0.€ <u>80</u> 2% \$0. 8 衛 19

Nonadiabatic Interactions Between Potential Energy Surfaces: Theory and Applications	1
By B. H. Lengsfield III and D. R. Yarkony	
DIABATIC POTENTIAL ENERGY SURFACES FOR CHARGE-TRANSFER PROCESSES	73
By V. Sidis	
MODEL POTENTIAL ENERGY SURFACES FOR INELASTIC AND CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISION	135
By F. A. Gianturco and F. Schneider	
QUANTUM-MECHANICAL TREATMENT FOR CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISIONS	187
By M. Baer	
SEMICLASSICAL APPROACH TO CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISIONS	243
By H. Nakamura	
THE SEMICLASSICAL TIME-DEPENDENT APPROACH TO CHARGE- TRANSFER PROCESSES	321
By E. A. Gislason, G. Parlant, and M. Sizun	
THE CLASSICAL TRAJECTORY-SURFACE-HOPPING APPROACH TO CHARGE-TRANSFER PROCESSES	423
By S. Chapman	
STATISTICAL ASPECTS OF ION-MOLECULE REACTIONS	485
By J. Troe	
AUTHOR INDEX	531
Subject Index	547

29 19. S

NONADIABATIC INTERACTIONS BETWEEN POTENTIAL ENERGY SURFACES: THEORY AND APPLICATIONS

BYRON H. LENGSFIELD III*

Theoretical Atomic and Molecular Physics Group Lawrence Livermore National Laboratory Livermore, CA

and

DAVID R. YARKONY[†]

Department of Chemistry
The Johns Hopkins University
Baltimore, MD

CONTENTS

- I. Introduction
- II. Theory
 - A. Evaluation of First-Derivative Nonadiabatic Coupling Matrix Elements and Energy Gradients: A Unified Approach
 - B. Molecular Orbital Derivatives
 - 1. Coupled-Perturbed MCSCF Equations
 - 2. Additional Constraints on the Molecular Orbitals
 - C. Second Derivative Nonadiabatic Coupling
 - 1. Evaluation of $k_{\alpha\beta}^{JI}(\mathbf{R})$ Using Analytic Gradient Techniques
 - 2. Analytic Evaluation of $\langle \phi_i | (\partial^2/\partial R_\alpha \partial R_\beta) \phi_i \rangle$

*Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy under Contract # W-7405-Eng-48 and by the Air Force Astronautics Laboratory under Contract #6761-01.

[†]Supported in part by NSF Grant CHE-87-23020 and AFOSR Grant 90-0051.

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.

- 3. Evaluation of $h_{\pi R}^{II}(\mathbf{R})$ Using Analytic Second Derivative Methods
- D. Body-Fixed-Frame Methods
- E. Avoided and Actual Surface Crossings: Direct Evaluation of the Energy Difference Gradient
 - 1. The Energy Difference Gradient
 - 2. Locating Actual/Avoided Crossings of Potential Energy Surfaces
- F. On the Existence of Rigorous Diabatic Bases

III. Applications

- A. Adiabatic Correction to the Born-Oppenheimer Potential Energy Curve for the $X^{1}\Sigma^{+}$ State of Lithium Hydride
- B. The He + $H_2(B^1\Sigma_u^+) \rightarrow He + H_2(X^1\Sigma_a^+)$ Reaction

IV. Future Directions

Appendices

- A. Evaluation of Terms of the Form Tr(MU) in the Atomic-Orbital Basis
- B. Contribution to Derivative Quantities from Inequivalent Core and Virtual Orbitals
- C. Coupled Perturbed State Averaged MCSCF (CP-SAMCSCF) Equations
- D. Contribution to Derivative Quantities from Inequivalent Active Orbitals
- E. The Second Derivative CP-SAMCSCF Equations References



DIABATIC POTENTIAL ENERGY SURFACES FOR CHARGE-TRANSFER PROCESSES

V. SIDIS

Laboratoire des Collisions Atomiques et Moléculaires, Université de Paris-Sud, ORSAY Cedex, France

CONTENTS

- I. Introduction
 - A. The Quasimolecular Model
 - B. Insufficiency of the BO Approximation
 - C. Historical Background
- II. Preliminaries
 - A. Coordinates
 - B. The Hamiltonian in the BF Frame
- III. The Adiabatic Representation
- IV. The Diabatic Representation
 - A. On the Transformation of an Arbitrary Representation to a Strictly Diabatic Representation
 - B. Nontrivial Strictly Diabatic Bases
- V. Characteristic Two-State Model Cases
- VI. Practical Construction of Diabatic States
 - A. 1. Case Study
 - 2. Philosophy
 - B. Preservation of Separated-Partner Characters: Orbitals
 - 1. The Case of Two Orbitals in Atom-Atom Systems
 - 2. The Case of a Few Orbitals in Atom-Atom Systems: A Hint at the Electron Translation Factor Problem
 - 3. (Quasi-)diabatic Orbitals of the Separated-Partner Type for Atom-Diatom Systems
 - C. Many-Electron Diabatic States for Electron-Transfer Processes
 - 1. Mutual Orthogonalization of Shells
 - 2. Improvement of Diabatic Prototypes
 - D. Extended Scope
 - 1. Bringing Out Characters
 - 2. Preservation of Characters

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.

