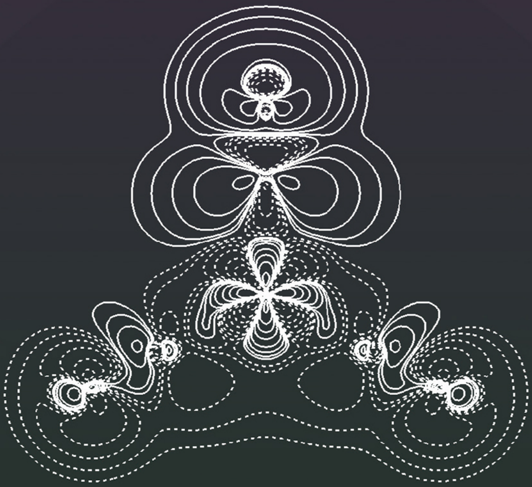
Third Edition

Electronic Structure and Properties of Transition Metal Compounds

Theory and Applications



Isaac B. Bersuker

Yang Liu

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Contents

Preface to the Third Edition *xvii*
Extract from the Preface to the Second Edition *xix*
Extracts from the Preface to the First Edition *xxiii*
Foreword to the First Edition *xxv*
Mathematical Symbols *xxvii*
Abbreviations *xxxiii*

1 Introduction: Subject and Methods *1*
1.1 Objectives *1*
1.1.1 Molecular Engineering and Intuitive Guesswork *1*
1.1.2 Main Objectives of This Book in Comparison with Other Sources *4*
1.2 Definitions of Chemical Bonding and Transition Metal Coordination System *8*
1.2.1 Chemical Bonding as an Electronic Phenomenon *8*
1.2.2 Definition of Coordination System *10*
1.3 The Schrödinger Equation *13*
1.3.1 Formulation *13*
1.3.2 Role of Approximations *15*
Summary Notes *16*
References *17*

2 Atomic States *19*
2.1 One-Electron States *19*
2.1.1 Angular and Radial Functions *19*
2.1.2 Orbital Overlaps: Hybridized Functions *25*
2.1.3 Spin–Orbital Interaction *29*
2.1.4 Relativistic Atomic Functions *31*

2.2 Multielectron States: Energy Terms 38
2.2.1 Electronic Configurations and Terms 38
2.2.2 Multielectron Wavefunctions 43
2.2.3 Slater-Condon and Racah Parameters 45
2.2.4 The Hartree–Fock Method 50
Summary Notes 54
Questions 55
Exercises and Problems 55
References 56

3 Symmetry Ideas and Group-Theoretical Description 59
3.1 Symmetry Transformations and Matrices 60
3.2 Groups of Symmetry Transformations 66
3.3 Classification of Point Groups 67
Example 3.1. The Symmetry Group of an Octahedral O_h System and Its Classes 69
3.4 Representations of Groups and Matrices of Representations 71
Example 3.2. The Rules of IrReps and Characters in C_{4v} Point Group 77
3.5 Classification of Molecular Terms and Vibrations, Selection Rules, and The Wigner–Eckart Theorem 78
Example 3.3. Energy Terms of Electronic Configuration e^2 81
3.6 Construction of Symmetrized Molecular Orbitals and Normal Vibrations 83
Example 3.4. Construction of E_g-Symmetry-Adapted σ MOs for Octahedral O_h Systems 86
Example 3.5. Construction of T_{2g}-Symmetry-Adapted π MOs for Octahedral O_h Systems 89
Example 3.6. Normal Coordinates of a Regular Triangular Molecule X_3 90
3.7 The Notion of Double Groups 92
Summary Notes 93
Exercises and Problems 94
References 95

4 Crystal Field Theory 97
4.1 Introduction 97
4.1.1 Brief History 97
4.1.2 Main Assumptions 98
4.2 Splitting of the Energy Levels of One d Electron in Ligand Fields 99

4.2.1 Qualitative Aspects and Visual Interpretation *99*
4.2.2 Calculation of the Splitting Magnitude *105*
Example 4.1. Splitting of a *d*-Electron Term in Octahedral Crystal Fields *107*
4.2.3 Group-Theoretical Analysis *111*
4.3 Several *d* Electrons *114*
4.3.1 Case of a Weak Field *114*
4.3.2 Strong Crystal Fields and Low- and High-Spin Complexes *120*
Example 4.2. High-Spin and Low-Spin Octahedral Complexes of Iron *124*
4.3.3 Energy Terms of Strong-Field Configurations *125*
4.3.4 Arbitrary Ligand Fields and Tanabe–Sugano Diagrams *127*
4.4 *f*-Electron Term Splitting *134*
4.5 Crystal Field Parameters and Extrastabilization Energy *137*
4.6 Limits of Applicability of Crystal Field Theory *141*
Summary Notes *143*
Questions *144*
Exercises and Problems *145*
References *146*

