

Revealing the nonadiabatic tunneling dynamics in solid-state high harmonic generation

Ruixin Zuo¹, Xiaohong Song^{2,*}, Shuai Ben², Torsten Meier^{1,†}, and Weifeng Yang^{2,‡}¹Department of Physics, Paderborn University, Warburger Strasse 100, D-33098 Paderborn, Germany²School of Science, Hainan University, Hainan 570288, China

(Received 5 January 2023; accepted 24 April 2023; published 24 May 2023)

Field-induced tunneling is one of the most fundamental quantum phenomena. In atoms this process has been successfully explored by attosecond interferometry based on high harmonic generation. Adapting this method to solids, the reconstruction of the subcycle tunneling dynamics calls for rigorous theoretical models that are able to properly map the experimental observables to the character of the tunneling process. Unlike in atomic gases, for crystalline solid-state systems the validity and applicability of the semiclassical trajectory-based model are still highly debated. Here we present a saddle-point analysis for solid-state systems which includes the quantum dynamics during tunneling. This allows us to quantify the initial conditions of electrons and holes when they emerge after the tunneling process in the classically allowed region. Our quantum trajectory simulations clarify the crucial role of the tunneling dynamics for the subsequent evolution and the harmonic emission from solids. Besides a nonzero initial electron-hole separation, a nonzero initial velocity of electrons/holes at the tunneling exits is revealed which arises from nonadiabatic tunneling. We find that depending on the ionization time, both inward and outward movements of the electron and its associated hole at the tunneling exit can occur. Our results provide intuitive insight into the nonadiabatic tunneling dynamics in solids and have direct implications for revealing fundamental quantum mechanical phenomena in solid-state systems with attosecond spectroscopic techniques.

DOI: [10.1103/PhysRevResearch.5.L022040](https://doi.org/10.1103/PhysRevResearch.5.L022040)

I. INTRODUCTION

Tunneling ionization driven by intense laser fields triggers many ultrafast nonlinear phenomena such as high-order harmonic generation (HHG), photoelectron holography, laser-induced electron diffraction, and molecular orbital tomography, which form the basis of the recently developed attosecond science [1–6]. More than half a century ago, Keldysh introduced an important dimensionless parameter known as the Keldysh parameter $\gamma_K = \sqrt{I_p/2U_p}$, where I_p is the ionization potential and $U_p = E^2/4\omega^2$ is the ponderomotive energy. The Keldysh parameter classifies photoionization into adiabatic tunneling for $\gamma_K \ll 1$ and multiphoton ionization for $\gamma_K \gg 1$ and treats ionization in gases and solids on equal footing [7]. In the multiphoton ionization regime, the electron is released by absorbing multiple photons along the “vertical” channel, shown by the red arrows in Fig. 1. However, adiabatic tunneling ionization means that electrons penetrate through the classically forbidden region of the potential barrier along the “horizontal” channel (see solid black arrow in Fig. 1).

Many real tunneling processes correspond to situations in between these two extreme limiting cases, which are denoted by “nonadiabatic” [8], as visualized by the dashed purple arrow in Fig. 1.

Attosecond chronoscopy techniques such as the attoclock and high harmonic spectroscopy have been developed to probe the tunneling dynamics of an electron through the atomic and molecular potential barrier [9–13]. It has been demonstrated that a small shift of the tunneling exit position can lead to clear fingerprints in the offset angle of attoclock measurements [14,15] and in the spectral amplitude and phase of HHG [13]. Semiclassical trajectory-based models have been employed to map the tunneling dynamics onto the experimental observations, which confirms the nonadiabaticity of the subcycle tunneling process [15–19]. Recently, attosecond science, especially HHG, was extended to solids [20–24] and therewith the semiclassical trajectory-based model [25–27]. However, in contrast to the great success for atomic and molecular gases, for solid-state systems the validity of the semiclassical trajectory-based model has been questioned by several studies, and it was suggested that the particlelike recollision picture would fail due to the spatial delocalization of the Bloch states [28–30].

In this Letter, we clarify that the failure of the solid-state semiclassical trajectory-based model is mainly due to inaccurate initial conditions of the electron and hole when they reappear after tunneling in the classically allowed region. We demonstrate the essential role of the tunneling dynamics in solids on the subsequent HHG by incorporating the tunneling process properly into a semiclassical

*song_xiaohong@hainanu.edu.cn

†torsten.meier@uni-paderborn.de

‡wfyang@hainanu.edu.cn

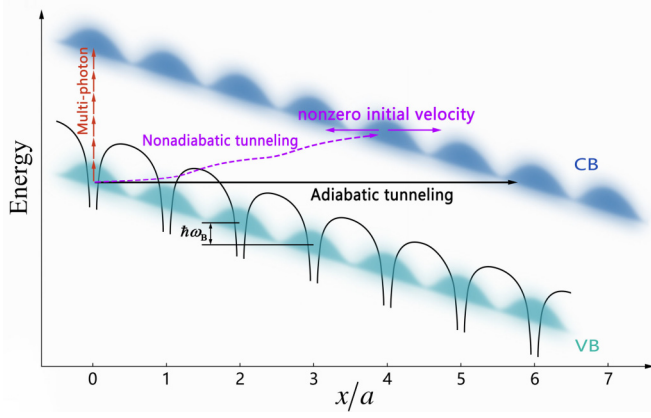


FIG. 1. Schematic illustration of multiphoton ionization (red arrows), adiabatic tunneling (black solid arrow), and nonadiabatic tunneling (dashed purple line) in crystalline solids in real space.

model for solid-state systems. Our quantum trajectory analysis reproduces simulations based on the semiconductor Bloch equations (SBEs) [31,32] very well and therefore builds a bridge between the experimental observable quantities in attosecond tunneling interferometry and the character of the tunneling process. Our study reveals the nonzero electron-hole separation and nonzero initial velocity of the electron/hole at the tunneling exit and provides deep insight into the subcycle nonadiabatic tunneling dynamics in solid-state HHG.

