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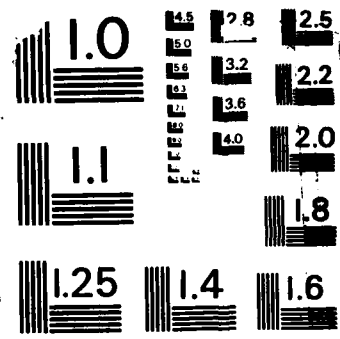
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The research under this grant was aimed at several closely related objectives involving studies in chemical dynamics and chemical kinetics. In the case of chemical dynamics, both gas-phase and gas-surface molecular collisions were studied with a special emphasis on the development and application of new techniques. In particular, an average wavefunction procedure was developed especially designed for treating the scattering from complex targets. Applications were made to gas-phase scattering as well as gas-surface scattering in the presence of defects. In the latter case, the focus was on the role that natural defects or adsorbed species have with regard to their influence on the chemical and physical properties of surfaces.

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22a. NAME OF RESPONSIBLE INDIVIDUAL
Major Larry P. Davis

22b. TELEPHONE (Include Area Code)
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FINAL TECHNICAL REPORT

**GAS-SOLID DYNAMICS AT DISORDERED AND
ADSORBATE COVERED SURFACES**

Sponsored by **AFOSR-84-0106B**

Herschel Rabitz

Herschel Rabitz

**Department of Chemistry
Princeton University**



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ABSTRACT

[The research under this grant was aimed at several closely related objectives involving studies in chemical dynamics and chemical kinetics. In the case of chemical dynamics, both gas-phase and gas-surface molecular collisions were studied with a special emphasis on the development and application of new techniques. In particular, an average wavefunction procedure was developed especially designed for treating the scattering from complex targets. Applications were made to gas-phase scattering as well as gas-surface scattering in the presence of defects. In the latter case, the focus was on the role that natural defects or adsorbed species have with regard to their influence on the chemical and physical properties of surfaces.] An enhanced degree of momentum transfer was found in the presence of surface defects. Scattering of helium atoms off of surface bound diatomic molecules was studied with the underlying lattice being in a finite temperature to include phonon effects. In this case, the strong phonon coupling was found to have a significant effect on the gas-surface energy transfer processes. In addition to this dynamics work, continuing development and applications of sensitivity analysis techniques were pursued for problems in chemical kinetics. Special applications of concern involve problems in combustion and atmospheric chemistry. Finally, research was also carried out in several other related areas stemming from these primary studies. In particular, applications of filtering theory to problems in quantum mechanics and chemical kinetics were investigated. This resulted in a new means for investigating these phenomena as well as providing insight into the degree that laboratory data may be inverted back to more fundamental information. Finally, a variety of variational techniques and their generalizations were explored for application to problems arising in quantum mechanics as well as other areas. Given below is a summary of these various research projects.

1. Semiclassical Perturbation Theory for Atom Scattering from Surfaces with Defects¹

Presented here is an extension of semiclassical perturbation theory (SCP) to gas-surface scattering incorporating surface defect sites with the restriction that the defects be diffuse enough such that they have no direct interaction. The formalism is applied to a corrugated surface with atoms missing, modelling a nearly complete layer of atoms adsorbed on a metal surface. The results show the redistribution of the Bragg intensities to a continuum of momentum transfers about the former peaks.

2. Atom Molecule Scattering with the Average Wavefunction Method²

The average wavefunction method (AWM) is applied to atom molecule scattering. In its simplest form the labor involved in solving the AWM equations is equivalent to that involved for elastic scattering in the same formulation. As an initial illustration, explicit expressions for the T-matrix are derived for the scattering of an atom and a rigid rotor. Results are presented for low energy scattering and corrections to the Born approximation are clearly evident. In general, the AWM is particularly suited to polyatom scattering due to its reduction of the potential in terms of a separable atom-atom potential.

