Time-independent quantum dynamics for diatom–surface scattering

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Two time-independent quantum reactive scattering methods, namely, the S-matrix Kohn technique to compute the full S-matrix, and the absorbing boundary Green's function method to compute cumulative reaction probabilities, are applied here to the case of diatom–surface scattering. In both cases a discrete variable representation for the operators is used. We test the methods for two- and three-dimensional uncorrugated potential energy surfaces, which have been used earlier by Halstead et al. [J. Chem. Phys. 93, 2359 (1990)] and by Sieweg et al. [J. Chem. Phys. 97, 684 (1992)] in studies of H₂ dissociating on metal substrates with theoretical techniques different from those applied here. We find overall but not always perfect agreement with these earlier studies. Based on ab initio data and experiment, a new, six-dimensional potential energy surface for the dissociative chemisorption of H₂ on Ni(100) is proposed. Two- and three-dimensional cuts through the new potential are performed to illustrate special dynamical aspects of this particular molecule–surface reaction: (i) the role of corrugation effects, (ii) the importance of the "cartwheel" rotation of H₂, and (iii) the role of the "helicopter" degree of freedom for the adsorbing molecule.

I. INTRODUCTION

The interaction of small particles with solid surfaces is of interest from both technological and scientific perspectives, ranging from spectroscopic techniques [e.g., low energy electron diffraction (LEED), or helium atom scattering (HAS)] to the vast field of heterogeneous catalysis. In addition to the practical importance of this branch of physical chemistry, interface problems represent a formidable challenge for theorists, in both the energetic and dynamical aspects.

The most complete (i.e., state-to-state) description of a molecule–surface collision process is provided by the scattering or S matrix, whose elements \( S_{\gamma_p,\gamma_0}(E) \) are the probability amplitudes for transitions between specific quantum states \( |\gamma_0\rangle \) of reactants to specific states \( |\gamma_p\rangle \) of products (at total energy \( E \)). Several exact quantum methods have been proposed during recent years with the aim to compute the S matrix for gas-phase scattering problems. For example, in a time-independent and variational framework, Miller and co-workers developed and applied a powerful technique which makes use of the S-matrix version of Kohn's variational principle. In this method scattering calculations essentially come down to a sequence of standard quantum mechanical operations, namely, the representation of the Hamiltonian in an appropriate basis and subsequent linear algebra computations. Recently the S-matrix Kohn technique has been reformulated in terms of a discrete variable representation (DVR) of the Hamiltonian. This variant was then applied to compute the S matrices for collinear (two-dimensional) and three-dimensional exchange reactions involving three atoms. A DVR introduces the additional attractive features, that (i) no multidimensional quadratures have to be performed to compute the required matrix elements, and (ii) the resulting matrices are (for systems of dimensionality higher than one) sparse, which makes the application of effective linear algebra methods favorable.

Clearly, knowledge of the full S matrix is highly desirable also in gas–surface chemistry where, for instance, one might want to tune the product state distribution by varying the solid substrate. Additionally, the S matrix gives the probabilities for nonreactive, i.e., elastic and inelastic scattering events, and is therefore of vital importance if one, for example, aims to interpret HAS spectra. In many applications, though, one is interested in a less detailed knowledge of a reaction than the complete state-to-state description. Of great interest in heterogeneous catalysis, for example, is the thermal rate constant

\[ k(T) = \frac{1}{2\pi \hbar} \int_{-\infty}^{\infty} dE e^{-E/kT} N(E), \]

which is expressed here in terms of the cumulative reaction probability (CRP), \( N(E) \), and the reactant partition function (per unit volume), \( Q_r(T) \). Since the CRP is the same for a reaction and its inverse, Eq. (1.1) clearly embodies the microscopic reversibility relation \( k_{f\rightarrow s} Q_s = k_{s\rightarrow f} Q_f \). Of specific interest in this paper is the reaction dissociative adsorption and its inverse associative desorption, often the rate-limiting steps in heterogeneous catalysis. \( N(E) \) is thus the same for these two reactions and its evaluation is the essential task in calculating the rates of these reactions.

The CRP, \( N(E) \) of Eq. (1.1), can be expressed in terms of the S-matrix elements,

\[ N(E) = \sum_{\gamma_p,\gamma_0} |S_{\gamma_p,\gamma_0}(E)|^2, \]
but if one is interested only in the CRP (and the thermal rate constant), then it is inefficient to have to compute all the state-to-state information (i.e., the $S$ matrix) first and use Eq. (1.2) to obtain the CRP. For these purposes a method which directly, but nevertheless rigorously (i.e., fully quantum mechanically) provides the CRP's, is advantageous.

Miller et al., using flux correlation analysis, were able to derive such a formally exact expression for $N(E)$ which does not require the knowledge of individual $S$-matrix elements. Instead, $N(E)$ is expressed in terms of flux and microcanonical density operators. Recently Seideman and Miller introduced an effective implementation by using a DVR for both the Hamiltonian and the flux operator, and by applying absorbing boundary conditions (ABC) to obtain a well-behaved representation of the outgoing Green's operator (which is in turn used to compute microcanonical density operators—see below). Again the technique has been tested for atom-exchange reactions in the gas-phase.

The methodological aspect of the present contribution is to adapt and apply the above mentioned direct and indirect approaches to compute $N(E)$ for the problem of diatomic molecules adsorbing on or desorbing from metal substrates. In this context, the $N(E)$'s are usually referred to as sticking probabilities. Also, we will demonstrate how the full $S$ matrix for gas–surface scattering can be computed with the aid of the $S$ matrix Kohn method.

During the adsorption of a small molecule on a solid, its molecular identity may either be essentially preserved (physisorption, molecular chemisorption), or chemical bonds within the molecule may be broken at the time when new bonds to the substrate atoms are formed (dissociative chemisorption). In the latter case, sometimes a physisorbed precursor towards dissociation is found. Type and extent of adsorption are governed by certain factors, namely the chemical nature, the structure, and the perfection of the surface, the nature of the adsorbate, a possible precoverage of the substrate, the pressure and finally the gas as well as surface temperatures. For example, $\text{H}_2$ dissociates easily on low-index surfaces of Ni even at low gas temperatures, but adsorbs exclusively molecularly on Mg(001). From a theoretical viewpoint it is clear that simplified models have to be selected to be able to deal with the complex problem of a dynamically evolving perturbation of an otherwise periodic (and infinite) system. If the interaction between substrate and adsorbate is not too strong (i.e., small ratio of the masses of adsorbate and surface atoms; small electrostatic forces), then the motion of surface atoms (i.e., phonons) can be neglected as a first approximation. [Similarly, we neglect electronic excitations (excitons).] Still, a diatomic adsorbing on a rigid substrate represents a six-dimensional problem—not a challenge for classical trajectory simulations, but nontrivial for an exact quantum treatment. However, for the "light-heavy" adsorption processes to be considered below, the concept of site selectivity, i.e., the distinct preference of the adsorbate for small spatial regions around certain crystallographic positions, holds (as shown by Kara et al. via classical dynamics) and may be exploited. Consequently, it is reasonable to fix the molecule’s center of mass above such a preferred site during the entire adsorptive event. In this way, as shown in Sec. II A, a four-dimensional Hamiltonian is obtained, which may be restricted even further.