II. METHODS

The SBEs describe the dynamical evolution of the microscopic interband polarizations $p_{\mathbf{k}}^{\lambda\lambda'}$ between bands λ and λ' and the carrier populations $n_{\mathbf{k}}^{\lambda}$ in band λ and read [31,32]

$$\begin{aligned} \frac{\partial}{\partial t} p_{\mathbf{k}}^{\lambda\lambda'} = & -\frac{i}{\hbar} \left(\varepsilon_{\mathbf{k}}^{\lambda} - \varepsilon_{\mathbf{k}}^{\lambda'} - \frac{i}{T_2} \right) p_{\mathbf{k}}^{\lambda\lambda'} \\ & - \frac{i}{\hbar} \mathbf{E}(t) \cdot \left[\sum_{\mu \neq \lambda, \lambda'} \mathbf{d}_{\mathbf{k}}^{\lambda\mu} p_{\mathbf{k}}^{\mu\lambda'} - p_{\mathbf{k}}^{\lambda\mu} \mathbf{d}_{\mathbf{k}}^{\mu\lambda'} \right] \\ & + \frac{e}{\hbar} \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} p_{\mathbf{k}}^{\lambda\lambda'}, \end{aligned} \quad (1)$$

$$\frac{\partial}{\partial t} n_{\mathbf{k}}^{\lambda} = -2\text{Im} \left[\sum_{\lambda' \neq \lambda} \mathbf{d}_{\mathbf{k}}^{\lambda\lambda'} \cdot \mathbf{E}(t) p_{\mathbf{k}}^{\lambda\lambda'} \right] + \frac{e}{\hbar} \mathbf{E}(t) \cdot \nabla_{\mathbf{k}} n_{\mathbf{k}}^{\lambda}. \quad (2)$$

Here $\mathbf{d}_{\mathbf{k}}^{\lambda\lambda'}$ is the interband transition dipole matrix element between bands λ and λ' . The time-dependent macroscopic polarization and intraband current are given by

$$\mathbf{P}(t) = \sum_{\lambda, \lambda', \mathbf{k}} \mathbf{d}_{\mathbf{k}}^{\lambda\lambda'} p_{\mathbf{k}}^{\lambda\lambda'}, \quad (3)$$

$$\mathbf{J}(t) = \sum_{\lambda, \mathbf{k}} n_{\mathbf{k}}^{\lambda} \nabla_{\mathbf{k}} \varepsilon_{\mathbf{k}}^{\lambda}. \quad (4)$$

The emitted field is $E_{\text{out}}(t) \propto \frac{\partial}{\partial t} \mathbf{P}(t) + \mathbf{J}(t)$, and the frequency spectrum of the emitted intensity is obtained by

Fourier transforming $E_{\text{out}}(t)$ and reads

$$I_{\text{out}}(\omega) = |E_{\text{out}}(\omega)|^2 \propto |\omega \mathbf{P}(\omega) + \mathbf{J}(\omega)|^2.$$

The solid-state semiclassical model is based on the saddle-point equations, as in the gas phase counterpart [25,27,33]. The three saddle-point equations describe the electron/hole dynamics during three steps: ionization, acceleration, and recombination (see Appendix A). Previously, as shown in [27], when solving the saddle-point equations, a classical approximation was performed by setting the band gap to zero, which ensures real solutions. This means that the quantum nature of the tunneling process and its effects on the electron-hole pair trajectories are disregarded. With this classical approximation, the initial electron-hole separation after the tunneling ionization is zero. This actually contradicts the well-studied tunneling dynamics in atoms and molecules in which the tunneling exit positions are usually nonzero [14,15]. Moreover, in the purely adiabatic tunneling regime, it has been predicted within the Wannier-Stark ladder picture that the separation between the electron and hole when tunneling occurs can be approximated as $\Delta \mathbf{r} = E_g/F(t)$, where E_g is the band gap and $F(t)$ is the electric field [8], which resembles the atomic adiabatic tunneling exit point, that is, $z_{\text{exit}} = I_p/F(t)$. Recently, a Wannier-function-based quasiclassical analysis revealed that an electron-hole pair can be born with a finite relative distance [34,35]. In the following, we demonstrate that accurately including the tunneling dynamics, especially the nonadiabatic tunneling, is very important for a proper description and interpretation of solid-state HHG by trajectory-based models and thereby provides a strong improvement over previously used simplified models.

Without invoking the classical approximation, the saddle-point equation $\frac{\partial}{\partial t'} S(\mathbf{k}_0, t', t) = \varepsilon_g(\mathbf{k}(t')) - \frac{i}{T_2} = 0$ has complex solutions. Closely following the tunneling picture in atoms and molecules in the strong field approximation, the complex solution of the saddle-point equation $t_s = t_r + it_i$ corresponds to the starting time of electron tunneling. The real part t_r denotes the ionization time when an electron tunnels through the barrier and reaches the tunneling exit. The imaginary part t_i is related to the weight of the electron trajectory. The tunneling through the classically forbidden barrier region corresponds to the evolution from t_s to t_r along the purely imaginary time axis. After the tunneling, the subsequent motions of the electron and hole evolve in real time until the recombination process occurs [25,27,33]. The initial tunneling exit positions of electrons and holes can be calculated according to $\Delta \mathbf{r} = \int_{t_s}^{t_r} d\tau \Delta \mathbf{v}(\mathbf{k}(\tau))$ [36], where $\Delta \mathbf{v}(\mathbf{k})$ is the velocity difference between the conduction and valence bands. The trajectories in the complex plane are known as quantum trajectories.

III. RESULTS AND DISCUSSION

To highlight the importance of the tunneling dynamics in the subsequent dynamics, we focus on HHG from ZnO crystals. On the one hand, it was demonstrated previously that the classical trajectory analysis is able to reproduce the emission time of harmonics in SBE simulation only for weak laser field strengths, whereas for strong fields striking differences appear [27]. On the other hand, SBE simulations agree

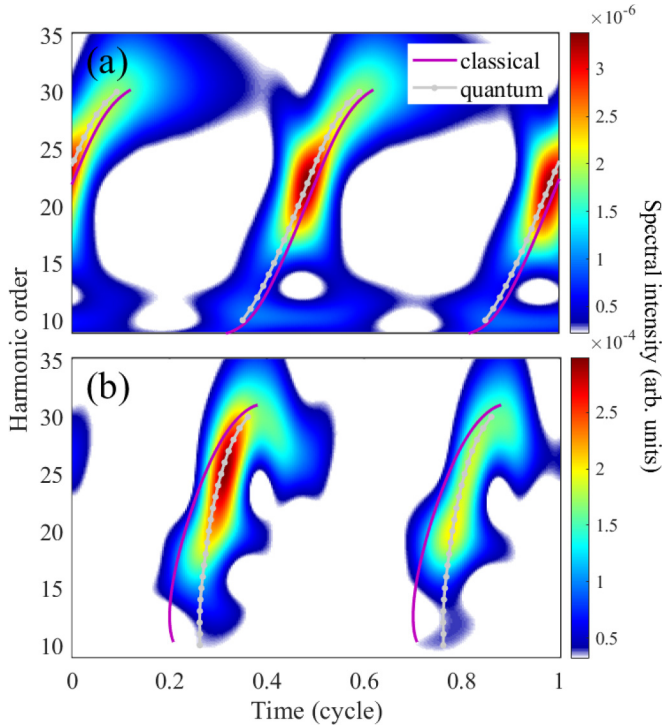


FIG. 2. The color-coded contours show the time- and frequency-dependent HHG obtained from quantum SBE simulations for ZnO in (a) lower- and (b) higher-field cases discussed in the text, respectively. The gray dotted and purple solid curves are the predictions of the emission time based on quantum and classical trajectory analyses, respectively.

well with attosecond tunneling interferometry measurements in ZnO [23], and therefore, we can adopt the SBE simulations as a benchmark to test the applicability and accuracy of our quantum trajectory-based analysis. The band structure of ZnO used in our simulations is the same as that used in [23,25,27] and is described in Appendix A. To make a comparison with the results shown in [27], the same laser parameters are employed in our simulations; that is, the laser central frequency is 0.014 a.u., corresponding to a $\lambda = 3.25 \mu\text{m}$ wavelength. The laser polarization is along the Γ - M direction.

