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ANALYSIS OF FORWARD AND INVERSE PROBLEMS IN
CHEMICAL DYNAMICS AND SPECTROSCOPY

by

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ABSTRACT

During the past several months, progress has continued on several interrelated aspects of research. The overall research is concerned with the development and application of advanced analysis tools for studying dynamics, kinetics, and spectroscopic phenomena from a forward and inverse perspective. In particular, the forward problem is concerned with understanding how detailed interatomic potential information maps onto a hierarchy of chemical dynamic and kinetic observables. The inverse aspects of the research are concerned with exactly the reverse of this process, whereby we desire to understand how particular measurements project back to yield information regarding the potential surface. Thus, in the latter domain, our research is concerned with the development of theoretically based tools ultimately aimed at applications to the inversion of quality laboratory data for the extraction of microscopic potential information.

PROGRESS SUMMARY

1. Inversion of gas-surface scattering data for potential determination using functional sensitivity analysis: II. Extraction of the full interaction potential from low energy diffraction data¹

We demonstrate that the full gas-surface potential can be successfully recovered from low energy elastic scattering intensities within the framework of functional sensitivity analysis and Tikhonov regularization as formulated previously. Specifically, we consider an extensive, but finite, set of simulated discrete data from specular scattering and three in-plane diffraction orders over a wide range of incident polar angles for the rigid, periodic, and corrugated He-Xe/C(0001) system at fixed beam energy and fixed azimuthal angle. It is found that the potential extracted from these input data resembles unambiguously the intended model potential. The recovered potential is only slightly steeper in the upper portion of the repulsive wall, and its minima are slightly deeper. Moreover, the repulsive walls of the recovered and true potentials cross the zero at almost the same distances from the surfaces. Finally, all of the details of the input data, namely the positions and shapes of the bound-state resonance extrema for all scattering channels under study, are accurately reproduced by the recovered potential.

2. Quantum Functional Sensitivity Analysis for the Collinear H + H₂ Reaction Rate Coefficient²

The effects of features in the potential energy surface on the collinear H + H₂ reaction rate coefficient are investigated by the method of quantum functional sensitivity analysis (QFSA). The calculations use QFSA to connect features in the microscopic realm, with their response upon macroscopic quantities of chemical interest, via the intermediary sensitivities of the reactive transition probabilities. While the sensitivities of the individual transition probabilities show considerable structure, there is an attendant loss of structure in the rate coefficient sensitivities because of the thermal averaging. For the range of temperatures used in our study (200 - 2400K), the most important region of the potential energy surface is found to be not at the top of the barrier, but rather, at the lower energy shoulders of the barrier. There are also regions near the barrier where an increase in the potential surface actually increases the reaction rate! The effects of using different underlying potentials (the PK2, LSTH, and DMBE surfaces) on the nature of the results were also compared. The absolute sensitivity magnitudes on the PK2 surface vary considerably from the other two, but the relative change in the rate coefficient is about the same on all three surfaces. Furthermore, the identified regions of importance on the potential surfaces remain essentially the same. The reactive scattering calculations were performed with the log-derivative version of the Kohn variational principle.

3. The rotation-vibration potential of He-H₂ and its connection with physical phenomena³

This paper examines the effect of infinitesimal functional variations in a three-dimensional vibration-rotation He-H₂ potential surface on several different levels of physical observables: inelastic cross sections, rate constants, and energy level populations. Earlier equations for a rigid-rotor system are extended and a comparison of the current results with earlier rigid-rotor results is made. A significant difference in the sensitivity of observables to the potential components has been observed between those observables which are purely rotationally inelastic and those which are vibrationally inelastic. The region of highest sensitivity is dependent upon the energy or temperature as well as the states related by the individual observable. Significant information loss has been observed in the transition from the microscopic observables to the macroscopic ones for those observables which are vibrationally inelastic.

4. Factorization of Certain Evolution Operators Using Lie Algebra: Convergence Theorems⁴

This work concerns convergence theorems with a sequence of $\bar{\xi}$ -approximants for exponential evolution operators with Lie operator arguments. A companion paper presents the formulation of the ξ -approximants. The theorems presented in this paper give the conditions which are sufficient for convergence of the sequences. Although the main

emphasis will be on convergence properties of the one-dimensional case, the generalization to multidimensional cases is quite straightforward.

5. Inversion of gas-surface scattering data for potential determination using functional sensitivity analysis: I. A case study for the He-Xe/C(0001) potential⁵

A general iterative inversion procedure based on functional sensitivity analysis is presented for determining the gas-surface interaction potential from low energy elastic scattering data. Formally, Tikhonov regularization, singular function analysis, and a recently developed exact transformation technique are implemented to render the inversion stable and efficient. Specifically, the simulation of helium scattering from a rigid periodic xenon monolayer on the graphite (0001) face is considered. It is found that the functional sensitivity densities of the diffraction intensities with respect to the He-Xe/C(0001) potential contain profound information, thus are invaluable in guiding the inversion of scattering data to yield the potential. Although unequivocal determination of the full three-dimensional potential from the inevitably incomplete experimental data may be difficult, we demonstrate that simulated input data consisting of a finite number of polar scan specular intensities can be used to accurately recover the underlying He-Xe/C(0001) potential. The recovered potential has been obtained without imposing any explicit functional form on the potential *per se*. The resulting procedure is quite promising for treating real laboratory data.

6. A General Analysis of Lumping in Chemical Kinetics⁶

A general lumping analysis has been developed for discrete reaction mixtures whose kinetics can be described by a first-order ordinary differential equation system with arbitrary reaction functions. The lumped species is considered as a linear combination of the original ones. The necessary and sufficient conditions of exact lumping have been obtained. These conditions are constructive so that all exact lumping schemes for a given reaction system can be determined by them. A uni- and bimolecular reaction system is utilized as an example to illustrate the method. Under some circumstances, exact lumping schemes may not exist, especially in the presence of constraints. For instance, some species may be required to be left unlumped or lumped by a given linear combination. In this case, approaches to determine the best approximate lumping schemes with different dimensions have been developed. The "Mobil 10-lump model" of cracking petroleum to produce gasoline is presented as an example. This analysis has been extended to reaction systems under nonisothermal conditions or coupled with diffusion. The lumping tools are general and can be also used in other areas, such as chemical engineering, control theory and classical molecular dynamics.

7. Sensitivity Analysis of a Steady-state, Premixed Laminar CO-H₂-O₂ Flame⁷

The direct and very efficient Newton method for obtaining sensitivities of two-point boundary value problems is utilized for detailed exploration of a reacting-diffusing CO+H₂+O₂ steady-state

premixed laminar flame. Sensitivity coefficients and Green's functions calculated for this system offer exhaustive characterization and new insights into the role of diffusion and exothermicity in carbon monoxide oxidation kinetics. In particular, the reactions of the hydroperoxy radical with hydrogen, oxygen and hydroxyl radicals are found to be extremely important at all temperatures in the fuel lean (40 torr) flame studied here. The diffusive mixing of chemical species from the low and the high temperature portions of the flame and the large heats of reaction associated with the hydroperoxy radicals are found to be responsible for the increased importance of these reactions.

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