To select an appropriate level of theoretical treatment for $\text{H}_2$–surface scattering, the distinct quantum nature of the light adsorbate must be kept in mind. Historically, however, the field was pioneered by the purely classical simulations of McCreey and Wolken, who studied $\text{H}_2$ on $\text{W}(100)$ with two-dimensional potential energy surfaces (henceforth PES's). The first exact quantum treatment of the sticking of $\text{H}_2$ and isotopomers on $\text{Ni}^{18}$ and $\text{Cu}^{19}$ surfaces used time-dependent wave packet propagation methods. Again, only two degrees of freedom, namely, the vertical distance of the molecule's center of mass to the substrate layer and its vibrational coordinate were considered. Meanwhile, wave packet studies have been carried out in three ($\text{H}_2$ and isotopomers on $\text{Ni}^{20}$ and $\text{Ni}^{21}$) and even in four dimensions (for the $\text{H}_2$/Cu system). Moreover, mixed classical-quantum schemes, classical transition state theory (sometimes with tunneling corrections and—once more—classical trajectories have been employed to illustrate higher-dimensional aspects of the adsorption/desorption problem.

Returning to the formally exact quantum treatment in two or three dimensions we note that studies based on time-independent formalisms are rare. Though from quite different viewpoints, the same amount of information may in principle be gained from either description. On the other hand, if a reaction is slow, such that a wave packet must be followed over many times steps, a time-independent picture is to be favored.

Whaley and Light used time-dependent approaches, namely the Wigner R-matrix and complex rotation of the Hamiltonian techniques, respectively, to study rotationally inelastic scattering of HD from Pt(111) and Ag(111). In both cases two degrees of freedom (the molecule’s distance from, and its angular orientation to a flat surface) were treated. Similarly, a 2D PES was used by Baer et al. in their time-independent formulation of reactive gas–surface scattering processes of the type $\text{A}+\text{B}+\text{S}\rightarrow\text{A}+\text{B}+\text{S}$ ($\text{A}+\text{B}$ is a molecule, S the surface). A broader class of reactions, the dissociation of diatoms on solids, has—for the special example of $\text{H}_2$ on $\text{Ni}(100)$—very recently been tackled by Sheng and Zhang. For that purpose, the authors used an uncorrugated 3D model-PES and the $S$-matrix version of Kohn’s variational principle with a continuous basis set (as opposed to discrete variable) representation.

The application of both time-independent formalisms sketched above to gas–surface scattering will be introduced as follows. In Sec. II we define the relevant Hamiltonians and discuss their manipulation within the contexts of the $S$-matrix Kohn and the ABC-Green’s function techniques, respectively. Subsequently (Sec. III), the methods are tested for 2D and 3D flat model-PES, since these have been used earlier in wave packet and time-independent dynamical studies on $\text{H}_2$ on metals.
There is a second motivation for the present contribution, namely that despite numerous presumably exact investigations, the published theoretical sticking probabilities for the standard problem $H_2$ on Ni(100) differ significantly from each other. (Additionally, though there is overall agreement with the main experimental trends observed by Hamza and Madix,29 measured details are not well reproduced.) We have strong evidence that these discrepancies are mainly connected with differences in the PES’s used in earlier work. Therefore, in Sec. IV A, a new six-dimensional PES [an extended version of McCreery and Wolken's London-Eyring-Polanyi-Sato (LEPS) forms37] is proposed for $H_2$ in Ni(100). The parametrization procedure is based on the most reliable experimental and ab initio data available. In Sec. IV B, several aspects of $H_2$ approaching Ni(100) are examined from a dynamical viewpoint. To do so, we use 2- and 3-dimensional cuts through the new PES and the ABC-Green's function method. A final Sec. V concludes our work.

II. METHODOLOGY

A. Hamiltonians

We consider a diatomic molecule approaching a solid surface [see Fig. 1 for the special case of a (100) layer]. Further we let $r = (r \sin \theta \cos \phi, r \sin \theta \sin \phi, r \cos \theta)$ be a vector pointing from atom 1 to atom 2, and $R = (X, Y, Z)$ be a vector specifying the position of the molecule's center of mass relative to a given reference point on the substrate. [In Fig. 1, this reference point is the atop position of the (100) layer.]

If one keeps the surface atom positions fixed, the molecule's motion relative to the substrate can be expressed in terms of the following 6D Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \nabla_r^2 - \frac{\hbar^2}{2M} \nabla_R^2 + V(r, R). \quad (2.1)$$

Here $\mu = (m_1 m_2)/(m_1 + m_2)$ is the molecular reduced mass, and $M = (m_1 + m_2)$. $m_{\text{solid}}/(m_1 + m_2 + m_{\text{solid}}) = m_1 + m_2$, and $m_{\text{solid}} \to \infty$ gives the reduced mass for the molecule moving relative to the substrate.

Starting from Eq. (2.1), one can derive lower-dimensional Hamiltonians which correspond to restricted molecular motions. For instance, by applying the concept of site-selectivity and fixing the molecule's horizontal center of mass coordinates ($X$ and $Y$) at constant values during the entire process, a 4D Hamiltonian is obtained:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \partial_{\theta}^2 - \frac{\hbar^2}{2M} \partial_Z^2 - \frac{\hbar^2}{2\mu} \sin \theta \partial_{\theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + V(r, Z, \theta; X, Y). \quad (2.2)$$

[The Hamiltonian, as opposed to Eq. (2.1), acts on a nuclear wave function $\Psi = r \cdot \Psi$ rather than $\Psi$.] Via the potential, Eq. (2.2) depends parametrically on $X$ and $Y$. Hence for different $X$ and $Y$, the Hamiltonians will be different. Consider an adsorption reaction, for example, then the situations $X = Y = 0, X = 0$, and $Y = d/2$ (or vice versa), and $X = Y = d/2$ would correspond to processes with different initial site-selectivity, namely, with atop $(a)$, bridge $(b)$, and center $(c)$ sites being the preferred positions, respectively.

Similarly, from Eq. (2.2) we may derive two important 3D Hamiltonians by fixing either $\phi$,

$$\hat{H} = -\frac{\hbar^2}{2\mu} \partial_{\theta}^2 - \frac{\hbar^2}{2M} \partial_Z^2 - \frac{\hbar^2}{2\mu} \sin \theta \partial_{\theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + V(r, Z, \theta; X, Y, \phi) \quad (2.3)$$

or $\theta$,

$$\hat{H} = -\frac{\hbar^2}{2\mu} \partial_{\phi}^2 - \frac{\hbar^2}{2M} \partial_Z^2 - \frac{\hbar^2}{2\mu} \sin \theta \partial_{\theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + V(r, Z, \phi; X, Y, \theta). \quad (2.4)$$

In the first case, the cartwheel rotation ($\theta$) is included, and the parametric dependence of $\hat{H}$ on $X, Y, \phi$, and $\phi$ shows that new processes are under consideration, for which site-selectivity not only for the initial, but also for the final states is assumed. Again from the point of view of adsorption, for example, $X = Y = \phi = 0$ describes the atop → bridge dissociation, whereas $X = Y = d/2, \phi = \pi/4$ stands for the center → atop case. In Eq. (2.4), on the other hand, the helicopter rotation ($\phi$) rather than the $\theta$ motion is accounted for. This will be important if not one particular final state is energetically clearly distinguished.