3. Applications of Filtering Theory for the Inversion of Temporal Chemical Systems³

This paper presents a method for inverting temporal experimental data from chemical models to obtain estimates of unknown parameters. Most of the models under consideration are deterministic and we assume that the measurements obtained from experimental observations are represented as the solution of a differential equation containing the variables of the model. To incorporate any extraneous laboratory effects that are not included in the model, we assume that these equations are perturbed by a white noise process so that the measurements become time dependent stochastic variables. A particular measurement is then equivalent to a realization of these variables and applying stochastic estimation theory this realization can be used to obtain estimates of the unknown parameters in the model. As an example of this estimation method, we consider chemical kinetics models with various observational equations and construct an estimator for the unknown reaction rate constants. We also show the estimators for the structural constants in a laser model depending on the representation of the experimental data. In some cases the observations are simulated numerically and we present the parameter estimates as a function of time. The efficiency of the estimation process is calculated as the ratio of the a-posteriori variance of the parameter estimator and the Rao-Cramer lower bound. Some issues in the numerical implementation of the filtering equations are discussed and a comparison is made between the minimum least square estimation method and the filtering method.

4. An Application of Filtering Theory to Parameter Identification in Quantum Mechanics⁴

In this paper we present a method for inverting observations on quantum mechanical systems to obtain estimates of unknown parameters residing in the Hamiltonian. The quantal system is represented in matrix form with respect to a chosen basis and it is assumed that the associated expansion coefficients are truncated to a finite dimension. The uncontrollable laboratory noise will be modelled by means of an inhomogeneous white noise process so that the experimental observations are represented as stochastic variables satisfying a stochastic differential equation. We will assume that measurements obtained from an experiment are now equivalent to a realization of these stochastic variables. It is known from filtering theory that the minimum variance estimate of the unknown parameters in the quantal model is now given by the expectation of the unknowns conditional on this realization. This estimator can be calculated analytically from the associated a-posteriori probability density if the original quantal system does not contain any random elements. We calculate this probability density for the unknown matrix elements and we demonstrate that for a full Hamiltonian matrix the asymptotic variance of the parameter estimator decreases as a third power in time and a fourth power in the initial conditions. Some differences with the minimum least square method are mentioned and a few issues of numerical implementation are discussed.

5. Time-dependent Resonant Fluorescence Spectrum of Two-level Atoms in Strong Short Pulsed Fields: A Nonperturbative Treatment⁵

A study is presented for the time-dependent resonance fluorescence spectrum of two-level atoms irradiating by hyperbolic secant pulsed lasers, allowing for an arbitrary spontaneous emission rate from the excited level to the ground one. Novel features of the temporally transient spectrum have been observed. The spectrum is dominated by a central peak which oscillates in time and is accompanied by multiple side peaks. Asymptotically (i.e., after the pulse has passed) the side peaks disappear leaving a tail at the line center which displays a Lorentzian shape of width equal to the sum of the spontaneous emission rate and the width of the spectrometer considered and of magnitude proportional to the instantaneous intensity of the pulse. The exact behavior of the spectrum is dictated by the area of the engaged pulse and by how the atom is prepared initially. In particular, it is found that the spectrum can be asymmetric even when the laser is tuned to exact resonance if the atoms are initially prepared in a certain class of proper coherent states, irrespective of how the field amplitude may vary in time. An analysis of the spectral symmetry without resorting to any explicit evaluation of the spectrum itself is also presented. Furthermore, the associated optical Bloch equations are solved analytically in terms of hypergeometric functions in a similar manner to that done previously for the undamped two-level Schrodinger equation. Specific numerical results are presented for pulses of area equal to π , 2π , 3π , 4π and 5π for both symmetric and asymmetric cases.

6. Sensitivity Analysis of Combustion Systems⁶

This paper presented an updated review of how sensitivity analysis techniques may be used to analyze chemically reacting flows with a particular emphasis on combustion phenomena. The paper included mathematical details as well as a particular emphasis on anticipated new directions for the field. Selected numerical examples were included to illustrate the material.

