

## Current trends in the theories of gas-surface interaction

HARJINDER SINGH and B M DEB

Department of Chemistry, Theoretical Chemistry Group, Panjab University, Chandigarh  
160 014, India

**Abstract.** Studies on gas-surface dynamics have acquired considerable importance recently not only for their intrinsic scientific interest but also for their technological potential. This article first briefly describes various experimental techniques and a number of interesting recent observations resulting from these techniques. It then discusses certain important theoretical methodologies being extensively used nowadays. There are *three* broad overlapping streams of theoretical works, viz classical, semi-classical and quantum-mechanical. There are also *three* basic problems in gas-surface interaction, viz (i) the interface presents a many-body problem; (ii) the solid surface is "rough"; (iii) the number of diffractive and inelastic channels is enormously large. The semi-classical approaches appear to dominate over the others in variety and quantity. But the sources of benchmark theoretical results are still the rigorous classical-trajectory and close-coupling quantum-mechanical calculations. The coming years are likely to witness not only increased numerical accuracy through refinements in semi-classical and quantum-mechanical approaches, but also certain special approximate methods designed to yield deeper physical insights into the nature of gas-surface interaction.

**Keywords.** Gas-surface dynamics; gas-surface interaction; adsorption; surface structure and reactivity.

PACS No. 82-65

### 1. Introduction: A bird's-eye view of techniques and features of gas-surface interaction

The interaction of gaseous atoms and molecules with the surface of a solid is perhaps the most widely explored subject in surface science. Indeed, the rapidly developing and basic scientific area of gas-surface dynamics has considerable potential impact on modern technology and vice versa. Thus, although most innovations in surface technology, e.g. microelectronics involving high miniaturization and high-tenacity surfaces of space-earth vehicles, were initially based on an inadequate understanding of surface structure and reactivity, they did lead to the realization that the physics and chemistry of interfaces abound with unanswered questions. For example, *heterogeneous reaction dynamics*, which has not yet matured, is essentially the study of chemical reactions occurring at gas-solid interfaces; the information sought here is relevant to a host of subjects ranging from catalysis to percolation\*. It is well known that many synthetic processes occur in the presence of metal surfaces. Further, certain problems in electrochemistry, e.g. corrosion and solar-energy research are akin to problems in gas-

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The authors felicitate Prof. D S Kothari on his eightieth birthday and dedicate this paper to him on this occasion.

\* Percolation is the flow of a fluid through a medium when a random noise or force is present in the system.

surface interaction which has therefore emerged, in the last two decades, as a major area of interdisciplinary research.

Historically, the first landmark experiments on the scattering of He and H<sub>2</sub> from alkali-halide surfaces contributed to the development of quantum scattering theory and were also useful in supplementing x-ray as well as neutron diffraction techniques. However, these techniques generally used sources which did not permit the isolation of the surface, either because of excess energy (x-rays) or because of no repulsive barrier just below the surface (neutrons). Inevitably, further interest in the subject waned, since surface discontinuity is too abrupt and too complex to permit a meaningful resolution from bulk interference (Adamson 1979; Morrison 1977; Somorjai 1981). Low-energy electron diffraction (LEED) avoids both these problems. Since low-energy electrons have greater wavelength than thermal neutrons, they do not penetrate more than one or two layers of bulk lattice. Today, this technique is extensively used and is also theoretically well-supported (Heinz 1982; Pendry 1984; Van Hove 1985; Van Hove and Tong 1979). Nevertheless, certain problems like multiple scattering of electrons on the surface remain and various modifications (Bernasek 1980) have been suggested to deal with these problems.

There are other experimental techniques. For example, *surface structure* can be studied by angle-resolved electron spectroscopy (Allyn *et al* 1977) and vibrational spectroscopy of adsorbed species (Citrin *et al* 1983; Hoffmann 1983; Ibach and Mills 1982, Stöhr *et al* 1983), while *surface composition* can be explored by photoelectron spectroscopy (Joyner 1977). Much useful information on *reactant and product characterization* comes from molecular beam methods (Cardillo 1981). Molecular beam studies have been accelerated by the recent availability of high-vacuum ( $< 10^{-10}$  torr) equipment providing reasonably long-lived *clean* surfaces.

Theoretical studies on gas-surface dynamics have picked up a rapid pace only recently. Until three decades ago, most theoretical studies focussed essentially on the improvement of empirical concepts such as adsorption isotherms, the BET equation and on the search for their fundamental basis. Since surfaces represent a many-body problem with special physicochemical effects arising because of surface discontinuities, rigorous work could not be done. Simplified classical-mechanical models using harmonic lattice structures or simple-cubic nearest-neighbour approximations were used even in the early sixties. Attempts were also made to solve the gas-surface dynamical problem in lower dimensions. Hard- and soft-cube analogues were used to mimic the surface potential (Goodman and Wachman 1976). Approximate quantum-mechanical methods of the distorted-wave Born approximation-type also developed in the late sixties. This period marked the beginning of "exact" quantum-mechanical and classical trajectory calculations (Celli and Evans 1982; Goodman and Wachman 1976; Tully 1980a). So far, semi- or quasi-classical approaches have been reasonably successful and quite popular. Among these are the quantum wave-packet, quasi-classical trajectory, sudden approximation and semi-classical perturbation methods. We will discuss these briefly in §2.

The nature and products of interaction between gas atoms/molecules and a solid surface depend on the energy with which projectiles approach the surface (both absolute and relative distribution in various degrees of freedom). As depicted in figure 1, a range of processes can be visualized (Tully and Cardillo 1984). Since the surface has a high free energy (hence, a high chemical potential), at reasonable (system-dependent) energies inelastic processes dominate the real events. However, study of elastic

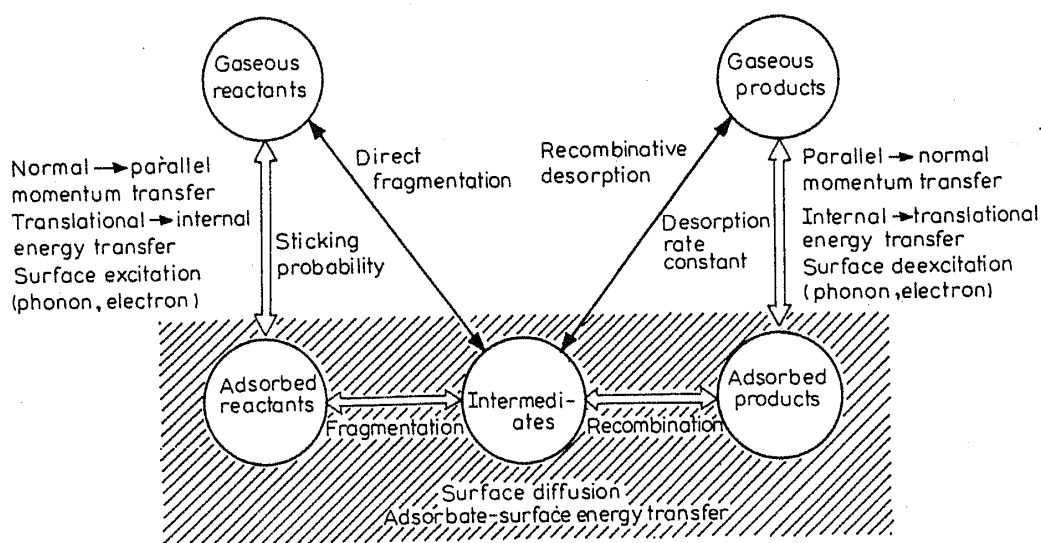


Figure 1. Schematic diagram showing various processes occurring on a solid surface as a gaseous reactant approaches it. (Reproduced with permission from Tully and Cardillo 1984).

processes (i.e., those accompanying momentum transfer to the solid) by themselves can be quite instructive.

Recent advances in experimental techniques and in computer technology have enabled researchers to focus increasingly on realistic events in heterogeneous dynamics involving various internal and reactive channels, e.g. *adsorption following dissociation or recombinative desorption*. Atomic dissociation products can have an inhibitory effect on molecular adsorption, e.g.  $O_2/O$  on  $Cu(110)$  (Didio *et al* 1984). The sticking probabilities\* on the surface obviously depend upon the nature of the adsorbate; for example,  $N_2$  and  $CH_4$  dissociatively adsorb on  $Cu(110)$ , with sticking probabilities depending explicitly on the total incident kinetic energy and the normal component of kinetic energy respectively (Auerbach *et al* 1984). Adsorption is sometimes accompanied by free-radical formation, e.g. the generation of  $(CH_3O)$  for the methanol/ $Ni(110)$  system was reported (Richter and Ho 1985) by using temperature-programmed electron-energy-loss spectroscopy (EELS). Indeed, many different experimental techniques have been used to study adsorbed materials, among which EELS (Bandy *et al* 1982) and angle-resolved UV photoemission studies (Dose 1981; Fauster and Himpsel 1983; Pendry 1981; Smith 1981) are abundant. Such studies sometimes reveal (Harris *et al* 1981; Hsu *et al* 1982; Opila and Gomer 1981; Tatarenko *et al* 1983) the presence of *hot precursor states* (transition states which are highly excited in internal modes) not in thermal equilibrium with the surface. Dissociated species tend to lose most of the perpendicular kinetic energy, reaching a thermal equilibrium. However, the parallel component has a rather long life-time, thermalizing eventually by diffusion processes.

