Survival of Floquet-Bloch States in the Presence of Scattering

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Supporting Information

Sample Growth

Bulk 2H-WSe_2 samples were grown via standard chemical vapor transport reactions.[1,2] For the growth of monolayer epitaxial graphene 6H-SiC wafers were graphitized in a modified Aixtron Black Magic reactor in Ar atmosphere at atmospheric pressure[3] using the parameters reported in Ref.[4] The resulting graphene samples were n-doped with the Fermi level ∼0.4 eV above the Dirac point. After growth all samples were transported in air and inserted into ultra-high vacuum for the tr-ARPES experiments. In order to obtain a clean surface the WSe_2 samples were cleaved *in situ* using Kapton tape and the graphene samples were annealed at a temperature of 800°C for 5 min.

Time- and Angle-Resolved Photoemission Spectroscopy (tr-ARPES)

We used a commercial Titanium:Sapphire amplifier (Legend Elite Duo from Coherent) delivering 35 fs pulses at a wavelength of 790 nm with a repetition rate of 1 kHz to generate femtosecond mid-infrared (MIR) pump and extreme ultraviolet (XUV) probe pulses. 10 mJ of output power were sent into a commercial optical parametric amplifier (HE-TOPAS from Light Conversion) where the fundamental of the laser was converted into signal and idler pulses at 1.34 μm and 1.92 μm, respectively. These pulses were overlapped on a GaSe crystal for difference frequency generation (DFG) of the pump pulse at $\lambda_{\text{drive}} = 4.45\,\mu$m ($\hbar\omega_{\text{drive}} = 280\,$meV, $T_{\text{drive}} = 15\,$fs). In order to block signal and idler pulses and to reduce the spectral width of the pump pulse the pump was sent through a bandpass filter centered at 4.45 μm with a full width at half maximum (FWHM) of 200 nm. The pump was then focused with a CaF_2 lens, yielding a pump fluence of $\sim 2\,$mJ/cm^2 at the focus. The polarization of the pump pulse was controlled with a combination of $\lambda/2$ and $\lambda/4$ waveplates.

XUV probe pulses were generated from the second harmonic of the remaining 2 mJ of output power by high harmonics generation in Argon. The 7th harmonic at $\hbar\omega_{\text{probe}} = 21.7\,$eV was selected with a time-preserving grating monochromator[5] and focused onto the sample with a toroidal mirror. P-polarized XUV pulses were used to eject photoelectrons from the sample. The photocurrent as a function of kinetic energy and emission angle of the photoelectrons was measured with a hemispherical analyzer (Phoibos 100 from SPECS). The signal on the two-dimensional detector was converted into snapshots of the energy and momentum dependent spectral function $A(E, \vec{k_{\|}})$ of the material under investigation. The energy resolution was 150 meV.

From the Gaussian full width at half maximum (FWHM) of the temporal profile of the replica band intensity we extract a pump-probe cross correlation of 300 fs. With a nominal XUV probe pulse duration of 120 fs we obtain a pump pulse duration of 270 fs. Therefore, the experimental conditions satisfy $\text{FWHM}_{\text{drive}} > \text{FWHM}_{\text{probe}} > T_{\text{drive}}$, where $T_{\text{drive}} = 15\,$fs is the period of the pump, required for the experimental observation of replica bands in periodically driven solids.[6]

From the experimental fluence of 2 mJ/cm^2 and the driving pulse duration of 270 fs we obtain a peak field strength of $E_{\text{vac}} = 2.4\,$MV/cm at the focus in vacuum. The field strength in the surface of the sample was calculated via $E_{\text{sample}} = 2E_{\text{vac}}/(1+\sqrt{\epsilon_\infty})$ where $\epsilon_\infty = 6.7$ for SiC[7] and $\epsilon_\infty = 15.6$ for WSe_2.[8] Note that the dielectric constant for epitaxial graphene on SiC(0001) remains controversial with values ranging from $\epsilon_\infty = 22$[9] to $\epsilon_\infty = 7.26$.[10] We would like to stress that using a different value of ϵ_∞ for our TDDFT simulations induces quantitative but no qualitative changes in the calculated ARPES spectra. Hence, the agreement with experiment cannot be improved by simply adapting the dielectric constant.

