

Attosecond diffraction imaging of electron dynamics in solids

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Visualizing the electron dynamics in four dimensions of space and time is crucial to the understanding of several ubiquitous processes in nature. Hence, ultrafast x-ray and electron imaging tools have been developed to probe the dynamics of matter by means of the time-resolved diffraction imaging (TRDI). In this work, we report an extension of the theory underlying the TRDI to the case of the laser-driven electron dynamics in solid-state systems. We demonstrate that the TRDI signal encodes essential information about the time-dependent electron density of the system under study and thus makes it possible to decipher the ultrafast quantum dynamics and the electron transfer phenomena in solids. We apply the developed approach to image the laser-driven electron dynamics in neutral graphene showing that the predictions made by the fully quantum version of the TRDI deviate significantly from those obtained with the conventional semiclassical approach.

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Recent advancements in attosecond technologies [1] have facilitated the observation and eventually control of ultrafast electron dynamics in atoms [2], clusters [3], molecules [4–6], liquids [7], and solids [8,9] with unprecedented resolution. However, the majority of previously utilized techniques, such as high-harmonic generation (HHG) [5], attosecond transient absorption [6], and photoelectron [10] and photofragmentation [4,11] spectroscopies, are specifically designed to capture the temporal evolution of a system but often provide insufficient information about the electron dynamics in the space domain.

Established experimental techniques that have been used for over a century to image the spatial structure of matter are x-ray [12,13] and electron diffraction [14–17] spectroscopies. With the advent of free-electron lasers [18,19] it is now possible to generate short coherent pulses in x-ray energy domain permitting thus direct observations of dynamics of matter with atomic spatial resolution. Even better temporal resolution has been recently demonstrated in attosecond electron diffraction microscopy experiment measuring the electron dynamics in the neutral multilayer graphene [20]. This attomicroscopy setup together with the free-electron laser facilities provide access to long-awaited real-space imaging of electron motion in matter on its natural time scales.

Theoretical description of x-ray and electron scattering from matter has been widely studied before [21,22]. A traditional semiclassical (SC) approach to connect the scattering signal with the properties of a system under study is based on a simple relation between the electron density $Q(\mathbf{r})$, where $\mathbf{r}$ denotes the real-space coordinate, and the intensity of the scattered beam $I(\mathbf{S})$, where $\mathbf{S}$ is the scattering vector. Under the first Born approximation and assuming the scattering is elastic, the scattering intensity is proportional to the absolute value of the Fourier transform of the electron density [21,22]: $I(\mathbf{S}) \propto |\hat{\mathcal{F}}_{\mathbf{S}}[Q(\mathbf{r})]|^2$, where $\hat{\mathcal{F}}$ denotes the Fourier transform operator. While in the past the computation of the electron density of a system $Q(\mathbf{r})$ was a complex problem by itself, the ever-growing computational power made the simulations of the ground-state electron density a routine task which, in turn, permitted the high-accuracy calculations of the scattering signal from complex systems.

Extending the SC approach to the case of a time-dependent target, one could assume that the intensities of the scattered beams will reflect the dynamics of the electron density in a similar manner [23–25]: $I(\mathbf{S}, t) \propto |\hat{\mathcal{F}}_{\mathbf{S}}[Q(\mathbf{r}, t)]|^2$. Indeed, if the duration of the probe pulse is much shorter than the time scale of the electron motion underlying the evolution of the electron density $Q(\mathbf{r}, t)$, the SC formalism seems to be a natural choice. The SC approach has been widely used in the recent past to describe the time-resolved diffraction imaging (TRDI) in atoms [26,27], molecules [26,28], and solids [29]. Even though its simplicity makes the SC methodology appealing, this approach has proven to be incomplete for describing the diffraction in the ultrafast regime as we explain next.

