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Overview of Electronic Structure Crystallography

1.1 Introduction

Electrons in materials, which are by nature de Broglie (probability) waves, have distribution both in space (i.e. electron density distribution in position space, or electron density for short) and in energy (i.e. electron density distribution in momentum space, or momentum density for short). These two distributions are highly complementary and together determine the properties of the material. The concepts of orbitals (e.g. s, p, and d orbitals) and chemical bonds (e.g. σ and π bonds), which describe the spatial properties of electrons, and the concepts of energy levels and energy bands, which describe the energy properties of electrons, can explain various physical and chemical phenomena.

In principle, the electronic structure of a material and its properties can be determined by quantum-mechanics-based first-principles computations, which generally involve wavefunction and density functional theory (DFT) calculations for molecular and crystalline systems, respectively. The wavefunction approach uses various approximations to simplify the Schrödinger equation to obtain an equation that can be easily solved, such as the Hartree–Fock equation, and involves self-consistent field iteration to obtain the material's electron wavefunction, with the electron wavefunction taking the form of a single Slater determinant in the Hartree–Fock framework. The DFT approach was proposed by Hohenberg and Kohn [1] with the basic idea that all the ground-state properties of a physical system can be determined by its electron density alone. Both electron wavefunction and density matrice are fundamental physical quantities that describe the electronic structure, and a pure-state electron wavefunction can be equivalently presented as an electron density matrix. The density matrix obtained by integrating all of the coordinates of $N - 1$ electrons in the complete N-electron density matrix can be denoted as a one-order reduced-density matrix (1-RDM) or a single-electron density matrix. Because all the properties of a single electron of interest can be obtained by the 1-RDM, any density matrix mentioned in this book actually refers to 1-RDM unless specified otherwise.

Although the electronic structures of materials are mainly obtained by first-principles computations, it is necessary to involve experimental measurements for determining electronic structures. First-principles computations typically introduce more approximations, leading to deviations between the theoretical

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computations and experimental results. Moreover, theoretical computations do not accurately consider the effects of external fields, and usually do not yield the electronic structure of a material under the working conditions; however, these limitations can be overcome to some extent by experimental means. Because electrons scatter X-rays and unpaired electrons scatter neutrons, it is possible to use X-ray and neutron scattering experiments to probe the electronic state of a material. In addition, the electron density distribution in a crystal determines the electrostatic potential and magnetic field inside it, which in turn affects electron scattering, suggesting that electron diffraction can also be used to study the electronic structure of a material. Scattering occurs in the form of coherent scattering (diffraction) and incoherent scattering (Compton scattering), of which X-ray diffraction is the most commonly used method for the structural characterization of materials and is the main experimental research tool in modern crystallography (X-ray crystallography).

Modern crystallography is an experimental science that aims to determine the arrangement of atoms (or ions) in solids, mainly to study the formation, morphology, composition, and structure, as well as the physical and chemical properties of crystals and crystalloids. The main experimental methods used to characterize the crystal structures of materials are X-ray diffraction, neutron diffraction, and electron diffraction, among which X-ray diffraction is the most developed and widely used. Modern crystallographic methods typically provide structural information of materials only on the atomic scale.

Electronic structure crystallography can be defined as an experimental crystallographic science that aims to determine the electronic structures (electron density, electron wavefunction, or density matrix) of ground and excited/distorted states of solids in real and momentum (or energy) space with combined experimental techniques in crystallography and other closely relevant disciplines. Electronic structure crystallography combines the quantum theory of electronic structure and the experimental methodology of scattering and energy spectroscopy, and is an interdisciplinary discipline and research hotspot in the current frontier of crystallography for the following main reasons. ① Electronic structure crystallography links the experimental observations of a material to its basic physical quantities, and the obtained electron density and wavefunction, in principle, contain all the electronic structure information of the material, allowing it to definitively calculate all of the ground-state properties of a material. ② For some special material systems, such as those with numerous atoms or complex electronic structures, it is difficult to obtain accurate and reliable electronic structure information by first-principles computations. Instead, electronic structure crystallography can be used to study their experimental electronic structures, which is of great significance for investigating the structural nature of material functions and revealing the material structure-property relationships. ③ The experimental measurements of electronic structures can be used to verify the results of theoretical computations, which is beneficial for improving the theoretical methods and computational models and promoting the further development of first-principles computations.

Reconstructing the experimental electronic structure of a material from scattering data first requires the construction of a parametric theoretical model of the electronic structure, which can be an electron density model, a density matrix model, or a wavefunction model, such as a pseudo-atom multipole model, a single Slater determinant wavefunction, an extremely localized molecular orbital (ELMO) wavefunction, or a 1-RDM model, all of which have currently attracted considerable attention. The unknown parameters in these models are associated with the observed quantities in scattering experiments, such as the X-ray diffraction structure factor associated with the electron density (diagonal element of the position-space density matrix) and the X-ray Compton profile associated with the electron momentum density (off-diagonal element of the position-space density matrix or diagonal element of the momentum-space density matrix). Constructing equations based on these relations, least-squares refinements using diffraction structure factors and/or Compton profile data can be performed to obtain an electronic structure model that best fits the experimental observations. These optimal models can be referred to as the experimental electronic structures. Because electron density can be fully determined by the experimental structure factor, and similarly, the 1-RDM can be fully determined by the structure factor and Compton profile, the electron density and 1-RDM obtained by refinement of the experimental scattering data can be referred to as the experimental electron density and experimental density matrix, respectively. Unlike the electron density and 1-RDM, the electron wavefunction is generally not considered an experimentally observable physical quantity; therefore, it is not a rigorous statement to say that the electron wavefunction can be determined exclusively by experimental methods. Rather, the experimental electron wavefunctions in this book were derived using refinement techniques with experimental data and contain certain experimental information. Because the number of refinement parameters in the electron wavefunction model is large, with a limited number of experimental structure factors, constraints such as energy minimization must be introduced during the experimental refinement of the wavefunction.

Because the concepts of electron density, density matrix, and wavefunction are not very intuitive and difficult for scientists in chemistry and materials science to use directly, after reconstructing the experimental electronic structure of a material from experimental data, as described above, it is necessary to further perform topological analysis on an experimental electronic structure to extract its topological indicators related to canonical concepts, such as topological atomic properties (charge, volume, and multipole moment) and topological bond properties (electron density, Laplacian value, and energy density at the critical point of the bond). Quantum theory of atoms in molecules (QTAIM) is the most widely used theory for the topological analysis of electronic structures.

In this chapter, we describe some basic concepts, principles, and methods for electronic structure crystallography and give a brief history of the development of electronic structure crystallography. To establish a connection between crystallography and quantum chemistry, Chapter 2 covers the first-principles computation methods for physical quantities (electron density functions) relevant to experimental electronic structures. Chapter 3 covers the theories for the topological analysis of electronic structures, including the commonly used QTAIM, the more generalized interacting quantum atoms (IQA) method, and the ω-restricted space partitioning method. Chapter 3 also presents an introduction to the computational methods of intermolecular interaction energies, as well as other analysis methods for chemical interactions (e.g. source function, electron localization function [ELF], and reduced density gradient function). Chapter 4 covers the experimental measurement techniques and refinement algorithms of electronic structures, with a special focus on the treatment of atomic thermal vibrations. The pseudo-atom models of electronic structures (mainly including the commonly used multipole models, with some descriptions of the classical X-ray atomic orbital (XAO) model, the X-ray molecular orbital (XMO) model, and the molecular orbitals with variable population numbers model, density matrix models, and wavefunction models (mainly including the X-ray constrained wavefunction (XCW) and ELMO wavefunction models) are described in detail in Chapters 5–7. Electronic structure crystallography has wide applications in inorganic and organic materials. Chapter 8 describes the concepts of functional electronic structure and functional motif of materials and illustrates the application of electronic structure crystallography in material research by presenting typical example of studying nonlinear optical functional motifs with in-situ electronic structure measurements.

1.1.1 History of Electronic Structure Crystallography

Although the concept of electronic structure crystallography was not formally introduced until recently [2], relevant research dates to the beginning of X-ray crystallography and quantum mechanics in the late nineteenth and early twentieth centuries.