5 Molecular Orbitals and Related Description of Electronic Structure *149*
5.1 Basic Ideas of the MO LCAO Method *149*
5.1.1 Main Assumptions *149*
5.1.2 Secular Equation *151*
5.1.3 Classification by Symmetry *152*
5.1.4 Symmetrized Orbitals *156*
5.1.5 Simplification of the Secular Equation *158*
5.1.6 A Short Note on Band Structure of Transition Metal Solids *160*
5.2 Charge Distribution and Bonding in the MO LCAO Method. The Case of Weak Covalency *161*
5.2.1 Atomic Charges and Bond Orders *161*
Example 5.1. Shortcomings of Mulliken's Definition of Atomic Charges in Molecules *163*
5.2.2 Bonding, Nonbonding, and Antibonding Orbitals *165*
5.2.3 Case of Weak Covalency *168*
5.2.4 Angular Overlap Model *170*
5.3 Methods of Calculation of MO Energies and LCAO Coefficients *173*
5.3.1 SCF MO LCAO Approximation *173*
5.3.2 Electron Correlation Effects *176*

5.3.3 Basis Sets and Pseudopotentials 182
Example 5.2. Calculate the CuF_2 Molecule Using Hartree–Fock and MP2 Methods 187
Example 5.3. Calculate the Absorption and Emission spectra of $[Cr(ddpd)_2]^{3+}$ (ddpd = N,N′-dimethyl-N,N′-dipyridin-2-ylpyridine-2,6-diamine) using CASSCF and CASPT2 Methods 190
5.4 Density Functional Theory 192
5.4.1 Hohenberg–Kohn (HK) Method 192
5.4.2 Exchange-Correlation Functional 196
5.4.3 Time-Dependent DFT (TD-DFT) 201
5.4.4 Density-Functional Tight Binding (DFTB) 202
Example 5.4. Calculation of $ZnCl_2$ by the DFT Method 203
Example 5.5. DFT Calculation of the Energy of Absorption of the O_2 on the Surface of CoN_4-ZnN_4/C Material 205
5.5 Electronic Structure Calculations for Large Polyatomic Systems 209
5.5.1 Fragmentary Calculations 209
5.5.2 Molecular Mechanics 213
Example 5.6. Application of Molecular Modeling to Transition Metal Complexes with Macrocycles 216
5.5.3 Combined Quantum/Classical (QM/MM) Methods 218
Example 5.7. Oxidative Addition of H_2 to $Pt(P(t\text{-}Bu)_3)_2$ Treated by ONIOM Version of QM/MM Methods 222
Example 5.8. Iron Picket-Fence Porphyrin Treated by the QM/MM Method with Charge Transfer (QM/MM/CT) 228
5.5.4 Machine Learning Force Fields (MLFF) Method 231
5.6 Comparison of Methods and Computer Programs 232
Summary Notes 239
Exercises and Problems 240
References 241

6 Electronic Structure and Chemical Bonding 249
6.1 Classification of Chemical Bonds by Electronic Structure and Role of *d* and *f* Electrons in Coordination Bonding 249
6.1.1 Criticism of the Genealogical Classification 249
6.1.2 Classification by Electronic Structure and Properties 252
6.1.3 Features of Coordination Bonds 254
6.1.4 Coordination Bonding by Pre- and Post-transition Elements 256

6.2 Qualitative Aspects and Electronic Configurations *258*
  6.2.1 Most Probable MO Schemes *258*
  6.2.2 Electronic Configurations in Low- and High-Spin Complexes *260*
  6.2.3 Covalence Electrons and Ionization Potentials *263*
6.3 Ligand Bonding *267*
  6.3.1 General Considerations: Multiorbital Bonds *267*
  6.3.2 Mono-orbital Bonds: Coordination of NH_3 and H_2O *272*
    Example 6.1. Ab Initio Numerical SCF CI Calculations of the Electronic Structure of Mono-orbital Bonds: $Ni(H_2O)_n$ and $Ni(PH_3)_n$, $n = 1, 2$ *273*
  6.3.3 Diorbital Bonds: Coordination of the N_2 Molecule *274*
    Example 6.2. Electronic Structure and Bonding in FeN_2 *276*
  6.3.4 Coordination of Carbon Monoxide *277*
    Example 6.3. Bonding and Charge Transfer in the Pt—CO Complex *278*
    Example 6.4. Bonding in M—CO with M = Cr, Fe, Co, Ni *279*
    Example 6.5. Bonding in Sc—CO, Ni—CO, and $Ni(CO)_2$ *280*
  6.3.5 $\sigma + \pi$ Bonding *282*
    Example 6.6. Electronic Structure of Transition Metal Hexacarbonils $M(CO)_6$ *283*
  6.3.6 CO Bonding on Surfaces *285*
  6.3.7 Bonding of NO *288*
    Example 6.7. Coordination of NO on the Ni(111) Surface *288*
  6.3.8 Coordination of C_2H_4 *289*
    Example 6.8. Ethylene Bonding to Transition Metal Centers *291*
    Example 6.9. Ethylene Bonding in $PtCl_3(C_2H_4)^-$ and $PdCl_3(C_2H_4)^-$ *292*
  6.3.9 Metal–Metal Bonds and Bridging Ligands *295*
    Example 6.10. Multiple Metal–Metal Bonds in $[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$ *296*
6.4 Energies, Geometries, and Charge Distributions *303*
  6.4.1 Ionization Energies *303*
    Example 6.11. Ab Initio Calculations of $Ni(C_3H_5)_2$ *305*
  6.4.2 Total and Bonding Energies, Geometries, and Other Properties *307*
6.5 Relativistic Effects *315*

