

TIME-DEPENDENT WAVEPACKET CALCULATIONS OF MOLECULAR SCATTERING FROM SURFACES

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An outline is given of time-dependent wavepacket methods as applied to calculations of molecular collisions with solid surfaces. The methods reviewed include numerical integration algorithms for the time-dependent Schrödinger equation, semiclassical wavepacket treatments, and approximations that treat some of the degrees-of-freedom quantum-mechanically and others classically. The computational and numerical characteristics of these methods are discussed, with emphasis on their particular advantages and relevance in the context of certain molecule/surface scattering problems. For the semiclassical and mixed quantal-classical treatments, the approximation errors and their physical origins are discussed. For the quantum wavepacket techniques a numerical error analysis is presented. The computational efficiency of the various algorithms is considered and examined in the context of several applications. The main focus is on diffractive scattering of atoms and light molecules from crystalline surfaces, on scattering of atoms from imperfect and disordered surfaces, and on rotational excitation of molecules in impact on solids. These are the most quantitative topics in the surface scattering field at the present state of the art. Guidelines for future applications are suggested, and some of the remaining problems in wavepacket calculations of surface scattering processes are discussed.

1. Introduction

The scattering of molecular beams has developed in recent years into one of the most powerful and versatile techniques for studying solid surfaces. Experiments using this method are carried out to explore questions such as the structure of the surface on the atomic scale [1], the vibrational frequency spectrum of the surface [2], and the physical mechanisms of energy transfer and chemical reaction processes in molecular–surface interactions [3,4]. Quantitative understanding of the dynamics of molecular collisions with surfaces is necessary for the interpretation and analysis of such experiments. This need played a major role in motivating much of the intensive activity in the theory of molecular collisions with surfaces and in methods of quantitative calculations in this field. The present review describes an important class of methods for calculating observables and describing the dynamics of certain types of molecule–surface collision processes. The methods are directed at cases where a quantitative quantum mechanical treatment is required for at least some of, though not necessarily all, the degrees of freedom. The aspect common to all the groups of methods considered here is that the dynamics is described in terms of wavepacket motion, the latter being computed either by numerical solutions of the time-dependent Schrödinger equation, or by semiclassical wavepacket approximations. Although relatively recent in use, these methods proved extremely useful, in particular in the field of surface scattering, and are attracting considerable interest due both to computational advantages and the simplicity by which physical insight can be extracted from such calculations. The field of molecule–surface collisions encompasses a vast variety of processes, which may require different methods and approaches. It should be useful to list and briefly discuss the processes for which time-dependent wavepacket methods seem particularly useful at the present state of the art.

1.1. Processes and systems treated

(a) *Diffraction scattering from crystalline surfaces*: The scattering of light atoms and molecules (e.g., He, H, Ne, H₂, etc.) from crystalline surfaces at thermal and hyperthermal energies give rise to well-resolved diffraction peaks [1]. The measured intensities are sensitive to the interaction between the projectile and surface, and can be used to determine this potential [5]. Moreover, since the interaction potential itself depends on the structure of the surface (although this dependence is neither simple nor fully understood), the measured diffraction intensities are a sensitive probe also of the structure of the surface on the atomic scale [1]. To extract either the interaction potential or the surface structure from experimentally measured diffraction data, it is necessary to have an algorithm for calculating the intensities for an assumed potential. This can be done by available time-independent methods, *provided that one can treat the surface as a rigid, nonvibrating target*. In this case the momentum transfer that takes place in the collision is restricted by Bragg's condition, namely:

$$\hbar\mathbf{K}' = \hbar\mathbf{K} + \mathbf{G}_{mn}; \quad \mathbf{G}_{mn} = \left(\frac{2\pi}{a_x}m, \frac{2\pi}{a_y}n \right), \quad (1.1)$$

where $\mathbf{K}'$, $\mathbf{K}$ are respectively the initial and final momentum components of the particle in parallel to the surface plane, $\mathbf{G}_{mn}$ are the reciprocal space vectors and a_x , a_y are the unit cell

vectors along the x , y directions of the surface lattice. Eq. (1.1) implies that the number of final momentum states in atom scattering from a rigid periodic lattice must be finite. Since (1.1) holds also for energetically-closed diffraction channels that can only play a role as intermediate states, it is seen that the set of momentum states involved in the process is a discrete one. This is explicitly taken advantage of in the time-independent scattering calculations that are routinely applied to this problem [5]. In the familiar close coupling technique, for instance, a truncated (but sufficient for convergence) set of momentum states is used as a basis for expanding the total wavefunction, and the resulting finite set of coupled-channel equations, for the scattering process is then solved numerically [5]. In this framework, the available time-independent methods are successful, but this depends on the validity of the rigid surface model. For a real, vibrating solid the collision involves energy transfer to surface phonons, and in principle a continuum of channels, associated with the continuum of phonon frequencies must be dealt with. This is beyond the scope of realistic close coupling calculations. The practical time-independent calculations hitherto carried out were thus confined to the rigid-surface model, and contact with experimental data was made by assuming the (approximate) Debye–Waller relation [6,7]:

$$I_{mn}(T) \approx F_{\text{DW}}(T) I_{mn}^0, \quad (1.2)$$

where I_{mn} is the intensity of (mn) diffraction peak for the real surface at temperature T , and I_{mn}^0 the corresponding diffraction intensity for a rigid, nonvibrating model of the same surface. Several explicit expressions different in details of approximation, were given for the Debye–Waller (DW) factor $F_{\text{DW}}(T)$ in (1.2) [6,7], and I_{mn}^0 can thus be extracted from the experimental intensities. However, (1.2) is an approximation, and recently significant deviations from the DW model were observed and discussed [1]. The theoretical derivation of the DW approximation (1.2) is most questionable, for instance, for collisions at near-grazing incidence angles and at low energies [7]. For further progress in the field, it should be extremely important to have a method for diffraction scattering calculations that can include the contributions of photons to the process. It will be seen later that this can be accomplished by the time-dependent wavepacket methods, and the latter thus open an important avenue for progress in diffraction scattering calculations, and in the extraction of surface structure and atom–surface potentials from diffraction data.

(b) Atom scattering from imperfect and disordered surfaces: Experimental and theoretical activity in this topic began only a few years ago, but it has grown very rapidly and the subject is attracting considerable interest. Important pioneering experiments by Comsa and collaborators [9] indicate that He scattering can serve as a powerful probe of noncrystalline surface systems, such as adsorbed overlayers (including at very low concentrations), vacancies in crystalline surfaces, random steps etc. [9]. Questions of great interest that can be explored via such experiments are, for instance, whether adsorbates on a surface attract or repel each other and whether they form clusters, what are the interactions between defects on surfaces, what are the activation energies associated with diffusion of adsorbates (or vacancies), and what is the nature of order–disorder phase transitions in adsorbed layers. A quantitative interpretation of experiments in this field requires a theory and computational algorithms for scattering from disordered surfaces. The development of the required theoretical tools for this subject is confronted by several difficulties. As pointed out earlier, in time-independent theories of scattering from

crystalline (nonvibrating) structures, surface periodicity is used to derive simplified scattering equations. Thus, the stationary scattering wavefunction is expanded in the form

$$\psi(x, y, z) = \sum_{m,n} \exp[i(\mathbf{G}_{mn} \cdot \mathbf{R} + \mathbf{K} \cdot \mathbf{R})] \chi_{mn}(z), \quad (1.3)$$

where $\mathbf{G}_{mn}$ as in (1.1) are the reciprocal space vectors, $\mathbf{K}$ is the incident wavevector component parallel to the surface, $\mathbf{R} = (x, y)$ is the position in the surface plane and z the distance from the surface. The discrete nature of the expansion (1.3) results in a manageable set of close coupling equations for the $\chi_{m,n}(z)$ that correspond to the different diffraction channels (m, n) . The expansion corresponding to (1.3) for a non-crystalline surface involves an integral over *continuum* values of the wavevector component in parallel to the surface plane. Thus the scattering problem is equivalent to a continuum of coupled-channel equations. In this case, unlike that of the previous topic (a), the continuum arises even at the level of a nonvibrating surface model, since scattering from noncrystalline systems is not necessarily diffractive. Time-independent approaches to this problem relied on simplifications of the dynamics such as the Sudden approximation (at high collision energies) [10] and the average wavefunction method (at low energies) [11], or employed models restricted to very special cases, e.g. an isolated adsorbed atom on a flat, infinitely hard surface [12,13]. Several of the studies reviewed in the present article showed that scattering from disordered surfaces can be treated quite powerfully and rigorously by wavepacket methods, for which case the occurrence of a continuum of open channels does not pose in general major computational difficulties.

(c) *Rotationally and vibrationally inelastic molecule-surface scattering*: A wealth of information was obtained in recent years in experimental studies of rotational energy transfer in molecular collisions with surfaces [3], but much less data are available as yet on the corresponding vibrational processes [14]. There are systems for which, at high energy collisions, phonon effects on the rotational energy distribution appear to be small, e.g. NO/Ag [15]. If the surface involved is also relatively smooth, then close-coupling calculations which neglect the roles of surface vibrations and surface corrugation become useful, and are definitely feasible [15,16]. If the rigid surface model can still be applied but the effects of surface roughness cannot be ignored, then time-independent coupled channel calculations get beyond the reach of presently available computers, for all but the lightest molecules, since the number of rotational and diffraction channels becomes extremely large. The scattering of H_2 from LiF(001) was studied recently by rigorous close-coupling calculations [17], but for most systems one must use approximations, and the Sudden method [18,19] seems quite successful in this context. For cases where phonon participation affects rotationally inelastic scattering, the only quantum-mechanical calculations reported so far utilize the Sudden approximation for both the rotational and the phonon degrees of freedom [20]. There is a scope and a need for new, additional methods whenever a detailed quantum-mechanical description of the final rotational state is sought in systems which either involve considerable surface corrugation or significant participation of surface vibration in the process (as reflected, e.g., in the dependence of the results on surface temperature). We stress that both these effects are the rule rather than the exception [3], and most experimental systems do correspond to these cases. It will be seen later on in this review that time-dependent processes do offer promising possibilities for dealing with phonon participation and with many diffraction

channels, hence their considerable potential importance in the study of rotational and vibrational energy transfer.

(d) Excitation of surface phonons and of electron–hole pairs: In the previous topics, the importance of treating surface phonons was mentioned in the context of the role these degrees of freedom may play in processes such as diffraction or rotational energy transfer. Coupling to phonons may significantly attenuate the intensities of such processes compared with the ideal reference case of a non-vibrating surface. However, atom scattering experiments can be used to probe, e.g., via time-of-flight techniques, the collisional excitation of the surface itself [2]. Methods for calculating the probabilities of such excitations are thus of considerable interest. Intensities for single phonon excitations can be calculated by approximate (distorted wave) time-independent quantum calculations [2], which are pertinent for instance to low energy He scattering from LiF(001). This method cannot, however, be extended in practical terms to multiphonon processes. It seems reasonable to assume that high-order multiphonon processes can be treated classically. An approach that can be applied also in the difficult, intermediate case of several phonon processes is to employ (time-dependent) wavepackets, in particular to treat surface vibrations by wavepackets. Studies of this type will be discussed later on. Time-dependent wavepacket methods may have a particularly crucial role in the study of electronic excitation of solids upon molecular impact on the surface. The role of electron–hole pair excitations in molecular interactions with metals and with semiconductors is a topic of fundamental interest. Recently, important progress was made in the direct experimental detection of such processes [21]. Two features make it very difficult to develop a computational approach to the study of such processes: The excited states form a continuum (as in the case of phonons), and classical approximations are not expected to work (unlike the case of phonons). Quantum wavepacket calculations seem a most promising route for overcoming these combined difficulties, and may be the only available computational tool in this respect in the field.

1.2. Advantages of wavepacket methods in surface scattering

The above survey of several types of surface scattering processes, and the computational requirements they give rise to, already indicated some of the points of strength of wavepacket methods. It should be useful at this point to systematically outline the motivations for pursuing wavepacket techniques for molecule–surface collisions.

(i) Surfaces give rise to problems of treating a continuum of scattering channels. Thus, in dealing with surface phonons a continuum of excitation channels is involved. In a topic such as scattering from a disordered surface, a continuum of final accessible “diffraction states” (or more precisely states labeled by the momentum value parallel to the surface) must be dealt with even within the model of a nonvibrating solid. Wavepacket methods offer a powerful tool of demonstrated applicability for problems involving a continuum of coupled scattering channels.

(ii) When solid degrees of freedom must be incorporated in the calculations, the complexity of the surface scattering problem is such that it is an enormous advantage to treat most of the degrees of freedom classically, whenever physical considerations justify such a simplification. On the other hand, the experiments that are being performed provide results that are quantum-state resolved for some of the variables (e.g. diffraction, final rotational distribution of scattered molecules). Methods that can treat consistently some of the degrees of freedom quantum

mechanically and the remainder classically are thus very advantageous for surface scattering. Time-dependent approaches which treat some modes by classical trajectories and others by quantum dynamics are very suitable in this respect, and are discussed in the present review.

(iii) One of the most rewarding approaches for incorporating phonon effects in surface scattering, pursued primarily in fully classical treatments, is based on using the Generalized Langevin Equation [22,23]: The influence of solid vibrations is represented as friction terms and as random forces. Quantum-mechanical time-dependent treatments of the scattered particle can readily utilize such time-dependent stochastic models of the target surface.

(iv) The issue of simple visualization and physical interpretation, always important for any computational result, seems to us particularly weighty for complicated processes such as surface collisions frequently are. Time-dependent wavepacket methods have great merit in this respect, and seem to us to offer physical insight much more directly and easily than, e.g., close coupling calculations.

(v) Most of the available, numerically-realized time-dependent wavepacket methods are based on algorithms that explicitly employ Cartesian coordinates. For surface scattering (although not e.g. for atom–molecule collisions), such coordinates are a natural and preferred choice. This technical reason has been an important factor in the many early applications of wavepacket methods to surface scattering.

1.3. Outline of the article

In section 2 we review grid methods for integrating the time-dependent Schrödinger equation, and discuss the computational efficiency and numerical properties of these schemes. Section 3 is dedicated to semiclassical wavepackets and their applications, with a discussion of the validity, scope and limitations of the approximations involved. Section 4 deals with methods that treat part of the degrees of freedom by quantum wavepackets and the remainder by classical trajectories. Methods that allow for consistency in the framework of such a mixed treatment are reviewed. The computations of the wavefunctions in the “quantum modes” in this framework is also discussed. Concluding remarks focusing on open problems and future outlook are presented in section 5.

2. Wavepacket propagations by grid methods

For surface scattering calculations, grid methods can be extremely useful. These methods are accurate and modular in structure. The numerical procedure can be divided in four steps: a) Setting the initial wavefunction on the grid. b) Establishing a method to calculate the Hamiltonian operation. c) Propagating the wavefunction in time. d) Analysing in the final propagated wavefunction. Because of this modular structure each step can be done separately by a variety of techniques, contributing to the versatility of grid methods. Accuracy can be controlled in each step separately. Time dependent grid methods resemble actual experiments in the sense that an initial state is scattered to a multitude of final states. This situation is equivalent to one column of the $\hat{\mathbf{S}}$ matrix. As a consequence using grid methods, simulations of actual experiments for which e.g. many diffraction peaks are resolved are possible, whereas a full $\hat{\mathbf{S}}$ matrix calculation is

prohibitively expensive. In grid methods very accurate results can be produced, which can be used as benchmarks to test other approximate methods. Surface scattering problems are easily adapted to these methods because Cartesian coordinates can be used and periodic boundary conditions can be matched to the unit cell of the lattice.

2.1. Discussion of grid methods for wavefunction representation

In quantum mechanics the state of the system is represented by the wavefunction ψ . All observable information on the system is extracted from this wavefunction. The time evolution of the wavefunction is governed by the Schrödinger equation:

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H}\psi. \quad (2.1)$$

A numerical construction of a solution to the time-dependent Schrödinger equation follows three stages: First the wavefunction ψ is discretized by representing it on grid points. (values of ψ between grid points are obtained by interpolation). Secondly, the Hamiltonian operator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} \quad (2.2)$$

and its operation on ψ , $\hat{H}\psi$ are calculated. Thirdly, a time propagation scheme is constructed which transforms an initial wavefunction to a final one. Different numerical methods can be classified by the way each of these steps is carried out.

Wavefunctions pertinent to our interest are continuous functions extended in space. All grid methods represent such a function at a set of discrete sampling points. The value of the wavefunction between sampling points is recovered by interpolation. The interpolation scheme chosen is the basis of the classification of different grid methods, the Finite Difference method (FD) and the Fourier method. The finite difference methods (FD) utilize polynomial interpolation schemes [24]. The Fourier method recovers the value between points by the $\text{sinc}(\sin x/x)$ interpolation procedure [25]. Derivatives of these interpolation schemes are the source of formulas, representing the different procedures used, for calculating numerical derivatives.

In grid methods, the size and shape of the grid have to be adapted to the physical problem. For two-dimensional surface scattering calculations, rectangular grids with uniform sampling points have been used. Although non-uniform grids maybe advantageous in special cases [26] no surface calculations have used them yet. The size of the grid must be large enough to contain the wavefunction from the initial state to the final one. In three-dimensional calculations the grid is matched to the unit cell. A parallelogram shaped grid is then adapted with uniform sampling points [27].

Boundary conditions of the grid are an important issue. The finite difference method is more flexible in the choice of boundary conditions because both fixed or periodic boundaries can be employed. The Fourier method is on the other hand restricted to periodic boundary conditions. Surface scattering problems require periodic boundaries matching the unit cell parallel to the surface and fixed boundaries perpendicular to the surface. In the Fourier method, fixed

boundaries are obtained by ending the grid with a strongly repulsive potential. For surface scattering problems the back side of the repulsive potential of the surface serves this purpose by preventing tunneling through the periodic boundaries of the grid. Absorbing boundary conditions also can be important in surface scattering. If placed at the far end of the grid they represent an extended open space. Such boundaries enable separation of the direct scattering amplitude from the absorbed amplitude. Absorbing boundaries are obtained by adding an imaginary optical potential at the far end of the grid [28].

