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Introduction: Subject and Methods

The electronic theory of transition metal systems, in the context of quantum chemistry of atomic matter, enriches the way of thinking in chemistry.

This chapter is intended to introduce the reader to the objectives and main purpose of the book, to define the subject and the methods of its exploration, and to determine its "ecological niche" in the rapid development of science and increasing demands for generalized information.

After a brief discussion of the main objectives and the role and place of this book among others available (Section 1.1), the definitions of chemical bonding and coordination systems are given (Section 1.2), followed by a very brief outline of the main ideas of quantum chemistry, mostly definitions employed in the subsequent presentation (Section 1.3).

1.1 Objectives

1.1.1 Molecular Engineering and Intuitive Guesswork

In the twenty-first century, at the beginning of the next millennium of human civilization, it is worthwhile to sum up the achievements in the past century and to relate our intentions to what is expected in the coming new age. In the twentieth century, the theory of structure and properties of transition metal coordination compounds, as well as polyatomic systems in general, advanced tremendously and reached impressive results. Following the discovery of quantum mechanics, basic understanding of the nature of chemical bonding and chemical transformations was reached, and the idea of purposeful synthesis of new compounds with specific properties acquired a new reality. As a result of the rapid development of this trend in science, especially in the second half of the century, the solution of the problem of *molecular engineering*, which includes the design and

Electronic Structure and Properties of Transition Metal Compounds: Theory and Applications,
Third Edition. Isaac B. Bersuker and Yang Liu.

consequent synthesis of newly designed compounds, advanced significantly. *Beginning with the twenty-first century the majority of new chemical compounds will be obtained on the basis of explicit molecular design, and we should be prepared, both practically and psychologically, to meet this challenge.*

Molecular engineering is based mainly on the knowledge of molecular structure, including electronic structure. To design a compound with specific properties, the laws that control the formation and structure of molecular systems, as well as the correlation between structure and properties, must be known in detail. Therefore, *the study of electronic structure and properties of polyatomic systems is one of the most important tasks of modern chemistry* in view of its trends and developments in the near future.

However, so far, the majority of chemical compounds with the required properties were obtained mainly on the basis of intuitive knowledge, without specialized molecular engineering. Thus far, the preparation of new compounds has depended mainly on the skills and intuition of the researcher. On the other hand, intuition, or intuitive knowledge, does not emerge from nothing; implicitly it is based on real knowledge or, more precisely, on *understanding* (see discussion below) of the phenomena lying at the base of the processes under consideration. Intuitive guesswork is also a kind of "engineering.". The in-depth understanding of chemical phenomena based on a correctly formulated way of thinking allows one to sidestep (circumvent, jump over) the lack of detailed information about the specific process under study, and to come to a correct result that from the outside appears to be "unexpected." The better the understanding in visual images, concepts, models, and comparisons, the more fruitful the intuitive thinking.

It is clear that the smaller the region of lack of knowledge (i.e., the less the volume of the "black box" of ignorance), the easier it is to "jump over" it. If this black box is large, the findings of intuitive guesswork are of a unique, accidental nature; they become more frequent and more purposeful with reduction of the black box. The volume of the black box decreases rapidly with the increase in our knowledge (although it may never be exactly zero). Hence, the preparation of new compounds based on intuitive thinking ultimately also depends on an in-depth understanding of the phenomena, an understanding based on the knowledge of the laws controlling the formation of new compounds and their properties.

Preparation of new compounds with specific properties based on either molecular engineering or intuitive conjecture requires (in both cases) knowledge of structures and properties of such compounds.

The term *understanding* used above is not trivial and needs some clarification. We use this term in the following sense: *to understand the origin of a new phenomenon means to be able to reduce it to more simple (usual), conventional images or concepts*. To deepen or extend the understanding means to introduce more complicated basic images to which the phenomena should be reduced. In the 1950s, the basic images in the understanding of the origin of properties of transition metal compounds were created by the *crystal field theory* (Chapter 4), which arose instead of and in addition to the image of a two-electron valence bond. Subsequently, a deeper understanding was reached by introducing more complicated images (concepts) of *molecular orbitals* that continue to serve as basic images (Chapters 5 and 6). In the more recent decades, new basic concepts based on *vibronic coupling* (Chapter 7) have emerged, which essentially involve excited states information, distortion, and transformation of molecular space configurations. Note that the new images of understanding, being more complicated, do not fully negate the old ones, but complement them with new content. New images (concepts) are produced by the theory. With the progress of science, the images become more complicated, approaching the reality.

