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GAS-SOLID DYNAMICS AT DISORDERED AND ADSORBATE COVERED SURFACES

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This report covers research carried out over the period of the grant. Two areas of activities were pursued: (1) Gas-surface dynamics, and (2) optimal control of molecular motion. In the first category, research was carried out to develop hybrid discrete-continuum techniques to study energy transfer and reactivity of surfaces, including bulk dynamics and surface defects. The second aspect of the research into quantum control theory laid the foundation for the rigorous introduction of theoretical tools capable of designing external optical fields for manipulating molecular scale events. A general formulation of the theory was developed, for treating rotational, vibrational, and electronic degrees of freedom. Both aspects of the research involve the development of formal theoretical techniques, as well as their numerical implementation on a variety of applications.

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ABSTRACT

During the period of this grant, two research activities were pursued. First, an initial development in the area of optimal control of quantum molecular motion was undertaken. Here, the objective was to control molecular motion through the introduction of external optical fields. The research laid the groundwork for introducing rigorous control theory techniques for the purpose of designing the external field, to achieve a variety of molecular scale objectives. The second aspect of the research is in the area of gas-surface dynamics. In this case, the research focused on the development of the comprehensive multiple scattering theory for reactivity at surfaces. The objective was to achieve an approach that was fully quantum mechanical, while still being capable of treating multiparticle dynamics. An integral part of this study was to include the response of the underlying bulk solid.

In both areas of research, a number of interrelated avenues of study were pursued. The goals of the research were achieved, thereby producing a general theoretical framework for both optimal control over molecular motion and gas-surface reactivity. During the period of this grant, one undergraduate, four graduate students, and three post-doctoral associates were supported to carry out the studies.

SUMMARY OF RESEARCH ACCOMPLISHMENTS

Described below is a summary of the particular research accomplishments achieved during the grant period. These activities are divided into two categories - A. Optimal Control of Molecular Motion, and B. Gas-Surface Dynamics.

A. Optimal Control of Molecular Motion

1. Optimal Control of Quantum-Mechanical Systems: Existence, Numerical Approximations, and Applications[1]

The optimal control of the path to a specified final state of a quantum-mechanical system is investigated. The problem is formulated as a minimization problem over appropriate functional spaces, and the well-posedness of this problem is established by proving the existence of an optimal solution. A Lagrange-multiplier technique is used to reduce the problem to an equivalent optimization problem and to derive necessary conditions for a minimum. These necessary conditions form the basis for a gradient iterative procedure to search for a minimum. A numerical scheme based on finite differences is used to reduce the infinite-dimensional minimization problem to an approximate finite-dimensional problem. Numerical examples are provided for the final-state control of a diatomic molecule represented by a Morse potential. Within the context of this optimal control formulation, numerical results are given for the optimal pulsing strategy to demonstrate the feasibility of wavepacket control, and finally, to achieve a specific dissociative wavepacket at a given time. The optimal external optical fields generally have a high degree of structure, including an early time period of wavepacket phase adjustment followed by a period of extensive energy deposition to achieve the imposed objective. Constraints on the form of the molecular dipole (e.g., a

linear dipole) are shown to limit the accessibility (i.e., controllability) of certain types of molecular wavepacket objectives. The nontrivial structure of the optimal pulse strategies emphasizes the ultimate usefulness of an optimal-control approach to the steering of quantum systems to desired objectives.

2. An Operator Method to Solve Differential Equations and Its Application for Solving the Determining Equations for Group Analysis of Differential Equations[2]

A Lie mapping-based operator algorithm combined with the method of characteristics is suggested to provide a general and practical way to solve the determining equations for an invariance group of transformations of a set of ordinary differential equations.

