Order Parameters of Quantum Materials and Electron Microscopy

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（量子材料序参量和电子显微学）

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Preface

Quantum materials represent a forefront topic in condensed matter physics, where their diverse phases and properties are intimately linked to multiple order parameters—including lattice, charge, spin, orbital, and topological degrees of freedom. Modern advanced electron microscopy has not only achieved sub-Ångström resolution but has also pioneered new methodologies for probing these order parameters. Furthermore, the ability to focus electron beams to nanometer scales, combined with energy resolution improvements to ~1 eV, enables techniques such as electron energy-loss spectroscopy (EELS), X-ray energy-dispersive spectroscopy (XEDS), and phonon spectroscopy. These methods provide critical insights into bonding, valence states, crystal fields, orbitals, and atomic positions within materials, offering a powerful toolkit for investigating order parameters and their correlation mechanisms in quantum materials.

Over the past 40 years, electron microscopy in China has advanced rapidly. My own journey into quantum materials and advanced electron microscopy spans the last decade. I am delighted that my creative young students and I have navigated the world of quantum material order parameters through the lens of electron microscopy.

This book aims to synthesize electron microscopy methods developed by Chinese electron microscopists for measuring and correlating order parameters in quantum materials. It also summarizes key findings from our studies on order parameters in ferrous materials, magneto-optical materials, high-temperature superconductors, and related systems.

I extend profound gratitude to the leadership and colleagues at Tsinghua University and the Beijing Iron and Steel Research Institute (BISRI). BISRI welcomed me with open arms, introduced me to electron microscopy—which became my lifelong pursuit—and guided me in applying it to advanced materials research aligned with national priorities.

Tsinghua University provided a high-level, interdisciplinary environment that enabled me to rapidly establish a new research frontier: probing quantum material order parameters via electron microscopy. I am also deeply indebted to Prof. J. M. Cowley at Arizona State University. During my visit to the Center for Solid State Science, he mentored me in the then-emerging fields of high-resolution

electron microscopy and high-spatial-resolution analytical electron microscopy. To my esteemed teacher: I have passed on the foundational knowledge you gave me to my students. This legacy has flourished on Chinese soil, yielding fruitful academic achievements.

I thank our era for its opportunities. The Beijing National Center for Electron Microscopy, nurtured in fertile soil and sustained by abundant resources, thrives through the dedication of exceptional talents.

I dedicate this book to my motherland and her people, who raised and shaped me.

Beijing, China Jing Zhu

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Order Parameters of Quantum Materials

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Abstract For quantum materials, the lattice, charge, spin, orbit, and topology order parameters are fundamentally correlated to enable the quantum materials to exhibit exotic and rich physics properties. The basic concepts for lattice, charge, spin, orbit, and topology order parameters for quantum materials are introduced. With continuous innovation in electron microscopy theories and techniques, modern advanced electron microscopy provides powerful tools for characterizing the order parameters in quantum materials and their interrelations at the atomic scale.

1.1 Quantum Materials

What is quantum material? Early reports often associated it with small size. In the late 1980s and early 1990s, some researchers employed materials containing fluorosilicone copolymers to manufacture aspherical contact lenses, due to their high oxygen permeability, for which a 1991 article in an ophthalmology journal referred to this kind of material as "quantum material." In 2012, Orenstein J., a scholar from University of California, Berkeley, proposed in Physics Today [1] that "the quantum materials refer to those materials in condensed matter physics that were once known as the strongly correlated electron systems." In 2016, Nature Physics published an editorial article titled "The rise of quantum materials" [2], whose main idea was: in 1960s and 70s the main approach for condensed matter physics study was to find measurable order parameters in system from perspective of symmetry. By the 1980s, there were two landmark achievements: one was a series of phenomena represented by topological insulators and the fractional quantum Hall effect, which jumped out

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of the Landau-Ginzburg theory; the other was the emergence of high-temperature superconductivity, which led to the so-called strongly correlated electron systems.

In 2015, the "Quantum Materials Symposium" held in Korea set up the following four sub-directions: ① High-temperature superconductivity; ② Multiferroic materials; ③ Strongly correlated systems; ④ Topological insulators. The focus was mainly on novel quantum phenomena arising from the correlation between charge, spin, and lattice.

