set of ten eigenvalues and eigenfunctions. The eigenvalues and their C_{2v} symmetry classification are shown in Fig. 3. Notice that the ionic surface has two B_1 states which can interact with the B_1 state of the neutral surface.

Most of the ingredients necessary for determining the sodium-surface interaction potentials and couplings have been constructed. What is left to do is to form the basis functions for the sodium-surface system and to use these in a PIM procedure to obtain the potentials and couplings. The Na atom is considered to have one valence $3s$ electron and excited states are neglected. The five neutral surface eigenfunctions and the ten ionic surface eigenfunctions will give a total of 15 sodium-surface basis functions. The ten basis functions for the ionic system are just the ten ionic surface eigenfunctions since there are no valence electrons on Na^+. The five basis functions for the neutral system are a little more difficult to construct. The basis functions for the neutral system can either have a total spin of 1 or 0. Since the $S = 1$ states do not interact with the ionic states $(S = 0)$ only

basis functions with $S = 0$ are considered. A straightforward way of constructing these is the following. The basis functions for the netural surface have an unpaired electron centered on one of the nuclei. These basis functions with the unpaired electron having an α (β) spin are combined with the sodium spin orbital that has a β (α) spin to form a bond. For example, one of the neutral surface basis functions given by Ref. 23 is

$$\Psi_1 = C\{|a\bar{b}cde| - |a\bar{b}\bar{c}de| - |\bar{a}bc\bar{d}e| + |\bar{a}b\bar{c}de|\}, \tag{5}$$

where in general $i(\bar{i})$ represents the spin orbital with an α (β) spin centered on nucleus "i" (see Ref. 23) and the unpaired electron is on nucleus "e". Following the above procedure leads to the sodium-surface function

$$\begin{aligned}\Psi_1' = C'\{&|a\bar{b}c\bar{d}e\bar{N}| - |a\bar{b}c\bar{d}\,\bar{e}N| \\ &- |a\bar{b}\bar{c}de\bar{N}| + |a\bar{b}\bar{c}d\,\bar{e}N| - |\bar{a}bc\bar{d}e\bar{N}| \\ &+ |\bar{a}bc\bar{d}\,\bar{e}N| + |\bar{a}b\bar{c}de\bar{N}| - |\bar{a}b\bar{c}d\,\bar{e}N|\}, \end{aligned} \tag{6}$$

where N represents the Na orbital. The neutral sodium-surface basis functions are given by

$$\Phi_i = C'\sum_j C_{ji}\Psi_j', \tag{7}$$

where the C_{ji}'s are the expansion coefficients of the neutral surface eigenfunctions and C' is a normalization constant.

The PIM Hamiltonian for this system is[24]

$$\hat{H} = \hat{H}_s + \hat{H}_g + \hat{V}_{sg} - \hat{H}_s^{at} - 5\hat{H}_g^{at}, \tag{8}$$

where

$$\hat{V}_{sg} = \hat{H}_{ag} + \hat{H}_{bg} + \hat{H}_{cg} + \hat{H}_{dg} + \hat{H}_{eg}, \tag{9}$$

$\hat{H}_s$ and $\hat{H}_g$ are the Hamiltonians for the surface and gas (Na) atom, respectively, in the absence of interactions, $\hat{V}_{sg}$ represents the interactions between the surface and Na, $\hat{H}_s^{at}$ is the atomic Hamiltonian for the surface which is a sum over the atomic Hamiltonians for each of the surface atoms, and $\hat{H}_g^{at}$ is the Hamiltonian for the Na atom. Numbering the basis functions from 1 to 15 with the corresponding surface eigenvalues, the result of $\hat{H}_s$ on an aribitrary basis function Φ_i will simply be $E_i^s\Phi_i$. Since the basis is orthonormal, the matrix representation of $\hat{H}_s$ is diagonal in the surface eigenvalues E_i^s. The matrix representation of $\hat{H}_g$ is similar. Taking the zero of energy to correspond to five tungsten atoms and a sodium atom, all in their ground electronic state, infinitely separated and at rest, the diagonal matrix of $\hat{H}_g$ will have five zeros correspond to the neutral states and ten entries equal to the ionization potential of Na (5.12 eV) corresponding to the ionic states. The matrix representation of the atomic Hamiltonians are found in an analogous way.

In order to calculate the interaction term $\hat{V}_{sg}$ the sodium–tungsten diatomic potentials are needed. The possible ways of assigning the two electrons are $W\bar{N}$, $\bar{W}N$, WN, $\bar{W}\bar{N}$, $W\bar{W}$, and $N\bar{N}$, where the " $-$ " above the orbital represents a β spin and lack of it an α spin and W is the space orbital on the tungsten atom. The last two assignments represent ionic configurations and $N\bar{N}$ is neglected. The basis functions are chosen to be

$$\Psi_1 = a_1(|\bar{W}N| - |W\bar{N}|) + b_1|W\bar{W}|, \tag{10}$$

$$\Psi_2 = a_2(|\bar{W}N| - |W\bar{N}|) + b_2|W\bar{W}|, \tag{11}$$

$$\Psi_3 = a_3(|\overline{W}N| + |W\overline{N}|), \tag{12}$$

$$\Psi_4 = \tfrac{1}{2}|\overline{W}\overline{N}|, \tag{13}$$

$$\Psi_5 = \tfrac{1}{2}|WN|. \tag{14}$$

One has that

$$\hat{H}_{WN}\Psi_1 = E_1\Psi_1, \tag{15}$$

$$\hat{H}_{WN}\Psi_2 = E_2\Psi_2, \tag{16}$$

where $\hat{H}_{WN}$ is the NaW diatomic Hamiltonian and E_1 and E_2 are the lowest two adiabatic energies ($E_1 < E_2$) and

$$\hat{H}_{WN}\Psi_i = E_3\Psi_i, \tag{17}$$

where $3 \leqslant i \leqslant 5$ and E_3 is the energy of the repulsive triplet state. Inverting the above equations gives

