

CONTENTS

PART I. THEORY

1. **The Nature of Intermolecular Forces**
By J. O. Hirschfelder and W. J. Meath 3
2. **Permanent and Induced Molecular Moments and Long-Range Intermolecular Forces**
By A. D. Buckingham 107
3. **New Methods for Calculating Long-Range Intermolecular Forces**
By A. Dalgarno 143
4. **Very Long-Range (Retardation Effect) Intermolecular Forces**
By E. A. Power 167
5. **Reaction Field Techniques and Their Applications to Intermolecular Forces**
By B. Linder 225
6. **Intermolecular Forces in Liquids**
By O. Sinanoğlu 283

PART II. EXPERIMENTAL DETERMINATIONS

7. **Methods for the Determination of Intermolecular Forces**
By E. A. Mason and L. Monchick 329
8. **Determination of Intermolecular Forces via Low-Energy Molecular Beam Scattering**
By R. B. Bernstein and J. T. Muckerman 389
9. **Microwave Pressure Broadening and Its Application to Intermolecular Forces**
By G. Birnbaum 487
10. **Intermolecular Forces Determined by Nuclear Magnetic Resonance**
By M. Bloom and I. Oppenheim 549
- Author Index** 601
- Subject Index** 619
- Cumulative Indexes to Volumes 1-13** 631

1. The Nature of Intermolecular Forces*

JOSEPH O. HIRSCHFELDER

*The University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin*

and

WILLIAM J. MEATH

*The University of Western Ontario Department of Chemistry
London, Ontario, Canada*

CONTENTS

I. Introduction	5
A. Interaction of Two 1s Hydrogen Atoms.	5
II. Concept of an Intermolecular Potential	8
A. The Born-Oppenheimer Approximation.	12
B. The Adiabatic Approximation	12
C. The Nonadiabatic Approximation	13
D. Coupling between the Electronic and Rotational Angular Momenta	14
E. Discussion	15
III. The Effective Potential	17
IV. Electrostatic Variational Calculations	21
A. Small and Intermediate Separations	22
1. The Ground $X^1\Sigma_g^+$ State of the Hydrogen Molecule	22
2. The Lowest Excited Bound State, $B^1\Sigma_u^+$, of Hydrogen	24
3. The Lowest Excited $^1\Sigma_g^+$ State of Hydrogen	25
B. Large Separations	25
V. Electrostatic Perturbation Calculations	29
A. Rayleigh-Schrödinger Perturbation Theory	29

* This research was supported in part by National Aeronautics and Space Administration Grant NsG-275-62 at the University of Wisconsin Theoretical Chemistry Institute. One of the authors (W.J.M.) wishes to thank the National Research Council of Canada for their grant which assisted him in this work. The other author (J.O.H.) wishes to thank the University of Florida Quantum Theory Project, Gainesville, Florida for their assistance.

B.	Large Separations	31
1.	The Multipole Expansion of V_e	31
2.	The Perturbation Problem	33
3.	Nonresonant Intermolecular Forces	34
a.	First-Order Energy	34
b.	Second-Order Energy	36
4.	Resonant Intermolecular Forces	39
a.	Resonance between Like Atoms	39
b.	First-Order Dipole Resonance	40
c.	First-Order Quadrupole Resonance	41
d.	The Second-Order Energy	41
e.	Resonance within One Molecule	42
5.	Almost Degeneracy Due to the Effects of Atomic Fine Structure	42
a.	(Λ, S) Coupling	43
b.	(J_a, J_b) Coupling	43
c.	Intermediate Coupling	43
C.	Intermediate Separations	45
1.	Charge-Transfer Interactions	49
D.	Very Small Separations	51
VI.	The Hellmann-Feynman Theorem	51
A.	The Generalized Hellmann-Feynman Theorem	52
B.	The Electrostatic Hellmann-Feynman Theorem	54
C.	Application of the Electrostatic Hellmann-Feynman Theorem to the Long-Range Interaction of Two Hydrogen Atoms	55
D.	Other Applications of the Hellmann-Feynman Theorem to the Long-Range Interaction of Two Atoms	60
1.	Cartesian Coordinates with Laboratory-Fixed Origin	60
2.	Electronic Coordinates Relative to the Associated Nucleus	60
3.	Confocal Elliptic Coordinates	61
E.	The Integral Hellmann-Feynman Theorem	62
VII.	The Role of Electron Correlations in Intermolecular Forces	63
A.	Large Separations	63
B.	Intermediate Separations	67
C.	Small Separations	69
D.	Discussion of Davidson's Double Minimum Excited H_2 Potential Energy Curve	70
VIII.	Magnetic or Relativistic Intermolecular Forces	71
A.	The Breit-Pauli Hamiltonian	71
B.	Small and Intermediate Separations	74
C.	Large Separations	75
1.	Calculation of the Interaction Energy	75
a.	The Multipole Expansion of H_{rel}	75
2.	Dispersion Energies	78
a.	Comparison with the Exact Retarded Dipole-Dipole Interaction Energy	79
b.	"Small R" Expansion	80
c.	"Large R" Expansion	82

