Electron–hole collisions in an atomically thin semiconductor

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Abstract. Strong-field biasing of a solid with intense lightwaves leads to simultaneous interband excitation and intraband acceleration of electron–hole pairs. These coupled dynamics result in high-harmonic emission from the bulk solid. For a controlled acceleration of quasiparticles with well-defined initial conditions, we prepare coherent electron–hole pairs by a resonant near-infrared pulse before a strong multi-terahertz field accelerates these entities. The ballistic dynamics manifests itself as high-order sidebands to the near-infrared excitation spectrum. This mechanism allows for the implementation of a quasiparticle collider in order to study those entities in close analogy to conventional collision experiments. Accelerating electrons and holes in a monolayer of a transition metal dichalcogenide extends this scheme to internal quantum degrees of freedom. We show how a strong lightwave can transport electron–hole pairs from one valley to the other faster than one oscillation of the carrier wave, effectively switching the valley pseudospin on a sub-cycle scale. This scheme paves the way to ultimately fast valleytronics.

1. Introduction

Light is an electromagnetic wave and consists of an oscillating electric and magnetic field. Owing to the transient nature of the fields, they may be harnessed as an ultrafast bias for solid state materials. While the photon energy may be well below the fundamental band gap of the semiconductor, the electric field can still promote carriers via Landau–Zener tunnelling [1]. Since the field is only applied for an optical half cycle, large peak amplitudes may be used without damaging the crystal by excessive carrier excitation [2]. These large peak fields can accelerate the carriers throughout a significant portion of the Brillouin zone once they reach a mobile state. If the corresponding Bloch wave even hits the edge of the Brillouin zone, it is Bragg reflected by the periodic lattice and undergoes a Bloch oscillation cycle [3]. Such dynamics can only be observed, however, as long as the coherence of the Bloch state is preserved. Ultrafast lightwave biasing accelerates charges faster than any scattering can occur and, hence, opens the door to studying and exploiting coherent strong-field processes in condensed matter.

Starting in the early 2000s, extremely nonlinear optical phenomena have been demonstrated in the terahertz and mid-infrared domain [4]. The first observation of non-perturbative high-harmonic generation in a solid was reported in 2011 [5]. These experiments have been modelled by pure intraband dynamics, which could explain salient features of the observed characteristics. By excluding the process of interband excitation, however, a major part of the microscopic light-matter interaction is left...
out. Not only the initial carrier distribution is set by the interband process, but it will also contribute to the macroscopic emission [6]. Subsequently, more refined models have been developed [7]-[10].

We have studied high-harmonic emission from bulk gallium selenide resulting from irradiation with intense multi-terahertz (THz) waveforms. The emitted harmonics cover the entire THz to ultraviolet spectral domain of almost 13 optical octaves in a single, phase-stable spectrum [7]. Gaining insight into the microscopic mechanism necessitates resolving the sub-cycle process on its natural timescale. To this end, we developed a cross-correlation technique capable of clocking the high-harmonic emission to the fundamental driving field [9]. These experiments reveal a distinctly different dynamics as compared to gaseous high-harmonic sources. Here, high-harmonic bursts are emitted synchronized to the field crests of one polarity only. The observed dynamics originate from a non-perturbative quantum interference of different excitation pathways, underpinning the influence of interband processes on high-harmonic emission [9]. The intricate mechanism can even be exploited to set the polarization state, the sub-cycle repetition rate, and to shape the high-harmonic carrier field by making use of crystal symmetry [10].

Although the relative contributions of interband excitation and intraband acceleration to high-harmonic emission can be controlled, they should be separated for a controlled acceleration of electrons and holes within a solid. In the following, we will show, how this can be achieved to realize coherent quasiparticle collisions on a sub-cycle timescale and how the scope of lightwave acceleration can be extended to quantum mechanical attributes such as the valley pseudospin in monolayer transition metal dichalcogenides (TMDCs).

2. Coherent electron–hole collisions

The processes of interband excitation and intraband acceleration are most elegantly separated by utilizing two different electromagnetic pulses. While a visible or near-infrared pulse creates coherent electron–hole pairs by resonant interband transitions, a strong lightwave can be used to accelerate these carriers within their bands. This scheme is illustrated in figure 1. When the lightwave drives only intraband currents, it will ballistically accelerate the wave packets during a half cycle (figure 1b). When the polarity of the field changes, however, electrons and holes are decelerated and set on a recollision path. If they reach spatial overlap again, they may annihilate and recombine (figure 1c), emitting their excess energy in the form of electromagnetic radiation. Since this process can occur periodically throughout the duration of the accelerator field, the light emission will be modulated and additional peaks to the resonance spectrum appear. This process is called high-order sideband generation and has been first observed for excitons in quantum wells driven by low-frequency terahertz fields [11].