$$\hat{H}_{WN}|W\overline{W}| = c[(E_2 a_1 b_2 - E_1 b_1 a_2)|W\overline{W}|$$
$$+ a_1 a_2(E_2 - E_1)|\overline{W}N|$$
$$- a_1 a_2(E_2 - E_1)|W\overline{N}|], \tag{18}$$

$$\hat{H}_{WN}|\overline{W}N| = \frac{c}{2}\{[(E_1 + E_3)a_1 b_2 - (E_2 + E_3)b_1 a_2]|\overline{W}N|$$
$$+ [(E_2 + E_3)a_1 b_2 - (E_1 + E_3)b_1 a_2]|W\overline{N}|$$
$$+ b_1 b_2 (E_1 - E_2)|W\overline{W}|\}, \tag{19}$$

and

$$\hat{H}_{WN}|W\overline{N}| = \frac{c}{2}\{[(E_3 - E_2)a_1 b_2 + (E_1 - E_3)b_1 a_2]|W\overline{N}|$$
$$+ [(E_3 - E_1)a_1 b_2 + (E_2 - E_3)b_1 a_2]|\overline{W}N|$$
$$- b_1 b_2 (E_1 - E_2)|W\overline{W}|\}, \tag{20}$$

where

$$c = 1/(a_1 b_2 - b_1 a_2). \tag{21}$$

From orthonormality requirements,

$$a_1 = \frac{1}{2}\sqrt{1 - 2b_1^2}, \tag{22}$$

$$a_2 = \frac{1}{2}\sqrt{1 - 2b_2^2}, \tag{23}$$

and

$$b_2 = -\left(\frac{1 - 2b_1^2}{2}\right)^{1/2}, \tag{24}$$

where b_1 is yet to be determined. The coefficients a_i, b_i are functions of the W–Na internuclear distance.

Once again there have been to our knowledge no experimental studies of the NaW diatomic. There has however been a theoretical study of this system based on the density function formalism.[30] In this study, the lowest adiabatic potential energy curve, the binding energy, equilibrium distance, and vibrational frequency were determined. This potential corresponds to the E_1 state above and is modeled with the Morse potential of Eq. (1). The values of the parameters are $D = 1.14$ eV, $a = 1.04$ Å^{-1}, and $r_0 = 2.80$ Å. The repulsive potential E_3 was again given the form of the Born–Mayer potential of Eq. (2) where the values of A and B are given by[27] 2700 eV and 3.64 Å^{-1}, respectively. These values were determined by using the combination rule of Eq. (3.25) in Ref. 27.

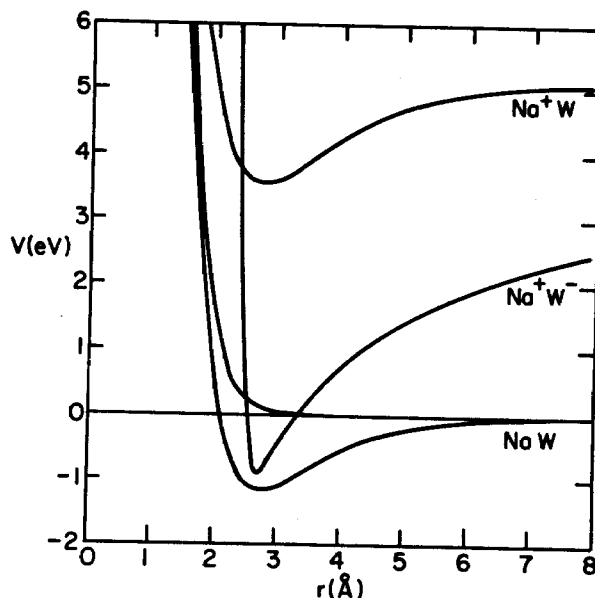The determination of E_2 is a bit more involved. At large

FIG. 4. Diatomic potentials for NaW, Na$^+$W$^-$, and Na$^+$W.

distances, the potential will have a Coulomb behavior, i.e.,

$$E_2(r) = -14.4 \text{ eV Å}/r + \text{I.P.}_{\text{Na}} - \text{E.A.}_{\text{W}}. \tag{25}$$

For smaller r, the potential should have a minimum and eventually become repulsive. The binding energy of the E_2 state is chosen to be due to covalent contributions only. Estimating the binding energy from Fig. 2 of Ref. 30 for the case of no charge transfer leads to a well depth of 0.88 eV. At $r = 2.85$ Å, the potential changes from the Coulomb potential [Eq. (25)] to a Morse potential [Eq. (1)]. With $D = 0.88$ eV, the two remaining parameters in Eq. (1) are chosen to fulfill the continuity requirements of the potential and its derivative at $r = 2.85$ Å. This leads to values of a and r_0 of 4.25 Å^{-1} and 2.74 Å, respectively. The calculations also showed that there is a 20% ionic contribution to the E_1 state at the equilibrium distance. Then b_1 varies from $\sqrt{0.2}$ at $r = 2.80$ Å to zero for large r. This is done by letting

$$b_1(r) = \left\{\frac{b_0}{2}\left(1 - \tanh[\alpha(r - r_x)]\right)\right\}^{1/2}, \tag{26}$$

where in this study the values of b_0, α, and r_x are given by 0.27, 0.75 Å^{-1}, and 3.5 Å, respectively. These choices indicate that some contribution from the ionic configuration is present up to $r \approx 6$ Å. The final potential needed here is for the (NaW)$^+$ diatomic. Again there is no information for this diatomic so that the procedures used for W$_2^-$ are also used for (NaW)$^+$. The values of the effective nuclear charges are $0.61e^-$ and $0.766e^-$ for sodium and tungsten, respectively. These were obtained by using the ionization potentials of sodium and tungsten (7.98 eV). Fitting the calculated potential with a Morse potential gave values of the well depth and exponential factor a of 1.56 eV and 0.890 Å^{-1}, respectively. The equilibrium distance was kept the same as for NaW, i.e., 2.80 Å. This potential is relative to the energy of Na$^+$ + W.

