ISSN (Print) : 2320 – 3765
ISSN (Online): 2278 – 8875

International Journal of Advanced Research in Electrical, Electronics and Instrumentation Engineering

*(A High Impact Factor, Monthly, Peer Reviewed Journal)*

*Website: www.ijareeie.com*

Vol. 4, Issue 6, June 2015

# Quantum Mechanics and Chemistry

**Dr. Vishramlal Bairwa**

Lecturer, Dept. of Chemistry, Govt. College, Karauli, Rajasthan, India

**ABSTRACT:** Quantum chemistry, also called molecular quantum mechanics, is a branch of physical chemistry focused on the application of quantum mechanics to chemical systems, particularly towards the quantum-mechanical calculation of electronic contributions to physical and chemical properties of molecules, materials, and solutions at the atomic level. These calculations include systematically applied approximations intended to make calculations computationally feasible while still capturing as much information about important contributions to the computed wave functions as well as to observable properties such as structures, spectra, and thermodynamic properties. Quantum chemistry is also concerned with the computation of quantum effects on molecular dynamics and chemical kinetics.

Chemists rely heavily on spectroscopy through which information regarding the quantization of energy on a molecular scale can be obtained. Common methods are infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and scanning probe microscopy. Quantum chemistry may be applied to the prediction and verification of spectroscopic data as well as other experimental data.

**KEYWORDS:** quantum chemistry, mechanics, wave functions, molecular dynamics, spectroscopy, chemical kinetics

## I.INTRODUCTION

Many quantum chemistry studies are focused on the electronic ground state and excited states of individual atoms and molecules as well as the study of reaction pathways and transition states that occur during chemical reactions. Spectroscopic properties may also be predicted. Typically, such studies assume the electronic wave function is adiabatically parameterized by the nuclear positions (i.e., the Born–Oppenheimer approximation). A wide variety of approaches are used, including semi-empirical methods, density functional theory, Hartree-Fock calculations, quantum Monte Carlo methods, and coupled cluster methods.[1]

Understanding electronic structure and molecular dynamics through the development of computational solutions to the Schrödinger equation is a central goal of quantum chemistry. Progress in the field depends on overcoming several challenges, including the need to increase the accuracy of the results for small molecular systems, and to also increase the size of large molecules that can be realistically subjected to computation, which is limited by scaling considerations — the computation time increases as a power of the number of atoms. Some view the birth of quantum chemistry as starting with the discovery of the Schrödinger equation and its application to the hydrogen atom in 1926. However, the 1927 article of Walter Heitler (1904–1981) and Fritz London,[2] is often recognized as the first milestone in the history of quantum chemistry. This is the first application of quantum mechanics to the diatomic hydrogen molecule, and thus to the phenomenon of the chemical bond. Hans Hellmann was first to publish a book on Quantum Chemistry in Russian [1] and in German languages [2] where he considered multi-particles interactions. In the following years much progress was accomplished by Robert S. Mulliken, Max Born, J. Robert Oppenheimer, Hans Hellmann, Linus Pauling, Erich Hückel, Douglas Hartree, Vladimir Fock, to cite a few. The history of quantum chemistry also goes through the 1838 discovery of cathode rays by Michael Faraday, the 1859 statement of the black-body radiation problem by Gustav Kirchhoff,[3] the 1877 suggestion by Ludwig Boltzmann that the energy states of a physical system could be discrete, and the 1900 quantum hypothesis by Max Planck that any energy radiating atomic system can theoretically be divided into a number of discrete energy elements ε such that each of these energy elements is proportional to the frequency ν with which they each individually radiate energy and a numerical value called Planck's constant[4]. Then, in 1905, to explain the photoelectric effect (1839), i.e., that shining light on certain materials can function to eject electrons from the material, Albert Einstein postulated, based on Planck's quantum hypothesis, that light itself consists of individual quantum particles, which later came to be called photons (1926). In the years to follow, this theoretical basis slowly began to be applied to chemical structure, reactivity, and bonding. Probably the greatest contribution to the field was made by Linus Pauling. The first step in solving a quantum chemical problem is usually solving the Schrödinger equation (or Dirac equation in relativistic quantum chemistry) with the electronic molecular Hamiltonian. This is called determining the electronic structure of the molecule. It can be said that the electronic structure of a molecule or crystal implies essentially its chemical properties[5]. An exact solution for the Schrödinger equation can only be obtained for the hydrogen atom (though exact solutions for the bound state energies of the hydrogen molecular ion have been identified in terms of the generalized Lambert W function). Since all other atomic, or molecular systems, involve the motions of three or more "particles", their Schrödinger equations cannot be solved exactly and so approximate solutions must be sought. Although the mathematical basis of quantum chemistry had been laid by Schrödinger in 1926, [6]it is generally accepted that the first true calculation in quantum chemistry was that of the German physicists Walter Heitler and Fritz London on the hydrogen ($H_2$) molecule in 1927. Heitler and London's method was extended by the American theoretical physicist John C. Slater and the American theoretical chemist Linus Pauling to become the valence-bond (VB) [or Heitler–London–Slater–Pauling (HLSP)] method. In this method, attention is primarily devoted to the pairwise interactions between atoms, and this method therefore correlates closely with classical chemists' drawings of bonds. It focuses on how the atomic orbitals of an atom combine to give individual chemical bonds when a molecule is formed, incorporating the two key concepts of orbital hybridization and resonance. An alternative approach was developed in 1929 by Friedrich Hund and Robert S. Mulliken, in which electrons are described by mathematical functions delocalized over an entire molecule. The Hund–Mulliken approach or molecular orbital (MO) method is less intuitive to chemists, but has turned out capable of predicting spectroscopic properties better than the VB method. This approach is the conceptual basis of the Hartree–Fock method and further post Hartree–Fock methods.[7]

