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STUDY OF RATE OF NONEQUILIBRIUM DECOMPOSITION OF ENERGETIC MOLE--ETC(U)  
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Final Technical Report

Study of Rate of Nonequilibrium Decomposition of Energetic Molecules (U)

R. A. Marcus

May, 1977

Picatinny Arsenal  
Dover, New Jersey 07801

Contract No. DAAA21-72-C-0679

Contractor: University of Illinois  
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Summary

The research accomplished during this research project is summarized. A statistical-dynamical method for treating the energy distribution of products of unimolecular decompositions was devised. Molecular beam reactions proceeding via long-lived complexes were treated. A numerical quantum mechanical description of simple molecules (three degrees of freedom) decomposing to products was developed. A practical semiclassical method for treating bound state problems and calculating their eigenvalues was formulated. In this way (and for the first time) it became possible to treat semiclassically dynamically nonseparable systems with smoothly varying potentials. The method involves using classical trajectories to obtain topologically independent phase integrals. Imposition of the Born-Sommerfeld quantization rules for these nonseparable systems yields the eigenvalues. Several investigations were undertaken on quantum mechanical treatment of decomposing small molecules (compound state resonances), on use of reduced-size basis sets for treating numerically the quantum mechanics of bimolecular collisions, and on collisional vibrational excitation.

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## Research Accomplished

### 1. On the Theory of Energy Distributions of Products of Molecular Beam Reactions Involving Transient Complexes

A theory for this purpose was developed under the present contract and published in J. Chem. Phys. 62, 1372 (1975), by R. A. Marcus under the above title. In this paper theoretical energy distributions of reaction products in molecular beam systems were described for reactions proceeding via transient complexes. Loose and tight transition states were considered for the exit channel. For a loose transition state and the case of  $l \gg j$ , the result was the same as of Safron *et al.* [Chem. Phys. Lett. 12, 564 (1972)]. Here,  $l$  denotes the orbital angular momentum of the products and  $j$  denotes their rotational angular momentum. For the case of a tight transition state exit channel efforts were included analogous to steric effects for the reverse reaction. It was shown how, via one mechanism, bending vibrational energy of that transition state can contribute to the translational energy of the reaction products. Expressions were derived for the energy distributions of the products when  $l \gg j$  and  $j \gg l$ .

This research was continued, after the present contract expired, and was then supported by the National Science Foundation. A forthcoming publication by G. Worry and R. A. Marcus [J. Chem. Phys. 67 (1977), August 15, 1977] is entitled "On the Theory of Translational Energy Distributions of Product Molecules of Molecular Beam Reactions Involving Transient Complexes. II." The work contained in that report represents an application of the 1975 paper. The results are described as follows.

A statistically-adiabatic model for chemical reactions involving a tight or loose transition state in the exit channel was used in Part I to obtain an integral equation for the individual reaction probabilities, i.e., for the magnitude of the S matrix elements. In this new paper (Part II) this integral equation was explicitly solved for the general case of product orbital ( $l$ ) and rotational ( $j$ ) angular momenta constrained only by energy and angular momentum conservation. The reaction probabilities were shown to be related to a contour integral of a product of canonical partition functions. The theory includes an effect of the evolution of the bending vibrations of the transition state into free rotations of the product molecules. The distribution of final translational energy for the general ( $l, j$ ) case was then obtained by averaging the reaction probabilities over various quantum states of the product molecules. The results were compared with the special cases in the literature for which (i) the transition state in the exit channel is loose ("phase space theory"), (ii) this case but with  $l \gg j$ , and

(iii) tight transition state theory with  $l \gg j$  (Part I). The results were also compared with experimental data obtained from the molecular beam reaction  $F + (CH_3)_2C = CH_2 \rightarrow F(CH_3)_2CCH_2^* \rightarrow CH_3 + FCH_2C = CH_2$ . The data and the theoretical results are now in better agreement.

In the treatment described in Parts I and II a loose transition state in the entrance channel was assumed. Expressions for the energy distribution were also given for the case when the entrance channel transition state was tight. Finally, a statistically-adiabatic S-matrix, which was useful for reactions proceeding through long-lived collision complexes having tight transition states was described, and its possible application to angular distributions and angular momentum polarization experiments were discussed.

## 2. Semiclassical Calculation of Bound States of a Multidimensional System

A paper on this topic and supported by the present contract was published by W. Eastes and R. A. Marcus in J. Chem. Phys. 61, 4301 (1974). In this paper the semiclassical quantum conditions for bound states were studied for a nonseparable system of two coupled oscillators which possesses a collection of quasiperiodic trajectories. The semiclassical energy levels were found to be in excellent agreement with the exact quantum levels. This treatment differed from previous work in that periodic trajectories were not needed and in that the potential surface was smooth and nonseparable in all regions.

