



# CONTENTS

A CRITICAL ASSESSMENT OF THE COUPLED CLUSTER METHOD IN QUANTUM CHEMISTRY	1
<i>By Josef Paldus and Xiangzhu Li</i>	
ON THE ELECTRONIC SPECTRA OF SMALL LINEAR POLYENES	177
<i>By Ruth McDiarmid</i>	
UNDERSTANDING ELECTRON CORRELATION: RECENT PROGRESS IN MOLECULAR SYNCHROTRON PHOTOELECTRON SPECTROSCOPY	215
<i>By A.D.O Bawagan and E.R. Davidson</i>	
DEVELOPMENTS IN PARALLEL ELECTRONIC STRUCTURE THEORY	267
<i>By G.D. Fletcher, M.W. Schmidt and M.S. Gordon</i>	
EXPERIMENTAL AND THEORETICAL BUBBLE DYNAMICS	295
<i>By W. Lauterborn, T. Kurz, R. Mettin and C.D. Ohl</i>	
ACID-BASE PROTON TRANSFER AND ION PAIR FORMATION IN SOLUTION	381
<i>By Koji Ando and James T. Hynes</i>	
STRUCTURES, SPECTROSCOPIES, AND REACTIONS OF ATOMIC IONS WITH WATER CLUSTERS	431
<i>By Kiyokazu Fuke, Kenro Hashimoto, and Suehiro Iwata</i>	





# CHAPTER 1

## A CRITICAL ASSESSMENT OF COUPLED CLUSTER METHOD IN QUANTUM CHEMISTRY

JOSEF PALDUS

*Max-Planck-Institute for Astrophysics, Karl-Schwarzschild Str. 1,  
Postfach 1523, 85740 Garching, Germany,  
and*

*Department of Applied Mathematics,\* Department of Chemistry,  
and Guelph-Waterloo Center for Graduate Work in Chemistry,  
University of Waterloo, Waterloo, Ontario N2L 3G1, Canada*

XIANGZHU LI

*Department of Applied Mathematics, University of Waterloo, Waterloo,  
Ontario N2L 3G1, Canada*

### CONTENTS

- Abstract
- I. Introduction
  - A. Historical Outline
  - B. Scope of the Review
- II. Methodology
  - A. Basic Notation: Second vs. First Quantization
  - B. Many-Body Perturbation Theory (MBPT): Origins of Coupled-Cluster (CC) *Ansatz*
  - C. Single-Reference Coupled-Cluster (SR CC) Approaches
    - 1. General Spin-Orbital Formalism
    - 2. Coupled-Cluster Method with Singles and Doubles (CCSD)
    - 3. Spin Adaptation
    - 4. Beyond CCSD
      - 4.1. Standard Full Approaches (CCSDT, etc.)
      - 4.2. Perturbative Approaches [CCSD(T), etc.]
      - 4.3. Other Approximate Approaches (ACCS, ACPQ, etc.)

---

\*Permanent address.



- D. Multireference Coupled-Cluster (MR CC) Approaches
  - 1. Effective Hamiltonian Formalism
  - 2. Proper MR CC Approaches
    - 2.1. Valence-Universal CC Methods
    - 2.2. State-Universal CC Methods
  - 3. State-Selective, or State-Specific (SS), Approaches
    - 3.1. SS MR CC Method of Adamowicz et al.
    - 3.2. Unitary Group Approach (UGA)-Based CCSD Methods
    - 3.3. Externally Corrected CCSD Methods
- E. Related Approaches
  - 1. Many-Body Perturbation Theory (MBPT)
  - 2. Quadratic Configuration Interaction (QCI)
- F. Coupled-Cluster Approaches to Properties
  - 1. Direct Calculation of Expectation Values
  - 2. Finite-Field Approaches
  - 3. Linear-Response (LR) Approaches
  - 4. Equations-of-Motion (EOM)-Based Approaches
- G. Computational Aspects
  - 1. Orbital Choice
  - 2. Basic Algorithms and Numerical Techniques
  - 3. Automated Generation of Computer Codes
- III. Applications
  - A. Correlation Energies
  - B. Potential-Energy Surfaces (PESs) and Related Properties
    - 1. Equilibrium Geometries
    - 2. Dissociation Energies
    - 3. Full Potential-Energy Surfaces
    - 4. Vibrational Frequencies
  - C. Ionization Potentials and Electron Affinities
  - D. Electronic Excitation Energies and Excited-State PESs
  - E. Static Properties (Dipole Moments, etc.)
  - F. Dynamic Properties
- IV. Conclusions and Future Prospects
- Appendix A: Algebra of Replacement Operators
- Appendix B: List of Acronyms
- Acknowledgments
- References





