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Review of Ultrafast Electron Diffraction Technology

Xiaoyang Li

School of Optoelectronic Engineering, Xi'an Technological University, Xi'an, China
15802917090@163.com

Abstract. Ultrafast Electron Diffraction (UED), built on the pump-probe framework, has long been an indispensable tool at the cutting edge of interdisciplinary research spanning physics, chemistry, and biology. Who would have thought that, with its dual advantages of femtosecond temporal resolution and sub-angstrom spatial resolution, it could directly "visualize" the ultrafast coherent coupling evolution of lattices, electrons, and spins in momentum space? This not only breaks the limitation that traditional spectroscopy can only indirectly infer molecular structural dynamics, but also truly pushes condensed-matter physics, photochemical reactions, and transient quantum materials into a new era of real-time atomic-scale visualization. This paper systematically reviews the landmark breakthroughs of UED in uncovering the microscopic mechanisms of extreme nonequilibrium states of matter, covering phase transition dynamics, electron-phonon coupling, molecular dynamics, and quantum ultrafast manipulation, fully demonstrating the irreplaceable scientific value of this technology.

Keywords: ultrafast electron diffraction, pump-probe, temporal resolution, space charge effect, molecular movie

1. Introduction

The physical framework of UED originates from the de Broglie matter wave hypothesis and the Bragg coherent scattering theory of crystal lattices. Since electron probes are simultaneously subjected to the Coulomb potential of atomic nuclei and extranuclear electron clouds, their elastic scattering cross-section is 4 to 6 orders of magnitude higher than that of X-rays, endowing this technology with extremely high detection sensitivity for surface and low-dimensional systems [1]. Early keV-level electron sources suffered from extremely weak accelerating electric fields, such that severe nonlinear space charge repulsion confined the temporal resolution to the picosecond regime. Over the past two decades, the large-scale application of radiofrequency (RF) photocathode technology has made it possible for MeV-level relativistic electron beams to dominate diffraction detection [2]. By increasing the Lorentz factor of electrons to suppress Coulomb distortion, the temporal limit of coherent observation has been successfully defined in the sub-100-femtosecond region, fully activating the real-time observation capability for cross-scale multi-body lattice dynamics [3].

The operation of UED detection systems is strongly dependent on a strictly optomechanically synchronized pump-probe experimental configuration (Figure 1). In a typical system, a polarized

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femtosecond laser beam coherently excites the sample to a non-equilibrium evolving state; after a controlled optical delay, an ultrashort electron pulse train shaped in reciprocal space with a Gaussian profile sweeps across the polarized region, and projects a coherent Bragg diffraction pattern carrying the transient crystallographic fingerprint. By high-resolution scanning of the delay domain, the three-dimensional configuration evolution of lattice broadening, distortion, and multi-body energy relaxation can be retroactively derived. This technology has become an indispensable tool for studying ultrafast dynamics in physics, chemistry, materials science, and structural biology, and every breakthrough in its temporal resolution has pushed forward the boundary of human cognition on dynamic processes in the microscopic world [4].

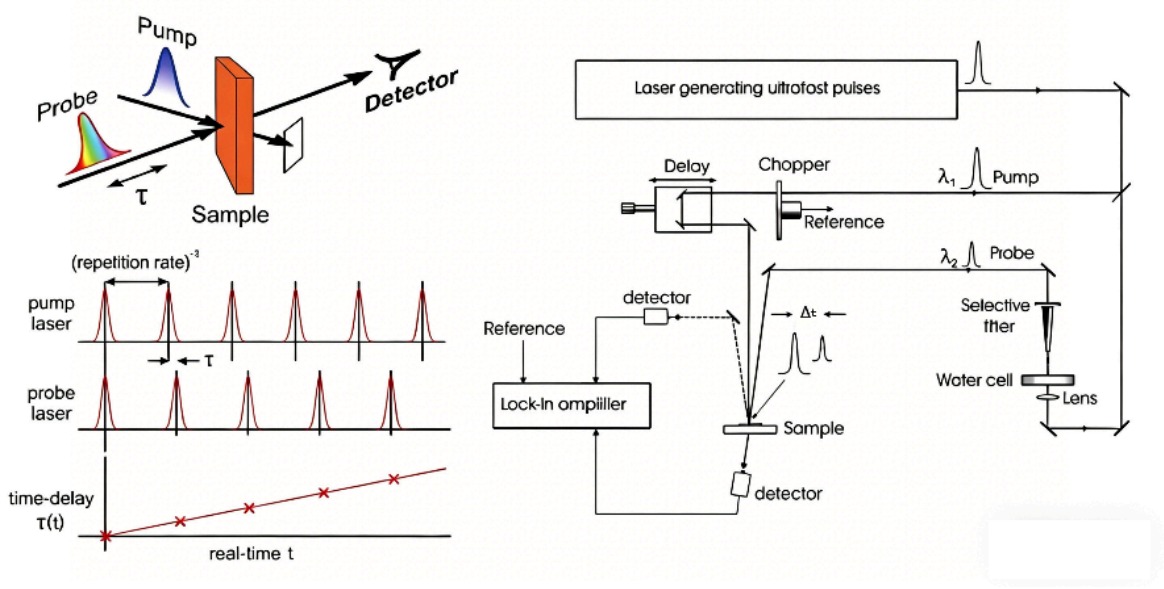

Figure 1. Schematic diagram of the pump-probe time-resolved experimental setup: The left panel shows the principle of the pump-probe technique: a strong pump pulse excites the sample, and a weak probe pulse with time delay τ detects the transient changes in the optical properties of the sample. By scanning τ, the dynamic evolution of the excited state can be obtained. The right panel shows the experimental optical path: an ultrafast laser is split into a pump beam (λ_1) and a probe beam (λ_2). The pump beam is used to adjust the time difference Δt through a delay line and modulated by a chopper, and then confocal with the probe beam onto the sample. The probe signal is received by a detector, and a lock-in amplifier is used to extract the transient signal and suppress noise. The timing diagram below shows the pulse synchronization relationship and the linear scanning process of the time delay τ