7. Vibrational Energy Transfer at the Gas-solid Interface: The Role of Collective and of Localized Vibrational Modes⁷

We present a study of energy transfer (kinetic to vibrational) in collisions of atoms with diatomic molecules adsorbed on the surface of a metal substrate, for hyperthermal collision energies (0.1 to 1.0eV). In order to make the many-body problem computationally tractable, atomic motions are restricted to one spatial dimension and the combined diatomic-metal target is modelled by a linear chain of coupled harmonic oscillators, so that vibrations of the target can be solved analytically for any arbitrary number of atoms. The collision is described in the semiclassical limit appropriate for hyperthermal velocities: translation of the projectile is obtained from a classical trajectory, while vibration of the target is treated quantum mechanically. The intensity of scattered atoms is obtained from the time-correlation function of the semiclassical transition operator. As a result, the intensity is evaluated analytically without need of internal-state expansions, and it includes the quantum-statistical average over the distribution of initial phonon states at nonzero temperature. The theory is applied to He projectiles scattered from OCPt_x , OCNi_x , N_2W_x , and from the pure metals.

The results are presented in the form of energy-loss spectra simulated for a typical experimental detector of finite resolution. The calculations are done with realistic values of force constants and He-target potentials. Hence, the one-dimensional model contains the basic vibrational features of the gas-solid interface, namely: a very large number of low-frequency modes involving collective vibrations of the target atoms and a few high-frequency modes whose atomic displacements are localized near the surface (the latter roughly correspond to the vibration of the free diatomic and to stretching of the diatom-substrate bond). The simulated spectra show rich structure due to many-quantum excitations of collective and localized modes. We show how the structure is related to the eigenfrequencies and eigenvectors of the target, and we examine how the contributions of each mode vary with collision energy and target temperature. We find that excitation of localized modes follow a Poisson distribution and only the first few transitions are significantly excited. In contrast, collective modes undergo many-quantum transitions characterized by a quasicontinuous and Gaussian distribution of energy transfer. We derive simple expressions that explain the amounts of energy transferred to each mode in terms of the physical parameters (force constants, atomic masses, temperature, thickness of the target, and strength of the potential). The simulations indicate that vibrational transitions of the adsorbed molecule can be resolved from the background of substrate phonons using present technology. They also suggest that lattice phonon structure could be observed using a thin substrate film weakly coupled to an underlying support. We also find that the spectrum is quite sensitive to small variations of the projectile-adsorbate potential, so that scattering experiments can yield information about how intermolecular forces are changed by chemisorption.

8. Autocorrelations in the Center Manifold of Dissipative Systems⁸

The phase-space contraction for the systems under consideration corresponds to an asymptotic-center manifold functional dependence of fast-relaxing variables X_f, j 's on the slowly-relaxing ones, the X_s, i 's. The propagation of perturbations along the center manifold is obtained from the Green-function sensitivity matrix. Scaling and self-similarity relations among the matrix elements are found. This fact allows for a simplification in the computation of the $X_f, j - X_f, j$ and the $X_s, i - X_s, i$ autocorrelations. The validity of the results is confirmed in two different contexts: (a) An analytical derivation of power spectra at the onset of periodic instabilities is performed. We demonstrate that in the infinite relaxation time limit for slow variables, the power spectra for all the X_f, j 's converge to the same distribution. This result is in accord with previous computations. (b) The power spectrum for a randomly driven anharmonic damped oscillator is computed at the asymptotic-center manifold regime and tested *vis-a-vis* previous plots exhibiting a very good agreement.

9. **Fundamental Sensitivity Propagators in Dissipative Systems with a Statistical Enslaving of Fast-relaxing Variables⁹**

We consider dissipative systems where the contraction in phase space corresponds asymptotically to the center-manifold-functional dependence of the fast-relaxing variables X_f 's on the order parameters given by the slow variables X_g 's. We derive analytically the Green-function sensitivity matrix to calculate the response on the subordinated variables to instantaneous perturbations on X_f or on X_g . We thus show how these perturbations propagate along the center manifold. This information is obtained from sensitivity measurements on the experimentally relevant variables X_g 's using also the center-manifold expansion. The results are applied to a randomly driven damped anharmonic oscillator. The spectral density is found by Fourier transforming the sum of the different contributions to the equilibrium correlation: The $X_g X_g$, $X_g X_f$, and $X_f X_f$ terms. The average local attractivity of the center manifold is calculated and used in this computation. The sensitivity functions involving only the subordinated degrees of freedom are used as fundamental propagators to calculate the $X_f X_f$ term. The results are tested against an analog computer simulation and *vis-a-vis* plots obtained from statistical linearization methods. A very good agreement is observed.