## CHAPTER 2

# ON THE ELECTRONIC SPECTRA OF SMALL LINEAR POLYENES

RUTH McDIARMID

*Laboratory of Chemical Physics, National Institute of Diabetes and  
Digestive and Kidney Diseases, National Institutes of Health,  
Bethesda, Maryland 20892-0510*

### CONTENTS

- I. Introduction
- II. Experimental Techniques
- III. Ethylene
- IV. Butadiene
- V. Hexatriene
- VI. Valence-Excited States
- VII. Evaluation of Numerical Calculations of Transition Energies in Polyenes
- VIII. Concluding Remarks
- References





## CHAPTER 3

# UNDERSTANDING ELECTRON CORRELATION: RECENT PROGRESS IN MOLECULAR SYNCHROTRON PHOTOELECTRON SPECTROSCOPY

A. D. O. BAWAGAN

*Ottawa-Carleton Chemistry Institute Carleton University,  
Ottawa, Ontario K1S 5B6, Canada*

E. R. DAVIDSON

*Department of Chemistry Indiana University, Bloomington,  
Indiana 47405, USA.*

## CONTENTS

- I. Introduction
- II. Experimental Details
- III. Theoretical Details
- IV. Survey of Synchrotron Photoelectron Spectroscopy of Molecules (Post-1986)
  - A. Alkanes and Alkenes
  - B. Intrinsic Correlations and Dynamic Correlations
  - C. Acetylene, Allene, and Butadiene
  - D. Other Molecular Systems
- V. Comparison of EMS and PES Intensities
- VI. Developing Practical Pictures of Electron Correlation Effects
- VII. Conclusions
- Acknowledgments
- References
- Appendix A



# CHAPTER 4

## DEVELOPMENTS IN PARALLEL ELECTRONIC STRUCTURE THEORY

G. D. FLETCHER, M. W. SCHMIDT, and M. S. GORDON

*Iowa State University, Ames, IA*

### CONTENTS

- I. Introduction
  - A. Porting versus Parallelization
- II. Parallel MP2 Gradient Algorithm
  - A. Integral Classes 1–4
  - B. Three-Virtual Terms
  - C. Solution of Z-Vector Equations
  - D. Back-Transformation
  - E. Summary
- III. Timings and Applications
  - A. Numeric MP2 Hessian of TATB
  - B. HEDM Molecular Structure
- IV. Conclusion
- Acknowledgments
- References





# CHAPTER 5

## EXPERIMENTAL AND THEORETICAL BUBBLE DYNAMICS

W. LAUTERBORN, T. KURZ, R. METTIN, and C. D. OHL

*Universität Göttingen, Göttingen, Germany*

### CONTENTS

- I. Introduction
- II. Classification of Cavitation Bubble Generation
- III. Cavitation Bubble Production Devices
- IV. Cavitation Threshold
- V. Single-Bubble Dynamics in a Sound Field
  - A. Experimental Observations
  - B. Theoretical Description
- VI. Single Laser-Induced Bubble Dynamics
  - A. Spherical Bubble Dynamics
  - B. Spherical Laser Bubble Luminescence
  - C. Aspherical Bubble Dynamics
  - D. Aspherical Laser Bubble Luminescence
- VII. Two-Bubble Systems
- VIII. Few-Bubble Systems
- IX. Many-Bubble Systems
  - A. High-Speed Cinematography
  - B. Cavitation Noise
  - C. Light Transmission
  - D. High-Speed Holographic Cinematography
  - E. Digital Image Processing
  - F. Multibubble Sonoluminescence
- X. Theory of Many-Bubble Systems
- XI. Summary
- Acknowledgments
- References