Finally, if no angular motion is allowed for at all, the familiar 2D Hamiltonians of the form

$$\hat{H} = -\frac{\hbar^2}{2\mu} \partial_{\theta}^2 - \frac{\hbar^2}{2M} \partial_Z^2 + V(r, Z; X, Y, \theta, \phi) \quad (2.5)$$

are regained.
We close this subsection by emphasizing the striking similarities between the Hamiltonians given above and those commonly used in gas-phase scattering and bound-state problems. For instance, Eq. (2.5) is formally identical to the Hamiltonian describing collinear \( A + B \rightarrow C \rightarrow A - B + C \) exchange reactions, when expressed in terms of Jacobi coordinates \( r \) (vibrational coordinate) and \( Z \) (scattering coordinate). Further, the 3D Hamiltonian in Eq. (2.3) closely resembles the \( J=0 \) Hamiltonian for a generally nonlinear triatomic molecule, characterized by Jacobi coordinates \( r,Z,\theta \).

It is this close correspondence which motivates our attempt to use methods proven powerful for gas-phase problems in the study of gas–surface scattering. However, there are differences, mainly connected with the periodicity of the adsorbent which leads to a potential periodical in some degrees of freedom, or in other words, a potential which accounts for corrugation effects.

**B. S-Matrix Kohn formalism for molecule–surface scattering**

The S-matrix Kohn formalism of molecule–surface scattering is a natural extension of the formalism for exchange reactions in the gas phase.\(^5\text{–}^7\) Though most of the basic equations reviewed below hold in general, some special relations are valid only for gas–surface scattering in two dimensions [with \( r \) and \( Z \) degrees of freedom; see Eq. (2.5)]. As mentioned earlier, a 3D variant (including the \( \theta \) motion) in a non-DVR formulation has been presented by Sheng and Zhang in Ref. 27.

In general, the objective of the S-matrix Kohn method is to compute the elements \( S_{\gamma'n'}{\gamma n} \) of the scattering matrix. [That is, the amplitudes for transitions from a channel \( \gamma n \), characterized by an index \( \gamma \) which specifies the topological arrangement of particles, and by a vector of quantum numbers \( n \), which labels the asymptotic internal (rovibrational) states, to a corresponding channel \( \gamma'n' \).] As shown in Ref. 5, the S-matrix Kohn variational principle leads to

\[
S = \frac{1}{2}(B - C^T \cdot B^{-1} \cdot C),
\]

with

\[
B = M_{00} - M_{0}^T \cdot M^{-1} \cdot M_{0}, \quad \text{(2.7a)}
\]

\[
C = M_{10} - M_{0}^T \cdot M^{-1} \cdot M_{0}. \quad \text{(2.7b)}
\]

The \( M_{00} \) and \( M_{10} \) are the so-called “free–free” matrices of dimension (number of open channels) \( x \) (number of open channels). To compute those, the free wave functions \( \{ \Phi_{\gamma n} \} \) must be known, since for instance

\[
(\Phi_{\gamma n})_{\gamma'n',\gamma'n} = \langle \Phi_{\gamma'n'} \rvert \hat{H} - E \rvert \Phi_{\gamma n} \rangle. \quad \text{(2.8a)}
\]

A similar expression holds for \( M_{10} \); in Eq. (2.8a), the same notation for matrix elements is used as in Ref. 5.] The exact form of the \( \{ \Phi_{\gamma n} \} \), which are products of asymptotically incoming (or outgoing) translational functions and asymptotic internal eigenfunctions, depends on the actual problem and will be specified later. Moreover, the square “bound–bound” and the rectangular “bound–free” matrices \( M \) and \( M_{0} \), respectively, are

\[
(M)_{\gamma'n'} = \langle \chi_{\gamma'n'} \rvert \hat{H} - E \rvert \chi_{\gamma n} \rangle. \quad \text{(2.8b)}
\]

\[
(M_{0})_{\gamma'n'} = -\langle \chi_{\gamma'n'} \rvert \hat{H} \rvert \Phi_{\gamma n} \rangle. \quad \text{(2.8c)}
\]

The \( \{ \chi_{\gamma n} \} \) are \( L^2 \) (square integrable) basis functions in the total space of all degrees of freedom; the only requirement is that they span the interaction region. These may—as shown in Refs. 7 and 8—be conveniently expressed in terms of a DVR scheme. Then, the “large” matrix \( M \), which according to Eq. (2.7) has to be inverted, will typically be sparse so that efficient iterative inversion techniques can be used.\(^{10(a)}\) Also, no numerical quadratures are required for the evaluation of Hamiltonian matrix elements. Both advantages may help to go beyond systems of dimensionality three. In this work, for vibrational and scattering coordinates we will use kinetic energy expressions based on a sinc-function DVR, as presented in Ref. 7. For these coordinates the grid is evenly spaced and should therefore be suited for scattering from nonsingular potentials. Also following Ref. 7, the “small” matrices \( M_{10} \) and \( M_{10} \) are still computed by numerical quadrature over non-discrete basis functions, whereas \( M_{0} \) is in a mixed representation and no integration is required to construct it.

To apply this formalism to molecule–surface scattering in two dimensions, the asymptotic arrangements \( \gamma \) must be specified. This is done in Fig. 2. Arrangement (a) provides a set of coordinates convenient for a vibrating diatomic molecule far from the substrate. Arrangement (b), on the other hand, is an appropriate choice if \( r_{0} \) is typically small and \( R_b \) is large, i.e., for two adsorbed atoms which translate relative to each other and collectively vibrate relative to the surface layer. Using these classifications, the asymptotic (i.e., \( R_v \rightarrow \infty \)) form of the free functions \( \Phi_{\gamma n} \) required for instance in Eq. (2.8a), is

\[
\lim_{R_v \rightarrow \infty} \Phi_{\gamma n} = \frac{e^{-ik_{\gamma n}R_v}}{\sqrt{\omega_{\gamma n}}} \Phi_{\gamma n}, \quad \text{(2.9a)}
\]

where \( \Phi_{\gamma n}(r) \) is a vibrational eigenfunction (indexed by \( n \)) of the asymptotic Hamiltonian \( \hat{H}_{as}^{\gamma n} \), i.e.,

\[
\begin{align*}
\Gamma_{\alpha} & \equiv r \\
R_{\alpha} & \equiv Z \\
R_{b} & \equiv Z
\end{align*}
\]