6.5.1 Relativistic Approaches *316*
6.5.2 Orbital Contraction and Valence Activity *319*
Example 6.12. Relativistic Effects in Catalytic Activity of Pt and Pd Complexes *322*
6.5.3 Bond Lengths, Bond Energies, and Vibrational Frequencies *322*
Example 6.13. Relativistic Effects in Metal Hydrides *323*
6.5.4 Correlation Between Spin-Orbital Splitting and Bonding *327*
Example 6.14. Relativistic Semiempirical Calculation of $PtCl_6^{2-}$ *329*
6.5.5 Other Relativistic Effects *331*
Summary Notes *332*
Exercises and Problems *333*
References *335*

7 Vibronic Coupling in Formation, Deformation, and Transformation of Polyatomic Systems. The Jahn–Teller Effects *343*
7.1 Molecular Vibrations *344*
7.1.1 Adiabatic Approximation *344*
7.1.2 Normal Coordinates and Harmonic Vibrations *347*
7.1.3 Special Features of Vibrations of Coordination Compounds *354*
7.2 Vibronic Coupling *356*
7.2.1 Vibronic Constants *356*
7.2.2 Orbital Vibronic Constants *358*
Example 7.1. Vibronic MO Description of Electronic Structure of N_2 and CO *361*
7.3 The Jahn–Teller Effects *363*
7.3.1 The Jahn–Teller Theorem *363*
7.3.2 The Pseudo-Jahn–Teller Effect *368*
7.3.3 *Hidden*-Jahn–Teller and *Hidden* Pseudo-Jahn–Teller Effects. Four Modifications of Jahn–Teller Effects *369*
Example 7.2. Hidden-JTE Origin of Instability of the High-Symmetry Configuration of the Ozone Molecule *372*
7.3.4 Configurations with *h*-PJTE and Spin Crossover *374*
Example 7.3. Hidden-PJTE Origin of Instability of the High-Symmetry Configuration of the CuF_3 Molecule *376*
7.3.5 The Renner–Teller Effect *378*
7.3.6 The Jahn–Teller Effect in a Twofold-Degenerate Electronic State *379*
7.3.7 Threefold-Degenerate Electronic States *391*

7.4 Pseudo-Jahn–Teller Effect and the Two-Level Paradigm 396
  7.4.1 Pseudo-Jahn–Teller (PJT) Instability 396
  7.4.2 Uniqueness of the Vibronic Mechanism of Structural Configuration Instability. The Two-Level Paradigm 404
    Example 7.4. Numerical Confirmation of the Pseudo-Jahn–Teller Origin of Instability of High-Symmetry Configurations of Simple Molecules 406
    Example 7.5. Numerical Calculations Confirming the Pseudo-Jahn–Teller Origin of Configuration Instability of Coordination Systems 407
  7.4.3 Further Insight into the Pseudo-JTE and Hidden JTE 409
    Example 7.6. Comparison of Covalence Versus Polarization Contributions to PJT Instability 411
    Example 7.7. Why Some ML_2 Molecules (M = Ca, Sr, Ba; L = H, F, Cl, Br) are Bent While Others Are Linear? 413
    Example 7.8. Direct Applications of the Jahn–Teller Effects in Materials Science and Engineering 414
Summary Notes 415
Exercises and Problems 416
References 417

8 Electronic Structure Investigated by Physical Methods 421
8.1 Band Shapes of Electronic Spectra 422
  8.1.1 Qualitative Interpretation of Vibrational Broadening 422
    Example 8.1. Broad and Narrow Bands in Light Absorption and Emission by Transition Metal Complexes 425
  8.1.2 Theory of Absorption Band Shapes 425
  8.1.3 Band Shapes of Electronic Transitions Between Nondegenerate States; Zero-Phonon Lines 428
  8.1.4 Types of Electronic Transitions on Intensity 432
    Example 8.2. Selection Rules for Polarized Light Absorption by the $PtCl_4^{2-}$ Complex 433
8.2 *d–d*, Charge Transfer, Infrared, and Raman Spectra 436
  8.2.1 Origin and Special Features of *d–d* Transitions 436
    Example 8.3. *d–d* Transitions in the Absorption Spectrum of $Mn(H_2O)_6^{2+}$ 436
    Example 8.4. Temperature-Dependent Absorption Spectra of K_2NaCrF_6 and Emerald 440
  8.2.2 Spectrochemical and Nephelauxetic Series 441
  8.2.3 Charge Transfer Spectra 445

