# Imaging Electron Dynamics in Graphene With Momentum Microscopy

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#### Abstract of the Dissertation

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2D quantum materials are often distinguished by their unique electronic properties determined by high-momentum electronic states near the Brillouin zone boundary. However, the dynamics initiated by photoexcitation are usually complex in these materials and often involve scattering to different locations in the Brillouin zone and many states that are optically dark. In this context, time- and angleresolved photoemission spectroscopy (time-resolved ARPES) based on high harmonic generation (HHG) can be a powerful technique for studying these complex dynamics owing to its capability of providing momentum-space information. Previously, most HHG-based time resolved ARPES systems have suffered from severe data-rate limitations imposed by space charge issues and low electron collection efficiency of photoelectrons from low repetition rate HHG sources. These limitations have largely precluded the study of intrinsic dynamics of excited particles in the perturbative low-fluence regime and restricted the parameter space (e.g. fluence, polarization, probe photon energy) that can be explored to extract meaningful physics.

To overcome these limitations, we have successfully combined a high repetition rate HHG source tunable over the range of 10 - 40 eV and time-of-flight (ToF) momentum microscopy to produce a unique instrument that can enable low-fluence measurements across the full Brillouin zone at a very high data rate. This dissertation demonstrates the feasibility of low-fluence excited-state ARPES experiments from  $\mu$ m-sized samples with coverage of large parameter space and the required instrumentation. Our beamline, consisting of a custom-built Yb:fiber frequency comb driver laser, a HHG enhancement cavity, subsequent beamline, and ToF-momentum microscope, has transitioned to the new 61 MHz repetition rate. To enable the demanding time-resolved micro-ARPES experiments in the perturbative limit, the beamline must be optimized in a way that a single isolated harmonic is focused to a small spot on the sample with sufficient flux and long-term stability. With the technical upgrades and optimizations, the new system provides a flux of  $\sim 10^{11}$  photons per second in a single isolated harmonic to the sample over the broad tuning range of 10 - 40 eV with a spot size of 24 × 16  $\mu$ m<sup>2</sup>, ideal for micro-ARPES.

The optimized system has made it possible for studying a variety of small 2D materials in a qualitatively new regime. This dissertation focusses on experiments in graphene. Using ToF-momentum microscopy with high data rate and high dynamic range, we report momentum-space measurements of optically excited electrons, and their subsequent relaxation. Specifically, we observe a pronounced non-thermal distribution of nascent photoexcited electrons with lattice pseudospin polarization in remarkable agreement with results of simple tight-binding theory. By varying the excitation fluence, we vary the relative importance of electron-electron vs. electron-phonon scattering in the relaxation of the initial distribution and study how these scattering mechanisms play a role on the relaxation.

**Dedication Page** 

To my husband Tom and my mom Chunja Jun

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# Chapter 1

# Introduction

# **1.1 Momentum-space representation**

The momentum-space concept is seldomly encountered in quantum chemistry of isolated atoms and molecules. The electronic properties of these simple matter can all be described in what is most familiar to us, position space. Take a chemical reaction as an example, where the motions of electrons and atomic nuclei change continually to break and to form chemical bonds as the reaction passes through its transition states. Within the Born-Oppenheimer approximation, we construct a potential energy surface against nuclear coordinates in this real space to visualize the reaction progress. We ultimately derive atomic or molecular wavefunctions and their electronic energy levels in position space to understand the microscopic details of chemical bondings.

On the other hand, when many atoms or molecules are condensed into crystalline solids, the subsequent quantum mechanics naturally changes its basis to socalled "momentum space". This is the Fourier conjugate of position space where electron wavevector k, related to crystal momentum  $\hbar k$ , specifies the coordinates of the space. The basic concepts of electron/phonon dispersion, scattering, or diffraction are all understood in momentum space. We formulate simple electronic problems within single-particle pictures [2,3] in a momentum-space basis and even more complex interaction problems for strongly correlated electron systems to study their electronic structures and new emerging phenomena [4–6].