Figures 2(a) and 2(b) show the emitted photon energy as a function of emission time for laser field amplitudes of $E_0 = 0.252 \text{ V/\AA}$ and $E_0 = 0.41 \text{ V/\AA}$, respectively. These two laser field amplitudes are referred to as the lower- and higher-field cases below. The color-coded contours are obtained by solving the SBEs. For comparison, the purple solid line and gray line with circles show the results obtained from classical and quantum trajectory simulations, respectively. In our analysis, we consider only short trajectories since they are responsible for the prominent emission obtained from the SBE simulations. It can be seen that the quantum trajectory analyses match well the quantum SBE simulations for both the low- and high-field cases (see Fig. 2). On the contrary, the deviation of the classical trajectory analysis from the SBE simulation is significant for higher field strength [27]. Our quantum trajectory analysis shows that recombination is most likely when the electron and its associated hole spatially overlap (not shown here), which is consistent with the classical trajectory simulation. Therefore,

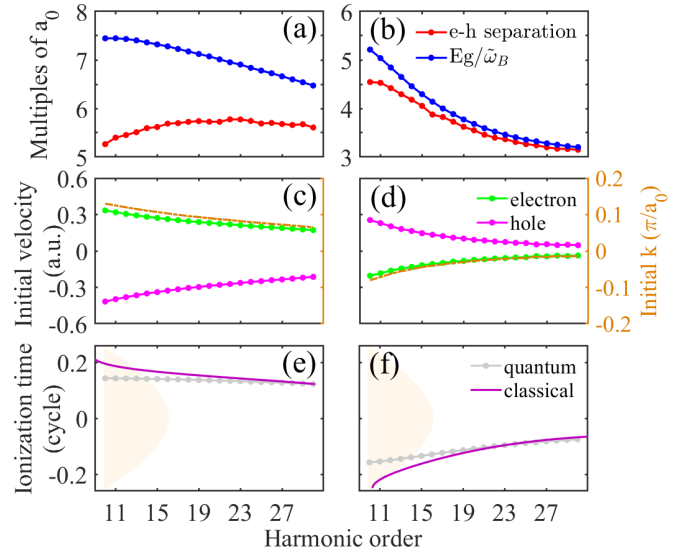


FIG. 3. Initial conditions of the electron and its associated hole in the classically allowed region after tunneling through the barrier in the lower-field (left column) and higher-field (right column) cases. (a) and (b) show the initial electron-hole separation in units of lattice constant with the quantum (red lines with circles) and purely adiabatic (blue lines with circles) analyses, respectively. (c) and (d) show the initial velocities of the electron (green lines with circles) and hole (magenta lines with circles) and initial crystal momenta of the electron/hole (yellow dashed lines). (e) and (f) compare the initial ionization times obtained with the quantum (gray lines with circles) and classical (purple solid lines) trajectory analyses. The yellow-shaded areas in (e) and (f) represent the half-cycle waveform of the electric field.

the discrepancy in the emission time between the quantum and classical analyses arises predominantly from the initial tunneling correction in the ionization process.

Using the quantum trajectory analysis, we quantify in Fig. 3 the tunneling characters at the tunneling exit for both the low (left column in Fig. 3) and high (right column in Fig. 3) laser fields. The red lines with circles in Figs. 3(a) and 3(b) show the harmonic energy dependent initial separations between the electron and hole at the tunneling exit, i.e., when the electron emerges in the conduction band after tunneling, for the quantum trajectory analysis. Clearly, these results differ from the assumption in the classical trajectory analysis that the electron and hole excursion starting from the same position. Moreover, they also differ from the adiabatic approximation analyses. In the lower-field case, the initial electron-hole separation at the tunneling exit predicted by the quantum trajectory analysis depends on the harmonic emission energy of about five to six lattice constants. This is about one to two lattice constants smaller than that predicted within the adiabatic approximation, indicating that nonadiabatic tunneling ionization occurs in this case. With increasing harmonic energy, the initial electron-hole separation at the tunneling exit increases first and then decreases slightly, which is in contrast to the adiabatic tunneling picture, where the electron-hole separation decreases continuously with the harmonic energy. In the high-field case, the two curves are almost synchronized, and the largest difference is less than

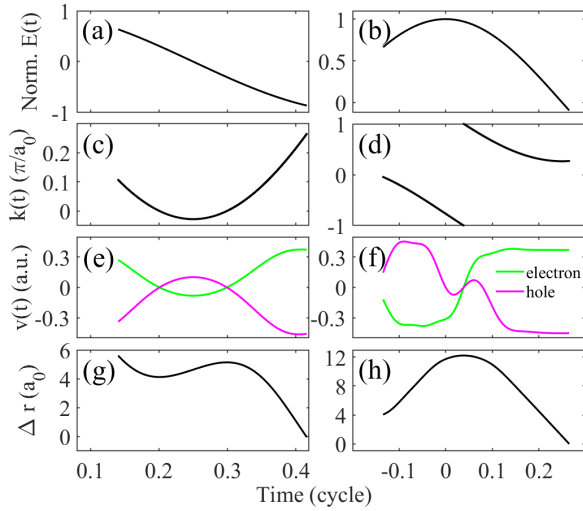


FIG. 4. Time-dependent evolution of trajectories associated with the 15th harmonic for the lower-field (left column) and higher-field (right column) cases, as discussed in the text, respectively. (a) and (b) The time-dependent electric fields, (c) and (d) the time-dependent crystal momenta $k(t)$, (e) and (f) the electron and hole velocities, and (g) and (h) the electron-hole displacements.

one lattice constant occurring at the low-order harmonics, indicating that nearly adiabatic tunneling is realized in this case, especially for the higher-order harmonics.