10. **Atom Scattering from Disordered Surfaces: Randomly corrugated Hard Walls and the Sudden Approximation¹⁰**

We used a randomly corrugated hard wall model and the sudden approximation to analyze two experiments on atom scattering from disordered surfaces. In one, the structural surface disorder was caused by ion bombardment. In the other, the disorder was due to an incomplete overlayer of adsorbed atoms. We also present a study of the scattering of a rigid rotor by a randomly corrugated hard wall using the sudden approximation.

11. **The Sudden Approximation for Scattering from Noncrystalline Surfaces: Applications to Models of Adsorbed Impurities and to Mixed Overlayers¹¹**

It was recently proposed that the sudden approximation should be a powerful tool for the calculation of the angular intensity distribution in high-energy atom scattering from one- and two-dimensional models of: (1) isolated adsorbed impurities on crystalline surfaces (Ar on Cu); (2) Mixed overlayers on an underlying surface (Xe+Ar mixtures on a smooth surface). The results are tested against numerically exact quantum-mechanical wave packet calculations. Except for very low collision energies, the sudden approximation gives results of excellent quantitative accuracy for both types of noncrystalline surfaces. At low energies, several features of the intensity distribution are not produced correctly by the sudden: These are found to be due mainly to double collision effects. The accuracy and validity range of the method are discussed in the light of the results obtained in the test calculations.

12. Variational Methods for Approximating Solutions of $\nabla^2 u(x) = f(x) + k(x)u(x)$ and Generalizations¹²

The iterative procedure of Guy, Sales, Brami-Depaux, and Joly-Cabaret (GSBJ) for approximately solving equations of the form $\nabla^2 u = f + ku$ is analyzed and generalized from the viewpoint of the calculus of variations. The GSBJ method involves a functional of the solution and either one or two auxiliary functions which are chosen empirically so as to make the iterations converge sufficiently fast, even for problems for which the corresponding Neumann series diverges or converges too slowly. In the case in which one of the auxiliary functions is identically unity, this functional is seen to be the scale-invariant form of the affine functional studied by Kahan, Rideau, Roussopoulos, and Pomraning (KRR)), and a systematic way of seeking appropriate auxiliary functions is developed by demanding that the functional be stationary about the true solution of the equation in question. The variational approach is tested on three simple example problems, and the numerical results are seen to compare favorably with those of GSBJ and with the exact solution. In addition, two new variational functionals are derived, various iteration schemes are discussed, the method is extended to more general equations, and further connections with other work are established.

13. Average Wave Function Method for Gas-surface Scattering¹³

The average wave function method (AWM) is applied to scattering of a gas off a solid surface. The formalism is developed for both periodic as well as disordered surfaces. For an ordered lattice an explicit relation is derived for the Bragg peaks along with a numerical illustration. Numerical results are presented for atomic clusters on a flat hard wall with a Gaussian-like potential at each atomic scattering site. The effect of relative lateral displacement of two clusters upon the scattering pattern is shown. The ability of AWM to accommodate disorder through statistical averaging over cluster configurations is illustrated. Enhanced uniform backscattering is observed with increasing roughness on the surface.

14. Local and Global Parametric Analysis of Reacting Flows¹⁴

This paper presents a selected overview of current techniques available for analyzing parametric behavior of dynamical systems including reactive flows. The paper is based on a series of lectures presented at Cornell University, and the discussion is broadly divided into the realms of local and global techniques. Local procedures are capable of addressing a rich variety of questions associated with the behavior of dynamical systems near a chosen operating point in parameter space. On the other hand, global procedures are specifically designed to map out solution behavior over wide ranges of parameter space for both statistical analysis as well as objective function mapping. Techniques for accomplishing all of these tasks are in various stages of development and comments on current research directions are mentioned when appropriate.