Lack of understanding means that we are unable to reduce the phenomenon to well-established conventional images; it requires the creation of new images. Sometimes the latter differ drastically from the usual ones. In the history of science, the most dramatic new images have been introduced by quantum mechanics. *The wave-particle duality*—the fact that a microscopic object (e.g., the electron) exhibits properties of both particles (i.e., it can be localized at a single point of space) and plane waves (i.e., it can be found delocalized over the whole space)—cannot be understood within the existing images, it must be taken as such in a conventional manner until it becomes usual.

In view of this *definition of understanding*, to make the book intelligible means to reduce the properties of transition metal compounds to basic images (concepts). Hence, we should describe the newest basic images that provide understanding most appropriate to the real phenomena. The main concepts in the theory of electronic structure of coordination compounds, mentioned above (crystal fields, molecular orbitals, vibronic coupling), should be presented such as to become usual elements of thinking in chemistry (in fact, molecular orbitals are now such elements). This, in turn, requires simplicity and visualization to the greatest extent possible. *Simplicity* in this aspect means a less abstracted presentation with more specific examples avoiding as much as possible bulky mathematical deductions. As pointed out by Werner Heisenberg [1.1], “even for the physicist description in plain language will be a criterion of the degree of understanding that has been reached.”

However, aspiring to simplicity involves the danger of *oversimplification*. The latter takes place when the phenomenon under consideration is presented by a “smoothed” picture in which “angles are cut off” and important details are omitted. For instance, in many books and papers, it is stated that as a result of the Jahn–Teller effect, distorted molecular configurations should be observed. This statement is an oversimplification because, in fact, the Jahn–Teller distortions can be observed only under some important additional conditions (Sections 7.3 and 9.2). Besides misunderstanding, oversimplification may create also illusions of “easy access to science,” whereas in fact much stronger efforts are needed; this may have a negative influence on education and scientific thinking.

1.1.2 Main Objectives of This Book in Comparison with Other Sources

Many books and review articles are devoted to the electronic structure and properties of transition metal coordination compounds or, more often, to particular aspects of this problem (see, e.g., Refs. [1.2–1.16] and references cited therein). The present book differs significantly from those sources in many respects.

First, this book attempts to give *a generalized view on the modern state of the art of the whole topic* beginning from the main ideas of quantum chemistry and atomic states through theories of electronic structure and vibronic coupling to physical methods of investigation and applications to various chemical and physical problems. The advantage of this presentation, as compared with many publications devoted to a narrower aspect of the problem, is that the latter gives a generalized view of what is going on in that narrow field, whereas this book generalizes the trend as a whole, including its main particular problems.

We emphasize that *the whole trend is not equal to the sum of particular trends* (more than 2000 years ago Aristotle claimed that “the whole is more than the sum of its parts”). A general view of the topic as a whole, given as an entire subject with direct interrelations between its different, more particular aspects, provides a significantly higher level of understanding of both the particular problems and the whole trend. Presented by the same author in a unified way and on the same level, different problems should be better understood by the reader. In some aspects, it is pleasing to see the unity of nature at work linking apparently unrelated observations together (see, e.g., the discussion of the statement that “nature tends to avoid degeneracies” in Section 7.4).

Many problems treated in this book are novel; they have not been fully considered before in books on coordination compounds. This is, first, *the concept of vibronic interactions* considered in Chapter 7, and then used to solve various problems of coordination compounds (Chapters 9–11). The treatment of *electronic structure, relativistic effects in bonding, optical band shapes, electronic and vibronic origin of stereochemistry, electron transfer in mixed-valence compounds, chemical activation by coordination*, etc., is also novel. Even for those problems that were solved long before and considered repeatedly in books and review publications, renewal of their presentation updated in accordance with the novel achievements of the theory is required periodically. The previous books on electronic structure of coordination compounds with goals similar to those of particular parts of this book have long been published [1.3–1.15]; two of the most recent books were published more than 25 years ago [1.14], not long after our first edition. Special attention in many publications was paid to methods of numerical computation [1.17–1.19, 1.21, 1.22]. The majority of the present book's sections include novel, original treatments for these "classical" problems too (see, e.g., the definition of the coordination bond given in Sections 1.2 and 6.1). In comparison with other books of this level, this book further explains the origins of phenomena based on first principles, which leads to a more in-depth understanding; it prefers physical meaning over pure description.

As mentioned in the Preface, the novelty of this book is also in its special efforts to promote a novel agenda with a higher level of theory and understanding of the role of electronic structure in the formation and transformation of matter. With regard to transition metal systems (TMSs), the first significant level of electronic theory was reached in the 1950s–1960s by the *crystal field theory*. It was essentially improved in the 1980s–1990s based on computer developments that allowed for full molecular orbital *electronic structure calculations*.