This paper systematically elaborates the core physical principles of ultrafast electron diffraction (UED) — the pump-probe mechanism based on de Broglie matter wave theory and Bragg diffraction law. It reviews the development of UED from hundreds of femtoseconds to tens of femtoseconds in temporal resolution and its progress toward the attosecond scale, dissects in detail the core components including electron source, beam shaping and transmission system, synchronization system and detection module, and clarifies the decisive role of key performance parameters such as beam brightness, pulse width and energy divergence on technical performance. The paper focuses on two core bottlenecks of UED technology: beam broadening and energy divergence caused by the space charge effect, and the limitation of temporal resolution imposed by timing jitter. It also deeply analyzes the technical routes of three innovative solutions: laser

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wakefield acceleration (LWFA) suppresses the space charge effect from the source through relativistic effects [5]; machine learning diagnosis technology realizes real-time prediction and dynamic correction of beam parameters [6]; and conditional guided diffusion model provides a high-precision tool for non-invasive monitoring of the space charge effect and timing jitter [7]. By summarizing landmark applications in cutting-edge fields such as transient evolution of charge density waves, thermal transport of lattice vibrations, capture of photoinduced phase transition intermediates and dynamic changes of molecular bonds [8, 9, 10], this paper intuitively demonstrates the unique advantages of UED technology in reconstructing "molecular movies" and fully restoring the ultrafast dynamic processes of matter with ultrahigh spatiotemporal resolution.

To intuitively illustrate the working principle and technical characteristics of the ultrafast pump-probe technique, a typical case of phase-randomized tomography is analyzed here, with relevant experimental results and device structure shown in Figure 2. This technical system takes the ultrafast pump-probe mechanism as the core and realizes multi-dimensional information characterization around phase-randomized tomography. Figure 2 (a) is the schematic diagram of the experimental optical path of ultrafast pump-probe phase-randomized tomography based on α-quartz and barium borate (BBO) crystals. The fundamental light output by the laser source is phase-modulated by α-quartz, then frequency-doubled and split by BBO crystal, and combined with a spatial light modulator (SLM) to complete phase encoding and beam shaping, finally constructing a complete pump-probe optical path to provide hardware support for phase-randomized tomography. Figure 2 (b) shows the two-dimensional spatial distribution characteristics of the Wigner quasi-probability. The azimuth angle φ is marked in polar coordinates, and the color scale on the right intuitively represents the positive and negative distribution of probability density (orange for positive, purple for negative), which clearly reflects the quantum state distribution law of the optical field under phase-randomized tomography and verifies the phase control ability of the system. Figure 2 (c) shows the evolution curve of photon number distribution $P(N)$ with coordinate X. Curves of different colors correspond to different parameters such as 1.65, 11.63 and 29.72, and the Poissonian fit results are also given, which quantitatively show the regulation effect of parameter changes on the statistical distribution of photon numbers and intuitively reflect the multi-parameter tunability of the system. Figure 2 (d) is a stacked histogram of photon counts #counts versus photon number *N*. Different colors correspond to photon number distributions of different components, and the stacked form clearly shows the superposition characteristics of multi-component distributions, which provides a quantitative basis for the analysis of photon statistical characteristics of phase-randomized tomography and further verifies the detection accuracy of the system.

Combined with the above cases, it can be further confirmed that ultrafast pump-probe technology can achieve high-precision detection of microscopic characteristics such as optical field phase and photon statistics through precise optical path construction and multi-dimensional quantum state characterization methods. This is also technically consistent with the core principles and development directions of ultrafast electron diffraction (UED) technology reviewed in this paper, providing an important reference for the subsequent phase manipulation and temporal resolution optimization of UED systems. Finally, this paper objectively analyzes the current limitations of UED technology in breaking through attosecond-level temporal resolution, balancing high charge and low space charge effects, and data analysis efficiency in complex systems. Combined with the latest research progress in the field, this paper prospects the future development directions of the technology toward higher temporal resolution (approaching the attosecond limit), lower influence of space charge effects (optimizing beam manipulation strategies), and wider application scenarios (expanding to extreme conditions and biological macromolecule systems) [7, 11, 12].

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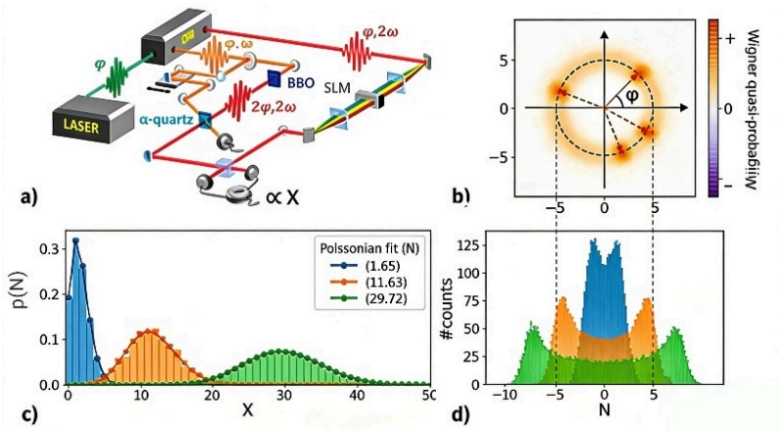