3. Optimal Control of Selective Vibrational Excitation in Harmonic Linear Chain Molecules[3]

A formalism for designing an optical field for selective vibrational excitation in linear harmonic chain molecules is presented, based on optimal control theory. The optimizing functional producing the field designs is flexible, to allow for the imposition of desirable laboratory and theoretical constraints. The designed optimal fields, which successfully lead to local bond excitations, exhibit complex structure on the time scale of 10 fs. Analysis of the optimal fields shows a high degree of cooperativity between the temporal structure of the fields and the dynamical capabilities of the molecules. It is generally impossible, using only spectral information, to devise the optical field needed to selectively excite a local bond in a polyatomic molecule. These results explain why the previous intuitively-based laboratory attempts at site specific chemistry have yielded disappointing results.

4. Systems Analysis at the Molecular Scale[4]

Problems involving physiochemical phenomena on both the microscopic and macroscopic scales often raise similar sets of generic issues and questions. The complexity of these problems is beginning to make inoperative the traditional intuition-based approaches to their analysis and solution. The common characteristics of large, multivariable, complex molecular systems call for a new, more systematic approach to guide theoretical and experimental efforts. With mathematical modeling becoming an essential ingredient in the studies, it is argued that molecular systems analysis, and especially the systematic tools of sensitivity analysis, can play an increasingly important role in understanding and finding solutions to complex, chemically-based problems.

5. Selective Excitation in Harmonic Molecular Systems by Optimally Designed Fields[5]

The goal of selective local excitation in a harmonic system can be achieved via *optimally designed* fields. For achieving a given primary objective of selective excitation in the molecular system, there may be a family of optimal fields that corresponds to a variety of additional physical concerns. The optimal fields *cooperate* with the dynamical behavior of the molecular system, and intramolecular energy transfer can be manipulated to help achieve the objective of selective local excitation. Long duration selective local excitation is studied, and the effect of the molecular polarizability on the optimal fields is considered. In some cases, the presence of polarization will not affect the quality of the finally achieved objective, while in other cases, its significant presence can make more difficult the achievement of selective local excitation.

6. Application of Optimal Control Theory for Selective Vibrational Excitation in Molecules Modeled as Harmonic Physical Systems[6]

The design of optimal electromagnetic fields producing selective vibrational excitation in molecules modeled as harmonic physical systems is shown to be equivalent to minimizing a quadratic cost functional balancing the energy distribution in the molecules and the fluence of the input. In the control problem, two approaches are employed to ensure that the final excitation is attained. One method uses a control strategy that employs a terminal constraint, and in the other approach, the cost functional is augmented with a terminal cost. The asymptotic form of the state and costate is investigated for both strategies in the limit that the final time approaches infinity, and some mathematical results on the form of the Lagrange parameter are presented for the first type of controller. These two results allow for a detailed discussion on the appropriate choice of practical design constants. For the example of a linear chain molecule, an approximation for the eigenvalues of the Hamiltonian matrix is derived for the limiting cases where the weighting on the fluence of the optical field in the cost functional increases to infinity. Also, for the linear chain, it is shown that the eigenvalues are bounded, and that this bound does not depend on the length of the chain.

7. Optimal Control of Selective Vibrational Excitation of Harmonic Molecules: Analytic Solution and Restricted Forms for the Optimal Fields[7]

Analytic solutions of the optimal fields giving selective local excitation in harmonic molecules are presented, and calculated by a numerically stable algorithm. It is shown that the optimal fields can be decomposed into a finite number of monochromatic laser fields, with the following properties: (a) the number of component frequencies is equal to the number of normal modes of the molecule; (b) the component frequencies

go to the molecular vibrational normal mode frequencies in the limit of low amplitude; (c) there is an inverse relationship between the amplitude of the fields (as controlled by the weighting factor for the field fluence term) and the time T at which the objective is reached; and (d) there exists a limiting form for the optimal fields as the controlling time $T \to \infty$ (which had been observed empirically in previous work, and now has a rigorous mathematical basis). The intensity of the component laser fields, and thus the optimal field, can be reduced to any desired level with a corresponding lengthening of the pulses. Thus, by varying the design criteria, one may determine a corresponding entire family of optimal fields with each member equivalently leading to the desired final local excitations. The optimization procedure clearly illustrates the trade-off between optimal pulse length and amplitude. In order to try and achieve the control objectives with consideration of laboratory constraints on the laser fields, a formalism is presented for designing the optimal fields with constrained functional forms. An illustration based on linear chain molecules shows that the objectives may be quite well achieved by using realistically constrained optimized fields.