All of the potentials for the NaW system are shown in Fig. 4. One notices the long range Coulomb tail of the ionic potential (Na$^+$W$^-$). This dominates the long range behavior of the sodium surface interaction potentials arising from the
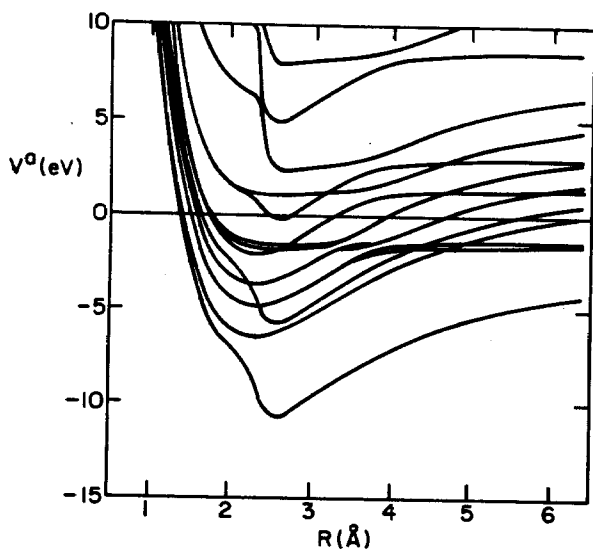
FIG. 5. Adiabatic potentials for the sodium atom interacting with the surface. The Na trajectory and definition of R are given in Fig. 1.

FIG. 6. Adiabatic potentials and coupling of B_1 symmetry for the sodium interacting with the surface. The Na trajectory is given in Fig. 1.

ionic configurations. Other treatments describe this type of interaction with an image potential.[31] In this treatment however, this interaction occurs quite naturally by including ionic configurations in the MO representation.

Using these potentials and following the procedure of Ref. 23 leads to a 15×15 secular equation. Diagonalizing it and choosing a trajectory for the sodium atom gives 15 interaction potentials, five of which are asymptotically neutral and ten asymptotically ionic. Choosing the Na trajectory to be normal to the surface and striking the center W atom (see Fig. 1) leads to the interaction potentials shown in Fig. 5. For this trajectory, the positions of the W nuclei are held fixed at the distances used for the surface calculation. This graph may look a little complicated but, by choosing the above trajectory, the C_{2v} symmetry is maintained. This leaves one with six A_1 states, four ionic and two covalent, and three each of A_2, B_1, and B_2 symmetry, two ionic and one covalent each. Since states of different symmetry designation do not interact for this particular angle of Na scattering, the picture is somewhat simplified.

The B_1 state is chosen to be the initial electronic state. The choice is somewhat arbitrary but it results in a two state problem which is a natural starting point for this study. There can be couplings between this state and the two B_1 states that are asymptotically ionic. The interaction potentials for these states with the trajectory mentioned above are shown in Fig. 6. One notices the avoided crossing around 4 Å. The lowest state interacts with the neutral state at around 12 Å but the coupling is extremely narrow (approximately a delta function). These two states are therefore treated as diabatic states whose off diagonal matrix element is zero (i.e., noninteracting). The coupling around the avoided crossing is shown in Fig. 6. These couplings are defined as

$$d^a = \left\langle \Psi_2^a \left| \frac{d}{dR} \right| \Psi_1^a \right\rangle, \qquad (27)$$

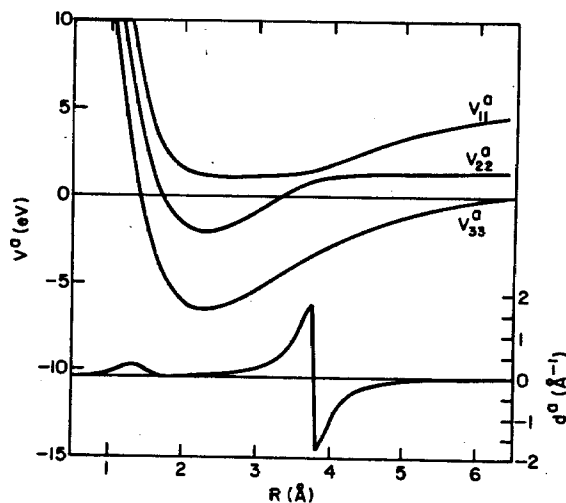where R is the distance from the Na to the central W atom and the superscript designates the adiabatic electronic representation. The subscripts on the eigenfunctions Ψ_i^a run from the highest to lowest eigenvalue. The abrupt change in the sign of the coupling indicates that the eigenfunction is changing from covalent (ionic) to ionic (covalent) in character. What is of concern is the absolute value of this coupling. These couplings were calculated using numerical differentiation and checked by comparing forward, backward, and symmetric difference formulas.

Since the couplings between Ψ_2^a and Ψ_3^a are very narrow one is left with a two electronic state problem. These have been studied extensively in gas phase collisions and some of the same techniques are used here. Initially the system starts in the state Ψ_2^a. The couplings between the electronic states with respect to the nuclear degrees of freedom determine the probability of ending up in the state Ψ_1^a. The formalism requires a diabatic electronic representation and this is introduced when appropriate.

Although the following development treats this two state problem for the perpendicular approach of the sodium, it is straightforward to extend this approach to include other trajectories and electronic states. This is discussed more fully in the final section.

III. GENERAL FORMALISM

In the Introduction it was pointed out that the treatments of nonadiabatic gas surface collisions required assumptions about the nuclear trajectories. Here a formalism is used that self-consistently determines the "nuclear" degrees of freedom along with the electronic transition amplitudes. Since this formalism has been presented in detail elsewhere,[21] only a brief outline of it is presented here.