The phenomenon of recombinative desorption is also system-specific. An interesting observation on the activated recombinative desorption of  $H_2$  from  $Cu$  is that the desorbed products do not show a Boltzmann distribution at the surface temperature

\* Sticking probability is the probability of adsorption of an impacting molecule.

(Barker and Auerbach 1984). Multi-phonon ionization combined with time-of-flight mass spectrometry shows a non-Boltzmann *rotational* distribution in this system (Kubiak *et al* 1985). The non-Boltzmann behaviour and its relative involvement in the gas-surface dynamics is more significant with *vibrational* levels. Actually, a shortlived ion is believed to be formed in the H<sub>2</sub>/Cu system (Kubiak *et al* 1985; Gadzuk 1983).

Information on the thickness of the adsorbed layer can be obtained by using metastable atom deexcitation spectroscopy (MADS) e.g. by employing excited metastable noble gas atoms as projectiles and analyzing the electrons emitted in the deexcitation process. Bozso *et al* (1983) used this technique (also known as surface penning ionization) to show that the adsorbed layer must be more than one atomic-diameter thick in order to prevent ionization of the metastable species. Often, adsorption occurs with a preferred orientation of the molecule on the surface; for example, N<sub>2</sub>O is adsorbed on Pt(111) in an erect configuration, with the N-end toward the metal (EELS (Avery 1983), MADS (Hagstrum 1984)). Note that *overlayer structures\** are also intricately involved in chemisorption systems, e.g. H/W(110) (Difoggio and Gomer 1982; Gonchar *et al* 1983). Atomic and molecular diffraction is widely used to gain information on elastic and inelastic scattering (non-reactive). Rainbows, including supernumerary\*\* ones, occur because of diffraction of He from both Ge(100) and Si(100); this observation is explained on the basis of disordered reconstructed lattice structures (Sakai *et al* 1984). Further, rotational inelasticity has been observed (Asscher *et al* 1982; Frenkel *et al* 1980, 1981; Kleyn *et al* 1981, 1982; Luntz *et al* 1982; McClelland *et al* 1981; Zacharias *et al* 1982) in a number of molecular beam studies. Kleyn *et al* (1981) reported that the rotational energy distribution for *specularly* scattered atoms shows a *non-Boltzmann* profile for *high* rotational excitations but a *Boltzmann-like* profile for *low* excitations. For some time, this remained a significant and controversial result until it was validated by theoretical studies (see §3). A further important observation is that of rotationally-mediated resonances in HD scattering from Ag and Pt surfaces (Cowin *et al* 1981; Whaley *et al* 1982). Beam-scattering from adsorbate-covered surfaces are now becoming more popular. These can reveal random adsorption at low coverages (Mason *et al* 1981) as well as formation of "large" islands (Poelsema *et al* 1982).

Of course, the major goal of surface experimentalists is to go beyond the above, somewhat limited, characterizations and ask questions on *reactive dynamics*. It is worthwhile to mention here several interesting observations. One particular feature, not satisfactorily understood yet, is the occurrence of *oscillations* in certain systems, e.g. CO-oxidation on noble-metal catalysts. The rate of this reaction is being studied using time-resolved FTIR reflection-absorption technique (Burrows *et al* 1984). It was proposed earlier (Sales *et al* 1982) that this system exhibits periodic formation and reduction of a subsurface oxide. Another interesting observation is *stimulated desorption*† followed by *two-hole resonances*‡, reported for the production of H<sup>+</sup> on

\* Overlayer refers to a layer of previously adsorbed species (adsorbed either deliberately or as an impurity).

\*\* Supernumerary rainbow structure is the additional quantum structure which occurs as satellite peaks next to the principal rainbow peak.

† Electron-, photon- or ion-stimulated desorption occurs when a surface core hole decays by an Auger process that leaves a localized two-hole final state on a surface atom.

‡ These are resonances caused by the correlation between two holes in metals and are well known in the Auger spectra for bulk systems such as Ni, Cu and Ag.

hydrogen-covered Si surfaces (Madden *et al* 1982). Such excitations rapidly self-trap on surfaces due to the production of local distortions in site geometry (Jennison and Emui 1983). The excitations themselves may be followed by the desorption of  $H^+$  and  $CH_3^+$  from condensed hydrocarbon overlayers (Kelber and Knotek 1982). Clearly, experiments have reached a level of sophistication necessary for understanding the dynamics of convoluted surface reactions. On the other hand, sophistication in theory cannot be said to have reached the desired level.

However, as mentioned before, recently there has been a rapid upsurge in theoretical studies on gas-surface interaction and a reasonable degree of success is already visible. The ultimate goal of these studies, as of the experiments, is to understand reaction dynamics in detail. Both rotational and vibrational motions of the interacting molecules as well as resonances in elastic scattering have been extensively studied (Tully 1980a, b). But it is difficult to see clear trends. The construction of a realistic potential for gas-surface interaction remains a primary objective. Model potentials continue to be invoked, though less frequently now than a few years ago. Surface hopping in classical-mechanical studies and multiple scattering in quantum-mechanical works are nowadays considered more frequently. Surface vibrations are also being taken into account. Interestingly, the source of benchmark calculations is still the close-coupling method in quantum mechanics and rigorous trajectory calculations in classical mechanics. In fact, semi-classical approaches appear to be dominant in quantity and variety. Within this category, one finds a greater number of studies which are "more classical" and have fewer quantum-mechanical features, e.g. the wave-packet and other quasi-classical trajectory approaches.

The preceding description has provided an overview of recent experimental and other studies on gas-surface dynamics. The present article intends to provide a review of certain current theoretical methods in this area, developed in the 1980's. However, constraints of space prevent us from reviewing other important and relevant areas including ion-beam and charged-particle interaction with surfaces (Van der Veen 1985), transport processes on surfaces (Wu and Montroll 1983), surface-enhanced Raman spectroscopy (Pockrand 1984), thermodynamic studies (e.g. phase diagrams), epitaxial growth, dynamical events involving considerable bulk interference and order-disorder transitions on surfaces (Sinha 1980).

In §2, we discuss several important theoretical methodologies being used today. Section 3 takes a comparative look at the results obtained by using these methodologies and a few concluding remarks are given in §4.

## 2. Theories of gas-surface interaction

The problem of gas-surface scattering has two important aspects: (i) the design of a suitable interaction potential, and (ii) the formulation of a methodology for obtaining the energy distribution of the products in various channels, elastic and inelastic (reactive and nonreactive modes). Since Hoinkes (1980) gives a comprehensive survey of the gas-surface interaction potential obtained from atom-diffraction experiments and Tully (1980a) describes various theoretical methods of determining this potential, in this section we will merely content ourselves by briefly mentioning those potentials which are used to obtain the results in §3. Although one must use realistic potentials for

benchmark (reference) calculations, for answering physical questions on reactive dynamics, or inelasticity in general, model potentials are often used.

There are *three* broad overlapping streams of theoretical works; classical, semi- or quasi-classical, and quantum-mechanical. The classical and some quasi-classical approaches use trajectory calculations. Although the meaning of "diffraction" is convoluted in the classical sense, these calculations provide a more direct insight into the dynamics and can produce, in principle, a frame-by-frame movie-like description of the interaction process. The quantum-mechanical approaches, on the other hand, yield results in terms of *S*-matrix elements for various open channels. The physics of the interaction is then interpreted from diffraction data. We will individually discuss the principles behind the more important of the various approaches. Note that, in what follows, the surface is taken as the *xy*-plane and the *z*-direction as the outward normal to the surface.

### 2.1 Gas-surface interaction in the classical framework

The most popular of the classical approaches, the stochastic trajectory approach (STA), is based on two simple ideas; (i) Many chemical events on surfaces actually take place in the midst of a very large assembly of atoms, i.e. they are localized in nature; (ii) the driving force in the dynamics is a generalized Langevin oscillator, with a fluctuating time-dependent part (Tully 1981). Trajectory calculations are also done using a rigid surface or simple harmonic oscillators (Polanyi and Wolf 1982, 1985). Mathematically, the STA can be expressed (Tully 1981) by the classical equations of motion for the primary atoms (in the local region of interest) and the secondary atoms (the less significant surrounding region),

$$\ddot{\mathbf{y}} = F(\mathbf{y}) - \Omega^2 \mathbf{z}, \quad (1)$$

$$\ddot{\mathbf{z}} = -\Omega^2 \mathbf{y} - \Omega_z^2 \mathbf{z}, \quad (2)$$

where  $\mathbf{y}$  and  $\mathbf{z}$  represent the primary and secondary atoms, respectively;  $\Omega^2$  and  $\Omega_z^2$  are the harmonic frequency matrices;  $F(\mathbf{y})$  represents the forces per unit mass, with anharmonic effects, acting on the primary atoms. Equation (2) can be solved formally (Lucchese and Tully 1984a, 1984b; Tully 1980b, 1981) for the *z*-coordinates of the secondary atoms and the results substituted into (1) for the primary atoms. One thus obtains a set of generalized Langevin equations (GLE) of motion where the 'redundant' secondary atoms have been eliminated, i.e.

$$\ddot{\mathbf{y}} = F'(\mathbf{y}) - \int_0^t \Lambda(t-t') \ddot{\mathbf{y}}(t') dt' + R(t). \quad (3)$$

Among the many advantages of such an approach is the fact that it treats the motions of surface atoms naturally and hence accommodates surface hopping. This can be dealt within quantum mechanics only if multiple scattering as well as nonadiabatic effects are included.