8. Quantum Mechanical Optimal Control of Physical Observables in Microsystems[8]

A quantum mechanical formalism for the optimal control of physical observables of microsystems is developed. The computational procedure for numerical implementation is presented. Three illustrative examples with a model Morse oscillator show that optimal pumping fields can be found to reach the physical objectives: selective excitations, steering a system to a specified state, and breaking a bond.

9. Optimal Control of Bond Selectivity in Unimolecular Reactions[9]

The optimal control theory approach to designing optimal fields for bond-selective unimolecular reactions is presented. A set of equations for determining the optimal fields, which will lead to the achievement of the objective of bond-selective dissociation is developed. The numerical procedure given for solving these equations requires the repeated calculation of the time propagator for the system with the time-dependent Hamiltonian. The splitting approximation combined with the fast Fourier transform algorithm is used for computing the short time propagator. As an illustrative example, a model linear triatomic molecule is treated. The model system consists of two Morse oscillators coupled via kinetic coupling. The magnitude of the dipoles of the two Morse oscillators are the same; the fundamental frequencies are almost the same, but the dissociation energies are different. The rather demanding objective under these conditions is to break the stronger bond while leaving the weaker one intact. It is encouraging that the present computational method efficiently gives rise to the optimal filed, which leads to the excellent achievement of the objective of bond selective dissociation.

10. Optimal Control of Molecular Motion: Nonlinear Field Effects[10]

This paper is concerned with some of the consequences of strong optical fields and corresponding nonlinear field effects upon the optimal control of molecular motion. It is shown that the presence of nonlinear interactions can give rise to the existence of multiple field solutions to the problem of optimally controlling molecular motion, where each of the fields produces exactly the same physical effects on the molecule. Secondly, it is argued that nonlinear field interactions may either act as a constraint on the control of molecular motion or an enhancement of that process, depending on the circumstances. These variation phenomena are

illustrated through consideration of control over the motion of harmonic molecules.

11. Optimal Control of Selectivity of Unimolecular Reactions Via An Excited Electronic State with Designed Lasers[11]

A molecular system is steered on the ground electronic surface from the initial state to a desired target state at time T via an excited electronic state by using optimally desired coherent laser fields. A new algorithm based on the SU(2) algebra is developed to solve the time-dependent Schröedinger equation for the systems involving two electronic states with time-dependent Hamiltonians. For the design of optimal fields with restricted functional forms, the rotating wave approximation is introduced for significantly reducing the computational effort. As a model of unimolecular reactions, a double-well switching problem is studied. The objective is to move the system from one well to the other. It is found that the unrestricted optimal fields which successfully move the system from one well to the other at the target time T are complicated. The objective is achieved through the cooperative interaction between the system and the driving field. The optimal fields with restricted functional forms, such as a train of Gaussian pulses with a single carrier frequency, can also lead to the satisfactory achievement of the objective. However, except for some propitious cases, a simple two-pulse pump-dump scheme does not achieve the control objective satisfactorily. Possible further potential applications are discussed briefly.

12. Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules: A Worst Case Analysis[12]

Recent research has demonstrated that optimal electromagnetic fields capable of producing selective vibrational excitation in molecules can be