However, in the last two or three decades a new, higher level of understanding of electronic structure and properties of matter emerged that is not yet fully apprehended by the lay chemist and physicist, and it still has not been introduced in teaching of this subject. Distinguished from the electronic structure of well-defined molecular shapes, the novel understanding is related to all kinds of spontaneous symmetry breaking and molecular transformation. The point is that quantum separation of ground and excited electronic states (as well as the definition of degenerate states) is valid only for given, fixed positions of the nuclei; these states become mixed by nuclear displacements, and this mixing is crucial in understanding nuclear configuration changes (Section 7.4). *Mixing degenerate electronic states, or sufficiently close ground and excited, 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 chemical reactions mechanisms, to mention only a few. For a given nuclear configuration, no changes are possible within just one electronic state—this is the *two electronic states in transformations* (TEST) paradigm.

Comprehending this nuclear-dynamical aspect of electronic structure elevates the theory to a new, higher level that facilitates a better understanding of chemical and physical phenomena. The intention of this book is also to instill this advanced way of thinking in physics and chemistry. It is given in many parts of this book, more noticeably and explicitly in Chapter 7, Section 7.3, with applications in subsequent chapters.

This book's symbiosis of theory and applications, namely, the presentation of the general theory of electronic structure (Chapters 2–5 and 7), together with applications to chemical bonding (Chapter 6), physical methods of investigation (Chapter 8), and various chemical problems (Chapters 9–11), accompanied by 70 *examples* of solutions of relevant specific problems, as well Summary Notes, Questions, Exercises, and Problems to each chapter, is very rare in the literature. Meanwhile, this presentation allows the reader, interested in the solutions of applied problems, to consult directly the theoretical background of these solutions and to consider their applicability to other problems. The treatment of different chemical properties from the same perspective also has the advantage of stimulating the search for new effects, rules, and laws that emerge from these direct comparisons.

To summarize, *the main objectives of this book are to give 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 and changed to "Theory and Applications" in the present third edition, already mentioned in the *Preface*. The "Introduction.." 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 mathematical background with sophisticated formulations and methodologies. Instead, the latest achievements of the theory are 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 literature [1.16–1.22]. 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 for this third edition.

An important question concerning the *theory* is the real meaning implied by this term. The theory of electronic structure forms one of the principal parts of modern quantum chemistry (others are molecular dynamics, intermolecular interactions, molecular transformations, interaction with external perturbations, etc.). Its particular trend—numerical computation of the electronic structure for fixed nuclei—is at present most advanced. Modern computers and supercomputers allow us, in principle, to compute the electronic structure of any coordination system of reasonable size and to get relatively accurate figures of its energies and wavefunctions, energy barriers of chemical reactions, spectroscopic properties, and so on (see Examples in Chapters 5, 6, and 11). Note that several decades ago metal-containing systems with active *d* and *f* orbitals were a challenge to quantum chemistry [1.17, 1.21]. With the development of computers and advanced computer algorithms and programs, these calculations tend to become routine (see Examples and Problems in Chapters 5, 6, and 11).

However, the numerical data of the computed electronic structure themselves cannot be regarded as a theory. Indeed, these data characterize a single compound (for which the computation has been carried out) and, in general, they cannot be directly transferred to other compounds. From this perspective, computer data seem to be similar to many other characteristics of the compounds obtained by different *experimental* facilities. *In fact, numerical results on electronic structure computation are outputs of a computer experiment*; the computer is thus similar to a numerical spectrometer that yields the energy spectrum and wavefunctions of the system.

To transform experimental data into a theory, these data should be properly accumulated and generalized. The latter means correlating the data with some *analytical models* obtained by simplifications and reasonable assumptions introduced in the first principles. In this way, the experimental data can be rationalized and shown to express some laws, rules, trends, and characteristic orders of magnitude. The same is true for computer numerical data. The latter are thus most appreciated when they are obtained for a series of compounds with similar structures and/or similar properties that can be directly generalized. In particular, this is true for different nuclear configurations of the same system—adiabatic potential energy surfaces (APES) and chemical reaction energy barriers [1.17, 1.21, 1.22] (see Chapters 6 and 11).

Note also that ab initio calculated wavefunctions of coordination compounds are given in thousands of determinants that in general can be neither read nor understood without specific rationalizations by means of physically grounded simplified schemes, or further processing by means of computer programs. Nevertheless, *the results of the numerical calculation are of inestimable value to the theory of electronic structure; together with other experimental data, they form the informational basis of the theory and allow one to discriminate the best theoretical models among the many possible.*

Finally, as mentioned above, the book is intended to be used also as a *textbook for graduate and advanced undergraduate students*. For this purpose, we introduced many examples (offset from the general text in box format) of specific applications of the theory, as well as end-of-chapter Summary Notes, Questions, Exercises, and Problems with solutions deemed to make this book more accessible to chemists and physicists, including graduate and advanced undergraduate students, and usable for teaching special courses. Such courses may not necessarily include the entire book material—they can be devoted to only parts of it—but because of the interrelation between these parts and cross-references, the student will be enriched with knowledge from other parts. The book is deemed to provide a solid background in and updated understanding of the laws controlling molecular properties, which is most important in pursuing further research and teaching activity on any narrower subject of this vast field.