Example 8.5. Some Ligand → Metal or Metal → Ligand Charge Transfer Spectra *447*
8.2.4 Infrared Absorption and Raman Scattering *449*
Example 8.6. Resonance Raman Spectrum of Red $K_2[Ni(dto)_2]$ in Solid State *453*
8.2.5 Transitions Involving Orbitally Degenerate States *454*
8.3 X-ray and Ultraviolet Photoelectron Spectra; EXAFS *457*
8.3.1 General Ideas *457*
Example 8.7. Photoelectron Spectra of Specific Coordination Systems and Their Interpretation *460*
8.3.2 Electron Relaxation; Shakeup and CI Satellites *462*
Example 8.8. Configuration Interaction Satellite to the K^+ 3*s* Emission Line in the UPS Spectrum of KF *465*
8.3.3 Chemical Shift *467*
Example 8.9. The 1s Line of Nitrogen in the XPS of Different Coordination Systems Reflecting the Variety of Its Bonding in Different Groups *470*
8.3.4 EXAFS and Related Methods *471*
Example 8.10. Applications of EXAFS Spectroscopy to a Variety of Problems *473*
8.4 Magnetic Properrties *474*
8.4.1 Magnetic Moment and Quenching of Orbital Contribution *474*
8.4.2 Paramagnetic Susceptibility *479*
8.4.3 Electron Spin Resonance (ESR) *481*
8.4.4 Magnetic Exchange Coupling *489*
Example 8.11. Magnetic Exchange Coupling in Binuclear Copper Acetate Hydrate *493*
Example 8.12. The Nature of Metal–Metal Bonding in Binuclear Copper Acetate Hydrate *494*
8.4.5 Spin Crossover *497*
8.4.6 Magnetic Circular Dichroism (MCD) *500*
8.5 Gamma-resonance Spectroscopy *503*
8.5.1 The Mossbauer Effect *503*
8.5.2 γ-Resonance Spectra *505*
8.5.3 Isomer Shift and Quadrupole Splitting in GRS *505*
8.5.4 Hyperfine Splitting *510*
Example 8.13. Magnetic Hyperfine Structure in GRS of Coordination Compounds with a ^{57}Fe Nucleus *511*
Example 8.14. Observation of Spin Crossover in the γ-Resonance Spectrum of $[Fe(phen)_2(NCS)_2]$ *513*

8.6 Electron Charge and Spin Density distribution in Diffraction Method 514
8.6.1 The Method of Deformation Density 514
Example 8.15. Deformation Density in Sodium Nitroprusside (Direct Inspection) 516
Example 8.16. Metal–Metal Bonding in $Mn_2(CO)_{10}$; Fragment Deformation Density 519
Example 8.17. Density Modeling for Fe(II)–Phthalocyanine and Co(II)–Tetraphenylporphyrin 522
8.6.2 Spin Densities from Neutron Scattering 524
Example 8.18. Spin Distributions in Some Coordination Systems Obtained from Neutron Scattering 525
Summary Notes 526
Exercises and Problems 528
References 532

9 Stereochemistry and Crystal Chemistry 539
9.1 Definitions. Semiclassical Approaches 539
9.1.1 The Notion of Molecular Shape 539
9.1.2 Directed Valences, Localized Electron Pairs, and Valence Shell Electron Pair Repulsion (VSEPR) 543
9.1.3 Nonbonding Orbitals and Nodal Properties 547
Example 9.1. Influence of Nonbonding MOs on Coordination Geometry 548
9.1.4 Complementary Spherical Electron Density Model 550
Example 9.2. The Inert-Gas Rule in Stereochemistry of Some Coordination Compounds 553
9.2 Vibronic Effects in Stereochemistry 555
9.2.1 Nuclear Motion Effects: Relativity to the Means of Observation and Vibronic Amplification of Distortions 555
9.2.2 Qualitative Stereochemical Effects of Jahn–Teller and Pseudo-Jahn–Teller Distortions 558
Example 9.3. Stereochemistry of MX_n Systems Controlled by Electronic Structure and Vibronic Coupling 560
Example 9.4. Pseudo-JT Origin of Distortions in $CuCl_5^{3-}$ Versus $ZnCl_5^{3-}$ 561
9.2.3 Off-Center Position of the Central Atom 564
9.2.4 Geometry of Ligand Coordination 566
9.2.5 Stereochemically Active and Inert Lone Pairs 570
9.2.6 Pseudorotations in Coordination Systems 574