designed, employing linear quadratic control methods using a cost functional that balances the energy distribution in the molecules, the fluence of the optical field, and a final cost to insure the desired excitation. Practical computations of molecular control theory for large molecules, especially with anharmonic potentials, become difficult to obtain due to the increased dimensionality and the accompanying uncertainty in the Hamiltonian. In this paper, we reduce the complexity of the problem by treating a portion of the molecule, including the target and optical dipoles, in full detail, while the remainder of the molecule is modeled as an external disturbance of bounded energy. The optimal control field now *minimizes* the cost functional which is simultaneously *maximized* with respect to the energy constrained external disturbance to assure robustness. This optimal design process is commensurate with taking the most pessimistic view of the disturbance. This conservative view was born out in the numerical calculations, such that practical laboratory studies should reach results much improved over the worst case design. As an illustration, we investigate disturbances of varying energy content for a truncated 20-atom molecule chain, where the uncontrolled remainder of the chain is the source of the system disturbance. The sensitivity of the system with respect to the disturbance was found to be strongly dependent on the distance of the disturbance to the target bond and the dipole arrangement. In addition, in the range of physically reasonable disturbance energy, the optimal field could be accurately predicted from an asymptotic expansion involving only the reference undisturbed case. Although the present research takes advantage of linear system techniques, the same robust optimal control procedure can be generalized to nonlinear systems by a variety of means.

13. Optimal Control of Molecular Motion[13]

This paper presents an overview of recent developments concerning the introduction of optimal control techniques into the molecular domain. The goal of this research is to identify the degree to which molecular dynamics may be controlled by external optical fields and provide a systematic means for designing optical fields for this purpose. Preliminary illustrations of molecular optimal control theory have been considered, involving rotational, vibrational, and electronic degrees of freedom. With the ultimate objective being laboratory implementation of the designed fields, the robustness of the designs is a critically important issue. These various topics are reviewed in this paper.

14. An Application of Minimax Robust Optimal Control Theory for Selective Vibrational Excitation in Molecules[14]

In recent investigations, control theory was applied to design electromagnetic fields capable of producing selective vibrational excitation in molecular systems. This approach has been applied to linear or nonlinear classical approximations of molecular systems or to quantal systems using distributed cost functionals. Practical computations of molecular optimal control theory for large molecules, especially with anharmonic potentials, become difficult due to the increased dimensionality and the mixed nature of the boundary conditions. This research proposes to approach the control design for such systems by treating a portion of the molecule containing the target and dipole bonds in full detail, while the effect of the remainder of the system is modelled as a disturbance of limited energy. The optimal field minimizes the cost functional, which is simultaneously maximized with respect to the disturbance. Such assumptions give rise to a robust controller akin to H_∞ theory of robust estimation. We investigate the various field designs for truncated harmonic systems associated with different disturbance energies

and demonstrate that the existence of the solution to the associated Ricatti equation insures the existence of the equilibrium game point. In addition, in the range of physically reasonable disturbance energy, the optimal field could be accurately predicted from an asymptotic expansion involving only the undisturbed reference case. As an application, we show the optimal field design for a 20-atom truncated molecular chain containing both the target bond (the 5th bond) and the dipole bonds (1st and 9th), where the disturbance only affects the end bond of the system attached to the remainder of the chain. In an effort to improve on the efficiency of the bond energy deposition, we investigate shortened target times and also a 40-atom truncated chain. This approach presents very conservative estimates of possible disturbances, but provides insight into the sensitivity of different configurations with respect to external disturbances. The mini-max approach can be generalized to nonlinear molecular systems by modelling the original system as a linear system plus an energy-constrained disturbance.

15. Effect of Defect Structures on Chemically Active Surfaces: A Continuum Approach[15]

A continuum approach is used to analyze the effect of defect structures on chemically active surfaces. The model comprises a linear diffusion equation with adsorption and desorption in which the defect structures are represented by nonlinear localized-reaction terms. The issue of multiple steady states and stability is treated, and a novel procedure is outlined that uses conformal mapping to derive stability criteria for these localized reaction diffusion equations. This conformal mapping procedure also provides insight into how the various physical processes affect the stability of the system. A class of reactive-trapping models is considered in which defects are assumed to act as sinks of material that ultimately desorbs as a chemical product. Other features

included in the model are nonlinear enhanced reactivity with concentration, and saturation effects. The continuum assumption is tested by direct comparison with a discrete reactive-trapping model and found to be a remarkably good approximation, even when the number of interdefect sites is as low as 20. We investigate the effect of relative defect locations on the balance between the desorptive processes that take place on the surface. The effect of defect locations on desorption is analyzed by considering symmetry-breaking perturbations to the defects in a periodic lattice. Two regimes of desorption are identified, depending on the level of adsorption on the surface and the defect spacing:

(i) Competitive - Defects that are moved closer by the perturbation *compete* for material, which reduces the trapping efficiency of the defect lattice and increases the bulk desorption rate; by considering the bulk desorption rate to be a function of the defect locations, we conclude that the situation of equally spaced defects is a local minimum of this function.

(ii) Cooperative - Defects that are moved closer by perturbation in this regime act *cooperatively* to reduce the saturation level locally, which enhances the trapping efficiency of the defect lattice and reduces the bulk desorption rate.

In this complex environment of competing physical effects, it would be difficult to determine the dominant process without the analysis presented here. In order to determine whether these phenomena persist when the defects undergo finite random perturbations, we solve the continuum equations numerically using the boundary-element technique. The phenomena identified by the small perturbation case do persist when finite defect variations are considered.

16. An Analysis of the Effect of Defect Structures on Catalytic Surfaces by the Boundary Element Technique[16]

The boundary element (BE) technique is used to analyze the effect of defects on one-dimensional chemically active services. The standard BE algorithm for diffusion is modified to include the effects of bulk desorption by making use of an asymptotic expansion technique to evaluate influences near boundaries and defect sites. An explicit time evolution scheme is proposed to treat the non-linear equations associated with defect sites. The proposed BE algorithm is shown to provide an efficient and convergent algorithm for modelling localized non-linear behavior. Since it exploits the actual Green's function of the linear diffusion-desorption process that takes place on the surface, the BE algorithm is extremely stable.

The BE algorithm is applied to a number of interesting physical problems in which non-linear reactions occur at localized defects. The Lotka-Volterra system is considered, in which the source, sink, and predator-prey interaction terms are distributed at different defect sites in the domain and in which, the defects are coupled by diffusion. This example provides a stringent test of the stability of the numerical algorithm. Marginal stability oscillations are analyzed for the Prigogine-Lefever reaction that occurs on a lattice of defects. Dissipative effects are observed for large perturbations to the marginal stability state, and rapid spatial reorganization of uniformly distributed initial perturbations is seen to take place. In another series of examples, the effect of defect locations on the balance between desorptive processes on chemically active surfaces is considered. The effect of dynamic pulsing at various time-scales is considered for a one species reactive trapping model. Similar competitive behavior between neighboring defects previously observed for static adsorption levels is shown to persist for dynamic loading of the surface. The analysis of a more

complex three-species reaction process also provides evidence of competitive behavior between neighboring defect sites. The proposed BE algorithm is shown to provide a useful technique for analyzing the effect of defect sites on chemically active surfaces.

17. Modelling the Effect of Changes in Defect Geometry on Chemically Active Surfaces by the Boundary Element Technique[17]

The boundary element (BE) technique is used to analyze the effect of defect structures upon desorption processes in two-dimensional chemically active surfaces. The standard BE algorithm for diffusion is modified to incorporate the effects of bulk desorption, and an explicit scheme is proposed for the treatment of the non-linear equations associated with localized defect structures. The BE algorithm proposed here provides an elegant representation of the effects of localized non-linear reactions which allows arbitrarily oriented defect structures to be modelled without having to perform mesh deformation.

A class of trapping reactions is assumed to occur along defect structures, and the effect of changes in defect geometry on the balance between the desorptive processes is explored. A number of interest competitive/cooperative phenomena are observed to occur for the various shapes of defect geometry, including strong intrinsic competition in circular defect structures that form islands of nearly constant concentration, a redistribution of material along V-shaped defect structures in a way that reflects relative competitiveness of defects on opposite sides of the defect structure, and a reduction of competitiveness for defect distributions that are less regular in shape.