A more careful consideration of the physics behind the time-resolved scattering process revealed fundamental issues with the applicability of the SC approach to the case

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of the scattering from a time-dependent system. In their pioneering work [30], Dixit and coworkers utilized a consistent description of light-matter interactions in the frame of quantum electrodynamics and employed the time-dependent perturbation theory to demonstrate that the time-resolved x-ray-scattering cross section deviates significantly from its SC analog. It has been shown [30,31] that the scattering signal at particular time instance t is related to a special form of the so-called density-density correlation function $\langle \Psi(t + \tau/2) | \hat{\rho}(\mathbf{r}') e^{-i\hat{H}\tau} \hat{\rho}(\mathbf{r}) | \Psi(t - \tau/2) \rangle$, where $|\Psi\rangle$ denotes the time-dependent wave function of the system evolving according to the Hamiltonian $\hat{H}$, $\hat{\rho}(\mathbf{r})$ and $\hat{\rho}(\mathbf{r}')$ are density operators, and the parameter τ accounts for the propagation of the probe pulse through the system. In parallel, Shao and Starace developed the theory of the time-resolved electron diffraction imaging using a more conventional approach based on the Lippmann-Schwinger equation under the first-order Born approximation [32]. While the chosen pathways for treating the time-dependent x-ray and electron scattering were different from each other, both led to the similar conclusion that the time-dependent diffraction in an ultrafast regime has a little overlap with the conventional SC approach. These fully quantum mechanical (QM) approaches to the x-ray and electron TRDI, QM-TRDI, have been applied to probe the pure electronic dynamics in atomic [30–39] and molecular systems [40–44], and also nonadiabatic molecular transitions at avoided crossings and conical intersections [45–49]. Interestingly, the applications of the QM-TRDI to solid-state systems have not been reported yet. This is especially surprising in view of the fact that the x-ray diffraction imaging as well as the electron microscopy have been initially invented [50,51] and then very successfully used [52,53] for studying the structure and properties of crystals for more than a hundred years.

In this Letter, we extend the theory underlying the QM-TRDI to the case of the laser-driven electron dynamics in solid-state systems. We show that under certain assumptions the x-ray and electron QM-TRDI are identical to each other up to a prefactor. We demonstrate that the simulations based on the QM-TRDI deviate substantially from that performed with more conventional SC-TRDI approach. We apply the developed formalism to probe the ultrafast laser-driven electron dynamics in neutral graphene, showing the possibility to trace the dynamics of the electron density, and thus demonstrate that the QM-TRDI can be a very useful technique to study the ultrafast electron motion in solids.

The choice of graphene is motivated by several reasons. First of all, graphene is one of the simplest solids which makes it computationally affordable to perform fully quantum modeling of the laser-driven electron dynamics and the subsequent simulations of the diffraction signal. Second, graphene has been extensively studied theoretically and thus both the electronic structure [54] and the laser dynamics [55–58] in this system are well understood. Furthermore, Yakovlev and coworkers demonstrated the application of the SC-TRDI to the case of graphene and identified certain characteristic features in their calculated diffraction signal [29]. Finally, and this is our third reason to study graphene, the electron dynamics in this system has been recently recorded experimentally by means of the attosecond electron diffraction [20] (see also

Refs. [59,60]). Importantly, the measured diffraction signal contradicts with the SC-TRDI simulations made by Yakovlev *et al.* [29]. Therefore, graphene turns out to be a perfect system to test the validity of the QM-TRDI approach and explain the difference between the previous theoretical simulations and the experimentally measured results.

Graphene is a monolayer material composed of carbon atoms arranged in a two-dimensional hexagonal honeycomb-lattice structure [54]. Each carbon atom of graphene possesses six electrons while four of them participate in the formation of valence bonds. Three of these (the so-called σ electrons) form tight bonds with the neighboring atoms in the plane while the fourth electron participates in the formation of π (bonding) and π^* (antibonding) bonds that lie above and below the plane formed by atomic nuclei. The unique structure and interactions of these delocalized π and π^* orbitals of graphene made this material a holy grail of solid-state physics attracting ever-growing interest from the community.