Figure 2. Ultrafast pump-probe phase-randomized tomography: a) Schematic of the experimental optical path for ultrafast pump-probe phase-randomized tomography based on α-quartz and BBO crystals, including core components such as α-quartz, BBO (barium borate crystal), and SLM (spatial light modulator); b) Two-dimensional spatial distribution of the Wigner quasi-probability with azimuthal angle φ marked in polar coordinates and the color bar representing the probability density; c) Evolution curve of photon number distribution $P(N)$ with coordinate X including Poissonian fit, with different colors corresponding to different parameters (11.63, 29.72, etc.); d) Histogram of photon counts #counts versus photon number N, where the stacked plot shows the multi-component distribution characteristics

2. Components of UED

Since probe electrons are elastically scattered by both the Coulomb potential of target nuclei and the wavefunction of extranuclear electron clouds, their cross-section must be strictly corrected according to the Mott-Bethe formula. Therefore, the design of the entire UED system is not a simple assembly of components, but a multi-objective extreme optimization for six-dimensional emittance, Mean Transverse Energy (MTE) and nonlinear Coulomb degradation under the law of Liouville's phase space volume conservation [13].

2.1. Photocathode physics and intrinsic emittance of electron sources

At present, high-performance UED systems widely rely on radio frequency (RF) photocathode emission cavities triggered by polarized lasers, dominated by 1.6-cell S-band structures. The initially photoemitted electron cloud is driven by an extreme gradient field of tens of MV/m in the microwave cavity and instantly jumps to the MeV relativistic energy regime. The brightness, charge quantity and pulse width of the electron source are key parameters determining the temporal resolution and the influence degree of the space charge effect. An ultrafast electron diffraction device based on a laser accelerator is shown in Figure 3, which focuses laser pulses into a gas cell via focusing mirrors to generate high-energy electron beams, achieves precise regulation of the pump-probe timing through laser pulses with accurately controllable phases, produces diffraction signals after the electron beams interact with the sample, and finally realizes "molecular movie" imaging of ultrafast structural dynamic processes at the detection end. However, during the envelope evolution stage, the inherent high-flux Coulomb repulsion inside the electron bunch, namely the space charge effect, induces longitudinal energy chirp leading to irreversible temporal broadening

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and energy dispersion on the one hand, and increases the transverse normalized emittance to collapse the coherent diffraction area on the other hand.

To suppress the space charge effect at the generation source, high-gradient superconducting radio frequency (SRF) systems and laser wakefield acceleration (LWFA) mechanisms have established benchmarks for cutting-edge exploration, and the latter, relying on plasma wakefields exceeding hundreds of GV/m, can accelerate electron beam probes to GeV within micrometer-scale distances while maintaining the pulse width at the femtosecond level, thus effectively avoiding divergence of the electron source [5, 14].

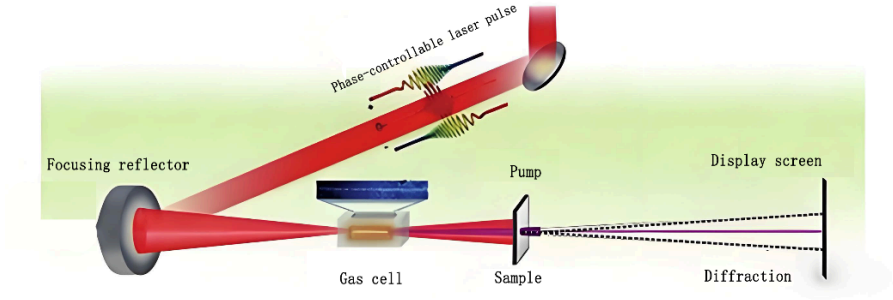

Figure 3. Schematic of the ultrafast electron diffraction experimental setup based on laser acceleration: This device focuses laser pulses into a gas cell using focusing mirrors to generate high-energy electron beams, realizes pump-probe timing control through phase-controllable laser pulses, produces diffraction signals after the electron beams bombard the sample, and finally completes the "molecular movie" recording of ultrafast structural dynamics on the detector screen

2.2. Beam shaping, transport and phase space conservation

This shaping and transport system aims to break the diffraction dispersion in single-particle dimension, with the core lying in linear diffraction compression of the beam and balancing of many-body mechanical distortions, so as to reconcile the mutual constraints between space charge and temporal resolution. Its key constraint modules are as follows:

Solenoid and quadrupole cold lens assembly – strictly controls electron position and divergence angle to match the Larmor focusing radius at the target plane, effectively delaying the evolution of the Coulomb-force-dominated divergent envelope;

Monochromator – one of the core components, usually composed of a set of bending magnets, used to select electrons with an extremely narrow energy bandwidth (e.g., $\frac{\Delta E}{E}$ ~10^{-5}), which not only reduces the contribution of energy spread to diffraction peak width (improving spatial resolution) but also indirectly suppresses energy dispersion caused by the space charge effect [6];

Radio frequency (RF) and THz bunch compression cavities – use an external strong axial time-varying electric field to precisely introduce velocity-space (or velocity-time) correlation, namely actively imposing a negative energy chirp. The high-energy particles at the tail then catch up with the low-energy particles at the head in the anomalous dispersion drift section, thereby achieving ballistic bunching of the longitudinal envelope, which can compress the pulse width to the femtosecond level [15].