Thus far, position- vs. momentum space representation may be merely seen as a mathematical parametrizaton of space and it is not so clear why momentum space is represented by k rather than the position vector r. The answer to this question lies in the band theory of solids. In a crystal lattice, the discrete energy levels of constituent atoms group into bands and a representation of these energy bands in momentum space is called the band structure of a solid. To calculate the band structure, one needs to solve the problem of an electron moving in a periodic lattice potential. In the independent electron approximation, this reduces to a single-particle Hamiltonian problem with the Hamiltonian given by  $\hat{\mathbf{H}} = -\hbar^2/2m\nabla^2 + \mathbf{U}(\mathbf{r})$  where the one electron potential  $\mathbf{U}(\mathbf{r}) = \mathbf{U}(\mathbf{r} + \mathbf{R})$  has the periodicity of the underlying lattice

for all lattice vectors  $\mathbf{R}$  [2, 3]. One can greatly simplify this problem by making use of periodic translational symmetry according to Bloch's theorem. We define a translation operator  $\hat{\mathbf{T}}_{\mathbf{R}}$  which, when acting on an arbitrary function  $f(\mathbf{r})$ , shifts the argument by  $\mathbf{R}$ ,  $\hat{\mathbf{T}}_{\mathbf{R}}f(\mathbf{r}) = f(\mathbf{r} + \mathbf{R})$  [2]. When  $\hat{\mathbf{T}}_{\mathbf{R}}$  acts on the crystal Hamiltonian  $\hat{\mathbf{H}}$ , it leaves  $\hat{\mathbf{H}}$  unchanged because of the periodicity of  $\hat{\mathbf{H}}$ .  $\hat{\mathbf{T}}_{\mathbf{R}}$  then becomes a good symmetry operator that commutes with  $\hat{\mathbf{H}}$ ,  $[\hat{\mathbf{H}}, \hat{\mathbf{T}}_{\mathbf{R}}] = 0$ , and  $\hat{\mathbf{H}}$  and  $\hat{\mathbf{T}}_{\mathbf{R}}$  can be diagonalized simultaneously. Hence,  $\hat{\mathbf{T}}_{\mathbf{R}}$  can be used to identify the eigenstates  $\Psi(\mathbf{r})$  of  $\hat{\mathbf{H}}$ ,  $\hat{\mathbf{T}}_{\mathbf{R}}\Psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{R}}\Psi(\mathbf{r})$ , which is true for the Bloch states. Here the electron wavevector  $\mathbf{k}$ , associated with the eigenvalue  $e^{i\mathbf{k}\cdot\mathbf{R}}$  of  $\hat{\mathbf{T}}_{\mathbf{R}}$ , becomes a good quantum number to label the Bloch eigenstates, similar to the atomic case where land m are associated with the eigenvalues of commuting operators  $\hat{\mathbf{L}}^2$  and  $\hat{\mathbf{L}}_z$  specify the atomic states. The corresponding energy eigenvalues, thus the energy bands,  $\varepsilon_n(\mathbf{k})$  of  $\hat{\mathbf{H}}$  depend only on the electron wavevector  $\mathbf{k}$  with the band index n. It is this quantum number  $\mathbf{k}$  that parametrizes the corresponding vector space as a result of periodic symmetry of the unit cell.

When discussing the band structures of solids, we often use the Fourier transformed unit cell, called the Brillouin zone, and  $\Gamma$ , K, or M points representing specific locations within the Brillouin zone. Band structures provide useful properties of materials. Bandgaps are useful for determining material types such as a metal, semiconductor, or insulator and optical properties such as absorption or emission. Band curvatures near the extrema determine carrier mobility through those bands. All of these are important for applications in optoelectronics and photovoltaics, where material designs by engineering bandgaps are critical for harvesting light.

# **1.2** Direct access to momentum space

Understanding the electronic structures of quantum materials is at the heart of modern condensed-matter physics. In these materials, interactions of electrons with many interacting degrees of freedom, such as electron interactions among themes-lves or with spin or phonons, often lead to exotic quantum effects and new quantum states ranging from unusual topological states protected by time-reversal symmetry for quantum computing to the Berry phase for spintronic applications to non-local entanglement of quantum states for teleportation to high-temperature superconductivity beyond the Bardeen–Cooper–Schrieffer limit [6–8]. The potential impact of applying these novel quantum effects into next generation technologies has motivated a wide range of scientists to investigate the electronic properties of quantum materials.

For characterizing ground states of quantum materials, angle-resolved photoemission spectroscopy (ARPES) has become a standard spectroscopic tool for direct momentum-space measurements [9, 10]. This technique is based on the photoelectric effect, the phenomenon first observed by Hertz [11] in 1887 and the concept later recognized by Einstein [12] in his 1905 paper. The great utility of ARPES is the direct provision of energy-momentum dispersion in crystalline solids based on simple conservation of energy and momentum. The periodic in-plane symmetry of the crystal along the surface preserves the parallel components of electron momenta inside  $(\mathbf{k}_{\parallel})$  and outside  $(\mathbf{K}_{\parallel})$  the material,