In 2017, Tokura et al. proposed to collectively refer to materials that simultaneously possess lattice, charge, spin, orbital, and topological order parameters with strong interactions between them as "quantum materials" [3].

1.2 Concepts of Order Parameters in Quantum Materials

1.2.1 Origin of the Term of "Order Parameter"

In the 1930s, the Soviet Union physicist Landau [4] pointed out that the nature of phase transitions in material systems could be summarized as the breaking or restoration of symmetry and the corresponding changes in materials ordering. He was the first to introduce the term of "order parameter": for phase transitions, Landau described the process from high symmetry to low symmetry as "symmetry breaking," and the reverse process as "symmetry restoration." Correspondingly, a degree of freedom in material system would undergo an ordered-disordered transition during the phase transition, which is referred to by Landau as the "order parameter." The 'symmetry' and the 'ordering' in material systems usually present opposite directions. For example, the more ordered structure (high ordering) presents the lower symmetry, and vice versa. The order parameter is the fundamental measure of the ordering degree in materials during the phase transition, which could be a scalar, vector, higher-order tensor, complex number, or in other forms, and different phase transitions require different types of order parameters to describe. In Landau's phenomenological theory model, the Gibbs free energy can be expanded as a power series of the order parameter near the changing point of the phase transition. If the $(n-1)^{th}$ derivative of the Gibbs free energy is continuous at the phase transition point, but the n^{th} derivative is discontinuous, the system is named to undergo an n^{th}-order phase transition. The Landau phenomenological theory model could well explain the phase transitions in material systems on a mesoscopic scale.

1.2.2 *Connotation of Order Parameters in Quantum Materials*

The order parameters described in the phenomenological model can be regarded as characteristic parameters related to multiple degrees of freedom on atomic scale, including lattice, charge, spin, orbit, and topology (see Fig. 1.1). These order parameters (lattice, charge, spin, orbit, topology) and their changes during phase transitions can largely determine the material phases and the macroscopic physical properties before and after phase transitions.

Tokura et al. [3] established the correlation between the ‘order parameters’ and ‘quantum materials’. In quantum materials, lattice, charge, spin, orbit, and topology are not acting as separate factors but are deeply coupled with each other at the fundamental level. They collectively determine the overall response of the material to external fields, resulting in macroscopic physical properties in electrical, magnetic, optical, thermal, and mechanical characteristics. For example, through strong interactions between electrons or the electron-lattice coupling, macroscopic exotic quantum phenomena could occur, such as high-temperature superconductivity, multiferroic materials, colossal magnetoresistance materials, and topological insulators. The exotic properties exhibited by the quantum materials are crucial for the development of next-generation quantum technologies, which can be applied in electronics, optoelectronics, thermoelectric energy harvesting, and secure quantum computing and communications. Quantum technologies based on modern quantum materials can meet the demands for sustainability, efficiency, and security in social development.

In this section, we first introduces briefly the concepts of different order parameters in quantum materials.

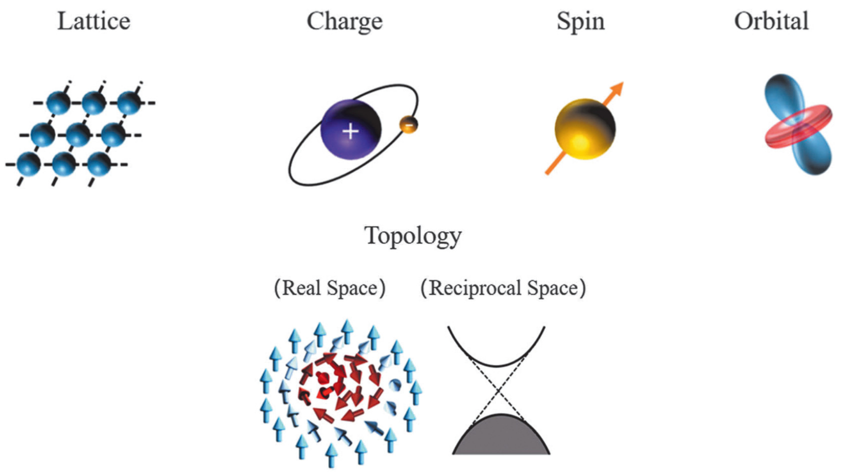

Fig. 1.1 Schematic to show order parameters of lattice, charge, spin, orbital and topology