1.1.2 The Beginnings of X-ray Crystallography and Quantum Mechanics

Electron structure and X-ray crystallography have been closely linked since the beginning of the two disciplines. The year 1895 saw the discovery of X-rays by Roentgen, which started a new era of probing the inner world of matter. In 1912, Laue discovered the diffraction of X-rays after they penetrated a crystal, and in the same year, the Bragg father and son team discovered that X-ray diffraction photographs could be used to determine the positions of atoms in a crystal; thus, pioneering the X-ray crystallography. During the same period, important breakthroughs were made in the understanding of electrons and the study of quantum theory, with Thomson's discovery of the electron in 1897 and Bohr's proposal of the atomic structure model in 1913, which introduced the concept of quantization for the study of electron motion within the atom. Recognizing the scientific revolution that could be brought about by X-ray crystallography techniques, Debye predicted in 1915 that "It seems that the experimental study of scattered radiation, in particular from light atoms, should get more attention, since along this way it should be possible to determine the arrangement of the electrons in the atoms." [3] This prediction gave impetus to the establishment and development of a theoretical atomic model that could be tested by diffraction experiments. Due to the limitations of the atomic scattering factor in Bohr's atomic model, the computed diffraction intensity was shown to differ significantly from the experimental value; thus, it has been difficult to use for structure determination. It was not until the quantum model of electron density in atoms was developed [4] that the determination of the structure of matter became possible. Subsequent developments in crystallography and chemical bonding theory enhanced the connection between crystallography and quantum chemistry, as well as facilitated advances in information technology for extracting the electronic structures of materials from experimental data.

1.1.3 The Nascent Period of Experimental Electronic Structure Research

It was not until 1958 that research related to electronic structure crystallography made new progress. Richard Weiss and his collaborators took the lead in conducting pioneering work on the experimental charge density, momentum density, and spin density of single-crystal samples by obtaining the outer electronic configurations of metal atoms Cu, Ni, Co, Fe, and Cr, determining the atomic scattering factors using X-ray single-crystal diffraction measurements [5], determining the electron momentum density of diamond, graphite, and carbon black by Compton scattering experiments [6], and by calculating the spin density information for Co from the magnetic form factors measured by polarized-neutron diffraction experiments [7]. The main purpose of the research efforts made by Richard Weiss was to extract electron wavefunction information directly from X-ray scattering experiments. In a book [8], Richard Weiss suggested that the experimentally determined scattering intensity could be used to correct the Hartree–Fock wavefunction, which itself can be computed theoretically without considering the correlation between opposite spin electrons. Richard Weiss' intuition provided inspiration for other researchers, whereby integrating crystallographic experimental methods and quantum chemical theoretical approaches, as well as electron density information in the position space and Fourier transform space (momentum space), it is feasible to reconstruct the electron wavefunction from X-ray and neutron scattering experiments.

1.1.4 Developments of Pseudo-atom Models

Beginning in the late 1960s, technology related to electronic structure crystallography branched out into two directions, namely, reconstructing electronic structures from experimental data based on atomic orbitals versus molecular orbitals. The atomic orbital-based approach originated from the generalized atomic scattering factor (GASF), which was developed by Stewart and was a concept first proposed by Dawson [9]. The atomic scattering factor is also known as the atomic form factor. Stewart's basic idea was to first calculate the GASF by projecting the quantum-mechanically computed electron density of a molecule onto the atomic orbital basis functions, and then use this GASF as an alternative to the isolated-atom scattering factor for structural refinement [10, 11]. The isolated-atom scattering factor can be obtained by quantum mechanical computations on isolated atoms without considering the interactions between the atoms present in the actual crystal, and has been widely used in crystal structure refinement. By contrast, the GASF takes into account the interactions between atoms, and can be obtained by projecting molecular electron density. An atomic model obtained by projecting the electron density of the molecule is referred to as a pseudo-atom model. In contrast to the almost spherical distribution of the outer electron orbitals of isolated atoms, where no interatomic interactions are considered, the outer electron orbitals of a pseudo-atom are stretched to various extents in different directions due to chemical bonding and can be expressed as multipolar spherical harmonics centered on the atom of interest. Therefore, a pseudo-atom model is also known as an aspherical or multipole model. Considering the complexity of theoretical computations of a molecular orbital wavefunction and its atomic orbital projection, the Stewart model eventually involved a relatively simple set of atomic orbital parameters to fit the experimental values of the structure factor [12]. Hence, in the structure refinement process, the electron density of a crystal unit cell can be projected on the atomic orbital wavefunction, followed by refining the atomic orbital parameters to minimize the difference between the theoretical and experimental structure factors. Similar to Stewart's idea, Hansen and Coppens [13] designed a modified multipole model in which the electron density of each atom can be expressed as the sum of the core electron density, the valence electron density, and the non-spherical electron density, where the core electron density is set to a constant value, assuming that the core electron density is less affected by chemical bonds and consequently not involved in structural refinement. The valence shell can be adjusted by refining the number of valence electrons and the contraction factor. Non-spherical electron density has been mainly used to describe the bonding states of atomic orbitals and can be further expressed as the sum of a series of spherical harmonics, providing better modeling of the expansion of valence electron orbitals in three dimensions when atoms form chemical bonds. Thus, by refining the number of electrons occupying each orbital and the orbital contraction factor, detailed information on atoms and bonding orbitals can be obtained. Meanwhile, the introduction of a local atomic coordinate system also confers good portability to the pseudoatom model, i.e. the atomic orbital parameters of a crystal or molecule obtained from refinement can be directly applied to another crystal or molecule, as long as the target atoms in both the crystals and molecules have similar chemical environments.

Among all versions of multipole models, the Hansen and Coppens multipole model is currently the most widely used pseudo-atom model. This model has undergone multiple rounds of development and improvement over the years to adapt it to different situations. In the 1990s and at the beginning of the twenty-first century, research in this area mainly focused on improving the quality of the radial part of the valence electron density and the non-spherical electron density [14]. This has also led to the development of certain refinement methods for contraction factors [15], as contraction factors are difficult to determine using experimental diffraction intensity during the refinement process. Over the past decade or so, efforts focused on improving multipole models have centered around refining the electron density distribution and spin density distribution while correcting for the distortion of the core electron shell. Meanwhile, some databases consisting of multipole model parameters have been established, which contain portable parameters of electron density. These can be used in the construction of electron density models for large or complex molecules (especially biological macromolecules), for which accurate electron density analysis is difficult.

These multipole model improvements stem from the flexibility of the Hansen and Coppens model, specifically due to the fact that the model defines each atom in a local coordinate system as independent of the crystal orientation matrix, allowing for the transfer of multipole moment parameters from one atom to another, as long as the two atoms have sufficiently similar chemical environments. The development of multipole models was originally intended to make model parameters portable; however, it was not until many years later that this concept was introduced [16]. The importance of multipole model portability was fully demonstrated only when the experimentally determined data of atomic multipole moments were sufficiently large to construct a database for a number of similar molecules [17], especially to improve the refinement results of some samples with poor diffraction quality and construct electrostatic potentials and moments. This approach was later adopted for the theoretical computations of atomic multipole moments with the advantage of computing the electron density of large molecules, for which experimental electron density models were generally difficult to construct [18–20]. These methods are now relatively well established and have found some new applications, such as in model construction for the electron diffraction-based analysis of crystal structures [21].

The flexibility of multipole models offers the possibility of probing special electronic structure features, such as studying small distortions in the electron density of atomic core electron shells in molecules or covalent crystals. For this reason, an extended Hansen and Coppens model was proposed [22]. In this model, the non-spherical electron distribution includes not only the valence shell, but also the core electron shell. The contraction factor of the core electron shell can also be refined during the refinement process, to not only provide a chemically reasonable interpretation, but to also correct for the temperature factor. For example, the carbon atoms in diamonds show a small yet significant contraction of the core electron shell, which can be interpreted as an indication of chemical bonding with the involvement of core electrons [22].

As another very important improvement, multipole models can be simultaneously used to describe the electron and spin densities, due to the development of X-ray diffraction and elastic neutron scattering techniques, allowing for the study of electron and spin densities, respectively. The neutron scattering cross-section is the superposition of cross-sections of both atomic scattering and magnetic scattering. In addition, magnetic scattering is affected not only by the atomic spin magnetic moment, but also by the atomic orbital angular momentum; thus, polarized neutron diffraction can be used to determine the spin density. Data from both X-ray and neutron diffraction experiments can be jointly refined using the same model, wherein the electron density can be split into spin-up and spin-down components. The high number of parameters in the joint refinement model can worsen the parameter correlation problem due to the very limited data generated by polarized neutron diffraction and their linear dependence on X-ray diffraction parameters. Even though current X-ray diffractometers can provide diffraction data at very high angles, only a small fraction of the low-angle diffraction data contains information on the electron density of valence shells. As a result, this physical limit cannot be fundamentally broken, which limits the flexibility of multipole models. However, joint refinement of charge and spin densities is possible for some paramagnetic metallic compounds or magnetic inorganics when certain constraints are imposed, with further progress laying a foundation for the application of multipole models in spintronics [23–25].