**FIG. 2.** Two asymptotic arrangements (a) and (b) for the dissociative adsorption of a diatom on a flat surface. Coordinates are expressed in terms of \( r \) and \( Z \), as well as in terms of Jacobi coordinates \( r, R_v \) (\( \gamma = a,b \)).
\[ \hat{H}^m_{\gamma} \psi_m(r_\gamma) = \left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + \lim_{r_\gamma \to \infty} V(r_\gamma, R_\gamma) \right] \psi_m(r_\gamma) = \epsilon_m \psi_m(r_\gamma). \]  

(2.9b)

Furthermore,

\[ v_m = \frac{2}{M_\gamma} \left( E - \epsilon_m \right) = \hat{H}_{\gamma} k_{\gamma m}. \]  

(2.9c)

are the translational velocities depending on the actual kinetic energies \( E - \epsilon_m \). The Jacobi coordinates \( r_\gamma \) and \( R_\gamma \) have already been defined in Fig. 2, and the vibrational and scattering masses \( \mu \) and \( M \) are for \( H_2 : \mu_a = M_a - 2m_H \) and \( \mu_b = M_a = 2m_H \) (with \( m_H \) being the hydrogen mass).

Hence, through Eq. (2.9) together with the 2D Hamiltonian (2.5), the free–free matrices \( M_0 \) and \( M_{10} \) are completely specified. It should be noted, however, that Eq. (2.9a) only holds for that, i.e., uncorrugated surfaces. Otherwise, the asymptotic behavior of the free function in arrangement (b) (i.e., for \( R_\gamma \to \infty \)) must be of Bloch rather than plane wave form, since the potential is then periodic in the coordinate \( R_\gamma \).

Next, the bound–bound matrix \( M \) must be specified. In the DVR proposed in Ref. 7 this matrix (2.5) is

\[ (M)_{ij,j'=i} = T'_{i,j} \delta_{jj'} + T'_{ij}, \delta_{jj'} + \delta_{ii} \delta_{jj'} V(r_i, Z_j) - \delta_{ii} \delta_{jj'} E, \]  

(2.10)

where \( r_i \to \delta_r \cdot \Delta_r \) (\( i = 1, 2, \ldots, \infty \)) and \( Z_j = j \cdot \Delta_Z \) (\( j = 1, 2, \ldots, \infty \) ) are the equidistantly distributed grid points with grid spacings \( \Lambda_r \) and \( \Delta_Z \), i.e., the “total” index \( \ell \) of Eqs. (2.8b) and (2.8c) is the composite grid point index \( (i,j) = \ell \). The kinetic energy matrix elements \( T'_{i,i} \) and \( T'_{jj} \) are given by Eq. (A8) in Ref. 7, the appropriate expressions for coordinates \( r_i, Z_j \in (0, \infty) \). This infinite grid has to be truncated in some practical calculations. This is achieved by discarding those points (1) which lie outside a region bound by large values \( \bar{r}_{\text{max}} \) and \( \bar{Z}_{\text{max}} \), and \( \phi = 0 \) (for which the condition \( V(r_i, Z_j) > V_c \) is fulfilled (\( V_c \) is an energy cutoff), i.e., points belonging to regions of the PES where the nuclear wave function is vanishingly small.

Finally, the bound–free matrix \( M_0 \) is given in this case by

\[ (M_0)_{ij,jm} = \sqrt{\Delta_r \Delta_Z} \langle r_i Z_j | \hat{H} - E | \Phi_m \rangle. \]  

(2.11)

Equations (2.8a), (2.10), and (2.11) constitute the fundamental equations on which the computation of \( S \)-matrix elements \( S_{r',n';r,n} \) via (2.6) is based. For \( \gamma' = \gamma \) \((= a \text{ or } b)\) we obtain amplitudes for elastic scattering (\( n' = n \); \( n', n \) being quantum numbers either for diatom or molecule–surface vibration) or inelastic scattering (\( n' \neq n \)). Moreover, the case \( \gamma' = \gamma \) describes reactive scattering. From the elements of the \( S \) matrix in the reactive block, cumulative reaction (sticking) probabilities can be extracted using Eq. (1.2) with (for an adsorptive process) \( n_r = (a, n_a) \) and \( n_s = (b, n_b) \).

### C. Cumulative sticking probabilities via Green’s functions with absorbing boundary conditions

The computation of a full \( S \) matrix can be computationally prohibitive. However, if only knowledge of the CRP’s is required (as in Eq. (1.1), for example), an alternative route may be followed, as recently shown by Seideman and Miller.\(^{11}\) Their direct scheme, based on earlier work of Miller et al.,\(^{11}\) makes use of two key elements, namely (1) a DVR for all operators involved and (2) the introduction of absorbing boundary conditions\(^{13}\) for the outgoing wave Green’s operator. Since the method requires less information of the PES (in particular, of its asymptotic regions) than the \( S \)-matrix Kohn technique, it should be more economical.

To give a brief review, we start with a formally exact expression for the cumulative reaction probability \( N(E) \)\(^{11}(b)\)

\[ N(E) = \frac{1}{2} \left( 2\pi \hbar \right)^2 \text{tr} \left[ \hat{f} \cdot \delta (E - \hat{H}) \cdot \hat{f} \cdot \delta (E - \hat{H}) \right], \]  

(2.12)

where \( \hat{H} \), \( \hat{f} \), and \( \delta (E - \hat{H}) \) being the Hamiltonian, flux, and microcanonical density operators, respectively. The latter can be rewritten in terms of an outgoing wave Green’s operator \( \hat{G}(E^+) = \lim_{q \to 0} (E + i\epsilon - \hat{H})^{-1} \), whereas \( \hat{f} \) is most generally expressed in the form of the commutator

\[ \hat{f} = \hbar \delta (H, h[f(q)]) \]  

(2.13)

where \( h \) is the Heaviside step function of some coordinate dependent \( \{q = (q_1, q_2, \ldots, q_F)\} \) function \( f(q) \). [This last quantity defines through the condition \( f(q) = 0 \) a dividing surface separating reactant from product regions.] If one uses these relationships together with a (not yet specified) DVR for all operators, one obtains\(^{12}\)

\[ N(E) = \sum_{jj'} G_{jj'} (E^+)^2 \Gamma_j (E^+_j), \]  

(2.14)

with \( q_j = (q_{j1}, q_{j2}, \ldots, q_{jF}) \) denoting a given grid point,

\[ G(E^+) = (E^+ + i\epsilon - H)^{-1} \]  

(2.15)

being the DVR of the outgoing wave Green’s operator, and

\[ \Gamma_j = (1 - h) \cdot \Gamma, \]  

(2.16a)

\[ \Gamma = 2\epsilon, \]  

(2.16b)

\[ \Gamma_e = h \cdot \Gamma, \]  

(2.16c)

denoting the DVR’s of the total, reactant, and product absorbing potentials, respectively. Note that these have been introduced in the course of a reinterpretation of the convergence factor \( \epsilon \) occurring in \( \hat{G} \) as a function of coordinates, i.e., \( \epsilon = \epsilon(q) \Gamma(q) / 2 \). Equivalently, \(-i\epsilon(q)\) can be understood as an imaginary potential which, when added to the physical Hamiltonian \( \hat{H} \), absorbs the flux exiting from the reaction region (in which \( \epsilon(q) \) is chosen to be effectively zero). This provides a well-defined representation for \( \hat{G}(E^+) \) since the outgoing wave boundary conditions are properly accounted for. The functional form of \( \epsilon(q) \) is usually chosen such that this purpose is opti-
mally fulfilled at a minimum of computational effort (see Ref. 12(a) for details). In the multidimensional case one conveniently takes

\[ \epsilon(q) = g[Q(q)] \]  

(2.17a)

with a function \( g \) determining the shape of the absorbing potential, and some function \( Q(q) \) fixing its location in configuration space. [With Eq. (2.17a), through Eqs. (2.16), the absorbing potentials are specified, once a dividing surface \( f(q) = 0 \) has been selected.]