1 Lattice Order Parameter

Based on the periodicity and symmetry of crystal structures, material crystals could be classified into 14 Bravais lattices, which is the crystallographic basis for characterizing the lattice order parameter. Various kinds of defects exist in material crystals deviated from the Bravais lattice. At the atomic scale (10^{-10} to 10^{-11} m), the lattice displacement could be introduced by lattice distortion, polarization, point defects, etc. On a larger scale (10^{-6} to 10^{-9} m), changes in lattice order parameter could possibly be introduced by dislocations, grain boundaries, stacking faults, domain walls, surfaces, and stress–strain gradients. The polarization would result in ions displacement at the atomic scale while generating polarized domains on the micro-nano scale. The lattice order parameter is also the base for other order parameters of orbit, charge, spin, and topology, which could have a direct impact on other order parameters.

2 Order Parameter of 'Orbital'

The orbitals of electrons in atoms can be labeled by quantum numbers (including principal quantum number *n*, angular quantum number *l*, magnetic quantum number *m*, and spin quantum number *s*). When atoms bind to form molecules or crystals, the overlapping between neighboring electrons leads to new electron orbitals. Bonding between atoms (including covalent bonds, ionic bonds, metallic bonds, σ bonds, π bonds, bonding, antibonding, hybrid bonding, etc.) could lead to different forms of electron orbitals. In crystals, under the crystal field the d-orbitals of transition metal cations would undergo degeneracy as well as the splitting of energy levels. Under different ligand fields within crystals, anion (e.g. O^{2-}) orbitals would present different configurations and densities of states. For strongly correlated systems, such as in colossal magnetoresistance (CMR) materials, orbital order can be associated with spin order to result in the 'orbital ordering' phenomenon.

3 Charge Order Parameter

The order parameter of charge describes the charge transfer and charge density distribution after atoms bonding in crystals. The charge density distribution relates to the orbital formation in the crystal: for example, the electron charge density distributions for different sp^2 and sp^3 hybrid orbitals are certainly different. The charge density distribution is also influenced by factors such as band structure, electric field distribution, and space charge layer. For charge transfer, in some strongly correlated systems, electron–electron interactions would cause splitting of the upper and lower Hubbard bands, allowing electron charge transfer between different energy bands to form the so-called charge transfer gap phenomenon. In high-temperature superconductors, due to the interactions between different order parameters, 'charge density wave' phenomenon would occur that the electron charge density presents non-commensurate structure.

4 Spin Order Parameter

The spin order parameter at the atomic scale refers to the orbital magnetic moment and spin magnetic moment of atoms. In crystals, the crystal field would cause the energy level splitting of the d-orbitals, resulting in electron orbitals in high-spin or low-spin state. The superstructural regular distribution of spins in lattice refers to the magnetic structure in crystal, which include paramagnetism, ferromagnetism, antiferromagnetism, ferrimagnetism, and non-collinear magnetism. At the micro-nano scale, the spin order parameter corresponds to the magnetic domain structure (magnetic domains are approximately at the scale of 10^{-9} cm^3), primarily formed due to the competition between demagnetizing field energy and domain wall energy. At the macroscopic scale, the spin order parameter refers to the macroscopic magnetic properties such as the magnetization polarization and magnetic susceptibility.

5 Topology Order Parameter

Topological materials are those whose properties remain unchanged under topological transformations, recently identified as a new type of quantum material. Using topological order parameters to classify the states of matter provides a completely new perspective for understanding the material world. Research on topological materials and topological phase transitions in materials was awarded the Nobel Prize in Physics in 2016.

In reciprocal space, electronic topological materials are those that maintain topological invariance in the reciprocal space (k-space or momentum space) of energy bands. Beyond traditional band theory, based on topological band theory and characteristics of topological order parameters, scientists have discovered and defined new material types such as topological insulators, topological semimetals, and topological superconductors.

In real space, materials can also have certain electric/spin polarization topological structures, such as in ferroelectric materials with spontaneous electric polarization and in magnetic materials with spontaneous magnetization polarization. Due to size effects or under certain interface coupling, various non-trivial (electrical or magnetic) polar topological structures can spontaneously appear, presenting different topological domain structures including flux-closure, vortices, antivortices, chiral skyrmions, etc.