In line with nonadiabatic tunneling through the atomic potential barrier, we find that the nonadiabatic tunneling process in solids also induces a nonzero initial velocity along the direction of the laser polarization for the electron (green lines with circles) and hole (magenta lines with circles) at the tunneling exit [see Figs. 3(c) and 3(d)]. This means that the electron does not emerge in the conduction band exactly at the Γ point and slightly deviates from it [see the yellow dashed lines in Figs. 3(c) and 3(d)]. Closer to the adiabatic regime [e.g., the high emission energy for the high-field case shown in Fig. 3(b)], this deviation is reduced, and so is the initial velocity of the electron and hole [see Fig. 3(d)]. For the lower-field case, HHG mainly originates from ionization after the crest of the electron field [see Fig. 3(e)]. We find for such an ionization phase that the direction of the initial velocity is opposite to the instantaneous acceleration of the electric field at the tunneling exit. In contrast, for the higher-field case where the HHG is dominated mainly by ionization before the crest of the laser field [see Fig. 3(f)], the direction of the initial velocity is opposite that for ionization after the electric field peak [see Figs. 3(c) and 3(d)].

Taking the 15th harmonic as an example, we present in Fig. 4 the evolution of the trajectories along the real axis of time, including their momenta $\mathbf{k}(t)$, electron-hole velocities, and relative displacements in real space. In the lower-field case, in contrast to the classical trajectory analysis, where the electron and hole separate quickly once they are created, here the electron and its associated hole first move toward each other until their velocities are decreased to zero and then move backward under the action of the laser field, as shown in Figs. 4(e) and 4(g). The subsequent motion is similar to that obtained from the classical trajectory analysis; that is, when

the direction of the laser field is reversed, it drives the electron and its associated hole to encounter each other again and emit a high harmonic photon whose energy is equal to the interband energy difference at the crystal momentum where they recombine. In the higher-field case the dynamics is different because the electron and its associated hole speed up away from each other directly after the tunneling [see Fig. 4(f)]. When they reach the boundary of the Brillouin zone, Bragg scattering makes the electron and its associated hole reverse their direction and leads to recombination [see Fig. 4(h)], as analyzed in [37].

In atomic gases, the nonadiabatic effect in the tunneling dynamics has been probed with HHG interferometry (also called attosecond tunneling interferometry) driven by the combination of fundamental and weak second harmonic probe laser fields [11–13]. The emitted harmonic pulses from the two consecutive half cycles constitute a temporal interferometer. The phase shift induced by the weak second harmonic field unbalances the interferometer, breaks the symmetry, and allows the generation of even harmonics [11]. The amplitude of the even harmonics depends sensitively on the relative phase between the two-color fields. In experiment and from the SBE simulations, the relative phase $\Phi_{\max}$ that maximizes the intensity of each even harmonic can be obtained by recording the modulation of the even harmonics versus the relative phase of the two-color field. To retrieve the tunneling characters, a quantitative analysis that can map the experimental observable $\Phi_{\max}$ to the tunneling characters is required. It was demonstrated in [11,12] that $\Phi_{\max}$ can be calculated according to the additional phase induced by the perturbative field, which is

$$\sigma(\mathbf{k}, t', t) = - \int_{t'}^t \mathbf{A}_{2\omega}(\tau) \Delta \mathbf{v}[\mathbf{k}^{(0)}(\tau)] d\tau, \quad (5)$$

where $\mathbf{A}_{2\omega}(t)$ is the vector potential of the second harmonic field and $\Delta \mathbf{v}[\mathbf{k}^{(0)}(t)]$ is the velocity difference between the electron and its associated hole in the unperturbed trajectories. With the semiclassical trajectory analysis, the ionization and recombination times of electron/hole trajectories can be calculated based on the saddle-point method, which allows us to calculate $\Phi_{\max}$; for further details see Appendix B. Therefore, as long as the calculated $\Phi_{\max}$ can reproduce quantitatively the experimental or SBE simulation results, it can serve as a bridge for mapping each harmonic to its ionization and emission times [11,12].

The color maps in Figs. 5(a) and 5(b) show the harmonic spectra versus the relative delay of the two-color fields as obtained from the SBEs for the lower and higher fundamental field cases discussed above. To get a clearer spectrum with discrete harmonics, a longer duration (10 cycles) of the laser pulse is used, whereas the other parameters are the same as adopted in Figs. 2 and 3. In Fig. 5, the white lines with circles and purple solid lines are the predictions with quantum and classical trajectory analyses, respectively. $\Phi_{\max}$ predicted by the classical trajectory analysis deviates strongly from that of the SBE simulations in the lower-field case. In contrast, the predictions based on the quantum trajectories agree very well with the SBE simulations for both lower- and higher-field cases. As for the deviations for the low-order harmonics (10th and 12th), we speculate that this might be related to near-resonance effects since resonant sidebands can be seen

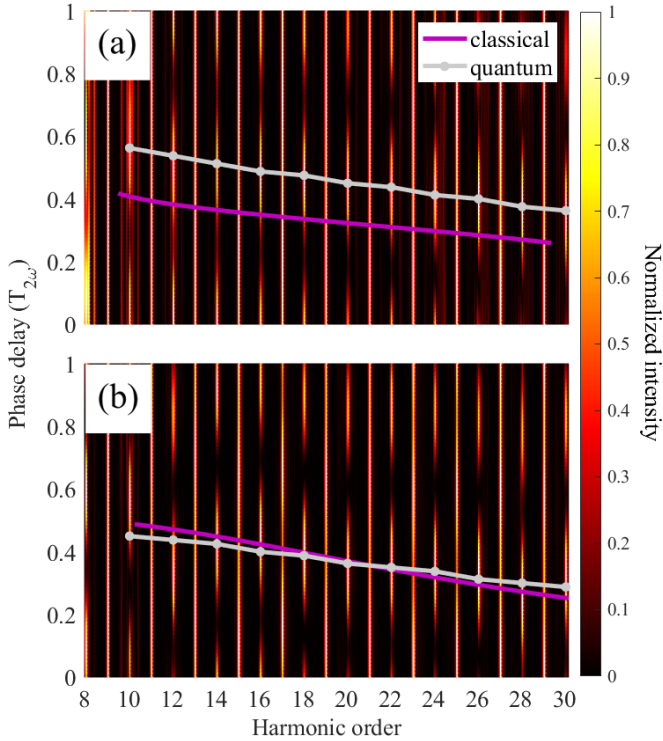


FIG. 5. High harmonic spectra versus the phase delay between the two-color fields for (a) the lower-field and (b) higher-field cases. The color contours are obtained from solutions of the quantum SBE, and the curves are the predictions of $\Phi_{\max}$ based on the classical (purple solid line) and quantum (white line with circles) trajectory analyses, respectively. The pulse duration is 10 optical cycles, and the other parameters are the same as those in Figs. 2 and 3.

around these harmonics in Fig. 5 [38]. With the quantum trajectory analysis, the calculated $\Phi_{\max}$ can also be expressed as a function of other tunneling characters at the tunneling exit, such as the initial electron-hole separations and the initial velocities of the electron and hole (for further details see Appendix B); thus, it provides an effective way to reveal the underlying tunneling dynamics in solids.