The Thomas–Fermi model was developed independently by Thomas and Fermi in 1927. This was the first attempt to describe many-electron systems on the basis of electronic density instead of wave functions, although it was not very successful in the treatment of entire molecules. The method did provide the basis for what is now known as density functional theory (DFT). Modern day DFT uses the Kohn–Sham method, where the density functional is split into four terms; the Kohn–Sham kinetic energy, an external potential, exchange and correlation energies. A large part of the focus on developing DFT is on improving the exchange and correlation terms. [8] Though this method is less developed than post Hartree–Fock methods, its significantly lower computational requirements (scaling typically no worse than $n^3$ with respect to n basis functions, for the pure functionals) allow it to tackle larger polyatomic molecules and even macromolecules. This computational affordability and often comparable accuracy to MP2 and CCSD(T) (post-Hartree–Fock methods) has made it one of the most popular methods in computational chemistry[9]. A further step can consist of solving the Schrödinger equation with the total molecular Hamiltonian in order to study the motion of molecules. Direct solution of the Schrödinger equation is called quantum dynamics, whereas its solution within the semiclassical approximation is called semiclassical dynamics. Purely classical simulations of molecular motion are referred to as molecular dynamics (MD).[10] Another approach to dynamics is a hybrid framework known as mixed quantum-classical dynamics; yet another hybrid framework uses the Feynman path integral formulation to add quantum corrections to molecular dynamics, which is called path integral molecular dynamics. Statistical approaches, using for example classical and quantum Monte Carlo methods,[11] are also possible and are particularly useful for describing equilibrium distributions of states. In adiabatic dynamics, interatomic interactions are represented by single scalar potentials called potential energy surfaces. This is the Born–Oppenheimer approximation introduced by Born and Oppenheimer in 1927. Pioneering applications of this in chemistry were performed by Rice and Ramsperger in 1927 and Kassel in 1928, and generalized into the RRKM theory in 1952 by Marcus who took the transition state theory developed by Eyring in 1935 into account. These methods enable simple estimates of unimolecular reaction rates from a few characteristics of the potential surface. Non-adiabatic dynamics consists of taking the interaction between several coupled potential energy surface[12] (corresponding to different electronic quantum states of the molecule). The coupling terms are called vibronic couplings. The pioneering work in this field was done by Stueckelberg, Landau, and Zener in the 1930s, in their work on what is now known as the Landau–Zener transition. Their formula allows the transition probability between two diabatic potential curves in the neighborhood of an avoided crossing to be calculated. Spin-forbidden reactions are one type of non-adiabatic reactions where at least one change in spin state occurs when progressing from reactant to product.[13]

## II.DISCUSSION

Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is different from chemical thermodynamics, which deals with the direction in which a reaction occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction. The pioneering work of chemical kinetics was done by German chemist Ludwig Wilhelmy in 1850.[1] He experimentally studied the rate of inversion of sucrose and he used integrated rate law for the determination of the reaction kinetics of this reaction. His work was noticed 34 years later by Wilhelm Ostwald.[14] After Wilhelmy, Peter Waage and Cato Guldberg published 1864 the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.[2][3][4]