The initial wavefunction

After the grid has been set up, the initial wavefunction has to be placed on it. For scattering calculations, the wavefunction is placed in the asymptotic region with an average momentum pointing to the surface. Because of the finite size of the grid the wavefunction has to be semi-localized. Two types of initial wavefunctions have been used for surface scattering calculations. Type I wavefunctions are localized both in the z direction perpendicular to the surface and in the x direction parallel to the surface. The type I choice is convenient for the study of local scattering from different regions of the surface. Type II wavefunctions are localized in the z direction, whereas they form a plane wave in the x and y directions. Usually the localization in the z direction is done by choosing a Gaussian wavepacket. A typical 3-D wave matched to the unit cell will have the form:

$$\psi(i, j, l) = (2\pi\sigma^2 A)^{-1/2} e^{-(z-z_0)^2/2\sigma^2} e^{i(i\Delta y k_x + j\Delta y k_y)}. \quad (2.3)$$

The i , j and l indices are the spatial indices of the grid in the directions x , y and z . Δz is the spatial displacement between grid points in z . Here $z = l\Delta z$, z_0 is the initial average position in z , σ the width in z . $\Delta x = a_x/N_x$ and $\Delta y = a_y/N_y$, where a_x and a_y are the lattice vectors and N_x and N_y are the numbers of grid points in the x and y directions. k_x and k_y are the wavenumber in the x and y directions. A is the area of the unit cell. The width of the Gaussian in z determines the width of the momentum and therefore the spread in energy. For a Gaussian of width σ the energy spread becomes:

$$\Delta E = \frac{\hbar^2}{2m} \frac{1}{\sigma^2} \quad (2.4)$$

By choosing a wide enough Gaussian the spread in energy can be minimized.

2.2. Hamiltonian operation for the Finite Difference (FD) method

The Hamiltonian operation can be partitioned to potential and kinetic parts. Because the potential energy operator is a local operator in coordinate space its operation is the simple multiplication at each spatial grid point. For a two-dimensional problem where i is the spatial index in x and l in z the operation becomes:

$$\hat{V}(i, l)\psi(i, l). \quad (2.5)$$

The potential energy operator can be time dependent to take into consideration thermal motion of the surface [29,30].

The main difficulty in the Hamiltonian operation arises from the kinetic energy operator because of its non-local character. McCullough and Wyatt [31] and later Kulander [32] and Askar and Cakmak [33], approximated the kinetic energy operator using a finite difference scheme (in 2-D)

$$\begin{aligned} & \frac{-1}{2m} \left(\frac{\partial^2 \psi(i, l)}{\partial x^2} + \frac{\partial^2 \psi(i, l)}{\partial z^2} \right) \\ & \approx \frac{-1}{2m} \left(\frac{\psi(i+1, l) + \psi(i-1, l) - 2\psi(i, l)}{\Delta x^2} + \frac{\psi(i, l+1) + \psi(i, l-1) - 2\psi(i, l)}{\Delta z^2} \right), \end{aligned} \quad (2.6)$$

where i and l are the spatial indices and Δx and Δz are the distances between grid points in x and z . This approximation is equivalent to the Laplacian of the quadratic interpolation scheme: If one considers the interval $x_{i-1} = (i-1) \Delta x \leq x \leq (i+1) \Delta x = x_{i+1}$ the interpolation scheme reads

$$f(x) = a(x - x_i)^2 + b(x - x_i) + c, \quad (2.7)$$

where

$$\begin{aligned} a &= \frac{f(x_{i+1}) + f(x_{i-1}) - 2f(x_i)}{2\Delta x^2}, \\ b &= \frac{f(x_{i+1}) - f(x_{i-1})}{2\Delta x}, \\ c &= f(x_i). \end{aligned}$$

Taking the second derivative of this formula at the point x_i , and using a similar formula for the z direction the result (2.6) can be recovered. The total Hamiltonian operation is then the sum of the potential and kinetic terms. Higher order finite difference schemes can be obtained by differentiating higher order polynomial schemes [34], but they have not been used for surface work.

Error analysis

The main source of error in the finite difference method is the semilocal approximation for the kinetic energy operator. The operator of equation (2.6) is a member of the family of convolution operators and therefore is diagonal in k space. Performing a Fourier transform on (2.6) the spectrum in k space of the FD kinetic energy operator is obtained (in one spatial dimension):

$$-\frac{\hbar^2}{2m} \frac{2(\cos(k \Delta x) - 1)}{\Delta x^2} = \frac{\hbar^2}{2m} \left(\frac{2 \sin(k \Delta x/2)}{\Delta x} \right)^2 \quad (2.8)$$

compared to the exact kinetic energy operator spectrum of $(\hbar^2/2m)k^2$, for $k \rightarrow 0$ the two

formulas coincide. For $k = 0.1 \times \pi/\Delta x$ the relative error for the operation becomes: 0.0041, which is tolerable in most cases. This is the origin of the thumb rule that at least 10 grid points are needed per wave length for an adequate approximation. For $k = 0.4\pi/\Delta x$ the relative error becomes: 0.065.

2.3. Hamiltonian operation for the Fourier method

The potential energy operation is calculated by multiplying $\mathbf{V}(\mathbf{i}, l)$ by $\psi(\mathbf{i}, l)$ as in the FD method. The simplicity of the operation comes about because the potential energy operation is local in the coordinate representation of the wavefunction. A local operation of the kinetic energy can be calculated in k space. The transformation from the coordinate space to the momentum space is the Fourier transform. At this step the k space wavefunction is multiplied by $-\hbar^2 k^2/2m$. The operation is completed by transforming back to coordinate space using an inverse Fourier transform. The numerical procedure is as follows: A) Transform $\psi(\mathbf{i}, l)$ to $\tilde{\psi}(\mathbf{n}, \mathbf{m})$ in k space by a two-dimensional discrete Fourier transform. B) Multiply $\tilde{\psi}(\mathbf{n}, \mathbf{m})$ by $-\hbar^2(k_n^2 + k_m^2)/2m$. C) Transform the result of B to coordinate space by an inverse 2-D Fourier transform. Numerical efficiency of the method is the result of the Fast Fourier Transform (FFT) algorithm [35,36]. For this algorithm numerical effort grows as $\mathcal{O}(N \log N)$ where N is the number of grid points. This is compared to a matrix transformation procedure from coordinate space to momentum space for which numerical effort grows as $\mathcal{O}(N^2)$ [37].

An important advantage of the method is that the communication relations of quantum mechanics, $[\hat{\mathbf{p}}, f(x)] = i\hbar \dot{f}(x)$ are preserved in the discrete representation [38,39]. This means that the discrete Hilbert space used for modeling the problem has the same commutation relations as the continuous Hilbert space and the correct operator algebra is mapped to the discrete world.

Error analysis

For a band limited function with finite support, the Fourier method is exact [25,37]. But for realistic wave functions, errors in the Fourier method are a result of two sources: a) The grid is not large enough to contain the wavefunction or does not match the periodic boundary conditions. b) The grid is not dense enough which results in undersampling of high momentum components of the wavefunction. For Gaussian type wavefunctions, the convergence of the method is exponential when increasing the grid size or grid density. Practically when constructing a grid care should be taken that the maximum momentum in the wave function does not exceed: $p_{\max} < \pi\hbar/\Delta x$.

2.4. Time propagation scheme

The next step in the grid methods is to propagate the wave function in time. The general solution of eq. (2.1) has the form:

$$\psi(t + dt) = \exp(-i\hat{\mathbf{H}} dt/\hbar)\psi(t). \quad (2.9)$$

For grid methods time propagation schemes have to be simple because they are applied on each grid point. This fact usually rules out predictor-corrector variable step integrators.

The Second Order Differencing scheme (SOD)

The simplest scheme for propagating eq. (2.1) is to expand the evolution operator $\hat{U} = \exp(-i\hat{H} dt/\hbar)$ in a Taylor series:

$$\exp(-i\hat{H} dt/\hbar) = 1 - i\hat{H} dt/\hbar + \dots \quad (2.10)$$

It has been found that a numerical scheme based on this expansion is not stable. This instability comes about because the scheme does not conserve the time reversal symmetry of the Schrödinger equation. With a symmetric modification of the expansion stability is obtained. One way to formulate the scheme is to use second order differencing (SOD) to approximate the time derivative in eq. (2.1). Another formulation uses the symmetric relation:

$$\psi(t + dt) - \psi(t - dt) = (e^{-i\hat{H}dt/\hbar} - e^{i\hat{H}dt/\hbar})\psi(t) \quad (2.11)$$

and then by expanding $\hat{U} = \exp(-i\hat{H} dt/\hbar)$ and $\hat{U}^*$ in a Taylor series the explicit second order propagation scheme is obtained:

$$\psi(t + \Delta t) \approx \psi(t - \Delta t) - 2i\Delta t\hat{H}\psi(t)/\hbar. \quad (2.12)$$

This formula is equivalent to the SOD form:

$$\frac{\partial \psi}{\partial t} \approx \frac{\psi(t + \Delta t) - \psi(t - \Delta t)}{2\Delta t}. \quad (2.13)$$

This is the time propagation scheme used in the finite difference method of Askar and Cakmak [33] and also in the Fourier method [38,39,40]. The advantage of the method is that it can propagate Hamiltonians which are time dependent.

Error analysis

Because the Schrödinger equation and also the SOD scheme are symmetric in time the error in propagation grows as $\mathcal{O}(\Delta t^3)$. If the Hamiltonian operation is Hermitian which is the case for both the FD method and the Fourier method the SOD propagations scheme preserves the norm and energy. A good way to investigate this scheme is to write it as a discrete mapping propagation scheme:

$$\begin{pmatrix} \psi^{n+1} \\ \psi^n \end{pmatrix} = \begin{bmatrix} 1 - 4\Delta t^2\hat{H}^2/\hbar^2 & -2i\Delta t\hat{H}/\hbar \\ -2i\Delta t\hat{H}/\hbar & 1 \end{bmatrix} \begin{pmatrix} \psi^{n-1} \\ \psi^{n-2} \end{pmatrix}, \quad (2.14)$$

where n is the index of the time step. The eigenvalues of this propagation matrix are:

$$\lambda_{1,2} = 1 - 2\Delta t^2\hat{H}^2/\hbar^2 \pm \frac{2\Delta t\hat{H}}{\hbar} \left(\frac{\Delta t^2\hat{H}^2}{\hbar^2} - 1 \right)^{1/2} \quad (2.15)$$

Because $\lambda_1\lambda_2 = 1$ this mapping is an area preserving mapping which is equivalent to the norm conservation (see next section):

$$\langle \psi_n | \psi_{n+1} \rangle = \text{const.} \quad (2.16)$$

In order to obtain the correct oscillatory solutions one obtains the stability criterion of the discrete map:

$$\frac{\Delta t^2 \hat{\mathbf{H}}^2}{\hbar^2} - 1 < 0$$

i.e.,

$$\Delta t \leq \frac{\hbar}{E_{\max}}, \quad (2.17)$$

where $E_{\max}$ is the largest eigenvalue of the discrete Hamiltonian. $E_{\max}$ can be estimated as the sum of the maximum potential and kinetic energy. For the Fourier method one obtains (for a 2-D problem):

$$E_{\max} \approx V_{\max} + \frac{\pi^2}{2m} \left(\frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right) \hbar^2, \quad (2.18)$$

where Δx and Δy are the spatial grid intervals. And for the FD method:

$$E_{\max} \approx V_{\max} + \frac{4}{2m} \left(\frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right) \hbar^2 \quad (2.19)$$

(The difference between (2.18) and (2.19) comes from eq. (2.4) where the high k values of the FD method have lower eigenvalues of the kinetic energy). If the time step exceeds the stability limit exponential solutions take over resulting in a numerical overflow. This fact can be used to empirically obtain the stability limit [38,39].

The norm and energy conservation of the SOD scheme is a consequence of the time reversal symmetry of the scheme and of the Hermitian property of the Hamiltonian operator both for the FD and Fourier methods. Consider first the conservation of the norm, eq. (2.1) is multiplied by ψ^{*n} :

$$i\hbar\psi^{*n}\frac{\partial\psi^n}{\partial t} = \psi^{*n}\hat{\mathbf{H}}\psi^n. \quad (2.20)$$

Next the conjugate of equation (2.1) is taken and multiplied by ψ^n to get

$$-i\hbar\psi^n\frac{\partial\psi^{*n}}{\partial t} = \psi^n\hat{\mathbf{H}}\psi^{*n} \quad (2.21)$$

After subtracting (2.20) from (2.21) and the summing over all points of the mesh, the result is:

$$i\hbar\left\langle\psi^{*n}\left|\frac{\partial\psi^n}{\partial t}\right.\right\rangle + i\hbar\left\langle\psi^n\left|\frac{\partial\psi^{*n}}{\partial t}\right.\right\rangle = \langle\psi^{*n}|\hat{\mathbf{H}}|\psi^n\rangle - \langle\psi^n|\hat{\mathbf{H}}|\psi^{*n}\rangle. \quad (2.22)$$

Because $\hat{H}$ is Hermitian the rhs vanishes, likewise eq. (2.13) implies

$$\psi^{*n} \frac{\partial \psi^n}{\partial t} + \psi^n \frac{\partial \psi^{*n}}{\partial t} = (\psi^{n+1} \psi^{*n} + \psi^{*n+1} \psi^n - \psi^n \psi^{*n-1} - \psi^{*n} \psi^{n-1}) / 2\Delta t. \quad (2.23)$$

The norm conservation will read:

$$\text{Re} \langle \psi^{n+1} | \psi^n \rangle = \text{const.} \quad (2.24)$$

The energy conservation is obtained in a similar way by multiplying eq. (1.1) by $\partial \psi^{*n} / \partial t$. The result is:

$$\text{Re} \langle \psi^{n+1} | \hat{H} | \psi^n \rangle = \text{const.} \quad (2.25)$$

Because of this norm and energy conservation the error in propagation accumulates in the phase. In order to obtain an estimate of this error consider the propagation of an eigenfunction ϕ_m with eigenvalue E_m . The eigenvalues of the propagation matrix become:

$$\lambda_{1,2} = 1 - \frac{2\Delta t^2 E_m^2}{\hbar^2} \pm \frac{2\Delta t E_m}{\hbar} \left(\frac{\Delta t^2 E_m^2}{\hbar^2} - 1 \right)^{1/2}. \quad (2.26)$$

Comparing with the exact expression of $e^{-2iE_m\Delta t/\hbar}$, one finds that the error in propagation by the SOD method per time step is

$$\text{error} \approx \frac{(\Delta t E_m)^3}{3\hbar^3}. \quad (2.27)$$

Propagating N times this error accumulates N times. First one should notice that the error is not uniform and is large for large eigenvalues of ψ . To minimize the error in phase it is customary to choose a time step Δt five times smaller than the stability limit. $\Delta t < \hbar/5E_{\text{max}}$. The resulting error for N steps becomes: $\text{error} \approx N/375$ which allows a few hundred propagation steps before error in interference terms become important. For calculations pertaining to a thermal surface, phase coherence is important only for relatively short periods of time. Therefore the SOD scheme is a good choice for these problems. One should notice that by shifting the energy and by adding a constant to the Hamiltonian one can predetermine the region in energy with minimum error.

Although there are other existing explicit and implicit propagation schemes based on a Taylor expansion of the evolution operator $\hat{U}$ such as the Crank–Nicholson method [31] or an implicit split method [32], none have been used for surface calculations.

The split time propagation scheme

Feit and Fleck [41] have introduced a split time propagation scheme in which the kinetic operator and potential operator are used to propagate the wavefunction separately:

$$e^{-i\hat{H}\Delta t/\hbar} \approx e^{-i(\hat{p}^2/2m)(\Delta t/2\hbar)} e^{-i\hat{V}\Delta t/2\hbar} e^{-i\hat{V}\Delta t/2\hbar} e^{-i(\hat{p}^2/2m)(\Delta t/2\hbar)}. \quad (2.28)$$

Each of these propagations is done in a local representation: First, the wave is transformed to k

space by an FFT procedure; then multiplied at each grid point by $\exp[-i(\mathbf{p}^2/2m)(\Delta t/2\hbar)]$; and then the wavefunction is transformed back to coordinate space by an inverse FFT procedure. Afterwards the wavefunction is multiplied by $\exp(-i\hat{\mathbf{V}} \Delta t/2\hbar)$, and one time step of propagation is complete. The next propagation step is done in reverse order the potential energy propagation before the kinetic energy propagation.

Error analysis

Norm is strictly conserved by the split time scheme, because each split time step is unitary. Error is due to the non-commutability of the kinetic and potential operators. Because of the alternating propagation scheme. The first term in the expansion $\Delta t^2[\mathbf{p}^2, \hat{\mathbf{V}}]/(8m\hbar^2)$ cancel. Therefore errors are of $\mathcal{O}(\Delta t^3)$.

$$\text{error} \approx \max\left(-i \frac{\Delta t^3}{16m} [\hat{\mathbf{V}}, [\hat{\mathbf{V}}, \mathbf{p}^2]], -i \frac{\Delta t^3}{32m^2} [\mathbf{p}^2, [\mathbf{p}^2, \hat{\mathbf{V}}]]\right)/\hbar^3 \quad (2.29)$$

This error accumulates in the phase and energy of the wavefunction.