In (3),  $R(t)$  may be taken to be a Gaussian random force. Inelasticity is introduced through the fluctuation-dissipation theorem,

$$\Lambda(t) = k_b T_s \langle R(t) R^\dagger(0) \rangle, \quad (4)$$

where  $\Lambda(t)$  is the friction kernel,  $k_b$  the Boltzmann constant and  $T_s$  the surface temperature;  $\Lambda(t)$  is also related to the phonon spectrum of the solid. Equation (4) is appropriately modified for internal degrees of freedom of the incident molecule.

## 2.2 Gas-surface interaction in the quasi-classical framework

2.2a *The semi-classical stochastic trajectory (SST) approach:* The STA allows for the simulation of rigid and hot surfaces, but processes such as transitions between various internal levels and electronic motions can be described "accurately" only by using quantum mechanics. The first method discussed here, which uses both classical and quantum concepts, is the SST approach (Richard and Depristo 1983). This method uses classical mechanics to describe the translations of the centre of mass of the molecule, while the internal degrees of freedom are described (either completely or partially) quantum mechanically. The motion of the surface atom (of the solid) is treated *via* the classical GLE. Thus, for the case of an atom undergoing no electronic transitions, the SST approach reduces to the STA.

The Hamiltonian for a gas molecule-solid surface scattering problem can be written as

$$H = H_0(\mathbf{r}, \mathbf{p}) + H'_0(\mathbf{r}', \mathbf{p}') + T(\mathbf{P}) + V(\mathbf{r}, \mathbf{r}', \mathbf{R}), \quad (5)$$

where  $H_0(\mathbf{r}, \mathbf{p})$  and  $H'_0(\mathbf{r}', \mathbf{p}')$  are the Hamiltonians of the noninteracting molecule and surface with collective position coordinates and momenta  $\mathbf{r}, \mathbf{p}$  and  $\mathbf{r}', \mathbf{p}'$  respectively;  $\mathbf{R}$  and  $\mathbf{P}$  are the C. M. coordinates and momenta of the gas molecule;  $V(\mathbf{r}, \mathbf{r}', \mathbf{R})$  is the coupling potential for the different degrees of freedom.

In the original formulation, a quantum-mechanical treatment is retained for the molecule's internal degrees of freedom. The wavefunction in the interaction representation is expanded as

$$\Psi^I(\mathbf{r}, t) = \sum_i c_i(t) \Phi_i(\mathbf{r}) \exp(-i\varepsilon_i t/\hbar), \quad (6)$$

where the molecular eigenstate  $\Phi_i(\mathbf{r})$  satisfies

$$H_0 \Phi_i(\mathbf{r}) = \varepsilon_i \Phi_i(\mathbf{r}), \quad (7)$$

$\varepsilon_i$  being the energy; the index  $i$  is a composite label ranging over all vibrational and rotational levels. The time-dependent Schrödinger equation in the interaction representation is

$$i\hbar \frac{d\Psi^I(t)}{dt} = V^I(t) \Psi^I(t), \quad (8)$$

where  $V^I(t) = \exp[i(H_0 + H'_0 + T)t/\hbar] V(\mathbf{r}, \mathbf{r}', \mathbf{R}) \exp[-i(H_0 + H'_0 + T)t/\hbar]$ . (9)

The right hand side of (8) is amenable to approximations. In the SST approach, the quantum mechanical co-ordinates  $\mathbf{r}'$  and  $\mathbf{R}$  are treated as classical, time-dependent variables  $\mathbf{r}'(t)$  and  $\mathbf{R}(t)$ . This makes  $H'_0$  and  $T$  commute with  $V$ . We then have

$$V^I(t) \approx \exp(iH_0 t/\hbar) V(\mathbf{r}, \mathbf{r}'(t), \mathbf{R}(t)) \exp(-iH_0 t/\hbar). \quad (10)$$

It is then possible to obtain (Richard and Depristo 1983),

$$i\hbar \frac{dc_i}{dt} = \sum_j V_{ij}(t) \exp(i\omega_{ij}t) c_j(t), \quad (11)$$

$$\text{where } V_{ij}(t) = \langle \Phi_i(\mathbf{r}) | V(\mathbf{r}, t) | \Phi_j(\mathbf{r}) \rangle \quad (11a)$$

$$= \langle \Phi_i(\mathbf{r}) | V(\mathbf{r}, \mathbf{r}'(t), \mathbf{R}(t)) | \Phi_j(\mathbf{r}) \rangle \quad (11b)$$

$$\text{and } \omega_{ij} = (\varepsilon_i - \varepsilon_j)/\hbar \quad (11c)$$

One invokes Ehrenfest's theorem to relate the phase space variables,

$$\dot{q}_k = \partial \langle H \rangle / \partial p_k, \quad (12a)$$

$$\dot{p}_k = -\partial \langle H \rangle / \partial q_k, \quad (12b)$$

$q_k$  and  $p_k$  being the position and momenta variables in the Hamiltonian dynamics framework. Note that two interesting features are introduced through (12): (i) The expectation value of the Hamiltonian  $\langle H \rangle$  effectively couples the motions of the classical coordinates at all times to the internal motions of the quantum coordinates; (ii)  $\langle H \rangle$ , which plays the role of an "effective Hamiltonian" in (12), is time-independent. Finally, the dynamics in terms of the molecule-solid-surface variables are given by the equations

$$\dot{\mathbf{r}}'_k = \partial H'_0 / \partial \mathbf{p}'_k, \quad (13a)$$

$$\dot{\mathbf{p}}'_k = -(\partial H'_0 / \partial \mathbf{r}'_k) - (\partial \langle V \rangle / \partial \mathbf{r}'_k), \quad (13b)$$

$$\dot{\mathbf{R}} = \partial T / \partial \mathbf{p}, \quad (14a)$$

$$\dot{\mathbf{p}} = -\partial \langle V \rangle / \partial \mathbf{R}, \quad (14b)$$

$$\text{where } \langle V \rangle = \sum_{ij} c_j^*(t) V_{ji}(\mathbf{r}', \mathbf{R}) c_i(t) \exp(i\omega_{ji}t). \quad (14c)$$

Just as (1) and (2) describe the time evolution of the positions of the surface atoms in the GLE model, for a given  $\Lambda(t)$  in (3), similarly (14a) and (14b) describe the time evolution of the molecule's C.M. Further, (10) gives the time evolution of the amplitudes of the internal states of the gas molecule.

**2.2b The semi-classical perturbation (SCP) approach:** The potential in this approach is divided into a zeroth order term plus a perturbation (Hubbard and Miller 1983), i.e.

$$V(x, y, z) = V_0(z) + V_1(x, y, z). \quad (15)$$

The SCP approach is based on using WKB phase shifts  $\eta_0$  and  $\eta_1$  in the zeroth and first order respectively. The phase shift  $\eta_1$  is an effect of the perturbation  $V_1$ , while  $\eta_0$  corresponds to  $V_0$ . The S-matrix element, i.e. the amplitude for scattering to the final diffractive channel characterized by quantum numbers  $n_x$  and  $n_y$  ( $n_x = n_y = 0$  defines



the specular channel) is given by,

$$S_{00}^{n_x n_y} = (a_x a_y)^{-1} \exp(2i\eta_0) \int_0^{a_x} dx_0 \int_0^{a_y} dy_0 \exp(-i\Delta k_x x_0) \\ \times \exp(-i\Delta k_y y_0) \exp[2i\eta_1(x_0, y_0)] \quad (16)$$

where  $\Delta k_x$  and  $\Delta k_y$  are the changes in the  $x$  and  $y$  components of momentum (in units of  $\hbar$ ), and are related to the diffraction-order quantum numbers by

$$\Delta k_x = 2\pi n_x/a_x, \quad \Delta k_y = 2\pi n_y/a_y. \quad (17)$$

Here  $a_x$  and  $a_y$  are the linear dimensions of the unit cell.

The first-order phase shift,  $\eta_1$ , is given by

$$2\eta_1(x_0, y_0) = - \int_{-\infty}^{\infty} dt V_1[x(t), y(t), z(t)]. \quad (18)$$

The trajectory  $[x(t), y(t), z(t)]$  is the one driven by the zeroth order potential  $V_0$ , i.e.  $z(t)$  is the inverse function of

$$t(z) = \pm \int_{z_0}^z dz' \left\{ \frac{2}{m} [E - V_0(z')] \right\}^{-1/2}, \quad (19)$$

and  $x(t) = x_0 + \frac{\bar{k}_x}{m} t, \quad (20)$

$$y(t) = y_0 + \frac{\bar{k}_y}{m} t, \quad (21)$$

where  $\bar{k}_x$  and  $\bar{k}_y$  are the averages of the initial and final values of the momenta.

