

Self-Heterodyne Diffractive Imaging of Ultrafast Electron Dynamics Monitored by Single-Electron Pulses

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The direct imaging of time-evolving molecular charge densities on atomistic scale and at femtosecond resolution has long been an elusive task. In this theoretical study, we propose a self-heterodyne electron diffraction technique based on single electron pulses. The electron is split into two beams, one passes through the sample and its interference with the second beam produces a heterodyne diffraction signal that images the charge density. Application to probing the ultrafast electronic dynamics in Mg-phthalocyanine demonstrates its potential for imaging chemical dynamics.

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Ultrafast electron diffraction (UED) has been widely employed to probe molecular structural dynamics in space and time [1–12]. A pump optical laser pulse initiates an excited state dynamics and is followed by a probe electron pulse whose diffraction pattern reveals the time-evolving molecular charge density. The recent development of mega-electron-volt radio-frequency (rf) electron guns has enabled UED to monitor femtosecond molecular dynamics with atomistic spatial resolution [13–17]. Elaborate computational methods are required for retrieving the molecular charge density $\langle \hat{\sigma}(\mathbf{r}) \rangle$ from UED signals. This is because standard homodyne detection gives the expectation values of products of charge-density operators $\langle \hat{\sigma}^\dagger \hat{\sigma} \rangle$, [18] while obtaining a real-space image requires the charge-density matrix itself in momentum space, including the phase, which goes beyond the expectation value of the charge density $\langle \hat{\sigma} \rangle$ alone [19]. Heterodyne-detected UED requires an additional reference wave that interferes with the scattered wave and can directly measure the time-evolving molecular charge density $\langle \sigma \rangle$ itself. It has been recently shown that the purely nuclear charge density can be singled out by subtracting the heterodyne x-ray scattering signal that images the electron density from heterodyne electron scattering signal [20,21]. Other diffraction and imaging techniques have been developed recently. Electron microscopies that utilize near field electron diffraction and

homodyne detection can image the system with high space-time resolution [22,23]. Homodyne-detected x-ray diffraction probes the modulus square of electron charge density in momentum space [24,25]. Electron holography, a transmission electron microscopy method that records the interference of reference electron wave and an imaging wave, utilizes heterodyne-detected near field electron diffraction to image nanostructures [26–35]. Heterodyne-detected electron diffraction, as a far field electron diffraction, can achieve better spatial resolution down to picometer and can image the total electronic and nuclear charge density. However, the experimental implementation of heterodyne-detected UED remains a challenge.

Here, we introduce a novel self-heterodyned UED technique for imaging ultrafast molecular dynamics (Fig. 1), which employs a 1 fs single-electron pulse [36–40] followed by an electron biprism, which splits the beam into two [41–43]. The electron wave packet generated in one path interacts with the photo-excited molecular sample (signal path) and exchange momentum, while the other (reference path) traveling parallel to the signal path does not interact with the sample. A second electron biprism is finally used to combine the two paths, and the phase information of the scattered electron in the signal path can be reconstructed from the interference pattern. A detector monitors the electron and records the diffraction pattern, thereby measuring the interference of the two paths. The time-resolved signal is recorded by varying the time delay between optical pump pulse and single-electron probe pulse. In analogy to photon self-interference as explained by Dirac [44], the electron of the single-electron pulse interferes with itself. Since the relative phase of the two electron beam paths must be controlled in order to recover the phase of the signal, single-electron pulses that exclude

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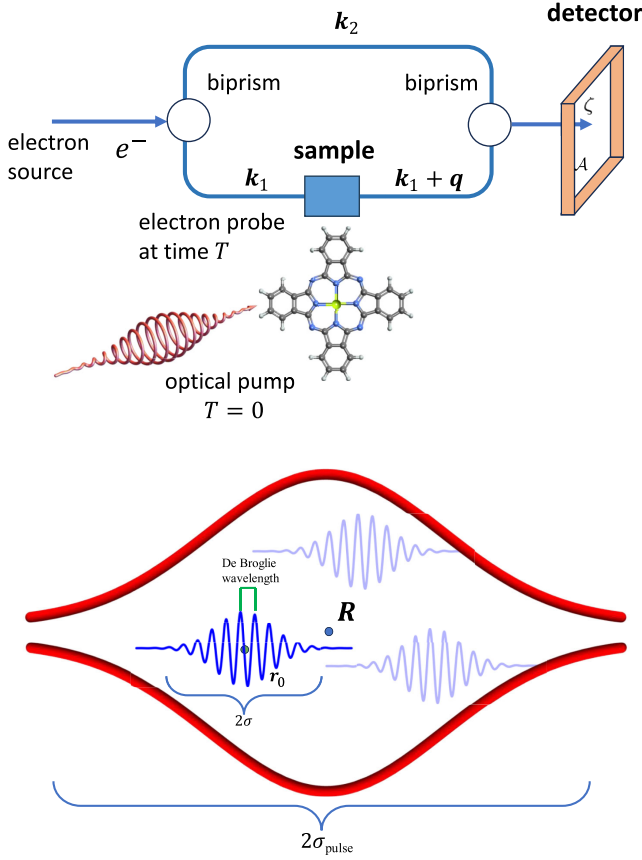