1.3 Measurement of Order Parameters in Quantum Materials

1.3.1 Techniques for Characterizing Order Parameters in Quantum Materials

Quantum materials exhibit exotic physical properties due to the interaction between different order parameters at the fundamental level. Therefore, how can we measure to understand the characteristic and order parameters of the quantum materials at atomic scale, which is of scientific and application significance? With the development of modern physics theories and instrument manufacturing, it provides powerful characterization techniques as well as advanced analysis theoretical foundation. Electron microscopy is one of the most important technologies. To characterize the lattice, orbital, charge, spin, and topological order parameters of quantum materials and their interactions, a variety of modern advanced characterization techniques, including electron microscopy, should be comprehensively employed. And a brief introduction is given below to compare between the mainly employed characterization techniques in measuring order parameters of quantum materials:

1. Measurement of Lattice Order Parameter

Since Laue confirmed the periodic arrangement of atoms in crystals by diffraction in 1912, X-ray diffraction has been the most basic and commonly used method for measuring the lattice order parameters of single/poly-crystalline materials. With the development of synchrotron radiation sources since the 1970s, modern synchrotron radiation sources possess features such as extremely high brightness (over a billion times brighter than conventional X-ray instrument), wide bandwidth (continuous and tunable wavelengths), high collimation, polarization modulation capability, and high precision. Utilizing the advantages of synchrotron radiation sources for high-resolution X-ray diffraction can significantly improve the resolution by several times to an order of magnitude compared to conventional X-ray diffraction, making it more suitable for accurately resolving the fine lattice structures in quantum materials.

Neutron diffraction, through the interaction between the incident neutrons and atomic nuclei, could avoid the strong scattering between X-rays and outer electrons. It can directly distinguish between different elements, which is particularly suitable for determining the occupancy of light elements in quantum materials. Additionally, neutron diffraction can differentiate between different isotopes of the same element. Characterization by neutron diffraction via introducing different isotopes in quantum materials can play an important role in understanding the changes in lattice vibration modes.

Scanning tunneling microscopy (STM) can provide ultra-high-resolution real-space imaging on surface of quantum materials. The lateral resolution of STM can reach atomic scale, and the vertical resolution can reach sub-angstrom scale, making it a powerful tool for revealing the local atomic structure on surface of quantum materials.

Transmission electron microscopy (TEM) possesses both the imaging and diffraction techniques, which could characterize the lattice order parameters of quantum materials with high resolution, either in real or reciprocal space. Compared with X-ray and neutron diffraction, electron diffraction can perform local diffraction analysis of materials with nanometer or even angstrom precision. With the development and maturity of aberration-corrected technology since the late twentieth century, the spatial resolution of (scanning) transmission electron microscopy for real-space imaging has been improved to sub-angstrom levels. Tsinghua University first introduced aberration-corrected transmission electron microscope into China in 2008, and started and developed the sub-angstrom-scale material characterization researches. In 2009, Xie Lin, Ling Tao, Zhu Jing, et al. [5] reported their work on preparing icosahedral iron nanoparticles using E. coli, and clearly revealing the atomic arrangements for the secondary and tertiary axes of the icosahedral iron nanoparticles using aberration-corrected electron microscopy. In 2010, Yu Rong and Zhu Jing achieved sub-angstrom resolution imaging of oxide nanoparticle surfaces [6]. In recent years, differential phase contrast (DPC) imaging has continued to develop and mature, allowing atomic-scale imaging of light elements such as Li element [7, 8]. Moreover, ptychography can further enhance the resolution of electron microscopy and even locate atoms in three dimensions [9]. The substantial progress made in advanced electron microscopy techniques has made electron microscopy an indispensable tool for characterizing the lattice order parameters of quantum materials.

2. Measurement of Orbital Order Parameter

Angle-resolved photoemission spectroscopy (ARPES) can collect the full momentum and energy information of photoelectrons emitted from materials upon light exposure, allowing precise characterization of the orbital and band structure information of quantum materials in momentum space. Modern ARPES technique, with high energy and momentum resolution, can even resolve the band renormalization information, caused by the electron–electron and electron–phonon interactions. These features are crucial for understanding the interactions between multiple order parameters in quantum materials.