IV. CONCLUSIONS

To summarize, the tunneling dynamics in solid-state HHG was studied using a quantum trajectory analysis. Our findings provide strong evidence that nonadiabatic tunneling through the periodic potential barrier is relevant in solid-state HHG. In addition to a reduced tunneling exit coordinate compared to the adiabatic picture, we found both inward and outward initial velocities of the electron and hole after nonadiabatic tunneling in solids. The quantitative agreement between the quantum trajectory analysis and the SBE simulations of attosecond tunneling interferometry allowed us to establish a direct mapping between experimentally observable quantities and the tunneling characters. Therefore, advancing attosecond spectroscopic schemes from atomic systems to more complex solid-state systems is feasible and allows one to reveal quantum phenomena encoded in high-field spectroscopy of solids.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Grants No. 12074240, and No. 12204136), the Hainan Provincial Natural Science Foundation of China (Grants No. 122CXTD504 and No. 122QN217), the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through TRR 142 “Tailored Nonlinear Photonics” (Project No. 231447078, Subproject No. A10), and the Sino-German Center for Research Promotion (Mobility Grant No. M-0031).

APPENDIX A: COMPLEX SOLUTIONS OF SADDLE-POINT EQUATIONS

The saddle-point method has been proven to be helpful and robust for analyzing attosecond phenomena induced by strong fields, providing intuitive physical insight into the underlying dynamics [39]. An electron-hole recollision model for solid-state high harmonic generation (HHG) was proposed based on the saddle-point equations [25], which read

$$\frac{\partial}{\partial t'} S(\mathbf{k}_0, t', t) = \frac{1}{\hbar} \varepsilon_g(\mathbf{k}(t')) - \frac{i}{T_2} = 0, \quad (\text{A1a})$$

$$\nabla_{\mathbf{k}_0} S(\mathbf{k}_0, t', t) = \int_{t'}^t d\tau \nabla_{\mathbf{k}_0} \varepsilon_g(\mathbf{k}(\tau)) = \mathbf{0}, \quad (\text{A1b})$$

$$\frac{\partial}{\partial t} S(\mathbf{k}_0, t', t) = \frac{1}{\hbar} \varepsilon_g(\mathbf{k}(t)) - \omega + \frac{i}{T_2} = 0, \quad (\text{A1c})$$

where $S(\mathbf{k}_0, t', t) = \int_{t'}^t d\tau \varepsilon_g(\mathbf{k}(\tau))$ is the action; $\mathbf{k}(\tau) = \mathbf{k}_0 + \mathbf{A}(\tau)$, with $\mathbf{k}_0$ being the canonical momentum; and $\mathbf{A}(\tau) = -\int_{-\infty}^{\tau} d\tau' \mathbf{F}(\tau')$ is the vector potential.

Without invoking the classical approximation, rigorous solutions of the saddle-point equations are complex valued; further details can be found in Refs. [33,40,41]. Here we briefly introduce the procedure for finding complex solutions to the saddle-point equations numerically. To obtain complex solutions to Eqs. (A1a)–(A1c), we first expand the band structure into a superposition of cosine functions with harmonics of lattice vectors, i.e., $\varepsilon_g(\mathbf{k}) = \sum_{j_1, j_2, j_3=0}^N \alpha_{g, j_1, j_2, j_3} \cos[(j_1 \mathbf{a}_1 + j_2 \mathbf{a}_2 + j_3 \mathbf{a}_3) \cdot \mathbf{k}]$. In the limit $\frac{i}{T_2} \rightarrow 0$ and considering the one-dimensional (1D) case, solving Eqs. (A1a)–(A1c) can be translated into finding the minima of the functions defined by the left sides of Eqs. (A1a)–(A1c). If the minima are sufficiently close to zero, the positions of the minima can be viewed as a reasonably accurate solution of the equations. We also compared several results for finite T_2 and found that the positions of the minima hardly change, which confirms our argumentation.

We study ZnO and describe the band structure by a 1D two-band model, as shown in Refs. [25,27]. The dispersion of the valence and conduction bands along the Γ - M direction is given by

$$E_v(k) = \sum_{j=0}^5 \alpha_v^j \cos(jka), \quad (\text{A2a})$$

$$E_c(k) = E_g + \sum_{j=0}^5 \alpha_c^j \cos(jka), \quad (\text{A2b})$$

with the lattice constant $a = 0.2814$ nm. The band gap at the Γ point $E_g = 3.3$ eV and the expansion coefficients $\alpha_{c/v}^j$ ($j = 0, 1, \dots$) are provided in [27]. The interband dipole matrix element used in our study is $d = 0.183$ nm. The quantum trajectory analysis based on the complex solution of saddle-point equations allows us to gain insight into the properties of electron-hole pairs at the point in time when they tunnel out of the periodic potential barrier like ionization instants, group velocities, and electron-hole separations, as shown in Fig. 2 of the main text.

APPENDIX B: TWO-COLOR EXCITATION SCHEME

Here we derive, in the presence of a weak second harmonic field, the oscillation of even and odd harmonics with respect to the relative time delay between the two colors [11]. Starting from the energy dispersion represented by the superposition of cosine functions $\varepsilon_g(k) = \sum_{j=0}^N \alpha_{g,j} \cos(jka)$, the action in terms of the time-dependent crystal momentum $k(t)$ is given by

$$S(k_0, t', t) = \int_{t'}^t d\tau \sum_{j=0}^N \alpha_{g,j} \cos[jk(\tau)a]. \quad (\text{B1})$$

In order to distinguish the contributions to the action when perturbed by the second harmonic field, perturbative expansions of the action $S(k_0, t', t) = \sum_{n=0}^{\infty} \lambda^n S^{(n)}$ and the momentum $\mathbf{k}(t) = \sum_{n=0}^{\infty} \lambda^n \mathbf{k}^{(n)}(t)$ are performed. With $k^{(0)}(t) = k_0 + A_{\omega}(t)$ and $\lambda k^{(1)}(t) = A_{2\omega}(t)$, the perturbation $\lambda k^{(1)}$ is small, i.e., $\lambda \mathbf{k}^{(1)} \approx 0$; then we arrive at

$$S^{(0)}(k_0, t', t) = \int_{t'}^t d\tau \sum_{j=0}^N \alpha_{g,j} \cos(jk^{(0)}a), \quad (\text{B2})$$

$$S^{(1)}(k_0, t', t) = - \int_{t'}^t d\tau \sum_{j=0}^N \alpha_{g,j} j a k^{(1)} \sin(jk^{(0)}a). \quad (\text{B3})$$