The extension of the formalism to molecule–surface scattering is straightforward. One simply uses the specific Hamiltonians of Sec II A for Eq. (2.15) and expresses them in an appropriate DVR. If 2D Hamiltonians of the form (2.5) are considered, a convenient representation is provided by the first three terms in Eq. (2.10), i.e., a sinc-function based DVR. In this case it is also reasonable to specify (2.17a) according to Ref. 12(a)

\[ \epsilon(r, Z) = \frac{2\lambda}{1 + \exp[Q(r, Z)/\eta]} \]  

(2.17b)

and

\[ Q(r, Z) = \begin{cases} Z_{\text{max}} - Z, & Z > r \\ r_{\text{max}} - r, & Z < r \end{cases} \]  

(2.17c)

i.e., to place two absorbing “strips” of Woods–Saxon form in the reactant and product regions. [Other forms \( g \) and \( Q \) in Eq. (2.17a) proved to be less effective for the present applications.]

In those calculations using the 3D Hamiltonians given by Eq. (2.3), we still use a sinc-function based DVR for the \( r \) and \( Z \) degrees of freedom, but use a Gauss–Legendre DVR for \( \theta \)-dependent operators. (A sinc-DVR for these operators, as given in Ref. 7, was found to be less efficient with respect to the number of angular points required.) Though in the 3D case \( \epsilon \) could in general be a function of \( r, Z, \) and \( \theta \), we retain the 2D form in Eq. (2.17b). This seems to be reasonable since in all cases studied here, the potential raises sharply with \( \theta \) leaving its equilibrium value—hence the corresponding points are discarded via the cutoff criterion \( V < V_c \) and no outgoing flux has to be absorbed.

Although the formalism relevant for gas-phase scattering can be adopted essentially unchanged for gas–surface problems, there is at least one important difference if corrugation effects are included. Namely, the parameter \( r_{\text{max}} \) in Eq. (2.17c) is then not any longer a convergence parameter (whereas \( Z_{\text{max}} \) still is). This is because the corrugation of the solid introduces periodicity in the potential with respect to \( r \). Therefore, different locations of the \( r \)-dependent absorbing strips correspond to different reactive events, e.g., a dissociation-only or a dissociation plus diffusion process (see Sec. IV).

III. DYNAMICS ON UNCORRUGATED SURFACES

In this section, the methods described in Sec. II will be applied to uncorrugated model-PES’s of two and three dimensions. Since the latter were used in earlier wave packet \(^{28(a)}\) and time-independent studies, \(^{27}\) the present section also serves to compare our results to those given there.

A. Two-dimensional case

With the objective of studying the influence of different PES topologies on dynamical observables for the dissociative adsorption of \( \text{H}_2 \) on metals, Halstead and Holloway \(^{28(a)}\) constructed a series of 2D model-PES (\( r \) and \( Z \) degrees of freedom). They started from a template of 1D Morse potentials for the \( r \) ("entrance channel") and \( Z \) ("exit channel") variables, their contours being connected by quarter circles in the "reaction zone." By superimposing a Gaussian barrier (of height \( V_0 = 0.538 \) eV) at different positions along the minimum energy path of the template, they arrived at model-PES’s with "early," "central," "late," and "very late" barriers (from the viewpoint of dissociation).

We performed calculations utilizing 2D Hamiltonians of the form (2.5) together with the PES’s of Ref. 28(a) to compare both time-independent approaches sketched above to the wave packet results of Ref. 28(a). Using the Green’s function technique to compute \( N(E) \) directly we
were able to confirm qualitatively all observations made by Halstead et al. However, as shown in Fig. 3(a), the quantitative agreement was not perfect, with our calculations predicting (i) a steeper rise of \( N(E) \) with \( E \), and (ii) no leveling-off of \( N(E) \) at higher energies for the early and late barriers. Careful convergence tests, during which all parameters affecting \( N(E) \) were systematically varied (\( \Delta_r \), \( \Delta_{Zr} \), \( V_c \), \( r_{\text{max}} \), \( Z_{\text{max}} \), \( \lambda \), \( \eta \)) did not lead to curves significantly different from those shown here. Also, different forms \( Q(r,Z) \) than the one given in Eq. (2.17) did not substantially affect the results. Further, failure (i) cannot be traced back to the finite width (in momentum space) of the wave packets used in Ref. 28(a): the reported uncertainty of \( \Delta k/k \sim 0.02 \) is simply too small to account for the distinct differences especially in the low-energy tails \( N(E) \), which are of particular importance if thermal rate constants are to be computed.

Therefore, we also computed \( N(E) \) using the indirect expression Eq. (1.2) in connection with the \( S \)-matrix Kohn method. Figure 3(b) gives (for the early barrier case only) sticking coefficients taken from Ref. 28(a) in comparison to those obtained with Eq. (1.2) or Eq. (2.14). We note that both time-independent methods yield virtually the same CRP's. The excellent agreement confirms also that the direct results are converged with respect to the parameters governing the absorbing potential [see Eq. (2.17)]. Provided the PES parameters published in Ref. 28(a) are correct, it is still an open question why our values differ somewhat from the wave packet data.

The converged computational parameters for the \( S \)-matrix Kohn results given in Fig. 3(b) are \( V_c = 1.95 \text{ eV} \), number of grid points per de Broglie wave length = 4.0 (this leads for instance at \( E(\text{total}) - E(H_2, v=0) = 0.53 \text{ eV} \) to \( \Delta_r = 0.214 \text{ a.u.} \) and \( \Delta_{Zr} = 0.107 \text{ a.u.} \). For \( r_{\text{max}} = Z_{\text{max}} \) we took large values (10.0 a.u.), to make sure that the asymptotic regions of the PES are well accounted for. It is interesting to note that the \( S \)-matrix Kohn results could be reproduced by the Green's matrix technique to within 1% and better for most energies, already if in the latter case \( r_{\text{max}} = Z_{\text{max}} = 4.5 \text{ a.u.} \) was chosen (with otherwise identical parameters). This shows once more that the Green's function approach to compute CRP's requires less information on the asymptotic regions, thus reducing the number of grid points. Further, the Green's function results shown in Fig. 3(b) were obtained with \( \lambda = 1.1 \text{ eV} \) and \( \eta = 0.40 \text{ a.u.}^{-1} \).