NATURE OF INTERMOLECULAR FORCES		5
3. First-Order Energies		86
a. Retarded First-Order Interaction Energies		86
b. Comparison with the Exact Retarded Dipole Resonance Energy		87
c. Nonretarded First-Order Interaction Energies		90
d. Example: The Interaction of Two Hydrogen Atoms		92
References		98

2. Permanent and Induced Molecular Moments and Long-Range Intermolecular Forces

A. D. BUCKINGHAM

*School of Chemistry, The University of Bristol
Bristol, England*

CONTENTS

I. Introduction	107
II. A Molecule in a Static Electric Field.	108
III. A Molecule in a Periodic Field	115
IV. Interaction of Two Molecules	122
V. Some Particular Molecular Interactions	128
A. A Point Charge and a Linear Molecule	129
B. A Point Charge and a Tetrahedral Molecule	130
C. A Spherical and a Tetrahedral Molecule	131
D. Two Linear Molecules	132
VI. Measurements of Molecular Moments and Polarizabilities	134
VII. Long-Range Dipolar Interactions.	138
References.	140

3. New Methods for Calculating Long-Range Intermolecular Forces

A. DALGARNO*

School of Physics and Applied Mathematics, The Queen's University of Belfast, Belfast, Northern Ireland

CONTENTS

I. Introduction	143
II. General Theory	144
III. Accurate Calculations	146
A. Atomic Hydrogen	146
B. Helium	148
C. Lithium	149
D. Molecular Hydrogen	150
IV. Semiempirical Methods	150
V. Hartree-Fock Theories	152
VI. Double Perturbation Theory	155
A. Sinanoğlu's Procedure	158
VII. Many-Body Perturbation Theory	160
VIII. Three-Body Forces	160
IX. Special Topics	162
A. Higher-Order Interactions	162
B. Long-Range Effects on Hyperfine Structure	162
X. Recommended Values	163
References	164

4. Very Long-Range (Retardation Effect) Intermolecular Forces

EDWIN A. POWER

*Mathematics Department
University College, London, England*

CONTENTS

I. Introduction to Very Long-Range Forces	167
A. General Background.	168
B. Historical Survey and Summary	173
II. Calculation of Dispersion Interaction: the Casimir-Polder Potential	187
A. Noncovariant Method	187
B. Feynman Method	194
III. Interaction Energies Involving Excited States	199
A. Concept of Potential	200
B. Energy Shifts with Excited States: Resonance Interaction	202
C. Excitation Present but Nonresonant	206
IV. Nondispersive Forces in the Long-Range Limit	209
A. Breit Operator	209
B. Pauli Approximation	216
References	222

5. Reaction-Field Techniques and Their Applications to Intermolecular Forces*

BRUNO LINDER

*Department of Chemistry, The Florida State University
Tallahassee, Florida*

CONTENTS

I. Introduction	226
II. The Reaction Field of a Static Moment in a Continuous Medium	228
A. The Reaction Field of a Nonpolarizable Dipole	229
B. The Reaction Field of an Arbitrary System of Charges	233
C. Critique of the Method	235
III. The Reaction Field of a Fluctuating Moment in a Medium of Arbitrary Distribution	237
A. General Formulation	237
B. Dielectric Description	239
C. Molecular Description	239
IV. Generalized Potential	243
V. Additive and Nonadditive van der Waals Potentials	249
A. Pair and Triple Potentials	250
B. Molecular Susceptibilities	251
1. Harmonic Oscillator	255
2. Rigid Rotor	255
C. Dispersion-, Orientation-, and Induction Forces	257
1. Pair Potentials	257
2. Triple Potentials	259
VI. Forces in Dense Media	260
A. Molecular Formulation	261
B. Dielectric Formulation	266
1. The Continuum Model	266
2. The Cavity Concept	268
VII. Two-Temperature Potentials	275
VIII. Concluding Remarks	279
References	280

* Supported (in part) by a grant from the Petroleum Research Fund, administered by the American Chemical Society, and (in part) by the Institute of Molecular Biophysics under contract with the Division of Biology and Medicine, U.S. Atomic Energy Commission.