The electronic structure of graphene can be described using a rather simple tight-binding model, leading to analytical solutions for the band energies, related eigenstates, and the corresponding electric-dipole matrix elements connecting these states with each other. Taking only π electrons into account, we form the two-band system consisting of the valence and the conduction bands of graphene (see Secs. I and II of the Supplemental Material (SM) [61] for details). These bands are highly symmetric in reciprocal space and touch each other at the so-called Dirac points forming thus conical intersections [54]. In case of graphene, the intersection points lie exactly at the Fermi level making this material a semimetal (zero-gap) character and leading to an enhanced transition probability from one band to the other at these points. Accordingly, in the following we will focus on the laser-driven electron dynamics occurring in the vicinity of the Dirac points of graphene.

We calculated the evolution of the electron density in reciprocal space of graphene driven by the interaction of the system with a laser field of the following wave form: $\mathbf{E}(t) = eE_0 \sin^4(\pi t/\tau) \cos(\omega t)$, where the peak field amplitude E_0 is chosen to be 2.5 V/nm, pulse duration τ is 21 fs, the photon energy ω is 1.55 eV which corresponds to the wavelength of 800 nm, and $\mathbf{e}$ denotes the unit vector in the direction of the field polarization. The chosen laser-pulse parameters are comparable to those utilized in the recent experiment in Ref. [20]. We numerically solved the semiconductor Bloch equation employing the dipole approximation and utilizing the time-dependent crystal-momentum frame evolving according to the Bloch acceleration theorem [62,63] $\mathbf{k}_t = \mathbf{k}_0 + e/\hbar \mathbf{A}(t)$, where e is the electron charge, $\mathbf{k}_t$ and $\mathbf{k}_0$ denote the time-dependent and the field-free reciprocal space vectors, respectively, and $\mathbf{A}(t) = -\int_{-\infty}^t \mathbf{E}(t') dt'$ is the vector potential associated with the applied laser pulse $\mathbf{E}(t)$. The detailed description of the employed computational procedure can be found in Sec. V of SM [61].

The action of the external field on graphene causes population transfer between the valence and conduction bands via two distinguishable mechanisms: (i) direct photon absorption occurring in the regions of reciprocal space where the energy gap between the bands matches the photon energy ω , and (ii) the so-called Landau-Zener transitions [64,65] resulting from