9.3 Mutual Influence of Ligands *580*
 9.3.1 The Model: *Trans* and *Cis* Influences in Stereochemistry *580*
 9.3.2 Electronic Factors *583*
 9.3.3 Vibronic Theory of Ligand Mutual Influence *586*
9.4 Crystal Stereochemistry *591*
 9.4.1 The Plasticity Effect *592*
 9.4.2 Distortion Isomers *596*
  Example 9.5. Origin of Distortion Isomers in $Cu(NH_3)_2X_2$, X = Cl, Br *597*
 9.4.3 Temperature-Dependent Solid-State Conformers *600*
 9.4.4 Cooperative Effects: Order-Disorder and “Displacive” Phase Transitions and Helicoidal Structures *603*
Summary Notes *610*
Exercises and Problems *612*
References *613*

10 Charge Transfer, Redox Properties, and Electron-conformational Effects *619*
10.1 Electron Transfer and Charge Transfer by Coordination *619*
 10.1.1 Intramolecular Charge Transfer and Intermolecular Electron Transfer *619*
  Example 10.1. Donor-acceptor Pt^{II} Complexes with Intramolecular Electron Transfer for Light Harvesting *623*
 10.1.2 Solvation-driven Charge Transfer *625*
 10.1.3 Redox Capacitance *625*
  Example 10.2. Charge Transfer by Coordination of Peroxide to Iron Porphyrin *629*
 10.1.4 Hard and Soft Acids and Bases *629*
10.2 Electron Transfer in Mixed-Valence Compounds *633*
 10.2.1 Mixed-Valence Compounds as Electronic Systems; a Two-Level Dimer *633*
  Example 10.3. The Creutz–Taube (CT) Ion as a Mixed-Valence System *636*
 10.2.2 Magnetic Properties *639*
 10.2.3 Mixed-Valence Trimers: Coexistence of Localized and Delocalized States *644*
  Example 10.4. Tricenter Ferredoxin *649*
10.3 Electron-Conformational Effects In Biological Systems *652*
 10.3.1 Distortions Produced by Excess Electronic Charge; Special Features of Metalloenzymes *652*
 10.3.2 Trigger Mechanism of Hemoglobin Oxygenation: Comparison with Peroxidase *656*

Summary Notes 661
Exercises and Problems 662
References 663

11 Reactivity and Catalytic Action 667

11.1 Electronic Factors in Reactivity 667
11.1.1 Chemical Reactivity and Activated Complexes 667
11.1.2 Transition (Activation) States of Chemical Reactions Are Controlled by the Pseudo-Jahn–Teller Effect 671
11.1.3 Frontier Orbitals and Perturbation Theory 673
11.1.4 Orbital Symmetry Rules in Reaction Mechanisms 678
Example 11.1. Orbital Symmetry Rules and Vibronic Coupling in Formation of Cyclobutane from Ethylene with Catalyst Participation 681
11.2 Electronic Control of Chemical Activation Via Vibronic Coupling 682
11.2.1 Chemical Activation by Electron Rearrangement 682
11.2.2 Activation of Small Molecules by Coordination 688
Example 11.2. Activation of Carbon Monoxide 690
Example 11.3. Numerical Estimate of CO Activation by Coordination to a NiO Surface 694
Example 11.4. Numerical Estimates of N_2, NO, and H_2 Activation by Coordination to Transition Metal Centers 694
Example 11.5. Activation of Oxygen by Hemoproteins 699
Example 11.6. Quantum-mechanical Tunneling Reactions in Jahn–Teller Distorted Cu(II)N_6 Complexes 703
11.3 Direct Computation of Energy Barriers of Chemical Reactions 706
11.3.1 Substitution Reactions: The *trans* Effect 707
11.3.2 Ligand Coupling and Cleavage Processes 713
11.3.3 Insertion Reactions 717
11.3.4 Photochemical Reactions of Organometallics 727
Example 11.7. Photochemistry of $Ru(bpy)_3^{2+}$ 732
Summary Notes 733
Questions and Problems 734
References 736

Appendix 1. Tables of Characters of Irreducible Representations of Most Usable Symmetry Point Groups and Direct Products of Some Representations *741*
Appendix 2. General Expressions for the Matrix Element $V_{mm'}$ of Perturbation of the States of one *d* Electron in Crystal Fields of Arbitrary Symmetry *747*
Appendix 3. Calculation of the Destabilization and Splitting of the States of One *d* Electron in Crystal Fields of Different Symmetries *751*
Appendix 4. Matrix Elements of Crystal Field Perturbation of a Two-Electron Term $F(nd)^2$, V'_{ij}, $i, j = 1, 2, \ldots, 7$ Expressed by One-Electron Matrix Elements $V_{mm'}$ Given in Appendix 2 *757*
Appendix 5. Matrix Elements of Crystal Field Perturbation of *f*-Electron States *759*
Answers and Solutions *763*
Subject Index *817*