6. Intermolecular Forces in Liquids

OKTAY SINANOĞLU

*Center for Theoretical Studies
University of Miami, Coral Gables, Florida
and
Sterling Chemistry Laboratory
Yale University, New Haven, Connecticut*

CONTENTS

I. Introduction	283
II. Effective Pair Potentials	284
III. The Two-Body Potential in the Gas Phase	289
IV. <i>N</i> -Body Potentials	292
V. Effective Nonpolar Pair Potentials in Liquids	298
A. Evaluation of L_{AB}	299
B. Evaluation of L_{AB} for $R < R_A + R_B + 4R_C$ and the Role of the Structure of the Liquid	306
1. Region 1	309
2. Region 2	310
3. Region 3— $R_A + R_B + 2\kappa R_C > R \geq R_A + R_B$	311
4. Region 4— $R_A + R_B > R > 0$	311
VI. Summary of the Effective Pair Potential $V_{AB}^{\text{eff}}(R, R_A/R_C, R_B/R_C, \rho_1)$ in the Liquid	315
A. The Lennard-Jones Case ($l = 0$)	315
B. The Kihara Case ($l \neq 0$)	316
VII. The Effective Potential in Other Density Ranges and Phases	319
VIII. Examples of Potentials in Some Nonpolar Liquids	319
References	326

7. Methods for the Determination of Intermolecular Forces*

E. A. MASON†

*Institute for Molecular Physics, University of Maryland
College Park, Maryland*

and

L. MONCHICK

*Applied Physics Laboratory, The Johns Hopkins University
Silver Spring, Maryland*

CONTENTS

I. Introduction	330
II. Quantal Calculations	331
A. <i>Ab Initio</i> Calculations	332
B. Semiempirical Calculations	333
1. Long-Range Forces	334
2. Short-Range Forces	338
3. Intermediate-Range Forces	345
C. Model Calculations	346
D. Survey of Accuracy	350
III. Spectroscopic Observations	350
A. Vibration-Rotation Bands	351
B. Predissociation	354
C. Intensity Distribution	355
D. Pressure Effects	357
IV. Beam Scattering	358
A. General Remarks	358
B. High-Energy Beams	361
C. Thermal-Energy Beams	364
1. Rainbows and Haloes	364
2. Shadows	367
3. Glories and Glorified Shadows	369

* This work was supported in part by the National Aeronautics and Space Administration (Grant NsG-5-59), and in part by the Bureau of Naval Weapons, Department of the Navy, under Contract N0w 62-0604-c.

† Present address: Brown University, Providence, Rhode Island.

V. Bulk Properties	370
A. Virial Coefficients	370
B. Transport Coefficients	372
C. Condensed Phases	375
VI. Relaxation Methods	377
VII. Final Remarks	379
References	379

8. Determination of Intermolecular Forces via Low-Energy Molecular Beam Scattering*

R. B. BERNSTEIN and J. T. MUCKERMAN

*Theoretical Chemistry Institute and Chemistry Department
University of Wisconsin, Madison, Wisconsin*

CONTENTS

I. Introduction	390
II. General Remarks	391
A. Short-Range Repulsive Forces	392
B. Intermediate- and Long-Range Attractive Forces	393
III. Description of the Measurements	397
A. Arrangement of the Experiments	397
B. Measured Quantities	398
IV. Description and Illustration of the Phenomena	401
A. General Angular Dependence of Scattering	402
1. Quantum Mechanical Preliminaries	402
2. Quantum Interferences.	405
3. Low-Angle Classical Behavior	408
4. Rainbow Scattering	409
B. Velocity Dependence of Total Cross Sections	413
1. General Dependence	413
2. Determination of C_6 Constants	414
3. Glory Extrema in $Q(v)$	414
V. Requirements for Suitability of Systems	418
A. Theoretical Requirements	419
B. Experimental Requirements	420
VI. Inventory of Scattering Measurements	424
A. Systems Studied	424
B. Types of Measurements	424
C. Annotated Bibliography	445

* This work received financial support from the National Aeronautics and Space Administration (Grant NsG-275-62) and the U.S. Atomic Energy Commission, Division of Research.