The probability of scattering into the final diffraction state  $(n_x, n_y)$  is given by

$$P_{00 \rightarrow n_x n_y} = |S_{00}^{n_x n_y}|^2. \quad (22)$$

**2.2c The wave-packet formalism:** Several time-dependent wave-packet approaches have been suggested (Agrawal and Raff 1982; Kumamoto and Silbey 1981; Drolshagen and Heller 1983). In the method formulated by Drolshagen and Heller (1983), a Gaussian wave-packet basis is chosen for the approaching gas molecule with average positions  $\mathbf{r}_t$  and momenta  $\mathbf{p}_t$  at time  $t$ , defined as dynamical variables in classical trajectories, i.e.

$$\Psi(\mathbf{r}, t) = \exp \left\{ \frac{i}{\hbar} (\mathbf{r} - \mathbf{r}_t) \mathbf{A}_t (\mathbf{r} - \mathbf{r}_t) + \frac{i}{\hbar} \mathbf{p}_t (\mathbf{r} - \mathbf{r}_t) + \frac{i}{\hbar} \mathbf{r}_t \right\} \quad (23)$$

$$= U(t) \Psi(\mathbf{r}, 0), \quad (24)$$

$U(t)$  being a unitary propagator. The matrix  $\mathbf{A}_t$  gives the spread in  $\mathbf{r}_t$  (in three dimensions) and the  $\mathbf{r}_i, \mathbf{r}_j$  correlation of the wave-packet. The term  $\mathbf{r}_t$  is a complex variable containing normalization and  $\mathbf{r}$ -independent phase of the wave packet. After determining the initial conditions, the wave packet is propagated in time along classical trajectories. The information on scattering is obtained by projecting the wave packet

onto the known asymptotic states. For a realistic simulation, one has to work with a superposition of a large number of trajectories. For a periodic surface, this superposition is expressed by an integral over a unit cell. The expansion into gaussians has to be done only in the  $xy$ -plane. The semi-classical  $S$ -matrix is finally given by

$$S_{00}^{mn} = c' \sqrt{k_z^{mn}} \sum_p \left( \frac{\pi^3}{\det A_i^p} \right)^{1/2} \exp \left[ -\frac{i\hbar}{4} (\mathbf{k}_i^p - \mathbf{k}^{mn}) (A_i^p)^{-1} (\mathbf{k}_i^p - \mathbf{k}^{mn}) - i\mathbf{k}^{mn} \cdot \mathbf{r}_i^p + i\mathbf{k}_0^p \cdot \mathbf{r}_0^p + \frac{i}{\hbar} \mathbf{r}_i^p \right], \quad (25)$$

where  $\mathbf{k}^{mn} = (k_x^m, k_y^n, k_z^{mn}),$  (26)

$$= \left( k_{x_i} + \frac{m2\pi}{a}, k_{y_i} + \frac{n2\pi}{a}, k_z^{mn} \right). \quad (27)$$

Here  $a$  is the lattice constant;  $m$  and  $n$  are the indices labelling a reciprocal lattice vector  $\mathbf{G}_{mn}$  involved in the interaction and

$$(k_z^{mn})^2 = k^2 - (\mathbf{K}_i + \mathbf{G}_{mn})^2. \quad (28)$$

The index  $i$  refers to the incident site;  $c'$  contains normalization and certain phase factors. There are many advantages of the wave-packet method (Drolshagen and Vollmer 1985). It needs no expansion in the target states, which is essential for close-coupling calculations (see § 2.3a). This makes it useful for high energies where a close-coupling calculation is virtually impossible because a large basis is necessary for reasonable accuracy, requiring large computer time and storage. For simple problems, analytical results can be obtained in the wave-packet approach. However, this method requires local harmonicity in the potential over the width of the packet.

*2.2d The sudden approximation:* Although we desist from discussing the quantum-mechanical methods until § 2.3, it is necessary to emphasize here that an important motivation behind semi-classical approaches is to reduce the labour involved in exact calculations. In particular, one is often interested in reducing the size of the matrices that arise in, e.g. the close-coupling method. One of the best-known methods to achieve this goal is the sudden approximation (Gerber *et al* 1980). This method is particularly useful for considering the inelastic modes. The approximation in it involves decoupling with respect to chosen degrees of freedom. For example, decoupling with respect to rotational levels can be introduced by assuming that the collision energy is large compared to the rotational levels of the molecule that are significantly involved in the collision, i.e.

$$E \gg \frac{\hbar^2}{2I} j(j+1). \quad (29)$$

Gas-surface interaction lends itself to a special choice of sudden approximation. Because of diffraction, changes in momentum (of the incident molecules) due to surface corrugation are thought to be very small compared to the change in the  $z$ -component of the momentum. This is a reasonable assumption since the surface potential has a 'large' component, the only effect of which is to produce a reflection at the repulsive wall of the

potential. This, together with rotational decoupling, is called the matrix diagonalization sudden (MDS) approximation. One has a set of coupled equations (compare with (45) later)

$$\left[ -\frac{d^2}{dz^2} \mathbf{I} + \mathbf{U}^D(z) - k_z^2 \mathbf{I} \right] \hat{\chi}(z) = 0, \quad (30)$$

where  $\mathbf{I}$  is the identity matrix;  $\mathbf{U}^D(z)$  is a reduced form of the exact coupling matrix  $\mathbf{U}(z)$

$$U_{GG'}^D(z) = \frac{1}{A_{\text{u.c.}}} \frac{2\mu}{\hbar^2} \int_{\text{u.c.}} \Phi_G^*(\mathbf{R}) V(\mathbf{R}, z) \Phi_{G'}(\mathbf{R}) d\mathbf{R}; \quad (31)$$

$A_{\text{u.c.}}$  is the area of the unit cell;  $\mathbf{G}$  and  $\mathbf{G}'$  refer to reciprocal lattice vectors;  $\mathbf{R}$  describes the  $(x, y)$  co-ordinate system as well as the internal co-ordinates (then  $U$  will be labelled by internal quantum numbers as well); the function  $\Phi_G(z)$  are the "exact" expansion coefficients of the total wavefunction in the reciprocal-lattice vector space;  $\hat{\chi}_G(z)$  is the approximate version of  $\Phi_G(z)$  corresponding to the decouplings introduced.  $\chi_G(z)$  is also labelled by rotational quantum numbers.

The  $S$ -matrix for the decoupled single-channel equations is given by

$$S_{jm_j, mn; j'm'_j, m'n'}^D = \exp(2i\eta_{jm_j, mn}) \delta_{jm_j, j'm'_j} \delta_{mn, m'n'}. \quad (32)$$

Here  $(j, m_j)$  refers to the rotational quantum numbers and  $(m, n)$  to the reciprocal lattice vector. The phase shifts  $\eta_{jm_j, mn}$  can be conveniently calculated by using the WKB approximation

$$\eta_{jm_j, mn} = \lim_{z \rightarrow \infty} \left( \int_{z_t}^z \{ [k_z^2 - U_{jm_j, mn}^D(z)]^{1/2} - k_z \} dz \right), \quad (33)$$

where  $z_t$  is the classical turning point associated with the integrand. The coordinate-representation sudden (CRS) approximation is analogous to the infinite-order sudden (IOS) approximation used in gas phase scattering. One way of arriving at CRS is to consider the MDS in the limiting case where all (infinitely many) diffraction and rotational channels are included for the sudden treatment. In other words, the total wavefunction is expanded in the bases of diffraction and molecular rotation states, i.e.

$$\Psi(\mathbf{R}, \theta, \phi) = \frac{1}{\sqrt{A}} \sum_{mn} \sum_{jm_j} \exp[i(\mathbf{G}_{mn} + \mathbf{K}) \cdot \mathbf{R}] Y_{j, m_j}(\theta, \phi) \chi_{jm_j, mn}(z). \quad (34)$$

Here  $\mathbf{R}$  denotes only the coordinates in the  $xy$ -plane;  $Y_{j, m_j}(\theta, \phi)$  are the spherical harmonics. The entire basis (34) is included in the treatment for the CRS approximation.

The final result for the  $S$ -matrix element is

$$S_{jm_j, mn}^{j'm'_j, m'n'} = \frac{1}{A} \int_A \exp\{i[\mathbf{G}_{mn} - \mathbf{G}_{m'n'}] \cdot \mathbf{R}\} \\ \times \int_0^{2\pi} Y_{j, m_j}^*(\theta, \phi) Y_{j', m'_j}(\theta, \phi) \exp\{2i\eta(\mathbf{R}, \theta, \phi)\} d\mathbf{R} \sin \theta d\theta d\phi, \quad (35)$$

where the phase shift is given by

$$\eta(\mathbf{R}, \theta, \phi) = \lim_{z \rightarrow \infty} \left( \int_{z_t}^z \left\{ \left[ k_z^2 - \frac{2\mu}{\hbar^2} V(\mathbf{R}, z, \theta, \phi) \right]^{1/2} - k_z \right\} dz \right) + k_z z_t. \quad (36)$$

Gerber *et al* (1980) suggest that the MDS method is much more efficient than the evaluation of the four-dimensional integral in (36). But, the CRS method provides greater insight for an analysis of transition probabilities.