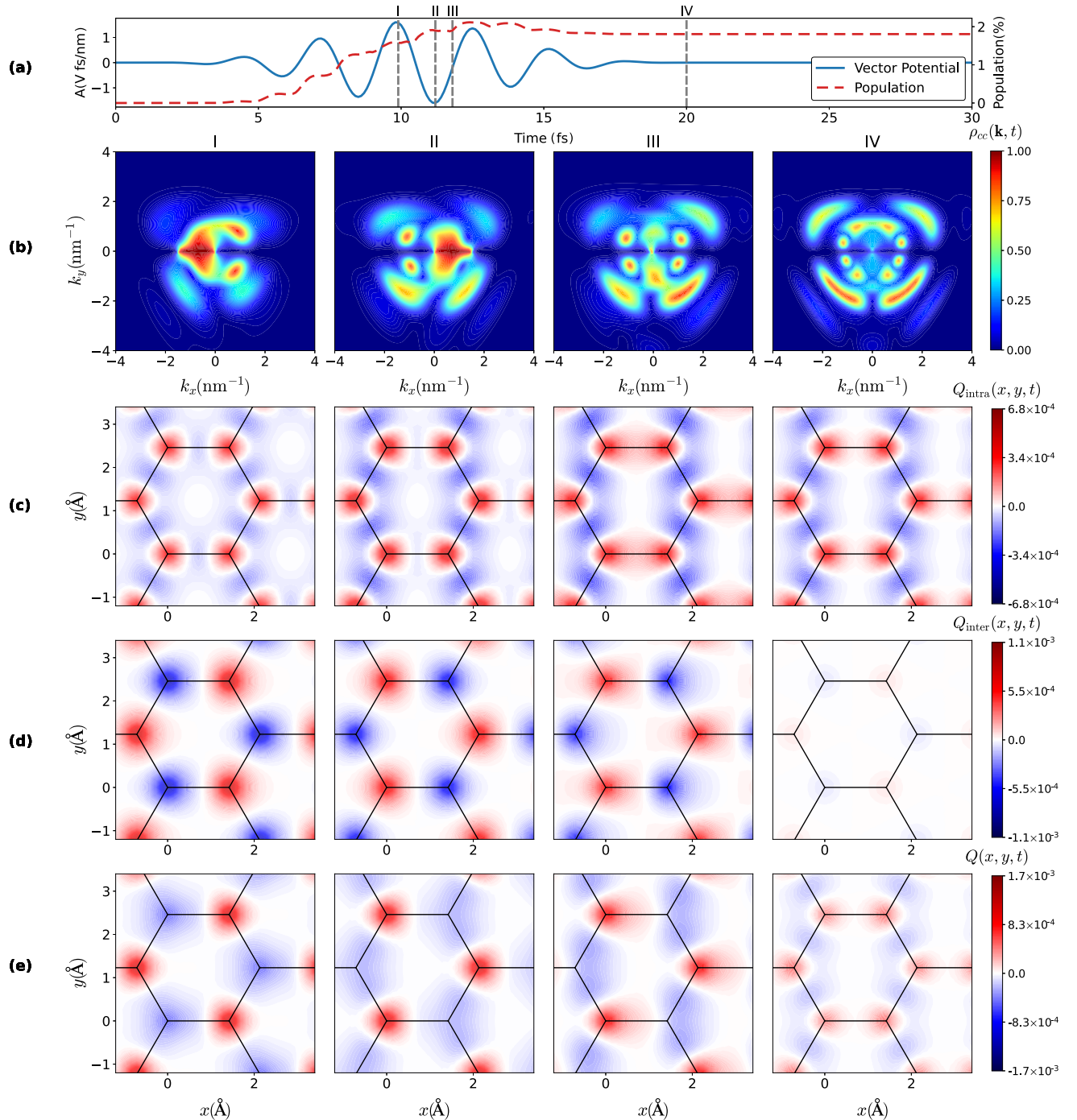


FIG. 1. Light-driven electron dynamics in graphene. (a) The blue curve represents the vector potential of the pump-laser field, while the red line depicts the evolution of the population of the conduction band of graphene. (b) The snapshots of the electron-density distribution in the reciprocal space of graphene in the vicinity of the Dirac point placed at the origin. The four columns depict the time instances $t_I = 9.8$ fs, $t_{II} = 11.2$ fs, $t_{III} = 11.8$ fs, and $t_{IV} = 20.0$ fs, indicated by the vertical grey dashed lines in (a). (c)–(e). The corresponding integrated real-space intraband, interband, and the total electron-difference densities, respectively, for the same time instances shown in (a) and (b).

the transfer of electrons through conical intersections in the vicinity of Dirac points. Figure 1 summarizes the results of the electron dynamics driven by the laser pulse described above and which is polarized along C–C bonds of the graphene sample (x direction in our simulations). The panel (a) of Fig. 1 depicts the vector potential $A(t)$ (blue solid line) and the corresponding population of the conduction band of graphene integrated over the unit cell in the reciprocal space (red dashed

line). As one can see, the population dynamics occurs continuously along the action of the field leading to about 2% electron transfer between the valence and conduction bands.

The panel (b) of Fig. 1 shows the snapshots of the matrix element $\rho_{c,c}(\mathbf{k}, t)$, where the index c denotes the conduction band, of the reciprocal space-density matrix $\rho(\mathbf{k}, t)$ in the vicinity of the Dirac point located at the origin. It is seen that the electron density is displaced towards negative values of

k_x direction when the vector potential is positive [snapshot I in Fig. 1(b), taken at $t_I = 9.8$ fs as indicated by the vertical dashed line in the panel (a)] and towards positive values of k_x when the sign of the vector potential is reversed (snapshot II, $t_{II} = 11.2$ fs). Importantly, at the moments of time when the vector potential is zero either during the action of the field (snapshot III, $t_{III} = 11.8$ fs) or when the field is over (snapshot IV, $t_{IV} = 20$ fs), the electron density in the reciprocal space remains symmetric with respect to the vertical line passing through the conical intersection.