Before leaving this subsection, we wish to demonstrate how the \( S \)-matrix Kohn method works in predicting state-resolved transition probabilities for gas-surface scattering. In Fig. 4(a), state-specific reaction probabilities are displayed for a very late barrier PES (i.e., the transition state is located at very large \( r \) or small \( Z \)), together with the \( N(E) \) curve. The latter shows some pronounced structure due to Feshbach resonances [see Ref. 28(a)]. We note that up to \( E = 0.514 \text{ eV} \) (all energies in the figures of this work are relative to the vibrational ground state of free \( H_2 \)) \( N(E) \) is solely determined by \( P_{n,\alpha} = |S_{n,\alpha}|^2 \), i.e., the reaction proceeds vibrationally adiabatic. (From the viewpoint of adsorption, two product channels are open in this energy range.) Above this energy, a second reactant channel opens (\( \gamma = a, n = 1 \)). Molecules starting from this excited state do not react adiabatically—in fact, \( P_{n,\alpha} < P_{n,\gamma} \) for all energies studied. Figure 4(b) demonstrates a strict correlation between \( N(E) \) and a elastic scattering probability, \( P_{\alpha,\alpha} \). This observation is a simple consequence of the conservation of probability in combination with the fact...
that from the initial state ($\gamma=a$, $n=0$) no inelastic channels can be reached up to $E=0.514$ eV. At this energy, however, inelastic probability $P_{a\gamma\gamma}$ begins to increase [Fig. 4(c)] and (together with a distinct population of now open reactive channels) to destroy the low-energy correlation observed in Fig. 4(b).

B. Three-dimensional case

Including one more degree of freedom ($\theta$), Sheng and Zhang recently performed three-dimensional wave packet calculation between both time-independent techniques appears to be good to within the convergence of both calculations. As a technical detail we note that for the low kinetic energies associated now, great care must be taken to choose appropriate convergence parameters, particularly for those responsible for the absorbing potentials. Also, to arrive at physical meaningful results, as many as 15 Gauss-Legendre abscissae were required for the DVR of $\theta$-dependent operators.

There is no easy way to compare our $N(E)$ graphs to the experimental sticking coefficients of Hamza and Madix.29 This is simply because these authors measure $N(E)$ as a function of kinetic energy, whereas we obtain them as a function of total energy (kinetic plus rotational). Hence there is a mismatch of energy scales, and there is no strict transformation between them since in Ref. 29 no information about the rotational state distribution is provided. However, the $H_2$ beams prepared in Ref. 29 are likely to be rotationally cold, and since the contributions of higher $j$'s to $N(E)$ are small in the energy range considered, Fig. 5 and the experiment should reflect similar trends. By comparing both curves, the following differences become apparent: (i) the theoretical data are shifted towards the low-energy regime, (ii) at higher energies, the predicted $N(E)$ seem to be too large; and (iii) there is no structure in the computed functions. Interestingly, the 3D wave packet results of Cruz and Jackson,22 who studied the same process as Sheng and Zhang, predict the $N(E)$ curve to be shifted relative to Fig. 5 towards higher energies by as much as $\sim 0.10$ eV and to be much less steep. In the search for an explanation of these clear differences between potentially exact methods, we note that the uncorrugated 3D PES proposed in Refs. 21 and 27 does not correctly reproduce the location and the height of the transition state towards dissociation as compared to ab initio data.21 Further, it predicts the adsorption to be slightly endoenergetic, while experimentally the heat of adsorption for $H_2$ on Ni(100) is found to be $-63$ kcal/mol.20 In contrast, Cruz and Jackson's PES nicely resembles ab initio data for the $\text{H}_2 \rightarrow \text{bridge } \text{event}$,21(a) but makes no reference to a more recent ab initio study, in which the energetically favorable $\text{H}_2 \rightarrow \text{center}$ path has been considered in detail.31 Therefore, the need to construct a new PES for the interaction of $H_2$ with Ni(100), which is based on the most reliable ab initio and experimental results, seems to be obvious. Such a parametrization will be given in the next section, and used for subsequent dynamical studies.

IV. DYNAMICS OF THE ATOP DISSOCIATION OF $H_2$ ON Ni(100)

A. The potential energy surface

Following the ideas of McCreery and Wolken17 (and of Cruz and Jackson22) we use a six-dimensional LEPS form to model the interaction of $H_2$ with Ni(100)

\[ V(x_1, y_1, z_1, x_2, y_2, z_2) = \sum_{i=1}^{3} U_i - \left[ A_i^2 + (A_1 + A_2)^2 - A_3(A_1 + A_2) \right]^{1/2}. \] (4.1)

Here the $(x_1, y_1, z_1)$ are the Cartesian coordinates of the two H atoms (see Fig. 1), and $U_i$ and $A_i$ denote Coulomb

\[ U_i = \frac{1}{4(1 + \Delta_i)} \cdot D_i [(3 + \Delta_i) e^{-(2\Delta \rho - r - \rho)]}, \] (4.2a)

and exchange terms,

\[ A_i = \frac{1}{4(1 + \Delta_i)} \cdot D_i [(3 + 3\Delta_i) e^{-2\Delta \rho - r - \rho)]}, \] (4.2b)

respectively, which are assumed to be of generalized Morse form. Further, the $\{\rho_i\}$ denote atom–surface $(\rho_1 = z_1; \rho_2 = z_2)$ or atom–atom $(\rho_i = r)$ distances (the $\{\rho_i\}$ being the corresponding equilibrium values), and $\{\alpha_i\}$ and $\{D_i\}$ denote the Morse exponential factors and well depths, respectively.

\[ N(E) \]

\[ E \text{ (TOTAL)} - E \text{ (H}_2\text{, } v=0) \text{ (eV)} \]

\[ 0.00 \quad 0.02 \quad 0.04 \quad 0.06 \quad 0.08 \quad 0.10 \]

\[ \Delta \text{ Ref. [27]} \quad \text{This work} \]
tively. To account for corrugation, we make the \( \{ \rho_\alpha \} \) and \( \{ D \} \) periodic functions of the horizontal atomic coordinates \( x_1, x_2, p_1, \) and \( p_2 \). Details of this procedure are given in the Appendix. Here we only stress that for the determination of parameters governing the asymptotic states (i.e., either the free \( \text{H}_2 \) molecule or singly adsorbed hydrogen atoms), we referred to spectroscopical data for the \( \text{H-H} \) interaction, and to experimental32 and theoretical33-35 dissociation energies,32(a),33-35 equilibrium distances32(b),33,34 and vibrational frequencies32(c),33 for the \( \text{H-S} \) surface interaction.