To begin with one needs the solutions of the time independent Schrödinger equation

$$(\hat{T}_{\text{nu}} + \hat{H}_{\text{el}})|\Phi(\mathbf{R})\rangle = E |\Phi(\mathbf{R})\rangle, \qquad (28)$$

where $\hat{T}_{\text{nu}}$ is the nuclear kinetic energy operator, $\hat{H}_{\text{el}}$ is the electronic Hamiltonian and $\mathbf{R}$, $|\rangle$ represent the nuclear, electronic coordinates. In order to make the treatment here as simple as possible, the trajectory of the previous section shown in Fig. 1 is used and the positions of the surface nuclei

are held constant. This gives a one dimensional problem with

$$\hat{T}_{nu} = -\frac{\hbar^2}{2m}\frac{d^2}{dR^2},\tag{29}$$

where R is the distance of the Na to the surface and m is the mass of the Na nucleus. In order to ensure that the operation on the left-hand side of Eq. (28) is Hermitian a diabatic electronic representation[32] is used. For this system, the electronic functions in this representation satisfy

$$\frac{d}{dR}|\Psi^d(R)\rangle = 0,\tag{30}$$

where $|\Psi^d(R)\rangle$ is a $1 \times n$ row matrix and the superscript "d" denotes the diabatic representation. These functions, assumed to be real, are related to the ones $|\Psi^a(R)\rangle$ in the adiabatic representation (Sec. II) by means of a 2×2 unitary matrix A. A general form of this matrix is

$$A = \begin{pmatrix} \cos\gamma(R,R_0) & \sin\gamma(R,R_0) \\ -\sin\gamma(R,R_0) & \cos\gamma(R,R_0) \end{pmatrix},\tag{31}$$

where[33]

$$\gamma(R,R_0) = \int_{R_0}^{R} dR' |d^a(R')|,\tag{32}$$

and $\gamma(R_0,R_0) = 0$. With Eq. (31) the diabatic representation is given by

$$|\Psi^d(R)\rangle = |\Psi^a(R)\rangle A(R,R_0).\tag{33}$$

Letting

$$|\Phi(R)\rangle = |\Psi^d(R)\rangle\phi(R),\tag{34}$$

where $\phi(R)$ is an $n \times 1$ column matrix and substituting in Eq. (28) results in

$$-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}\phi(R) + V^d\phi(R) = E\phi(R),\tag{35}$$

where

$$V^d = \langle\Psi^d|\hat{H}_{el}|\Psi^d\rangle\tag{36}$$

and $\langle\text{---}|\text{---}\rangle$ denotes an integration over electronic coordinates only. The matrix elements ϕ_i are related to the probability of being in the electronic state "i." The first step involves writing the amplitudes in the form

$$\phi(R) = \chi(R)e^{\frac{i}{\hbar}S(R)},\tag{37}$$

where χ is an $n \times 1$ column matrix. This form of ϕ is called the common eikonal since the eikonal $S(R)$ is the same for all electronic channels.

Substituting Eq. (37) into Eq. (35) and requiring that

$$\frac{(dS/dR)^2}{2m} + \overline{V} = E\tag{38}$$

results in

$$-\frac{\hbar^2}{2m}\frac{d^2}{dR^2}\chi - \frac{i\hbar}{m}\left(\frac{dS}{dR}\right)\frac{d}{dR}\chi - \frac{i\hbar}{2m}\left(\frac{d^2S}{dR^2}\right)\chi + V^d\chi - \overline{V}\chi = 0,\tag{39}$$

where $\overline{V}$ is to be determined. The next step consists of using the short wavelength approximation which allows one to neglect the first term in Eq. (39) so that

$$-\frac{i\hbar}{m}\frac{dS}{dR}\frac{d}{dR}\chi - \frac{i\hbar}{2m}\left(\frac{d^2S}{dR^2}\right)\chi + V^d\chi - \overline{V}\chi = 0.\tag{40}$$

Taking $\chi^\dagger$ times Eq. (40) and adding it to the adjoint of Eq. (40) times χ gives

$$\overline{V} = \chi^\dagger V^d\chi,\tag{41}$$

where $\chi^\dagger\chi = 1$. As will be seen, $\overline{V}$ plays the role of a potential in a set of equations that has the form of Hamilton's equations of motion. That it is not a pure classical potential is manifested by its dependence on the amplitudes χ.

The final step involves making a transformation into time, i.e.,

$$R \to R(t),\tag{42}$$

$$\frac{dS}{dR} \to \frac{dS(t)}{dt} = P(t),\tag{43}$$

and

$$\chi(R) \to C(t)\exp\frac{i}{\hbar}\left\{\int_{t'}^{t} dt'\left[\overline{V}(t') - \frac{\hbar}{i}\frac{d}{dt'}\ln P^{1/2}\right]\right\},\tag{44}$$

where the exponential factor in Eq. (44) has been included for convenience. Transforming Eq. (40) into time and using Eqs. (42) through (44) gives

$$\frac{\hbar}{i}\frac{dC}{dt} + V^dC = 0\tag{45}$$

and now

$$\overline{V} = C^\dagger V^dC.\tag{46}$$

From Eq. (38),

$$\frac{P^2}{2m} + \overline{V} = E,\tag{47}$$

which has the form of a Hamilton–Jacobi equation. Defining the Hamiltonian as

$$H(R,P,C) = \frac{P^2}{2m} + \overline{V}\tag{48}$$

and letting

$$C = \frac{1}{\sqrt{2\hbar}}(C^R + iC^I),\tag{49}$$

where C^R and C^I are real matrices, Eq. (45) can be rewritten as

$$\frac{dC_j^R}{dt} = -\frac{\partial H}{\partial C_j^I}\tag{50}$$

and

$$\frac{dC_j^I}{dt} = \frac{\partial H}{\partial C_j^R}.\tag{51}$$

Conservation of energy can be achieved, i.e.,

$$\frac{dH}{dt} = 0\tag{52}$$

by requiring that

$$\frac{dR}{dt} = \frac{\partial H}{\partial P}\tag{53}$$

and

$$\frac{dP}{dt} = -\frac{\partial H}{\partial R}. \tag{54}$$

By multiplying $C^\dagger$ times Eq. (45) and subtracting it from the adjoint of Eq. (45) times C one finds that

$$\frac{dC^\dagger C}{dt} = 0, \tag{55}$$

i.e., the probability is conserved. Equations (50), (51), (53), and (54) are in the form of Hamilton's equations of motion. The real and imaginary parts of the amplitudes play the roll of canonical variables as well as the "nuclear" variables. One should remember that the nuclear variables were defined by the conservation of energy [Eq. (52)] so that they cannot be strictly interpreted as a classical position and momentum. They can however offer some understanding of the collision event.