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2.3. Pump-probe and synchronization system

The synchronization accuracy of the pump-probe mode directly determines the upper limit of temporal resolution. The pump beam (usually a tunable femtosecond laser) and the laser for generating probe electrons originate from the same master oscillator, and femtosecond-level synchronization is realized through a precise optical delay line [3]. Timing jitter mainly comes from the stability of this synchronization link and is a key factor restricting the actual temporal resolution. To verify the feasibility of the terahertz-driven electron beam compression scheme and the system timing stability, relevant experiments were carried out on the HIGGINS dual 100 TW laser platform. The results are shown in Figure 4, which shows the electron bunch compression characteristics and system timing jitter performance. The details of each subplot are as follows:

Figure 4 (a) shows the variation of the electron beam full width at half maximum (FWHM) with the terahertz electric field strength ETHz. The red squares represent experimental data, and the black solid line is the theoretical fitting curve, showing typical V-shaped compression characteristics. The inset shows the electron beam temporal profile before compression (black) and after optimal compression (red), intuitively reflecting the temporal compression effect of the terahertz field on the electron beam.

Figure 4 (b) shows the simulated evolution of the electron beam pulse width along the beamline under different terahertz driving field strengths. The blue shaded area is the dielectric-loaded waveguide (DLW) interaction region, and the green shaded area is the sample test position, providing a theoretical basis for experimental layout and parameter optimization.

Figure 4 (c) shows the long-term temporal jitter ΔT measurement of the electron beam under optimal compression conditions. The root-mean-square (rms) temporal jitter of the electron beam is 3.8 fs within 5 minutes, which fully verifies that the system has ultra-high temporal stability and can meet the stringent requirements of time-resolved experiments such as ultrafast electron diffraction.

The researchers achieved precise spatiotemporal overlap of the two laser beams via shadowgraphy, with the synchronization error controlled at the femtosecond level, guaranteeing the recording of high-temporal-resolution "molecular movies" [5, 16].

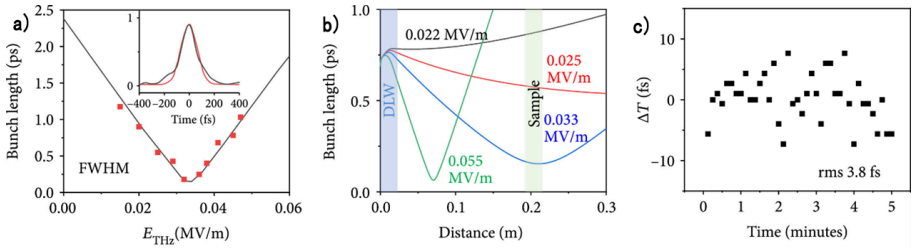

Figure 4. Electron bunch compression and system timing jitter: a) Compression effect of THz electric field strength on electron bunch pulse width (FWHM); b) Evolution of electron bunch length along propagation distance under different THz field strengths; c) Long-term stability monitoring of electron beam temporal jitter (ΔT) (rms = 3.8 fs)

2.4. Detector topology and cross-time-coherent sampling mode

Stroboscopic Ensemble Averaging: Dedicated to fully reversible state evolution. Relying on extremely high photoexcitation repetition rates, phase-space ensemble averaging with extremely high signal-to-noise ratio is achieved through linear geometric superposition of millions of coherent scattering cross sections under the constraint of extremely low intrinsic charge (fully suppressing

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Coulomb effects within a single pulse). This also approaches the physical limit of electron scattering sensitivity.

Single-shot Transient Capture: For irreversible dynamics such as photoablation and free radical fragmentation, it is mandatory to stack an extremely wide transverse coherent cross-sectional area (usually more than 10^5–10^7 electrons) within an extremely short time window (single pulse period). This operation pushes the physical boundary into the nonlinear many-body Coulomb explosion regime and relies heavily on the extremely high electromagnetic gradient provided by laser wakefield acceleration (LWFA) to suppress Coulomb explosion [5].

MHz Electron Detector: Using high-sensitivity, low-noise electron microscopy cameras (such as direct electron detection cameras) combined with components such as Ce:YAG scintillation screens, it can rapidly record two-dimensional diffraction patterns and achieve high-resolution imaging, providing hardware support for increasing the frame rate of "molecular movies" [5, 17].

Intelligent diagnostic assistance: Based on a condition-guided generative diffusion model, high-resolution 1024×1024-pixel longitudinal phase space (z, E) images of electron beams can be generated through a 15-dimensional conditional input vector including 5 accelerator parameter setpoints and 10 non-invasive beam measurements, realizing fast virtual diagnosis of accelerator beam phase space and real-time monitoring of beam variations induced by the space charge effect [7].

Specifically, the operating mechanism of the conditional diffusion module used to generate XTCAV images of the longitudinal phase space projection (z, E) of the beam is as follows, with the detailed process shown in Figure 5: the model takes accelerator parameters ($c_1, c_2, \ldots, c_{15}$) as conditional embeddings, combined with time embeddings and noisy latent images, to generate the beam longitudinal phase space (Δz - ΔE) distribution measured by XTCAV through the diffusion process. This architecture provides solid feedback support for dynamic optimization of accelerator temporal resolution.