1.2 Definitions of Chemical Bonding and Transition Metal Coordination System

1.2.1 Chemical Bonding as an Electronic Phenomenon

Chemical bonding is usually defined as an interaction between two or several atoms that causes the formation of a chemically stable polyatomic system (molecule, radical, molecular ion, complex, crystal, chemisorbed formation on surfaces, etc.). However, this formulation is not sufficiently rigorous, because without additional explanation it is not clear when the system should be considered as chemically stable. In fact, in this definition, admitting that chemical bonding is a kind of interaction, we introduce for the characterization of the latter a new term "chemically stable system," which is no clearer than the initial one, the chemical bond.

One may try to discriminate chemical bonding from other (say, intermolecular) interactions by the bonding energy. However, the latter, as is well known from experimental data, is not sufficiently informative for this purpose; for chemical bonds, the bonding energy varies from several to several hundred kilocalories per mole (kcal/mol), as it is thus both smaller and larger than intermolecular interaction (which reaches about 20 kcal/mol) and the hydrogen bond (1–8 kcal/mol) (compare with the energies of the bond UBr_5—Br equal to 13 kcal/mol, or the reaction $ClO_2 \rightarrow Cl + O_2$ equal to 4 kcal/mol [1.23]). It can also be shown that bond lengths are not always sufficiently informative with respect to the nature of the bonding.

A more rigorous discrimination of the chemical bonding can be based on the differences in electronic structure. *The main feature of chemical interaction is that it results in a significant reorganization (restructuring) of the electronic shells of the bonding atoms.* This reorganization is characterized by "collectivization" of the valence electrons and *charge transfer* (in case of different atoms). Electron collectivization is a more general characteristic of the bond since it can take place without charge transfer, whereas charge transfer cannot be realized without collectivization; the limit case of pure (100%) ionic bonds does not exist.

We define the *chemical bond* as an interaction between atoms associated with a collectivization of the valence electronic orbitals [1.24]. This definition is sufficiently rigorous and allows one to distinguish chemical bonding from, say, intermolecular interaction or physical adsorption on surfaces (according to this definition, the hydrogen bond, which is associated with electron collectivization and charge transfer, is a type of chemical bonding).

Any rigorous definition of a physical quantity should contain, explicitly or implicitly, an indication of the means of its observation. In the definition of the chemical bonding given above, the means of its observation are implied; the collectivization of the electrons affects all the main physical and chemical properties of the system, and therefore, the set of all these properties forms an experimental criterion of chemical bonding. In this set, such an important characteristic of the bond as its energy, which is an integral feature of the bond, may be less sensitive to the electronic structure than, for instance, the electronic spectra. In the example described above, the bond UBr_5—Br with a bonding energy of ~13 kcal/mol (which is less than the intermolecular limit of 20 kcal/mol) could be attributed to intermolecular bonding, but the electronic spectra testify to chemical bonding. Besides bonding energy and electronic spectra, chemical bonding affects essentially all other spectra in whole-range spectroscopy, magnetic and electric properties, electron and X-ray diffraction, and so on.

The electronic nature of chemical bonding leads directly to the conclusion of its quantum origin. The motions of the electrons in atomic systems can be correctly described only by means of quantum mechanics. The nature of the bonding between two neutral atoms in the hydrogen molecule was first revealed by Heitler and London in 1927 by means of a quantum-mechanical description [1.25]. It was shown that the bonding results from the so-called exchange part of the energy, which is negative and results from the *undistinguishability* of the electrons and the *Pauli principle*; the exchange energy is a quantum effect and has no classical (nonquantum) analog. The Heitler-London approximation lies at the base of the quantum electronic theory of chemical bonding and quantum chemistry.

However, it is incorrect to state that the chemical bonding is due to exchange forces that keep the neutral atoms together. The analysis of the Heitler-London approximation for the H_2 molecule clearly shows that the only forces that lead to the formation of the chemical bond are the electrostatic interaction forces between the four particles: two protons and two electrons. In fact, the bonding is caused by the quantum wave properties of the electrons. The interference of the wavefunctions of the two electrons from the two bonding hydrogen atoms, under certain conditions, results in extra electronic charge concentration in the region between the two nuclei (constructive interference), thus keeping them bonded. In many cases, a significant part of the bonding energy is due to the reduction of the kinetic energy of the collectivized electrons. The separation of the exchange part of the energy results from the assumed one-electron approximation in the wavefunction when there are two or more electrons. For instance, in the case of H_2^+ with a single electron, there is still chemical bonding (resulting from the same interference of the two wavefunctions occupied by one electron) in spite of the absence of exchange interaction.