Data Analysis

The experimental EDCs at negative pump-probe delay were fitted with the following function

$$f(E) = \left(\sum_n \text{Peak}(E, E_n, w_n) + \text{BG}_{\text{Shirley}} \right) f_{\text{FD}}(E, \mu, T) \tag{1}$$

where Peak is either a Lorentzian or a Gaussian, E_n and w_n are peak position and full width at half maximum, respectively, $\text{BG}_{\text{Shirley}}$ is the Shirley background, f_{FD} is the Fermi-Dirac distribution, μ is the chemical potential, and T is the electronic temperature. The replica bands in the presence of the driving pulse were included like this

$$F = (1-2a)f(E) + af(E - \hbar\omega_{\text{drive}}) + af(E + \hbar\omega_{\text{drive}}) \tag{2}$$

where a is the intensity of the replica bands, and ω_{drive} is the driving frequency.

Time-Dependent Density Functional Theory (TDDFT)

We compute the photoemission spectra using density-functional theory as implemented in the Octopus code.[11] In this method the time evolution of an electronic structure under the influence of pump and probe lasers in the dipole approximation is computed by propagating the Kohn-Sham equations in time.[12,13] The photoelectron spectrum is then obtained from the flux of ionised electronic states through an analyser surface placed at an appropriate distance away from the surface.[14] The electronic structure of WSe_2 and graphene was obtained using the local density approximation for the DFT exchange-correlation potential and HGH pseudo potentials.[15] The states of WSe_2 and graphene where represented in the unit cell on a real space grid with a spacing of 0.4 Bohr and 0.36 Bohr, respectively, and with k-point samplings of $6 \times 6 \times 1$ and $12 \times 12 \times 1$. In both cases the time evolution was evaluated with steps of 0.002 fs and the analyser surface was placed at 90 Bohr from the surface of the material. A complex absorbing boundary with a width of 30 Bohr[16] was used to prevent unphysical rescattering.

Photon-Dressed States

Unfortunately, it is impossible to disentangle Volkov and Floquet-Bloch contributions to the replica band intensity of a photoelectron spectrum using TDDFT. Therefore, in order to calculate the intensity of the nth order Volkov replica band, we use the model from Madsen.[17] This model also includes the contribution of the ponderomotive energy U_p which is neglected in the more recent model from Park et al.[18] In Madsen's model[17] the normalized intensity of the nth order Volkov replica band is given by

$$I_n/I_0 \propto J_n^2\left(\vec{\alpha}\vec{q}_f, \frac{U_p}{2\omega_{\text{drive}}}\right) \tag{3}$$

where $\vec{\alpha} = \vec{A}/\omega_{\text{drive}}$, $\vec{q}_f$ is the momentum of the photoelectron, and $U_p = A^2/4$ is the ponderomotive energy. The generalized Bessel functions $J_n(u, v)$ have the following property:

$$J_n(u, v) = \sum_{k=-\infty}^{\infty} J_{n-2k}(u) J_k(v). \tag{4}$$

Also, $J_n(0) = 0$ for $n \neq 0$ and $J_0(0) = 1$. With $u = \vec{\alpha}\vec{q}_f = 0$ (which is the case for sp driving pulses in the present study) and $v = \frac{U_p}{2\omega}$ we get

$$J_n(0,v) = \sum_{k=-\infty}^{\infty} J_{n-2k}(0) J_k(v) \tag{5}$$

$$J_{n=2k}(0,v) = \sum_{k=-\infty}^{\infty} J_0(0) J_k(v) \tag{6}$$

$$= \sum_{k=-\infty}^{\infty} J_k(v) \tag{7}$$

where we used that $J_{n-2k}(0) \neq 0$ only if $n = 2k$. This means that, if $\vec{\alpha}\vec{q}_f = 0$, we will only get even-order Volkov replica bands. Hence, the Volkov contribution to the first order replica band is zero. Therefore, any first-order replica band that we observe in tr-ARPES using sp driving pulses necessarily needs to be a Floquet-Bloch state.

