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# **Introduction To Ligand Field Theory**

***GEORGE CHRISTOU Indiana  
University, Bloomington I am no  
doubt representative of a large  
number of current inorganic***

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***chemists in having obtained my undergraduate and postgraduate degrees in the 1970s. It was during this period that I began my continuing love affair with this subject, and the fact that it happened while I was a student***

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***in an organic laboratory is beside the point. I was always enchanted by the more physical aspects of inorganic chemistry; while being captivated from an early stage by the synthetic side, and the measure of creation with***

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***a small c that it entails, I nevertheless found the application of various theoretical, spectroscopic and physicochemical techniques to inorganic compounds to be fascinating, stimulating,***

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***educational and downright exciting. The various bonding theories, for example, and their use to explain or interpret spectroscopic observations were more or less universally accepted as belonging within the***

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***realm of inorganic chemistry, and textbooks of the day had whole sections on bonding theories, magnetism, kinetics, electron-transfer mechanisms and so on. However, things changed, and subsequent***

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***inorganic chemistry teaching texts tended to emphasize the more synthetic and descriptive side of the field. There are a number of reasons for this, and they no doubt include the rise of diamagnetic organometallic***

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***chemistry as the dominant subdiscipline within inorganic chemistry and its relative narrowness vis-d-vis physical methods required for its prosecution.***

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***organometallic and metallobiochemical systems. This is an excellent reference for chemists, researchers and teachers, and advanced undergraduate and graduate students in inorganic,***

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***coordination, and organometallic chemistry.***

***Aimed at senior undergraduates and first-year graduate students, this book offers a principles-based approach to inorganic chemistry that, unlike other***

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***texts, uses chemical applications of group theory and molecular orbital theory throughout as an underlying framework. This highly physical approach allows students to derive the greatest benefit of topics such as***

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***molecular orbital acid-base theory, band theory of solids, and inorganic photochemistry, to name a few. Takes a principles-based, group and molecular orbital theory approach to inorganic chemistry The first***

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***inorganic chemistry textbook to provide a thorough treatment of group theory, a topic usually relegated to only one or two chapters of texts, giving it only a cursory overview Covers atomic and molecular term symbols,***

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***symmetry coordinates in vibrational spectroscopy using the projection operator method, polyatomic MO theory, band theory, and Tanabe-Sugano diagrams Includes a heavy dose of group theory in the primary***

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***inorganic textbook, most of the pedagogical benefits of integration and reinforcement of this material in the treatment of other topics, such as frontier MO acid--base theory, band theory of solids, inorganic***

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***contrast different theories of bonding in order to allow for a more rigorous treatment of their application to molecular structure, bonding, and spectroscopy Informal and engaging writing style; worked***

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In this book, a synthesis of old and new notions straddling the disciplines of physics and chemistry is described.

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analysis of vibrational spectra and molecular orbital theory are essential knowledge for the undergraduate student of inorganic chemistry. The second edition of Group Theory for Chemists uses diagrams and problem-solving to help students test

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and improve their understanding, including a new section on the application of group theory to electronic spectroscopy. Part one covers the essentials of symmetry and group theory, including symmetry, point groups and

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representations. Part two deals with the application of group theory to vibrational spectroscopy, with chapters covering topics such as reducible representations and techniques of vibrational spectroscopy. In part three, group

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theory as applied to structure and bonding is considered, with chapters on the fundamentals of molecular orbital theory, octahedral complexes and ferrocene among other topics. Additionally in the second edition, part four focuses on the application

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comprehensive study of group theory and its applications, an invaluable resource to students of chemistry as well as those in related fields seeking an introduction to the topic Presents diagrams and problem-solving exercises to help

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students improve their understanding, including a new section on the application of group theory to electronic spectroscopy Reviews the essentials of symmetry and group theory, including symmetry, point groups and

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and everyday life. Differing from other foundational texts with this emphasis on applications and examples, the text uniquely begins with a focus on the shapes (geometry) dictating intermolecular forces of attractions, leading to

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Carboranes and Metallocarboranes and their applications in Catalysis, Medicine and Pollution Control. Throughout the book, illustrative examples bring inorganic chemistry to life. For instance, biochemists and students will be interested in how

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coordination chemistry between the transition metals and the ligands has a direct correlation with cyanide or carbon monoxide poisoning (strong-field Cyanide or CO ligand versus weak-field Oxygen molecule).