15. Dynamics and Kinetics on Surfaces Exhibiting Defects¹⁵

This paper considers dynamics and kinetic phenomena on surfaces with defect structures. Quantum mechanical scattering as well as kinetics and diffusion processes are treated as examples. In the case of quantum mechanics, a theoretical formulation is presented capable of handling atomic disorder on surfaces. The approach is based on an approximation which is best in the quantum long wave-length regime. Some simple illustrations considering scattering off ordered and disordered lattices will be presented. The second part of the paper considers the steady state non-linear reaction-diffusion equations used to describe adsorption, desorption, diffusion and reaction on surfaces with macroscopic scale defects. These latter defects may arise due to inherent faulting of the lattice or foreign material on the surface. Defects within a mean diffusion length of each other are shown to exhibit cooperativity in their chemical properties. Finally, in the last portion of the paper reaction-diffusion models are again considered from a different perspective. In this case, all of the non-linear chemical or descriptive aspects of the problem are restricted to the edges of the defect sites and the intervening surface is assumed to be characterized by adsorption, desorption and simple diffusion. These physically realistic models clearly show the capability of multiple steady states existing on active chemical surfaces. A variety of non-linear surface phenomena could possibly be important in appropriate gas-surface systems.

Publications Resulting from AFOSR Support:

1. **Semiclassical Perturbation Theory for Atom Scattering from Surfaces with Defects**, L.M. Hubbard and H. Rabitz, J. Chem. Phys. (to be published).
2. **Atom Molecule Scattering with the Average Wavefunction Method**, H. Singh, D.K. Dacol, and H. Rabitz, Chem. Phys., 1987 (in press).
3. **Applications of Filtering Theory for the Inversion of Temporal Chemical Systems**, J.G.B. Beumee and H. Rabitz, J. Chem. Phys. 1987 (in press)
4. **An Application of Filtering Theory to Parameter Identification to Quantum Mechanics**, J.G.B. Beumee and H. Rabitz, J. Math. Phys. 1987 (in press).
5. **Time-dependent Resonant Fluorescence Spectrum of Two-level Atoms in Strong Short Pulsed Fields: A Nonperturbative Treatment**, T-S. Ho and H. Rabitz, Phys. Rev. A, 1987 (submitted).
6. **Sensitivity Analysis of Combustion Systems**, H. Rabitz, The Mathematics of Combustion, J. Buckmaster, editor, (SIAM, Philadelphia, 1985).
7. **Vibrational Energy Transfer at the Gas-solid Interface: The Role of Collective and of Localized Vibrational Modes**, E. Vilallonga and H. Rabitz, J. Chem. Phys., 85, 2300 (1986).
8. **Autocorrelations in the Center Manifold of Dissipative Systems**, A. Fernandez and H. Rabitz, Phys. Rev. A, 33, 3314 (1986).
9. **Fundamental Sensitivity Propagators in Dissipative Systems with a Statistical Enslaving of Fast-relaxing Variables**, A. Fernandez and H. Rabitz, Phys. Rev. A, 33, 1913 (1986).
10. **Atom Scattering from Disordered Surfaces: Randomly Corrugated Hard Walls and the Sudden Approximation**, D.K. Dacol, H. Rabitz, and R.B. Gerber, J. Chem. Phys., 86, 1616 (1987).
11. **The Sudden Approximation for Scattering from Noncrystalline Surfaces: Applications to Models of Adsorbed Impurities and to Mixed Overlayers**, A.T. Yinnon, R.B. Gerber, D.K. Dacol and H. Rabitz, J. Chem. Phys., 84, 5955 (1986).
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13. Average Wave Function Method for Gas-surface Scattering, H. Singh, D.K. Dacol and H. Rabitz, J. Chem. Phys., 84, 1852 (1986).
14. Local and Global Parametric Analysis of Reacting Flows, H. Rabitz, Physica 20D, 67-81 (1986).
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