Moreover, the flexibility of multipole models allows them to be used for studying certain substances under unconventional conditions such as laser irradiation, electric fields, high pressures, or temperatures, and even some powder samples [26]. In these cases, certain typical conditions beneficial for obtaining accurate electron densities cannot be met. For example, atomic vibrations dramatically intensify at high temperatures, seriously compromising the feasibility of obtaining electron densities from thermal motion by inverse convolution. Sometimes, it is the external field that allows the material to possess interesting properties, as demonstrated by some studies of crystals under high pressure [27–29]. Unlike high-temperature conditions, high pressure is not a factor that affects the accurate acquisition of electronic structures of crystals. However, the diamond anvil cell (DAC) commonly used in high-pressure studies can severely affect the quality of diffraction data, particularly by affecting the region of the reciprocal space where diffraction data can be measured, producing severe background signals. Another disadvantage is that pressure above a certain threshold cannot be uniformly transmitted to the crystal sample under investigation and can likely result in fracturing of the sample, thus, affecting the collection of diffraction data. Pressurization reduces atomic vibrations, especially for molecular crystals without strong supramolecular interactions. Studies [27, 28, 30] have shown that isostatic pressing under 5–10 GPa is equivalent to exposing a sample to a low temperature of 100 K in terms of decreasing the amplitude of the temperature factor. Low-temperature measurements under the purging of liquid nitrogen are a benchmark of experimental electronic structure studies. Though, to achieve the same effect that helium purging temperature has on the temperature factor, an isostatic pressure of more than 100 GPa is required, which is almost impossible for diffraction experiments in practice. Despite some difficulties and drawbacks, examples of the successful determination of electronic structures of high-pressure molecular crystals have been reported by means of multipole refinement [28].

In the 1970s, a number of other models were proposed in addition to the most famous multipole model proposed by Stewart and Coppens, all of which were based on the same general ideas but lacked the quantum mechanical basis of the Stewart model. Among these models, the Hirshfeld atom model is well-established [31]. This model uses the theoretical electron density of an isolated ground-state atom (spherical) as the basis for projection computations, similar to the atomic electron density used in traditional crystal structure refinement. In projection computations, the electron density of the whole molecule or crystal can be expressed as the sum of spherical atom electron densities and then decomposed onto each atom according to the projection weights to obtain the scattering factors of Hirshfeld atoms for subsequent structural refinement. The Hirshfeld atom refinement (HAR) model provides an operationally easy decomposition scheme for different types of electron density data, such as those originating from multipole model refinement or wavefunction computations. In electronic structure crystallography, Hirshfeld atoms are mainly used for three purposes: (i) to perform atomic charge population analysis on experimental or DFT electron densities [32], (ii) to construct molecular Hirshfeld surfaces [33], and (iii) to perform HAR [34].

In contrast to research on atomic orbital-based electronic structure reconstruction, research on molecular orbital-based electronic structure reconstruction faces more obstacles. The main idea of the second method is to obtain molecular orbital wavefunctions by direct refinement against diffraction or other scattering experimental data. Coppens and his collaborators made attempts in this regard [35], but found that the implementation of the process, even for medium-sized molecules, was very complicated, mainly because the computational process required refinement of the coefficients of the product of two atomic-orbital wavefunctions, which was not possible due to the relatively severe correlation between the wavefunction parameters.

1.1.5 Developments of Experimental Electron-density Matrix Models

Since 1969, the systematic method proposed by Clinton, Massa, and their collaborators has shown to be a landmark advance in electronic structure crystallography for extracting the 1-RDM from theoretically computed electron densities or structure factors [36–43]. This method constructs an iterative computation equation containing a density matrix and structure factor by introducing the electrostatic theorem, the virial theorem, and the Hellman–Feynman theorem, indicating the electron density that best conforms to the structure factor by solving the equation. Because the density matrix must obey the Pauli exclusion principle, it must be obtainable by integrating an N-electron antisymmetric wavefunction, a type of constraint referred to as N-representability conditions. A 1-RDM satisfying the N-representability conditions can be used to fully determine the experimental wavefunction. To make the obtained density matrix satisfy N-representability conditions, Clinton and Massa imposed certain constraints on the density matrix, such as using a single-Slater-determinant wavefunction and requiring the 1-RDM to be at least Hermitian, idempotent (i.e. the density matrix must be a projection operator), and normalized (the trace of the density matrix is the number of electrons N) [44], with the normalization condition ensuring an eigenvalue of the 1-RDM between 0 and 1.

The methods proposed by Clinton and Massa were later improved upon to some extent. For example, this strategy was extended to single-determinant wavefunctions for open-shell systems [45], in which Frishberg and Massa used high-quality theoretical X-ray structure factors to fit wavefunctions for a number of simple atomic and molecular systems, obtaining more accurate single-electron properties than the variational approach, despite the inability to obtain two-electron properties. In addition, Pecora obtained density matrices that not only satisfied the idempotency condition but also simultaneously provided a better fit of the experimental observables by introducing the steepest descent algorithm [46]. The most important advance in this line of research was made by Massa et al., who directly obtained the idempotent density matrix of beryllium from the analysis of X-ray diffraction data for the first time [47].

Howard and his collaborators constructed a variant of Clinton's scheme and used a simulated annealing algorithm to fit single-determinant wavefunctions for large systems, such as methylamine and formamide [48]. Snyder and Stevens used high-resolution single-crystal X-ray diffraction data to obtain an idempotent density matrix for azide anion in potassium azide [49]. Notably, the deformation density fitted using the density matrix showed a negative peak near the nucleus, a feature that was predicted for theoretical deformation density but not observed in the deformation density refined by the multipole model, suggesting that density matrix refinement could provide finer electronic structure features than multipole model refinement. According to X-ray diffraction structure factors, Tanaka proposed the XAO method [50, 51] to simulate heavy atomic orbital distortions due to crystal field effects. Based on this achievement, the XMO method was subsequently proposed[52].

The Clinton method, as well as similar methods described above, all impose idempotency constraints on the density matrices (i.e. single-Slater-determinant wavefunctions). To overcome this drawback, Hibbs, Waller, and their collaborators designed a novel method using experimental structure factors to optimize the occupation numbers of a predetermined set of (occupied or empty) molecular orbitals [53, 54]. This method, known as the molecular orbitals with variable occupation numbers (MOON) method, has the advantage of linearly increasing the number of refinement parameters with the scale of the refinement system, making it easy to perform property computations, even for very large systems.

In some more advanced methods, the idempotency condition can be replaced by more stringent N-representability conditions. In 1985, researchers noticed that the chemical bonding information hidden in the inelastic Compton scattering data could be used to reconstruct the 1-RDM [55, 56]. Subsequently, Weyrich [57], Gillet [58, 59], and their collaborators systematically proposed a method of reconstructing the 1-RDM through joint refinement of the diffraction and Compton scattering data, i.e. determining the diagonal elements of the density matrix by the structure factor of X-ray diffraction and determining the off-diagonal elements by the Compton scattering profile. For the spin density matrix, the diagonal matrix elements can be determined by polarized neutron diffraction and, in principle, by magnetic X-ray diffraction, while the off-diagonal matrix elements can be determined by magnetic Compton scattering experiments.

In 2007, Gillet designed a method to extend the Hansen–Coppens multipole model of charge density distribution to a single-particle density matrix [60]. Although tested only in simple diatomic systems (HF and CO), this approach allows the main features of chemical bonding to be extracted from complementary (diffraction and Compton scattering) experimental data. De Bruyne and Gillet used orthogonal atomic basis functions to describe the single-electron density matrix and introduced N-representability conditions into the least-squares refinement of the density matrix by using the semidefinite programming method. This approach was subjected to basic testing with dry ice crystals and was found to be in good agreement with the periodic quantum-mechanical computations [61].

Based on the fundamental research of the spin density of $YTiO_3$ in the coordinate space and momentum space by polarized neutron diffraction and magnetic X-ray Compton scattering [62, 63], a more advanced model, called the spin-resolved 1-RDM (1-SRDM) model, was proposed [64]. In this model, the density matrix was expanded by using atomic Gaussian basis functions, similar to the approach of De Bruyne and Gillet, in dealing with the closed-shell case [61]. However, unlike in the De Bruyne and Gillet approach, the exponent of the Gaussian function in 1-SRDM is not fixed and can be adjusted during the refinement process. Once the optimal exponent of the Gaussian function is obtained, the matrix elements of 1-SRDM can be obtained by minimizing the difference between the computed and experimental values (magnetic structure factor and magnetic Compton profile). Similarly, a quantum-mechanically rigorous 1-SRDM can be obtained by satisfying N-representability conditions. The study observed that the joint refinement indeed led to more accurate results than those obtained from polarized neutron diffraction data alone when the model was applied to an artificially modified magnetic crystal model based on a urea structure. The researchers also observed that the magnetic Compton profile not only affected the off-diagonal 1-SRDM elements but also improved the diagonal matrix elements, which was beneficial for obtaining a generally more accurate estimate of spin density. This technique was later used to determine the 1-SRDM of $YTiO_3$, and the refinement results could explain the magnetic properties of the Ti–O–Ti chemical bonds [65].