Here, we demonstrate coherent electron–hole collisions on a sub-cycle timescale in the bulk semiconductor tungsten diselenide (WSe$_2$) [12]. We inject coherent carriers into this material by addressing the excitonic resonance of bulk WSe$_2$ with a 100-fs near-infrared pulse. The exciton binding energy amounts to 60 meV [13], which provides stable excitons even at room temperature. Intense THz pulses are collinearly focused on the crystal and are used to ionize, accelerate and recollide the coherent electron–hole pairs. The combined interaction of the near-infrared and the THz pulses results in the emission of a broadband high-order sideband spectrum (figure 2a). The sideband peaks exhibit a spacing of twice the driving THz frequency. By Fourier transformation, this translates into a temporal periodicity

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Figure 1. (a) A resonant optical pulse (orange) creates coherent electron–hole pairs (red and blue wave packets) in the conduction and valence band (parabolas), respectively. (b) A strong lightwave (black) accelerates the wave packets within the bands. (c) In the following half cycle, electrons and holes are recollided and emit high-order sideband radiation.
of half the driving period. Hence, coherent electron–hole collisions occur for both field polarities equally, in accordance with the inversion symmetry of bulk WSe$_2$.

For a better understanding of the microscopic mechanism, we prepare coherent electron-hole pairs with an 8-fs near-infrared pulse and track the sub-cycle dynamics of this process. When we delay the ultrashort injection pulse with respect to the THz field, we observe certain delay times $t_{ex}$ of high and low sideband intensity and, hence, good and bad injection times, respectively (figure 2b). Interestingly, the sideband intensity only peaks after the crest of a THz half cycle, evidencing a ballistic origin of the sidebands: electrons and holes have to be injected after the field maximum, so that they are accelerated at first, but the following half cycle is strong enough to invert their motion and to recollide them at high velocity. With a full quantum-mechanical calculation of the light-matter interaction based on the

**Figure 2.** (a) High-order sideband spectrum obtained from bulk tungsten diselenide. The interband resonance is addressed with a 100-fs near-infrared pulse in resonance with the excitonic absorption peak (order 0). When the THz bias is applied even-order sidebands appear, spanning the entire visible-to-ultraviolet spectrum. Inset: Pictogram of the experimental scheme. (b) A sub-cycle injection of excitons with an 8-fs optical pulse allows for tracking the ballistic dynamics. We observe good and bad excitation times (high and low sideband intensity). (c) The experimental results are well reproduced by a quantum mechanical calculation.

**Figure 3.** (a) Relative sub-cycle delay of individual sideband peaks with respect to the nearest THz field crest, shown for experiment (orange) and calculation (blue). The error bars depict the standard deviation obtained from 25 consecutive measurements. (b) Calculated trajectory (blue) of an electron with respect to the hole residing at position 0 for a bad excitation time of $t_{ex} = -4$ fs. The black line shows the THz field and time $t = 0$ is set to mark the peak intensity of the injection pulse (dashed line). The intensity of the blue curve encodes the density of coherent electron–hole pairs, which are driven apart by the THz field. (c) Same as (b) for a good excitation time of $t_{ex} = 7$ fs. The trajectory crosses position 0 again, indicating a collision between electrons and holes.
semiconductor Bloch equations, we are able to reproduce the dynamics of the experiment (figure 2c) [12]. Intricate details such as the relative sub-cycle delay of the sideband peaks with respect to the nearest THz field crest, are reproduced in great detail (figure 3a). A cluster expansion approach allows us to include many-body correlations and to track the average electron–hole separation during lightwave acceleration by their mutual correlation [12]. This allows for an extraction of relative electron–hole trajectories, which directly underpin the ballistic acceleration for bad excitation times (figure 3b, no recollision) and good excitation times (figure 3c, recollision).

This approach offers a completely novel way to study many-body excitations in the condensed phase. It brings the powerful tools developed for high-energy particle physics to the solid state and allows for an implementation of the same principles in studying quasiparticles. This scheme may be extended to other correlated phenomena such as Cooper pairs in high-temperature superconductors or Dirac-like fermions in topological insulators.

3. Excitons in monolayer transition metal dichalcogenides

Particularly interesting quasiparticles for future nano-electronic applications are excitons in monolayer transition metal dichalcogenides. This bound state is defined by its centre of mass momentum \( K \) and discrete quantum numbers, describing the relative electron–hole motion. Due to the reduced dimensionality and the non-uniform, weak screening in these materials, the excitons exhibit a large binding energy in excess of 0.2 eV and a non-hydrogenic Rydberg series in their excitation spectrum [14].