The calculated reciprocal space-density matrix $\rho(\mathbf{k}, t)$ gives access to the real-space time-dependent electron density $Q(\mathbf{r}, t)$:

$$Q(\mathbf{r}, t) = \frac{1}{\mathcal{N}} \sum_{n,m} \int_{\text{unit cell}} \rho_{n,m}(\mathbf{k}, t) Q_{m,n}(\mathbf{k}, \mathbf{r}) d\mathbf{k}, \quad (1)$$

where the indices n and m iterate over the valence (v) and conduction (c) bands, the integration is performed over the unit cell in the reciprocal space, $\mathcal{N}$ is the normalization factor accounting for the volume of the unit cell and the number of active electrons [$\mathcal{N} = (2\pi)^2/\sqrt{3}a^2$ for graphene, where $a = 2.46$ Å is the lattice constant], and $Q_{m,n}(\mathbf{k}, \mathbf{r})$ denote the $\mathbf{k}$ - and $\mathbf{r}$ -resolved electron densities of π/π^* bands ($m = n = v/c$, respectively), or the corresponding transition densities connecting the bands with each other ($m \neq n$). The total real-space electron density $Q(\mathbf{r}, t)$ can be decomposed in two contributions: $Q(\mathbf{r}, t) = Q_{\text{intra}}(\mathbf{r}, t) + Q_{\text{inter}}(\mathbf{r}, t)$, where the first term $Q_{\text{intra}}(\mathbf{r}, t)$ represents the diagonal portion of Eq. (1) ($n = m \in \{v, c\}$) and thus is referred to as the intraband electron density, while the second term $Q_{\text{inter}}(\mathbf{r}, t)$ is composed from the off-diagonal elements responsible for the coherent interband electron motion (see Sec. I of SM for the detailed derivation [61]). In the follow-up discussion we will use the real-space electron-difference densities (EDDs) integrated over z axis for convenience: $Q(x, y, t) = \int [Q(\mathbf{r}, t) - Q(\mathbf{r}, 0)] dz$, where we removed, in addition, the static portion of the density to make the corresponding figures more representative.

The panels (c), (d), and (e) of Fig. 1 depict the snapshots of the intraband $Q_{\text{intra}}(x, y, t)$, interband $Q_{\text{inter}}(x, y, t)$, and the total $Q(x, y, t)$ EDDs for the same time instances I, II, III, and IV discussed before. As one can see, the intraband EDDs for time instances I and II [columns I and II in Fig. 1(c)] are nearly identical to each other up to a scaling factor reflecting the difference in the overall population of the conduction band. At the same time, the corresponding reciprocal space densities [Fig. 1(b), I and II] mirror each other with respect to the y axis passing through the origin as we already discussed in the previous paragraph. The identical real-space EDDs for the distinguishable reciprocal space densities arise due to the symmetry of the $Q_{m,n}(\mathbf{k}, \mathbf{r})$ densities with respect to the Dirac point in graphene. In a difference, the corresponding interband EDDs, shown in Fig. 1(d), I and II, are antisymmetric with respect to each other. Accordingly, the total EDDs for time instances I and II [Fig. 1(e), I and II], which are combinations of the intra- and interband contributions, are also antisymmetric yet qualitatively identical to each other. The intraband EDDs for time instances III and IV are also similar to each other [Fig. 1(c), III and IV], same as the corresponding reciprocal

space densities [Fig. 1(b), III and IV]. We note, however, a significant difference between the intraband EDDs and the reciprocal space densities for time instances I/II and III/IV, respectively. The interband EDD at time instance IV [Fig. 1(d), IV] has nearly disappeared due to the fast decoherence of the matrix element $\rho_{vc}(\mathbf{k}, t)$ and its complex conjugate. As the result, the total EDD is composed almost entirely from the intraband component shortly after the action of the pulse on the system is over [see Fig. 1(e), IV]. The complete movie of the laser-driven electron dynamics in graphene can be found in SM Video I [61].