The proposed BE algorithm is shown to provide a useful technique for modelling the effect of defect structures on chemically active surfaces.

18. Calculation of Scattering Wavefunctions by a Numerical Procedure Based on the Møller Wave Operator[18]

We present a procedure that numerically evaluates the scattering wavefunction. The solution to the time-dependent Schröedinger equation is calculated by a novel combination of: (a) the Møller operator of scattering theory, (b) time-dependent wavepackets whose shape is unconstrained, and (c) efficient wavepacket propagation on a dynamically-adapted grid. The superposition of packets appropriate to the scattering boundary conditions yields the full wavefunction, from which scattering amplitudes are then obtained. Since the procedure does not make use of basis-set expansions, its computational cost is independent of the number of open channels. It explicitly calculates the wavefunction not only in the asymptotic region, but also within the interaction region, so it allows one to evaluate additional information beyond the scattering amplitude, as well as the functional sensitivity of transition probabilities with respect to changes in the potential. Applications here are illustrated by two simple examples: one-dimensional tunneling through a potential barrier, and elastic scattering from a one-dimensional periodic surface (i.e., a two-dimensional scattering problem). Extensive applications to imperfect surfaces, including sensitivity analysis, are separately presented in other research.

19. Evolution of Reactions on Surfaces Exhibiting Defect Structures[19]

This paper considers the time and spatial dependent behavior of an active surface exposed to two reactants which may diffuse on the surface, desorb, and also react. The surface is assumed to contain defect structures corresponding to either inherent lattice faults or foreign material on the surface. A number of case studies are examined corresponding to different assumptions about the desorption and kinetic

characteristics of the defect sites. The surface concentration profiles are examined to gain physical insight into the competing surface processes. The net effect of surface defects on chemical production rates was examined by integrating the local production rate over a test region on the surface. Of special interest was the study of the poisoning effective of the product species on the diffusion and reaction of the reactants. The reaction-diffusion equations of the models were solved by the alternating direction collocation technique, which shows promise for providing an efficient numerical procedure capable of handling practical large scale problems.

20. A Hybrid Model for Vibrational Energy Transfer at the Gas-solid Interface: Discrete Surface Atoms Plus a Continuous Elastic Bulk[20]

We introduce a discrete-continuum hybrid treatment of solid vibrations in order to describe the collisional excitation of adsorbate and defect modes by atom impacts. The inhomogeneous surface is represented by: (a) one or more atom clusters corresponding to the defect sites and their immediate neighbors, which are harmonically coupled to (b) an elastic continuous bulk. The model thus aims at reproducing the long-wavelength spectrum of the lattice, as well as the high-frequency localized modes contributed by adsorbates and surface defects. The hybrid model is tested against lattice results in one-dimensional simulations that allow for analytic solution of the surface motion (which would be unfeasible for three-dimensional imperfect lattices); hybrid and lattice results are thus compared in detail under identical conditions. The model is also evaluated under the worst possible conditions for the continuum approximation, since collinear collisions correspond to three-dimensional situations in which the transferred momentum and, therefore, short wavelength excitations are maximal. Comprehensive tests are presented for He atoms scattering from CO chemisorbed on Pt and on Ni substrates, and

from N_2 adsorbed on W. The scattering dynamics is treated by time-correlation functions of the transition operator previously developed for polyatomic targets [*J. Chem. Phys.*, 84, 3162 (1987); 85, 2300 (1987); 86, 750 (1987)]. All the energetically open states are thus incorporated, as well as the thermal average over initial states, without need of basis-set expansions. Distributions of transferred energy are presented as would be observed in a one-dimensional scattering "experiment" using impact energies between 0.1 and 1 eV and with the solid at non-zero temperature. The collisional spectra obtained from the hybrid models are found to be in excellent agreement with those of the corresponding inhomogeneous lattices throughout wide ranges of impact velocity, surface initial temperature (including 0 K) and transferred energy. The results indicate that discrete-continuum treatments provide a powerful tool for analyzing the transfer of energy at the gas-adsorbate-solid interface.