In order to give a feeling for the equations above, a qualitative description of the collision event is presented. Well before the collision takes place the system is in one electronic state determined by the initial conditions. In this case, $\overline{V}$ is just the diabatic potential corresponding to this state and R and P behave as classical quantities in the usual sense. During the course of the collision the diabatic potentials can cross and the off-diagonal matrix elements of the diabatic potentials drive probability from one channel to another. After the collision occurs, the off-diagonal potential matrix elements are zero but the final amplitudes depend on the collision process. After the collision, $\overline{V}$ becomes a linear combination of the diagonal elements of the diabatic potential matrix whose coefficients are the final probabilities of being in the corresponding electronic state. The nuclear variables R and P will evolve on an average potential and this is why they can not be interpreted as classical variables.

A more physical set of canonical variables for the amplitudes are the probability and phase, i.e.,

$$C_j = P_j^{1/2} e^{(i/\hbar)\theta_j}. \tag{56}$$

These however have the disadvantage of containing an essential singularity when P_j is zero (i.e., initial conditions). In practice the calculations are done with the variables of Eq. (49) and since

$$P_j = \frac{1}{2\hbar}(C_j^{R\,2} + C_j^{I\,2}) \tag{57}$$

and

$$\theta_j = -\hbar \tan^{-1}(C_j^I / C_j^R), \tag{58}$$

the results are transformed into the more easily understood variables P_j and θ_j.

IV. PRELIMINARY RESULTS

In this section the formalism of the previous section is applied to the two electronic state problem discussed in Sec. II. Since there are two electronic states, six first order differential equations in time need to be simultaneously integrated. These equations are

$$\frac{dR}{dt} = \frac{P}{m}, \tag{59}$$

$$\frac{dP}{dt} = -\frac{\partial H}{\partial R}, \tag{60}$$

$$\frac{dC_1^R}{dt} = -\frac{1}{\hbar}(V_{11}^d C_1^I + V_{12}^d C_2^I), \tag{61}$$

$$\frac{dC_1^I}{dt} = \frac{1}{\hbar}(V_{11}^d C_1^R + V_{12}^d C_2^R), \tag{62}$$

$$\frac{dC_2^R}{dt} = -\frac{1}{\hbar}(V_{22}^d C_2^I + V_{12}^d C_1^I), \tag{63}$$

and

$$\frac{dC_2^I}{dt} = \frac{1}{\hbar}(V_{22}^d C_2^R + V_{12}^d C_1^R). \tag{64}$$

The object is to start the calculation at an initial time $t = 0$ and integrate the equations to a final time when the sodium no longer interacts with the surface. The initial value of R is chosen large enough so that the sodium-surface interaction is negligible. The initial value of P is related to the initial kinetic energy of the system, i.e.,

$$P_{in} = \sqrt{2mE_k^i}, \tag{65}$$

where E_k^i is the initial kinetic energy which is varied. The total energy of the system originating in the neutral state is

$$E_{tot} = E_2^s + \frac{P_{in}^2}{2m}, \tag{66}$$

where E_2^s corresponds to the energy of the neutral surface B_1 state discussed in Sec. II. The initial values of the amplitudes are found by letting $P_2 = 1$, $\theta_2 = \theta_1 = P_1 = 0$. Setting θ_2 equal to zero is arbitrary but it oscillates rapidly throughout the trajectory and should not affect the results.

As seen in Eqs. (61) through (64), the electronic Hamiltonian must be formulated in the diabatic representation. The transformation matrix to this representation depends on the angle defined in Eq. (32). In order to simplify things, the absolute value of the coupling was modeled with a Gaussian function so that

$$|d^a(R)| = Be^{-b(R - R_x)^2}, \tag{67}$$

where B is given by the maximum value of $|d^a|$, 1.75 Å^{-1}, and R_x is the value of R at the maximum of $|d^a|$, 3.8 Å. The value of b was chosen so that the area under the curve of $|d^a|$ equaled the area under the curve of Eq. (32). Its value turns out to be 3.97 Å^{-2}. The coupling along with $|d^a|$ is shown in Fig. 7. With this choice of coupling, the angle is determined analytically and one has that
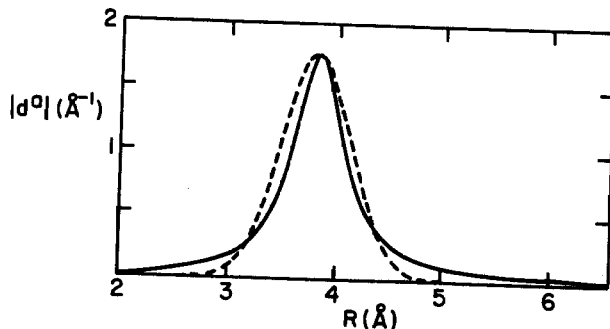