Engaging discussion of key

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concepts with examples from the real world Valuable coverage from the foundations of chemical bonds and stereochemistry to advanced topics, such as organometallic, bioinorganic, carboranes and environmental chemistry Uniquely

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begins with a focus on the shapes (geometry) dictating intermolecular forces of attractions, leading to reactivity between molecules of different shapes

An Introduction to Transitional-metal Chemistry

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*Electronic Structure and  
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*Theory [by] Leslie E. Orgel  
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*and Letters, April 4 and 5, 1986  
To appreciate the  
chemistry and physical  
properties of complexes  
of the transition  
series, an understanding  
of metal-ligand*

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*interactions applied to complexes of the d-block is needed. Metal Ligand Bonding aims to provide this through an accessible, detailed, non-mathematical*

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*approach. Initial chapters detail the crystal-field model, using it to describe the use of magnetic measurements to distinguish complexes*

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*with different  
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chapters look at the  
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*complexes using a pictorial approach. Bonding in octahedral complexes is explored and electronic spectra and magnetic properties are given extensive*

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biology constitutes the  
subject called  
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*detailed analysis which follows. Pathways of metal assimilation, storage and transport, as well as metal homeostasis are dealt with next. Thereafter,*

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sodium and potassium,  
magnesium, calcium,  
zinc, iron, copper,  
nickel and cobalt,  
manganese, and finally*

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*molybdenum, vanadium,  
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*life is chemical and isotopic traces, not fossils, preserved in rocks.*

*Geochemistry has allowed us to unravel the history of the ice ages and thereby deduce their cause.*

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*determine the temperatures and pressures at which rocks have been metamorphosed, and the rates at which ancient magma chambers cooled and crystallized. The field has grown rapidly more sophisticated, in both analytical techniques that can determine elemental concentrations*

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level as well as the angular behavior of the wavefunctions. This text then examines the problem of obtaining the energy eigenvalues and eigenstates of the two-electron systems, in which two electrons are

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accommodated in the  $t_{2g}$  and  $e_g$  shells in a variety of ways. Other chapters discuss the ligand-field potential, which is invariant to any symmetry operation in the group to which symmetry of the system belongs. This

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consistent field theory of Hartree-Fock. This book is a valuable resource for research physicists, chemists, electronic engineers, and graduate students.

Inorganic Complexes

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describes the particular features of inorganic complex chemistry, as it has developed since 1950. The chemical information recorded in this book is intimately connected with the theoretical approach

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applying M.O. theory, which is also called ligand field theory in the special case of transition group complexes with a partly filled shell, for classification of the energy levels and rationalization

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of the absorption spectra. This text also discusses the aqua, hydroxo, oxo, fluoro, chloro, bromo, and iodo complexes; nitrogen-, oxygen-, and sulfur-containing ligands; amino acids and other N,O-

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containing ligands; and intermetallic bonding and cooperative effects. This publication is a good source for chemists and students conducting work on inorganic complex chemistry.

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treatment of ligand field theory and its applications  
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interactions in transition metal compounds, and the way it is used to interpret the physical properties of the complexes. It examines the traditional electrostatic crystal field model, still widely used by physicists,

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as well as covalent approaches such as the angular overlap model, which interprets the metal ligand interactions using parameters relating directly to chemical behavior.

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broadens the book's field of interest beyond transition metal chemistry into the many other areas where these metal ions play an important role. As clear and accessible as Brian Figgis's 1966 classic Introduction to

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Ligand Fields, this new book provides inorganic and bioinorganic chemists as well as physical chemists, chemical physicists, and spectroscopists with a much-needed overview of the many significant changes that

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It has long been recognized that metal spin states play a central role in the reactivity of important biomolecules, in industrial catalysis and

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in spin crossover compounds. As the fields of inorganic chemistry and catalysis move towards the use of cheap, non-toxic first row transition metals, it is essential to

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understand the important role of spin states in influencing molecular structure, bonding and reactivity. Spin States in Biochemistry and Inorganic Chemistry provides a

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complete picture on the importance of spin states for reactivity in biochemistry and inorganic chemistry, presenting both theoretical and experimental perspectives.