The perturbation contribution to the action $S^{(1)}(k_0, t', t)$ is denoted as $\sigma(k, t', t, \phi)$ and is related to the unperturbed group velocity and second harmonic vector potential as follows:

$$\sigma(k, t', t, \phi) = - \int_{t'}^t A_{2\omega}(\tau, \phi) \nabla_k \varepsilon_g[k^{(0)}(\tau)] d\tau. \quad (\text{B4})$$

In the single-color case, the signals are identical but have opposite signs in consecutive half cycles, $\mathbf{j}_R^{(0)}(t - \pi/\omega) = -\mathbf{j}_L^{(0)}(t)$, where R and L represent the right and left arms of the electron interferometer. The signal generated from the two-color excitation is the sum over all optical cycles and is expressed in terms of the unperturbed one as

$$\mathbf{j}(t) = \sum_{\text{No.c.}} \mathbf{j}_L^{(0)}(t) e^{i\sigma} - \mathbf{j}_L^{(0)}(t + \pi/\omega_0) e^{-i\sigma}. \quad (\text{B5})$$

Fourier transforming the signal into the frequency domain, the higher-order harmonics are

$$\mathbf{j}(n\omega_0) = \mathbf{j}_L^{(0)}(n\omega_0) (e^{i\sigma} - e^{in\pi - i\sigma}). \quad (\text{B6})$$

From this we obtain the relation between the spectrum and the second harmonic field. The even and odd harmonics are

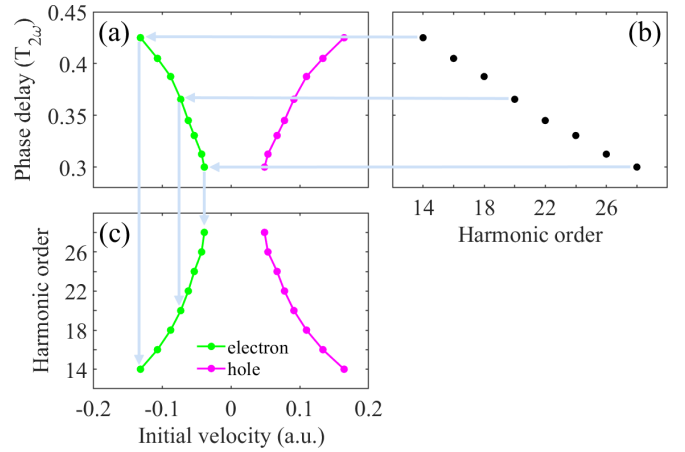


FIG. 6. (a) The obtained relation between $\Phi_{\max}$ and the initial velocities of the electron and hole. (b) $\Phi_{\max}$ of the even harmonic orders resulting from solutions of the SBE. (c) The reconstructed initial velocities for each harmonic from comparing the data in (a) and (b).

modulated as a function of the relative time delay between the two colors:

$$I_{2N+1} \propto |\cos[\sigma(k, t', t, \phi)]|^2, \quad (\text{B7})$$

$$I_{2N} \propto |\sin[\sigma(k, t', t, \phi)]|^2. \quad (\text{B8})$$

As theoretically analyzed, in the two-color scheme, the second harmonic field is added perturbatively, which hardly modifies the stationary solutions of saddle-point equations, i.e., ionization and recombination instants [11,42]. Using Eqs. (B4) and (B8), we calculate the $\Phi_{\max}$ that maximizes the generation of even order harmonics as a function of the set of unperturbed parameters $\{k_0, t', t\}$. The measured dependence of the HHG from ZnO on the relative phase delay of two-color fields was reported in Fig. 1 of Ref. [23]. By solving the SBEs, we are able to reproduce the reported HHG spectrum up to the 18th harmonics. Hence, solving

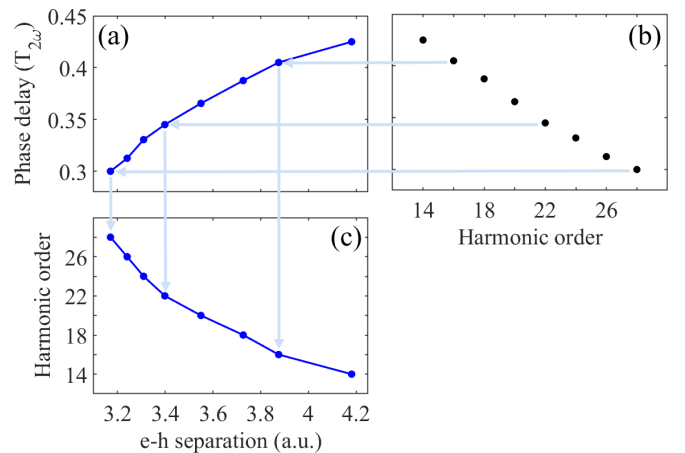


FIG. 7. (a) The obtained relation between $\Phi_{\max}$ and the initial displacement of the electron and hole. (b) $\Phi_{\max}$ of the even harmonic orders resulting from solutions of the SBE. (c) The reconstructed initial separation of the electron-hole pair for each harmonic from comparing the data in (a) and (b).

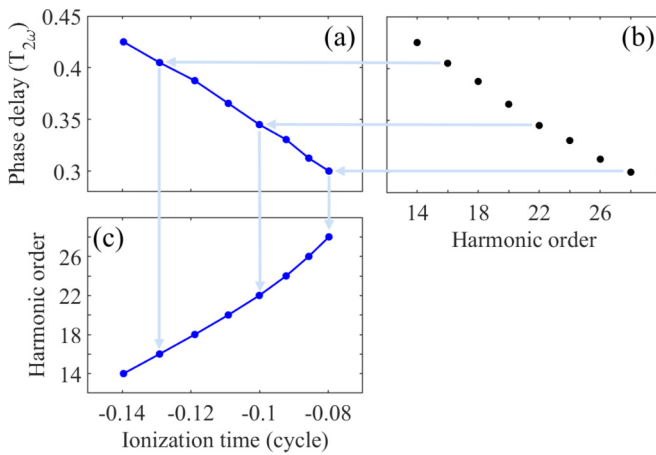


FIG. 8. (a) The obtained relation between $\Phi_{\max}$ and the ionization time. (b) $\Phi_{\max}$ of the even harmonic orders resulting from solutions of the SBE. (c) The reconstructed ionization time for each harmonic from comparing the data in (a) and (b).