In contrast to these asymptotic data, for which abundant and reliable information is available, not much is known about the interaction region modeled by the Sato parameters \( \Delta_i \) in Eq. (4.2). The concept of site selectivity, though probably adequate for \( \text{H}_2/\text{Ni} \), does not say anything about the preferred position itself. Indeed, the latter for \( \text{H}_2 \) on \( \text{Ni}(100) \) is still somewhat controversial.16,23(b),36 Siegbahn et al., based on their cluster calculations31 and on experiments,37 suggest that \( \text{H}_2 \) approaches the atop position (i.e., \( X=Y=0 \)) most easily in a parallel orientation. In particular, they find a small (classical) barrier (0.191 eV) for the \( \text{atop} \rightarrow \text{bridge} \) dissociation (\( X=Y=0, \phi=0 \))31(a) and—more recently—no barrier at all for the more exothermic \( \text{atop} \rightarrow \text{center} \) reaction (\( X=Y=0, \phi=\pi/4 \)).31(b) Along the latter reaction path also a metastable molecular adsorbed precursor towards dissociation can be identified at large \( Z \) and small \( r \). We used Siegbahn's energy and geometry results on the transition state (TS) for the \( \text{atop} \rightarrow \text{bridge} \), as well as the physisorption well and the TS towards dissociation for the \( \text{atop} \rightarrow \text{center} \) reactions to parametrize the interaction region (see the Appendix for details).

In Fig. 6 we present 2D cuts through the new PES, modeling the \( \text{atop} \rightarrow \text{bridge} \) (a) and \( \text{atop} \rightarrow \text{center} \) (b) chemisorptions of \( \text{H}_2 \) on \( \text{Ni}(100) \). In the figure caption, the target values for characteristic points in the interaction region, as defined in the Appendix, are compared with the actual values predicted with the present parametrization scheme. The agreement is very good. Further, by construction, the asymptotic regions are represented well, too. Hence the proposed PES should give a realistic description of the energetics at least for the atop adsorption of \( \text{H}_2 \) on \( \text{Ni}(100) \).

### B. Dynamical simulations

In this subsection, three particular dynamical aspects of the atop approach of \( \text{H}_2 \) to \( \text{Ni}(100) \) are investigated with the help of the ABC-Green's function method and our new PES. They are (i) the role of corrugation, (ii) the role of the cartwheel \( \phi \) motion, (iii) and the role of the helicopter \( \phi \)-degree of freedom.

To illustrate the first point, Fig. 7(a) shows \( N(E) \) curves for the \( \text{atop} \rightarrow \text{bridge} \) event, obtained with the 2D Hamiltonian in Eq. (2.5) (\( X=Y=\phi=0, \theta=\pi/2 \)). As noted earlier, for \( \text{corrugated potentials} \) \( r_{\text{max}} \) in Eq. (2.17c) is not a convergence parameter. Rather, by centering the product (from the point of view of adsorption) absorbing region around different \( r_{\text{max}} \), different physical processes are described. For example, \( r_{\text{max}} \sim 6 \) a.u. would only allow for a pure \( \text{atop} \rightarrow \text{bridge} \) dissociation, whereas \( r_{\text{max}} \sim 14 \) a.u. [see Fig. 6(a)], corresponds to a combined dissociation plus diffusion event. Hence we first optimized our true convergence parameters \( \lambda, \eta, Z_{\text{max}}, \Delta_r \) and \( \Delta_\phi \), and then scanned the corrugated PES by continuously increasing \( r_{\text{max}} \). \( N(E) \) expectedly appeared to be rather insensitive to moderate variations of \( r_{\text{max}} \) in the approximate interval 5 a.u. \(< r_{\text{max}} < 9 \) a.u., where only dissociation is possible. The case \( r_{\text{max}} \sim 7 \) a.u. is shown in Fig. 7(a). For \( r_{\text{max}} \geq 9 \) a.u., however, the physical potential for the \( \text{bridge} \rightarrow \text{bridge} \) diffusion process turns on and considerably deforms the \( N(E) \) curve. This is also shown in Fig. 7(a) for \( r_{\text{max}} = 14 \) a.u., where the full combined process obtains. The former, structureless \( N(E) \) rises quickly and without a visible energy threshold. (The classical barrier is small and furthermore reduced due to the zero-point energy released along the reaction path; also, \( \text{H}_2 \) tunnels to a significant extent.) In contrast the latter \( N(E) \) curve is shifted to the right and shows distinct peaks and valleys patterns at low energies. The shift is due to a large barrier for diffusion [1.165 eV relative to free \( \text{H}_2 \) or 1.44 eV relative to the dissociation well in Fig. 6(a)]. The structure can be attributed to res-

![FIG. 6. Two-dimensional (\( \theta=\pi/2 \)) cuts through the new PES modeling the \( \text{atop} \rightarrow \text{bridge} \) (a) and \( \text{atop} \rightarrow \text{center} \) (b) adsorptions of \( \text{H}_2 \) on \( \text{Ni}(100) \). The contour spacing is 300 meV. Geometries and energies (relative to the classical ground state of free \( \text{H}_2 \)) for the TS's towards dissociation in (a) ("TS1") and (b) ("TS2") and the physisorption precursor well in (b) ("phys") are with the present parametrization (target ab initio values in brackets): \( r_{\text{TS1}}=2.33 \) a.u. (2.37), \( Z_{\text{TS1}}=2.42 \) a.u. (2.51), \( E_{\text{TS1}}=-190 \) meV (+191); \( r_{\text{phys}}=2.25 \) a.u. (2.3), \( Z_{\text{phys}}=2.62 \) a.u. (2.5), \( E_{\text{phys}}=-87 \) meV (87); \( r_{\text{phys}}=1.52 \) a.u. (1.69), \( Z_{\text{phys}}=2.84 \) a.u. (2.84), \( E_{\text{phys}}=-486 \) meV (-477).]
Next, the influence of the \( \theta \)-motion on \( N(E) \) has been examined for dissociation-only processes. In Fig. 7 (b), we compare 3D results, as obtained with Hamiltonians (2.3) for \( X = Y = \phi = 0 \) and \( X = Y = 0, \phi = \pi/8 \) to the corresponding 2D curves, where \( \theta \) was kept fixed at \( \pi/2 \). Referring to the \( \phi = 0 \) case (atop \( \rightarrow \) bridge) we observe a remarkable shift to the right, and a flattening of \( N(E) \) in the higher-dimensional example. This strong dimensionality effect has been found earlier for gas-surface problems,\(^{18(a)}\) and is in complete analogy to gas-phase dynamics. For example, for the \( \text{H} + \text{H}_2 \) reaction exactly the same trend for the cumulative reaction probabilities is observed in going from the collinear to the 3D case. The general behavior is mainly a consequence of the fact that the energetically favored 2D geometries (collinear \( \text{H}_3 \) and \( \text{H}_2 \) parallel to a surface, respectively), are a small fraction of the space available in the 3D system.