Utilizing the formalism discussed above, the intensities of Bragg diffraction peaks in the SC-TRDI approximation can be expressed as

$$I_{\text{SC}}(\mathbf{S}, t) = |\hat{\mathcal{F}}_{\mathbf{S}}[Q(\mathbf{r}, t)]|^2$$

$$= \frac{1}{\mathcal{N}} \left| \sum_{n,m} \int_{\text{unit cell}} \rho_{n,m}(\mathbf{k}, t) \hat{\mathcal{F}}_{\mathbf{S}}[Q_{m,n}(\mathbf{k}, \mathbf{r})] d\mathbf{k} \right|^2, \quad (2)$$

where the scattering vector $\mathbf{S} = h\frac{2\pi}{a}(1/\sqrt{3}, 1) + l\frac{2\pi}{a}(1/\sqrt{3}, -1)$ is composed from the corresponding reciprocal space vectors of graphene, and h and l are integers (see Sec. III of SM for details [61]). We note that in the semiclassical regime the x-ray and electron scattering amplitudes are different from each other only by a $1/|\mathbf{S}|^2$ prefactor which we eliminate in the further discussion by considering the scattering intensities in units of the scattering from a free electron. We simulated the SC-TRDI for the first-order Bragg peaks of graphene. Due to the high symmetry of the graphene structure, which is reflected in the corresponding symmetries of the Fourier transforms $\hat{\mathcal{F}}_{\mathbf{S}}[Q_{m,n}(\mathbf{k}, \mathbf{r})]$ contributing to Eq. (2), only two signals $I_{\text{SC}}(\mathbf{S}_1, t)$ ($[h=1, l=0]$, $[0, 1]$, $[0, -1]$, $[-1, 0]$) and $I_{\text{SC}}(\mathbf{S}_2, t)$ ($[1, 1]$, $[-1, -1]$) are distinguishable from each other. Figure 2 depicts the correspondence between the applied vector potential (blue solid line in the top panel) and the simulated “normalized” (excluding the static background and the part responsible for the population transfer) SC-TRDI signal for the two families of Bragg spots $I_{\text{SC}}(\mathbf{S}_1, t)$ and $I_{\text{SC}}(\mathbf{S}_2, t)$, shown by the red dashed lines in the middle and bottom panels, respectively. As one can see, the diffraction intensities at the maximum ($t_I = 9.8$ fs) and minimum ($t_{II} = 11.2$ fs) values of the vector potential have the same sign and comparable magnitudes with each other. This is again due to the symmetry of the Fourier transform $|\hat{\mathcal{F}}_{\mathbf{S}}[Q(\mathbf{r}, t)]|^2 = |\hat{\mathcal{F}}_{\mathbf{S}}[Q(-\mathbf{r}, t)]|^2$. The total EDDs, as well as their components, are either fully symmetric [$Q_{\text{intra}}(x, y, t)$, Fig. 1(c), I and II] or antisymmetric [$Q_{\text{inter}}(x, y, t)$ and $Q(x, y, t)$, Fig. 1(d) and 1(e), I and II] with respect to each other at time instances I and II. Accordingly, the absolute values of their Fourier transforms are comparable to each other which makes the SC-TRDI signal oscillating with twice the frequency of the applied external field.

Let us turn to the simulations employing the QM-TRDI approach. In Sec. IV of the SM document [61], we demonstrate that the time-resolved x-ray and electron diffraction can be considered on the same footing and can even become identical