- 3. Diabatic Basis Changes
- 4. Diabatic Vibronic Bases
- 5. Exotic Diabatic States: Hydrogenic States in Heavy-Light-Heavy Systems

VII. Conclusions

MODEL POTENTIAL ENERGY SURFACES FOR INELASTIC AND CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISIONS

F. A. GIANTURCO

Department of Chemistry, The University of Rome, Città Universitaria, Rome, Italy

F. SCHNEIDER

Central Institute for Physical Chemistry, Rudower Chaussee 5, Berlin, Germany

CONTENTS

- I. Introduction
- II. The DIM Method
 - A. General Formalism
 - B. The Symmetry-Adapted Basis Functions
 - C. The DIM Hamiltonian
 - D. The Nonadiabatic Coupling
 - E. The Implementation of the Method
- III. Triatomic Ion-Molecule Systems
 - A. The H₃⁺ Case and Related Models
 - B. The HeH 2 System
 - C. The FH; Interaction
 - D. The BH, Surfaces
 - E. The O₂H⁺ Charge-Transfer Interactions
- IV. More Complex Cases
 - A. Rare-Gas Clusters
 - B. Interactions on Surfaces
 - V. Final Considerations

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.

QUANTUM-MECHANICAL TREATMENT FOR CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISIONS

MICHAEL BAER

Department of Physics and Applied Mathematics, Soreq Nuclear Research
Center, Yavne, Israel

CONTENTS

- I. Introduction
- II. Theory
 - A. The Schrödinger Equation
 - B. The Collinear System
 - 1. The Schrödinger Equation
 - 2. The Adiabatic-Diabatic Transformation
 - 3. The Quasi-Adiabatic-Diabatic Transformation
 - 4. The Two-Surface Case
 - C. The Diatomic-in-Molecule Potential
 - D. The Treatment of Reactive Systems
 - E. The Three-Dimensional System—The Introduction of Infinite-Order Sudden Approximation
- III. Studies of Specific Systems
 - A. Background
 - B. The $H_2(D_2, HD) + H^+$ System
 - 1. Differential Cross Sections
 - 2. Integral Cross Sections
 - 3. On the Mechanism of Charge Transfer in the $H_2(v=0) + H^+$ System
 - C. The $(Ar + H_2)^+$ System
 - 1. The Three-Surface System
 - 2. The Study of CT in the High-Energy Region
 - 3. The Study of Charge Transfer, Exchange, and Spin Transitions in the Low-Energy Region
 - 4. Discussion
 - D. $(H + O_2)^+$ System
- VI. Summary

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.



SEMICLASSICAL APPROACH TO CHARGE-TRANSFER PROCESSES IN ION-MOLECULE COLLISIONS

HIROKI NAKAMURA

Division of Theoretical Studies, Institute for Molecular Science, Myodaiji, Okazaki, Japan

CONTENTS

- I. Introduction
- II. Basic Mechanisms and Their Characteristics
- III. Semiclassical Theory of Nonadiabatic Transition
 - A. Dynamical State (Generalized Adiabatic State) Representation
 - B. Landau-Zener-Type Nonadiabatic Transition
 - C. Rosen-Zener (Demkov)-Type Nonadiabatic Transition
- IV. Multichannel Curve Crossing Problem
 - A. General Formulation of Electronic Transitions in Diatomic Systems
 - 1. The Case Without Closed Channel
 - 2. General Case Involving Closed Channels
 - B. VibronicTransition in Ion-Molecule Collisions
 - C. Numerical Examples
 - 1. Vacancy Migration in the Ne⁺ + Ne Collision—Catalysis Effect
 - 2. Li⁺ + Na and Li + Na⁺ Collisions
 - 3. Three- and Four-Level Model Systems
 - 4. Application of the BFG Model to Vibronic Transitions
 - V. Chemical Reaction—Particle Rearrangement
 - A. Orbiting (Langevin) Model for Ion-Molecule Collision
 - B. Classical S-Matrix Theory
 - C. Hyperspherical Coordinate Approach
- VI. Semiclassical Treatment of Electronically Nonadiabatic Chemical Reaction—Future Developments
- VII. Summary

Acknowledgements

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.



THE SEMICLASSICAL TIME-DEPENDENT APPROACH TO CHARGE-TRANSFER PROCESSES

ERIC A. GISLASON

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois

GÉRARD PARLANT^a

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

MURIEL SIZUN

Laboratoire des Collisions Atomiques et Moleculaires,^b Université de Paris-Sud, Orsay, France

- I. Introduction
- II. Classical Path Formulation
 - A. Classical Path Equations
 - B. Basis Set
 - C. Coupled Equations
 - D. Vibrationally Sudden Approximation
 - E. Classical Trajectory

^aPermanent address: Physico-Chimie des Rayonnements (UA 75, Associé au CNRS), Bâtiment 350, Université de Paris-Sud, 91405 Orsay Cedex, France.