Cassam-Chenaï pointed out the importance of using a density matrix ensemble that satisfies N-representability conditions, considering the relatively large number of parameters to be refined by the density matrix approach and the fact that the amount of X-ray or neutron diffraction data is limited by the Ewald sphere, where a density matrix ensemble can be described by a pre-computed wavefunction, using experimental structure factors to refine a small number of coupling coefficients [66]. These coupling coefficients provide information on the electronic structure in terms of intra- and intermolecular electronic correlations as well as spin-orbit coupling. This method was later used to analyze polarized neutron diffraction data to obtain the magnetic moment density of $CoCl_4^{2-}$ polyanions in Cs_3CoCl_5 crystal [67].

Of note, for the density matrix model, satisfying N-representability conditions may still be insufficient. Indeed, according to the theories of Gilbert [68] and Coleman [69], a given electron density distribution can, in principle, be expressed by an infinite number of 1-RDMs that satisfy the N-representability conditions. Thus, fitting the electron density data alone, as in the case of all previous fitting strategies, is insufficient to ensure that the experimental wavefunction or density matrix obtained by refinement is physically realistic. To address this problem, Henderson and Zimmerman suggested that among all the single-Slater-determinant wavefunctions that fit experimental electron densities, the best one would minimize the Hartree–Fock energy [70]. Inspired by this idea, a new strategy for improving the Clinton equations was proposed and applied to the analysis of theoretical structure factor data of LiH. A new alternative scheme was subsequently proposed by

Levy and Goldstein [71], who argued that if a single-Slater-determinant wavefunction could not be uniquely determined by the experimental data, the wavefunction should allow for the minimization of electron kinetic energy. Following this idea, Parr and his collaborators [72–74] designed methods to extract Kohn–Sham orbitals from the electron density data obtained from theoretical wavefunctions or quantum Monte-Carlo computations. These strategies have also been used to generate new DFT functionals.

1.1.6 Developments of Experimental Electron Wavefunction Models

In recent years, inspired by the Levy-constrained search method [75], Jayatilaka proposed a technique that is easier to implement than the Henderson and Zimmerman idea, called the X-ray constrained wavefunction (XCW) method [76–83], where an exact wavefunction can reproduce the experimental electron density distribution while also minimizing the total energy of a given material. By using the Lagrange multiplier method and minimizing a new summation function, this method can obtain a single-Slater-determinant wavefunction that minimizes energy while also fitting the experimental structure factor within the experimental error. This summation function is the sum of the single-Slater-determinant energy and the agreement factor between calculated and experimental diffraction data. Lagrange multipliers can also be used to adjust the weights of experimental diffraction data in computation minimization, and the iterative computation process can be performed by gradually increasing the Lagrange multiplier until the theoretical and experimental structure factors are in best agreement. In practice, the XCW technique can be usually combined with the HAR technique [84], namely, to alternately perform HAR and XCW refinement computations until the structure converges. The HAR technique mainly refines crystal structure parameters (i.e. atomic positions and temperature factors), while the XCW technique mainly refines electronic structure parameters (e.g. coefficients of a single-Slater-determinant molecular orbital wavefunction). Some refinement examples of amino acids and peptides have demonstrated that this new XCW approach can yield crystal structures and charge densities that are more consistent with experimental diffraction data than traditional multipole model refinement. Of note, Jayatilaka's XCW and other similar methods use the term "constrained," referring to minimizing the wavefunction energy under the constraints of the experimental scattering data (mainly X-ray diffraction data).

Jayatilaka's XCW method is likely the most promising among all the constrained methods developed so far. In addition to obtaining the experimental electron density distributions of practical relevance, the XCW method has certain advantages, namely, it can successfully obtain the physical and chemical properties of molecular crystals, such as dipole moments, polarizabilities, and refractive indices [85–87]. By contrast, because multielectron interactions are not considered, the electron density distribution obtained by multipole model refinement cannot be used to accurately determine the polarizability and refractive index of a molecule or crystal. In principle, XCW does not satisfy the sum-over-state (SOS) requirements for polarizability computations (involving excited states); however, with reasonable approximation, a ground-state wavefunction can suffice to estimate the polarizability of a molecule.

Moreover, XCW considers the chemical environment of a crystal; thus, it can be regarded as a realistic ground-state wavefunction, with good agreement between the refractive indices of certain molecular crystals computed using XCW and experimental measurements. Later, Cole et al. further exploited the Jayatilaka method and applied it to the research of certain nonlinear optical crystals [86, 88]. These studies showed that when the nature of the two-electron effect contribution had to be considered, the XCW method outperformed the multipole model refinement technique in capturing information on solid-state effects from experimental data when properties depending on two-electron terms were concerned. In addition, the XCW method was successfully applied to reveal the functional motifs [89] of nonlinear optical crystals by Jiang and Guo et al. For example, the B–O motif $[B_3O_5]-$ was experimentally confirmed as the NLO functional motif of LiB_3O_5 (LBO) by comparing the in-situ electron density and wavefunction of LBO in the dark versus under laser irradiation at 360 and 1064 nm, where an NLO functional motif served as the structural unit with a large micro-polarizability and was the main contributor to the macroscopic NLO properties of the crystal. This work was the first to experimentally confirm the functional motif of an NLO material [90].

Macchi et al. investigated the potential of the Jayatilaka method for obtaining information regarding the crystal field and electron correlation effects [91, 92]. Because the Jayatilaka method can be regarded as a modification of the Hamiltonian quantities for both effects, the obtained experimental electron wavefunctions contain information on both the crystal field and electron correlation effects. Bučinský et al. developed unrestricted open-shell and relativistic XCW [93–96], further extending the application system of the XCW method. This unrestricted open-shell approach can obtain experimental spin densities, corresponding to those obtained by multipole models and 1-RDM. Still, the relativistic XCW method paves the way for studies on the experimental electron wavefunctions of compounds containing heavy atoms, as heavy atoms are strongly affected by relativistic effects.

However, the chemical interpretation of the electron density distribution obtained by the Jayatilaka method is not sufficiently intuitive, as the molecular orbitals are completely delocalized. Jayatilaka et al. attempted to overcome this drawback, e.g. by directly extracting the ELF [97], the electron localization index [98, 99], and the Roby index [100] from the obtained XCW. The direct introduction of traditional, chemically intuitive interpretations to XCW methods has been an important research direction in recent years, with most of the advances in this area based on the concept of ELMO [101–107], i.e. dividing a molecule into many fragments according to predetermined rules or chemical intuition, and describing each fragment using an ELMO localized on the fragment in question. Therefore, by introducing this fragmentation into the XCW framework of Jayatilaka, X-ray-constrained ELMOs (XC-ELMOs) strictly correspond to atoms, chemical bonds, lone pairs of electrons, and functional groups can be obtained [108–111]. Hence, it is possible to obtain X-ray-constrained molecular orbitals corresponding to the traditional chemical intuition of chemists. This endows the XCW technique with an ability originally available only in the multipole model, namely, regarding the total electron density of a molecule or crystal as the sum of the contributions of the individual fragments. One could even argue that the ELMO concept is as important to XCW as the pseudo-atom concept to the multipole model. In fact, XC-ELMOs act as transferable units as multipole model pseudo-atoms, i.e. the XC-ELMO parameters of a molecular fragment refined in one molecule or crystal can be directly used to refine the electronic structures of the same molecular fragments in other molecules or crystals. Theoretical ELMO libraries have been developed [112–114] and applied to the development of multiscale quantum chemistry embedding techniques [115, 116], the rapid detection of noncovalent interactions in large systems [117], and the refinement of crystal structures of peptides and small proteins in the framework of HAR [118].

ELMOs have also been used to develop the so-called X-ray-constrained ELMO valence bond method (XR-ELMO-VB) [27, 119], which can be considered the first prototype of the multideterminant XCW technique. Based on X-ray diffraction data, this strategy can be used to determine the weights of resonant molecular structures, i.e. the system wavefunctions can be written in the form of linear combinations of multiple ELMOs with different resonance structures. This technique has been used to study the charge density of syn-1,6:8-13-bicarbonyl[14]annulene (BCA) under isostatic pressure, a compound whose aromaticity has been shown to be partially suppressed with increasing pressure [28]. XR-ELMO-VB computations have confirmed the trend that, at ambient pressure the two resonance structures of BCA are basically equivalent, at high pressure, one of the two becomes clearly predominant [27].

To extract useful chemical information from X-ray diffraction data, the more recent X-ray constrained spin-coupled method (XRSC) has been introduced, resulting from the coupling of the Jayatilaka method with the spin-coupled technique of the valence bond theory [120–124]. This method can be considered a step forward compared to the previous XR-ELMO-VB strategy. In fact, in this novel XRSC method, it is possible to extract both the orbitals and resonance structure weights from the X-ray diffraction data without requiring any localization schemes or *a priori* wavefunctions. Several computations have shown that the spin-coupled orbital and resonance structure weights obtained by the XRSC method present a non-negligible difference compared to those obtained through conventional gas-phase spin-coupled computations. This has further demonstrated the intrinsic capability of the Jayatilaka method in accounting for the crystal field effects on electronic structures.