the SBEs, which can be viewed as a numerical experiment, provides the characteristic modulation of the harmonics with varying delay of two-color fields and produces the correct spectrum up to the cutoff energy. The theoretical calculation of the relative phase delay that maximizes the even harmonics for the higher-field case discussed in the main text is presented in Figs. 6(b)–9(b). The predictions of the initial conditions, i.e., initial electron and hole velocities, their separation, ionization time, and momentum, obtained from the

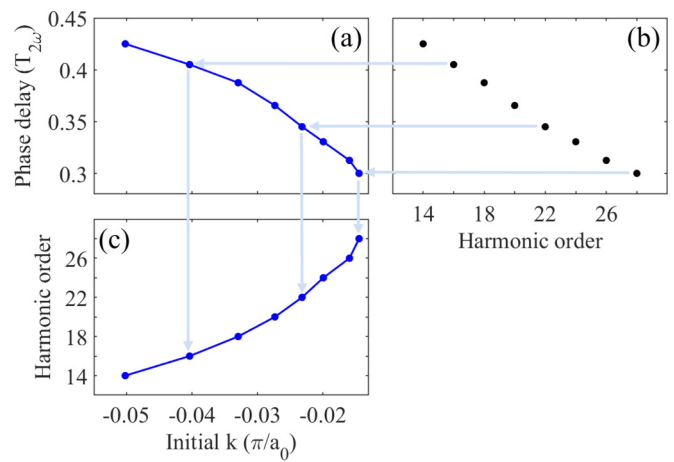


FIG. 9. (a) The obtained relation between $\Phi_{\max}$ and the initial momentum where the transition occurs. (b) $\Phi_{\max}$ of the even harmonic orders resulting from solutions of the SBE. (c) The reconstructed initial crystal momentum for each harmonic from comparing the data in (a) and (b).

quantum trajectory analysis are presented in Figs. 6(a)–9(a), respectively. Relating Figs. 6(a)–9(a) and 6(b)–9(b), each harmonic number is mapped to its initial conditions, as described in Figs. 6(c)–9(c). Thus, the information about the tunneling dynamics, more specifically, the subcycle ionization instants, the crystal momentum where transition happens, electron-hole separation, and their respective velocities, can be retrieved from experimental observations of two-color spectroscopy.

- [1] M. Hentschel, R. Kienberger, Ch. Spielmann, G. A. Reider, N. Milosevic, T. Brabec, P. Corkum, U. Heinzmann, M. Drescher, and F. Krausz, Attosecond metrology, *Nature (London)* **414**, 509 (2001).
- [2] M. Meckel, D. Comtois, D. Zeidler, A. Staudte, D. Pavičić, H. C. Bandulet, H. Bépín, J. C. Kieffer, R. Dörner, D. M. Villeneuve, and P. B. Corkum, Laser-induced electron tunneling and diffraction, *Science* **320**, 1478 (2008).
- [3] Y. Huismans, A. Rouzée, A. Gijsbertsen, J. H. Jungmann, A. S. Smolkowska, P. S. W. M. Logman, F. Lépine, C. Cauchy, S. Zamith, T. Marchenko, J. M. Bakker, G. Berden, B. Redlich, A. F. G. Van Der Meer, H. G. Muller, W. Vermin, K. J. Schafer, M. Spanner, M. Yu. Ivanov, O. Smirnova, D. Bauer, S. V. Popruzhenko, and M. J. J. Vrakking, Time-resolved holography with photoelectron waves, *Science* **331**, 61 (2011).
- [4] O. Smirnova, Y. Mairesse, S. Patchkovskii, N. Dudovich, D. Villeneuve, P. Corkum, and M. Yu. Ivanov, High harmonic interferometry of multi-electrodynamics in molecules, *Nature (London)* **460**, 972 (2009).
- [5] F. Krausz and M. Ivanov, Attosecond physics, *Rev. Mod. Phys.* **81**, 163 (2009).
- [6] M. Nisoli and G. Sansone, New frontiers in attosecond science, *Prog. Quantum Electron.* **33**, 17 (2009).
- [7] L. Keldysh, Ionization in the field of a strong electromagnetic wave, *Sov. Phys. JETP* **20**, 1307 (1965).
- [8] S. Yu. Kruchinin, F. Krausz, and V. S. Yakovlev, Strong-field phenomena in periodic systems, *Rev. Mod. Phys.* **90**, 021002 (2018).
- [9] P. Eckle, M. Smolarski, P. Schlup, J. Biegert, A. Staudte, M. Schöffler, H. G. Muller, R. Dörner, and U. Keller, Attosecond angular streaking, *Nat. Phys.* **4**, 565 (2008).
- [10] P. Eckle, A. N. Pfeiffer, C. Cirelli, A. Staudte, R. Dörner, H. G. Muller, M. Büttiker, and U. Keller, Attosecond ionization and tunneling delay time measurements in helium, *Science* **322**, 1525 (2008).
- [11] N. Dudovich, O. Smirnova, J. Levesque, Y. Mairesse, M. Yu. Ivanov, D. M. Villeneuve, and P. B. Corkum, Measuring and controlling the birth of attosecond XUV pulses, *Nat. Phys.* **2**, 781 (2006).
- [12] O. Pedatzur, G. Orenstein, V. Serbinenko, H. Soifer, B. D. Bruner, A. J. Uzan, D. S. Brambila, A. G. Harvey, L. Torlina, F. Morales, O. Smirnova, and N. Dudovich, Attosecond tunneling interferometry, *Nat. Phys.* **11**, 815 (2015).
- [13] O. Kneller, D. Azoury, Y. Federman, M. Krüger, A. J. Uzan, G. Orenstein, B. D. Bruner, O. Smirnova, S. Patchkovskii, M. Ivanov, and N. Dudovich, A look under the tunnelling barrier via attosecond-gated interferometry, *Nat. Photon.* **16**, 304 (2022).
- [14] A. N. Pfeiffer, C. Cirelli, M. Smolarski, D. Dimitrovski, M. Abu-samha, L. B. Madsen, and U. Keller, Attoclock reveals