The Chebychev time propagation method

For time-independent Hamiltonians, a propagation scheme exists which can eliminate the error in propagation almost completely [42]. The strategy chosen for the propagation scheme is to expand the evolution operator $\hat{\mathbf{U}} = \exp(-i\hat{\mathbf{H}} dt/\hbar)$ in a polynomial series in the operator: $-i\hat{\mathbf{H}} dt/\hbar$. The problem then becomes a choice of the best polynomial approximation for this series. It has been shown [20] that this problem reduces to approximating the scalar function e^z by a polynomial expansion where z belongs to the domain which includes all the eigenvalues of the operator $-i\hat{\mathbf{H}} dt/\hbar$. It is known [43] that the best approximation is achieved by an expansion based on the complex Chebychev polynomials ϕ_k . (The reason is the uniform character of the complex Chebychev polynomials in distributing the errors in the interval $[-i, i]$.) These polynomials are a complex version of the Chebychev polynomials and they are defined as:

$$\phi_k(\omega) = i^k T_k(-i\omega), \quad \omega \in [-i, i] \quad (2.30)$$

and the T_k are the Chebychev polynomials of the first kind. The ϕ_k are orthogonal on the imaginary interval $[-i, i]$ with respect to the following inner product.

$$\langle f, g \rangle = -i \int_{-i}^i \frac{f(\omega) g^*(\omega)}{\sqrt{(1 - |\omega|^2)}} d\omega. \quad (2.31)$$

The domain of the eigenvalues of the Hamiltonian $\hat{\mathbf{H}} = \mathbf{p}^2/2m + \hat{\mathbf{V}}$ depends on the discretization scheme. In the Fourier method the eigenvalues are real because the Hamiltonian is Hermitian [28]. (This is also true for the FD method.) The domain of the eigenvalues can be estimated as follows. The maximum kinetic energy is $P_{\max}^2/2m$. If the minimum of the potential (represented on the grid) is $V_{\min}$ and its maximum $V_{\max}$, the range of the eigenvalues of $\hat{\mathbf{H}}$ is

$$\lambda \in \left[V_{\min}, V_{\max} + \frac{\hbar^2 \pi^2}{2m(\Delta x)^2} \right]. \quad (2.32)$$

Where Δx is the spatial grid interval in one dimension, and the Fourier method is assumed. The scalar function z is choen to be in the range of $i\lambda \, dt$. Defining

$$R = dt \left(\frac{\hbar^2 \pi^2}{2m \Delta x^2} + V_{\max} - V_{\min} \right) / 2\hbar, \quad G = V_{\min} dt / \hbar$$

and

$$\omega = (z - iR - iG)/R$$

one obtains:

$$e^z = e^{i(R+G)} e^{R\omega}, \quad \omega \in [-i, i]. \quad (2.33)$$

At this step e^z is expanded in the Chebychev series:

$$e^z \approx \sum_{k=0}^N a_k \phi_k(\omega), \quad (2.34)$$

where:

$$a_k = -i e^{i(R+G)} \int_{-i}^i \frac{e^{R\omega} \phi_k(\omega)}{\sqrt{(1-|\omega|^2)}} d\omega = e^{i(R+G)} C_k J_k(R) \quad (2.35)$$

and $C_k = 1$ for $k = 1$ and $C_k = 2$ for $k > 1$. J_k are Bessel functions of the first kind of order k . The high accuracy of this expansion can be traced to the fact that when k is greater than R , $J_k(R)$ goes to zero exponentially fast. Thus the degree N of the expansion has to be at least R . In this work N was chosen to be αR where $\alpha > 1$. The value of α depends on the degree of accuracy needed and can be chosen to bring errors below the accuracy of the computer. The propagation scheme is obtained by substituting $-i\hat{H} \, dt/\hbar$ for z in (2.34) and using (2.35)

$$\hat{U}(dt) \approx \sum_{k=0}^N a_k \phi_k \left(\frac{-i\hat{H} \, dt}{\hbar R} \right), \quad (2.36)$$

where the Chebychev polynomials in the operator $i\hat{H} \, dt/\hbar R$ are computed by the recurrence relation satisfied by the polynomials $\phi_k(\hat{\mathbf{X}})$

$$\phi_k(\hat{\mathbf{X}}) = 2\hat{\mathbf{X}}\phi_{k-1}(\hat{\mathbf{X}}) + \phi_{k-2}(\hat{\mathbf{X}}) \quad (2.37)$$

and

$$\phi_0(\hat{\mathbf{X}}) = \hat{\mathbf{I}}, \quad \phi_1(\hat{\mathbf{X}}) = \hat{\mathbf{X}},$$

where $\hat{\mathbf{X}}$ is the operator $-i\hat{H} \, dt/\hbar R$ and where $\hat{H}$ is shifted by $-\hbar R/(2dt) + V_{\min}$, in order to distribute the eigenvalues evenly in the interval $[-i, i]$. As a result $R + G = 0$ in eqs. (2.34)–(2.36).

The basic algorithm is then used as a one step propagator obtaining the solution at the final time $t + dt$ directly from the initial data, or as a marching scheme if one is interested in intermediate results. The size of the time step dt depends only on the information one wants to get out of the numerical procedure. R and the order N are determined accordingly. The refinement of the scheme is then based on increasing the order of the expansion and not by decreasing the time step.

A modification of the Chebychev method enables to obtain bound states on the grid. This is done by propagating an initial wavefunction in negative imaginary time. This wavefunction relaxes to the ground state. Excited states are obtained by projecting out the lower states from the Hamiltonian operation and repeating the propagation [44].

Error Analysis

In the above Chebychev propagation scheme errors are both in phase and in energy. The errors are distributed uniformly in the domain of the eigenvalues. Because of the exponential decay of the Bessel expansion coefficients this error can be chosen to be lower than the numerical precision of the computer by using enough expansion coefficients.

2.5. Examples using the FD method: 2-D scattering from a dynamical surface

Agrawal and Raff [29] and Smith, Agrawal and Raff [30] introduced the FD method to surface scattering. The system that was investigated is a model for the scattering of a beam of hydrogen atoms by a dynamical tungsten surface.

Formulation

The initial wavefunction was chosen to have a uniform momentum distribution in the direction of the beam and a flat distribution in coordinate space perpendicular to the motion. If the incident angle is θ_i , then

$$\psi(x, y, 0) = G(q_1)F(q_2), \quad (2.38)$$

where

$$q_1 = x \cos \theta_i + y \sin \theta_i$$

and

$$q_2 = y \cos \theta_i - x \sin \theta_i,$$

x is the direction parallel to the surface, and y perpendicular to it. The following functions were chosen for G and F :

$$G(q_1) = \frac{e^{-ik_0 q_1} \sin(\Delta k(q_1 - q_1^0))}{(q_1 - q_1^0)(\pi(\Delta k))^{1/2}} \quad (2.39)$$

and

$$F(q_2) = \begin{cases} (2a)^{-1/2} & \text{for } -a \leq q_2 \leq a, \\ 0 & \text{for } q_2 < -a \text{ or } q_2 > a, \end{cases}$$

where

$$a = (R_e/2 + \Delta y) \cos \theta_i$$

and R_e is the equilibrium lattice spacing. A grid of 240×520 was used with $\Delta x = \Delta y = 0.2 \text{ \AA}$ covering an area of $12 \times 26 \text{ \AA}^2$. Fixed boundary conditions were used, which is the reason for the large grid to ensure that the wavefunction did not reach the boundary during the propagation. The initial average energy was $\langle E_i \rangle = 0.089 \text{ eV}$. The average momentum associated with this energy required a grid with $0.165 \text{ \AA}$ spacing compared to the used grid of $0.2 \text{ \AA}$. This meant that the calculation included much numerical dispersion. The choice of the initial wave function was not optimal. A uniform distribution in momentum space in the q_1 direction meant that the wings of the distribution in coordinate space decay only as $1/q_1$. This meant that a significant portion of the wave is on the surface before the beginning of the collision. Also the rectangular distribution in coordinate space in the q_2 coordinate meant a momentum distribution of the shape

$$\sin(ak_2)/k_2(\pi a)^{1/2} \quad (2.40)$$

having significant contributions from high momentum states for which numerical dispersion is high.

The potential used in the calculation was a time dependent potential describing the thermal motion of the solid. The surface atoms were assumed to move according to a harmonic force field (see section 4). Only a set of primary atoms were moved, three in the case of the two dimensional surface calculation [29], and nine in the case of the 3-D surface calculation [30]. A Runge-Kutta propagator was used to propagate the classical motion describing the motion of the solid atoms. The lattice motion was assumed to be classical and unperturbed by the incident atomic beam. Such a treatment does not conserve energy for the total system. The atom surface potential was chosen as the sum of pairwise $LJ(12, 6)$ potentials with minimum position $\sigma = 2.74 \text{ \AA}$ and well depth $\epsilon/k_B = 38.5 \text{ K}$. The initial surface state was taken to be the symmetric set of outer classical turning points with initial surface energy equipartitioned into all pairwise bonds. Phase averaging over initial surface states has been omitted.

The propagation of the initial wavefunction was carried out by the FD method of Askar and Cakmak [33] with a time step of $d\tau = 4 \times 10^{-16} \text{ s}$. Upon the completion of the collision the wave function was analysed by calculating the average final kinetic energy, the probability density and the probability current density. Also a Fourier transform to momentum space was carried out to examine the momentum distribution.

Results

A linear relation between the final kinetic energy, and the surface temperature and initial kinetic energy was found for both 2-D and 3-D surface calculations. (The wavefunction in both

cases was 2-D.) This is in qualitative agreement with the experimental result of Janda et al. [45] for Ar scattering from a tungsten surface. In the momentum distribution inelastic peaks from multiphonon processes could be identified resembling the power spectra of the solid. Debye–Waller factors were extracted by calculating the average momentum transfer in the z direction.

To summarize: this work is significant in the sense that it demonstrates the possibility of using grid methods to obtain physically relevant information corresponding to scattering from thermal surfaces. The actual numerical results have only semiquantitative value because of the large numerical dispersion and undersampling.

2.6. Examples using the Fourier method in surface scattering

The Fourier method has been applied to scattering both from static as well as from dynamical surfaces.

Scattering from static surfaces

2-D calculations using the Fourier method have been applied to scattering from stepped surfaces [40], disordered surfaces [46,47] and surfaces with impurities [48]. Also surface calculations using the Chebychev method were reported [42,50]. In all cases the initial wavefunction was constructed by a Gaussian in the z direction and a plane wave in the x direction (and y direction for 3-D calculations), utilizing the periodic boundary conditions of the grid. First, a comparison was done with established coupled channel calculations (CC) [51]. A two-dimensional repulsive Lennard-Jones–Devonshire potential was employed [40] with parameters of the He–W system. A small grid of 32×32 with $\Delta x = 0.97125$ a.u. and $\Delta z = 0.6$ a.u. was used. In order to compare to fixed energy CC calculations a wide Gaussian in the z direction was used. The Gaussian width was 7 a.u. and the mean momentum was 3.43 a.u. This means a relative spread in energy of 0.17%. The propagation was done by the SOD scheme was $\Delta t = 50.0$ a.u. Diffraction peak intensities were within 0.4% of the CC calculation. Even more accurate result were obtained by using the Chebychev propagation method [42]. A grid of 64×64 was used, with $\Delta x = \Delta z = 0.6475$ a.u. The propagation was carried out for 80 000 atomic time units which means a Chebychev expansion of order 580. The third diffraction peak could be resolved although it is by six orders of magnitude less than the specular peak. Also the results compared very well with the CC calculations. In these calculations one should notice that the mean momentum was 70% of the maximum, with a spread of 4%. This means that the error due to the finite momentum representation is minimal.

The same method was then used to study surface scattering from very rough surfaces. The system He–Cu(1, 1, 7) was studied, where the unit cell is large due to the stepped structure. Both for high and low energies multiple rainbows could be distinguished. For low energy selective adsorption occurred. By employing absorbing boundary conditions the rate of adsorption was calculated. The fraction adsorbed (13.7%) was found to be larger than for classical trajectory studies (8.4%) at the same energy.

The effect of an isolated impurity on the diffraction pattern was also studied by the same method [46,47]. The system studied was the He–Cu system with an Ar impurity. A Lennard-Jones–Devonshire potential was used with a pair potential between the Ar and the He atoms.

The main results are: The diffraction peaks of the pure He–Cu system prevail but a broad shallow background peak is superimposed on each diffraction line. Diffraction peaks due to the impurity could be resolved. These peaks correspond to classical rainbows. Scattering intensities thus contain useful detailed information on impurity location.

A study of He scattering from a mixed disordered surface overlayer consisting of two species was carried out [48]. This is a first example of an exact scattering calculation from a disordered surface. The surface was modeled by 18 Xe or Ar atoms chosen randomly from a distribution of different average compositions. The results were averaged for the different possible atom distributions. The potential was a sum of atom–atom gas phase pair potentials. The main results are: Peaks at the Bragg position of the pure Xe layer persist even for the 50% Xe : 50% Ar. On the other hand, the peaks at the pure Ar positions disappear already for the 80% Ar : 20 Xe ratio. For 70% Ar : 30 Xe all diffraction features have collapsed by the intensity has some structure of weak oscillations due to scattering from structure of the type Xe–Ar–Ar–Xe.

These studies showed the ability of the Fourier method to calculate diffraction patterns from very large finite surfaces clusters. Due to the continuum of the momentum states this calculation would be prohibitively expensive in a CC method.

The 3-D parallelogram

In 3-D calculations the unit cell may have a skewed shape. It is desirable to match the grid to the unit cell using periodic boundary conditions to represent an extended perfect surface. This unit cell forces a non-Cartesian set of coordinates in x and y . The Fourier method is able to cope with this situation [27,49]. The kinetic energy operator is still diagonal in momentum space but includes mixed derivatives in x and y which are calculated by multiplying the transformed wavefunction by $ik_x ik_y$. The Laplacian in these coordinates has the form

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} - 2 \cos \beta \frac{\partial}{\partial x} \frac{\partial}{\partial y} \right) \frac{1}{\sin^2 \beta} + \frac{\partial^2}{\partial z^2}, \quad (2.41)$$

where β is the skewing angle of the unit cell. 3-D calculations of He scattering from metal and rare gas surfaces are in progress. Also bound states of He on a Pt(111) surface were calculated using the Chebychev bound state method [44].

3-D Rotationally inelastic molecular surface scattering

3-D H_2 surface scattering is a major computational problem. There are six degrees of freedom which have to be treated simultaneously. On the other hand good experimental data exist which makes it worthwhile to overcome the computational challenge. The Fourier method has been applied to the problem [49,50] as well as CC [52] and semiclassical methods [53]. A straight forward approach would put a grid on r , θ and ϕ . But for low energy collisions it was found that a hybrid method which uses the Fourier method for the translational degrees of freedom and an expansion in $Y_{lm}(\theta, \phi)$ for the rotation is more economical. The wavefunction has the form:

$$\psi(x, y, z, \theta, \phi) = \sum_{jm} Y_{jm}(\theta, \phi) \chi_{jm}(x, y, z, t) \quad (2.42)$$

A set of time dependent coupled equations is obtained by substituting eq. (2.42) in eq. (4.1) and then multiplying by $Y_{j'm'}^*$ and integrating over θ and ϕ . In matrix form the equation become:

$$i \frac{\partial \tilde{\chi}(\mathbf{R}, t)}{\partial t} = \left[\tilde{\mathbf{I}} \left(-\frac{\hbar^2}{2m} \nabla_{\mathbf{R}}^2 \right) + \tilde{\epsilon} + \tilde{\mathbf{U}}(\mathbf{R}) \right] \tilde{\chi}(\mathbf{R}, t), \quad (2.43)$$

where $\mathbf{R}$ is the vector x, y, z , $\tilde{\mathbf{I}}$ is the identity matrix, $\tilde{\chi}$ is a column vector, $\tilde{\epsilon}$ is a diagonal matrix with the elements $\epsilon_j = j(j+1)/2\mu r^2$, and $\tilde{\mathbf{U}}(\mathbf{R})$ is the potential energy matrix:

$$\tilde{\mathbf{U}}_{j'm',jm}(\mathbf{R}) = \int_0^{2\pi} \int_0^\pi Y_{j'm'}^*(\theta, \phi) V(\mathbf{R}, \theta, \phi) Y_{jm}(\theta, \phi) \sin \theta d\theta d\phi. \quad (2.44)$$

The time propagation has been done by the Chebychev scheme equation (2.36) which has been adopted to integrate coupled equations. This technique has been termed by Mowrey and Kouri as the close coupling wavepacket approach (CCWP).