FIG. 1. Top: the self-heterodyned UED setup. The molecular sample is excited by an optical pump pulse at time 0. The electron source ejects a single electron, going through a biprism and separated into two replicas. One replica is scattered by the sample at time τ and changes its wave vector from \mathbf{k}_1 to $\mathbf{k}_1 + \mathbf{q}$. The other replica has wave vector \mathbf{k}_2 . The two interfere at the detector. Bottom: the single electron pulse at the reference time t_0 .

the interference of different electrons and remain coherent with themselves are most suitable for the proposed setup. In contrast, for multielectron pulses, when the beam electrons are incoherent, the interaction of incoherent electrons cannot recover the phase information. Besides the well-controlled phase information, single-electron pulses also overcome the space charge problem that limits the temporal duration of multielectron pulses [36–40,45]: due to Coulomb repulsion, multielectron pulses become longer during propagation from the source to the sample. Space charge is absent in pulses containing a single electron at a time. Femtosecond single-electron pulses with several keV electrons have been applied recently [46–48] to ultrafast microscopy and diffraction [45,49,50], demonstrating the feasibility of the proposed technique. Self-heterodyne diffraction can be alternatively performed with coherent multielectron pulses, where the pulse electrons remain coherent within the relevant spatiotemporal window [73,74], i.e., retain their phases. Measurements of electron diffraction with such multielectron pulses have improved

data collection. However, multielectron pulses do not have the femtosecond temporal resolution required for measuring ultrafast electronic dynamics in molecular systems. Single-electron pulses are thus ideal for ensuring coherence of the electron beam and for ultrashort time resolution.

Heterodyne-detected diffraction can image the charge density on atomistic scale and with femtosecond time resolution. We demonstrate this by simulating this signal for Mg-phthalocyanine (MgPc) electronic dynamics with frozen nuclei. The signal probes the charge density temporal evolution in the current migration process, where the coherent ring currents created by an optical pump pulse redistribute among different locations within the MgPc molecule [75]. Similar to charge migration [76–84], current migration is caused by the time evolution of a coherent superposition of excited states.

In the proposed pump-probe setup, as illustrated in Fig. 1, an optical pump at time 0, first launches the electronic dynamics. The sample molecule excited by the optical pump pulse evolves according to the time-dependent Schrödinger equation

$$i \frac{\partial |\psi(t)\rangle}{\partial t} = [H_{\text{mol}} - \boldsymbol{\mu} \cdot \mathcal{E}(t)] |\psi(t)\rangle, \quad (1)$$

where $\mathcal{E}(t)$ is the optical pump electric field, $\psi(t)$ is the electronic wave function that may be expanded as $|\psi(t)\rangle = \sum_A c_A(t) |\psi_A\rangle$, and A runs over ground state and excited states. The charge-density operator in real space is given by

$$\hat{\sigma}(\mathbf{r}) = e \left(\sum_{\alpha} Z_{\alpha} \delta(\mathbf{r} - \mathbf{R}_{\alpha}) - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right), \quad (2)$$

Here, Z_{α} and \mathbf{R}_{α} are nuclear charges and coordinates, α runs over the nuclei, \mathbf{r}_i is the coordinate of electron i , and e is unit charge. The real-space charge density at time t is given by $\sigma(\mathbf{r}, t) = \langle \psi(t) | \hat{\sigma}(\mathbf{r}) | \psi(t) \rangle$, or in momentum space,

$$\tilde{\sigma}(\mathbf{q}, t) = \int_{\mathbb{R}^3} d\mathbf{r} e^{-i\mathbf{q} \cdot \mathbf{r}} \sigma(\mathbf{r}, t). \quad (3)$$