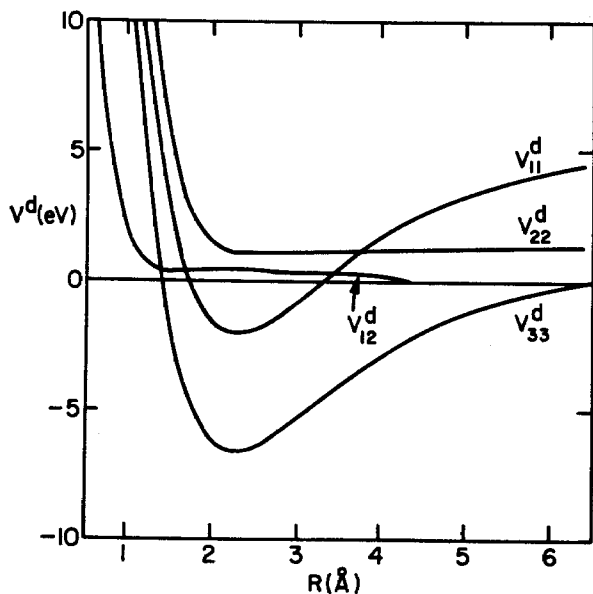FIG. 7. Comparison of $|d^a|$(—) and the model coupling of Eq. (67)(---). The Na trajectory is given in Fig. 1.

FIG. 8. Diabatic potentials of B_1 symmetry for the sodium atom interacting with the surface. The Na trajectory is given in Fig. 1.

$$\gamma(R,R_0) = B(\pi/4b)^{1/2}\{\mathrm{erf}\left[\sqrt{b}(R - R_x)\right]$$
$$- \mathrm{erf}\left[\sqrt{b}(R_0 - R_x)\right]\}, \qquad (68)$$

where erf is the error function.[34] From Eqs. (33) and (36) the matrix elements of V^d are

$$V^d_{11}(R) = V^a_{11}(R)\cos^2\gamma(R,R_0) + V^a_{22}\sin^2\gamma(R,R_0), \qquad (69)$$

$$V^d_{22}(R) = V^a_{11}(R)\sin^2\gamma(R,R_0) + V^a_{22}\cos^2\gamma(R,R_0), \qquad (70)$$

and

$$V^d_{12}(R) = V^d_{21}(R) = (V^a_{11} - V^a_{22})\sin\gamma(R,R_0)\cos\gamma(R,R_0). \qquad (71)$$

These are plotted in Fig. 8. One notices that since the integral of Eq. (67) does not exactly equal $\pi/2$, the off-diagonal matrix elements V^d_{12} diverge for small R. Worth noting is the general behavior of these potentials. V^d_{22} corresponds to the interaction of a neutral sodium with the surface. This potential is flat at larger distances, has a shallow well at around 2.5 Å and becomes repulsive at short distances. The ionic potential V^d_{11} is a long range interaction, exhibits a much deeper well before becoming repulsive at short range. If the sodium approaches the surface on V^d_{22} and then crosses to the state V^d_{11}, there will be a rather large variation in the potential energy of the system. Several treatments of this problem use the atomic state of Na and a band state of the surface. It is known that the level of the atomic state varies in the neighborhood of the surface but the treatments of this variation have been rather arbitrary and not from first principles. It is seen here that variations in the potential energy occur quite naturally by the use of a MO picture.

The results to be presented here were obtained by integrating Eqs. (59) through (64) using a standard subroutine based on Adam's formula.[35] The criteria used to terminate the calculation was for the particle to be on its outward trajectory and further than 10 Å from the surface and its mo-
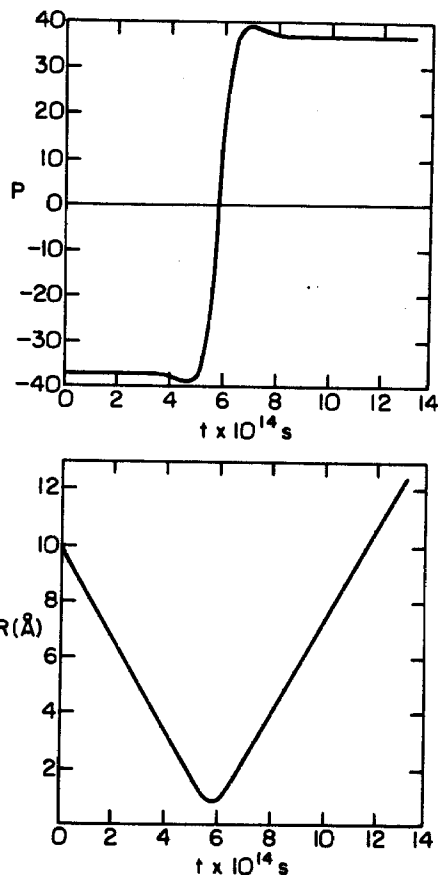

FIG. 9. R and P vs t. The initial kinetic energy is 30 eV. The unit of P is 3.8×10^{-17} g cm/s.

mentum constant. The results to be presented here were taken from calculations performed with the initial kinetic energy varied between 5 and 60 eV.

The results for the nuclear variables and potentials are taken from the calculation where the initial kinetic energy was 30 eV. This gives a total energy of 31.38 eV which was checked for invariance throughout the calculation. The collision event is typically over in about 200 fs (1fs = 10^{-15} s) and the velocity range is between 6.5×10^5 and 2.3×10^6 cm/s. The results for R and P are shown in Fig. 9. One sees that R decreases from its initial value of 10 Å to less than 1 Å at around 60 fs and then increases as the sodium leaves the surface. In other words, the sodium atom approaches the surface, undergoes a single collision with it and then leaves. During the initial part of the trajectory (less than 20 fs), P remains constant and equal to its initial value. As the potentials cross, P becomes more negative which corresponds to motion on the ionic potential curve. At the distance of closest approach, P changes sign and becomes positive as the distance from the surface increases. On the outward path, the magnitude of P is initially larger due to motion being on the ionic potential. As the potentials again cross, the behavior of P becomes more constant which indicates motion primarily on the neutral surface. As mentioned earlier, the constancy of P on the outward path is used to terminate the calculation.