The quantum nature of the chemical bond is stipulated by the quantum-mechanical description of the motions of the electrons and nuclei.

The quantum origin of chemical bonding contributes directly to the understanding of the main property of a chemical compound—its existence and stability. Therefore, *in the study of the composition-structure-property correlation the* *electronic structure plays a key role.* Note that in general, the term *electronic structure* implies that in addition to the ground-state energy and electron distribution (the wavefunction), the *excited states* are also known. The latter allows one to describe vibronic coupling and spectroscopic properties, as well as the behavior of the system under the influence of external perturbations, including intermolecular interactions and chemical reactions (Sections 10.1 and 11.1).

However, the electronic structure does not describe all the properties of the compound. In particular, the temperature dependence of the properties may be determined rather by *the dynamics in the nuclear subsystem.* An important feature of the system is also *the coupling of the electronic distribution to the nuclear configuration and nuclear dynamics (vibronic coupling).*

The electronic structure, vibronic coupling, and nuclear dynamics describe in principle all the properties of isolated molecules. To describe chemical compounds in their different aggregate states—ensembles of interacting molecules—*quantum-statistical, thermodynamic, and kinetics studies should be employed.*

1.2.2 Definition of Coordination System

The definition of a coordination system (coordination bond, coordination compound) is not trivial and encounters difficulties. Many previous attempts to give a compact definition based on empirical data were unsuccessful (see, e.g., the text by Cotton and Wilkinson [1.15] and Section 6.1). In view of the discussion given below in this section, these attempts failed because they tried to define the coordination compound according to the genealogy (prehistory) of its formation, whereas in fact the properties of any molecular system are determined by its structural features, primarily by its electronic structure, regardless of the method of its preparation [1.24] (properties of chemical compounds are functions of state, not functions of pass).

The usual definition of a coordination system that can be traced back to the *coordination theory* created by Alfred Werner more than a century ago [1.26] is that a complex or a coordination compound is formed by a *central atom* (CA) *or ion* M that can bond one or several ligands (atoms, atomic groups, ions) L_1, $L_2, \ldots$, resulting in the system $ML_1L_2, \ldots, L_n$ (all the ligands L_i or some of them may be identical). This definition is so general that any molecular system can be considered as a coordination compound. For instance, methane can be presented as C^{4+} (M) + $4H^-$ ($4L$), that is, as a coordination compound ML_4 [1.15]. To avoid this misunderstanding, it was required that the ions M and ligands L_i, be "real," existing under the usual chemical conditions, and that the reaction of complex formation takes place under the usual conditions.

Even with these limitations, the definition above is invalid, and there are many cases when it is misleading. For example, SiF_6^{2-} has many features of coordination compounds (Section 6.1), whereas, when presented as required by the definition of $Si^{4+} + 6F^-$, we encounter conflict with the fact that Si^{4+} does not exist under usual conditions. This example can be treated as a more real composition: $SiF_4 + 2F^-$; then, to include it in the definition, we must assume that M can be also a molecule, but this assumption gives rise to new controversies and misunderstandings. This and many other examples show explicitly that *it is impossible to give a general definition of coordination systems based on the genealogy of their formation.*

On the other hand, the properties of molecular compounds as functions of state are determined by their electronic structure. This statement leads directly to the idea of the classification of chemical bonds and definition of coordination systems *on the basis of electronic structure* [1.24]. At present, when the electronic structure of coordination compounds is relatively well studied, the tendency to classify the chemical compounds on their methods of preparation seems somewhat old-fashioned. However, it was not old-fashioned at the time when coordination chemistry was rapidly developing, while the knowledge about electronic structure was rather poor and could not serve as a basis for classification. Note also that the way of thinking in chemistry was (and in a great measure is) more appropriate to *preparative chemistry*, but it is gradually changing to *structural chemistry*.

It is quite understandable that the definition of coordination systems based on electronic structure is more convenient to discuss after the study of electronic structure. Therefore, the classification of chemical bonds and chemical compounds is given in more detail in Section 6.1. According to Section 6.1, chemical bonds can be classified after their electronic structure into three main classes (Table 6.1). The first is that of *localized valence bonds* formed by two electrons with opposite spins, by one from each of the bonding atoms, and these two electrons occupy one localized bonding orbital. These valence bonds follow the usual rules of valence of organic compounds, which can be described by one valence scheme without the assumption of resonance structures (superposition of valence schemes). Localized double, triple,…, bonds are also included in this class. The compounds with localized valence bonds can be called *valence compounds*.