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The successes and pitfalls of theoretical methods such as DFT, ligand-field theory and coupled cluster theory are discussed, and these methods are applied in studies throughout the

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book. Important spectroscopic techniques to determine spin states in transition metal complexes and proteins are explained, and the use of NMR for the analysis of

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and gas phase reactions  
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pharmaceutical chemistry. Twenty years ago Tanabe and Sugano published the first ligand field energy diagrams which are applicable to  $d^n$  electronic configurations.

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These diagrams are limited in scope in that they can be used only for octahedral symmetry and for a limited number of terms. The present volume is an attempt to fill the

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gap by providing a reasonable number of complete and accurate ligand field energy diagrams for  $d^n$  configurations in the most commonly encountered

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symmetries. Despite their limited nature, the diagrams of Tanabe and Sugano were extensively used in the past in order to rationalize optical and luminescence spectra and

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to discuss various electronic properties of transition metal ions, their coordination compounds and solids. Moreover, Tanabe-Sugano diagrams have an

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established place in the theory of transition metal compounds and are included in most textbooks of inorganic and coordination chemistry. It is expected that the present diagrams

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Group Theory and Quantum  
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Fundamental Theory and  
Applications  
Multiplets of Transition-  
Metal Ions in Crystals  
*"The Theory of Atomic Spectra",*

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*surrernanzlllg all that was then known about the quantum theory of free atoms; and in 1961, J.S. Griffith published "The Theory of Transition Metal Ions", in which he combined the ideas in Condon and Shortley's book with those of Bethe, Schlapp, Penney and Van Vleck. All this work, however, was done by physicists,*

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*and the results were reported in a way which was more accessible to physicists than to chemists. In the meantime, Carl J. Ballhausen had been studying quantum theory with W. Moffitt at Harvard; and in 1962 (almost simultaneously with Griffith) he published his extremely important book, "Introduction to Ligand Field*

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*Theory". This influential book was written from the standpoint of a chemist, and it became the standard work from which chemists learned the quantum theory of transition metal complexes. While it treated in detail the group theoretical aspects of crystal field theory, Carl J. Ballhausen's book also emphasized the*

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*limitations of the theory. As he pointed out, it is often not sufficient to treat the central metal ion as free (apart from the influence of the charges on the surrounding ligands): - In many cases hybridization of metal and ligand orbitals is significant. Thus, in general, a molecular orbital treatment is needed to*

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*As it results from the very nature of things, the spherical symmetry of the surrounding of a site in a crystal lattice or an atom in a*

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*molecule can never occur. Therefore, the eigenfunctions and eigenvalues of any bound ion or atom have to differ from those of spherically symmetric respective free ions. In this way, the most simplified concept of the crystal field effect or ligand field effect in the case of individual molecules can be introduced. The*

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*conventional notion of the crystal field potential is narrowed to its non-spherical part only through ignoring the dominating spherical part which produces only a uniform energy shift of gravity centres of the free ion terms. It is well understood that the non-spherical part of the effective potential "seen" by open-shell electrons*

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*localized on a metal ion plays an essential role in most observed properties. Light adsorption, electron paramagnetic resonance, inelastic neutron scattering and basic characteristics derived from magnetic and thermal measurements, are only examples of a much wider class of experimental results dependent on it. The*

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*influence is discerned in all kinds of materials containing unpaired localized electrons: ionic crystals, semiconductors and metallic compounds including materials as intriguing as high-Tc superconductors, or heavy fermion systems. It is evident from the above that we deal with a widespread effect relative*

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*to all free ion terms except those which can stand the lowered symmetry, e.g. S-terms. Despite the universality of the phenomenon, the available handbooks on solid state physics pay only marginal attention to it, merely making mention of its occurrence. Present understanding of the origins of the crystal field potential*

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