VII. Summary and Appraisal of the More Reliable Determinations . . .	459
A. Semiempirical Aids to Correlation of Data	460
B. "Best" Potential Parameters for Systems of Atoms and/or Diatomics	464
C. Regularities and Systematics	465
VIII. Concluding Remarks: Scope of the Method	479
References	484

9. Microwave Pressure Broadening and Its Application to Intermolecular Forces

GEORGE BIRNBAUM

*North American Aviation Science Center
Thousand Oaks, California*

CONTENTS

I.	Introduction	488
A.	Scope of this Review	488
B.	Historical Survey of Theories of Spectral Line Shape and Width ..	489
C.	The Impact Approximation	491
II.	Widths of Resonant Lines	493
A.	Anderson's Theory of Pressure-Broadened Lines	493
1.	Appendix. Intermolecular Potentials	505
B.	Simplifications of Anderson's Theory	509
C.	Gordon's Theory of Pressure-Broadened Lines	513
III.	Comparison of Theoretical and Experimental Line Widths	515
A.	Introduction	515
B.	Linear Molecules.....	516
1.	OCS	516
2.	HCl	523
3.	BrCN	525
4.	N ₂ O	525
5.	O ₂	526
C.	Symmetric Top Molecules. Rotational Lines	527
D.	Asymmetric Top Molecules	527
1.	H ₂ O	527
2.	SO ₂	528
E.	Inversion Spectrum of NH ₃	529
1.	Self-Broadening	529
2.	Foreign-Gas Broadening	531
F.	Summary	533
IV.	Molecular Quadrupole Moments	535
V.	Nonresonant Absorption and Relaxation	539
A.	Introduction	539
B.	Theory	540
C.	Comparison of Theory and Experiment	543
VI.	Conclusions	545
References	545

10. Intermolecular Forces Determined by Nuclear Magnetic Resonance

MYER BLOOM*

*Department of Physics, University of British Columbia, Vancouver,
British Columbia, Canada*

and

IRWIN OPPENHEIM†

*Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts, and Department of Chemistry and Institute
for Radiation Physics and Aerodynamics, University of California, San
Diego, La Jolla, California*

CONTENTS

I. Introduction	550
A. Macroscopic Measurements	550
B. Physical Significance of the Relaxation Time Measurements	553
II. Theory of Nuclear Spin Relaxation in Dilute Hydrogen Gas	555
A. Intramolecular Correlation Functions	556
B. The Number of Distinct Correlation Functions	559
C. Exact Correlation Function in the Low-Density Region	561
D. Relationship of the Correlation Function to the Master Equation	562
1. Weak-Collision Approximation	564
III. Application of the Theory to Some Special Cases	567
A. Infrequent Transitions Between States of Different J	567
B. The Two-Level System	568
IV. Correlation Functions of Anisotropic Intermolecular Potentials	572

* Research supported by National Research Council of Canada.

† This research was supported in part by the Advanced Research Projects Agency (Project DEFENDER) and was monitored by the U.S. Army Research Office, Durham under Contract DA-31-124-ARO-D-257; and the National Science Foundation.

V. Calculation of the Intermolecular Correlation Functions	578
A. High-Temperature Approximation to the Intermolecular Correlation Functions	579
B. The Constant Acceleration Approximation (CAA)	581
VI. Interpretation of Some Experiments Using the CAA	585
A. Infrequent Transitions Between States of Different J	585
B. Application to Pure H_2 Gas	587
C. Effect of Transitions Between Rotational States in H_2	591
D. Quadrupole-Quadrupole Interactions Between H_2 and Diatomic Molecules Having Large Moments of Inertia	592
VII. Miscellaneous Topics	594
A. Other Theoretical Work	594
B. Spin Diffusion Constant in H_2	596
C. Nuclear Spin Relaxation in HD and D_2	596
D. Nuclear Spin Relaxation in Polyatomic Molecules	597
References	598