Scanning tunneling spectroscopy (STS) attached on scanning tunneling microscopy (STM) can probe the tunneling current in response to the voltage applied to the material surface, which allows high energy resolution detection and characterization of the energy density of states near the Fermi surface of quantum materials with meV precision.

In probing orbital order parameters, X-ray absorption spectroscopy (XAS) based on synchrotron radiation sources and electron energy loss spectroscopy (EELS) in analytical electron microscopy are quite similar. Both techniques can characterize the orbital order parameters by detecting the transition of inner-shell electrons to the unoccupied states above the Fermi level, to obtain the orbital information of quantum materials under influence of crystal field environment, lattice distortion, etc. Compared to EELS, XAS generally has a higher signal-to-noise ratio and is more suitable for high-energy range detection (greater than 2000–3000 eV). EELS, however, has the advantage of high spatial resolution, allowing the detection of local orbital information for quantum materials at the atomic scale.

3. Measurement of Charge Order Parameter

Scanning tunneling spectroscopy (STS) can adjust the bias voltage relative to the Fermi level to observe the corresponding tunneling current. For quantum materials, STM combined with STS can specify the energy near the Fermi surface and further obtain the two-dimensional distribution mapping of the charge density at the corresponding energy level, which is valuable for studying high-temperature superconductors, charge density waves, topological vortices, and other quantum materials and properties [10–12].

With respect to electron microscopy techniques, convergent beam electron diffraction (CBED), differential phase contrast (DPC) imaging, and 4D-STEM techniques can explore the electric potential, electric field, and charge density distribution within materials. Aberration-corrected STEM can converge the electron beam down to sub-angstrom diameter to image the sample. Combining STEM with DPC or utilizing 4D-STEM can obtain information on the local electric field and charge density distribution within the sample at sub-angstrom resolution in real space. The progress in electron microscopy in these areas could help better discover the characteristics of charge density distribution within quantum materials.

4. Measurement of Spin Order Parameter

For macroscopic magnetic measurements of quantum materials, superconducting quantum interference device (SQUID) magnetometry is a highly sensitive instrument capable of measuring weak magnetic fields down to 10^{-11} Gauss. It is valuable for studying the magnetic properties of superconducting and magnetic quantum material.

Both magneto-optical Kerr effect (MOKE) technique based on conventional light sources and X-ray magnetic circular dichroism (XMCD) based on synchrotron radiation sources depend on principle of the magnetic circular dichroism. MOKE can image the micro-nano magnetic domains on surface of materials through the magneto-optical Kerr effect, useful for studying the magnetic domain dynamics of magnetic quantum materials as well as spintronic devices. XMCD can measure the magnetic circular dichroism spectrum of magnetic quantum materials to obtain element-specific quantitative magnetic moments information. X-ray magnetic linear dichroism (XMLD) based on synchrotron radiation can measure the magnetic linear dichroism spectrum of materials to obtain quantitative information related to the antiferromagnetic structures. Photoemission electron microscopy (PEEM) combined with XMCD/XMLD can achieve magnetic domain imaging with high spatial resolution at nanoscale resolution.

Neutron diffraction can quantitatively determine the strength and orientation of magnetic moments for atoms in crystal lattice, through magnetic diffraction analysis between neutron magnetic moments and atomic magnetic moments, making it a primary tool for studying and determining the magnetic structures of the quantum materials.

Spin-polarized angle-resolved photoemission spectroscopy (spin-polarized ARPES) can characterize the spin-resolved band structure of superconducting, magnetic, and topological quantum materials. Spin-polarized STM can provide atomic-resolution real-space imaging of spin-resolved electron charge distribution on surface of quantum materials, useful for observing and investigating important quantum phenomena like spin density waves (SDW).