An important observation of Mowrey and Kouri is that from one time dependent calculation scattering amplitudes can be obtained for a range of energy values. In the asymptotic region far from the potential energy can be determined by the momentum alone. The transition probabilities are obtained by calculating the moments of the final wavefunction with the asymptotic eigenfunctions of the Hamiltonian. The asymptotic wavefunction which describes a molecule in the rotational state $j'm'$ and diffractive state l' and n' with total energy E is:

$$\phi_{j'm'}^{ln}(\mathbf{R}, \theta, \phi) = \left(k_{z,j'}^{l'n'} \right)^{-1/2} e^{i(k_{z,j'}^{l'n'} z + (\mathbf{K} + \mathbf{G}_{ln})\mathbf{R} - Et/\hbar)} Y_{j'm'}(\theta, \phi), \quad (2.45)$$

where: $\mathbf{G}_{ln} = (2\pi l/a, 2\pi n/b)$ is the reciprocal lattice vector and

$$\hbar k_{z,j'}^{l'n'} = \left[2m(E - \epsilon_j) - (\mathbf{K} + \mathbf{G}_{ln})^2 \right]^{1/2}.$$

Multiplication of eq. (2.42) by the complex conjugate of (2.45) and integrating over spatial coordinates gives the amplitude for the transition as:

$$a_{j'm'l'n',jmln}(E) = \left(k_{z,j'}^{n'l'} \right)^{-1/2} \int e^{-i(k_{z,j'}^{l'n'} z + (\mathbf{K} + \mathbf{G}_{ln})\mathbf{R} - Et/\hbar)} \chi_{jmln}(\mathbf{R}, t) d\mathbf{R}, \quad (2.46)$$

χ carried the index of its initial state. The $\mathbf{S}$ matrix element for the transition from state $j, m, 0$, 0 to $j'm', l, n$ becomes:

$$S_{j,m,0,0 \rightarrow j',m',l,n}(E) = \frac{a_{j'm'l'n',jmln}(E)}{\left[\sum_{jmik} |a_{j'm'i'k',jmnl}(E)|^2 \right]^{1/2}}. \quad (2.47)$$

Results

The method was applied to scattering of H_2 from a flat and corrugated surface. The potential

used was the surface-dumbbell model:

$$\begin{aligned}
 V(\mathbf{R}, \theta, \phi) = 2A e^{-\alpha z} [& \cosh(\alpha r \cos \theta/2) \\
 & + \beta (\cosh(\alpha r \cos \theta/2) (\cos(2\pi x/a) \cos(\pi r \sin \theta \sin \phi/a) \\
 & + \cos(2\pi y/b) \cos(\pi r \sin \theta \sin \phi)) \\
 & + \sinh(\alpha r \cos \theta/2) (\sin(2\pi x/a) \sin(\pi r \sin \theta \cos \phi/a) \\
 & + \sin(2\pi y/b) \sin(\pi r \sin \theta \sin \phi/b))] , \tag{2.48}
 \end{aligned}$$

where $\alpha = 1.94012 a_0^{-1}$, $r = 1.4011 a_0$, $a = 4A \text{ \AA}$, $b = 2A \text{ \AA}$ and $A = 1.5 \text{ eV}$. For the flat surface calculation $\beta = 0$. The initial wavefunction was a Gaussian in z in the $j=0$ $m=0$ state. The grid was of 128 points with an interval $\Delta z = 0.25 \text{ a.u.}$. The initial position was 8.0 a.u. with a width of 1.118 a.u. The average energy was of 0.1 eV which corresponds to an initial momentum of -5.195 a.u. Considering the grid interval of $\Delta z = 0.25 \text{ a.u.}$, the maximal momentum which could be represented on the grid is 4π . Considering the mean energy of the calculation the results of the computation are converged. The results were compared to CC calculations with an exeelent agreement. One run was sufficient to obtain results in a wide range of energy.

Basically the same method was applied to a corrugated surface with $\beta = 0.1$. The other potential parameters as in the flat surface calculation. The grid parameters were: A grid of $8 \times 8 \times 64$ with 7 rotational channels, $\Delta x = 0.944804 \text{ a.u.}$, $\Delta y = 0.472433 \text{ m a.u.}$, $\Delta z = 0.25 \text{ a.u.}$. The same initial wavefunction was used. A comparison was made with CC and semiclassical calculations and the CCWP method was the most exact differing only a few tenth of a percent from the CC calculation and 29% from the semiclassical calculation.

Comparing the amount of computer time needed to carry out the calculation the CC calculation took approximately 12 times longer. Increasing the number of rotational channels to $j = 4$ (15 channels) the calculation was feasible for the WPCC method (50.4 minutes of CPU of FPS-164) but prohibitively expensive for the CC method which scales as the number of channels cubed (approximately 40 hrs). As a conclusion it seems that the CCWP is as accurate as the CC method and much more efficient especially when a large number of scattering states are participating.

3-D Scattering from dynamical surfaces

This type of calculation is quite close to a true simulation of an inelastic atom-surface scattering. This means that the surface phonons are included in the calculation. The system chosen [54] was He on Pt(100). The initial wavefunction was chosen to be a Gaussian in z and a plane wave in x and y . For scattering calculations the wavefunction was positioned out of the reach of the surface potential $z_0 = 16.5 \text{ a.u.}$ For desorption calculations, the wavefunction was put in the potential well. A grid of $64 \times 16 \times 16$ was used with: $\Delta x = 0.45 \text{ a.u.}$, $\Delta y = 0.45 \text{ a.u.}$ and $\Delta z = 0.4 \text{ a.u.}$ Absorbing boundaries were used at the far end of the grid. The potential was a sum of pair potentials between the he and the first layer of Pt atoms plus a background contribution of a (3, 9) potential in the z direction. The calculation was carried out using a mixed

quantum-classical method where for the He coordinates a wave packet representation was used and for the heavy Pt atoms classical mechanics were used. Such mixed classical-quantum calculations are discussed in section 4 of the review.

To take into consideration thermal motion of the surface, a generalized Langevin approach was adopted. The equation of motion of the surface motion were the same as in the work of Grimmerman, Tully and Helfand [55]. The propagation method was SOD combined with a fourth-order Runge–Kutta propagator for the classical Langevin motion of the surface atoms. A time step of 5 a.u. was used which was determined empirically as 1/5 of the stability limit.

Results

Diffraction peaks for two temperatures were calculated. The effect of the temperature was to broaden the peaks due to inelastic processes. Strong out-of-plane scattering was observed indicating the importance of full 3-D calculations.

Desorption calculations were performed and compared to 1-D classical and quantum calculations. Absorbing boundary conditions were used and the desorption rate was calculated by the loss of amplitude as a function of time. Two mechanisms for desorption were identified: A low temperature ladder mechanism, and a high temperature direct mechanism. The 3-D rate of desorption was found to be 10 times slower than the 1-D rate pointing to the dominant role the out-of-plane modes contribute to desorption. It is important to emphasize the ability of a quantum mechanical calculation to describe the rare event of desorption naturally.

For lower temperatures a quantum mechanical treatment of the phonons must be carried out. A 1-D model calculation of energy accommodation for low temperatures can be found in ref. [46]. This calculation shows the importance of sticking to the correct calculation of energy accommodation in low temperatures.

In this work the possibility of a 3-D simulation of scattering from a thermal surface was demonstrated. A moderate grid of $16 \times 16 \times 64$ was adequate to describe an experimentally realistic energy (the initial momentum was a third of the maximum allowed by the grid spacing). The classical description of the motion of the surface atoms is realistic for high temperatures but would need modification for describing scattering experiments done on cold surfaces because of the zero point motion of the surface atoms.

2.7. Comprehensive assessment of grid methods

Considering the vast amount of experimental and theoretical effort devoted to surface scattering and the ability of experiments to resolve high order diffraction peaks, grid methods are only at the first stage of their development. A critical evaluation of grid methods is due, considering the following aspects: 1) Adaptability to realistic experimental surface scattering problems. 2) Relative comparison of different grid methods. 3) Comparison of grid methods to alternative schemes such as CC on the one hand and Semiclassical and Sudden approximation on the other.

Experimental problems for which one would expect grid methods to be advantageous are limited to low and moderate momentum. This means either a low mass of the colliding particle like He or H₂ or very low energy, measured from the minimum of the potential well. Systems of this type are He and H₂ scattering from ordered and disordered surfaces. This experimental situation will be used for comparison between different grid methods.

The grid

The grid size is a critical parameter in determining the feasibility of a calculation. This size is determined by the surface to be covered and by the maximum momentum of the incoming particle acquired in the potential well. The surface grid size varies from one unit cell to an area consisting of 20–30 atoms in a moderate disordered surface calculation. The momentum is determined by the mass and energy of the incoming particle. This limits most calculations to H, He or H₂ scattering. Energy, typically 0.1 eV, is mostly determined by experimental considerations. This means for He a momentum of ≈ 7 a.u. For an FD calculation needing 10 grid points per wave length the grid displacement would become $\Delta x = 0.04$ a.u., while for the Fourier method a displacement of $\Delta x = 0.2$ a.u. would be adequate. To cover a unit cell of 4×4 a.u. and a distance of 16 a.u. in the z direction would require a grid of $100 \times 100 \times 400 = 4\,000\,000$ points for a finite difference calculation and a grid of $16 \times 16 \times 64 = 16\,384$ for the Fourier method. In both methods the storage requirements are at least four times this number. Moreover, because the wavefunction is complex the storage requirements are doubled. On existing computers this fact prohibits the use of FD methods for 3-D calculations because of limitations on storage. Considering scattering from disordered surfaces which is currently being studied a grid of $64 \times 64 \times 64$ is being used. This means that only the Fourier method is feasible.

Hamiltonian operation

Two issues should be considered; accuracy and efficiency. For very accurate calculations the Fourier method has no alternative. The convergence of the Fourier method upon increasing the grid is exponential [37] while the convergence of the FD method is only cubic.

Efficiency depends on the number of operations. In the FD method two multiplications and two additions per grid point complete the operation. In the Fourier method $2 \log_2 N$ operations are needed [35], which is significantly more operations. But considering that the FD method requires 5 times more grid points per spatial dimension the number of operations becomes equal for 2-D calculations. For 1-D calculations the Fourier method is inferior and for 3-D calculations the Fourier method is superior from the point of view of numerical efficiency. These considerations are altered by the existence of very fast machine dependent FFT routines, as on the Cray, CDC 205 or the FPS-164. These routines are up to 10 times faster than equivalent Fortran routines. Moreover the introduction of new parallel computers such as the hyper cube architecture, optimizes the data flow in the FFT routine. This fact can reduce the numerical effort from $N \log N$ to $\log N$ with N parallel processors. This availability of optimized FFT routines shortens the period a code can be optimized on a new architecture, and eliminates expensive assembly coding.

Time propagation

For time-dependent problems the Chebychev propagation scheme is the choice scheme because it is more efficient and more accurate than other methods. This method is also adaptable to the FD scheme. Together with the Fourier scheme for calculating the Hamiltonian operation, an accurate and highly efficient general method thus exists for solving the time-dependent Schrödinger equation. One of the main advantages of this combined method is the slow increase in numerical effort with the increase in the size of the problem. As a function of M (the total number of grid points) numerical effort grows as $\mathcal{O}(M \log M)$. As a function of the energy,

numerical effort grows as $\mathcal{O}(E^{3/2})$. This is a slow rate compared to other methods.

For scattering from time-dependent potentials, the SOD scheme has to be used with the drawback of reduced accuracy and speed.

The basic features which make these methods adaptable to surface scattering is the flexibility of these methods to describe the single collision event in which an initial state evolves to a multitude of final states. This description is equivalent to one column of the $\hat{\mathbf{S}}$ matrix. Moreover scattering matrix elements for a whole range of energies can be obtained from one time dependent calculation.

3. Semiclassical wavepacket computations

3.1. Physical considerations

Classical dynamics is often an adequate tool for treating various types of molecule surface collision processes. Basically, typical conditions realized in molecular beam scattering experiments (e.g., the energies used) imply that the classical limit is approximately attained, at least in the sense that the de Broglie wavelength is small on the scale of the potential range. However, it is essential in several respects to be able to provide a treatment at the quantum mechanical level: (1) There are quantum effects such as tunneling, interference etc. that may play a role. It should be noted that interference, for instance, can be pertinent also to cases where the incident momentum is high (short de Broglie wavelength). (2) Even when interference, tunneling etc. are absent, a quantal treatment may be required. Such cases typically occur when the experiments at hand focus on individual quantum states e.g. the diffractions measured and resolved in light atom scattered off periodic surfaces. A quantum mechanical approach is also necessary in the study of specific rotational states measured in molecule-surface scattering. These examples emphasize that it is imperative in studies of surface scattering to have a method at hand that may handle both classical and quantal effects. Semiclassical methods fulfill this goal by providing an elegant and efficient route for treating this combination of classical and quantal motion.

Two alternative avenues of approaching the semiclassical limit of quantum mechanics to surface scattering have emerged. The first involves time independent scattering theory. Expansion in powers of $\hbar$ [57,58] leads to a WKB type of approximation. A more general treatment has used the correspondence between the stationary phase approximation applied to the quantum mechanical propagators and classical paths [59–61]. The classical $\mathbf{S}$ -matrix approach has been applied to the surface scattering problem by Doll [62,63] and by Masel et al. [64,65]. The second trend involves the idea of a time dependent wavepacket picture. The wavepacket approach to semiclassical scattering has been introduced to molecular dynamics by Heller and his coworkers [66–81] and into surface scattering by Drolshagen and Heller [82–85] and used by Drolshagen and Vollmer [87]. A similar approach has been suggested by Weissman and Jortner [86]. This pioneering work utilizes the localized nature of classical motion. Semiclassical wavepackets are thus governed at each instant by a small portion of the potential only.

The purpose of a semiclassical wavepacket theory is to solve the Schrödinger equation by representing the wavefunction in terms of approximate wavepackets having an apriori chosen form. These approximate wavepackets (e.g. Gaussians) depend on several time dependent

parameters. The “time evolution” of these parameters often resembles classical equations of motion, but this alone does not mean that the physical classical limit has been reached. Rather, important quantum mechanical effects may still be present, e.g. interference. What is gained is some intuitive physical insight as well as computational efficiency usually present in classical mechanics. This point has been emphasized by Metiu and his co-workers [88–92] when applying the wavepacket methods to surface scattering.

The semiclassical limit is properly reached only under more restrictive conditions. As asserted by Heller [66], the correspondence between classical dynamics and quantum mechanics is obtained for localized wavepackets on smooth potentials. This correspondence has led Heller to use locally harmonic potentials with narrow wavepackets. Gaussian wavepackets prove to be a natural form to chose in this case, as for harmonic potentials an initial Gaussian wavepacket remains Gaussian.

Consider the collision of a structureless particle (atom) with a rigid nonvibrating surface, which for simplicity is taken to have a square lattice structure. To treat such processes, the initial states are represented by a superposition of wavepackets. The wavepackets are propagated and after the collision they are projected onto the final asymptotic states, the center of the individual packets following classical trajectories. The initial positions of these centers are chosen to form a grid that covers the surface area of one unit cell. The initial finite superposition of Gaussian wavepackets $G(\mathbf{r}, \mathbf{k}, t)$ takes the form [82,83]

$$\Psi_{\text{in}}(\mathbf{r}, \mathbf{k}_0, t_0) = \frac{1}{\sqrt{k_{z,0}}} \exp[i\mathbf{k}_0 \cdot \mathbf{r}] = c \sum_{p=1}^N G_p(\mathbf{r}, \mathbf{r}_0^p, \mathbf{k}_0^p, t_0), \quad (3.1)$$

with $\mathbf{k}_0^p$ being the initial momentum of an individual Gaussian wavepacket chosen to be identical for all p 's i.e. $\mathbf{k}_0^p = \mathbf{k}_0$ in (3.1). In addition, the parameters $\mathbf{r}_0^p = (x_0^p, y_0^p, z_0^p)$ are chosen such that $z_0^p = z_0$ and $-a/2 \leq x_0^p \leq a/2$; $-a/2 \leq y_0^p \leq a/2$; a being the lattice constant i.e. x_0^p, y_0^p cover the surface area of the unit cell, and z_0 is the distance from the surface and has to be taken sufficiently large i.e. far from the surface to be outside the range of the potential. After the collision has been completed at time t , Ψ_{in} evolves into Ψ_{out} which is assumed also to be expressible as a superposition of propagated Gaussian packets:

$$\Psi_{\text{out}}(\mathbf{r}, \mathbf{k}, t) = c \sum_p G_p(\mathbf{r}, \mathbf{r}_t^p, \mathbf{k}_t^p, t). \quad (3.2)$$

The equations of motion for the parameters describing the Gaussian G_p are presented in subsections (3.2) and (3.3). It will be seen that the equation for the parameter $\mathbf{r}_t$ is closely related to classical dynamics.

The semiclassical **S**-matrix can be obtained by projecting Ψ_{out} onto Ψ_{in} in the usual way in scattering theory:

$$\mathbf{S} = \langle \Psi_{\text{out}} | \Psi_{\text{in}} \rangle \quad (3.3)$$

Defining **S** in terms of individual diffraction states such that

$$\Psi_{\text{out}}(\mathbf{r}) = \sum_{mn} S_{mn} \frac{1}{\sqrt{k_z^{mn}}} \exp[i(k_z^{mn} z + (\mathbf{K} + \mathbf{G}_{mn}) \cdot \mathbf{R})], \quad (3.4)$$

where $\mathbf{K} = (k_x, k_y)$, $\mathbf{R} = (x, y)$ and the reciprocal lattice vector $\mathbf{G}$ is given by:

$$\mathbf{G}_{mn} = (\Delta k_x, \Delta k_y) = \left(m \frac{2\pi}{a}, n \frac{2\pi}{a} \right) \quad (3.5)$$

and k_z^{mn} is given by

$$|k_z^{mn}|^2 = k^2 - (\mathbf{K} + \mathbf{G}_{mn})^2, \quad (3.6)$$

S_{mn} is the scattering matrix element and $|S_{mn}|^2$ is the probability for scattering into the final diffraction states (m, n) .

The scattering matrix elements S_{mn} may be obtained by matching the propagated superposition of Gaussian wavepackets eq. (3.2) with the known asymptotic form eq. (3.4) to give:

$$S_{mn} = c' \int \frac{1}{\sqrt{k_z^{mn}}} \exp(-i \mathbf{k}^{mn} \cdot \mathbf{r}) \Psi_{\text{out}}(\mathbf{r}) d\mathbf{r}, \quad (3.7)$$

where $\mathbf{k}^{mn} = (k_x^0 + m2\pi/a, k_y^0 + n2\pi/a, k_z^{mn})$. The integration in eq. (3.7) may be performed in closed form for Ψ_{out} of eq. (3.2) as it amounts to Fourier transforming the Gaussian functions G_p in (3.2). c in (3.2) and c' in (3.7) are constants containing the normalization factors as well as some parts of the phase, and therefore do not affect the scattering intensities.

The ensuing section is organized as follows. In subsection 3.2 we review the usage of locally quadratic potentials as introduced by E.J. Heller. Subsection 3.3 discusses the Minimum Error Method (MEM) introduced by Metiu and his co-workers to extend the original pioneering work of Heller, (3.2) and (3.3) are meant to provide the working equations of the methods. In (3.4) we include a discussion of the approximations involved in the semiclassical wavepacket methods and examine their reliability and applicability. Subsection (3.5) describes the numerical implementation of the semiclassical methods. In (3.6) we present applications to stepped crystalline surfaces, scattering from imperfect and disordered surfaces and collisions with a linear vibrating chain.