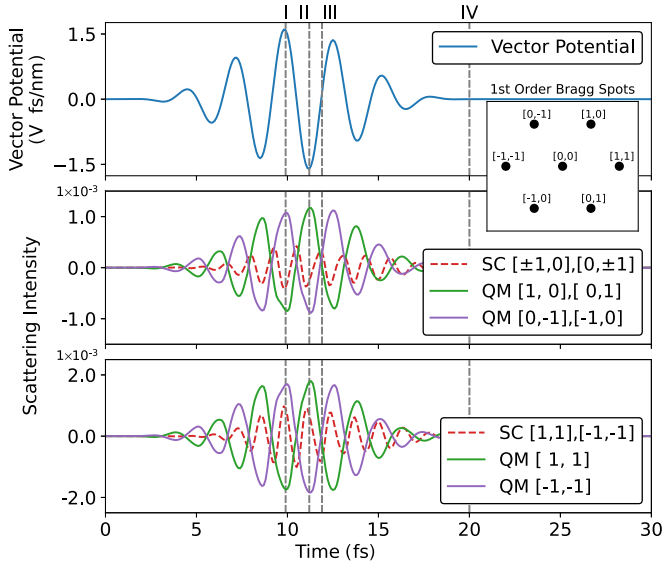


FIG. 2. Comparison of the time-resolved Bragg diffraction intensities in graphene computed with the semiclassical (SC, red dashed lines) and quantum mechanical (QM, green and purple solid lines) approaches. Top panel: Vector potential of the pump field (blue solid line). Middle and bottom panels: SC and QM diffraction intensities measured at $[\pm 1, 0]$, $[0, \pm 1]$ and $[1, 1]$, $[-1, -1]$ Bragg spots, respectively. Note that SC intensity is scaled by a factor of four for better visibility. The vertical grey dashed lines indicate the four time instances depicted in Fig. 1. The inset schematically shows positions of the zero- and first-order Bragg spots of graphene.

to each other up to a prefactor under certain assumptions. In particular, the difference between the two originates from the nature of the interaction mechanisms between the system and the beam: x-rays interact via electromagnetic forces while electrons “feel” the system via Coulomb potential. In the latter case, if the beam of electrons has sufficiently high kinetic energy, the effect of the Coulomb potential becomes negligible, making the scattering event instantaneous and taking place only when the electrons of the target and the beam approach each other. A similar instantaneous interaction mechanism is the basis of the perturbative treatment of the light-matter interactions. Accordingly, under these approximations the scattering of x-rays and electrons become conceptually indistinguishable from each other and will be considered in the same framework in the followup discussion.

Assuming the duration of the probe pulse is infinitely short and that the energy transfer between the beam and the target during the scattering event is small, such that $|\mathbf{k}_s| \approx |\mathbf{k}_{in}|$, the QM-TRDI intensities can be calculated as (see Sec. IV of SM for details [61])

$$I_{QM}(\mathbf{S}, t) = \frac{1}{\mathcal{N}} \sum_{n,m,f} \int_{\text{unit cell}} \rho_{n,m}(\mathbf{k}, t) \hat{\mathcal{F}}_{\mathbf{S}}^*[Q_{f,m}(\mathbf{k}_t, \mathbf{r})] \times \hat{\mathcal{F}}_{\mathbf{S}}[Q_{f,n}(\mathbf{k}_t, \mathbf{r})] d\mathbf{k}, \quad (3)$$

where the index f runs over the final electronic states reached by the scattering process. As one can see from Eq. (3), the resulting signal depends linearly on the reciprocal space-electron densities $\rho_{n,m}(\mathbf{k}, t)$, while in the case of the

SC-TRDI, Eq. (2), the intensity is obtained as an absolute value of the sum of the corresponding quantities. Therefore, the negative [Fig. 1(b), I] and positive [Fig. 1(b), II] displacements of the electron density in the reciprocal space become spectroscopically distinguishable from each other in the frame of the QM-TRDI approach. Furthermore, the linearity of Eq. (3) makes the total diffraction signal a simple sum of the intra- and interband contributions, which is not the case for the SC-TRDI, Eq. (2) (see Sec. V of SM for the detailed discussion [61]). Interestingly, we found that the QM-TRDI signal originates almost entirely from the intraband dynamics with a small portion of the overall intensity coming from the interband motion (see Fig. 4 in SM [61]). This, together with the linearity of the intraband dynamics dictated by the Bloch acceleration theorem, allows us to anticipate a simple single-frequency response from the time-resolved diffraction measurements as opposed to other complicated highly nonlinear outcomes, e.g., such as those observed in the HHG spectra of solids [66].