*2.2e Miscellaneous quasi-classical methods:* A number of other semi-classical works exist. Sometimes approximations are developed specific to a potential form. Thus, Maniv and Cohen (1984) obtained an interesting relationship for the transition amplitude from incoming momentum  $\mathbf{k}$  to the outgoing momentum  $\mathbf{k}'$ ,

$$T(\mathbf{k}, \mathbf{k}') = |\bar{k}_z| (4\pi^2 \Omega)^{-1} \int d^2 K f(\mathbf{k}; \mathbf{K}) f^*(\mathbf{k}', \mathbf{K}') / (k^2 - K^2)^{1/2}, \quad (37)$$

where 
$$f(\mathbf{k}, \mathbf{K}) = \frac{\mu}{ik_z} \int d^3 r V(\mathbf{r}) A_{\mathbf{K}}(\mathbf{r}) \exp \{ i[\mathbf{k} \cdot \mathbf{r} - S_{\mathbf{K}}(\mathbf{r})/\hbar] \}. \quad (38)$$

$S_{\mathbf{K}}(\mathbf{r})$  is the classical action integral corresponding to the fully distorted incident wave with an asymptotic momentum  $\mathbf{K}$  parallel to the surface plane;  $A_{\mathbf{K}}(\mathbf{r})$  is the amplitude of the corresponding semi-classical wavefunction;  $\mu$  is the particle's reduced mass;  $|\bar{k}_z| = \frac{1}{2}|k_z - k'_z|$ ;  $\Omega$  is the surface area exposed to the incoming atoms or molecules.

Field-theoretical models using creation and annihilation operators are becoming common particularly in dealing with the surface phonons. Brako (1982) introduced the Hamiltonian

$$H = \frac{p^2}{2m} + V(z) + \sum_k \varepsilon_k b_k^\dagger b_k + \sum_k f_k(\mathbf{r})(b_k^\dagger + b_k). \quad (39)$$

The substrate modes coupled to the adatom (the projectile) moving close to the surface are assumed to be harmonic phonons. The operators  $b_k^\dagger$  and  $b_k$  are the usual phonon creation and annihilation operators respectively. The constants  $f_k(\mathbf{r})$  represent the strength of coupling. The first two terms (the kinetic and the potential energy respectively) in (34) represent the adatom exclusively and can be dealt with in terms of a classical trajectory approach. The third (free-surface Hamiltonian) and fourth terms are dealt with by quantum mechanics. The effect of the first two terms is studied as a perturbation on the quantum-mechanical problem defined by the rest of the terms. In principle, one has a thermal spread in the description of a trajectory (positions and momenta) because each initial state corresponds to a trajectory at a finite surface temperature. Brako (1982) uses a trajectory approximation where this spread is neglected and a unique trajectory is taken to describe a scattering event at a given initial energy and angle.

### 2.3 Gas-surface interaction in the quantum-mechanical framework

*2.3a Scattering from a periodic surface:* The Schrödinger equation for a particle of mass  $\mu$  with incident vector  $\mathbf{k}_i = (k_x, k_y, -k_z)_i \equiv (\mathbf{K}, -k_z)_i$ , scattering from a potential

$V(r)$  can be written as,

$$\left[ -\frac{\hbar^2}{2\mu} \nabla_r^2 + V(\mathbf{r}) - \frac{\hbar^2 k^2}{2\mu} \right] \Psi(\mathbf{r}) = 0. \quad (39)$$

For a periodic potential  $V(r)$ , we have

$$V(\mathbf{r}) = V(\mathbf{R}, z) = V(\mathbf{R} + \mathbf{A}, z), \quad (40)$$

$\mathbf{A}$  being a lattice vector. The asymptotic conditions are chosen at  $t = \mp \infty$ , i.e. the incoming and outgoing waves respectively, as

$$\Psi_{t=-\infty}(\mathbf{r}) = \frac{1}{\sqrt{k_{zi}}} \exp[i(-k_{zi}z + \mathbf{K} \cdot \mathbf{R})]. \quad (41)$$

Due to corrugation in the  $xy$ -plane, the scattered particle is diffracted, with the asymptotic description at  $t = +\infty$ ,

$$\Psi_{\text{out}}(\mathbf{r}) = \sum_{mn} S_{00}^{mn} \frac{1}{\sqrt{k_z^{mn}}} \exp[ik_z^{mn}z + (\mathbf{K}_i + \mathbf{G}_{mn}) \cdot \mathbf{R}]. \quad (42)$$

The momentum exchange is described in terms of the reciprocal lattice vector,

$$\mathbf{G}_{mn} \equiv (m, n) \equiv (\Delta k_x, \Delta k_y) = \left( \frac{m2\pi}{a}, \frac{n2\pi}{a} \right), \quad (43)$$

where  $m, n = 0, \pm 1, \pm 2, \dots$ ;  $a$  is the lattice constant and  $k_z^{mn}$  is given by (28).  $S_{00}^{mn}$  is the scattering matrix element such that  $|S_{00}^{mn}|^2$  is the probability for scattering into the final diffraction states  $(m, n)$ .

The close-coupling approach (Wolken 1973) is analogous to the multi-channel expansion for inelastic scattering in the gas phase. The total wavefunction is expanded as a Fourier series in the reciprocal lattice space, i.e.

$$\Psi(\mathbf{r}) = \sum_{\mathbf{G}} \phi_{\mathbf{G}}(z) \exp[i(\mathbf{K}_i + \mathbf{G}) \cdot \mathbf{R}]. \quad (44)$$

A multi-channel expansion in a basis for internal modes is necessary even here, if inelastic effects are to be included.

Using the above expansion, the Schrödinger equation is now transformed to a set of coupled equations

$$\left[ \frac{d^2}{dz^2} \mathbf{I} + (\mathbf{k}_z^{mn})^2 - \mathbf{U}(z) \right] \phi(z) = 0, \quad (45)$$

where  $\mathbf{I}$  is the identity matrix;  $\mathbf{k}_z^{mn}$  is a diagonal matrix with elements  $k_z^{mn}$ ; the coupling matrix  $\mathbf{U}(z)$  is defined by (31).

Numerical methods can now be utilized to solve these coupled equations. Exact diffraction intensities can, in principle, be obtained using  $S$ -matrix elements  $S_{\mathbf{G}\mathbf{G}'}$  and the asymptotic condition,

$$\Phi_{\mathbf{G}\mathbf{G}'}(z) = \frac{1}{\sqrt{k_z^{mn}}} \{ \exp[-ik_z^{mn}z] S_{\mathbf{G}\mathbf{G}'} - S_{\mathbf{G}\mathbf{G}'} \exp[ik_z^{mn}z'] \} \quad (46)$$

for the open channels  $[(k_z^{mn})^2 > 0]$ .

The probability of scattering into the final diffraction state ( $m, n$ ) is

$$P_{00 \rightarrow mn} = |S_{00}^{mn}|^2. \quad (47)$$

In practice, one has to truncate the sum in (49) after a finite number of terms. Still, the computational labour involved is considerable. For  $M$  terms, a set of  $N$  coupled equations has to be solved, where

$$N = 1 + 2(M^2 + M). \quad (48)$$

The computing time rises roughly with  $N^3$ . Clearly, only a few diffraction orders can be considered in a real calculation. This is much more so if inelastic effects are considered. In the case of a rigid surface, (44) is replaced by

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} \sum_{jm_j} \phi_{\mathbf{G}, jm_j}(z) Y_{jm_j}(\theta, \phi) \exp [i(\mathbf{K} + \mathbf{G}) \cdot \mathbf{R}], \quad (49)$$

while each term in (45) carries the rotational indices in addition to the lattice indices such that

$$k_z^{mn^2} = \frac{2\mu}{\hbar^2} \left[ E - \frac{j(j+1)\hbar^2}{2I} \right] - (\mathbf{K} + \mathbf{G})^2; \quad (50)$$

(compare (50) with (28)) and (31) is replaced by

$$\begin{aligned} \frac{\hbar^2}{2\mu} U_{\mathbf{G}'jm'_j}^{\mathbf{G}jm_j}(z) &= A_{\text{u.c.}}^{-1} \int_{\text{u.c.}} d\mathbf{R} \int Y_{jm_j}^*(\theta, \phi) \phi_{\mathbf{G}}^*(\mathbf{R}) V(\mathbf{r}, \theta, \phi) \\ &\times \phi_{\mathbf{G}'}(\mathbf{R}) Y_{j'm'_j}(\theta, \phi) \sin \theta d\theta d\phi \end{aligned} \quad (51)$$

**2.3b Approximations in the quantum-mechanical framework:** Among the earliest quantum-mechanical approximations, the first-order distorted-wave Born approximation (FODWBA) (Goodman and Wachman 1976) and its various improvements became popular. In particular, the CCGM (named after Cabrera *et al*; for this work see Goodman and Wachman 1976, and references therein) approximation has the advantage of giving a unitary  $S$ -matrix as the final result. To discuss these, let us first consider the formal theory of scattering for the interaction of gas atoms/molecules with a surface. The interaction potential can be represented as

$$V = V_0 + V_1. \quad (52)$$

The first term ( $V_0$ ) represents a 'large' potential, e.g., the potential of a gas atom approaching in a direction normal to the surface. This part has to be dealt with exactly or by a convenient approximation. The effect of  $V_0$  is mostly a specular reflection. The  $T$ -matrix for the entire problem can be written as

$$T_{fi} = \langle \psi_f | V_0 + V_1 | \Psi_i^\dagger \rangle \quad (53)$$

$$= \langle \psi_f | V_0 | \chi_i^\dagger \rangle + \langle \chi_f^- | V_1 | \Psi_i^\dagger \rangle, \quad (54)$$

where the wavefunctions  $\psi$  and  $\chi^\pm$  refer to the zeroth order solution (i.e., for  $H_0$ , the total Hamiltonian being  $H_0 + V$ ) and the scattering state solutions of  $H_0 + V_0$  (+ for