This work was the starting point for a substantial body of subsequent research on semiclassical eigenvalues of nonseparable problems, by the writer and coworkers, and W. H. Miller and coworkers in this country, and by I. Percival et al. and N. C. Handy et al. in Great Britain. Among our own subsequent work there was the following work: "Semiclassical Calculation of Bound States in a Multidimensional System. Use of Poincaré's Surface of Section" by D. W. Noid and R. A. Marcus, J. Chem. Phys. 62, 2129 (1975), and supported by the present contract. In this work a method utilizing integration along invariant curves on Poincaré's surfaces of section was described for semiclassical calculation of eigenvalues. The systems treated were dynamically nonseparable (as in the Eastes-Marcus paper) and were quasiperiodic. Use was also made of procedures developed in that previous paper. The calculated eigenvalues for an anharmonically coupled pair of oscillators agreed well with the exact quantum values. They also agreed with the previous semiclassical calculations in this laboratory, which instead used integrations along the caustics. This second paper increased the number of systems capable of being treated. Using numerical counter examples for nondegenerate systems, it was also shown that an alternative view

in the literature, which assumes that periodic trajectories alone suffice, leads to wrong results for the individual eigenvalues.

A second follow-up publication was "Semiclassical Calculation of Bound States in a Multidimensional System for Nearly 1:1 Degenerate Systems" by D. W. Noid and R. A. Marcus, supported by the National Science Foundation, to be published in J. Chem. Phys. 67 (1977) [July 15, 1977]. In this work the method was devised to calculate eigenvalues semiclassically for an anharmonic system whose two unperturbed modes are 1:1 degenerate, by introducing a curvilinear Poincare surface of section. The results were in reasonable agreement with the quantum ones. The classical trajectories also frequently showed a large energy exchange among the two unperturbed normal modes. Implications for Slater's theory of unimolecular reactions, which neglects this effect, and for "quantum ergodicity" were described.

A third follow-up publication with NSF support was an entirely new semiclassical method for obtaining the properties of isolated molecules, "A Spectral Analysis Method of Obtaining Molecular Spectra from Classical Trajectories" by D. W. Noid, M. L. Koszykowski and R. A. Marcus, J. Chem. Phys. 67 (1977) [July 15, 1977]. Several other related papers are in preparation, including some on the application to actual molecules to calculate their vibrational spectra and compare with experiment.

Thus, in summary, the original support of this research by Picatinny Arsenal provided the basis for the many subsequent developments in this field.

### 3. Dynamical Effects in Chemical Reactions

A paper on this topic, supported under the present contract was published by R. A. Marcus in "Proceedings of the Conference on Mechanisms of Explosion and Blast Waves" Naval Weapons Station, Yorktown, Va., November 13-15, 1973 (N. Slagg, Picatinny Arsenal, editor). In this work it was noted that experimental and theoretical studies in the past have focused on rate constants for reactions and on their activation energies, that in highly nonequilibrium situations more detailed dynamical data such as reaction cross sections are utilized instead, and that a large body of new information is now becoming available on these and allied dynamical topics. Some recent and earlier results were discussed for bimolecular and unimolecular reactions.

#### 4. Compound State Resonances in the Collinear Collision of an Atom with a Diatomic Oscillator

In this work, supported by the present contract, a paper by W. Eastes and R. A. Marcus was published in J. Chem. Phys. 59, 4757 (1973) under the above title. In that paper compound state resonance effects were reported in exact, numerical calculations of the collinear collision of a particle with a harmonic oscillator with a Morse interaction potential. They were shown to be due to the formation of a long-lived complex or quasibound state and were much more narrow than resonances reported previously for this type of system. The stable eigenvalues resulting from a variational calculation with a bound state basis set were found to be in excellent agreement with the resonance energies, and such a variational calculation was found to be a good way of locating these resonances.

#### 5. S Matrix Elements for Excited Rotational State Transitions

This study was undertaken by W. Eastes as a preliminary step toward treating more complicated collisions by testing numerical procedures. The results were published under the above title in J. Chem. Phys. 59, 3534 (1973). The main problem in numerical quantum mechanical treatments of collisions is associated with the large number of rotational-orbital-vibrational states to be considered, requiring very large quantum mechanical basis sets for the wave function. In this paper it was found how to reduce the size of the basis set by neglect of low lying states: Exact S-matrix elements were presented for atom-rigid rotor scattering for transitions between the  $j = 6, 8, \text{ and } 10$  rotational states. Enough channels were included in the close coupling scheme to ensure convergence. It was found that one may neglect the lower lying rotational states if one is interested only in S-matrix elements for transitions between excited states.

#### 6. Semiclassical Calculation of the Harmonic Oscillator Transition Probability for a Collinear Hard Sphere Collision

Another collision problem treated in the collisional part of the present study was that in an article under the above title, by W. Eastes and J. D. Doll of this laboratory. The work was published in J. Chem. Phys. 60, 297 (1974). In this study closed form expressions were obtained for the vibrational transition probabilities in a semiclassical formulation for the inelastic hard sphere collision of an atom with a harmonic oscillator. The uniform semiclassical expression was found to be in excellent agreement with the numerically computed quantum mechanical transition probabilities. Expressions were also

obtained for the average energy transfer in this collision and for the scattering of atoms from a hard cube model surface.

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