The calculated normalized QM-TRDI intensities for all first-order Bragg peaks of graphene are shown in the middle and bottom panels of Fig. 2. In contrast to the SC-TRDI results, the QM-TRDI signals oscillate with the same frequency as the applied external field. Furthermore, the intensities measured at spots located opposite to each other in space oscillate out of phase with respect to each other.

The major physical effect not captured by the SC-TRDI approach is, ironically, the motion of electrons, which is only partially reflected in the time dependence of the corresponding electron density. In the SC treatment of diffraction, the beam measures an instantaneous shape of the electron density in the real space. However, identical real-space electron densities can have different underlying electron momenta making them distinguishable in the scattering process. The QM-TRDI approach is sensitive not only to the instantaneous positions of the electrons of the target in space but also to their momenta. In our simulations, the electric field polarized along x axis accelerates the electrons towards negative/positive direction when the amplitude of the corresponding vector potential is positive/negative [see panel (b) of Fig. 1]. Accordingly, the electrons possessing extra momentum towards certain direction increase the intensities of Bragg spots located along that direction and decrease the intensities of the opposite spots, as shown in Fig. 2.

Before concluding, we emphasize that Eqs. (2) and (3) become identical in case of the elastic ($f = j$) scattering from the target present in a specific electronic state [$\rho_{n,m}(\mathbf{k}, t) = \delta_{n=m=j}$]. We note that such conditions do not necessarily preclude the existence of the electron dynamics since the intraband motion can still be present in the system as it is naturally taking place in a particular electronic band. Another possible scenario occurs from consideration of a crystal made of identical electronic wave packets placed at each lattice site [31] or a crystal prepared as an incoherent mixture of unit cells present in different but well-defined electronic eigenstates [37]. In all these special cases, expressions for modeling the diffraction signal share certain similarities with those arising within the SC treatment. In general, however, the QM-TRDI formalism is not equivalent to a straightforward extension of the SC approach to the case of the time-dependent electron

density. Most importantly, the calculations based on the SC-TRDI approach produce the diffraction signal that oscillates with twice the frequency of the driver laser field, which was already predicted earlier [29] (see Sec. VII of SM [61] for the detailed comparison of our approach and the one reported in Ref. [29]). Our new results demonstrate, and this agrees well with the recent experimental measurements of the electron diffraction in graphene [20], that the diffraction signal should oscillate with the same frequency as the driver field. This discrepancy between the SC and QM results arises because the SC approach ignores the momenta of the moving electrons. We would like to note that the formalism reported in our paper is not limited to simulating the electron dynamics and diffraction in a simple two-band tight-binding model of graphene and could easily be generalized to include more electronic bands into consideration or be applied to an arbitrary periodic solid (see Sec. VI of SM [61] for details).

In conclusion, we have demonstrated the application of QM-TRDI to probe the ultrafast laser-driven electron dynamics in solid-state systems. We presented the extension of the theory underlying QM-TRDI to the case of solids and derived a simple expression that connects the dynamics of electron density in the reciprocal space with the intensities of the scattered beams. We made a first attempt to unify the time-dependent x-ray and electron QM-TRDI showing that they share many similarities and can even become identical

to each other up to a prefactor under certain assumptions. We performed fully quantum simulations of the electron dynamics in neutral graphene sample and demonstrated that QM-TRDI signal deviates significantly from that obtained with the SC-TRDI approach. Finally, we identified more complicated symmetry relations between the diffraction signals measured at different Bragg spots in comparison to those present in the SC-TRDI simulations. This, in turn, could be beneficial for the corresponding experimental measurements since more information about the dynamics of the system under study is fingerprinted in the spectra. The investigation of possible computational schemes capable of recovering the dynamics of electron density from diffraction images is a promising direction of further research. We hope that our work will motivate such studies.

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