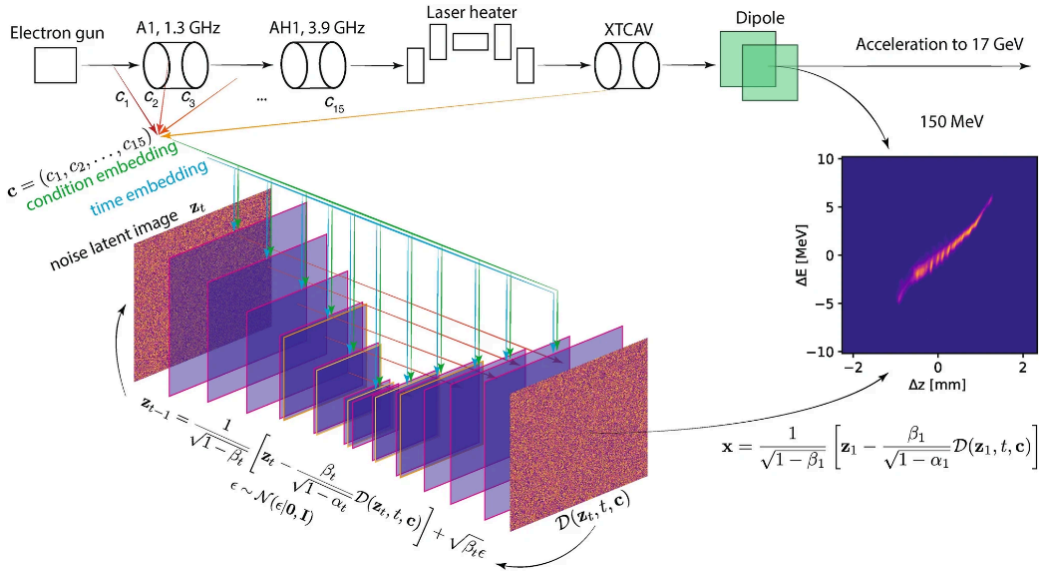

Figure 5. Schematic of the conditional diffusion module for generating XTCAV images of the beam longitudinal phase space projection (z, E): The model takes accelerator parameters ($c1$, $c2$, … , $c15$) as conditional embeddings, combined with time embeddings and noisy latent images, to generate the beam longitudinal phase space (Δz–ΔE) distribution measured by XTCAV through the diffusion process, realizing fast virtual diagnosis of accelerator beam phase space

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3. Technical limitations and solutions of UED

Through research focusing on the core components of the UED system and ultrafast dynamics characterization, a preliminary analysis has been conducted on fundamental physical issues such as Coulomb explosion and space charge effect, clarifying their influence mechanisms on electron beam quality. On this basis, further investigation reveals that the performance limit of UED technology is essentially determined by a set of core contradictions: the balance between improving temporal resolution and suppressing the space charge effect. To achieve femtosecond-level temporal resolution, electron bunches must be compressed to the sub-picosecond or even femtosecond scale. However, the high charge density brought by short pulses induces severe space charge effects, leading to beam broadening and timing jitter, which directly offset the improvement in temporal resolution. The natural trade-off between the two constitutes the core challenge in the development of UED technology [6]. In addition, issues such as timing synchronization jitter, group velocity mismatch, the trade-off between beam flux and resolution, and the limitations of destructive diagnostics further restrict the application potential of UED technology in "molecular movie" recording and ultrafast dynamics research. The core challenges and corresponding innovative solutions are analyzed in detail below.

3.1. Space charge effect (Coulomb explosion)

In the free unshielded drift section, nonlinear Coulomb repulsion between electron bunch sequences (also known as space charge degradation) dominates the degradation of probe quality. Longitudinal electrostatic repulsion directly drives bunch energy spread broadening and physical pulse stretching, leading to an exponential degradation of the temporal resolution extracted by the detector. Meanwhile, transverse repulsion causes real-space spot diffusion and reduces the transverse coherent length of the Brillouin zone, which is manifested as the broadening of high-order Bragg diffraction peaks. The single-shot mode for detecting irreversible transient physics poses an extreme challenge to the load of a single pulse (which needs to carry more than 10^6 particles). In this case, severe spatial distortion easily induces physical "Coulomb explosion" in phase space, resulting in complete overlap and distortion of structural scattering signals. Solutions are developed along two paths: "source suppression" and "process manipulation".

Use of relativistic-energy electron beams (MeV scale): Electron velocity approaches the speed of light (e.g., 2 MeV electrons travel at approximately 0.98 c), significantly shortening the interaction time between electrons and limiting the space charge effect to within 10% [3]. Experiments at the Weizmann Institute show that the space charge broadening of a 152 MeV relativistic electron beam is only 1/5 that of a non-relativistic beam [1, 5].

Optimization of electron gun phase and laser injection conditions: By precisely adjusting the phase of the RF electron gun (e.g., the optimal phase of a 1.4-cell gun is 6°) and the spot size and pulse duration of the laser pulse, the initial emittance of the electron beam is reduced to below 10 nm·rad at the source, weakening the internal Coulomb interaction of the beam [11].

Adoption of a highly selective monochromator: Electrons with an extremely narrow energy bandwidth ($\frac{\Delta E}{E} \sim 10^{-5}$) are selected using bending magnets to filter out energy-dispersed electrons caused by the space charge effect, indirectly mitigating its impact on resolution, although approximately 70%–80% of the beam flux is sacrificed [6].

Exploration of laser wakefield acceleration (LWFA) electron sources: Using the strong wakefield excited by lasers in plasma (acceleration gradient > 100 GV/m), femtosecond-scale electron beams with ultra-low emittance (<1 mm·mrad) are generated, which inherently feature weak space charge

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effects. The single-pulse charge can reach 92±33 pC with a pulse width maintained within 2 fs [5, 14].

Induction of wakefield reverse bias shielding: High-amplitude reverse currents excited by transverse plasma wakefields can provide a reverse Lorentz magnetic field, which significantly suppresses the unsteady space charge divergence envelope through intrinsic self-shielding [2].

Development of superconducting radio frequency (SRF) electron guns: The zero-resistance property of superconductors enables a higher acceleration electric field gradient (>50 MV/m), producing high-brightness electron beams at lower charge levels to balance the space charge effect and detection flux [18].