the outgoing and – for the incoming waves) respectively: the function  $\Psi$  is the solution for the total Hamiltonian; the indices  $i$  and  $f$  denote the initial and the final states respectively. The  $T$ -matrix is related to the  $S$ -matrix as

$$S_{fi} = \delta_{fi} - 2\pi i \delta(E_f - E_i) T_{fi}. \quad (55)$$

The first term (Kronecker delta) can be removed for the case of gas-surface scattering (since  $f = i$  implies completely forward scattering). A ‘reduced  $T$ -matrix’ is now defined as

$$t_{fi} = \langle \chi_f^- | V_1 | \Psi_i^+ \rangle \exp(-i\xi_s) \quad (56)$$

where the phase factor  $\xi_s$  has the information about  $V_0(z)$ , viz,

$$S_{fiV_1 \rightarrow 0} = \exp(i\xi_s) \delta(f, s). \quad (57)$$

The index  $s$  represents the specular state. It can be shown (Goodman and Wachman 1976) that

$$|T_{fi}|^2 = |t_{fi} + \frac{i}{2\pi\rho_s} \delta(f, s)|^2, \quad (58)$$

where  $\rho_s$  is the density of specularly scattered states in the energy space. In the FODWBA,

$$t_{fi} = \langle \chi_f^- | V | \chi_s^- \rangle. \quad (59)$$

Comparing (56) and (59), we see that  $\Psi_i^+$  is replaced by  $\chi_s^-$  and  $\xi_s$  is taken as zero. This corresponds to a rigid surface, when  $V_0(z)$  is a hard wall. The function  $\chi_s^-$  is then the same as  $\chi_i^+$ . Thus, the replacement of  $\Psi_i^+$  by  $\chi_s^-$  is a first-order Born approximation and since  $V_0$  has been separately dealt with, it is a distorted wave approximation. In the CCGM approximation, one considers a few more terms like

$$t_{fi} = \langle \chi_f^- | V | \chi_s^- \rangle + \sum_{\{n_{mb}\}} \sum_{|k_b|} \sum_{k_{b_z}} (E_i - E_b)^{-1} \langle \chi_f^- | V | \chi_b^- \rangle t_{bi} - i\pi \left\{ \sum_{\{n_{mc}\}} \sum_{|K_c|} \rho_c \langle \chi_f^- | V | \chi_c^- \rangle t_{ci} \right\}_{E_c = E_i}, \quad (60)$$

where  $\{n_m\}$  denotes the set of phonon states; the indices  $b$  and  $c$  refer to bound and continuum states;  $E_c = E_i$  refers to the fact that only energy-conserving continuum states are considered. Equation (56) differs from the ‘exact’ expression in that a complicated matrix integral term has been removed, by putting

$$\sum_{\{n_{mc}\}} \sum_{K_c} \mathbf{P} \int dE_{cz} (E_i - E_c)^{-1} \rho_c \langle \chi_f^- | V | \chi_c^- \rangle t_{ci} = 0. \quad (61)$$

Here  $\mathbf{P}$  indicates the principal value of the integral; the summation includes all those continuum states which do not conserve energy. This makes it possible to preserve unitarity of the  $S$ -matrix, which is not possible in the FODWBA framework.

Several approaches start with the formulation of an effective Hamiltonian that is

valid in restricted regimes. Singh *et al* (1986a) used a self-conjugate effective potential which is a sum of non-local separable interactions. Each term in the sum operates on the "exact" total wavefunction projecting it to its weighted average in the vicinity of each surface atom. One starts with the integral formulation of scattering theory, i.e., the Lippman-Schwinger equation

$$\Psi_{\mathbf{k}}^{\dagger}(\mathbf{r}) = \chi_{\mathbf{k}}^{\dagger}(\mathbf{r}) + \sum_i \int G_+(\mathbf{r}, \mathbf{r}') v_i(\mathbf{r}' - \mathbf{r}_i) \Psi_{\mathbf{k}}^{\dagger}(\mathbf{r}') d\mathbf{r}', \quad (62)$$

where  $G_+(\mathbf{r}, \mathbf{r}')$  is the outgoing Green's function of the Schrödinger equation with potential  $V_0(\mathbf{r})$  (see (48)) and  $G_{\pm}^0(\mathbf{r} - \mathbf{r}')$  are the usual free-space Green's functions; the functions  $\chi_{\mathbf{k}}^{\pm}(\mathbf{r})$  are the scattering states of the potential  $V_0(\mathbf{r})$ , i.e.,

$$\chi_{\mathbf{k}}^{\pm}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \int G_{\pm}^0(\mathbf{r}, \mathbf{r}') V_0(\mathbf{r}') \chi_{\mathbf{k}}^{\pm}(\mathbf{r}') d\mathbf{r}', \quad (63)$$

where  $\phi_{\mathbf{k}}(\mathbf{r})$  is a plane wave (with wave vector  $\mathbf{k}$ ) multiplied by a suitable normalization constant; the sum over  $i$  represents an assumed description of  $V_1$  in (52) as a sum of pairwise interactions between the approaching gas phase atom/molecule and each surface atom. Now, replacing the wavefunction in the integrand by a weighted average of its value at the atomic locations, we have

$$\bar{\Psi}_{\mathbf{k}}(\mathbf{r}) = \phi_{\mathbf{k}}(\mathbf{r}) + \sum_i \lambda_i \gamma_i \int d\mathbf{r}' G_+(\mathbf{r}, \mathbf{r}') v_i(\mathbf{r}' - \mathbf{r}_i) \omega_i(\mathbf{r}'), \quad (64)$$

where  $\gamma_i = \int d\mathbf{r} \omega_i^*(\mathbf{r}) v_i(\mathbf{r} - \mathbf{r}_i) \bar{\Psi}_{\mathbf{k}}(\mathbf{r}), \quad (65)$

and  $\lambda_i^{-1} = \int d\mathbf{r} |\omega_i(\mathbf{r})|^2 v_i(\mathbf{r} - \mathbf{r}_i), \quad (66)$

$\omega_i(\mathbf{r})$  being a weighting factor, the choice of which is crucial to determine a particular scheme among the family of approximations defined by (64). A different approach is to look at the effective Hamiltonian that corresponds to these approximations. The potential  $V_1(\mathbf{r})$  (see (52)) is being replaced here by a non-local separable interaction, i.e.

$$V_1(\mathbf{r}) \Psi(\mathbf{r}) \rightarrow \bar{V}(\mathbf{r}) \Psi(\mathbf{r}) = \sum_i \lambda_i v_i(\mathbf{r} - \mathbf{r}_i) \omega_i(\mathbf{r}) \int d\mathbf{r}' \omega_i^*(\mathbf{r}') v_i(\mathbf{r}' - \mathbf{r}_i) \Psi(\mathbf{r}'). \quad (67)$$

The quality of the approximation depends strongly on the choice of  $\omega_i(\mathbf{r})$ . It has been shown (Singh *et al* 1986) that it is amenable to a non-perturbative iteration process, where even the first-order term has information on multiple scattering.

The need for a good approximation scheme arises from the enormously high cost of computation involved in an "exact" calculation. A major problem is the 'roughness' of a realistic solid surface. While perfect surfaces can be used for testing various theoretical approaches, randomness to a reasonable degree has to be invoked for results comparable to experiments. Stochastic and other statistical theories have been used for this purpose. Lapujoulade (1981) has studied the case of a random arrangement of steps on the surface. A random statistical surface having a slope defined by a isotropic normal



or gaussian probability function with standard deviation  $\sigma$  and an isotropic correlation coefficient  $C(\tau_{ij})$  have also been used (Garcia and Cabrera 1980). Here

$$C(\tau_{ij}) = \exp(-\tau_{ij}^2/T^2) \quad (68)$$

where  $\tau_{ij}$  is the distance between points  $i$  and  $j$  on the surface;  $T$  is the correlation distance. The wavelength of surface oscillations due to impurities and random defects is inscribed in  $T$ .

Normally, statistical theories based on ensemble-averaging cannot be used for a realistic surface because of computational limitations. We leave the discussion here by referring to a recent work by Spadacini and Tommei (1983), which is designed for a static, hard surface such that the surface level is described by a Markov process. The differential scattering probability in their work (see also Levi *et al* 1981, 1982 and Tommei *et al* 1985) is calculated by using the eikonal approximation.

An important feature not discussed adequately here is the multiple scattering expansion for gas-surface collisions. In particular, reactive dynamics on a surface cannot be dealt with without a multiple-scattering expansion. However, this necessitates enormous computational labour and the only way out of it is, again, to invoke a system-specific approximation. Elber and Gerber (1985a, b), for instance, developed a method for diatomic scattering from inert surfaces (whose chemical activity is negligible for the relatively high energy of the incident molecules).