Van 't Hoff studied chemical dynamics and in 1884 published his famous "Études de dynamique chimique".[5] In 1901 he was awarded by the first Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions".[6] After van 't Hoff, chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. Elementary reactions follow the law of mass action, but the rate law of stepwise reactions has to be derived by combining the rate laws of the various elementary steps, and can become rather complex. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction.[15]

Gorban and Yablonsky have suggested that the history of chemical dynamics can be divided into three eras.[7] The first is the van 't Hoff wave searching for the general laws of chemical reactions and relating kinetics to thermodynamics. The second may be called the Semenov--Hinshelwood wave with emphasis on reaction mechanisms, especially for chain reactions. The third is associated with Aris and the detailed mathematical description of chemical reaction networks.[16]

### Factors affecting reaction rate

#### Nature of the reactants

The reaction rate varies depending upon what substances are reacting. Acid/base reactions, the formation of salts, and ion exchange are usually fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be slower.

The nature and strength of bonds in reactant molecules greatly influence the rate of their transformation into products.

#### Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in separate phases, the reaction is limited to the interface between the reactants. Reaction can occur only at their area of contact; in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant the greater its surface area per unit volume and the more contact it with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches — one does not start with large logs right away. In organic chemistry, on water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions ( are those reactions in which solute and solvent not mix properly)[14]

Surface area of solid state

In a solid, only those particles that are at the surface can be involved in a reaction. Crushing a solid into smaller parts means that more particles are present at the surface, and the frequency of collisions between these and reactant particles increases, and so reaction occurs more rapidly. For example, Sherbet (powder) is a mixture of very fine powder of malic acid (a weak organic acid) and sodium hydrogen carbonate. On contact with the saliva in the mouth, these chemicals quickly dissolve and react, releasing carbon dioxide and providing for the fizzy sensation. Also, fireworks manufacturers modify the surface area of solid reactants to control the rate at which the fuels in fireworks are oxidised, using this to create diverse effects. For example, finely divided aluminium confined in a shell explodes violently. If larger pieces of aluminium are used, the reaction is slower and sparks are seen as pieces of burning metal are ejected.

Concentration

The reactions are due to collisions of reactant species. The frequency with which the molecules or ions collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will usually result in the corresponding increase in the reaction rate, while a decrease in the concentrations will usually have a reverse effect. For example, combustion will occur more rapidly in pure oxygen than in air (21% oxygen).

The rate equation shows the detailed dependence of the reaction rate on the concentrations of reactants and other species present. The mathematical forms depend on the reaction mechanism. The actual rate equation for a given reaction is determined experimentally and provides information about the reaction mechanism. [12]

Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.The effect of temperature on the reaction rate constant usually obeys the Arrhenius equation , where A is the pre-exponential factor or A-factor, $E_a$ is the activation energy, R is the molar gas constant and T is the absolute temperature.[8]

At a given temperature, the chemical rate of a reaction depends on the value of the A-factor, the magnitude of the activation energy, and the concentrations of the reactants. Usually, rapid reactions require relatively small activation energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the $\alpha$ (temperature coefficient) is often between 1.5 and 2.5.

The kinetics of rapid reactions can be studied with the temperature jump method. This involves using a sharp rise in temperature and observing the relaxation time of the return to equilibrium. A particularly useful form of temperature jump apparatus is a shock tube, which can rapidly increase a gas's temperature by more than 1000 degrees.[10]

Catalysts

A catalyst is a substance that alters the rate of a chemical reaction but it remains chemically unchanged afterwards. The catalyst increases the rate of the reaction by providing a new reaction mechanism to occur with in a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis–Menten kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation.

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.[8]

In addition to this straightforward mass-action effect, the rate coefficients themselves can change due to pressure. The rate coefficients and products of many high-temperature gas-phase reactions change if an inert gas is added to the mixture; variations on this effect are called fall-off and chemical activation. These phenomena are due to exothermic or endothermic reactions occurring faster than heat transfer, causing the reacting molecules to have non-thermal energy distributions (non-Boltzmann distribution). Increasing the pressure increases the heat transfer rate between the reacting molecules and the rest of the system, reducing this effect.

Condensed-phase rate coefficients can also be affected by pressure, although rather high pressures are required for a measurable effect because ions and molecules are not very compressible. This effect is often studied using diamond anvils.