The total time-dependent charge density can be decomposed as

$$\tilde{\sigma}(\mathbf{q}, t) = \sum_{A \in g_{\text{Jex}}} \rho_{AA}(t) \tilde{\sigma}_{AA}(\mathbf{q}) + \sum_{A, B \in g_{\text{Jex}}, A \neq B} \rho_{AB}(t) \tilde{\sigma}_{AB}(\mathbf{q}), \quad (4)$$

where A, B denote the electronic states, $\rho_{AB}(t) = c_A^*(t) c_B(t)$ is the density-matrix element. $\rho_{AA}(t)$ is the population of state A , while $\rho_{AB}(t)$ is the coherence between states A, B . The optical pump brings the system from the ground state to a superposition of excited states via the electric dipole interaction, Eq. (1). When the pump

pulse is over, the populations are stationary, while the electronic coherences ρ_{AB} oscillates with a period $[h/(E_A - E_B)]$, reflecting the difference of phase evolution of states A and B . The time-dependent charge density is thus solely attributed to electronic coherences.

The electron source ejects the probe electron, which is then split by an electron biprism into two beams. At a reference time t_0 before the probe electron interacts with the sample, the probe electron density matrix is $\rho_f(\mathbf{r}_1, \mathbf{r}_2; t_0)$ [or $\rho_{\mathbf{k}_1, \mathbf{k}_2}(t_0)$ in momentum space]. Starting at time t_0 , the probe electron $\rho_{\mathbf{k}_1, \mathbf{k}_2}(t_0)$ propagates in the two beams. Electron beam 1 propagates according to the Coulomb potential created by the sample charge density,

$$u(\mathbf{r}, \tau) = \int_{\mathbb{R}^3} d\mathbf{r}_\mu \frac{\langle \sigma(\mathbf{r}_\mu, \tau) \rangle}{|\mathbf{r} - \mathbf{r}_\mu|}, \quad \tilde{u}(\mathbf{q}, \tau) = 4\pi \frac{\langle \tilde{\sigma}(\mathbf{q}, \tau) \rangle}{q^2}, \quad (5)$$

scatters off the sample at time τ , changing its wave vector from \mathbf{k}_1 to $\mathbf{k}_1 + \mathbf{q}$. Beam 2 propagates freely with a fixed wave vector \mathbf{k}_2 . The magnitude distribution of the \mathbf{k}_2 is narrow, however its direction distribution should be wide enough to cover the range of \mathbf{q} . This interaction is described in Supplemental Material [50], Fig. S1. Treating the Coulomb potential Eq. (5) perturbatively, the probe electron density matrix at a later time t , $\rho_{\mathbf{k}_1 + \mathbf{q}, \mathbf{k}_2}(t)$ is calculated in Liouville space, as explained in Supplemental Material. Finally, the electron counting detector captures the probe electron from the two beams and measures the electron flux. Truncating the perturbative expansion of the density matrix to first order in the electron-sample interaction, we obtain the electron density matrix at time t , given as Eq. (S16) in Supplemental Material. By integrating the current density on surface \mathcal{A} on the detector to calculate the electron flux, we obtain the expression for the electron diffraction signal at time t_D ,

$$\mathcal{S}_0(\mathcal{A}; \mathbf{q}; t_D) = \frac{ie}{\hbar} \int_{t_0}^{\infty} d\tau \frac{\langle \tilde{\sigma}(\mathbf{q}, \tau) \rangle}{q^2} W_0(\mathcal{A}; t_D, \mathbf{q}, \tau) + c.c., \quad (6)$$

where W_0 is the window function defined in Eq. (S22). Details of the window function are discussed in Sec. S2 of Supplemental Material.

The signal that reveals the time-dependent charge density in q space convoluted with the window function depends on the detection time t_D , the wave vector \mathbf{q} , and the detector area \mathcal{A} . Here, the single electron pulse diffraction signal is derived by neglecting the Coulombic interaction between the electrons in the pulse. This derivation also holds for multielectron pulses provided the number of electrons in the pulse is low and their Coulombic interaction can be neglected.

In the interaction of the probe electron and the sample, we neglected the contribution of inelastic scattering that involves vibrational state changes. We have also neglected the free-free transition where an electron passing close to an ion accelerates, and the laser assisted electron scattering where the probing electron is scattered by neutral matter in the process of laser, since the electron and the laser pulse have no temporal overlap in this proposed experiment.