3.2. Locally quadratic potentials and the equations of motion for systems of several variables

Following Heller [66–85] let us assume that the scattering of an atom from a static surface may be described by an effective Hamiltonian

$$H^{\text{eff}}(t) = \frac{1}{2} \mathbf{P} \mathbf{m}^{-1} \mathbf{P} + V_t^{\text{eff}}(\mathbf{q}), \quad (3.8)$$

where $V_t^{\text{eff}}(\mathbf{q})$ replaces the exact potential $V(\mathbf{q})$. $V_t^{\text{eff}}(\mathbf{q})$ is a time-dependent harmonic potential obtained by a Taylor expansion of $V(\mathbf{q})$ about the point $\mathbf{q}_t$ at time t .

$$V_t^{\text{eff}}(\mathbf{q}) = V(\mathbf{q}_t) + V'(\mathbf{q}_t)(\mathbf{q} - \mathbf{q}_t) + \frac{1}{2}(\mathbf{q} - \mathbf{q}_t)V''(\mathbf{q}_t)(\mathbf{q} - \mathbf{q}_t). \quad (3.9)$$

It will be seen later than $\mathbf{q}_t$ has the significance of a classical trajectory describing motion of the wavepacket center.

It is well known that for harmonic potentials, nonstationary Gaussian wavefunctions remain Gaussians. The form of the wavepacket is taken to be

$$G(\mathbf{q}, t) = \exp\left(\frac{i}{\hbar} \left[(\mathbf{q} - \mathbf{q}_t) \mathbf{A}_t (\mathbf{q} - \mathbf{q}_t) + \mathbf{p}_t (\mathbf{q} - \mathbf{q}_t) + \gamma_t \right]\right). \quad (3.10)$$

The classical coordinates $\mathbf{q}_t$ and momenta $\mathbf{p}_t$ give the central location of $G(\mathbf{q}, t)$ in $\mathbf{q}$ space and the Fourier Transform $\Psi(\mathbf{p}, t)$ in $\mathbf{p}$ space, respectively. $\mathbf{A}_t$ is a complex matrix giving the $\mathbf{q}$ distribution spread and the $\mathbf{q}\mathbf{q}_j$ correlation of the wavepacket. The complex scalar γ_t gives the normalization and phase of the wavepacket.

Inserting (3.10) into the time dependent Schrödinger equation

$$i\hbar \frac{\partial G(\mathbf{q}, t)}{\partial t} = H^{\text{eff}}(t) G(\mathbf{q}, t) \quad (3.11)$$

leads to the following “equations of motion” for the parameters of the wave packet

$$\dot{\mathbf{q}}_t = \left. \frac{\partial H^{\text{eff}}}{\partial \mathbf{p}} \right|_{\mathbf{p}=\mathbf{p}_t} = m^{-1} \mathbf{p}_t, \quad (3.12)$$

$$\dot{\mathbf{p}}_t = - \left. \frac{\partial H^{\text{eff}}}{\partial \mathbf{q}} \right|_{\mathbf{q}=\mathbf{q}_t} = -V'(\mathbf{q}_t), \quad (3.13)$$

$$\dot{\mathbf{A}}_t = -2\mathbf{A}_t m^{-1} \mathbf{A}_t - \frac{1}{2} V''(\mathbf{q}_t), \quad (3.14)$$

$$\dot{\gamma}_t = i\hbar \text{Tr}(m^{-1} \mathbf{A}_t) + \mathbf{p}_t \cdot \dot{\mathbf{q}}_t - E, \quad (3.15)$$

where $E = \frac{1}{2} \mathbf{p}_t m^{-1} \mathbf{p}_t + V(\mathbf{q}_t)$ is the classical energy. If the true potential in (3.9) is at most quadratic i.e. $V(\mathbf{q}) = V_t^{\text{eff}}(\mathbf{q})$ then the eqs. (3.12)–(3.15) give the exact solution of the problem.

Heller has derived eq. (3.9) and (3.10) and proposed their use for an arbitrary $V(\mathbf{q})$. The potential is thus expanded about the instantaneous center of the wavepacket and $\mathbf{q}_t$ and $\mathbf{p}_t$ follow a “classical motion” on a smooth potential.

The effective Hamiltonian $H^{\text{eff}}(t)$ may serve to construct a basis of Gaussian wavepackets $G_j(\mathbf{q}, t)$. Hence the exact wave function may be expanded in this propagated set in the form

$$\Psi(\mathbf{q}, t) = \sum_{j=1}^{\infty} d_j(t) G_j(\mathbf{q}, t). \quad (3.16)$$

If the propagated wavepacket $\Psi(\mathbf{q}, t)$ remains localized about its center $\mathbf{q}_t$ at all times, only a few (N) terms may suffice in eq. (3.16).

The time dependent Schrödinger equation for $\Psi(\mathbf{q}, t)$ reads:

$$i\hbar \frac{\partial \Psi(\mathbf{q}, t)}{\partial t} = [T + V(\mathbf{q})] \Psi(\mathbf{q}, t) = (H^{\text{eff}}(t) + [V(\mathbf{q}) - V_t^{\text{eff}}(\mathbf{q})]) \Psi(\mathbf{q}, t). \quad (3.17)$$

Using the Frenkel–McLachlan [93] Variational principle, Lee and Heller [78] obtain the time dependence of the coefficients $d_j(t)$ for a non-overlapping set of Gaussians from:

$$i\hbar \dot{d}_j(t) = \sum_{k=1}^N d_k(t) \langle G_j(\mathbf{q}, t) | (V(\mathbf{q}) - V_t^{\text{eff}}(\mathbf{q})) | G_k(\mathbf{q}, t) \rangle. \quad (3.18)$$

This set of equations is integrated with the initial conditions $d_j(0)$ defining the initial wavepacket $\Psi(\mathbf{q}, 0)$.

In the above described scheme, each basis function $G_j(\mathbf{q}, t)$ is independently propagated to the time t , as if its center moves along a classical trajectory. The advantage of such a scheme is that it retains the computational efficiency and physical intuitive insight of classical dynamics.

3.3. Minimum Error Method (MEM)

In the previous section we have seen how the choice of locally quadratic potentials has motivated the use of Gaussian wavepackets. One may wonder whether keeping the same Gaussian form yet relaxing the quadratic approximation in the potential, may improve the results. This line has recently been taken by Metiu [88–92] and his co-workers.

Let us focus on the case of a single Gaussian $G(\mathbf{q}, t)$ in a one-dimensional space q . In the MEM one assumes that this Gaussian packet remains Gaussian at all times and one tries to minimize the error functional, defined by:

$$\text{Err} = \int dq \left(i\hbar \frac{\partial G}{\partial t} - HG \right)^* \left(i\hbar \frac{\partial G}{\partial t} - HG \right). \quad (3.19)$$

Err is a quadratic form in the variables $\dot{q}_t$, $\dot{p}_t$, $\dot{\alpha}_t$ and $\dot{\gamma}_t$ where $\alpha(t) = A_{11}(t)$ for a one-dimensional Gaussian in eq. (3.10).

The “equations of motion” for the parameters q_t , p_t , α_t , γ_t are then:

$$\dot{q}_t = p_t/m, \quad (3.20)$$

$$\dot{p}_t = \frac{-V_1}{M_2} = -\frac{\partial}{\partial q_t} \left(\frac{\langle G | V | G \rangle}{\langle G | G \rangle} \right) = -\left\langle G \left| \frac{\partial V}{\partial q} \right| G \right\rangle. \quad (3.21)$$

$$\dot{\gamma}_t - p_t \dot{q}_t - \frac{i\hbar}{m} \alpha_t + \frac{1}{2} m p_t^2 = -\frac{(M_4 V_0 - M_2 V_2)}{(M_0 M_4 - M_2^2)}, \quad (3.22)$$

$$\dot{\alpha}_t + \frac{2\alpha_t^2}{m} = \frac{(M_2 V_0 - M_0 V_2)}{(M_0 M_4 - M_2^2)} = -\frac{1}{2} \frac{\partial^2}{\partial q_t^2} \langle G | V | G \rangle = -\frac{1}{2} \left\langle G \left| \frac{\partial^2 V}{\partial q^2} \right| G \right\rangle, \quad (3.23)$$

where

$$V_i(Q) = \langle G | V(q)(q - Q)^i | G \rangle = \int dq V(q)(q - Q)^i G^*(q) G(q), \quad (3.24)$$

$$M_i(Q) = \langle G | (q - Q)^i | G \rangle = \int dq (q - Q)^i G'(q) G(q), \quad (3.25)$$

$$M_0(Q) = 1. \quad (3.26)$$

These equations reduce to eqs. (3.12)–(3.15) for a one-dimensional Gaussian, if one expands the potential $V(q)$ up to a quadratic term about the center q_i of the Gaussian.

If the wavepacket is taken to be constructed of a sum of Gaussians, i.e.

$$\Psi(q, t) = \sum_j G_j(q, t), \quad (3.27)$$

one may repeat the minimum error procedure (3.19)–(3.26) and obtain “equations of motion” for the various parameters of the different Gaussians. The resulting equations may be summarized in the condensed matrix form:

$$\mathbf{MX} = \mathbf{V}, \quad (3.28)$$

where

$$\mathbf{M} = \begin{pmatrix} M(10|10) \dots \\ \vdots \\ \vdots \end{pmatrix}, \quad (3.29)$$

$$M(An|Bj) = \int_{-x}^x dr (r - q_A)^n (r - q_B)^j G_A(r)^* G_B(r), \quad (3.30)$$

$$\mathbf{X} = \begin{pmatrix} \frac{p_1^2}{2m} - p_1 \dot{q}_1 - \frac{i\hbar}{m} \alpha_1 + \dot{\gamma}_1 \\ \vdots \\ \frac{p_N^2}{2m} - p_N \dot{q}_N - \frac{i\hbar}{m} \alpha_N + \dot{\gamma}_N \\ 2\alpha_1 \left(\frac{p_1}{m} - \dot{q}_1 \right) + \dot{p}_1 \\ \vdots \\ 2\alpha_N \left(\frac{p_N}{m} - \dot{q}_N \right) + \dot{p}_N \\ \dot{\alpha}_1 + 2\alpha_1^2/m \\ \vdots \\ \dot{\alpha}_N + 2\alpha_N^2/m \end{pmatrix}, \quad (3.31)$$

$$\mathbf{V} = \begin{pmatrix} \sum_{i=1}^N V(10|i0) \\ \vdots \\ \sum_{i=1}^N V(N0|i0) \\ \vdots \\ \sum_{i=1}^N V(11|i0) \\ \vdots \\ \sum_{i=1}^N V(N1|i0) \\ \vdots \end{pmatrix}, \quad (3.32)$$

where

$$V(An|Bj) = \int_{-x}^x dr V(r) (r - q_A)^n (r - q_B)^j G_A^*(r) G_B(r). \quad (3.33)$$

3.4. Discussion on the approximations

The minimum error method (MEM) provides the best set of equations for a wavepacket constructed from a superposition of Gaussians. However, the physics of the problem may require the use of many Gaussians. In such a case, the complexity of the problem may increase rapidly so that eventually one is led to propagate an enormous number of parameters. For each individual Gaussian additional four parameters are added, c.f. eqs. (3.19)–(3.23). For a three-dimensional problem the number of parameters is accordingly enlarged. The disadvantage of such a brute force approach is the loss of simplicity which motivated the use of the method in the first place.

In this subsection we follow the presentation of Metiu and his co-workers [88–92], in which the approximations inherent in Heller's work emerge from the more accurate MEM method.

Two main approximations leading to Heller's approach are: (1) The assumption that the Gaussians $G_j(q, t)$ in (3.27) are linearly independent at all times (Independent Gaussian Approximation IGA). (2) The premise that each independent Gaussian is narrower than the spatial range over which the potential changes appreciably throughout the collision event. In such a case one may expand the potential in a power series around the center of the Gaussian and retain the terms up to quadratic, i.e. the potential is given by eq. (3.9). This approximation is termed the Local Harmonic Approximation (LHA). It is our task in this subsection to examine the two approximations mentioned above.

Metiu and his coworkers have viewed these two approximations through the following physical analog. One may imagine a set of trajectories coupled to one another and to "external

time dependent fields" $\alpha_1 \cdots \alpha_N, \gamma_1 \cdots \gamma_N$, which are responsible for the width and phase of the individual Gaussians. Independent Gaussian Approximation eliminates the coupling among the trajectories whereas Local Harmonic Approximation eliminates the coupling to the external fields.

The Independent Gaussian Approximation

As stated in the previous subsection, the various Gaussians in eq. (3.27) are coupled to one another in eq. (3.28). The Independent Gaussian Approximation (IGA) is obtained by neglecting all the coupling terms in (3.28)–(3.33). This amounts to using only the diagonal part of the matrix $M(Am|Bn) = M(Am|An)\delta_{AB}$ and using the matrix $V(Am|Bn) = V(Am|An)\delta_{AB}$. The elements of the vector X are decoupled and the equation for each element is identical to eqs. (3.20)–(3.25) for a single Gaussian.

The most obvious case for the IGA to be valid is when the Gaussians do not overlap. If the wavefunction of the problem splits into spatially disjointed pieces, the off diagonal integrals $M(Am|Bn)$ and $V(Am|Bn)$ above vanish.

An example in which the validity of the IGA seems reasonable is the case where the integrals $M(Am|Bn)$ and $V(Am|Bn)$ oscillate rapidly around zero. The oscillatory behaviour may arise from the phases of the product of two different Gaussians, or from a time-dependent oscillation around zero due to the time-dependent phase value of these complex integrals. In both cases, IGA is justified if the oscillation of these integrals is characterized by a wavelength much smaller than the characteristic length of the quantities of interest (e.g. the width of the product of two Gaussians).

A second valid application of IGA to apply is the case of imposing the Local Harmonic Approximation. This may be intuitively expected when remembering that a Gaussian wavefunction maintains its form if the interaction is described by a quadratic Hamiltonian. As shown by Metiu et al. IGA indeed follows exactly when LHA is imposed.

The Local Harmonic Approximation

The Local Harmonic Approximation (LHA) is defined in eq. (3.9) where the potential is expanded up to quadratic terms around the center q_i of the wavepacket. Clearly this expansion is valid as long as the potential changes slowly as a function of q around q_i over a range equal to the width of the Gaussian.

In order to quantitatively examine the LHA, Metiu et al. have compared it to the MEM equation. They show that by adding the next order term (third order) in the expansion of the potential and plugging it into the MEM eq. (3.21) one obtains:

$$\frac{\dot{p}_{\text{MEM}} - \dot{p}_{\text{LHA}}}{\dot{p}_{\text{LHA}}} = \frac{l^2(t)}{4} \frac{\partial^3 V}{\partial q^3} \bigg|_{q_i} \bigg/ \frac{\partial V}{\partial q} \bigg|_{q_i} + \mathcal{O}(l^4). \quad (3.34)$$

Here $\dot{p}_{\text{LHA}}$ is given by eq. (3.13) and is the Local Harmonic Approximation for the momentum p_i of the wavepacket $\dot{p}_{\text{MEM}}$ is the Minimum Error Method value of $\dot{p}$, when the third order term is included in the expansion of the potential. The length $l(t)$ of the Gaussian is given by

$l(t) = (\hbar/(2\text{Im}\alpha(t)))^{1/2}$. The error made by using $\dot{p}_{\text{LHA}}$ instead of $\dot{p}_{\text{MEM}}$ is less than say 10% if

$$\frac{l^2}{4} \frac{\partial^3 V}{\partial q^3} \bigg|_{q_n} \bigg/ \frac{\partial V}{\partial q} \bigg|_{q_i} < 0.1. \quad (3.35)$$

Metiu and his co-workers have found by a similar analysis, that the errors in other quantities of the LHA (eqs. (3.12)–(3.15)) are smaller than 10% if (3.35) is satisfied, i.e. the LHA eq. (3.13), which describes the “classical motion” of the center of the Gaussian, is the one giving the largest error.

It turns out that the expectation value, i.e. average of $-\partial V/\partial q$ in eq. (3.21) and the classical force $-\partial V/\partial q|_{q_i}$ of eq. (3.13) can differ considerably in calculations of scattering of He atoms from solid surfaces [89] and for other systems involving significantly anharmonic potentials, and low collision energies.

Both the original Heller and the MEM extension of Metiu are subject to the following limitations. 1) These methods are expected to fail in cases where resonances occur. Also for nonresonant scattering at low energies, the approximations used in the methods may breakdown. 2) It is not clear how to apply or extend the methods to cases where the wavepacket breaks into many small peaces. 3) When the center of the wavepacket penetrates into the classical forbidden region, it is not possible to use these methods. These limitations are still open for further investigations.

3.5. The numerical implementation

In both the MEM and Heller’s original method, one is faced with solving a closed set of coupled-first-order differential equations, these equations determining the propagation in time of the values of the parameters of the Gaussians. Once these parameters are known at the asymptotic limit, the scattering information may be extracted, see e.g. eq. (3.7). To solve these equations one may choose one of the standard methods such as the Runge–Kutta, a Prediction–Corrector or the Adams method with variable step size.

A grid of wavepackets has to be chosen to define the initial conditions. The choice of the width of the Gaussians is the most problematic one as it is rather arbitrary. It may be done by using a least-square-fit to a given initial state and determining the initial parameters. This procedure has proven efficient in minimizing the number of Gaussians to be used. Drolshagen and Heller [82–84] have observed that improved convergence may be achieved when the width of the wavepacket is chosen such that it “collects itself” in the vicinity of the target surface. This may be approximately obtained if one chooses the initial conditions in such a way that the original packet when propagated via the free hamiltonian is of minimal width at the surface. In any case the procedure of choosing the initial conditions is delicate due to the arbitrariness inherent in the particular combination of Gaussians used. One has to make sure that the final results are rather insensitive to the particular combination of Gaussians chosen.