21. Sensitivity of Elastic Gas-surface Scattering to the Potential: A Functional Sensitivity Approach Based on Wave Packet Dynamics[21]

Functional sensitivity analysis is used to study the effect of potential structure upon the elastic scattering of He atoms from a one-dimensional surface. The calculations are implemented by computing the total scattering wave functions from a wave packet calculation by a Møller wave operator method. The functional sensitivities of the various diffraction probabilities for several angles of incidence and surface corrugation are studied. The method is extended to examine the role of potential structure for a surface with adsorbed impurities. It was observed that the various diffraction processes draw from local regions of the potential in very different ways. At high angles of incidence for back scattering, and particularly, for strong surface corrugation, the

large protruding portions of the surface cast a "shadow" of lower dynamical sensitivity. Results of this type should ultimately be insightful for the inversion of experimental data to obtain the interaction potential.

22. Applications of Stochastic Mechanics to Polyatomic Lattices[22]

Stochastic quantization in the sense of Nelson provides an alternative interpretation of some aspects of quantum mechanics in the coordinate representation, and it was combined recently with the Ford, Kac, and Mazur approximation [*J. Math Phys.*, **6**, 504 (1965)] for large lattices to construct a quantum analog to the Brownian motion process. In this paper, a similar approach is applied to model the effect of temperature fluctuations in a one-dimensional ordered chain of atoms with nearest-neighbor linear forces. However, we do not make use of the FKM approximation, and as a consequence, the statistical properties of the involved processes are exactly determined by the lattice force field. In particular, we evaluate the covariance matrix for the fluctuations, and we examine its high- and low-temperature behavior. Because of the translation invariance of the interaction potential, the covariance matrix for the fluctuations becomes singular, implying that the associated probability density has equal density along the zero eigenvector of the interaction matrix. This behavior is readily interpreted in terms of the motion of the center of mass of the system, which corresponds to a stochastically perturbed translation, while all other modes are bounded with a probability of 1. As is well known, the transformation to internal (bondlength) coordinates leads to a Hamiltonian specified by a nonsingular interaction matrix. We examine the variance of the fluctuations for the internal coordinates, and we show that in the high-temperature limit, the result agrees with that of classical statistical mechanics. Both the position and bondlength of the surface atom decrease with time as is

expected for a semi-infinite lattice. However, the position of the surface atom is less dependent on substrate-atom positions than is the surface bondlength on substrate bondlengths. Finally, the autocorrelation function of the surface bondlength in the case of a semi-infinite lattice limit is investigated for low- and high-temperature limits.

23. Matrix Elements of the Transition Operator Evaluated off the Energy Shell: Analytic Results for the Hard-core plus Square-well Spherical Potential[23]

An analytic expression is presented for the off-shell T-matrix elements for scattering from the spherical hard-core plus square-well potential. Various analytical properties of the off-shell T matrix, such as symmetry and unitarity, are examined. The typical behavior of the off-shell T matrix is shown numerically. It is found that the behavior strongly depends on the three independent quantities (i.e., the energy, and the initial and final momenta) which can be off the energy shell. These results, combined with multiple-scattering theory, can be used to study high-energy many-body collision processes, such as collision-induced dissociation.

24. Discrete-continuum Hybrid Model for Gas Surface Collisions I: Trajectories with Single Multiple Collisions and Capture[24]

This paper presents a model and calculations for the scattering of atomic and molecular beams from solid surfaces. In this model, the solid is represented as an elastic continuum for the energy exchange processes and phonon propagation, while the particulate nature of the projectile, as well as the corrugation due to the discreteness of the solid lattice is retained. This hybrid continuum/discrete representation of the solid is a suitable description for relaxation dynamics of adsorbates on surfaces and low energy collisions of gas particles with surfaces. The projectile-

surface interaction is described in terms of compliance coefficients which are effective spring and damping constants for the solid. This makes the handling of the solid extremely practical. The full set of compliance coefficients for all possible surface forces and moments are given. As applications, trajectory calculations are presented, using the parameters of the He + LiF system, as well as models with deeper wells and softer solids. Although with the parameters of the He + LiF system, only single collisions and elastic wave excitation are observed, the model calculations display additional interesting phenomena such as multiple collisions, resonances, and capture of the projectile.