The results of the diabatic potentials and $\bar{V}$ for $E^i_k = 30$ eV are shown in Fig. 10. One sees that the results agree with the qualitative discussion given in the previous
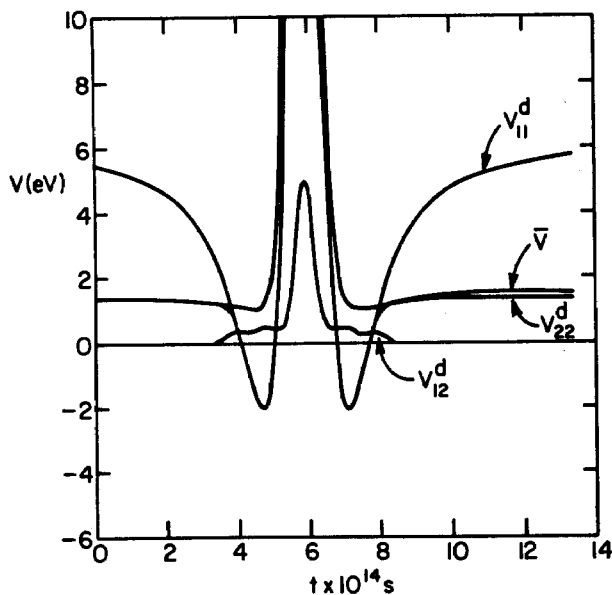
FIG. 10. Diabatic potentials (V_{ij}^d) and average potential $(\overline{V})$ vs t. The initial kinetic energy is 30 eV.

section. For times earlier than around 20 fs, $\overline{V}$ and V_{22}^d coincide. This is because the trajectory begins in a pure electronic state, i.e., $P_2 = 1$ so that the expression for $\overline{V}$ [Eq. (46)] reduces to V_{22}^d. In the neighborhood of 20 fs the potentials V_{11}^d and V_{22}^d cross and the off-diagonal term V_{12}^d becomes nonzero. In this region, $\overline{V}$ changes from values close to V_{22}^d to values that are closer to V_{11}^d. This signifies that there has been a large increase in P_1 and a large decrease in P_2. That $\overline{V}$ does not equal V_{11}^d means that the transition did not occur with unit probability. As the Na approaches the surface (time < 50 fs) its potential energy decreases due to the deeper well of the ionic potential. This is compensated by the increase in its momentum shown in Fig. 9. At small distances, the short range repulsive forces dominate and there is an abrupt increase in the potential energy. After reaching the turning point (≈ 60 fs) it begins the outward part of the trajectory and the potential energy rapidly decreases. The potential again becomes negative due to the ionic well. At around 80 fs the diabatic states again cross and the behavior of $\overline{V}$ becomes much more like that of V_{22}^d. That it does not equal V_{22}^d means that P_1 does not equal zero. In other words, there is a rather small but noticeable probability that reaction occurs. Since P_1 does not equal zero at large time, $\overline{V}$ is a linear combination of V_{11}^d and V_{22}^d. This emphasizes the point made earlier that after the collision, R and P do not necessarily correspond to the classical position and momentum of the particle.

The results of the nuclear variables and potentials for an E_k^i of 30 eV are fairly typical of the results obtained at the other energies. Since the system is rather restricted (fixed surface nuclei and the one dimensional sodium trajectory) they offer little insight into the contribution of the nuclear degrees of freedom to the probability of reaction. If the conditions were relaxed, e.g., letting the surface atoms move and varying the impact parameter of the Na colliding with the center W, information about the effect of momentum trans-
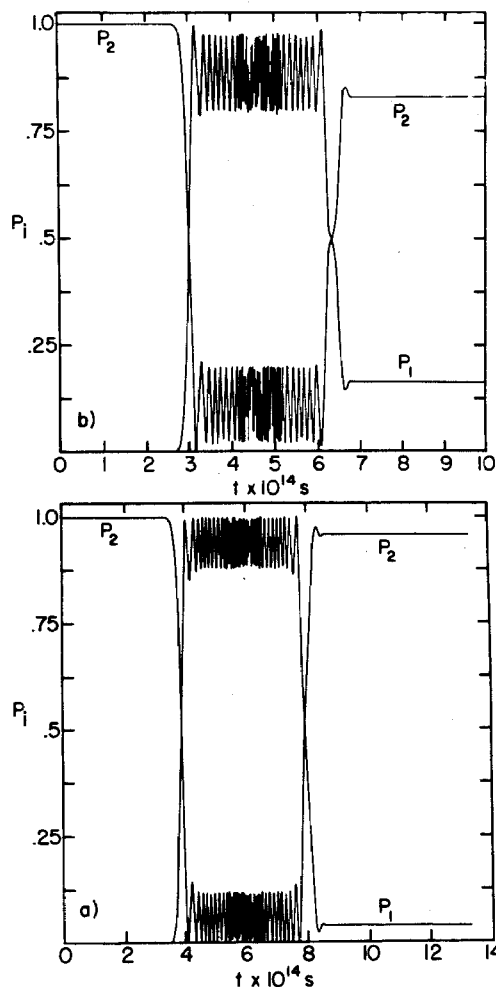

FIG. 11. P_1 and P_2 vs t. Initial values of P_1 and P_2 are 0 and 1, respectively. The initial kinetic energies are (a) 30 eV; (b) 50 eV.

fer or multiple collisions on the reaction probability could be obtained. The results presented here are meant to help familiarize the reader with this type of description of the collision event.

Considering now the transition probabilities, the results for P_1 and P_2 for an E_k^i of 30 and 50 eV are shown in Fig. 11. Common to both cases are two regions where the probabilities make abrupt changes. These correspond to regions where the diabatic potentials cross. Considering the E_k^i equal 30 eV figure, initially ($t = 0$) the system is in the neutral state so that $P_2 = 1$ and $P_1 = 0$. At around 35 fs, the diabatic potentials cross and P_1 increases to values close to one and P_2 decreases to small values. These changes are driven by the nonzero V_{12}^d term. Between 40 and 80 fs both P_1 and P_2 have small rapid oscillations. These occur because V_{12}^d is not zero in this region. At around 80 fs there is again a large change in P_1 and P_2 which is again in the region where the diabatic curves cross. The final values of P_1 and P_2 are about 0.05 and 0.95, respectively.