In the implementation of the MEM method, extra caution has to be exerted, to avoid the singularity of the equations when linear dependencies of the various Gaussians emerge. The problem is that at a particular time the set of Gaussians may behave perfectly well in

representing the wavefunction, but at a later (or earlier) time the representation could be disastrous due to linear dependencies. This demands the manual interference of the programmer in the course of the computation – an undesirable feature.

Another source of numerical difficulty is the quadratic dependence of the width parameter in eqs. (3.14) or (3.5), i.e. the term containing α_t^2 . This term demands very small time steps to account for the oscillatory behaviour. In some cases this oscillatory behaviour leads to a dramatic failure in the attempt to solve the differential equations. These problems are caused by the instability of the equations due to the α_t^2 term. A transformation designed by Heller to overcome this difficulty introduces two new matrices $\mathbf{X}_t$ and $\mathbf{Z}_t$ in such a way that $\mathbf{A}_t$ in eq. (3.14) is given by:

$$\mathbf{A}_t = \frac{1}{2}\mathbf{X}_t\mathbf{Z}_t^{-1}, \quad (3.36)$$

where

$$\dot{\mathbf{Z}}_t = m^{-1}\mathbf{X}_t. \quad (3.37)$$

Inserting (3.36) into (3.14) one finds:

$$\dot{\mathbf{X}}_t = -V''(q_t)\mathbf{Z}_t. \quad (3.38)$$

Equations (3.37) and (3.38) are first solved with the initial conditions $\frac{1}{2}\mathbf{X}_0 = \mathbf{A}_0$, $\mathbf{Z}_0 = 1$, and $\mathbf{A}_t$ is then determined from (3.36). Direct solution of the coupled matrix equations (3.37), (3.38) has shown best numerical stability at low scattering energies and high surface corrugation. At higher energies it has been shown that the matrices $\mathbf{X}_t$ and $\mathbf{Z}_t$ may be extracted better directly from adjacent trajectories. This may be seen by inspecting the transformed Hamiltonian

$$H = \frac{1}{2}\mathbf{X}_t m^{-1}\mathbf{X}_t + \mathbf{Z}_t V''(q_t)\mathbf{Z}_t \quad (3.39)$$

which results in the following equations for $\mathbf{X}_t$, $\mathbf{Z}_t$:

$$\begin{pmatrix} \mathbf{X}_t \\ \mathbf{Z}_t \end{pmatrix} = \begin{pmatrix} \left. \frac{\partial \mathbf{p}_t}{\partial \mathbf{p}_0} \right|_{q_0} & \left. \frac{\partial \mathbf{p}_t}{\partial \mathbf{q}_0} \right|_{p_0} \\ \left. \frac{\partial \mathbf{q}_t}{\partial \mathbf{p}_0} \right|_{q_0} & \left. \frac{\partial \mathbf{q}_t}{\partial \mathbf{q}_0} \right|_{p_0} \end{pmatrix} \begin{pmatrix} 2\mathbf{A}_0 \\ 1 \end{pmatrix}. \quad (3.40)$$

The partial derivatives in eq. (3.40) may be constructed directly from ordinary classical trajectories, centered about $\mathbf{r}_0$ and $\mathbf{p}_0$. For example finite differences may approximate these derivatives.

3.6. Applications

The discussion in the present section focuses attention on diffractive scattering from a static crystalline surface and on a model for collisional excitation of surface vibrations [82–85]. First

the test case of He + LiF scattering is presented and semiclassical calculations are compared to quantum mechanical ones. Next, the more challenging cases of diffraction from surfaces with imperfections are considered. Various stepped surfaces are regarded as examples of imperfections distributed regularly or randomly. A study of scattering off corrugated surfaces with adsorbed atoms is also presented once again with regular and random distributions. Finally the collision induced energy transfer in a linear chain is considered, this example serving as a pilot model of phonon excitation in atom surface collisions.

(a) He + LiF scattering

In order to test the wavepacket (WP) method, Drolshagen and Heller [82] have applied it to He scattering off the LiF surface. The results have been compared to quantum mechanical coupled channel (CC) calculations. Over a wide range of energies and several orders of magnitude of the diffraction probabilities, the comparison has been remarkably good. The behaviour of the diffraction peaks due to surface corrugation has also been tested, showing that the wavepacket method may reproduce the CC calculations. While for low incident energies (in this particular study below $k = 10$ a.u.) the CC calculations are still feasible, the semiclassical WP approach has permitted extending the energy up to any desired large value. For such high energies even several hundred diffraction channels may be open and a converged CC calculation would be almost impossible. This emphasizes an advantage of the WP method.

An interesting question arises regarding the performance of the wavepacket method in classical forbidden regions. Penetration of the wavefunctions to such regions may in some cases be the origin of observed transitions. The comparison has shown that the WP method may reproduce the classically forbidden transitions encountered at high energies, as the tail of the wavepacket penetrates into the classical forbidden region. At lower energies, the results of the WP method predict too small diffraction probabilities. This may be due to the insufficient penetration into the target vicinity.

Another interesting issue emerges when considering pure crystalline surfaces. It is intrinsic in the CC method that the diffraction probabilities appear as delta function Bragg peaks. The periodical symmetry of the crystal is taken into account exactly, thus assuring that the correct behaviour is built in. In the WP method there is no need to include the assumption of an infinite perfect surface so that it may be applied to surfaces with imperfections in a straight forward manner. However, in the case of vibrating crystalline surfaces one has to include more and more unit cells in order to approach the limit of delta peaks. For such vibrating periodical and large surfaces, the feature of a necessary finite width in the WP method is a limitation, since it introduces a complication of separating the width due to phonon effects from the width due to the finite size. On the other hand, with the very new techniques now appearing [94–97], it becomes feasible to consider portions of the surface having the size of about 1000 Å. In such cases it is advantageous to have a method which may obviate the need for the assumption of a perfectly periodic surface.

(b) Scattering from stepped crystalline surfaces

In this section, a report of an application of He scattering is presented again. In this study, Drolshagen and Heller have used a stepped Pt(997) surface describing the scattering by the

potential [82–84]:

$$V(z) = D \exp[2\alpha(z_0 - z)], \quad (3.41)$$

$$z_0(x) = \begin{cases} m(x - a); & a \leq x \leq a + b, \\ \frac{2}{a^3}(ma - h)x^3 - \frac{3}{a^2}(ma - h)x^2 + mx - h; & 0 \leq x \leq a, \end{cases} \quad (3.42)$$

with the parameters: $D = 10$ meV; $\alpha = 1.0 \text{ \AA}^{-1}$; $a = 2.5 \text{ \AA}$; $b = 17.5 \text{ \AA}$; $h = 2 \text{ \AA}$; $m = -h/b$.

The two-dimensional potential $V(x, z)$ is periodic in the x -direction, and for simplicity, no corrugation is introduced in the y -direction

$$z_0(x \pm (a + b)) = z_0(x). \quad (3.43)$$

The relative scattering intensities as functions of momentum exchange in the x -direction have been calculated at several incident angles. The qualitative features of the physical effects observed by Lapujoulade et al. [98] have been reproduced. The main point is that the method is capable of handling a complicated case in which as many as 49 Bragg peaks are open. Moreover, even the effect of multiple scattering can be traced. In this respect, one should stress that these are short range multiple scattering events and it is doubtful whether the method could handle multiple scattering in the presence of long range attractive forces, where resonances may emerge [40,99]. We anticipate that in such a case the assumption of local harmonic forces will break down. Moreover, the Gaussians should interact coherently upon entering the resonance region of the trapped state. This type of interaction is beyond the scope of the GWP approaches. We note that the asymmetry in the intensity distribution caused by scattering off the step edges is reflected by the method.

The effects of a random mixture of steps of different sizes have also been tested. Steps twice as large (i.e. $a' = 2a$, $b' = 2b$, $h' = 2h$ in eq. (3.42)) have been inserted gradually into the sample, this resulting in a distortion of the regular pattern of Bragg peaks. Furthermore, the background between the Bragg peaks has increased. The buildup of half order peaks due to the double sized steps has appeared smoothly without any sudden jumps. Due to the finite size of the surface sample, the diffraction pattern has shown heavy oscillations. Thus, only the average of these size-dependent oscillations may be compared to experimental data.

(c) Scattering from imperfect and disordered surfaces

In this discussion we return to the scattering of He atoms off the LiF surface. In this example, the wavepacket approach is applied by Drolshagen and Heller to a full three-dimensional surface modeled by the potential:

$$V(x, y, z) = V_0 + V_{ad}, \quad (3.44)$$

$$V_0 = D \exp[2\alpha(z_0 - z)] + V_1(z)Q(x, y), \quad (3.45)$$

$$V_{ad} = A \exp(-\gamma d), \quad (3.46)$$

with:

$$Q(x, y, z) = \exp(2\pi x/a) + \cos(2\pi y/a), \quad (3.47)$$

$$V_1(z) = -2\beta D \det[2\alpha(z_0 - z)], \quad (3.48)$$

$$d(x, y, z) = [x^2 + y^2 + (z - z_a)^2]^{1/2}. \quad (3.49)$$

The parameter values used are: $D = 7.63$ meV, $\alpha = 1.1 \text{ \AA}^{-1}$, $\beta = 0.8$, $a = 2.84 \text{ \AA}$, $A = 3$ eV, $\gamma = 6 \text{ \AA}^{-1}$, $z_a = 0.8 \text{ \AA}$, $z_0 = 1 \text{ \AA}$.

The model still oversimplifies a realistic description of scattering of atoms off surfaces with adsorbed particles as the various interactions are non-additive, but serves as an excellent example of the capability of the wavepacket approach.

Inspection of the relative scattering probabilities has made it possible to identify the effect of adsorbed atoms. In between the well separated Bragg peaks, a background emerges when addatoms are introduced. Furthermore, for the specific simple model used, a well-organized monolayer can be constructed having an intensity distribution very similar to the original bare surface. By looking at the scattering intensity for various choices of momentum transfer, the results have shown preference to scattering in certain directions. It is useful to have a method capable of tracing such trends in the scattering probability distribution. One should mention in this respect, that further study is needed, in order to assess the ability to cope with a more realistic model in which attractive forces are included, and in cases where the potential is distorted due to the presence of an addatom over a range longer than a single unit cell. One way to tackle the latter case is to try and extend the area of sampling of the wavepacket over several unit cells. There is a need to design a preaveraging procedure for the wavepacket method to avoid the oscillations obtained due to the finite size of the sample which tend to obscure fine structure of physical relevance and broadening of the Bragg peaks. These delicate effects are detectable by present experimental techniques [36–39].

(d) Collisions with a linear vibrating chain

The ability to probe phonon excitation and collision-induced energy transfer has long been a challenge in surface scattering. The linear vibrating chain may serve as a pilot model for describing these complicated effects.

Drolshagen and Heller [28,39] have inspected the translational energy spectrum for various chain lengths, different projectile masses and local potentials to force the individual atoms in the chain to remain near their equilibrium position. The potential parameters have been chosen to represent scattering of Ar atoms on the W(100) surface. In these studies the energy distribution is calculated by Fourier Transforming autocorrelation functions using directly the time dependence in the method. That allows calculating an energy spectrum with finite resolution without explicit use of final target states. The results show that it is possible to obtain the intensity distribution for large targets as a function of energy and it is possible to trace normal mode excitation of various chain lengths. A detailed study as to the accuracy of the Frozen Gaussian Approximation has shown that this approximation is encouragingly good for most cases, especially in the high

energy regime. We stress that in all these calculations trapping does not occur and cannot be treated by Gaussian Wavepacket Methods.

The observation that the Frozen Gaussian approximation is a reliable one in the direct scattering regime is very important, as the computational effort required in the Frozen Gaussian Approximation is comparable to that needed in classical trajectory calculations. Thus, in the Frozen Gaussian Approximation it would be permissible to treat almost any scattering system quantitatively where classical trajectory calculations can be performed. The more accurate wave packet calculation with non-frozen Gaussians is probably still considerably easier to compute than a full quantum mechanical calculation. In closing we mention that calculations of correlation functions have been applied only to the case of a zero temperature. Calculations for finite temperature are still difficult and reflect a limitation of the method.

4. Methods mixing classical and quantal degrees of freedom

It is inherent in the physical properties of many realistic molecule/surface scattering systems that some (often most) of the degrees of freedom involved can be treated adequately at the purely classical level. This gives importance to the methods that treat by wavepackets those modes for which quantum effects are expected while describing all other degrees of freedom by classical dynamics. The choice as to which degrees of freedom may be treated classically obviously depends on the system and on the scattering conditions (e.g., surface temperature, collision energy). Low energy scattering of He or H₂ from a solid of heavy-mass atoms calls for a quantum description of the projectile combined with a classical description of the surface vibrations. On the other hand, the study of electron-hole pair excitations in heavy-molecule impact on metal surfaces requires a quantum approach to the dynamics of the solid electrons, while the projectile may be adequately described in the classical framework. Similarly, a quantum-mechanical treatment may be required for surface phonons at low temperatures of the solid even in the collision processes at high energies, when the colliding atom or molecule behaves classically. The detailed considerations involved will be clarified in the context of examples mentioned below. The main issue common to all these problems is *how to combine the classical and the quantum-mechanical treatments of different degrees of freedom in a consistent way*. This question is familiar from corresponding methods in gas-phase scattering [100], and proposed approaches must be examined with regard to energy conservation, time-reversal invariance and other properties that may be pertinent in a given process. In any case, methods that treat the quantum degrees of freedom by time-dependent wavepackets can relatively easily be combined with a classical trajectory description of the other modes. Time-independent quantum mechanical algorithms do not generally have the same advantage of being easily combined with a classical calculation for part of the system. Once an approach for coupling classical and quantum wavepacket dynamics is adopted, this may impose restrictions on the algorithm for solving the time-dependent equations of motion. For instance, the potential that governs the wavepacket evolution is typically a “dynamical”, i.e., time-dependent one, representing energy exchange with the classical modes. This excludes the Chebychev algorithm for the time propagation of the wavepacket (see section 2) that requires a stationary Hamiltonian for the quantum-mechanical part of the problem.

4.1. Scattering of a quantum-mechanical projectile from a classical vibrating surface

The methods discussed in this subsection are pertinent to the scattering at low energies of a light atom or molecule from a solid surface of heavy constituent atoms. It is supposed that the solid temperature is sufficiently high to justify a classical treatment of surface vibrations. It is also assumed at the background of all these methods that electron–hole pair excitations can be neglected, and thus excluded from the model Hamiltonians used. The objective of the methods discussed here is to treat processes such as diffraction and those of rotationally inelastic scattering (when the projectile is a molecule) within a framework that includes the effects of lattice vibrations at the classical level.

Mixed classical / quantal Time-Dependent Self-Consistent Field (TDSCF) approximation

This method is one of the general schemes for treating consistently some degrees of freedom classically, other quantum-mechanically, allowing at least approximately for energy exchange between the two groups of modes. The basis of the approach is the quantum-mechanical TDSCF approximation, which dates back to the earliest stage of quantum theory [10]. Mixed quantal-classical TDSCF was developed in recent years for a variety of gas-phase collision and unimolecular dissociation processes, e.g. by Schatz [102] and by Gerber et al. [103,104]. Consider the method in the specific context of an atom colliding with a vibrating surface. Let $\mathbf{r}$ be the position vector of the atom, and denote by $\mathbf{q}$ the phonon coordinates. In the TDSCF approximation it is assumed that the time-dependent wavefunction of the whole system can be approximately factorized as follows:

$$\Psi(\mathbf{r}, \mathbf{q}, t) = \phi_a(\mathbf{r}, t) \phi_{\text{ph}}(\mathbf{q}, t) \quad (4.1)$$

This is substituted in the time-dependent Schrödinger equation for $\Psi(\mathbf{r}, \mathbf{q}, t)$:

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[H_{\text{ph}}(\mathbf{q}) - \frac{\hbar^2}{2\mu} \nabla_r^2 + V(\mathbf{r}, \mathbf{q}) \right] \Psi, \quad (4.2)$$

where $H_{\text{ph}}(\mathbf{q})$ is the surface (phonon) Hamiltonian, $V(\mathbf{r}, \mathbf{q})$ the molecule–surface interaction, and μ the mass of the colliding atom. This leads to the quantum-mechanical TDSCF equations for the scattered atom and for the phonons:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_r^2 + V_a^{\text{eff}}(\mathbf{r}, t) \right] \hat{\phi}_a(\mathbf{r}, t) = i\hbar \frac{\partial \hat{\phi}_a(\mathbf{r}, t)}{\partial t}, \quad (4.3a)$$

$$\left[H_{\text{ph}}(\mathbf{q}) + V_{\text{ph}}^{\text{eff}}(\mathbf{q}, t) \right] \hat{\phi}_{\text{ph}}(\mathbf{q}, t) = i\hbar \frac{\partial \hat{\phi}_{\text{ph}}(\mathbf{q}, t)}{\partial t}, \quad (4.3b)$$

where

$$\hat{\phi}_a(\mathbf{r}, t) = \exp[i\sigma_a(t)] \phi_a(\mathbf{r}, t), \quad (4.4a)$$

$$\hat{\phi}_{\text{ph}}(\mathbf{q}, t) = \exp[i\sigma_{\text{ph}}(t)] \phi_{\text{ph}}(\mathbf{q}, t). \quad (4.4b)$$

The phase factors $\exp[i\sigma_a(t)]$, $\exp[i\sigma_{ph}(t)]$ are of no physical importance and the explicit expressions for these quantities will not be given here. The effective, mean field potentials $V_a^{\text{eff}}(\mathbf{r}, t)$, $V_{ph}^{\text{eff}}(\mathbf{q}, t)$ are given by

$$V_a^{\text{eff}}(\mathbf{r}, t) = \langle \hat{\phi}_{ph}(\mathbf{q}, t) | V(\mathbf{r}, \mathbf{q}) | \hat{\phi}_{ph}(\mathbf{q}, t) \rangle_{\mathbf{q}}, \quad (4.5a)$$

$$V_{ph}^{\text{eff}}(\mathbf{q}, t) = \langle \hat{\phi}_a(\mathbf{r}, t) | V(\mathbf{r}, \mathbf{q}) | \hat{\phi}_a(\mathbf{r}, t) \rangle_{\mathbf{r}}. \quad (4.5b)$$

Eqs. (4.3), (4.5) are the quantum-mechanical TDSCF equations.