- natural coordinates of the laser-induced tunneling current flow in atoms, *Nat. Phys.* **8**, 76 (2012).
- [15] D. Trabert, N. Anders, S. Brennecke, M. S. Schöffler, T. Jahnke, L. Ph. H. Schmidt, M. Kunitski, M. Lein, R. Dörner, and S. Eckart, Nonadiabatic Strong Field Ionization of Atomic Hydrogen, *Phys. Rev. Lett.* **127**, 273201 (2021).
- [16] J. Tong, X. Liu, W. Dong, W. Jiang, M. Zhu, Y. Xu, Z. Zuo, P. Lu, X. Gong, X. Song, W. Yang, and J. Wu, Probing Resonant Photoionization Time Delay by Self-Referenced Molecular Attoclock, *Phys. Rev. Lett.* **129**, 173201 (2022).
- [17] M. Li, J. Geng, M. Han, M. Liu, L. Peng, Q. Gong, and Y. Liu, Subcycle nonadiabatic strong-field tunneling ionization, *Phys. Rev. A* **93**, 013402 (2016).
- [18] R. Boge, C. Cirelli, A. S. Landsman, S. Heuser, A. Ludwig, J. Maurer, M. Weger, L. Gallmann, and U. Keller, Probing Nonadiabatic Effects in Strong-Field Tunnel Ionization, *Phys. Rev. Lett.* **111**, 103003 (2013).
- [19] M. Klaiber, K. Z. Hatsagortsyan, and C. H. Keitel, Tunneling Dynamics in Multiphoton Ionization and Attoclock Calibration, *Phys. Rev. Lett.* **114**, 083001 (2015).
- [20] Z. Tao, C. Chen, T. Szivási, M. Keller, M. Mavrikakis, H. Kapteyn, and M. Murnane, Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids, *Science* **353**, 62 (2016).
- [21] L. Seiffert, Q. Liu, S. Zherebtsov, A. Trabattoni, P. Rupp, M. C. Castrovilli, M. Galli, F. Süßmann, K. Wintersperger, J. Stierle, G. Sansone, L. Poletto, F. Frassetto, I. Halfpap, V. Mondes, C. Graf, E. Rühl, F. Krausz, M. Nisoli, T. Fennel, F. Calegari, and M. F. Kling, Attosecond chronoscopy of electron scattering in dielectric nanoparticles, *Nat. Phys.* **13**, 766 (2017).
- [22] S. Ghimire, A. D. DiChiara, E. Sistrunk, P. Agostini, L. F. DiMauro, and D. A. Reis, Observation of high-order harmonic generation in a bulk crystal, *Nat. Phys.* **7**, 138 (2011).
- [23] G. Vampa, T. J. Hammond, N. Thiré, B. E. Schmidt, F. Légaré, C. R. McDonald, T. Brabec, and P. B. Corkum, Linking high harmonics from gases and solids, *Nature (London)* **522**, 462 (2015).
- [24] G. Ndabashimiye, S. Ghimire, M. Wu, D. A. Browne, K. J. Schafer, M. B. Gaarde, and D. A. Reis, Solid-state harmonics beyond the atomic limit, *Nature (London)* **534**, 520 (2016).
- [25] G. Vampa, C. R. McDonald, G. Orlando, D. D. Klug, P. B. Corkum, and T. Brabec, Theoretical Analysis of High-Harmonic Generation in Solids, *Phys. Rev. Lett.* **113**, 073901 (2014).
- [26] S. Ghimire, A. D. DiChiara, E. Sistrunk, G. Ndabashimiye, U. B. Szafruga, A. Mohammad, P. Agostini, L. F. DiMauro, and D. A. Reis, Generation and propagation of high-order harmonics in crystals, *Phys. Rev. A* **85**, 043836 (2012).
- [27] G. Vampa, C. R. McDonald, G. Orlando, P. B. Corkum, and T. Brabec, Semiclassical analysis of high harmonic generation in bulk crystals, *Phys. Rev. B* **91**, 064302 (2015).
- [28] Y. S. You, D. A. Reis, and S. Ghimire, Anisotropic high-harmonic generation in bulk crystals, *Nat. Phys.* **13**, 345 (2017).
- [29] L. Yue and M. B. Gaarde, Imperfect Recollisions in High-Harmonic Generation in Solids, *Phys. Rev. Lett.* **124**, 153204 (2020).
- [30] L. Li, P. Lan, X. Zhu, and P. Lu, Huygens-Fresnel Picture for High Harmonic Generation in Solids, *Phys. Rev. Lett.* **127**, 223201 (2021).
- [31] D. Golde, T. Meier, and S. W. Koch, High harmonics generated in semiconductor nanostructures by the coupled dynamics of optical inter- and intraband excitations, *Phys. Rev. B* **77**, 075330 (2008).
- [32] H. Haug and S. W. Koch, *Quantum Theory of the Optical and Electronic Properties of Semiconductors*, 5th ed. (World Scientific, Singapore, 2009).
- [33] O. Smirnova and M. Ivanov, Multielectron high harmonic generation: Simple man on a complex plane, in *Attosecond and XUV Physics* (Wiley, Hoboken, NJ, 2014), Chap. 7, p. 201.
- [34] A. M. Parks, G. Ernotte, A. Thorpe, C. R. McDonald, P. B. Corkum, M. Taucer, and T. Brabec, Wannier quasi-classical approach to high harmonic generation in semiconductors, *Optica* **7**, 1764 (2020).
- [35] E. N. Osika, A. Chacón, L. Ortmann, N. Suárez, J. A. Pérez-Hernández, B. Szafran, M. F. Ciappina, F. Sols, A. S. Landsman, and M. Lewenstein, Wannier-Bloch Approach to Localization in High-Harmonics Generation in Solids, *Phys. Rev. X* **7**, 021017 (2017).
- [36] V. Popruzhenko, G. G. Paulus, and D. Bauer, Coulomb corrected quantum trajectories in strong-field ionization, *Phys. Rev. A* **77**, 053409 (2008).
- [37] R. Zuo, A. Trautmann, G. Wang, W.-R. Hannes, S. Yang, X. Song, T. Meier, M. Ciappina, H. T. Duc, and W. Yang, Neighboring atom collisions in solid-state high harmonic generation, *Ultrafast Sci.* **2021**, 9861923 (2021).
- [38] V. Gruson, Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron, *Science* **354**, 734 (2016).
- [39] P. B. Corkum, Plasma Perspective on Strong Field Multiphoton Ionization, *Phys. Rev. Lett.* **71**, 1994 (1993).
- [40] A. Nayak *et al.*, Saddle point approaches in strong field physics and generation of attosecond pulses, *Phys. Rep.* **833**, 1 (2019).
- [41] G. Vampa, J. Lu, Y. Y. You, D. R. Baykusheva, M. Wu, H. Liu, K. J. Schafer, M. B. Gaarde, D. A. Reis, and S. Ghimire, Attosecond synchronization of extremely ultraviolet high harmonic from crystals, *J. Phys. B* **53**, 144003 (2020).
- [42] A. J. Uzan-Narovlansky, Á. Jiménez-Galán, G. Orenstein, R. E. F. Silva, T. Arusi-Parpar, S. Shames, B. D. Bruner, B. Yan, O. Smirnova, M. Ivanov, and N. Dudovich, Observation of light-driven band structure via multiband high-harmonic spectroscopy, *Nat. Photon.* **16**, 428 (2022).