1.1.7 Developments in Electron Diffraction-Based Studies of Electronic Structures

In addition to X-ray and neutron scattering, the use of electron diffraction techniques to explore the experimental electronic structure of materials has long attracted the attention of researchers. The convergent-beam electron diffraction method (CBED) [125] converges electron beams with a certain cone angle into a small, unbent region with a uniform thickness on the sample. In addition to the usual diffraction spots, diffraction disks are produced, with an integrated diffraction intensity comparable to the theoretical values computed from the electron diffraction dynamics. Therefore, diffraction disks can be used to directly and accurately determine the low-index structure factor, and this advantage allows them to be used in reconstructing the electron density of certain simple inorganic substances, allowing CBED to outperform X-ray diffraction in terms of determining the crystal systems and space groups of materials [126]. Nakashima showed that the charge density distribution of metallic Al extracted by the quantitative CBED method was more reliable than theoretical or X-ray diffraction results, and matched well with the experimental results of the anisotropic elasticity coefficients of Al [127]. Zuo et al. studied the electron density information of Cu—Cu bonds in Cu_2O and interpreted the deformation density around Cu as an electron shift from Cu-3d to Cu-4s orbitals [128]. In addition, Palatinus et al. used precession electron diffraction tomography to determine the exact position of H atoms in nanocrystals [129]. These studies demonstrated the potential of the CBED method for studying the experimental electronic structures of materials.

1.2 Basic Descriptors of Electronic Structure

1.2.1 Electron Density

In quantum chemistry, electron density is a function of the wavefunction. For a molecular system containing M atoms and N electrons, the ground-state electron wavefunction ψ_{el} is considered a function of the electron spin and spatial coordinates ($\boldsymbol{t}_i = (\boldsymbol{s}_i, \boldsymbol{r}_i)$; $i = 1, 2, \cdots, N$). Under the Born–Oppenheimer approximation, when the spatial coordinates of nucleuses ($\boldsymbol{R}_k$; $k = 1, 2, \cdots, M$) are fixed and the influence of other electrons is not considered, the probability of finding an electron in the volume element d$\boldsymbol{r}$ at any location $\boldsymbol{r}$, $\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r}$ can be written as

$$\rho(\boldsymbol{r})\mathrm{d}\boldsymbol{r} = N \int |\psi_{\mathrm{el}}|^2 \, \mathrm{d}\boldsymbol{t}'\mathrm{d}\boldsymbol{r}, \tag{1.1}$$

where d$\boldsymbol{t}'$ denotes the integration over the spin and spatial coordinates of all but one electron, $\rho(\boldsymbol{r})$ is the density of electrons in the position space or electron density (electron density), and the total charge density is the sum of the charge densities of electrons and nuclei in the position space. When addressing electron density distribution, the term "charge density" can be used interchangeably with the term "electron density," as is the case in this book.

In crystallography, the electron density is closely related to the structure factor. X-ray diffraction is a phenomenon of electron–photon interactions, and in principle, it cannot be understood well without knowledge of quantum mechanics. However, some reasonable simplifications are often made in practical applications. In kinematical theory, the amplitude of coherent elastic scattering (diffraction), i.e. the structure factor $F(\boldsymbol{H})$, is the Fourier transform of the unit cell electron density $\rho(\boldsymbol{r})$. Thus, $\rho(\boldsymbol{r})$ can be obtained by the inverse Fourier transformation of $F(\boldsymbol{H})$:

$$\rho(\boldsymbol{r}) = \int F(\boldsymbol{H}) \exp(-2\pi \boldsymbol{i}\boldsymbol{H} \cdot \boldsymbol{r})\mathrm{d}\boldsymbol{H}, \tag{1.2}$$

where $F(\boldsymbol{H})$ is the complex structure factor, which has been corrected for anomalous scattering. In addition, the scattering vector $\boldsymbol{H} = h\boldsymbol{a}_1^* + k\boldsymbol{a}_2^* + l\boldsymbol{a}_3^*$ corresponds to certain discrete lattice points in the reciprocal space, where h, k, l is an integer and $\boldsymbol{a}^*_{i,i=1,3}\left(\boldsymbol{a}_i\boldsymbol{a}^*_j = \delta_{ij}\right)$ is the reciprocal lattice basis vector.

Because $F(\boldsymbol{H})$ can be defined over the discrete $\boldsymbol{H}$, the integral Eq. (1.2) can be converted into summation form:

$$\rho(\boldsymbol{r}) = V^* \sum_{\boldsymbol{H}} F(\boldsymbol{H}) \exp(-2\pi \boldsymbol{i}\boldsymbol{H} \cdot \boldsymbol{r}), \tag{1.3}$$

where V^* is the unit cell volume of the reciprocal lattice, i.e. $1/V$, where V is the unit cell volume in real space.

Because electron density is a real function, the right-hand side of Eq. (1.3) must also be real, and $F(\boldsymbol{H})$ can now be written in complex form:

$$F(\boldsymbol{H}) = |F(\boldsymbol{H})| \exp i\,\varphi(\boldsymbol{H}) \equiv A(\boldsymbol{H}) + iB(\boldsymbol{H}), \tag{1.4}$$

$$A(\boldsymbol{H}) = |F(\boldsymbol{H})| \cos\varphi; B(\boldsymbol{H}) = |F(\boldsymbol{H})| \sin\varphi, \tag{1.5}$$

where $\varphi(\boldsymbol{H})$ is the phase of the structure factor. After substituting Eq. (1.4) into Eq. (1.3), the expression can be reorganized to remove the imaginary part. Moreover, the $F(\boldsymbol{H})$ and $F(-\boldsymbol{H})$ contributions can be summed up by using relationships $A(\boldsymbol{H}) = A(-\boldsymbol{H})$ and $B(\boldsymbol{H}) = -B(-\boldsymbol{H})$, as suggested in Eq. (1.5). Thus, the unit cell electron density can be written as

$$\rho(\boldsymbol{r}) = \frac{2}{V} \sum_{1/2} \{A(\boldsymbol{H}) \cos(2\pi\boldsymbol{H} \cdot \boldsymbol{r}) + B(\boldsymbol{H}) \sin(2\pi\boldsymbol{H} \cdot \boldsymbol{r})\}, \tag{1.6}$$

or

$$\rho(\boldsymbol{r}) = \frac{2}{V} \sum_{1/2} [|F(\boldsymbol{H})| \cos\{2\pi\boldsymbol{H} \cdot \boldsymbol{r} - \varphi(\boldsymbol{H})\}]. \tag{1.7}$$

Thus, each structure factor contributes a plane wave with wave vector $\boldsymbol{H}$ and phase angle φ to the total electron density.

1.2.2 Residual Density

The density difference $\Delta\rho(\boldsymbol{r})$ between the total electron density $\rho(\boldsymbol{r})$ and reference density $\rho_{\mathrm{ref}}(\boldsymbol{r})$ reflects the degree of adequacy of the reference density to describe the system. Thus, ΔF can be defined as the difference between the observed value of the structure factor $F_{\mathrm{obs}}(\boldsymbol{H})$ and the computed value $F_{\mathrm{calc}}(\boldsymbol{H})$, i.e.

$$\Delta F = F_{\mathrm{obs}}(\boldsymbol{H})/k - F_{\mathrm{calc}}(\boldsymbol{H}), \tag{1.8}$$

where k is a scale factor. Because $F_{\mathrm{obs}}(\boldsymbol{H})$ and $F_{\mathrm{calc}}(\boldsymbol{H})$ are complex numbers, ΔF is considered a vector in the complex plane. In addition, $\Delta\rho(r)$ can be obtained by the Fourier transformation of ΔF:

$$\Delta\rho(\boldsymbol{r}) = \rho_{\mathrm{obs}}(\boldsymbol{r}) - \rho_{\mathrm{calc}}(\boldsymbol{r}) = \frac{1}{V} \sum_{\boldsymbol{H}} \Delta F \exp(-2\pi i\boldsymbol{H} \cdot \boldsymbol{r}). \tag{1.9}$$

Similar to Eq. (1.9), the density difference $\Delta\rho(\boldsymbol{r})$ can be written as:

$$\Delta\rho(\boldsymbol{r}) = \frac{2}{V} \left\{ \sum_{1/2} (A_{\mathrm{obs}} - A_{\mathrm{calc}}) \cos 2\pi H \cdot r + \sum_{1/2} (B_{\mathrm{obs}} - B_{\mathrm{calc}}) \sin 2\pi\boldsymbol{H} \cdot \boldsymbol{r} \right\}. \tag{1.10}$$

If the structure model used to calculate F_{calc} is obtained by the least-squares refinement of the observed structural factor, and if the phase angle of F_{calc} is specified, the density map obtained from Eqs. (1.9) and (1.10) can be referred to as the residual density map (RDM). In structural analysis, residual density is a very useful tool from which the least-squares refinement process and the soundness of the structure model can be evaluated.