The present self-heterodyne electron diffraction technique can be applied to single molecule or molecules aligned in periodic structure, preferably on a single layer of molecular film on lattice position, since the random orientation or position of molecules will make the self-heterodyne signal vanish. For a periodic sample, the diffraction signal Eq. (6) becomes a function of discrete value of $\mathbf{q} \in L_B$, where L_B is the periodic structure's corresponding Bragg lattice [Eqs. (S17),(S18)]. When the focal point of the electron beam is at the molecular location that only covers a single molecule, the measurement of a periodic system is equivalent to single molecule diffraction.

To obtain an analytical form for the window function, we assume that the probe electron has a Gaussian profile around the reference time t_0 . The heterodyne electron diffraction of the single electron pulse should be measured repeatedly to accumulate enough signal strength for the detection of the diffraction pattern [39]. For each single electron pulse, the position of the Gaussian center \mathbf{r}_0 has a random variation [39]. We thus describe the probe electron as an ensemble of single electron pulses described by a mixed-state density matrix at time t_0 ,

$$\rho(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2\pi}\sigma_{\text{pulse}}} \int d\mathbf{r}_0 \exp\left[-\frac{(\mathbf{r}_0 - \mathbf{R})^2}{2\sigma_{\text{pulse}}^2}\right] \rho^{\text{pure}}(\mathbf{r}_1, \mathbf{r}_2). \quad (7)$$

This contains the pure state density matrix (ρ^{pure}) of Gaussian wave packet centered at \mathbf{r}_0 , whose wave function in real space is

$$\phi(\mathbf{r}) = \frac{1}{\sqrt{2\pi}\sigma} e^{-ik_0 r} \exp\left[-\frac{(\mathbf{r} - \mathbf{r}_0)^2}{2\sigma^2}\right], \quad (8)$$

while its center \mathbf{r}_0 is distributed around \mathbf{R} with a Gaussian weight factor $\exp\{-[(\mathbf{r}_0 - \mathbf{R})^2/2\sigma_{\text{pulse}}^2]\}$, as depicted in the lower panel of Fig. 1. Here, \mathbf{k}_0 is the average electron wave vector, σ denotes the spatial width of single electron at the reference time, σ_{pulse} is the width of the Gaussian wave center \mathbf{r}_0 distribution. We use the same width in the longitudinal and transverse directions. We further used an electron average energy of $E_0 = 100$ keV, $|\mathbf{k}_0| = 85.7$ (\hbar/a_0), where a_0 is Bohr radius, c is the speed of light and m_0 is electron mass. Its De Broglie wavelength 3.88 pm, determines the spatial resolution, i.e., the upper