### 3. A comparative discussion of theoretical methodologies and their results

If one knows the interaction potential reasonably well and has access to excellent computational facilities, the close-coupling method is the best approach to use. For instance, Celli *et al* (1985) have recently tested the superiority of the interaction potential derived using semi-*ab-initio* pair potentials, *vis-a-vis* a Morse model. A much better description of bound states and diffraction intensities was obtained using the derived potential in the close-coupling calculations of elastic scattering of He atoms from the LiF(001) crystal surface, leading to a very good agreement with available (Frankl *et al* 1978; Boato *et al* 1976) experimental data (see figure 2). Close-coupling calculations show that retaining only two Fourier components in describing the corrugation potential gives reasonable agreement between experiment and theory (Jonsson *et al* 1984). Drolshagen *et al* (1985) have done benchmark calculations on the H<sub>2</sub>/LiF(001) system using the interaction potential,

$$V(\mathbf{r}, \theta) = [V_0(z) + \beta V_1(z)Q(R)][1 + \lambda P_2(\cos \theta)],$$

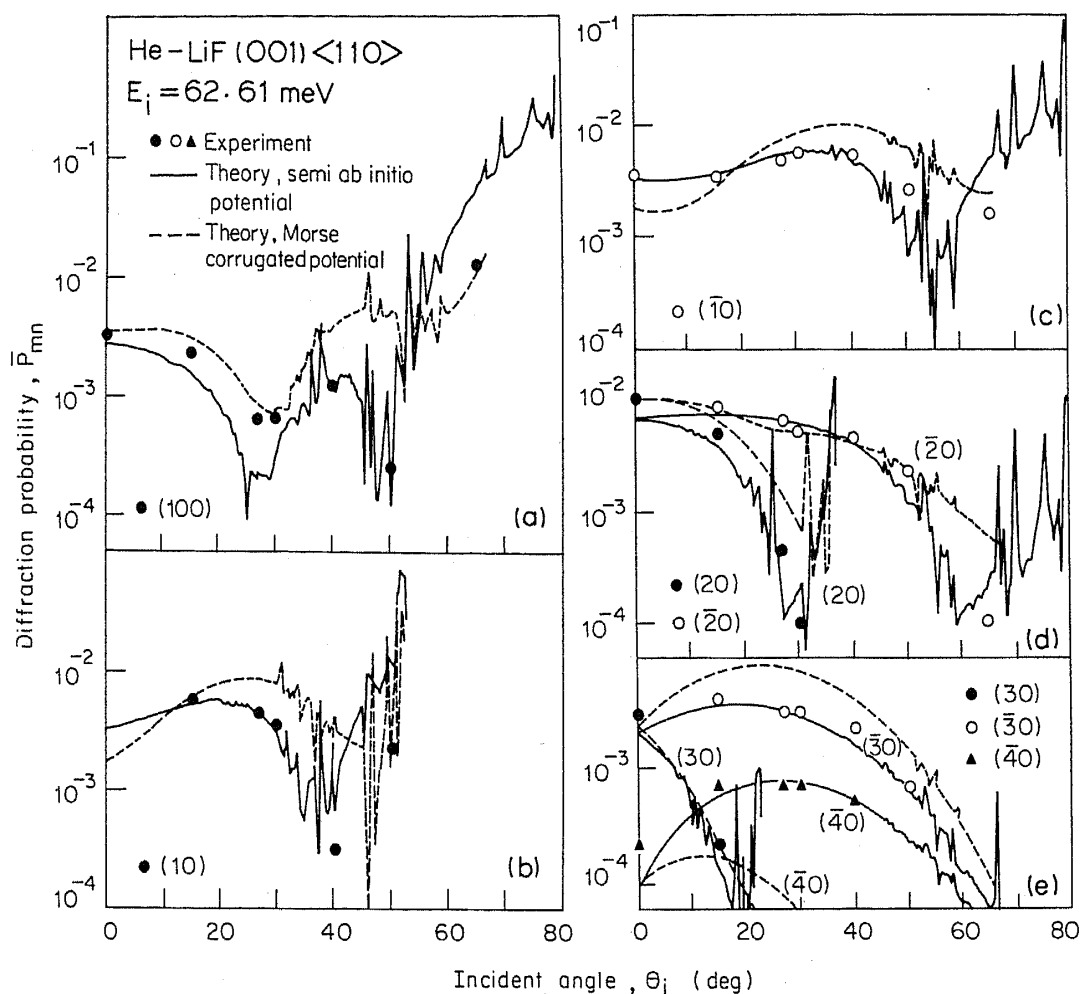
with 
$$V_0(z) = D \{ \exp[2\alpha(z_0 - z)] - 2 \exp[\alpha(z_0 - z)] \},$$

$$V_1(z) = D \exp[2\alpha(z_0 - z)],$$

$$Q(R) = \cos \frac{2\pi x}{a} + \cos \frac{2\pi y}{a},$$

$$\alpha = 1.14 \text{ \AA}^{-1}, \quad \lambda = 0.24, \quad a = 2.84 \text{ \AA}, \quad D = 38 \text{ MeV}.$$

The surface is taken as rigid and the diffraction as well as the rotation parts to  $U_{G_j}^{G_j'}$  can be factored out. However, a complete decoupling of the diffraction and rotation parts

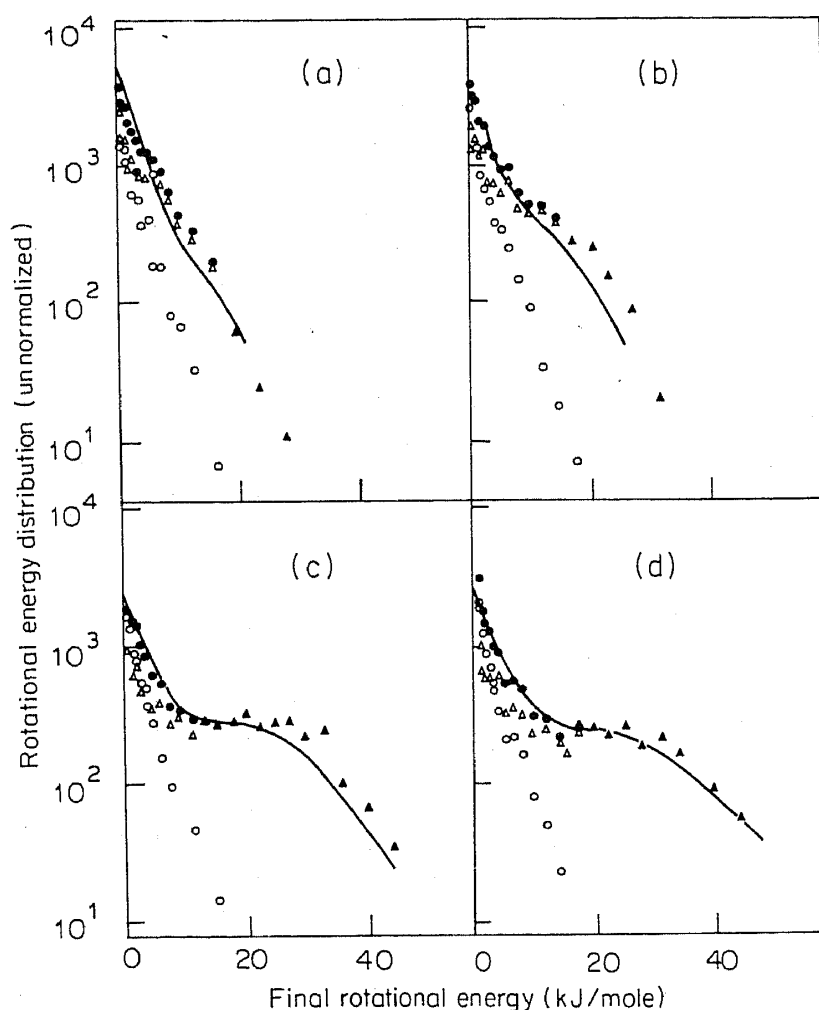


**Figure 2.** Diffraction probabilities as a function of incident polar angle  $\theta_i$  for He-LiF(001) scattering with  $E_i$  (incident kinetic energy) = 62.61 meV along the 110 direction. (a) the specular beam; (b) the (10); (c) the ( $\bar{1}0$ ); (d) the (20) and ( $\bar{2}0$ ); (e) the (30), ( $\bar{3}0$ ) and ( $\bar{4}0$ ) beams. Solid and open circles and the open squares are three different sets of experimental data (Boato *et al* 1976). The theoretical results are obtained *via* the close-coupling method using a semi-*ab-initio* potential (full lines) and a Morse corrugated potential (dashed lines). (Reproduced with permission from Celli *et al* 1985).

would mean neglecting all terms containing a product of  $\beta$  and  $\lambda$ . This has been explored earlier by Gerber *et al* (1980) within the sudden approximation. It is seen that for a widely used range of approximations such a decoupling is valid ( $\lambda \leq 0.24$ ,  $\beta \leq 0.05$  and for the relatively large energies  $E_i \geq 0.5$  eV). This implies that the relative distributions of the molecular states should be the same for all diffraction states. In other words, surface corrugation has no effect on the diffractively summed rotational transition probabilities and the anisotropy in the molecular potential does not effect the rotationally averaged transition probabilities among diffraction states.