$F(\tau)$ can be defined as the Fourier transform of $f(t)$. In the discussion below, Parseval's theorem is given by:

$$\int_{-\infty}^{\infty} |f(t)|^2 \, \mathrm{d}t = \int_{-\infty}^{\infty} |F(\tau)|^2 \, \mathrm{d}\tau. \tag{1.11}$$

Because $\Delta\rho$ is the Fourier transform of ΔF, Eq. (1.11) indicates that minimizing $\int (\rho_{\mathrm{obs}} - \rho_{\mathrm{calc}})^2 \, \mathrm{d}\boldsymbol{r}$ is equivalent to minimizing $\int (F_{\mathrm{obs}} - F_{\mathrm{calc}})^2 \, \mathrm{d}\boldsymbol{H}$; thus, minimization of the structure factor will also lead to the minimization of residual density. When only some of the values of $f(t)$ are known, Eq. (1.11) still holds. In diffraction experiments, only structure factors no more than $\boldsymbol{H}_{\max}$ will be experimentally available due to the limited structural resolution.

The Patterson function $D(\boldsymbol{u})$ can be defined as the autocorrelation of $\Delta\rho$:

$$\begin{aligned} D(\boldsymbol{u}) &\equiv \int \Delta\rho(\boldsymbol{r})\Delta\rho(\boldsymbol{r} - \boldsymbol{u})\mathrm{d}\boldsymbol{r} = \Delta\rho(\boldsymbol{r}) * \Delta\rho(-\boldsymbol{r}) \\ &= \frac{1}{V}\sum_{\boldsymbol{H}} \Delta\boldsymbol{F}(\boldsymbol{H}) \cdot \Delta\boldsymbol{F}(-\boldsymbol{H}) \exp(-2\pi\boldsymbol{H} \cdot \boldsymbol{u}) \\ &= \frac{2}{V}\sum_{1/2} (\Delta F)^2 \cos 2\pi\boldsymbol{H} \cdot \boldsymbol{u} \end{aligned} \tag{1.12}$$

The first line of the above equation follows the relationship between autocorrelation and convolution (* denotes convolution), while the second line uses the convolution theorem of Fourier transform, i.e. the Fourier transform of the convolution of two functions is equal to the product of the Fourier transforms of the individual functions. Moreover, the third line does not contain the imaginary part, because $\Delta\rho$ is a real number. At $\boldsymbol{u} = 0$, Eq. (1.12) becomes:

$$D(0) = \frac{2}{V}\sum_{1/2} (\Delta F)^2 = \int \Delta\rho(\boldsymbol{r})^2 \mathrm{d}\boldsymbol{r}. \tag{1.13}$$

In fact, minimization computation in the position space (or direct space) is not strictly equivalent to the reciprocal space, because during minimization, additional weight factors are added to each structure factor in the reciprocal space to participate in the computation, as is the case for electron density in the position space.

1.2.3 Deformation Density

The deformation density is defined as the difference between the total electron density and the electron density computed by the reference model. As is the case of computing the residual density according to Eq. (1.9), the deformation density can also be obtained through Fourier transformation, except F_{calc} is computed from the reference model and compared to the experimental electron density.

A commonly used reference density, also known as the promolecule density, is the superposition of spherically averaged atomic charge densities, which are each centered on the coordinates of the corresponding nucleus, where a promolecule represents a collection of independent atoms without the existence of interatomic interactions in a real crystal, only forming a hypothetical entity. However, electrostatic interactions will occur between the atoms in a promolecule, and a promolecule will be stable if interatomic interactions other than electrostatic interactions are absent. The deformation density computed by using the promolecule density as a reference density is the commonly used (standard) deformation density, i.e. the difference between the total density $\rho(\boldsymbol{r})$ and total density $\rho_{\mathrm{pro}}(\boldsymbol{r})$ of the spherical ground-state atoms at the $\boldsymbol{R}_i$ position:

$$\Delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho_{pro}(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \sum_{\mathrm{all}} \rho(\boldsymbol{R}_i). \tag{1.14}$$

Deformation density can be used to determine whether a covalent bond has formed. The presence of charge aggregation (bond charge maximum) between two adjacent atoms is an indicator of two atoms forming a covalent bond, but not vice versa, i.e. the absence of a bond charge maximum between the two atoms does not necessarily indicate the absence of bond formation. This is because atoms in promolecules are neutral and for an element with both half-filled and fully filled orbitals, the number of electrons in a half-filled orbital (where there is only one electron) is mistakenly subtracted by more than 1. For example, when subtracting the electron density of a spherical O atom with electron configuration $(1s)^2$ $(2s)^2$ $(2p)^4$ from an O atom in an actual crystal, each valence orbital will be subjected to subtraction of 1.333 electrons, resulting in a lack of bonding charge when the extra 0.333 electrons exceed the bonding charge. This explains why the O—O bond in hydrogen peroxide has a lack of bond charge. Sometimes some other reference states, such as an oriented atomic state and a molecular fragment state, must be used to gain insight into the formation of chemical bonds.

Deformation density can be obtained by different experimental methods. The first method involves a combination of X-ray diffraction and neutron diffraction techniques. In this method, the exact atomic coordinates and temperature factors required to compute the reference-state density can be obtained by neutron diffraction, followed by difference Fourier transformation to derive the deformation density. However, this method involves both X-ray diffraction data and neutron diffraction data, and the experimental conditions are not the same for both sets of data, thus causing large systematic errors. The second method uses the same set of X-ray diffraction data. Because valence-electron scattering mainly occurs in the low-angle region (also known as the low-order region or low-resolution region) [130] and that high-angle (i.e. high-order or high-resolution) diffraction data are mainly contributed by core-electron scattering, it is possible to obtain exact atomic coordinates and temperature factors by refining the high-angle diffraction data, and then deriving the deformation density by performing difference Fourier transformation of the full-resolution structure factor:

$$\rho_{\mathrm{deformation}}(\boldsymbol{r}) = \frac{1}{V} \sum_{\boldsymbol{H}} (F_{\mathrm{obs}} - F_{\mathrm{calc,high\ order}}) \exp(-2\pi i \boldsymbol{H} \cdot \boldsymbol{r}). \tag{1.15}$$

The distinction between high- and low-angle scattering is compound-specific, and it is difficult to obtain the widely accepted criterion. It is generally recommended that the cut-off scattering angle satisfy the conditions of $\sin\theta/\lambda = 0.5$ Å^{-1} or $\lambda/2\sin\theta = 1.0$ Å.

In electron density analysis, dynamic model deformation density (DMDD) and static model deformation density (SMDD) are also commonly used, where the term dynamic means that the effect of atomic thermal vibrations is accounted for, while the term static means that the effect of atomic thermal vibrations is not considered.

DMDD can be defined as:

$$\Delta\rho_{\text{model}}(\boldsymbol{r}) = \rho_{\text{model}}(\boldsymbol{r}) - \rho_{\text{reference}}(\boldsymbol{r}), \tag{1.16}$$

where the total model density is given by:

$$\rho_{\text{model}}(\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{H}} F_{\text{calc,model}}(\boldsymbol{H}) \exp(-2\pi i\boldsymbol{H}\cdot\boldsymbol{r}), \tag{1.17}$$

where the model-calculated structure factor $F_{\text{calc,model}}$ takes into account the effect of atomic thermal vibrations.

SMDD generally refers to the deformation density of a multipole model and can be expressed as:

$$\begin{aligned}\Delta\rho_{\text{model}}(\boldsymbol{r}) = \sum_{i}^{\text{all atoms}} & \Big\{P_{i,c}\rho_{\text{core}}(r) + P_{i,v}\kappa^{3}\rho_{\text{valence}}(\kappa_i\boldsymbol{r}) \\ & + \sum_{l=0}^{l_{\max}} \kappa'^{3}_{i} R_{i,l}\left(\kappa'_i r\right) \sum_{m=0}^{l} P_{i,lm\pm} d_{lm\pm}(\boldsymbol{r}/r)\Big\} - \rho_{\text{reference}}(\boldsymbol{r})\end{aligned} \tag{1.18}$$

Please refer to Chapter 5 for additional details regarding the multipole model. Because the structure model acts as a noise filter during the refinement process, the bond charge maximum will be higher in the SMDD map than in the DMDD map.

The true phase of a structure factor generally differs from one computed by an independent-atom model, and the difference will introduce errors into the computation of deformation density. The phase of structure factor is fixed at 0 or π in centrosymmetric structures, whereas in non-centrosymmetric structures, only the phases of certain diffraction spots formed by centrosymmetric projection are fixed, such as the *hk*0, *h*0*l,* and 0*kl* diffraction spots in the $P2_12_12_1$ space group.