$$\mathbf{k}_{\parallel} = \mathbf{K}_{\parallel} = \frac{\sqrt{2mT}}{\hbar} \cdot \sin\theta = 0.512 \text{\AA}^{-1} \sqrt{T[\text{eV}]} \cdot \sin\theta, \qquad (1.1)$$

where  $\theta$  is the angle of photoelectrons emitted from the sample and T is their kinetic energy determined from the energy conservation statement  $T = h\nu - (\Phi + |E_B|)$ with  $h\nu$  the incident photon energy,  $\Phi$  the material workfunction, and  $E_B$  the binding energy of electronic states inside the material. By measuring the emission angles and kinetic energies of photoelectrons, one can directly extract the energymomentum dispersion of electronic structures of various condensed-matter systems for many decades, which is why every syncrotron has a beamline dedicated to ARPES stations for ground-state photoemission measurements.

# **1.3** Technical challenges in time-resolved ARPES

Conventional ground-state ARPES can be extended into the time domain via pump-probe spectroscopy using a pair of ultrashort pulses. In time-resolved ARPES, the first optical pulse, called the pump, excites electrons to unoccupied states and the second delayed pulse, called the probe, tracks the population of the excited electrons by photoemission. Subsequent relaxation dynamics of excited quasi-particles after photoexcitation are usually complex because they often couple to other interacting degrees of freedom [13] and involve many states that are optically dark [14–16]. In this regard, time-resolved ARPES provides direct energy and momentum selective dynamics, inaccessible by any other optical spectroscopy, with the possibility of disentangling complicated interactions. However, the implementation of time-resolved ARPES presents a number of technical challenges. For example, time-resolved studies with commonly used 6 eV light sources can achieve high performance, but are restricted to small momentum electronic states only around the Brillouin zone center due to the limited photon energy [17–21].

# **1.3.1** Brillouin zone coverage

Many interesting ultrafast dynamical processes in quantum materials occur at high momentum electronic states near the edge of the Brillouin zone as well. High-lighted examples are conical band dispersion in graphene [22, 23], exciton physics in transition metal dichalcogenides [24–27], and the antinode of copper oxide based high-temperature superconductors [28,29]. The first Brillouin zone of these systems typically extends to the range of 0.7 - 2.0 Å<sup>-1</sup> [30]. To cover this range of the full Brillouin zone, the minimum photon energies of ~ 20 eV are needed.

There are different methods for accessing the XUV spectral region. Synchrotron radiation has been the main choice for XUV ground-state ARPES for many decades, but the long pulses produced by equilibrated recirculating electron bunches are not not suitable for ultrafast time-resolved measurements. Alternatively, the free-electron lasers can provide fs-pulses but their low repetition rates are not high enough to perform time-resolved ARPES experiments [31]. High harmonic generation (HHG) has often been the best choice until now for generating ultrashort XUV pulses suitable for time-resolved ARPES. In a typical HHG process, high-energy ultrashort infrared laser pulses (>100  $\mu$ J) are focused onto a noble gas medium to intensities of ~ 10<sup>14</sup> W/cm<sup>2</sup>. Harmonics of the fundamental driving laser frequency at odd integer multiples are created during the frequency upconversion process. Previously, the repetition rate has been limited to kHz level by available average power from existing commercial laser systems, posing a data-rate challenge for performing time-resolved XUV ARPES, especially in the limit of low excitation.

# **1.3.2** Low-fluence time-resolved ARPES

Excitation fluence has a profound impact on excited-state dynamics. For this reason, pump-probe experiments on condensed-matter systems are generally divided into two regimes, non-perturbative high-fluence and perturbative low-fluence experiments [5]. High-fluence experiments are particularly useful for the study of photo-induced phase transitions such as ultrafast melting of charge order [32, 33], metal-to-insulator transition [34], or ultrafast demagnetization [35]. They typically use  $\sim$  mJ/cm<sup>2</sup> fluence, where optical excitation produces substantial changes in the electron band structures. Here, the dynamics are due to a more collective response [5] from a large density of excited particles. Under the  $\sim$  mJ/cm<sup>2</sup> regime, the electronic temperature is usually several thousand kelvins, as observed in Mott insulator [17] or graphene/graphite [36–38], leading to rapid thermalization.