However, only the optically bright excitons with vanishing centre of mass momentum can be accessed by optical spectroscopy. Here, we study the intra-excitonic transitions, irrespective of the electron–hole pair’s centre of mass momentum, by employing phase-locked THz probe pulses, tracking the \( 1s-2p \) resonance. This technique reveals unique and direct insight into the entire exciton ensemble, its many-body interactions, and ultrafast dynamics [15].

In a pump-probe geometry, we resonantly create excitons within the light cone by a 90-fs near-infrared pulse (figure 4a). A THz probe pulse then addresses intra-excitonic transitions, which are tracked by its absorption. With electro-optical detection, we resolve pump-induced changes in the electric field of the THz waveform, which allow us to extract the real part of the optical conductivity \( \Delta \sigma_1 \) and the dielectric function \( \varepsilon_1 \). We observe a clear absorption peak in \( \Delta \sigma_1 \) and a zero-crossing in \( \varepsilon_1 \), which are caused by the \( 1s-2p \) transition (figure 4b-c). A two-dimensional hydrogen model of the Wannier excitons including nonlocal dielectric screening confirms this assignment and allows for an extraction of the

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oscillator strength [15]. Furthermore, we directly observe the temporal evolution of the exciton density upon photo-excitation (figure 4d): the exciton density rises quickly, but features an ultrafast decay afterwards, followed by a more moderate decay dynamics. This behaviour is caused by the large dipole moment of excitons in monolayer TMDCs, resulting in an ultrafast radiative decay. On longer timescales, excitons may scatter to optically dark states, where the main mechanism is Auger recombination [15].

These results represent the first-ever direct observation of the ultrafast radiative decay of excitons in monolayer TMDCs, highlighting their strong coupling to light and new possibilities to utilize internal orbital resonances for future quantum control of these materials.

4. Lightwave control of the valley pseudospin

Excitons in monolayer TMDCs also feature an additional degree of freedom, hitherto untapped by lightwave electronics: the valley pseudospin. This quantum mechanical attribute is a spin-like quantity describing whether an electron resides in one of two distinguishable energy minima of the band structure. It can be used as a binary quantum information carrier, opening the field of valleytronics [16]. Here, we demonstrate a sub-cycle control scheme for the valley pseudospin. To this end, we utilize atomically strong THz fields to accelerate and collide electrons and holes in monolayer WSe$_2$. We read out changes in the pseudospin by the polarization of the emitted high-order sidebands [17].

As a first step, we compare high-order sideband generation in bulk and monolayer WSe$_2$. Figure 5a illustrates typical spectra. While the bulk crystal (orange curve) exclusively shows even orders, also odd orders appear in the monolayer spectrum, when the semiconductor is biased along its zigzag direction (red curve). In the armchair case (blue curve), virtually no odd orders are observed. The electronic structure in reciprocal space reveals that the zigzag direction connects K and K’ valleys (inset to figure 5a), while the armchair direction only connects valleys of the same type. The odd orders, therefore, directly reflect the influence of the valley pseudospin. Additionally, the optical selection rules connected with the valley degree of freedom selectively rotate the polarization state of the odd orders perpendicular to the driving field (figure 5a, arrows) [17].

To determine, if we can switch the valley pseudospin on a sub-cycle timescale, we prepare coherent excitons selectively in the K valley by a right-handed circularly polarized light pulse (figure 5b, orange...
spheres). The sidebands, however, exhibit a strongly elliptical polarization, resulting from admixtures of the non-excited valley with opposite helicity. We quantify the intervalley transport by modelling the microscopic dynamics quantum mechanically. The calculations reproduce the polarization state of the sidebands (figure 5c). The coherent electron–hole polarization $p_{k}$ is proportional to the density of electrons and holes and allows us to track their excursion in the band structure. Figure 5d illustrates a snapshot near a zero-crossing of the THz field. Here, all excitons remain in the K valley. After a few femtoseconds, the THz field has accelerated a significant portion of electrons and holes towards the K’ valley (figure 5e). The peak prevailing in the K valley originates from continued excitation by the 100-fs injection pulse. We predict, however, a transfer fidelity as high as 96% for a 5-fs excitation pulse [17].

5. Summary
In conclusion, we demonstrate that THz pulses can not only probe many-body excitations in solids extremely sensitively, but they can also control their dynamics and quantum properties. We accelerate and collide coherent excitons in bulk WSe$_{2}$, demonstrating quasiparticle collisions on a sub-cycle scale. We expect this to be a useful tool in the investigation of emergent and correlated effects in condensed matter. Going to the monolayer limit of WSe$_{2}$, we study the internal structure and ultrafast radiative decay dynamics of optically excited excitons using ultrasensitive THz probing. In a second step, we extend the scope of lightwave acceleration in solids to quantum degrees of freedom and introduce a sub-cycle control scheme of the valley pseudospin in monolayer TMDCs. This paves the way to ultimately fast quantum information processing in nano-materials.

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