The second class contains *linearly delocalized bonds with possible ramifications* in which the valence electrons occupy one-electron molecular orbitals that are delocalized over all or a part of (but more than one) interatomic bonds (e.g., conjugated organic molecules, metallic chain structures, or solids). These bonds can be called *conjugated*, or *orbital, bonds*. In fact, this class of bonds includes all organic and main-group-element compounds that cannot be described by one valence scheme.

The third class contains *the bonds that are three-dimensional delocalized around a center: coordination bonds*. Distinct from the conjugated bonds, which are delocalized along the bonding line, the coordination bond is *three-dimensionally center-delocalized*. In other words, the coordination bond is formed by a coordination center to which the ligands are bonded via electrons that occupy one-electron orbitals, each of which involves all or several ligands. This means that, in general, there are no localized CA–ligand bonds; they are collectivized by the three-dimensionally (i.e., along several bonds CA–ligand) delocalized bonding electrons. It can be shown that the delocalization of the one-electron orbitals is realized via the *d* or *f* orbitals of the CA, which have many lobes differently oriented in space (Section 2.1), while *s* and *p* electrons can provide only localized or linearly delocalized orbitals.

This definition allows one to discriminate the coordination bonds from valence and conjugated bonds. For instance, the two tetrahedral systems, CH_4 and $CuCl_4^{2-}$, differ essentially in electronic structure: CH_4 has four localized two-electron bonds C—H (hybridized sp^3 valence bonds), whereas in $CuCl_4^{2-}$, the bonding electrons are delocalized over all the ligands via the copper *d* electrons (coordination bond). Note that by this definition, the bonds in NH_4^+ and BH_4^- are valence bonds analogous to CH_4 [1.27]; similarly, BF_3—NH_3 is a valence compound since its electronic structure is analogous to CF_3—CH_3.

In the SiF_6^{2-} example considered above, SiF_4 is a valence compound because of its localized Si—F bonds (analogies of C—F), while the bond in SiF_6^{2-} can be considered as a coordination bond because the octahedral coordination involves partially the low-lying *d* orbitals of Si, making the one-electron bonding states delocalized (Section 6.1).

With this classification of chemical bonds, the following definition of the coordination compound or, more general, coordination system can be given: *a coordination system* $ML_1L_2,\ldots, L_n$ *consists of a coordinating atom* (*coordination center*) *M ligated to n atoms or groups of atoms* (*ligands*) $L_1, L_2,\ldots, L_n$ *by coordination bonds that are delocalized over all or several ligands*. Following this definition, two main structural features characterize the coordination system: the coordination center and the three-dimensionally center-delocalized (coordination) bond. These features determine the main properties of coordination bonding discussed in this book; for a brief summary, see Table 6.2.

Transition metal compounds are mostly coordination systems: even in the solid state of ionic crystals (as well as in the pure metallic state) the local features of the system are controlled by the coordination centers with properties that, in essence, are quite similar to those of isolated coordination systems. The main reason for this similarity between molecular and local crystal properties lies in the specific role of the *d* electrons in both cases. Since these electrons may be active also as low-lying excited states, this book, which is devoted to TMSs, mostly coordination systems, also includes partly pre- and posttransition and rare-earth systems. As emphasized in Section 6.1, in principle any atom may serve as a coordination center; active *d* states lacking in the free atom may occur as a result of a corresponding chemical interaction that results in *d*-state activation and coordination bonding.

1.3 The Schrödinger Equation

This section presents some basic notions of quantum chemistry, the Schrödinger equation, and the main approximations used in its solution for molecular systems, which we give here mainly to introduce appropriate denotations used below. There are quite a number of textbooks on this topic: the reader is referred to several texts [1.28–1.32], to mention only some of them.

1.3.1 Formulation

Following the formal scheme of quantum mechanics [1.28], each physical quantity L (energy, momentum, coordinate, etc.) is correlated with an *operator* $\mathbf{L}$ (a symbol that denotes a certain mathematical operation), such that the experimentally observed values of this quantity $L = L_n$, $n = 1, 2, \ldots$, are the eigenvalues of the following *operator equation*

$$\mathbf{L}\Psi_n = L_n\Psi_n, \quad n = 1, 2, \ldots \tag{1.1}$$

The eigenfunction Ψ_n (the wavefunction) contains information about all properties of the system in the state with $L = L_n$.