While close-coupling results are highly accurate, calculations for inelastic modes are restricted to a few channels and either to a static surface (in the case of a molecule) or to one/two surface phonons (in the case of an atom). Perhaps the best results on dynamics involving surface vibrations have come from the other extreme, viz the classical

trajectory approach. Muhlhausen *et al* (1985) have used stochastic trajectory simulations employing empirical potential energy surfaces, to describe the nondissociative interaction of NO with the (111) faces of Ag and Pt (for experiments on this system see Serri *et al* 1982). Their results agree with the experimental data of Kleyn *et al* (1981) reproducing the observed rotational energy distributions of scattered molecules, including rainbow features (figure 3). These rotational rainbows have attracted a lot of interest recently (Tanaka and Sugano 1984; Schinke 1982; Voges and Schinke 1983). Tanaka and Sugano (1984) showed that the observed Boltzmann-like profile for low excitations in the system can be ascribed to the first of the two rotational peaks. They used three different types of potentials and found that the semi-classical infinite-order

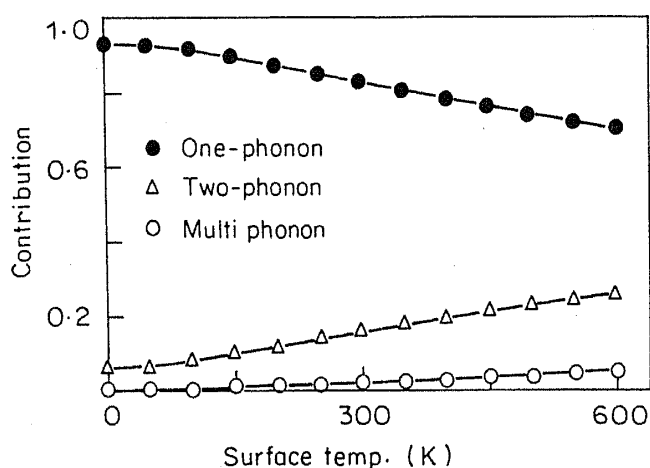


**Figure 3.** Rotational energy distribution for NO scattered from Ag(111). The non-exponential behaviour at high rotational energies is attributed to 'rotational rainbows'. Solid curves are experimental results of Kleyn *et al* (1981); solid circles are calculations using an empirical potential (Muhlhausen *et al* 1985); open circles refer to similar calculations for orientation angle,  $\theta < 60^\circ$ , open squares are for  $\theta > 60^\circ$ . (a) Incident translational energy  $E_i = 0.32$  eV, incident approach angle  $\theta_i = 40^\circ$ . (b)  $E_i = 0.32$  eV,  $\theta_i = 15^\circ$ . (c)  $E_i = 0.75$  eV,  $\theta_i = 15^\circ$ . (d)  $E_i = 10$  eV,  $\theta_i = 15^\circ$ . Surface temperature and initial rotational temperature are 650 and 20 K respectively, for all cases (reproduced with permission from Muhlhausen *et al* 1985).

sudden (SIOS) results were a good approximation to those obtained by using classical trajectory (CT) calculations. Earlier, Voges and Schinke (1983) had shown that the rotational rainbows will always occur in the collision of a diatomic molecule with a solid surface provided the collisions were mostly impulsive and many rotationally open channels were available. Rotational rainbows arise due to constructive interference of trajectories with different initial coordinates (rotor angles), all leading to the same final rotational state. A comparative discussion on the use of various classical trajectories (i.e., starting with different driving forces) was presented by Polanyi and Wolf (1982, 1985). The generalized Langevin oscillator was found to best describe surface adsorption. In fact, the other possibilities, namely, rigid surface and a simple harmonic oscillator, both give poor or no meaningful picture of reactive dynamics.

Inelasticity is sometimes introduced in classical dynamics as a constraint through a Lagrange multiplier. Wolf *et al* (1985) have followed this procedure to study the product polarization as a function of the product rotation for a rotor scattering from a solid surface. In general, it is found to decrease with increasing value of  $j'$ , the final rotational quantum number (Wolf *et al* 1985; Muhlhausen *et al* 1985). Elber and Gerber (1985c) have done classical trajectory calculations to assess the effect of surface vibrations on the rotational transitions. For the system, high energy  $I_2/MgO(100)$ , they show that inclusion of surface vibrations does not significantly change the rotational distribution after scattering compared to a rigid surface. This is because the time scale involved in administering the rotational torque to the molecule is faster than the time scale over which the surface vibrations are excited. This behaviour is expected to be typical of high-energy impact of heavy molecules on solids of light surface atoms. This is different from the sudden treatment, where the rigidity of the solid surface is an inherent assumption in the theory (Schinke and Gerber 1985). Nowadays, phonon scattering is becoming somewhat easier to handle as more is being known about it both experimentally (Mattera *et al* 1982; Brusdeylins *et al* 1983; Allison and Feuerbacher 1980; Mason and Williams 1980) and theoretically (Micha 1981; Hubbard and Miller 1984; Park and Bowman 1984; Meya and Levine 1984; Billing 1984; Schinke and Gerber 1985). Park and Bowman (1985) have computed the two-phonon transition intensities for He/Si(100)-(2X1) system by a classical trajectory quantum-field oscillator method called DESCENT. Time-of-flight spectra were simulated for three different surface temperatures and the contribution of one-, two- and multi-phonon terms to the total energy transfer was compared. It was shown that unless the surface temperature is very high, multi-phonon contributions are minimal (figure 4). The Debye-Waller attenuation factor has also been evaluated to include the effects of surface vibrations by many research groups (Celli and Maradudin 1985; Garcia and Maradudin 1982). However, this has many problems; for example, the use of this factor obtained from neutron scattering (Lapujoulade *et al* 1980) has been questioned (Jackson and Metiu 1985). Close-coupling theory followed by perturbation is also not quite accurate, since this goes against the spirit of expanding the wavefunction in the reciprocal lattice space using the periodic nature of the gas-surface interaction potential. The time-dependent wave-packet method is found to be more helpful to overcome this difficulty. It accounts very well for the surface-temperature-dependence of diffraction peak intensities, even though the method needs to be improved in order to reduce computational labour.

The interaction with defects or impurities on the surface is a dominant effect in molecular beam studies (Tully and Cardillo 1984). These experiments are conducted under conditions of low coverage of the adsorbate molecules on the metal surface. It is



**Figure 4.** One-, two- and multi-phonon contributions to the total energy transfer versus surface temperature for the He/Si(100)-(2X1) system (Reproduced with permission from Park and Bowman 1985).

believed that the interaction of gas atoms/molecules with such impurities on the surface is dominated by long-range forces since even a small coverage of adsorbed molecules causes a large decrease in the specular beam intensity (Mason *et al* 1981; Poelsema *et al* 1982a, b; Rieder and Wilsch 1983). Bosanak and Sunjic (1985) have interpreted this as arising from the orientation of the dynamic dipole of the adsorbed molecule.

Reactive scattering on a surface is one of the most difficult problems. This has been addressed in the IOS framework by Baer (1981). Processes like  $AB + S \rightarrow AS + B$  or  $BS + A$  ( $S$  denotes the surface), occurring without adsorption and desorption, were studied in a recent work (Baer 1985). A modified LEPS (London, Eyring, Polanyi and Sato) potential surface was used for calculating the transition probabilities for a reaction involving (HCl, S) and (HI, S) systems. The findings reveal that the only threshold for the reaction to occur is the zero-point energy of the diatomic molecule. The reaction seems to proceed faster if the reactants were translationally, rather than vibrationally, excited. Ron *et al* (1985) have also done quasi-classical studies on diatomic systems for the exchange collision mentioned above. The dissociation channel is found to be a used channel, which simplifies the problem. Reaction dynamics on a solid surface have also been studied in an effective Hamiltonian framework by Billing and others (Billing 1984; Billing and Caccitore 1985). The surface phonons are taken as a set of coupled harmonic oscillators with a frequency spectrum. This semi-classical approach was used for the oxidation process  $C + O \rightarrow CO$  on the Pt(111) surface.

Before we conclude this section, it is worthwhile to consider a question posed by the randomness of a realistic solid surface: *What role, if any, does nonlinearity play in gas-surface interaction?* Although this question has not been tackled yet in the context of gas-surface dynamics, an attempt has been made (Deb and Chattaraj 1986) to examine this problem in the case of ion-atom collisions, e.g. high-energy (non-reactive) proton-neon collisions. Within the framework of time-dependent density-functional theory and quantum fluid dynamics (Ghosh and Deb 1982; Deb 1984), it is possible to obtain a time-dependent Kohn-Sham-type equation in three-dimensional space in which "time" is explicitly embedded as a parameter. The equation is of the nonlinear Schrödinger-type, the solution of which describes the time-evolution of the electron density

(regarded as a "fluid") of the interacting system and an effective potential; in other words, one can directly follow the interaction process from start to finish within the novel framework of a (time-dependent) *pulsating potential* surface. Although, in this approach one has to solve a highly nonlinear integro-differential equation, it is still likely to result in considerable computational economy because it contains only *three* space variables (apart from "time"). The extension of this work to obtain new physical insights into gas-surface dynamics is a future possibility.

#### 4. Conclusion

Theoretical surface physics is an enormously rich but inadequately explored area. This article has presented a summary of some of the current activity in this field. We emphasize again the basic problems in gas-surface interaction: The interface presents a many-body problem. There is significant "roughness" on the surface and this has to be accounted for in theoretical formulations. Further, the number of diffractive and inelastic channels for gas-surface interaction is very large. As the present article indicates, considerable effort is under way to tackle these problems on a realistic footing. While numerical accuracy is being sought by using rigorous classical-trajectory and close-coupling quantum-mechanical approaches, approximate methods based on stronger assumptions are yielding better physical insights into the nature of gas-surface dynamics. Progress in this area may drastically alter our perceptions of catalytic processes and certain electrochemical processes such as corrosion. Better pollution control and the improvement of the quality of solid surfaces used in daily life are among the likely technological "spin-offs" of studies on surface structure and reactivity.

#### Acknowledgement

BMD would like to thank the Council of Scientific and Industrial Research for a research grant.

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