Preface to the Third Edition

In the present, third edition of this book, as compared to the previous two editions [1, 2], significant changes are related, first of all, to the attempt to take into account the latest achievements in this field in both the theory and applications, and to add more illustrative examples, along with other minor corrections. Significant additions and improvements are introduced in all the 11 chapters, especially in Chapters 3, 5, 6, 7, and 11, and in questions, problems, appendixes, and references, as well as in the resolution of most figures. On a more fundamental view, the new edition explores in much more details the role of the nuclear framework and the electron–nuclear (vibronic) interactions in the formation of space configurations of polyatomic systems and their transformations, directly related to the observable properties, including chemical reactions. More introductory information for the reader is presented below in the *Prefaces* to, respectively, the second and the first editions of this book, as well as in the *Foreword* to the first edition, written by the *classics* of coordination chemistry A. Cotton and J. Fackler [1]. But much more detailed information about the role and scope of the book is given in its special *Chapter 1,* titled *"Subject and Methods."*

As a very brief summary, ***the main objectives of this book are to reveal a general and most modern view on the theory of electronic structure and properties of transition metal compounds with applications to various chemical and physical problems, presented in a way intelligible to students, researchers, and teachers, and usable also as a textbook for graduate and advanced undergraduate students.***

Some comments are worthwhile about the meaning of the notion "Introduction to the Theory" given as a subtitle to the title of the first two editions of this book [1, 2] and changed to "Theory and Applications" in the present third edition. The "*Introduction to the Theory*" notice was meant to emphasize that the book is addressed also to those who have not studied any special theory of electronic structure of transition metal coordination compounds (but who have some background in quantum theory in the volume of a regular course for chemists). It also implied that the book is not devoted to the advances of the theory itself, its sophisticated formulations and methodologies. Instead, the latest achievements of the theory were presented together with explanations of how they have been obtained (but without bulky mathematical deductions) and how they can be used to solve physical and chemical problems. Further developments of the theory itself form a part of quantum chemistry, well presented in the literature. With the extensions and additions to this volume, and following many notices of the readers, the subtitle "*Theory and Applications*" seems to be more appropriate to this third edition.

In view of the increased volume of information in this field and to reduce the time for preparation of this edition, Dr. Yang Liu from Harbin Institute of Technology, China, a high-level expert in this field, agreed to coauthor this third edition of the book, for what Dr. Bersuker is very thankful.

Isaac B. Bersuker
Yang Liu
May, 2024

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1 I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, Wiley, New York, 1996.
2 I. B. Bersuker, *Electronic Structure and Properties of Transition Metal Compounds. Introduction to the Theory*, 2nd ed., Wiley, New York, 2010.

Extract from the Preface to the Second Edition

In rewriting the first edition of this book, two goals were pursued. The first one is educational, to make the book more accessible to graduate and advanced undergraduate students and to supplement the presentation with additional "infrastructure" that allows the reader to use the book as a textbook for special courses. The second goal, although more usual, is no less important; it strives from the necessity to renew the material of the book in view of the fast development of this field during the last two decades.

For the educational goal the narrative is given in maximum possible plain language accompanied by many boxed "Examples" showing explicitly how the theory is applied to solving specific chemical problems, and each chapter is supplemented by "Summary Notes," "Questions," "Exercises," and "Problems." These supplements serve as a guide to learning and adoption of the subject by the students, and to help the instructor of the course. Some of these additions are on the level of chemical problem-solving with detailed solutions given at the end of the book.

Beside these essential educational improvements, the book preserves and enhances the first edition's role as a source of information on the basics of electronic structure and properties of transition metal systems (TMSs) in its most modern understanding, and with emphasis on origins and physical meaning. All the chapters are corrected and updated, but essential changes were introduced in Chapters 5–9, especially in Chapters 5 and 8. In particular, in Chapter 5 combined quantum–classical (QM/MM) methods of modeling large organometallic systems are described and examples of QM/MM calculations for specific TMS are given. In the same chapter, an extended presentation of the density-functional methods of electronic structure calculations (which have reached widespread use also by nonexperts) is given together with examples of computations using free programs downloaded from the Internet. Similar examples are also given for semiempirical and ab initio methods of computation. In Chapter 8 some important physical methods of investigation are added, including a section on gamma-resonance spectroscopy, as well as further description of IR, Raman, and charge transfer spectra.

The special boxed “Examples” in nine chapters of the book (a total of 70) supplement the theoretical methods and results, making them more accessible and understandable. They may serve also as separate essays—solutions of chemical problems by means of theoretical methods, and therefore they are indicated on a separate line in the book Contents.

The role and place of this book among others available is outlined in the introductory Chapter 1, but I should like to note here the (unique of this kind) attempt to promote a novel, more general agenda (with a higher level of theory and understanding) of the role of electronic structure in formation and transformation of matter. With regard to TMS, the first significant level of electronic theory was reached in the 1950s–1960s by *crystal field theory*. A higher level of theory was achieved in the 1980s–1990s, based on computer developments that allowed for full molecular orbital and density-functional *electronic structure calculations*.