For the main physical quantities, the form of the operator $\mathbf{L}$ is well known. In quantum chemistry, the most important quantity is the energy of the system E. The operator of energy is the Hamilton operator $\mathbf{H}$, called the *Hamiltonian*. Therefore, the operator equation for the energy is

$$\mathbf{H}\Psi_n = E_n\Psi_n \tag{1.2}$$

This is the *Schrödinger equation for stationary states* (for which the energy has a definite value). For nonstationary states that are time-dependent, the Schrödinger equation is ($\hbar$ is the Planck constant and i is the imaginary unit, $i^2 = -1$):

$$i\hbar\frac{\partial\Psi}{\partial t} = \mathbf{H}\Psi \tag{1.3}$$

Equation (1.2) is a particular case of Eq. (1.3).

The Hamiltonian H (hereafter we denote operators in italic type) includes the operators of the kinetic energies of the electrons and nuclei T and the potential energy of all the interactions between them U, $H = T + U$. In the *nonrelativistic approximation,* these interactions are purely electrostatic. Taking account of relativistic effects, the dependence of the masses on velocity, as well as magnetic spin-orbital and spin-spin interactions, should be included. This can be done on the basis of the *Dirac equation* discussed in Sections 2.1, 5.4, and 6.5.

The total kinetic energy is the sum of the kinetic energy operators of each particle $T = p^2/2\mu$, where $\vec{p} = -i\hbar\vec{\nabla}$ is the operator of the momentum ($\vec{\nabla}$ is a gradient vector with components $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$; do not confuse the imaginary unit i, $i^2 = -1$, with the summation index, which is often also expressed as i) and μ is its mass:

$$T = \sum_i \frac{-\hbar^2\Delta_i}{2\mu_i} \tag{1.4}$$

This equation accounts for the fact that $p^2 = (-i\hbar\nabla)^2 = -\hbar^2\Delta$, where Δ is a usual differential operator ($\vec{\nabla}^2 = \Delta$), $\Delta_i\Psi = \partial^2\Psi/\partial x_i^2 + \partial^2\Psi/\partial y_i^2 + \partial^2\Psi/\partial z_i^2$.

The operator U contains the sum of the Coulomb attractions and repulsions. The attraction of the ith electron to the α nucleus is $U_{i\alpha} = -Z_\alpha e^2/r_{i\alpha}$, where e is the numerical value of the charge of the electron, Z_α is the order number of the element in the periodic table equal to the positive charge of the nucleus, $r_{i\alpha} = |\mathbf{r}_i - \mathbf{R}_\alpha|$ is the electron-nucleus distance, and $\mathbf{r}_i$ and $\mathbf{R}_\alpha$ are the radius vectors of the electron and nucleus, respectively. The Coulomb repulsion between the electrons is $U_{ij} = e^2/r_{ij}$, and between the nuclei, it is $U_{\alpha\beta} = Z_\alpha Z_\beta e^2/R_{\alpha\beta}$, where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\mathbf{R}_{\alpha\beta} = |\mathbf{R}_\alpha - \mathbf{R}_\beta|$ are the interelectron and internuclear distances, respectively.

Thus, the Schrödinger equation for a molecular system of n electrons with mass m and N nuclei with masses M_α can be expressed as

$$[T + U]\Psi_k = E_k\Psi_k$$

or in a more explicit form as

$$\left[\sum_i^n \frac{-\hbar^2\Delta_i}{2m} + \sum_\alpha^N \frac{-\hbar^2\Delta_\alpha}{2M_\alpha} - \sum_i^n\sum_\alpha^N \frac{Z_\alpha e^2}{r_{i\alpha}} + \sum_{i<j}\frac{e^2}{r_{ij}} + \sum_{\alpha<\beta}\frac{Z_\alpha Z_\beta e^2}{R_{\alpha\beta}} - E_k\right]\Psi_k(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) = 0 \tag{1.5}$$

This equation is in fact a linear differential equation of the second order (of elliptical type) with respect to $3(n + N)$ variables $\mathbf{r}_i$ and $\mathbf{R}_\alpha$. It yields a nontrivial solution for only discrete values E_k, which are thus the only possible stationary energy values of the system, as well as their corresponding wavefunctions Ψ_k. The latter, as mentioned above, contains the information of all the (nonrelativistic) properties of the system in the state with the energy E_k. In particular, Ψ_k also contains complete information about the electronic and nuclear charge distribution: $\Psi|(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{R}_1, \mathbf{R}_2, \ldots,)|^2$ equals the probability of finding the first electron at $\mathbf{r}_1$, the second at $\mathbf{r}_2$, and so on (Section 5.2).

The exact solution of the Schrödinger equation allows one, in principle, to determine a priori all the properties of any polyatomic system and its behavior in different *conditions*. Note that in all cases, when exact solutions of Eq. (1.5) have been obtained, they were in good agreement with the experimental data, and in many cases, the results of calculation have an accuracy rivaling experiment.