3.2. Timing jitter

Optical-RF Phase Locking and Direct Photoconductive Switching: A femtosecond-level phase-locked loop is used to cut off low-frequency phase-difference coupling between the high-frequency master clock and the cascaded amplification stages. Direct photoconductive driving eliminates jitter accumulation in microwave transmission lines, compressing the system mutual-alignment uncertainty well below a single microwave period (5 fs limit) [15].

Machine Learning Correction in Data Post-Processing: A neural network model based on Bragg diffraction patterns can inversely deduce beam pointing jitter (RMS error 0.11 μrad) and energy jitter (RMS error 3.44×10^{-5}) from peak position shifts, and perform algorithmic compensation to indirectly improve effective temporal resolution [7]. Experiments at Brookhaven National Laboratory show that this method reduces resolution degradation caused by jitter by 40% [4, 10].

Design of Isochronous Optical Transport Lines: By optimizing the arrangement of magnetic lenses and bending magnets, electrons of different energies are made to travel identical path lengths, eliminating energy-time correlated jitter induced by the space charge effect and improving temporal resolution by 20%–30% [11].

Real-Time Correction Based on Conditional-Guided Diffusion Models: Physical transitions of beam states under different accelerator parameters are realized via latent space interpolation, dynamically compensating for jitter accumulation caused by parameter drift and superimposed space charge effects, improving jitter stability to within 8 fs [7].

Transverse Broadband THz All-Optical Clock Phase-Locking Control: Since ultra-broadband strong THz fields and the excitation beam path share absolute homologous optical path time-translation invariance, a crossed deflection waveform is constructed, which essentially eliminates long-range phase-uncertain oscillations introduced by external independent RF sources, thereby suppressing jitter to the sub-femtosecond level [15].

3.3. Group velocity mismatch

In non-collinear grazing-incidence configurations for transparent media or transmission-type dynamics characterization limited by finite macroscopic thickness, the group velocity mismatch (GVM) between the pump optical wave packet and the sub-relativistic electron probe is particularly significant. Because the phase velocity of low-energy electron probes lags behind that of optical pulse excitation, the "time zero" of the excitation moment is severely dispersed along the sample crystal axis, resulting in sample-thickness-dependent temporal broadening. For example, a 100 nm thick silicon sample can induce a broadening of approximately 50 fs. To break the GVM limitation in material systems such as thick complex epitaxial heterostructures, the physics community has proposed various targeted solutions, including ultra-thin two-dimensional free-standing sample

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preparation, tilted pump wavefront compensation, two-color pump-probe schemes, or direct implementation of MeV-scale isochronous electron sources to approach the vacuum limit [19].Your paper must provide the email address of the corresponding author.

Use of ultra-thin samples (tens of nanometers thin films): Samples with thickness <50 nm are prepared via focused ion beam (FIB) or ultrasonic exfoliation techniques, reducing the propagation path difference between the pump light and the electron beam, so that the temporal broadening caused by group velocity mismatch is reduced to below 10 fs [2]. Studies show that a 20 nm thick graphene oxide sample can suppress such broadening to within 8 fs [1, 8].

Selection of gas-phase or surface experimental systems: In gas-phase samples, both pump light and electron beams propagate in vacuum, making the group velocity difference negligible; surface experiments only involve the sample surface layer (<10 nm), effectively avoiding the influence of the medium on temporal resolution [5].

Adoption of tilted pump wavefront compensation: Optical components are used to tilt the pump laser wavefront, synchronizing the propagation path of the pump light within the sample with the electron beam, achieving consistent time zero at different depths. After compensation, temporal broadening can be reduced by more than 60% [6].

Development of two-color pump-probe schemes: Two pump lights of different wavelengths are used to excite the surface and deep layers of the sample respectively, eliminating the effect of group velocity mismatch through time delay calibration, suitable for complex samples with thickness >100 nm [13, 19].

3.4. Trade-off between flux and resolution

The conflict between high temporal resolution and high flux is another core challenge of UED technology: high temporal resolution requires narrow electron pulses (femtosecond scale) and low charge density (to suppress the space charge effect), but low charge results in weak diffraction signals and poor signal-to-noise ratio; while high flux (high charge) can improve signal strength, it easily induces severe space charge effects and degrades resolution [5]. This contradiction is particularly acute in single-shot mode, limiting the detection of weakly scattering systems such as biological macromolecules and light-element samples 12]. Solutions focus on efficient beam utilization and the development of high-brightness electron sources.

Development of high-efficiency monochromator designs: Reverse bending magnets are adopted to optimize beam transmission efficiency. While maintaining energy resolution ($\frac{\Delta E}{E}$ ~ 10^{-5}), the transmission efficiency of the monochromator is increased from the traditional 13% to over 25%, reducing flux loss [6].

Development of ultra-high-brightness electron sources: Semiconductor photocathodes (such as GaAs-based cathodes) can reduce the thermal emittance of electron beams to several nm·rad (e.g., 5 nm·rad), improving beam brightness (>10^{12} A/(m²·sr)) while ensuring low space charge effects, thus balancing flux and temporal resolution [12, 14].

Adoption of direct electron detection cameras: Compared with traditional scintillator+CCD detection systems, the quantum efficiency of direct electron detection cameras is increased to over 70%, enabling high signal-to-noise ratio diffraction images at lower beam flux and reducing dependence on high-charge beams [16, 17].

Development of multi-pulse accumulation and coherent superposition techniques: In studies of reversible processes, signal strength is improved through cumulative averaging of millions of pulses; in coherent superposition techniques, diffraction signals from multiple low-charge pulses are

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coherently superimposed, avoiding space charge effects caused by high charge in a single pulse while ensuring signal flux [11].