A reaction's kinetics can also be studied with a pressure jump approach. This involves making fast changes in pressure and observing the relaxation time of the return to equilibrium.

Absorption of light

The activation energy for a chemical reaction can be provided when one reactant molecule absorbs light of suitable wavelength and is promoted to an excited state. The study of reactions initiated by light is photochemistry, one prominent example being photosynthesis.[6]

## III.RESULTS

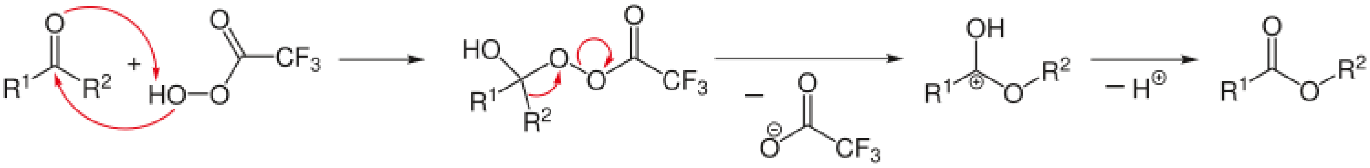
A chemical reaction is a process that leads to the chemical transformation of one set of chemical substances to another.[1] Classically, chemical reactions encompass changes that only involve the positions of electrons in the forming and breaking of chemical bonds between atoms, with no change to the nuclei (no change to the elements present), and can often be described by a chemical equation. Nuclear chemistry is a sub-discipline of chemistry that involves the chemical reactions of unstable and radioactive elements where both electronic and nuclear changes can occur.[4]

The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change, and they yield one or more products, which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations, which symbolically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Chemical reactions happen at a characteristic reaction rate at a given temperature and chemical concentration. Typically, reaction rates increase with increasing temperature because there is more thermal energy available to reach the activation energy necessary for breaking bonds between atoms.

A reaction may be classified as redox in which oxidation and reduction occur or non-redox in which there is no oxidation and reduction occurring. Most simple redox reactions may be classified as a combination, decomposition, or single displacement reaction.[3]

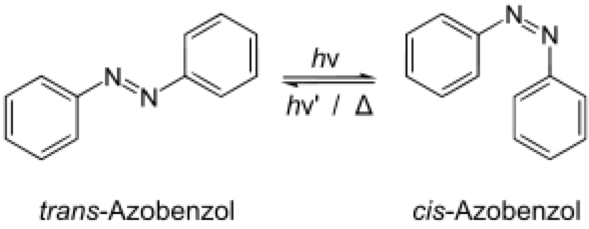
Different chemical reactions are used during chemical synthesis in order to obtain the desired product. In biochemistry, a consecutive series of chemical reactions (where the product of one reaction is the reactant of the next reaction) form metabolic pathways. These reactions are often catalyzed by protein enzymes. Enzymes increase the rates of biochemical reactions, so that metabolic syntheses and decompositions impossible under ordinary conditions can occur at the temperature and concentrations present within a cell. The general concept of a chemical reaction has been extended to reactions between entities smaller than atoms, including nuclear reactions, radioactive decays and reactions between elementary particles, as described by quantum field theory. Chemical equations are used to graphically illustrate chemical reactions. They consist of chemical or structural formulas of the reactants on the left and those of the products on the right. They are separated by an arrow (→) which indicates the direction and type of the reaction; the arrow is read as the word "yields".[10] The tip of the arrow points in the direction in which the reaction proceeds. A double arrow (⇌) pointing in opposite directions is used for equilibrium reactions. Equations should be balanced according to the stoichiometry, the number of atoms of each species should be the same on both sides of the equation.[1]



An example of organic reaction: oxidation of ketones to esters with a peroxycarboxylic acid

The elementary reaction is the smallest division into which a chemical reaction can be decomposed, it has no intermediate products.[13] Most experimentally observed reactions are built up from many elementary reactions that occur in parallel or sequentially. The actual sequence of the individual elementary reactions is known as reaction mechanism. An elementary reaction involves a few molecules, usually one or two, because of the low probability for several molecules to meet at a certain time.[14] The most important elementary reactions are unimolecular and bimolecular reactions. Only one molecule is involved in a unimolecular reaction; it is transformed by isomerization or a dissociation into one or more other molecules. Such reactions require the addition of energy in the form of heat or light. A typical example of a unimolecular reaction is the cis–trans isomerization, in which the cis-form of a compound converts to the trans-form or vice versa.[15]