1.3.2 Role of Approximations

In the early stages of the development of quantum mechanics, the Schrödinger equation raised some hopes that it could describe the entire chemistry, rendering many experimental approaches unnecessary. In a 1929 publication [1.33], one of the founders of quantum mechanics, P. A. M. Dirac, stated that "the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble." After 95 years, this statement remains valid; there are still principal difficulties in obtaining exact solutions of Eq. (1.5) for molecular systems with many particles, although the achievements in this field are impressive. With the growth of computers, exact solutions of Eq. (1.5) or even more complicated equations that include relativistic effects become possible for a limited number of electrons and nuclei. This number is increasing, but for relatively large numbers of particles, the results of numerical computations become difficult to perceive and almost impossible to interpret directly.

For instance, as mentioned above, the wavefunction of a system with tens of particles emerges from the numerical calculations spread on thousands of determinants. With the increase in the number of particles, the numerical information yielded by the computer becomes so vast that it is useless. To rationalize these data and to be able to solve Eq. (1.5) for larger molecular systems, *simplifications* by introducing *approximations and/or analytical models* are absolutely necessary (see also the discussion at the end of Section 5.5).

Thus, *the exact numerical solution of the Schrödinger (Dirac) equation for large molecular systems is at present, in general, an irrational task.* The problem of electronic structure can be solved by introducing approximate methods of solution of Eq. (1.5) that allow one to obtain energies E_k and wavefunctions Ψ_k in a convenient form and to evaluate the physical and chemical observable quantities with the required accuracy. The choice of the approximation that is optimal for the solution of a specific problem for a given molecular system and analysis of the results in view of the approximations made is one of the most important (and sometimes most difficult) problems of quantum chemistry.

Most approximations used in modern quantum chemistry are aimed at the separation of variables in Eq. (1.5). These approximations can be divided into three main groups:

1) Separation of the nuclear dynamics from the electronic motions—the adiabatic approximation (Section 7.1).
2) Substitution of the local interactions between the electrons given by the Coulomb terms e^2/r_{ij} by some averaged interaction that is an additive function of r_i and r_j (neglect of correlation effects)—the one-electron approximation, followed by an account for correlation effects by different methods (Section 5.3).
3) Presentation of the one-electron function of many centers—molecular orbitals (MOs), by a sum of one-center functions; atomic orbitals (AOs), the approximation of molecular orbitals as linear combinations of atomic orbitals (MO LCAO) (Section 5.1); and related approximations in the density-functional approaches (Section 5.4).

These approximations are discussed in Chapters 2, 4, 5, and 7.

Summary Notes

1) *Molecular engineering* of new compounds—the forefront of modern chemistry—is based on knowledge and understanding of the laws that control the structure and properties of molecular systems. Intuitive guesswork is an art of the researcher based on the same premises.
2) *Understanding* a new phenomenon means being able to reduce it to already-known (conventional) images and conceptions. New images and conceptions are produced by the theory that is a generalization of experimental data.
3) *The chemical bond* is defined as an interaction between atoms that collectivizes the motion of some or all of their valence electrons. The bonding is produced by electrostatic forces between the electrons and nuclei, their motion being described by means of quantum mechanics.
4) Different kinds of *chemical bonds should be classified by their electronic structure*, not by the way they are obtained—properties of chemical compounds are functions of state, not functions of pass.
5) Coordination compounds are defined as having a central atom—a coordination center forming *three-dimensionally delocalized bonds* with two or more ligands. Such bonds are produced by significant participation of *d* or *f* electrons, which are present in transition metal atoms, but can be activated in some other atoms under the ligand influence or by excitation.
6) The basis of electronic structure studies is quantum chemistry, the main equation of which is the *Schrödinger equation*. To solve this equation for practically important molecular systems, three *main simplifications* are employed: (1) separation of electronic and nuclear motions (adiabatic approximation), (2) separation of the variables of the electrons (one-

electron approximation), and (3) presentation of the molecular orbitals as a linear combination of atomic orbitals (MO LCAO approximation).

7) One of the main goals of this book is to promote a general view (understanding) of the whole subject by presenting the theory of electronic structure interlinked with physical methods of investigation and applications to a variety of chemical problems. The whole subject is more than a sum of its particular topics considered elsewhere.
8) Another goal is to make the book accessible to lay chemists and physicists, including graduate and advanced undergraduate students, and usable also as a textbook for corresponding courses. For this purpose, the discussions of the topics are presented together with many examples and illustrations of applications of the theory to specific transition metal systems, as well as Summary Notes, Questions, Exercises, and Problems.

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