The wavefunctions and effective potentials associated with the $\mathbf{q}$ and $\mathbf{r}$ modes must be solved self-consistently. It is the time-dependence of the effective potentials that allows for the energy exchange between the modes within the TDSCF scheme, since the effective Hamiltonians for the $\mathbf{r}$ and for the $\mathbf{q}$ subsystems do not separately conserve energy. For a range of gas-phase problems, it was found that energy transfer with the TDSCF framework is roughly of the correct magnitude [103,104]. However, this can definitely not be regarded as a general conclusion, and it remains to be established also for surface scattering problems that the TDSCF does not underestimate or overestimate systematically the amount of energy transferred between the modes involved. This requires a test against “exact” calculations for suitable model systems, and such computations in the context of surface scattering have not yet been reported. The availability of formally separate Hamiltonians for the $\mathbf{r}$ and the $\mathbf{q}$ subsystems respectively, makes it possible to treat very simply any one of them (or both, when justified) classically without leading to any inconsistency in the treatment of the second subsystem. The classical equations of motion for the phonons are:

$$\dot{q}_i = [\partial H_{ph}^{\text{eff}}(\mathbf{q}, t) / \partial p_i], \quad (4.6a)$$

$$\dot{p}_i = -[\partial H_{ph}^{\text{eff}}(\mathbf{q}_i, t) / \partial q_i], \quad (4.6b)$$

where

$$H_{ph}^{\text{eff}}(\mathbf{q}, t) = H_{ph}(\mathbf{q}) + V_{ph}^{\text{eff}}(\mathbf{q}, t) \quad (4.7)$$

is the *classical* effective Hamiltonian for the phonons, and i is a label for the phonon modes. The mean-field acting on the atom becomes, when the phonons are treated classically,

$$V_a^{\text{eff}}(\mathbf{r}, t) = \frac{1}{n_T} \sum_{\alpha=1}^{n_T} V(\mathbf{r}, \mathbf{q}_{\alpha}(t)), \quad (4.8)$$

where α is an index labelling the various initial values used in sampling over the different initial conditions in the $\mathbf{q}$ -modes, n_T is the number of $\mathbf{q}$ -trajectories calculated. The mixed classical-quantal TDSCF equations involve solving self-consistently the trajectory eqs. (4.6) for the $\mathbf{q}$ -modes with the time-dependent Schrödinger eq. (4.3a) for the atom, and with eqs. (4.5a), (4.8) for the effective potentials involved. General properties of these equations are discussed by Gerber et al. [103] in the context of gas-phase dissociation processes. The classical-quantal TDSCF conserves total energy, time-reversal invariance, and other symmetry properties implied

by the full, true Hamiltonian of the system. Since this is quite a general approach for coupling a classical and a quantal subsystem, it can also be applied (as will be discussed below) to problems where surface modes must be handled quantum mechanically while the behavior of the projectile may be described by classical dynamics.

Mixed quantum mechanical/classical trajectory calculations that use the TDSCF approximation to couple classically-described surface vibrations with the quantum-mechanical scattering of a light particle were reported by Kosloff and Cerjan [54]. They studied the dynamics of He desorption and scattering from a Pt surface at the temperature range of 100–800 K. To integrate the time-dependent Schrödinger equation for the scattered atom, Kosloff and Cerjan employed the Fast Fourier algorithm, with the second-order differencing for the time propagation (see section 2). Note that in this case only a propagation method which is applicable to an explicitly time-dependent potential can be used. To calculate the motions of the solid atoms, Kosloff and Cerjan use the Generalized Langevin Equation (GLE) method as developed by Adelman and Doll [22] and by Tully [23]. In this approach, the solid atoms are divided into “primary zone” and “secondary zone” atoms. It is assumed that only the “primary zone” atoms (typically those at the outermost surface layer) are directly coupled to the incoming particle. The secondary-zone atoms, pertaining to inner layers of the solid, interact and exchange with the surface layer, but are assumed not to be directly coupled to the scattered particle. The GLE scheme assumes the harmonic approximation for the secondary zone atoms, and then models their effect on the motions of the primary zone particle via a time-dependent friction term, and a stochastic fluctuating force. Using matrix notation, the equations of motion take the following form in the GLE scheme [22,23]:

$$\dot{\mathbf{p}}_i = \mathbf{G}_i[\mathbf{r}_i(t)] - \int_0^t \Delta(t-t') \mathbf{r}_i(t') dt' + \mathbf{R}(t), \quad (4.9a)$$

$$\dot{\mathbf{r}}_i = \mathbf{M}_i^{-1} \mathbf{p}_i(t). \quad (4.9b)$$

Here $\mathbf{p}_i$, $\mathbf{r}_i$ are, respectively, the momentum and position of the primary-zone atom i , M_i is its mass. $\mathbf{G}_i[\mathbf{r}_i]$ is the local force function acting on atom i . $\mathbf{R}(t)$ is a fluctuating “stochastic” force representing part of the influence of secondary zone atoms on the motions of the primary zone particles. Another effect is given by the integral in (4.9a), which is a friction term representing energy dissipation into the secondary zone, and which includes memory effects. The friction kernel $\Delta(t'-t)$ and the fluctuating force are related by the “Second Fluctuation–Dissipation Theorem”, familiar from nonequilibrium statistical mechanics:

$$\Delta(t) = k_B T \langle \mathbf{R}(t) \mathbf{R}(0) \rangle_T \quad (4.10)$$

i.e., $\Delta(t)$ is a correlation function of the random force. In the GLE, the atoms that are treated explicitly by equations of motion are only those of the primary zone (in addition to the scattered particle), the number of which in practical applications is of the order of 5–50 [23]. However, the GLE as applied in real cases is not exact in the classical framework, but rather uses various models to construct simply the random force and the memory kernel. (The kernel is constructed e.g. to represent approximately the phonon spectrum of the solid.) A detailed discussion of the

GLE scheme lies outside the scope of the present review, which focuses on the quantum part of the problem. We only note here that the GLE equations for the solid particles as employed in the calculations of Kosloff and Cerjan [54] use a local force function G_i which is obtained from the TDSCF potential field (4.5b), that is an average of the full potential function of the system over the time-dependent wavepacket of the scattered atom. A summary of the results is contained in section 2.

For low temperatures the classical description of the GLE is not adequate because of the quantal effects due to zero point motion of the solid surface. An attempt to overcome this difficulty employed a semigroup representation for the phonon motion [56]. In this method The Liouville–Von Neumann equation of motion is solved for the phonons including relaxation terms which lead to the correct temperature effect. A semigroup description of the dynamics in the Heisenberg picture reads:

$$\dot{\mathbf{X}} = \mathbf{L}(\mathbf{X}) = \mathbf{L}_H(\mathbf{X}) + \mathbf{L}_D(\mathbf{X}), \quad (4.11)$$

where $\mathbf{X}$ is an operator in the Hilbert space of the system. $\mathbf{L}$ is the superoperator governing the dynamics.

$$\mathbf{L}_H(\mathbf{X}) = i[\mathbf{H}, \mathbf{X}] \quad (4.12)$$

and

$$\mathbf{L}_D(\mathbf{X}) = \sum_i \gamma_i (\mathbf{V}_i \mathbf{X} \mathbf{V}_i^\dagger - \frac{1}{2} [\mathbf{V}_i \mathbf{V}_i^\dagger, \mathbf{X}]_+),$$

where $[\mathbf{A}, \mathbf{B}]_+ = \mathbf{AB} + \mathbf{BA}$, $\mathbf{V}_i$ is an operator in the Hilbert space, and the parameters γ_i determine the rate of relaxation and the equilibrium state.

In the description of the surface motion, the phonon motion was assumed harmonic with a relaxation rate leading to equilibrium. If one excludes the relaxation terms this description is similar to the forced-oscillator method described in section (4.3). A TDSCF description was used to couple the phonon motion to the he degrees of freedom.

The importance of mixed semigroup/quantal TDSCF calculations of the type reported by Kosloff and Cerjan [56] is that they are capable of predicting the large energy accommodation effects in very low energy collisions of atoms with surfaces of temperatures close to zero. Time-independent quantum-mechanical approximations that were applied to such processes in the past [e.g. 105] gave an artificial result of energy accommodation which goes to zero as both the surface temperature and the collision energy tend to zero. The difficulty stemmed from the use of the distorted wave approximation for the scattered particle (with a rigid surface model employed to define the zero-order wavefunctions), and of the approximation of a one phonon process [105]. The mixed semigroup/quantal TDSCF approach avoids these approximations, and seems to yield reasonable magnitudes for energy transfer at low surface temperatures and collision energies.

Semiclassical stochastic trajectory method This approach was developed in recent years by De Pristo and his coworkers [106–110] and applied to a wide range of molecule–surface collision

problems. The method makes the assumption that the motion of the colliding molecule, or atom, along its distance coordinate from the surface z , can be treated classically. Similarly, a classical trajectory description, in the specific form of the GLE scheme discussed earlier, is used for the surface vibrations. Other degrees of freedom such as the diffraction coordinates (the coordinates (x, y) of the molecular center of mass motion in parallel to the surface), the vibrational and rotational degrees of freedom of the colliding molecule, are all treated by time-dependent quantum mechanics. To couple the classical z -motion in perpendicular to the surface to the other, quantum-mechanical modes, a condition representing energy conservation in the collision is imposed. For the case of a nonvibrating surface, this condition implies that the energy flow from or into the z -motion of the molecular c.m. equals the gain (or loss) of energy by all the other, quantum-mechanical, degrees of freedom. As for handling the equations of motion for the quantum modes, this is done by expanding in a basis of stationary states, and solving for the time-dependent coefficients.

We give explicit dynamical equations of this mixed quantal/classical method for one of the simplest cases to which it was applied, namely that of atom scattering from a nonvibrating crystalline surface, as presented by Grote and De Pisto [106]. The motion in the diffraction coordinates $\mathbf{R} = (x, y)$ which are parallel to the surface, as described by a time-dependent wavepacket

$$\psi(x, y, t) = \sum_{mn} C_{mn}(t) \exp(i[\mathbf{K} + \mathbf{G}_{mn}] \cdot \mathbf{R}) \times \exp(iE_{mn}t/\hbar) \quad (4.13)$$

where E_{mn} is the energy in the $\mathbf{R}$ -coordinates corresponding to the (mn) diffraction state:

$$E_{mn} = \frac{\hbar^2}{2\mu} (\mathbf{K} + \mathbf{G}_{mn})^2, \quad (4.14)$$

here μ is the mass of the scattered atom, $\mathbf{K}$ – the component of the incident wavevector along the surface plane, and $\mathbf{G}_{mn}$ the (mn) reciprocal space vector defined in section 1. The probability of scattering into the (mn) diffraction state is given by

$$I_{mn} = |C_{mn}(t \rightarrow +\infty)|^2, \quad (4.15)$$

while initially:

$$C_{mn}(t \rightarrow -\infty) = \delta_{m0}\delta_{n0}. \quad (4.16)$$

The dynamical equations for the $C_{mn}(t)$ in De Pisto's method are:

$$i\hbar \dot{C}_{mn}(t) = \sum_{m'n'} V_{mn,m'n'}(z(t)) \exp(i\omega_{mn,m'n'}t), \quad (4.17)$$

where

$$V_{mn,m'n'}(z(t)) = \frac{1}{A} \int e^{-i[\mathbf{G}_{mn} - \mathbf{G}_{m'n'}] \cdot \mathbf{R}} V(\mathbf{r}, z(t)) d\mathbf{R}, \quad (4.18)$$

where the integral is over the unit cell of area A $\omega_{mn,m'n'}$ is defined by:

$$\omega_{mn,m'n'} = (E_{mn} - E_{m'n'})/\hbar. \quad (4.19)$$

The equation of motion in the classical degree of freedom z is given by:

$$\dot{P}_z = - \sum_{mm'n'} C_{mn}(t) \left\{ \frac{\partial}{\partial z} V_{m'n',mn}(z(t)) C_{m'n'}^*(t) \right\} \exp(i\omega_{m'n',mn}t), \quad (4.20a)$$

with

$$\mu \dot{z} = P_z. \quad (4.20b)$$

Eqs. (4.17) and (4.20) are solved simultaneously. The method is thus of the TDSCF type in the way it coupled the classical z mode with the quantum degrees of freedom $\mathbf{R}$. In test calculations for He scattering from LiF(001) at low initial kinetic energies ($E = 20$ meV and $E = 60$ meV), the method produced results in semiquantitative agreement with exact quantum (close coupling) calculations, and with experimental data available for this system. Nevertheless the results are not of the quantitative accuracy required in diffraction calculations, and at the lower energy of 20 meV some of the individual diffraction peak intensities are very seriously in error (the specular $(m, n) = (0, 0)$ peak is too small by a factor of 5). However, the real force and purpose of the method is in applicability to problems which cannot be tackled by more rigorous algorithms. In this context, De Pisto's method proved to be one of considerable computational efficiency and versatility. The introduction of surface vibrations via the GLE scheme is feasible and was pursued in several applications [107–110], and the method was used also to study vibrationally and rotationally inelastic scattering of molecules from surfaces. Thus, Clary and De Pisto [109] carried out calculations on vibrationally inelastic scattering of CO₂ from Pt(111) (in this case the large manifold of rotational states involved was treated in the Sudden approximation). Lee et al. [108] calculated vibrational and rotational transition probabilities in H₂ scattering from Pt(111), and De Pisto et al. [110] calculated physisorption probabilities for H₂, D₂/Cu(100) and H₂/Ag(111), processes in which rotationally inelastic scattering is involved. In fact, in a recent study De Pisto et al. incorporated also the effects of electron-hole pair excitation in the treatment, albeit in a very heuristic way, by introducing pertinent terms in the GLE friction forces and calibrating the latter to fit information available on the electron-hole pair interactions.

De Pisto's method has, however, several limitations and problems. Conceptually, it does not seem satisfactory in general to treat the z -motion classically, while all other molecular degrees of freedom (the $\mathbf{R} = (x, y)$ coordinates, the rotation) are approached quantum mechanically. Such a distinction between the modes seems justifiable physically if, e.g., the energy in the z motion is throughout the collision much higher than that associated with the (x, y) -coordinates. However, this condition is not satisfied at least for some of the systems and scattering conditions to which the method was applied. Obviously, the method is expected to break down when quantum effects in the z -motion are important. One pertinent case is when the potential for the motion of the molecule towards the surface has a barrier, and tunneling in the z -direction occurs. More

frequently found in actual applications are systems that give rise to quantum interference along the z axis. Such cases are well known, e.g. in He scattering from stepped surfaces [98]. Consider, for another example, a model surface consisting of a layer of spheres: The specular scattering from the tops of the spheres can interfere with the scattering from the “valleys” between the spheres. Such effects take place for surfaces of high corrugation, thus the applicability of the method to such systems is questionable. Interference effects in the z motion may also be important in resonance (trapping) processes. Grote and De Pisto [106] drew attention to another difficulty which may arise in the case of trapping: eqs. (4.17), (4.20) couple the z and the $\mathbf{R} = (x, y)$ motions by a TDSCF type of approximation. For at least some of the resonances in He scattering from LiF(001) strong correlations occur between the z and the $\mathbf{R}$ motions, to the point that the above approximation is no longer valid.

In conclusion, the semiclassical method of De Pisto offers an efficient algorithm which is feasible also for collisions of small polyatomic molecules with surfaces. The method seems on the whole justifiable on physical grounds and by the success of test calculations in the regime of direct scattering. Strong correlations between the classical and the quantum degrees of freedom, and also the possible occurrence of interference may lead to failure of the method in cases of collisions that involve trapping.