The situation found for \( \phi = \pi/8 \) demonstrates a second dimensionality effect, also known from gas-phase dynamics: The possibility that structure in CRP curves will be softened out if more degrees of freedom are involved. With the present PES one finds for \( X = Y = 0, \theta = \pi/2, \phi = \pi/8 \) a resonancelike structure at \( E(\text{total}) - E(\text{H}_2, v = 0) = 0.08 \) eV. This is because in going from \( \phi = 0 \) to \( \phi = \pi/4 \) the activation barrier for dissociation is smoothly diminished while a distinct precursor well emerges (see Fig. 6). Also, along the reaction path zero-point energy is released due to differences in reduced masses. Consequently, for intermediate \( \phi \), a dynamical well effective in temporarily trapping flux may occur, as observed for \( \phi = \pi/8 \). In three dimensions, however, the PES appears on average to be smoother than in 2D, and hence the dynamic structure is averaged out as in Fig. 7 (b).

Figure 7(b) indicates already that not only the \( \theta \), but also the \( \phi \)-degree of freedom appears to be important. This point is emphasized with the help of Fig. 7 (c), which depicts \( N(E) \) curves resulting from 3D calculations [\( r, \theta, \phi \) see Eq. (2.3)] at different but fixed \( \phi \) values for \( \phi = 0, \phi = \pi/8, \) and \( \phi = \pi/4 \). Again, the (classical) barrier is gradually turned on with decreasing \( \phi \). Therefore, \( N(E, \phi = \pi/4) \) is very steep and saturates at low energies, whereas \( N(E, \phi = 0) \) turns on smoothly (due to tunneling) and is as a whole shifted towards higher energies. The case \( \phi = \pi/8 \) is somewhere in between. Figure 7 (c) also explains why the sticking probabilities in Ref. 22 are so different from those in Ref. 27 (or Ref. 21). In the first case, a
distinct barrier towards dissociation (0.19 eV) is predicted—hence the corresponding CRP results are much like our $\phi=0$ case in Fig. 7(c). In Refs. 27 and 21, however, the PES used estimates the barrier to be small (0.127 eV)—hence the resulting $N(E)$ curve is more like in our $\phi=\pi/8$ situation. The large dependence of $N(E)$ on $\phi$, as found here, relies on the validity of our PES, and may actually be smaller because Siegbahn et al. used slightly different methods in Refs. 31(a) and 31(b). Nevertheless, a more thorough inclusion of the $\phi$-degree of freedom via Eq. (2.4) or Eq. (2.2) seems advisable.

V. CONCLUSIONS

In the present work two exact time-independent quantum reactive scattering methods have been applied to the special case of molecule–surface scattering. The $S$-matrix Kohn technique (which has been used earlier in gas–surface scattering$^{27}$) provides the complete $S$ matrix at a given energy, whereas the ABC-Green’s function method gives the cumulative reaction probability $N(E)$ directly without making explicit reference to the $S$ matrix and asymptotic channels, thereby being computationally more efficient. For both methods we expressed the operators in a DVR, which makes the Hamiltonian matrices sparse and avoids multidimensional quadratures in order to construct them.

From the viewpoint of applications we note that in real systems, like $H_2$ on $Ni(100)$, even if the concept of site-selectivity may hold and if phonons do not play a crucial role (experimentally, the sticking coefficients are independent of surface temperature over a wide range$^{28}$), all four remaining degrees of freedom seem to be of vital importance. The use of restricted dimensionality Hamiltonians has shown, that at least a four-dimensional treatment via Eq. (2.2) is required for a realistic description of this system. Although in this preliminary study we did not emphasize them, two features of the physical problem and its present formulation may be exploited for this purpose: (i) The sparsity of the Hamiltonian, and (ii) the symmetry properties of the potential function. Within the context of the $S$-matrix Kohn approach, iterative matrix inversion techniques which utilize the sparsity of the Hamiltonian, have already successfully been used$^5$. This improves the computational scaling to obtain the entire $S$ matrix from $N^0$ ($N$ is the dimension of the Hamiltonian matrix) to quasiquadratic. For the ABC-Green’s matrix method, potential complex iteration schemes are complex Lanczos$^{10(b)}$ generalized minimum residual (GMRES),$^{10(c)}$ or a power series expansion of the Green’s function.$^{10(d)}$ Whereas the latter has already been successfully implemented and,$^{10(d)}$ the usefulness of the former two is still a matter of active research. Further, the point symmetry inherent in the problem may be utilized to block diagonalize the Hamiltonian.$^{38}$ In particular, for the atop adsorption of $H_2$ on $Ni(100)$, there is a fourfold symmetry of the potential with respect to $\phi$, and a twofold symmetry with respect to $\theta$, thus confining the effective range of the angular variables to the interval $(0, \pi/2)$. The implementation of these possibilities is presently under investigation.

There is a second type of symmetry inherent in the problem, namely, the translational one, reflected by the corrugation of the potential. Our analysis in Sec. IV has shown that—as soon as corrugation is included—there is a strong coupling between dissociation and surface diffusion. Hence the elementary steps of heterogeneous catalysis may in general not be treated as a sequence of independent single steps. Here, however, we included corrugation only in connection with the Green’s matrix method and also only in quite an approximate manner by placing product absorbing potentials at various positions in configuration space. A more proper treatment within the $S$-matrix Kohn scheme, for instance, would be to introduce Bloch-type boundary conditions for surface channel outgoing waves. Alternatively, one might still try to compute individual $N(E)$’s for each elementary step involved in a typical surface reaction, and then construct a composite $N(E)$ for the entire process.$^{39}$ These possibilities are objects of our current research.

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APPENDIX

In this Appendix we show how the parameters occurring in Eq. (4.2) have been determined.

The $H-H$ interaction. The $H-H$ interaction parameters $\alpha_1=1.028$ 10 a.u., $\alpha_2=1.400$ 83 a.u., and $D_3=4.745$ eV were taken from Refs. 17 and 22. The values represent an optimum Morse fit to the experimentally observed $H-H$ potential energy curve.

The $H-Ni(100)$ interaction. Due to symmetry we have $D_1=D_2$, $\rho_{10}=\rho_{20}=\rho_{0}$, $\alpha_1=\alpha_2$. To account for corrugation, the $D_0$, $\rho_{0}$, and vibrational frequencies $\omega_i$ (from which the Morse exponents $\alpha_i$ will be deduced) have been forced to be periodic functions of the horizontal atom coordinates $x_i$ and $y_i$ ($i=1,2$). For instance, we choose

$$D_0-D_0 \left[ 1+a_D \cos \cos \frac{2\pi x_i}{d} + \cos \cos \frac{2\pi y_i}{d} + P_D(x_i, y_i) \right], \quad (A1a)$$

with

$$P_D(x, y_i)=b_D \left[ \cos \frac{2\pi x_i}{d} - 1 \right] \cdot \left[ \cos \frac{2\pi y_i}{d} - 1 \right] - 4 + 2 \quad (A1b)$$

and $d$ standing for the lattice constant for the $Ni(100)$ surface ($d=4.69$ a.u.). The three parameters $D_0$, $a_D$, and $b_D$.
For the center adsorption of H on Ni(100), an experimental value \(\Delta_{10} = 0.2635\), \(\Delta_{11m} = 0.0535\), \(\Delta_{30} = 0.356\), \(\Delta_{3m} = 0.106\).