1.2.4 Electron Wavefunction and Density Matrix

In the method of linear combination of atomic orbitals (LCAO), a molecular orbital χ_i can be described as a linear combination of atomic basis functions ϕ_μ:

$$\chi_i = \sum_{\mu} C_{i\mu}\phi_{\mu}. \tag{1.19}$$

To satisfy the Pauli exclusion principle, the many-electron wavefunction must be antisymmetric with respect to the permutation of electrons. This wavefunction can be written in the form of a Slater determinant, i.e. antisymmetric combinations of occupied molecular orbitals. In the Hartree–Fock method, a wavefunction contains only a single-Slater determinant, and each electron is assumed to be influenced by the average potential field of the other electrons.

For an n-electron system, the single-determinant wavefunction can be written by:

$$\psi = (n!)^{-1/2} \begin{vmatrix} \chi_1(1) & \cdots & \chi_n(1) \\ \vdots & & \vdots \\ \chi_1(n) & \cdots & \chi_n(n) \end{vmatrix}, \tag{1.20}$$

where the number i in parenthesis denotes the i-th electron ($i = 1, 2 \ldots n$), and the coefficient $(n!)^{-1/2}$ in front of the determinant is a normalization factor. The single-determinant wavefunction can often be abbreviated in the following form:

$$\psi = |\chi_1(1)\chi_2(2)\cdots\chi_n(n)\rangle. \tag{1.21}$$

According to the rule of determinant computation, Eq. (1.20) can be expanded:

$$\psi = \sum_i \sum_{j\geqslant i} \widehat{P}_{ij}(\chi_1(1)\chi_2(2)\cdots\chi_n(n)), \tag{1.22}$$

where $\widehat{P}_{ij}$ is an electron permutation operator that permutates $\chi_1, \chi_2, \cdots, \chi_n$, whose eigenvalues -1 and $+1$ denote an odd and even number of electron permutations, respectively. The permutation of the two rows (or columns) in the Slater determinant changes the sign of the wavefunction, where the determinant value is zero when any two rows (or columns) are identical. Thus, the Slater determinant wavefunction obeys the fermionic Pauli exclusion principle.

Because the n-electron wavefunction is a function of $3n$ spatial coordinates and n spin variables, the single-electron density $\rho(\boldsymbol{r})$ can be obtained by integrating over the spatial coordinates and spin variables of all but one of the electrons:

$$\rho(\boldsymbol{r}) = \int |\Psi|^2 \, (\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_n, s_1, s_2, \ldots, s_n)\mathrm{d}\boldsymbol{r}_2 \cdots \mathrm{d}\boldsymbol{r}_n \mathrm{d}s_1 \cdots \mathrm{d}s_n. \tag{1.23}$$

Since electrons are indistinguishable and molecular orbitals are orthogonal, the overlap integral of two molecular orbitals is 0, which allows $\rho(\boldsymbol{r})$ to be simplified:

$$\rho(\boldsymbol{r}) = \sum_i n_i \chi_i^2. \tag{1.24}$$

If χ_i is a spin-orbital that contains both space and spin components, then $n_i = 1$. If χ_i is a spatial orbital, spin is not considered; thus, $n_i = 2$.

To obtain the electron density of atomic orbitals, Eq. (1.19) can be substituted into Eq. (1.24) to obtain:

$$\rho(\boldsymbol{r}) = \sum_\mu \sum_v P_{\mu v} \phi_\mu(\boldsymbol{r}) \phi_v(\boldsymbol{r}), \tag{1.25}$$

where $\boldsymbol{P}$ is the density matrix, and the matrix element $P_{\mu v}$ is the population of the orbital product $\phi_\mu(\boldsymbol{r})\phi_v(\boldsymbol{r})$, i.e.

$$P_{\mu v} = \sum_i n_i C_{i\mu} C_{iv}. \tag{1.26}$$

The wavefunction ψ contains all of information regarding the joint probability density of electrons. For example, the two-electron density can be obtained by integrating all of the other spatial and spin variables, except for the two-electron spatial coordinates, to describe the joint probability of simultaneously finding electron 1 at $\boldsymbol{r}_1$ and electron 2 at $\boldsymbol{r}_2$.

A single-Slater determinant obeys the Pauli exclusion principle by considering the correlation between parallel-spin electrons, but ignores the correlation between opposite-spin electrons. Computations based on a single-Slater determinant will show that the probability of simultaneously finding two opposite-spin electrons at the same position is not zero, which is practically impossible.

More advanced methods than the Hartree–Fock method include excited-state determinants in the wavefunctions. If the occupied orbitals are denoted by a, b, c while denoting the empty orbitals by r, s, t, a single excited configuration generated by the promotion of an electron from a to r can be expressed by:

$$\left|\psi_a^r\right\rangle = |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_n\rangle. \tag{1.27}$$

A multi-configuration wavefunction can be expressed by:

$$|\psi\ \rangle = c_0|\psi_0\ \rangle + \sum_{ra} c_a^r\left|\psi_a^r\right\rangle + \sum_{\substack{a<b\\ r<s}} c_{ab}^{rs}\left|\psi_{ab}^{rs}\right\rangle + \cdots. \tag{1.28}$$

For a multi-Slater determinant wavefunction, molecular orbitals can be defined similarly to Eqs. (1.24) and (1.25), and these molecular orbitals are known as natural spin orbitals, where n_i is no longer necessarily an integer, but can be a fractional number between 0 and 1. Accordingly, Eq. (1.25) contains both one-center and two-center terms, with the same nucleus position for ϕ_μ and ϕ_ν in the one-center term and different nucleus positions for ϕ_μ and ϕ_ν in the two-center term. The two-center term represents the bond charge density, with observable values only when ϕ_μ and ϕ_ν are in the same spatial region, which can be neglected for distantly separated atoms.

1.3 Experimental Characterization of Electronic Structure

Scattering data generated by a variety of instruments or large-scale scientific facilities can be used for the refinement of experimental electronic structures. Typical examples of these datasets include X-ray diffraction data, polarized neutron diffraction data, and X-ray Compton scattering data, which are generated and collected by X-ray single-crystal diffractometers (in a laboratory setting), synchrotron X-ray single-crystal diffractometers, or neutron single-crystal diffractometers. Among these instruments, synchrotron and neutron sources are expensive and time-consuming. The most readily available instruments are small laboratory X-ray single-crystal diffractometers; however, X-ray single-crystal diffractometers used for experimental electronic structure measurement have more rigorous requirements for some technical specifications compared to instruments used for conventional crystal structure measurements, such as the technical specifications of the intensity and wavelength of X-ray light sources. Specifically, for in-situ electron structure measurements under an external field, the diffractometer host requires some additional external devices, such as laser and cryogenic systems.

Electron structure refinement requires near-perfect diffraction data, where changes by a few thousandths of diffraction intensity can have a significant impact on the shape of the refined electron cloud. To obtain high-precision diffraction data, it is necessary to strictly control the crystal quality, instrument accuracy (mainly depending on X-ray source quality, goniometer accuracy, and detector sensitivity), and data correction.

1.3.1 Experimental Electronic Structure Measurement with X-ray Single-crystal Diffractometer

1.3.1.1 X-ray Source

The fourth-generation synchrotron radiation source and rotating X-ray anodes are cutting-edge X-ray light sources used in large-scale scientific facilities and laboratories, respectively. Significant advances have been achieved in X-ray free-electron lasers at synchrotron radiation facilities; however, more in-depth research is needed to explore whether this technology can benefit experimental electron density studies. For laboratory X-ray sources, an important advancement is the use of microfocus X-ray spots, which allows for the generation of X-rays with higher optical density, but with a lower uniformity of spot intensity distribution compared to conventional (non-microfocus) sources.

Refinement of high-precision electronic structures requires X-ray single-crystal diffraction data with high structural resolution ($\lambda/2\sin\theta < 0.4$ Å). According to the Bragg law $d_{hkl} = \lambda/2\sin\theta$, structural resolution can be improved by using a short-wavelength ($\lambda = 0.71073$ Å) Mo-target X-ray source and collecting high-angle diffraction spots with sufficient intensity. Because X-ray diffraction intensity decays sharply with increasing diffraction angle, the high-angle diffraction spot intensity can be increased by increasing the exposure time, using a high-power X-ray generator and high-performance 2D detector, as well as using X-ray focusing and enhancing techniques.

Highly-precision diffraction data place high demands on the monochromaticity, uniformity, and high intensity of the X-ray source. Compared to synchrotron radiation, the X-rays from the Mo target of a laboratory X-ray single-crystal diffractometer is a mixture of $K_{\alpha1}$ (0.7093 Å), $K_{\alpha2}$ (0.71359 Å), and K_{β} (0.632288 Å) lines, which degrades the monochromaticity. When improving the monochromaticity, a monochromator can be used to filter out the K_{β} line and even the $K_{\alpha2}$ line, leaving only the most intense line –the $K_{\alpha1}$ line. However, this will greatly reduce the intensity of the X-ray to be used. Because a Mo-target X-ray source is a multiwavelength source, a diffraction spot will split into several at different locations, making it difficult to locate the diffraction spots and integrate the intensity, especially at high angles. However, this problem can be overcome by improving the integration algorithm.