4. Advanced application cases of UED (typical scenarios of "molecular movies")

Ultrafast Electron Diffraction (UED), relying on its unique pump-probe timing control mechanism and combining the dual advantages of femtosecond-scale temporal resolution and atomic-scale spatial resolution, overcomes the bottleneck that traditional characterization methods cannot capture transient dynamics. It can intuitively reconstruct the structural evolution, charge transfer, and energy transfer processes of matter on the femtosecond-to-picosecond scale in the form of "molecular movies". This technology transforms static diffraction patterns into dynamic time-series images, providing direct experimental evidence for cutting-edge research in condensed matter physics, photochemistry, quantum materials, accelerator physics, and other fields, and promoting innovative understanding of ultrafast dynamic mechanisms. The following elaborates on the advanced application achievements of UED in recording "molecular movies" around five typical scenarios.

4.1. Charge density wave and complex phase transition dynamics

The multi-dimensional competition among charge density waves (CDWs), Mott edge states, and pseudogap superconducting phases in quasi-two-dimensional transition-metal dichalcogenides—is this not an ideal platform for studying strongly correlated many-body systems? The answer is yes. With precise pump-probe timing control and extremely low background noise, UED has become the core technique for resolving the transient evolution of CDWs. In classical systems such as $NbSe_2$ and TaS_2, researchers used femtosecond laser excitation and high-energy electron beam probing to capture the full process of photoinduced quenching and relaxation recovery of CDW order at a limiting temporal resolution of 50 fs. Does this not clearly prove that strong electron-lattice coupling is the dominant mechanism driving CDW phase transitions? The answer is unquestionable. It provides the most intuitive "molecular movie" evidence for quantum state manipulation in strongly correlated systems [1, 8].

Moreover, the iterative advancement of ultrafast electron diffuse scattering has further expanded the application scope of UED. In systems such as Ni metal and WSe_2, researchers optimized electron beam quality and probe optics to suppress the space charge effect below 10%, greatly improving the signal-to-noise ratio and accuracy of diffraction signals. Momentum-resolved electron-phonon coupling dynamics were successfully observed, quantitatively characterizing phonon-mediated energy transfer across different momentum channels, and strengthening the theoretical framework of many-body interactions in two-dimensional quantum materials [2, 9].

4.2. Lattice thermalization and phonon transport

What exactly is the underlying nature of light-matter interaction and energy conversion hidden in laser-induced lattice thermalization and phonon transport? This question has long puzzled the academic community. Traditional characterization methods struggle to dynamically track nonequilibrium carrier cooling, lattice vibrational excitation, thermal diffusion, and other ultrafast processes—yet UED, with atomic-scale spatial resolution and femtosecond temporal resolution, precisely fills this gap. Taking laser-excited gold thin films as an example, UED records the full time series of lattice thermalization at 100 fs resolution: nonequilibrium hot carriers generated by pump pulses transfer energy to the lattice within an extremely short time, causing a rapid decay of the

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Debye-Waller factor; the lattice then expands isotropically, and thermal energy diffuses spatially via phonon transport. The entire dynamic process is resolved into 200 consecutive frames, allowing precise quantification of hot-carrier cooling rate, phonon group velocity, and thermal diffusivity, providing direct experimental support for ultrafast thermal dynamics modeling of metallic materials [8, 13].

In the modification of functional two-dimensional materials, the combination of UED and infrared vibrational spectroscopy demonstrates extraordinary power. Taking the photoreduction of graphene oxide as an example, the team distinguished acoustic vibrational modes corresponding to photoinduced and thermally induced reduction at sub-picosecond resolution. The "molecular movie" clearly reveals the selective cleavage and removal of epoxy groups and the evolution of lattice defects, offering direct experimental guidance for the precise optical modification of two-dimensional carbon materials [9, 14].

4.3. Molecular structural dynamics and photochemical reactions

The essence of photochemical reactions lies in bond breaking and reformation, yet the formation, structural isomerization, and evolution of transient intermediates — is this not one of the most difficult observational challenges in photochemistry? Indeed, traditional spectroscopy only provides indirect dynamic information, whereas UED directly reflects changes in molecular geometry through electron diffraction patterns, turning microscopic photochemical reactions into visible molecular movies and enabling accurate calibration of reaction coordinates. In the photodissociation of cyclopentadiene, a pump-probe UED system captures the entire bond-breaking process at 80 fs resolution: upon photoexcitation, the stable bicyclic structure becomes unstable and rapidly transforms into an open-ring radical intermediate, which further dissociates into final products. The complete structural evolution pathway from reactants, intermediates to products is fully reconstructed, and experimental results agree excellently with reaction coordinates from high-precision theoretical calculations, firmly verifying the reliability of the photodissociation mechanism [3, 8].

For sequential photochemical reactions in complex hybrid systems, the multimodal strategy combining UED and optical spectroscopy shines. In halogen-bonded hybrid systems, researchers integrated femtosecond spectroscopy and UED to record the sequential dynamics of spin crossover, radical formation, and dimer softening at femtosecond resolution. Key transient intermediates were located via "molecular movies", and their lifetime was measured to be approximately 3 ps, clarifying the halogen-bond-mediated spin-structure coupling mechanism and providing experimental guidance for designing novel photofunctional molecules [12, 16].