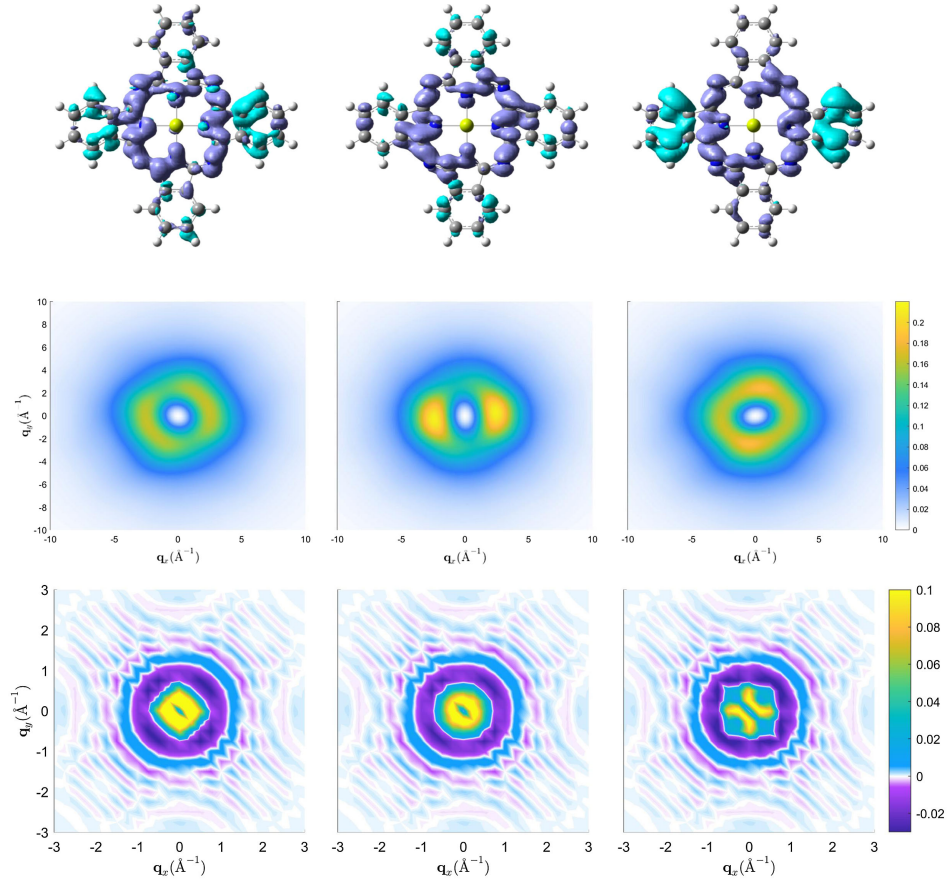


FIG. 2. Top row: real space charge density at time τ minus the charge density at the initial time step, $[\sigma(\mathbf{r}, \tau) - \sigma(\mathbf{r}, -3.9 \text{ fs})]$. Second row: the real part of charge density in q -space, $(\Re[\tilde{\sigma}(\mathbf{q}, \tau) - \tilde{\sigma}(\mathbf{q}, -3.9 \text{ fs})])$. Analytical integral Eq. (3) is evaluated with the algorithm of Ref. [92]. Third row: the diffraction signal $[S'_0(\mathbf{q}; t_D) - S'_0(\mathbf{q}; -3.9 \text{ fs})]$. The first, second, and third columns are at times 2.1 fs, 8.1 fs, 17.1 fs, respectively.

limit of $|\mathbf{q}|$ in the diffraction pattern. \mathbf{R} is set at the origin, while $\sigma = 22.066 \text{ \AA}$, $\sigma_{\text{pulse}} = 1103.3 \text{ \AA}$. The probe pulse duration 1.18 fs is the pulse length ($2\sigma_{\text{pulse}}$) divided by electron velocity. The electron coherence time is given by its coherence length (2σ) divided by its velocity, 0.047 fs. The window function is Eq. (S42) in Supplemental Material. Using Eq. (6), we define the signal as

$$S'_0(\mathbf{q}, \mathcal{A}; t_D) = \mathbf{q}^2 S_0(\mathbf{q}, \mathcal{A}; t_D). \quad (9)$$

We have applied this technique to probe the electronic dynamics in Mg-phthalocyanine (MgPc) initiated by a circularly polarized light pump pulse. Details of the dynamics are discussed in Supplemental Material and in Refs. [50,75]. Phthalocyanines have many applications in, e.g., dye-sensitized solar cells [85,86] and as photosensitizers for cancer photodynamic therapy [87]. MgPc has a rigid structure, which remains stable upon electronic excitation [88,89]. It is a planar molecule consisting of a center porphyrin ring and four corner benzene rings (see Fig. 1). Its high density of excited states in the 2 to 4 eV

regime, facilitates the coherent excitation of multiple excited states by a broadband pump pulse [75]. The circularly polarized pump drives the electron in the conjugated π bond moving in a circle, resulting in ring currents proportional to the electronic state coherence, $\mathbf{j}(t) = \sum_{A,B,A \neq B} \rho_{AB} \mathbf{j}_{AB}$, where \mathbf{j}_{AB} is transition current density, analogous to the coherent charge density in Eq. (4). These coherent ring currents vary with time due to the superposition of multiple electronic states. Since different coherent currents have distinct spatial profiles, some concentrated in the central ring while others reside in the corner rings, the ring currents redistribute among different regions of the molecule with time, resulting in a current migration process between the central and the corner rings [75]. Similar to current migration, the interplay of coherent charge-density oscillations induced by multiple pairs of coherences causes the dynamics of charge density, i.e., the charge density redistributes among the central porphyrin and the corner benzene rings, as depicted in the first row of Fig. 2 and Fig. S2 in Supplemental Material. The charge density is more pronounced on the central ring and left and right rings, and moves to the top and bottom

rings, and back. Such change can also be reflected in the real part of q -space charge density (second row of Fig. 2) and the diffraction pattern (third row of Fig. 2). Although electron diffraction does not directly image the current density, it images the charge density, originating from the same electronic coherence ρ_{AB} . However, the continuity relation $-(\partial\rho/\partial t) = \nabla \cdot \mathbf{j}$ connects the time evolution of the charge density to the divergence of the current density [90,91].