References

(1) Traving, M.; Boehme, M.; Kipp, L.; Skibowski, M.; Starrost, F.; Krasovskii, E. E.; Perlov, A.; Schattke, W. Electronic structure of WSe_2: A combined photoemission and inverse photoemission study. *Phys. Rev. B* **1997**, *55*, 10392–10399.

(2) Buck, J.; Iwicki, J.; Rossnagel, K.; Kipp, L. Surface photovoltage effect at the *p*-WSe_2:Rb surface: Photoemission experiment and numerical model. *Phys. Rev. B* **2011**, *83*, 075312.

(3) Emtsev, K. V.; Bostwick, A.; Horn, K.; Jobst, J.; Kellogg, G. L.; Ley, L.; McChesney, J. L.; Ohta, T.; Reshanov, S. A.; Röhrl, J.; Rotenberg, E.; Schmid, A. K.; Waldmann, D.; Weber, H. B.; Seyller, T. Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide. *Nature Materials* **2009**, *8*, 203.

(4) Rossi, A.; Büch, H.; Rienzo, C. D.; Miseikis, V.; Convertino, D.; Al-Temimy, A.; Voliani, V.; Gemmi, M.; Piazza, V.; Coletti, C. Scalable synthesis of WS2 on graphene

and h-BN: an all-2D platform for light-matter transduction. *2D Materials* **2016**, *3*, 031013.

(5) Poletto, L.; Frassetto, F. Time-preserving grating monochromators for ultrafast extreme-ultraviolet pulses. *Appl. Opt.* **2010**, *49*, 5465–5473.

(6) Sentef, M.; Claassen, M.; Kemper, A.; Moritz, B.; Oka, T.; Freericks, J.; Devereaux, T. Theory of Floquet band formation and local pseudospin textures in pump-probe photoemission of graphene. *Nature Communications* **2014**, *6*, 7047.

(7) Patrick, L.; Choyke, W. J. Static Dielectric Constant of SiC. *Phys. Rev. B* **1970**, *2*, 2255–2256.

(8) Laturia, A.; Van de Put, M. L.; Vandenberghe, W. G. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Materials and Application* **2018**, *2*, 6.

(9) Walter, A. L.; Bostwick, A.; Jeon, K.-J.; Speck, F.; Ostler, M.; Seyller, T.; Moreschini, L.; Chang, Y. J.; Polini, M.; Asgari, R.; MacDonald, A. H.; Horn, K.; Rotenberg, E. Effective screening and the plasmaron bands in graphene. *Phys. Rev. B* **2011**, *84*, 085410.

(10) Hwang, C.; Siegel, D. A.; Mo, S.-K.; Regan, W.; Ismach, A.; Zhang, Y.; Zettl, A.; Lanzara, A. Fermi velocity engineering in graphene by substrate modification. *Scientific Reports* **2012**, *2*, 590.

(11) Tancogne-Dejean, N. et al. Octopus, a computational framework for exploring light-driven phenomena and quantum dynamics in extended and finite systems. *The Journal of Chemical Physics* **2020**, *152*, 124119.

(12) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133–A1138.

(13) Runge, E.; Gross, E. K. U. Density-Functional Theory for Time-Dependent Systems. *Phys. Rev. Lett.* **1984**, *52*, 997–1000.

(14) De Giovannini, U.; Hübener, H.; Rubio, A. A First-Principles Time-Dependent Density Functional Theory Framework for Spin and Time-Resolved Angular-Resolved Photoelectron Spectroscopy in Periodic Systems. *J. Chem. Theory Comput.* **2017**, *13*, 265.

(15) Hartwigsen, C.; Goedecker, S.; Hutter, J. Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. *Phys. Rev. B* **1998**, *58*, 3641–3662.

(16) De Giovannini, Umberto,; Larsen, Ask Hjorth,; Rubio, Angel, Modeling electron dynamics coupled to continuum states in finite volumes with absorbing boundaries. *Eur. Phys. J. B* **2015**, *88*, 56.

(17) Madsen, L. B. Strong-field approximation in laser-assisted dynamics. *American Journal of Physics* **2005**, *73*, 57–62.

(18) Park, S. T. Interference in Floquet-Volkov transitions. *Phys. Rev. A* **2014**, *90*, 013420.