The results for the final values for the probability of electron transfer over a range of E_k^i are shown in Table I. There are two main points that should be noticed about these results. The first is that they are not trivial, i.e., the final values of P_2 are not always 1. Thus even with this restricted

TABLE I. Final values for the probability of electron transfer (P_f) for different values of the initial kinetic energy (E_k^i). The initial value of P_i is zero.

E_k^i(eV)	P_f
5	$< 10^{-4}$
10	0.0026
20	0.0578
30	0.0425
40	0.168
50	0.166
60	0.209

system, noticeable reaction probabilities are obtained. The second is that they depend on the E_k^i of the sodium atom. This suggests that momentum transfer and multiple collisions might play an important role in determining the reaction probability especially on the outward part of the trajectory. This could allow one to test the assumptions used in other theories such as a dependence of the probability on only the normal component of the particles velocity with respect to the surface or the binary collision approximation. Although the results are much too preliminary to compare with experiment, it is hoped that by including surface motion and variable impact parameters quantitative comparisons with experiment can be made.

V. DISCUSSION

This paper has been primarily concerned with three major aspects of the description of gas–surface collisions. These were the characterization of the surface, the determination of the gas–surface interaction potentials and couplings and the description of the evolution of the nuclear and electronic variables. The scheme for making systematic improvements is described below.

As described in Sec. II the surface was characterized as a system of five atoms. Although this is a microscopic view of the surface, it allows one to use well known electronic structure techniques (DIM, CNDO, Hartree–Fock, etc.) to obtain the eigenvalues and eigenfunctions. It would be of interest to determine the effect on the eigenvalues and vectors of including more surface atoms or a layer of atoms beneath the surface. This could be done with the DIM procedure given in Ref. 23. Also of interest would be to determine how the eigenvalues and eigenfunctions are affected by changing the positions of the surface atoms. This will be the subject of future work.

It is unfortunate that more information about either metal dimer interaction potentials or potentials between a gas and metal atom is not available. These potentials are necessary in this approach (and most other approaches too) and it would be informative to find out how a better diatomic electronic description would affect these results. It is hoped that this information becomes available in the near future.

An important aspect of this work has been the description of the gas–surface interaction potentials and couplings. In contrast to much of the previous work done in this area, here the shapes and magnitudes of these potentials and couplings are not assumed. Instead they are obtained in a syste-

matic way by means of the DIM and PIM methods. The employment of a MO picture allows one to formulate the problem in a discrete electronic basis. Other authors have formulated the problem with a continuous set of surface states which interact with the atomic state of the gas atom. Although this may physically seem to be more reasonable, the evolution of these states as a function of time or distance from the surface is difficult if not impossible to calculate. This difficulty leads to many of their assumptions. It has been shown here how this problem can be avoided.

The results presented in the last section were obtained by keeping the positions of the surface nuclei fixed and choosing the trajectory of the sodium atom to be perpendicular to the surface and colliding with the center W atom. These conditions considerably simplified the problem which led to results that were relatively easy to understand. For the low energies considered here, fixing the positions of the surface atoms should not be a bad approximation since there is almost an order of magnitude difference between the masses of W and Na. For higher energies, however, these atoms should be allowed to move. The restrictions placed on the trajectories can be easily relaxed so that a sampling over impact points could be done. The trajectories done here at the single impact point correspond somewhat with the models used in some other approaches. For example, Hagstrum[3,4] treats the surface more like an electron gas and does not consider the actual positions of the surface nuclei. This is similar to the model used here in the sense that only one set of interaction potentials and couplings were considered, i.e., all impact points are equivalent. Since Hagstrum's model was developed for larger energies than used here, it would be interesting to determine whether varying the impact point at these low energies appreciably changes the transition probabilities. Work along these lines is currently underway.

An important point to be made about this approach is that all of the approximations that are made can be either made more accurate or eliminated altogether. This is in contrast to other approaches that for example assume the form of the coupling matrix element. Once this assumption is made, it is not clear how improvements can be made. The end result is a few parameters whose values must be either arbitrarily chosen or fit to experiment. The treatment presented here does not contain these kind of parameters in that all of the quantities that were introduced can be obtained from first principles.

Another advantage in this method is that the approximations can be systematically eliminated which allows one to determine the relative importance of each approximation. For example, the results for the restricted system presented here can be compared to the results obtained by letting the surface atoms move. This would indicate the importance of gas–surface momentum transfer on the reaction probability. Making these comparisons as a function of increasing kinetic energy could establish a region of energy where this approximation is valid. This could be done for other quantities such as the impact parameter and perhaps provide a valuable tool for testing the assumptions made in other theories.

Ultimately this method will be applied to SIMS experiments where the sputtering of a particle can be thought of in

a localized way. Currently a small surface similar to the one used here can be embedded in the surface of a much larger solid. The positions of the nuclei can be assumed to evolve via classical equations of motion. The electronic problem for the particle absorbed on the small surface can be calculated with the techniques used here. When the solid transfers energy to the small surface, the desorption of the particle will be governed by the equations of motion given in Sec. III. The results would give the final probabilities for being in the electronic states and the trajectories for the nuclear variables could offer insight into the desorbing mechanism.

In conclusion, this paper has tried to focus on the basic ideas involved in describing a surface and the gas–surface interactions and couplings. The trajectories presented here were rather restricted but they should be an aid in understanding future work along these lines. It has been shown that surface chemistry can be done from first principles so that the approximations used in other approaches can be avoided. We expect that this microscopic view will lead to a greater understanding of processes that occur on surfaces.

ACKNOWLEDGMENTS

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