Alternatively, a microfocus light source can be used to increase the X-ray intensity, but the intensity of the microfocus light source in the radial direction (i.e.

in the cross-section perpendicular to the direction of X-ray incidence) will follow a Gaussian distribution instead of a constant profile; thus, the uniformity will not be satisfactory. By nature, using a microfocus light source involves sacrificing monochromaticity and uniformity in favor of high intensity, which is necessary for collecting high-angle diffraction data from crystals, because such data are usually weak. High data intensity due to a microfocus light source can greatly reduce the diffraction data collection time and allow for the measurement of samples with relatively weak diffraction ability.

1.3.1.2 Goniometer

Based on the Bragg equation ($d_{hkl} = \lambda/2\sin\theta$), when using the Mo-target X-ray with $\lambda = 0.71073$ Å to achieve the structural resolution required for high-precision electronic structure refinement ($\lambda/2\sin\theta < 0.4 =$ Å), the diffraction angle 2θ should reach 125°, which is much higher than the diffraction angle of 50.7° required for conventional measurement of crystal structures (typically requiring a structural resolution of 0.83 Å). Therefore, the X-ray source, goniometer, detector, beamstop, and camera components must be mounted in a compact manner to ensure that the detector can be turned relatively close to this angle without component collisions.

The accuracy of the goniometer is also an important factor to consider, especially for microfocus X-ray sources. If the goniometer is not sufficiently accurate, the crystal will be more or less off-center during crystal measurement, resulting in a negative impact on the intensity and absorption correction of the diffraction data. Although this effect can be mitigated to some extent through complex absorption corrections, a high-precision goniometer is still desirable, as it can produce high-quality diffraction data. In general, the accuracy of goniometers decreases with use due to mechanical wear.

1.3.1.3 X-ray Detector

It is important to accurately measure the intensity of the Bragg peak, and unlike earlier point detectors, where only one diffraction spot could be measured at a time, a 2D digital detector can quickly collect diffraction photographs of the entire reciprocal space. A significant advantage of 2D detectors is that they can obtain high-redundancy data, which greatly improves statistical accuracy; however, this requires more corrections for absorption, attenuation, source instability, and dispersion.

Two important parameters of 2D detectors are the dynamic range of the readings and the reading time. The exposure time of a single photograph during diffraction data collection for electronic structure refinement is generally long, and it may be very long for generating some particularly strong diffraction spots, suggesting that the dynamic range of the detector's individual pixels should be wide. Otherwise, the intensity of the diffraction spots on these pixels may exceed their thresholds; thus, accurate measurement will be difficult.

1.3.1.4 Cryogenic Systems

Low temperatures are important for obtaining high-quality electron density distributions for two main reasons: (i) atomic vibrations reduce the scattering intensity, whereas low temperatures allow atoms to vibrate as close to the equilibrium position as possible, and (ii) with large thermal vibration factors, it is difficult to separate the electron density parameters from the thermal vibration parameters during refinement. However, exactly how low a temperature is needed for accurate electron density analysis is difficult to define, depending on the material under study. In general, the lower the temperature, the better the result. However, even when collecting data at 0 K, it is still impossible to completely avoid thermal vibrations of atoms because of the presence of zero-point vibrations. Modern cryogenic techniques in laboratories are sophisticated, including measurement at temperatures near the boiling point of liquid nitrogen, which generally generates stable and reliable data, and measurement at temperatures near the boiling point of liquid helium, which represents a more advanced technique.

Low temperatures play multiple roles in experimental electron density analysis. (i) Most importantly, low temperatures allow us to reduce the thermal motion of atoms, making the pseudo-atom approach a reasonable assumption in structural refinement, where the smaller the thermal vibrational factor, the smaller the correlation coefficients between the parameters, and the more reliable the refinement results. (ii) In addition, a smaller thermal vibrational factor makes the simple harmonic vibrational model of atoms more effective. Of note, although higher-order models of atomic vibrations, such as the Gram-Charlier expansion, can be used, this introduces too many parameters. Mallinson et al. showed that peak intensity distribution of residual map of non-harmonic vibrations was somewhat similar to that of deformation charges, making it difficult to identify true electron-density features [131]. Therefore, the physical significance of the Gram-Charlier parameter must be verified when approximating the refined temperature factor by high-order nonharmonics. Another advantage of low temperatures is the high accuracy of the diffraction intensity that can be obtained, especially for high-angle diffraction spots. Although the refinement of bond-charge density features generally does not require high-angle data (since high-angle diffraction spots are mainly a result of the scattering from core electrons), high-angle, high-intensity diffraction data are important for the refinement accuracy, especially when refining atomic positions and thermal vibration factors (except for H atoms). Moreover, low temperatures can significantly reduce the dispersion of high-angle diffraction spots; thus, allowing for high-precision intensity integration.

1.3.2 Key Aspects of Experimental Electronic Structure Measurement

1.3.2.1 Single-crystal Samples

Nearly defect-free single-crystal samples with high quality are crucial for obtaining high-quality diffraction data, as high-precision analysis of experimental electronic structure data is generally difficult when atomic disorder exists in the crystal structure. In practice, a single-crystal sample to be measured should not be too large, in most cases (e.g. mean size of less than 0.3 or 0.5 mm), otherwise, the sample may have strong X-ray absorption, degrading the accuracy of diffraction data. However, the sample should not be too small, such as mean size of less than

0.1 mm; otherwise, the diffraction intensity will be significantly reduced, and a longer exposure time will be required to obtain the diffraction data with a high signal-to-noise ratio. In general, to increase the intensity noise (S/N) ratio by a factor of n for the same sample using a single photograph, the exposure time of the photograph must be increased by a factor of n^2. Of note, an infinitely long exposure time will not lead to an indefinitely large S/N ratio, as there is an inherent limit to the S/N ratio achieved by the instrument. Meanwhile, an appropriate sample size will also depend on the diffracting power of the sample, the X-ray spot size, the light source intensity, and the acceptable duration of data collection.

1.3.2.2 Measurement Process

Diffraction data collection requires that the crystal sample be relatively stable and not shifted during goniometer rotation. Collecting a set of electron structure diffraction data by a laboratory light source typically takes a long time, ranging from 3–5 days to 1–2 weeks. Ensuring that the crystal position does not shift during such a long test time is not easy, especially under low-temperature gas purging, as it usually requires that the crystal carrier is in good condition and that the glass filament (or other materials such as metal rods) and glue used to adhere the crystal are strong.

Collecting a large number of diffraction photographs and achieving a data/parameter ratio above 10 are desirable; however, the data/parameter ratio will be much lower than 10 in many practical circumstances. Inter-parameter correlations during electronic structure refinement can be well reduced if a sufficient number of high-angle diffractions are available.

1.3.2.3 Data Correction

Raw diffraction data collected on a single-crystal diffractometer should be carefully corrected for various errors before subsequent electronic structure refinement. The main sources of diffraction intensity errors include the intensity instability of the X-ray source, the non-monochromaticity and non-uniformity of the X-ray source, the spherical aberration of the goniometer, the X-ray absorption by the crystal sample, and the irregularities of the crystal shape. Therefore, a suitable error model is required to correct the raw diffraction data.

The X-ray absorption coefficients are generally large for crystals containing heavier atoms, and the diffraction data usually need to be corrected for absorption before they can be used for electronic structure refinement. When using a microfocus light source, the X-ray intensity will have a distorted Gaussian distribution in the radial direction of the light, causing far greater X-ray absorption near the center of the crystal than at the crystal edge when the X-rays pass through the crystal; thus, the distorted Gaussian distribution should be taken into account when correcting for absorption.

Multiple scattering is less likely to occur in single-crystal diffraction experiments; however, because the volume of diffraction data required for electronic structure refinement is generally large, multiple scattering can significantly alter the intensity of a few diffraction spots. However, it should be mentioned that this effect cannot be eliminated through scale factor correction and absorption correction. The intensity and error of diffraction data should satisfy the requirements for general electronic structure refinement, which were indicated by a number of statistical metrics such as consistency factors R_{int} and R_{sigma} around 0.03 in the full resolution range, χ^2 around 1, $I/\text{sig}(I) \sim \log10(I)$ curves in a sinusoidal pattern [132], and the normalized scale factors within ±0.3 around 1.

1.3.2.4 Examination of the Quality of Electronic Structure Refinement

Electron structure refinement includes electron density refinement, density matrix refinement, and wave function refinement. Compared to the conventional crystal structure model, the number of refinement parameters in the electronic structure model is generally higher; thus, some statistical indicators have to be examined after the least-squares refinement to determine whether the refinement results are reliable. The statistical metrics for the multipole model refinement should normally have the following features: symmetric DRK plots with their central parts passing through the origin, mirror-symmetric plots of fractal dimensions of residual electron density, and errors within ±0.05 for the curve of $F_{\text{obs}}/F_{\text{calc}}$ versus the structure resolution.

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