Figures S2 and S5 display the charge density in real space and the diffraction pattern of the system prior to the pump pulse where no current density exists. First row of Fig. 2 depicts the charge-density difference $[\sigma(\mathbf{r}, \tau) - \sigma(\mathbf{r}, -3.9 \text{ fs})]$, where the charge density at time -3.9 fs before the pump is subtracted from the charge density at time τ . The second row displays the charge density difference in q -space $\tilde{\sigma}(\mathbf{q}, \tau) - \tilde{\sigma}(\mathbf{q}, -3.9 \text{ fs})$, while the third row depicts the diffraction signal difference $\mathcal{S}'_0(\mathbf{q}, \mathcal{A}; t_D) - \mathcal{S}'_0(\mathbf{q}, \mathcal{A}; -3.9 \text{ fs})$. The diffraction signal is simulated by convoluting the charge density and the instrumental window function. The window function has both real and imaginary parts. Once integrated over the charge density, both parts contribute to the diffraction pattern. The real (imaginary) part of the charge density is an even (odd) function of \mathbf{q} [see Eq. (3)]. We find that the resulting diffraction pattern is dominated by the stronger real part.

During the optical pump, the excited state population ρ_{AA} increases, inducing a population ring current [75,93] and charge density [first term in Eq. (4)]. Since the electronic state population is time-independent once the pump pulse is over, the time dependence of the signal after the optical pump pulse only comes from electronic coherences. If the pump has a narrow bandwidth that only covers one pair of excited state and one coherent ring current like in Refs. [93–95], the corresponding coherent ring current and coherent charge density oscillate with the coherence, i.e., the coherent current density reverses direction while the coherent charge density changes sign at the frequency of coherence. For a broad band pump, the superposition of multiple pairs of coherence causes current migration and a redistribution of charge density among different regions of the molecule, as seen in the diffraction signal Fig. 2 and Supplemental Material Fig. S5. The electronic dynamics involves excited states of irreducible representation E_u . Since E_u in D_{4h} point group has character -2 with respect to inversion, the charge-density change is symmetric for inversion. For this reason, the charge-density change of the electronic dynamics in real space has a central symmetry. The diffraction signal integrates the window function and the momentum-space charge density. The real (imaginary) part of $\tilde{\sigma}(\mathbf{q}, \tau)$ is central symmetric (antisymmetric). The resulting diffraction pattern has central symmetry, as the real part of window function dominates. The diffraction signal changes mostly occur within -2 to 2 \AA^{-1} , since the

window function decays rapidly for larger $|\mathbf{q}|$. The diffraction signal is thus only clear when the scattering wave vector $|\mathbf{q}|$ is smaller than some threshold. To measure the signal in a broader range of \mathbf{q} , higher energy single-electron pulses should be employed.

In a future study, we will apply relativistic theory for describing higher energy probing electrons and simulating their self-heterodyne diffraction signal. Reconstruction of the real-space charge density from the diffraction signal requires the inverse Fourier transform of the three-dimensional momentum-space charge density $\tilde{\sigma}(\mathbf{q}, \tau)$. The diffraction signal integrates the window function with $\tilde{\sigma}(\mathbf{q}, \tau)$, thus mixing its real and imaginary parts. Obtaining $\tilde{\sigma}(\mathbf{q}, \tau)$ requires: (1) measuring the diffraction signal at various q_z ; (2) performing phase-shifting [43,96–98] measurement, i.e., varying the relative phase of the signal and reference electron beam to separately obtain real and imaginary parts of the complex valued function; (3) deconvoluting the window function.

In summary, we have proposed a self-heterodyne electron diffraction method for imaging the molecular charge density in real time and space. A single probe electron is split into two beams, where only one travels through the sample. The diffraction signal is obtained by the interference of these two paths. This ultrafast imaging of the charge density in q space can monitor electron dynamics in real time. It is demonstrated by simulating the time-resolved signal of MgPc electronic dynamics initiated by a UV-visible circularly polarized light pulse. The proposed technique is not limited to probing electronic dynamics like current and charge migration, but can be also applied to the imaging of various light-induced ultrafast chemical processes.

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