Mean trajectory semiclassical method This approximation was proposed and pursued in the context of surface scattering by Metiu and coworkers [53,111]. We consider here the method in the specific context of rotationally inelastic and diffractive scattering of molecules from a static, corrugated surface as presented by Jackson and Metui [53]. In this scheme, the molecular center of mass motion is described by semiclassical Gaussian wavepackets, as in Heller’s method, while the rotational degree of freedom is treated quantum-mechanically, using an expansion in a basis of stationary states. The rotational and translational wavepackets are separated by a TDSCF approximation, hence the trajectory describing the propagation of the center of the Gaussian is obtained from a potential function averaged over the quantum-mechanical degrees of freedom. Therefore the name Mean Trajectory Approximation (MTA) used by the authors. Jackson and Metiu [53] employ the following wavefunction for a rotor scattered from a surface:

$$\psi(\mathbf{r}, \theta, \phi, t) = \sum_{\alpha=1}^N C_{\alpha}(t) G_{\alpha}(\mathbf{r}, t) \sum_{i=1}^n C_{\alpha i}(t) Y_i(\theta, \phi) \exp(iE_i t/\hbar), \quad (4.21)$$

where the $Y_i(\theta, \phi) = Y_{jm}(\theta, \phi)$ are the spherical harmonics, used as a basis for the rotational wavepacket, and E_i are the rotational energies. The Gaussian wavepackets have the form (see section 3 on Heller’s method):

$$G_{\alpha}(\vec{\mathbf{r}}, t) = \exp\left\{\frac{1}{\hbar}[\mathbf{r} - \mathbf{r}_{\alpha t})\mathbf{A}_t(\mathbf{r} - \mathbf{r}_{\alpha t}) + \mathbf{p}_{\alpha t}(\mathbf{r} - \mathbf{r}_{\alpha t})]\right\}, \quad (4.22)$$

where the matrix $\mathbf{A}_t$ and the vectors $\mathbf{p}_{\alpha t}$, $\mathbf{r}_{\alpha t}$ are time-dependent. (Note that an additional time dependent complex phase factor which appears in Heller’s scheme is here incorporated in $C_{\alpha}(t)$). The coefficients $C_{\alpha}(t=0)$ are so chosen that the sum $\sum_{\alpha} C_{\alpha}(0)G_{\alpha}(\mathbf{r}, t=0)$ represents a plane wave in the coordinates $\mathbf{R} = (x, y)$ parallel to the surface, and a normalized Gaussian in the z

coordinate. The equations of motion for this method are obtained by substituting (4.21) in the time-dependent Schrödinger equation for the molecule/surface system, and also by simplifying the expressions using the locally quadratic approximation for the potential pertaining to the semiclassical degrees of freedom. The equations for propagating the parameters $\mathbf{r}_{\alpha t}$, $\mathbf{p}_{\alpha t}$, $\mathbf{A}_t$, are thus the same as in Heller's method. The effective potential which appears in these dynamical equations in the present case is:

$$\bar{V}(\mathbf{r}, t) = \sum_i \sum_k C_{\alpha k}^*(t) C_{\alpha i}(t) \exp[-i(\epsilon_i - \epsilon_k)t/\hbar] \langle Y_k | V(\mathbf{r}, \theta, \phi) | Y_i \rangle_{\theta, \phi} \quad (4.23)$$

where $V(\mathbf{r}, \theta, \phi)$ is the full molecule/surface interaction potential and the $C_{\alpha i}(t)$ are the coefficients of the rotational wavefunction defined in (4.9). The dynamical equations for the $C_{ik}(t)$ derived in this method are:

$$i\hbar \dot{C}_{i\alpha}(t) = B_{\alpha}(t) C_{i\alpha}(t) + \sum_k C_{\alpha k} V_{ik}(\mathbf{r}_{\alpha t}) \exp[-i(\epsilon_k - \epsilon_i)t/\hbar], \quad (4.24)$$

where

$$V_{ik}(\mathbf{r}) = \langle Y_i | V(\mathbf{r}, \theta, \phi) | Y_k \rangle, \quad (4.25)$$

$$B_{\alpha}(t) = \frac{1}{2\mu} \mathbf{p}_{\alpha t}^2 - \mathbf{p}_{\alpha t} \dot{\mathbf{r}}_{\alpha t} - i\hbar \text{Tr } \mathbf{A}_t / \mu. \quad (4.26)$$

Thus, in this method eqs. (4.22) for the coefficients of the wavepacket of the “quantum” mode are solved simultaneously and consistently with the Heller equations for the Gaussian parameters $\mathbf{r}_{\alpha t}$, $\mathbf{p}_{\alpha t}$, $\mathbf{A}_t$ that describe the propagation of the semiclassical degree of freedom.

The MTA can be viewed as an improvement of De Pisto's scheme, to which it is closely related, since it does include also quantum interference effects in the motion perpendicular to the surface. For systems where such influence is important, e.g. in diffraction scattering from stepped surfaces, the method can be expected to give results that differ significantly from those of De Pisto. In test calculations by Jackson and Metiu [53] on H_2 scattering from a model of LiF(001), the deviations between the two methods were not large (and the above possible physical cause for substantial differences is not present). However, the Gaussian wavepackets fail to describe resonance scattering, as discussed in section 3, so the MTA can be relied upon only for direct scattering. (This limitation applies also to De Pisto's scheme.) Also cases where the wavepacket breaks up in the z direction, or when tunneling in that coordinate is involved, are outside the scope of the MTA. As in De Pisto's method, the MTA involves a TDSCF approximation through which the full quantum and the semiclassical modes are coupled, and cases involving strong correlations between the two types of degrees of freedom could result in a breakdown of the approximation. This can definitely arise in scattering resonances, but may also occur in some direct collision problems (little is as yet known on this). More exhaustive studies on the validity regimes of both De Pisto's scheme and the MTA seem strongly desirable.

4.2. Excitation of metal electrons by impact of a classical particle

Electron–hole pair excitation in atomic impact on surfaces are processes of fundamental importance in gas–solid interactions. Very little is known on the role of electronic degrees of freedom in energy transfer and chemical reaction processes in molecule–surface collisions, and tentative arguments were presented that such effects could be of major significance. From the methodological point of view central to the present article, such processes are of interest because they demand quantum treatment of surface degrees of freedom. The de Broglie wavelength of electrons occupying the Fermi level of a metal, typically of the order of 1 Å, is too long (on the scale of the interactions involved) for either classical or semiclassical treatments to be valid. Furthermore, it turns out that the classically forbidden region for the electron, somewhat outside the outermost layer of solid ions, plays a dominant role in the process. Excitation of metal electrons in atom–surface collisions thus requires a quantum mechanical treatment of the electrons. Although this subject was pursued in many theoretical studies, e.g. [112–115], nearly all these investigations employed relatively crude methods such as first-order perturbation theory as well as highly simplified models for the atom–electron interactions and for electronic surface states. The most quantitative treatment presented so far for solving the dynamical equations, although carried out for a simplistic model of the electronic states and interactions, was presented by Kirson et al. [116,117]. In this study the metal electrons are described as particles in a potential box, and the independent-electron approximation is assumed to hold for the excitation process during the collision. Thus, the dynamical problem becomes one of a single electron undergoing excitation upon impact of an atom or molecule on the surface. Fermi–Dirac temperature averaging over the initial electron states is carried out in the calculations. The method used involves a TDSCF approximation in which the motion of the colliding atom is described classically, while a time-dependent wavepacket treatment is used for the electron. As stressed above, semiclassical wavepacket algorithms are inapplicable in this case, since the coupling between the atom and the electron comes mainly from the classically forbidden region of the latter particle. Kirson et al. [115] employed a variational principle for solving the time-dependent Schrödinger equation for the electron, having used a variational trial form for the wavepacket with explicit time-dependent parameters, Frenkel’s variational functional is [93,118]:

$$I\{\psi, \theta\} = \int |H\psi - \theta|^2 dz, \quad (4.27)$$

where the integration is over the entire configuration space (a 1-D model is treated here). I vanishes if $\theta = i\hbar \partial\psi/\partial t$. The variational property of $I\{\psi, \theta\}$ is that it is stationary in $\delta\theta$, i.e., to first order in $\delta\theta$:

$$\delta I = 2 \operatorname{Re} \int \delta\theta^* (H\psi - \theta) dz = 0. \quad (4.28)$$

To apply the method a time-dependent trial function is chosen on physical grounds. Assume the initial state $\psi(t_0)$ is given at t_0 , then for a small time-increment:

$$\psi(z, t_0 + \Delta t) = \psi(z, t_0) - i\theta(z, t_0)\Delta t/\hbar. \quad (4.29)$$

Eq. (4.28) is solved for $\theta(z, t_0)$, eq. (4.29) is used and the process is repeated until the entire time-evolution is obtained. In the study of Kirson et al. the following form was used for the 1-D model of an electron in a metal:

$$\psi(z, t) = \int_{k=0}^{\infty} g_k(t - t_0) f_k(z) \exp[iE_k(t - t_0)/\hbar] dk, \quad (4.30)$$

where $f_k(z)$ are stationary eigenstates of the electrons in the metal and $g_k(t - t_0)$ is taken to be a Gaussian in the wavevector, the *center* and the *width* of which are employed as time-dependent variational parameters, and solved for. Kirson et al. [116], carried out such wavepacket calculations of electron-hole pair excitation for He, Ar and H in collisions with a model of a Li surface for collision energies in the range of [0.0–1.0 eV]. In another study, Kirson et al. [117] examined electron-hole pair excitations by this method for the collisions of molecular dipoles, representing CO and HCl, with an Al surface. One of the main conclusions drawn from these studies is that electron-hole pair excitation due to He collisions is of negligible importance (at a collision energy of 0.01 eV, the fraction of energy converted into electron excitations is $\approx 0.2\%$). On the other hand, for H atom collisions with metals the energy transfer can be rather large ($\approx 10\%$ of the incidence energy at 0.01 eV). Also, electron-hole pair excitations can lead to large trapping probabilities in very low energy impact of H on a low-temperature metal. Physically the low excitation probability in He collisions is due to the fact that the He is stopped by the repulsive part of its interaction with the surface far outside the Jellium edge. The short range He/electron interaction then couples significantly to the electron only in the deeply classically forbidden region where electron density, determined by the nonclassical tail of the wavefunction is very low. H has a much nearer turning point to the surface, and its interaction with the metal electron is chemical, and much longer in range. Hence in the case of H the atom/electron coupling occurs over regions of relatively large electron density.

It should be remembered that calculations for physically realistic systems of electron-hole pair excitations in atom/surface collisions were not carried out yet. Evidence from the simplistic models suggests that methods treating the electrons by time-dependent quantum-mechanical wavepackets should prove a very useful tool also for the realistic cases.

4.3. Forced-oscillator methods for the excitation of surface phonons

Several models were proposed for studying phonon excitations which are based on the availability of an analytic solution for the forced harmonic oscillator problem. These models are related to those developed previously for vibrational excitation in gas-phase atom-diatom collisions [100]. A feature common to all these methods is that a classical trajectory $\mathbf{R}(t)$ for the incoming atom is generated using some reference potential, or the full potential function of the system. This, when substituted in the expression for the forces acting on the surface atoms, and when the motions of the latter are treated in the harmonic approximation, gives rise to a forced-oscillator problem for each surface mode. From the solution of the quantum-mechanical forced oscillator problem, probabilities are obtained for the single and multiple quantum transitions in each phonon mode. These methods are time-dependent wavepacket methods only in an implicit sense, as they are based on the availability of an analytic solution for the

time-dependent Schrödinger equation for the forced harmonic oscillator. In practical terms, the methods employ directly the final solutions for the transition probabilities. There are several available forced oscillator methods for phonon excitation in molecular impact on surfaces, which differ e.g. in the choice of the potential function used to determine the trajectory of the molecule, by either including or not including the effect of energy transfer on the trajectory obtained, etc. [119–124]. We describe here the scheme of Park and Bowman [121,122] which is based on the DECENT approximation [100] for vibrational excitation in gas-phase atom–molecule collisions. The procedure of Park and Bowman [121,122] is the following: First a classical trajectory calculation is carried out for the atom-surface collision. In this calculation the solid atoms are initially at rest in their equilibrium positions, i.e. $\mathbf{u}_j(t=0) = 0$, $\dot{\mathbf{u}}_j(t=0) = 0$, where $\mathbf{u}_j$ is the displacement vector from equilibrium of the j atom. Having propagated the trajectory calculation until the end of the collision, the final energy transferred to each phonon mode can readily be computed. The phonon modes are related to the atom displacements by a linear transformation, i.e.

$$Q_{j\beta} = \sum_{\alpha=1}^3 \sum_{l=1}^N (\mathbf{L}^{-1})_{j\beta l\alpha} q_{l\alpha}, \quad (4.31)$$

where $q_{l\alpha}$, $\alpha = 1, 2, 3$ are the Cartesian components of the vector $\mathbf{q}_l = \sqrt{m_l} \mathbf{u}_l$, m_l is the mass of the l -surface atom, and $\mathbf{L}$ is the transformation matrix from atom displacements to normal (phonon) modes. The post-collision energy in any normal mode is obtained from

$$E_{j\beta} = \frac{1}{2} \dot{Q}_{j\beta}^2 + \frac{1}{2} \omega_{j\beta}^2 Q_{j\beta}^2. \quad (4.32)$$

Generally, a whole ensemble of trajectories must be calculated, each corresponding to a different initial lateral position of the incoming atom within the surface unit cell. Denote by $\langle E_{j\beta} \rangle$ the mean energy transfer over the n_T trajectories used. The quantum-mechanical transition probability expression for a forced harmonic oscillator can now be used. It gives the probability $P_{i \rightarrow f}^{(l\alpha)}$ for exciting the $(l\alpha)$ mode from an initial state i to any final state f in terms of the mean energy transfer $\langle E_{l\alpha} \rangle$:

$$P_{i \rightarrow f}^{(l\alpha)} = i!f! \exp(-\epsilon_{l\alpha}) \epsilon_{l\alpha}^{i+f} (K_{i \rightarrow f}^{(l\alpha)})^2, \quad (4.33)$$

where

$$K_{i \rightarrow f}^{(l\alpha)} = \sum_{l=0}^{\min(i,f)} \frac{(-i)^l \epsilon_{l\alpha}^{-1}}{(i-l)!l!(f-l)!} \quad (4.34)$$

and

$$\epsilon_{l\alpha} = \langle E_{l\alpha} \rangle / \hbar \omega_{l\alpha}. \quad (4.35)$$

From the elementary, single mode transition probabilities, one can readily compute multimode transition probabilities, thermally averaged results, etc.

Bowman and Park applied their DECENT-type forced oscillator method to phonon excitation in He scattering from Si(100)-(2 × 1) [121,122]. They found a high specificity of the energy transfer for different types of phonon modes. The geometric nature of the displacement appears to be a critical factor in determining the effectiveness of the coupling to the colliding particle, and it is very different for different groups of modes.

Other forced oscillator methods for phonon excitation were proposed by Billing [119,120] by Newns [123] and by Brenig [124]. Billing's approach involves a TDSCF-type of approximation through which the motion of the projectile and the solid vibrations are coupled. Billing considered also simplification of the basic method by a stochastic approximation for the collision dynamics. Another interesting feature of Billing's approach is his derivation of an effective potential for the colliding atom that depends on surface temperature [119,120].

Newns developed a force oscillator approximation for multiphonon excitation that starts from path-integral representation of the transition probabilities [123]. Explicit, practical expressions are then obtained by applying an expansion based on the stationary phase approximation to the integral. Newns then derives a hierarchy of approximations which include the influence of the energy transfer to the oscillators on the collision trajectory through a certain effective, optical potential [123]. Forced oscillator methods for phonon excitation should be most helpful when applied to collisions with a very low temperature solid, in which case quantum effects may arise. The DECENT and related forced oscillator techniques proved quite successful in applications to various processes of vibrational excitation in atom-molecule collisions. One may reasonably expect satisfactory results also for phonon excitations. Note, however, that high-impact energy collisions may result in very anharmonic shock-wave like excitations as demonstrated e.g. in the case of Hg/MgO(100) [125]. In such cases the forced-oscillator approach is clearly invalid. The validity of the approach remains also to be tested for low energy collisions, when trapping effects can play a major role. A treatment on different footing of the surface vibrations and of the projectile dynamics is probably not justified in this case.

5. Concluding remarks

The weight of available results suffices to establish time-dependent wavepacket methods as tools of great power and versatility for surface scattering calculations. Perhaps the greatest asset of these methods from a computational point of view is that they can be used to tackle problems that involve a continuum of scattering channels. This is an important requirement for many surface scattering problems, obvious examples being processes involving phonon or electron-hole pair excitations. From a broader perspective, not less important is the convenient physical insight and interpretation offered by wavepacket methods which resembles the usefulness of trajectory calculations in the classical regime.

Applications of wavepacket methods are, however, very new and therefore still at a relatively early stage of development. We list several of the open problems, where progress can perhaps be expected before long.

(1) Non-Cartesian coordinates: The available, practical algorithms for both semiclassical and quantum-mechanical wavepacket calculations are confined to Cartesian coordinates. There are several applications of importance, e.g. rotational excitation, which should best be described by

angular degrees of freedom. Early steps for extending wavepacket methods for such coordinates were recently taken (both in the semiclassical framework [128] and the quantum-mechanical one). Progress in using non-Cartesian coordinates, could be of impact on molecule-surface scattering, since the rotational mode is often of major importance. Presently the best approaches for such problems are those mixing a wavepacket treatment of the translational modes with a close-coupling treatment of the rotation.

(2) Resonance scattering: The semiclassical Gaussian method available does break down in this case. The exact quantum-mechanical algorithms (e.g. the Fourier method) were demonstrated to work, but their efficiency is in question, mainly due to the long integration times required and the great sensitivity in the resonance regime to even small numerical errors. Development of new wavepacket methods geared to be effective in the resonance regime seems a challenge of considerable importance. It is conceivable, in our opinion, that e.g. variational methods could prove useful in this respect.

(3) Tunneling effects in surface scattering: Such effects exist in several systems, e.g. due to the corrugation barrier to motion of the colliding atom in the direction parallel to the surface. As with resonance scattering, the available Gaussian semiclassical wavepacket schemes cannot deal with such processes, and “exact” wavepacket algorithms may be very time-consuming when “deep” (i.e. very slow) tunneling is involved. Also in this case new wavepacket methods capable of adequately dealing with such processes are desirable.

(4) Mixed quantum-mechanical/semiclassical wavepacket treatments: It should be very useful in many surface scattering problems to deal with most degrees of freedom (e.g. solid vibrations) by the very efficient Gaussian wavepacket algorithm, while applying the exact quantum treatment to only few coordinates (the scattered particle, for instance). This will be a natural improvement over the mixed classical/quantum-mechanical treatments discussed in Sec. IV. Work along this line is in progress, e.g. [126].

(5) Electron processes: Two types of electron processes may benefit from the applications of wavepacket techniques: Scattering of electrons from surfaces, e.g. LEED [127]; and excitation of surface electrons by collisional impact. The latter topic, collisional excitation of electron-hole pairs was briefly discussed in section 4. The Gaussian semiclassical wavepacket methods are not suitable in general for these electron processes, and the quantum-mechanical grid methods have not yet been applied to such systems. It should be very useful to apply available quantum-mechanical algorithms for these electronic processes and to develop new ones, if necessary.

We believe, in light of the above, that not only will wavepacket methods remain important tools of application to surface scattering, but they are likely to grow as a field of research, with ample scope for improvements of existing schemes and with prospects of completely new approaches being injected.

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