^bUnité associé au CNRS-No. 281.

- F. Differential Cross Sections
- G. Numerical Procedures
 - 1. Vibrational Matrix Elements
 - 2. Average Over Initial Conditions
 - 3. Numerical Solution of Coupled Equations
 - 4. Examples
- III. Classical Path Calculations—Total Cross Sections
 - A. Paper of Bates and Reid
 - B. Work of Moran, Flannery, and Co-workers
 - C. DePristo's Work
 - D. Work of Kimura and Co-workers
 - E. Work of Spalburg and Co-workers
 - F. Work of Parlant and Gislason on $(Ar + N_2)^+$
 - 1. Introduction
 - 2. Theoretical Procedures
 - 3. Potential Energy Surfaces and Couplings
 - 4. Calculations for $N_2^+(X,A) + Ar$
 - 5. Charge-Transfer Collisions Between $Ar^{+}(^{2}P_{J}) + N_{2}$
 - 6. Inelastic Collisions of $Ar^{+}(^{2}P_{J})$ and N_{2}
 - G. Work of Archirel, Gislason, Parlant, and Sizun on (Ar + CO)+
 - 1. Introduction
 - 2. Theoretical Procedures
 - 3. Potential Energy Surfaces and Couplings
 - 4. Calculations for $Ar^{+}(^{2}P_{J}) + CO$ Collisions
 - H. Work of Sidis and Co-workers on Dissociative Charge Transfer
- IV. Classical Path Calculations—Differential Cross Sections
 - A. Work of Grimbert, Sidis, and Sizun
 - B. Work of DePristo
- V. General Features of Charge-Transfer Collisions
 - A. The Franck-Condon Principle
 - B. Adiabatic Vibronic Potential Energy Surfaces
 - C. Energy Dependence of Charge-Transfer Cross Sections
- VI. Future Developments Involving the Classical Path Procedure Acknowledgements
 References



THE CLASSICAL TRAJECTORY-SURFACE-HOPPING APPROACH TO CHARGE-TRANSFER PROCESSES

SALLY CHAPMAN

Department of Chemistry
Barnard College, Columbia University
New York, NY

- I. Introduction
- II. Nonadiabatic Molecular Collisions: Background
 - A. The Semiclassical Description of Nonadiabatic Transitions
 - B. Two-State Systems
 - 1. Adiabatic and Diabatic States
 - 2. The Landau-Zener Model
 - 3. The Demkov Model
- III. Trajectory-Surface-Hopping Methods
 - A. Foundations
 - 1. The General Concept
 - 2. Tully and Preston
 - 3. Miller and George
 - B. Alternate Methods for Locating the Seam and Predicting Hopping
 - 1. Stine and Muckerman
 - 2. Kuntz, Kendrick, and Whitton
 - C. Combining TSH with the Time-Dependent Semiclassical Equations
 - 1. Blais and Truhlar
 - 2. Parlant and Gislason
 - D. Electron-Detachment Processes
- IV. Applications
 - A. Ion-Molecule Reactions: Charge-Transfer and Competing Processes
 - 1. H⁺
 - 2. ArH,
 - 3. HeH,
 - 4. NeHe,*

State-Selected and State-to-State Ion-Molecule Reaction Dynamics, Part 2: Theory, Edited by Michael Baer and Cheuk-Yiu Ng. Advances in Chemical Physics Series, Vol. LXXXII. ISBN 0-471-53263-0 © 1992 John Wiley & Sons, Inc.

- 5. HeN₂⁺
- 6. ClH₂
- 7. H₂O⁻
- 8. H₄⁺
- B. Electron Transfer Reactions
 - 1. Introduction
 - 2. Alkali Plus Halogen
 - 3. Alkali Plus Oxygen
- C. Neutrals: A Sampling of Systems Studied
- V. Discussion and Future Developments References

STATISTICAL ASPECTS OF ION-MOLECULE REACTIONS

JÜRGEN TROE

Institut für Physikalische Chemie, Universität Göttingen, Göttingen, Germany

- I. Introduction
- II. Basic Relationships of Statistical Rate Theories
 - A. Bimolecular Processes
 - B. Unimolecular Processes
- III. Adiabatic Channel Eigenvalues and Channel Threshold Energies
 - A. Rigid Activated Complexes
 - B. Isotropic Potentials
 - C. $\cos \theta$ Anisotropies for Atom + Linear Reactant Systems
 - D. $\cos \theta$ Anisotropies for Atom + Symmetric Top Reactant Systems
 - E. $\cos^2 \theta$ Anisotropies for Atom + Linear Reactant Systems
 - F. Nonadiabatic Effects
- IV. Capture Rate Constants and Cross-Sections
 - A. Isotropic Potentials
 - B. Anisotropic Charge-Linear Dipole Potentials
 - C. Anisotropic Charge-Nonlinear Dipole Potentials
- V. Bimolecular Ion-Molecule Reactions with Redissociating Collision Complexes
 - A. Specific Rate Constants for Rigid Activated Complexes
 - B. Specific Rate Constants for Loose Activated Complexes
 - C. Reaction Yields for Vibrational and Rotational Channel Switching References