However, in the last two to three decades a new, higher level of understanding of the role of electronic structure in properties of matter emerged that has not yet been assimilated by the lay chemist and physicist, and still has not been introduced in teaching of this subject. The novel understanding is related to the ways in which the electrons control molecular transformation. It turns out that nuclear configuration changes are dependent on the electronic structure that essentially *involves excited electronic states*. The point is that quantum separation of ground and excited electronic states is valid only for given, fixed positions of the nuclei; any displacement of the latter mixes the initial ground and excited or degenerate states, and this mixing is crucial in understanding the origin of nuclear configuration changes. *Mixing electronic states, ground and excited, degenerate and nondegenerate, solely determines all possible nuclear configuration instabilities, distortions, and transformations*, including formation of molecular shapes and crystal lattices, conformational changes and phase transitions, chemical activation, and mechanism of chemical reactions, to mention a few.

Comprehending this nuclear-dynamical aspect of electronic structure elevates the theory to a new, higher level and facilitates a better understanding of chemical and physical phenomena. The intention of this book is to instill this advanced way of thinking in physics and chemistry. It is given in many parts of the book as a paradigm, more noticeable and explicitly in Section 7.4 with applications in subsequent chapters, especially Chapters 9–11.

In preparation of this book, I benefited from the help of my students and colleagues, many of whom were mentioned in the Preface to the first edition. For the present (second) edition, I received further assistance from J. E. Boggs, P. Garcia-Fernandez, V. Z. Polinger, B. S. Tsukerblat, M. D. Kaplan, S. A. Borshch, S. S. Stavrov, G. I. Bersuker, L. F. Chibotaru, I. Ya. Ogurtsov, N. N. Gorinchoy, Wenli Zou, and Yang Liu. I am grateful also to F. A. Cotton and J. P. Fackler, Jr., for their foreword to the first edition. Special thanks are due to Professor Charles Dismukes (Princeton University), who used the first edition as a textbook to his courses and provided us with a variety of comments and questions, as well as corrections to misprints and omissions.

Isaac B. Bersuker
Austin, Texas, March 2009

Extracts from the Preface to the First Edition

Presently transition metal compounds form a number of research fields with vast applications ranging from a variety of magnetic, ferroelectric, and superconducting materials to all kinds of catalysts, to metallobiochemical systems of vital importance. The main goal of this book is to provide a comprehensive discussion of the latest developments in the study of electronic structure and related properties of transition metal coordination systems, and to present the subject in a form suitable for chemists and physicists—students, researchers, and teachers.

Most attention is paid to a better understanding of the basic principles, general features, and specifics of electronic properties affecting ligand bonding, stereochemistry and crystal chemistry, chemical reactivity, electron transfer and redox phenomena, as well as spectroscopic, magnetic, and electronic density distribution properties. The discussion of relativistic effects in bonding, presented in a book context for the first time, elucidates the origin of important properties including, for instance, the "nobleness" and the yellow color of gold.

Quite novel are the implications of vibronic effects in chemical and physical phenomena presented in this book. The concept of vibronic interactions developed during the last two decades as a perturbational approach to the coupling between the electronic motion and nuclear configuration contributes significantly to the solution of a number of problems. These include, for instance, band shapes of electronic and photoelectron spectra, local stereochemistry and structural phase transitions in crystals, plasticity, distortion isomers, and temperature dependent conformers, molecular pseudorotations, chemical activation by coordination, and electron-conformational effects in biological systems.

One of the special features of this book is that it includes both the theory of electronic structure and its applications to various problems. Significant efforts were made to present the whole topic in a unified fashion with indications of direct and indirect links between its numerous more specific aspects and to make the presentation understandable without oversimplification. Many examples are provided, which will assist the reader in understanding how theoretical concepts can be applied to laboratory problems.

During the preparation of this book, I benefited from the help and cooperation of my students and co-workers, as well as from suggestions of many colleagues throughout the world. I am very grateful to all of them.

Isaac B. Bersuker
Austin, Texas, April 1995

Foreword to the First Edition

While several major treatises have been published in the English language that purport to cover the topic of this volume, none has appeared in more than a decade. Advances in computing during this time have put the tools of the theoretical chemist in the hands of the experimentalist. The use of these tools requires a working knowledge of the basis for understanding the electronic structure and properties of the transition elements and their compounds. Therefore, theoretical features of the electronic structure of transition metal compounds are an important component of the training of both the experimental and theoretical chemist contributing solutions to problems in this area. Since this chemistry permeates industrial and biological chemistry as well as catalysis, solutions to problems in this field take on considerable importance. The field of transition metal chemistry is, indeed, fortunate that Isaac Bersuker, the leading contributor to the theory of transition metal electronic structure in the late period of the former Soviet Union, has translated and edited his numerous contributions published originally in Russian and combined them with new work into this modern English language text.