25. Discrete-continuum Hybrid Model for Gas Surface Collisions II: Closed Form Perturbation Solutions for Single Collisions[25]

A perturbation scheme for the scattering of particle beams from single crystal surfaces is presented. The procedure is based on the assumption that displacements of the lattice points are small compared to the lattice spacing, and that surface corrugation is weak. The phonon interaction is accounted for by representing the crystal as an elastic continuum following the hybrid model introduced in the preceding paper. The projectile-surface interaction is described in terms of compliance coefficients which are effective spring and damping constants of the solid. This makes the handling of the solid extremely practical. The perturbation theory and the linear solid model permit the study of collision-induced waves and the thermal waves separately. The total energy exchange is obtained as the sum of the energy exchanges between the projectile and the two types of waves. The perturbation solution yields closed form expressions for the energy exchange, with both the exponential repulsive and Morse potentials. These results compare favorably with the exact (i.e., numerical) calculations of the preceding paper, when multiple collisions, resonances, and capture are absent. The availability of

explicit expressions for the energy transfer permits the calculation of the necessary thermal averages in closed form as well. Quantitative results indicate in addition, that for the Morse potential, results are markedly different from those with the purely repulsive cases that is commonly used for its simplicity. At high energies, the results of the two potentials converge, as expected.

26. Sensitivity analysis of the potential for elastic gas-solid scattering from surface defects[26]

The role of surface defects in elastic gas-solid collisions is investigated by means of a recently developed numerical procedure based on the Møller operator and wavepackets. Since the procedure explicitly evaluates the scattering wavefunction, it yields the probabilities for scattering from the given initial state into all possible final states, as well as the sensitivity of the probabilities with respect to variations in the gas-surface potential. Probabilities and their functional sensitivities are calculated fro a simulated Pt surface exhibiting various configurations of vacancies: isolated sites, "interacting" di-vacancies, and closely packed tri-vacancies. The functional sensitivities indicated which regions of the gas-defect-solid potential are most relevant to the scattering dynamics. The resultant physical insight should be ultimately helpful for inverting experimental data to obtain the interaction potential.

27. A Hybrid (Discrete-Continuum) Model for Vibrational Energy Transfer at the Gas-Solid Interface: II. The Evolution of Solid-Surface-Atom Displacements[27]

We further analyze a recently developed hybrid treatment of the vibration of inhomogeneous surfaces, whereby surface defects and their surroundings are properly treated as discrete atoms while the remainder of

the solid is represented by an elastic continuum of equivalent mass-density and elasticity. Such a model is aimed at describing collective vibration (i.e., long-wavelength lattice phonons) as well as defect-localized excitation in vibrationally-inelastic gas-surface scattering. We assess how the hybrid model reproduces the response of the surface by following the quantum-statistical moments of atom displacements as the collision progresses. Hybrid and lattice results are compared in detail using one-dimensional simulations of diatomic molecules chemisorbed on metal substrates. The results indicate that the discrete-continuum approach can provide a powerful tool for describing collisional excitation of defect-laden surfaces within a fully quantal treatment of surface motion.

PUBLICATIONS RESULTING FROM THE RESEARCH

A. OPTIMAL CONTROL OF MOLECULAR MOTION

1. Optimal Control of Quantum-Mechanical Systems: Existence, Numerical Approximations, and Applications, A. Peirce, M. Dahleh, and H. Rabitz, Phys. Rev. A, 37, 4950 (1988).
2. An Operator Method to Solve Differential Equations and Its Application for Solving the Determining Equations for Group Analysis of Differential Equations, S. Shi and H. Rabitz, Appl. Math. Comp., 25, 101 (1988).
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