In a typical dissociation reaction, a bond in a molecule splits (ruptures) resulting in two molecular fragments. The splitting can be homolytic or heterolytic. In the first case, the bond is divided so that each product retains an electron and becomes a neutral radical. In the second case, both electrons of the chemical bond remain with one of the products, resulting in charged ions. Dissociation plays an important role in triggering chain reactions, such as hydrogen–oxygen or polymerization reactions.[3]



Isomerization of azobenzene, induced by light (hv) or heat (Δ)

## IV.CONCLUSIONS

The Schrödinger equation is a linear partial differential equation that governs the wave function of a quantum-mechanical system.[1]: 1–2 It is a key result in quantum mechanics, and its discovery was a significant landmark in the development of the subject. The equation is named after Erwin Schrödinger, who postulated the equation in 1925, and published it in 1926, forming the basis for the work that resulted in his Nobel Prize in Physics in 1933.[2][3]

Conceptually, the Schrödinger equation is the quantum counterpart of Newton's second law in classical mechanics. Given a set of known initial conditions, Newton's second law makes a mathematical prediction as to what path a given physical system will take over time. The Schrödinger equation gives the evolution over time of a wave function, the quantum-mechanical characterization of an isolated physical system. The equation can be derived from the fact that the time-evolution operator must be unitary, and must therefore be generated by the exponential of a self-adjoint operator, which is the quantum Hamiltonian.[14]

The Schrödinger equation is not the only way to study quantum mechanical systems and make predictions. The other formulations of quantum mechanics include matrix mechanics, introduced by Werner Heisenberg, and the path integral formulation, developed chiefly by Richard Feynman. Paul Dirac incorporated matrix mechanics and the Schrödinger equation into a single formulation. When these approaches are compared, the use of the Schrödinger equation is sometimes called "wave mechanics".[16]

## REFERENCES

1. Hellmann, Hans (1937). Einführung in die Quantenchemie. Deuticke, Leipzig und Wien.
2. Atkins, P.W. (2002). Physical Chemistry. Oxford University Press. ISBN 0-19-879285-9.
3. Atkins, P.W.; Friedman, R. (2005). Molecular Quantum Mechanics (4th ed.). Oxford University Press. ISBN 978-0-19-927498-7.
4. Atkins, P.W.; Friedman, R. (2008). Quanta, Matter and Change: A Molecular Approach to Physical Change. ISBN 978-0-7167-6117-4.
5. Bader, Richard (1994). Atoms in Molecules: A Quantum Theory. Oxford University Press. ISBN 978-0-19-855865-1.
6. Gavroglu, Kostas; Ana Simões: Neither Physics nor Chemistry: A History of Quantum Chemistry, MIT Press, 2011, ISBN 0-262-01618-4
7. Karplus M., Porter R.N. (1971). Atoms and Molecules. An introduction for students of physical chemistry, Benjamin–Cummings Publishing Company, ISBN 978-0-8053-5218-4
8. Landau, L.D.; Lifshitz, E.M. (1977). Quantum Mechanics:Non-relativistic Theory. Course of Theoretical Physic. Vol. 3. Pergamon Press. ISBN 0-08-019012-X.
9. Levine, I. (2008). Physical Chemistry (6th ed.). McGraw–Hill Science. ISBN 978-0-07-253862-5.
10. McWeeny, R. (1979). Coulson's Valence. Oxford Science Publications. ISBN 0-19-855144-4.
11. Pauling, L. (1954). General Chemistry. Dover Publications. ISBN 0-486-65622-5.
12. Pauling, L.; Wilson, E. B. (1963) [1935]. Introduction to Quantum Mechanics with Applications to Chemistry. Dover Publications. ISBN 0-486-64871-0.
13. Pullman, Bernard; Pullman, Alberte (1963). Quantum Biochemistry. New York and London: Academic Press. ISBN 90-277-1830-X.
14. Scerri, Eric R. (2006). The Periodic Table: Its Story and Its Significance. Oxford University Press. ISBN 0-19-530573-6. Considers the extent to which chemistry and especially the periodic system has been reduced to quantum mechanics.
15. Simon, Z. (1976). Quantum Biochemistry and Specific Interactions. Taylor & Francis. ISBN 978-0-85626-087-2.
16. Szabo, Attila; Ostlund, Neil S. (1996). Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory. Dover. ISBN 0-486-69186-1.