# CHAPTER 6

## ACID–BASE PROTON TRANSFER AND ION PAIR FORMATION IN SOLUTION

KOJI ANDO

*Institute of Materials Science, University of Tsukuba, Tsukuba,  
Ibaraki 305-8573, Japan*

JAMES T. HYNES

*Department of Chemistry and Biochemistry, University of Colorado,  
Boulder, Colorado 80309-0215, USA*

### CONTENTS

- I. Introduction
- II. General Issues and Model Studies
  - A. Some General Considerations
  - B. Valence Bond Study in a Dielectric Continuum Solvent
  - C. Molecular Dynamics of Acid–Base Proton Transfer
- III. Ionization of Hydrochloric Acid in Water
  - A. Introduction
  - B. Potentials and Computational Methods
  - C. Second Proton-Transfer Step
  - D. Ionization of Hydrofluoric Acid in Water
- IV. Concluding Remarks
- Acknowledgments
- References





# CHAPTER 7

## STRUCTURES, SPECTROSCOPIES, AND REACTIONS OF ATOMIC IONS WITH WATER CLUSTERS

KIYOKAZU FUKE

*Department of Chemistry, Kobe University, Kobe, 657-8501 Japan*

KENRO HASHIMOTO

*Computer Center, Tokyo Metropolitan University, Minami-Ohsawa,  
Hachioji, 192-0397 Japan*

SUEHIRO IWATA

*Institute for Molecular Science, Okazaki, 444-8585 Japan*

### CONTENTS

- I. Introduction
- II. Group 1 (Alkali) Metals
  - A. Size Dependence of the Ionization Energy
    - 1. Experimental Study
    - 2. Theoretical Study
  - B. Photoelectron Spectroscopy of Solvated Metal Anions
    - 1. Experimental Study
    - 2. Theoretical Study
  - C. Ammoniated Metal Anions for Comparison with Hydrated Clusters
    - 1. Experimental Study
    - 2. Theoretical Study
- III. Group 2 Elements
  - A. Collision Reactions of Metal Ions with Water Clusters
    - 1. Product Switches
    - 2. Ab initio MO Studies
    - 3. Analysis of the Product Switches

**B. Photodissociation Spectra and the Dissociation Process**

1. Photodissociation Spectra of  $\text{Mg}^+(\text{H}_2\text{O})_n$
2. Ab initio MO Studies of the Vertical Excitation Energies
3. Photodissociation Spectra of  $\text{Ca}^+(\text{H}_2\text{O})_n$
4. Photodissociation Process of  $\text{Mg}^+(\text{H}_2\text{O})_n$  and  $\text{Ca}^+(\text{H}_2\text{O})_n$

**IV. Group 13 Elements**

- A. Photoionization of  $\text{Al}(\text{H}_2\text{O})_n$
- B. Photodissociation of  $\text{Al}^+(\text{H}_2\text{O})_n$
- C. Unimolecular Fragmentation Reactions
- D. Intracuster Reactions of  $[\text{B}(\text{H}_2\text{O})_n]^+$  Studied by a Hybrid Procedure of Ab Initio MO Calculations and Monte Carlo Samplings

**V. Halogen–Water Cluster Anions**

- A. Incremental Enthalpy Changes and Structures of the Clusters
- B. Photoelectron Spectra of  $\text{X}^-(\text{H}_2\text{O})_n$
- C. Vibrational Spectroscopy
- D. MD and MC Simulations of the Clusters

**VI. Summary and Concluding Remarks**

Acknowledgments

References