Isaac Bersuker became recognized as an authority in the Soviet Union on transition metal chemistry theory with publication of his 1962 book, which in many ways covered the same material that was published in English as *An Introduction to Transition-Metal Chemistry* by L. E. Orgel (Butler and Tanner Ltd., Frome, Somerset. England, 1960). While Orgel's book was "must" reading for transition metal chemists in the West in the 1960s, Bersuker's book served the same role in the Soviet Union. To our knowledge, Bersuker's Russian language book was never fully translated into English, although one of us (JPF) had a Russian-speaking student translated much of it for him in the late 1960s. As Bersuker's interaction with Western scientists increased during the 1970s and 1980s, his contribution to the understanding of the electronic structure of metal systems became increasingly known and appreciated. While in the former Soviet Union, Bersuker directed a powerful Academy of Sciences program in Kishinev, Moldova which focused on problems involving coupling between electronic and vibrational phenomena. In 1993, he moved to the United States (Austin, Texas), where he continues to be active. He recently authored a major review on “The concept of vibronic interactions in crystal stereochemistry of transition metal compounds,” *J. Coord. Chem.* **289**, 338 (1995).

Many readers of this Foreword will be familiar with Isaac Bersuker’s contributions to the understanding of the Jahn–Teller effect. His book *The Jahn–Teller Effect and Vibronic Interactions in Modern Chemistry* (Plenum Press, New York, 1984) is an important contribution used by persons interested in evaluating those systems in which vibrational and electronic states have similar energy separations that interact with each other. The useful concept of *orbital vibronic constants* is first presented in text form in the Jahn–Teller volume. This topic is brought into focus for the reader of this book in Chapter 7, following along after several introductory chapters that build the basic theory of transition metal chemistry. Incidentally, relativistic effects for transition metal compounds are treated for what is perhaps the first time in a book directed toward inorganic chemistry. Molecular orbital methods are introduced and compared, various bonding types are classified, electronic band shapes are interpreted, and magnetic properties are discussed. Stereochemistry is a fundamental and important part of this book, with symmetry and group theory widely used throughout, including the classification of terms, selection rules, crystal structures, and vibronic effects (vibronic stereochemistry). The book concludes with an investigation of the electronic properties of transition metal complexes, including the use of modern techniques such as EXAFS and the development of the concepts associated with electron transfer, a topic of fundamental importance to biological catalysis. Chemical activation and the direct calculation of energy barriers in chemical reactions complete the coverage in the book. Thus the student of this text is armed with an important, even essential arsenal of theory with which to handle virtually any electronic structure problem in transition metal chemistry.

We trust that this book will be a suitable primer for every serious practitioner of modern transition metal chemistry.

F. A. Cotton
J. P. Fackler, JR.

Mathematical Symbols

A	electron affinity
	hyperfine constant
A	atomic core
A, B	nondegenerate terms
A, B, C	Racah parameters
$\mathbf{B}$	magnetic induction
C	redox capacitance
$C^{(i)}$	anharmononicity correction coefficients
c	speed of light
c_{ij}	LCAO coefficients
D	activation energy
	barrier height
D_s, D_t	low-symmetry crystal field corrections
d	atomic state
	barrier width
E	energy
E, e	double degenerate representation term
E_{JT}	Jahn-Teller stabilization energy
e	electronic charge
e_σ, e_π	AOM parameters
F	linear vibronic constant
F_k	radial components of crystal field matrix elements
$F^{(k)}$	Slater-Condon parameter
$F\,(S)$	structure factor in X-ray scattering
$F(\Omega)$	form function for spectroscopic band shapes
f	angular dependence function in ESR spectra
	atomic state
	linear orbital vibronic constant
	multiplicity of degeneracy

	oscillator strength
	probability of nuclear zero-phonon transition
G	atomic term
	quadratic vibronic constants
	symmetry operator
G_{ij}	group overlap integral
g	g factor
	quadratic orbital vibronic constant
H	Hamiltonian
ΔH	heat of reaction
$\mathcal{H}$	magnetic field intensity
$\mathcal{H}_n$	Hermite polinomial
I	ionization potential
	light intensity
$\mathbf{I}$	nuclear spin
I_{ij}	Coulomb interaction
i, j	atomic and molecular states
	multiply used index
$\mathbf{j}_i$	total one-electron momentum
J	exchange coupling constant
	quantum number
	total momentum
$K_{i,j}$	exchange interaction
$K^{\Gamma}_{\Gamma*}$	force (elastic) constant, APES curvature
$K_{\Gamma*}(\Gamma)$	vibronic reduction factor
$K(\Omega)$	coefficient of light absorption
k	reaction rate
$k(\Omega)$	spectral density of absorption
k^i	force constant coefficients
$\mathbf{L}$	Operator
	orbital momentum
L	orbital momentum quantum number
L_i	Ligand
L^i_k	Laguerre polynomial
l,m,n	direction cosines
	quantum numbers of atomic states
	vibronic energy levels
$\mathbf{M}$	magnetic (electric) dipole moment
	magnetization