4.4. Ultrafast control in quantum materials

Composite quantum states protected by the Berry phase — such as topological insulating surface states and strongly spin-orbit-coupled Mott semiconductors — exhibit remarkable robustness against external fields. Yet who would have imagined that coherent optical depopulation could destroy or reconstruct topologically protected interfaces via nonadiabatic abrupt changes that break time-reversal symmetry? In Bi_2Se_3, UED microscopically captures the evolution of surface electronic order at 60 fs resolution: immediately after pump laser excitation, the topological protection of surface-state electrons is rapidly lost and the electronic structure reconstructs; driven by lattice relaxation and electron-phonon scattering, topological surface states recover within 200 fs. Lattice displacements directly validate the multiscale topological recovery competition model

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between photoinduced decoherence and driven phonon revival, successfully producing a "molecular movie" of optical-field-controlled surface electronic order [2, 9].

In laser plasma acceleration, UED has also achieved breakthrough applications in the dynamic characterization of relativistic electron bunches. Researchers used UED to record the spatiotemporal evolution of transverse charge density distributions, clearly revealing the correlation between laser polarization direction and beam asymmetry, and analyzing the divergence and compression behavior of electron beams in plasma environments, providing direct "molecular movie" data for optimizing beam quality in laser plasma accelerators [5, 14].

4.5. Non-invasive monitoring of large accelerator beams

The electron beam quality of large-scale free-electron laser (FEL) facilities directly determines the performance of light pulses. Yet traditional beam diagnostics suffer from invasive interference and insufficient temporal resolution, making real-time monitoring at MHz repetition rates impossible. Is there really no better way? Virtual diagnostic technology integrating UED principles and artificial intelligence algorithms provides exactly the new solution. At the European XFEL, a UED virtual diagnostic system based on conditionally guided diffusion models generates "molecular movies" of electron beam longitudinal phase space at MHz repetition rates with 1 ms temporal resolution, enabling real-time monitoring of key parameters such as beam broadening and energy spread induced by the space charge effect [4, 7].

This technique requires no direct beam sampling and completely avoids invasive disturbance to beam quality. Meanwhile, deep learning algorithms enable rapid diffraction pattern reconstruction and parameter inversion, providing real-time beam quality feedback critical for dynamic control of FEL pulses and ensuring stable temporal resolution in downstream ultrafast and structural biology experiments [6, 19].

5. Deficiencies and prospects

5.1. Existing deficiencies

Even though UED has made remarkable progress in "molecular movie" imaging, it still faces unavoidable core challenges.

Temporal resolution bottleneck: Attosecond-scale resolution remains limited by the space charge effect and synchronization jitter. The most advanced current systems only reach approximately 20 fs, still far from the attosecond target — is this not the most pressing technical shortcoming?

Incomplete suppression of space charge effects: In single-shot mode, when the charge exceeds 100 pC, pulse broadening caused by space charge exceeds 30%, making high charge and high temporal resolution incompatible.

Conflict between frame rate and image quality: High repetition rates easily damage samples, while low rates fail to capture short-lived intermediates. Moreover, the space charge effect further degrades the signal-to-noise ratio of diffraction signals, greatly weakening observational performance.

High system complexity: High-performance UED setups rely on large-scale accelerator platforms, which are costly and bulky, making them difficult to deploy in ordinary laboratories.

Difficult data processing: Multidimensional structural information must be extracted from each diffraction frame, yet efficient analysis algorithms are still lacking for amorphous and partially ordered systems, undoubtedly limiting the popularization of the technology [4, 10].

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5.2. Future prospects

Today, the development of UED has long moved beyond the initial stage of single-parameter optimization. Future breakthroughs will surely center on three goals: higher temporal resolution, weaker space charge effects, and higher-quality molecular movies.

Innovation in electron sources and acceleration technologies: High-gradient RF guns, superconducting guns, X-band guns, and novel schemes such as laser wakefield acceleration (LWFA) and terahertz acceleration will continue to evolve. LWFA can suppress the space charge effect below 5% and push temporal resolution beyond 10 fs; THz acceleration is perfectly synchronized with lasers, further reducing timing jitter and turning attosecond "molecular movies" from dream into reality [5, 11, 14].

Intelligent beam manipulation and diagnostics: Deep integration of artificial intelligence and machine learning is irresistible. Next-generation virtual diagnostic systems based on conditionally guided diffusion models enable real-time monitoring of dynamic space charge variations; adaptive feedback adjustment of electron gun parameters can improve temporal resolution stability by three times [4, 7].

Upgrading "molecular movie" capabilities: The combination of ultrafast electron energy-loss spectroscopy and diffraction will equip "molecular movies" with both structural and electronic state information, visualizing coupled structure-electron evolution. 4D UEM technology enables seamless switching between real-space imaging and diffraction modes, expanding spatial dimensions from 2D to 3D and directly revealing nanoscale inhomogeneous dynamics [1, 6, 8, 13].

Expanding application boundaries: Extreme conditions (high pressure, low temperature, strong fields) and complex systems (solid–liquid interfaces, living cells, heterostructures) will become new frontiers. Challenges such as the metallization of hydrogen under high pressure and the formation pathway of superconducting states at low temperatures are expected to be conquered one by one [4, 15].

Miniaturization and popularization: Tabletop UED systems are coming. Compact LWFA electron sources and low-cost virtual diagnostic modules can reduce the volume to 1/10 of traditional setups while maintaining temporal resolution within 100 fs, meeting routine "molecular movie" requirements and truly entering ordinary chemistry and biology laboratories [7, 11, 13].

Centered on the pump-probe scheme, UED continues to upgrade "molecular movie" quality through breakthroughs in temporal resolution and suppression of space charge effects, and has long been an indispensable tool for revealing the ultrafast microscopic evolution of matter [3]. It can be predicted that with continuous innovations in electron sources, detection techniques, and data analysis methods, UED will play an increasingly critical role in basic scientific research and cutting-edge technological development, pushing human understanding of the dynamic microscopic world to a new height [5, 6, 7, 8, 12].

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