Modern electron microscopy has developed various techniques to characterize the spin order parameters of quantum materials on different scales. Lorentz microscopy and electron holography can perform static or dynamic in-situ imaging of the magnetic domain structures within materials at nanometer resolution, allowing the observation and study of small nanometer-scale magnetic domain structures, such as skyrmions in quantum materials. Inspiring by XMCD technology, the counterpart of electron energy loss magnetic chiral dichroism (EMCD) has been developed to measure the magnetic properties of materials in TEM. In Tsinghua University, Prof. Zhu Jing, Wang Ziqiang, Zhong Xiaoyan, and Song Dongsheng further developed innovative high spatial resolution quantitative EMCD techniques with site-specific, in-plane-magnetic-moment-measurable, and atomic-plane specific capabilities, which are valuable for studying multiferroic, magneto-optical, superconducting quantum materials [13–15]. The newly developed differential phase contrast (DPC) imaging method and 4D-STEM technology can further achieve real-space imaging of magnetic information within materials at nanometer or even atomic resolution. In 2022, Professor Shibata Naoya's research group from the University of Tokyo combined DPC technology with magnetic field free aberration-corrected STEM to achieve the atomic-scale magnetic structure imaging [16]

5. Measurement of Topological Order Parameter

For investigating topological electronic states in topological materials, angle-resolved photoemission spectroscopy (ARPES) possesses powerful capability in characterizing the detailed band structure, which could directly verify the presence of non-band-gap edge state in topological insulators.

For the novel electric or spin polarization topological structures exhibited in quantum materials, aberration-corrected (scanning) transmission electron microscopy with sub-angstrom resolution can be employed to direct observe the non-trivial polar topological structures such as closed loops, vortices, and chiral skyrmions. Techniques such as Lorentz microscopy can be used to image the spin topological domain structures, such as magnetic skyrmions, on a micro- to nanoscale [17, 18].

1.3.2 Advantages of Electron Microscopy in Characterizing Order Parameters of Quantum Materials

Compared with other techniques for characterizing order parameters of quantum materials, advanced electron microscopy has the following two distinct features.

1. Comprehensiveness

Various techniques integrated on the electron microscope platform can characterize the lattice, orbital, charge, spin, and topological order parameters of quantum materials. Therefore, on a single modern advanced electron microscope, different electron microscopy methods can comprehensively characterize the various order parameters of quantum materials locally at the atomic scale. This strong comprehensive synergy of electron microscopy is rarely matched by other characterization techniques. In the exploration of quantum materials, the comprehensiveness of electron microscopy characterization is indispensable, as it can deeply explore and reveal multiple order parameters of quantum materials and their interactions, playing a crucial role in understanding the fundamental mechanisms in quantum materials.

2. High Spatial Resolution

With the maturation of aberration-corrected technology, the spatial resolution of modern transmission electron microscope in real-space imaging has reached sub-angstrom levels, which is difficult to achieve by other characterization techniques. While scanning tunneling microscopy (STM) has a spatial resolution comparable to electron microscope, it is limited to high-resolution imaging of conductive sample surface. The high spatial resolution capability of electron microscope allows direct observation of the lattice structure of quantum material at the atomic scale, as well as the lattice distortions of quantum materials under different preparation methods, in defects, or under internal and external fields. The sub-angstrom spatial resolution capability of aberration-corrected electron microscopes can be combined with other analytical electron microscopy techniques to achieve high spatial resolution characterization of the orbital, charge, spin, and topological order parameters of quantum materials at atomic scale. Important phenomena and deep coupling mechanisms of multiple order parameters in quantum materials occur at the atomic scale, making the high spatial resolution capability of electron microscopy indispensable for their study.

The powerful characterization capabilities of modern advanced electron microscopy are the result of significant progress in electron microscopy principles and hardware technology over the past few decades. These advancements include:

(1) The development of aberration-corrected imaging technology, which has brought sub-angstrom spatial resolution capabilities for real-space imaging.
(2) The development of technologies such as chromatic aberration correction and direct electron detector, which could improve the energy resolution as well as the signal-to-noise ratio of the electron energy loss spectroscopy (EELS); breakthroughs in principles and applications of momentum-resolved EELS and electron magnetic circular dichroism (EMCD) for characterizing the orbital and spin order parameters of materials.
(3) The development of differential phase contrast (DPC) and 4D-STEM technologies, which enables imaging of light elements, improves the spatial resolution in obtaining information of atomic arrangements in sample, and possesses real-space imaging capabilities of electric potential, electric fields, charge density, and even magnetic information.

Furthermore, the development of in situ electron microscopy techniques enables the investigation of order parameters of quantum materials under different external fields (electric, magnetic, mechanical, thermal, optical) and environmental conditions (gas, liquid). Additionally, with the development and integration of new methods from artificial intelligence, future electron microscopy will have more powerful intelligent analysis and automatic operation capabilities.