Low-fluence experiements study intrinsic dynamics of individual excited quasiparticles with ~  $\mu$ J/cm<sup>2</sup> fluence [5, 39–42]. In this low-fluence regime, the system is perturbed as gently as possible [5] such that weak pumping initially creates only a small number of individual quasiparticles in the conduction bands. In this way, interactions of excited particles are substantially suppressed such that the dynamics are more likely due to those moving in the material's intrinsic bands as opposed to a large collection of excited particles moving in transiently modified bands in highfluence experiments. This perturbative-excitaition regime is important to study materials with low transition temperatures [17, 18] and to probe the dynamics within a given phase of a certain material [5]. Also, this is the regime where electronphonon scattering is expected to be the dominant scattering mechanism and therefore one can effectively study a nonthermal distribution of nascent photoexcited electrons that have not yet relaxed into a Fermi-Dirac distribution. By gradually varying the fluence, one can control the relative importance of electron-electron vs. electron-phonon scatterings and study how electron-phonon coupling plays a role in the relaxation. The trouble with studying these individal quasiparticle dynamics is that pump-induced photoemission signals are usually small and nearly indicernible from statistical noise in the electron distributions [40], in contrast to the  $\sim$  mJ/cm<sup>2</sup> regime where photoexcitation produces large discernible changes visible on a linear scale. High data acquisition rate is then important for recording such measurements at high dynamic range.

The most critical factor that limits data rate in time-resolved photoemission experiments is the so-called vacuum space charge effect. In photoemission, interactions between electrons emitted from a sample surface during a short laser period cause shifting and broading of photoelectron spectra, where the shifting and broadening scale with the number of electrons per probe pulse [43–47]. When ultrashort pump pulses are added to photoemission techniques, they can intensify this space charging via multiphoton processes [48–50]. The space charge effect fundamentally limits the number of electrons that can be extracted from a sample, and hence the number of photons that can be applied to it. For XUV probe pulses, the number of electrons per pulse should be 100 - 1000 to limit the resolution to 100 meV [51].

Given the attainable data rate set by the fundamental space-charge constraint, the data-rate problem becomes particularly acute for time-resolved photoemission measurements in the low fluence limit. The signal of interest in a typical pumpprobe measurement comes from only a small fraction of ground-state electrons excited by the pump, which is typically orders of magnitude smaller than the signal at  $E_F$ . In the low fluence regime of ~  $\mu$ J/cm<sup>2</sup>, corresponding pump-induced signals become even smaller, orders of magnitude lower than the ~mJ/cm<sup>2</sup> regime. To extract the dynamics of excited states, data should be recorded at several pump-probe delays at a minimum, and often with varying fluence, polarization, and photon energy to extract meaningful physics. Complete low-fluence time-resolved ARPES experiments covering all these parameters then demand increasingly long acquisition time. Therefore, low-fluence experiments have been very difficult, especially with space-charge limited HHG-based photoemission setups.

Given these limitations, to avoid the detrimental space charge problem and thus to record data with reasonable acquisition time, it is necessary to perform experiments at high repetition rates. Significant improvements have been made recently to achieve high repetition rate HHG sources and they have been successfully applied to time-resolved photoemission measurements [41, 52–54]. High repetition rate ultrashort XUV pulses can be generated via single-pass HHG with tight focusing [54–56] or cavity-enhanced techniques [52, 57]. In single-pass HHG, the required ~100  $\mu$ J pulse energy for a HHG process is delivered by a high power commercial laser and focused onto a gas medium. In cavity-enhanced HHG, low-energy ~1  $\mu$ J driving pulses from a femtosecond optical frequency comb are resonantly enhanced in a passive optical resonator to pulse energies > 100  $\mu$ J [58, 59]. While cavity-enhanced HHG provides ultrashort XUV pulses at higher repetition rates, usually up to ~ 100 MHz [60–62], single-pass HHG outputs XUV pulses typically at kHz repetition rates, with a few examples of ~ 1 MHz [54], limited by available powers from commercial lasers.

Experimentalists can also optimize data rate for low-fluence time-resolved ARPES by adopting the new technique of time-of-flight momentum microscopy (ToF-MM) [63, 64] for photoelectron detection. ToF-MM provides simultaneous detection of

2D momenta  $(k_x, k_y)$  and energies E of photoelectrons emitted from the full  $2\pi$  solid angle, dramatically increasing data rate by several orders of magniude higher than conventional hemispherical analyzers. It can also select photoemission signals from a micron-sized region of interest on the sample surface via an insertable aperture in the real-space image plane of the electron microscope, enabling micro-ARPES from small samples. Over the past few years, several research groups have benefited from combining ToF-MM and HHG-based time-resolved ARPES system operating at 500 kHz - 1 MHz and achieved high-performance measurements in the low-fluence limit or close [16, 54, 65, 66]. However, the data rate with these repetition rates can still be a problem to scan a range of experimental parameters, especially the probe photon energy as needed to study the matrix element effect or samples with strong  $k_z$  dispersion.

# 1.4 Low-fluence time-resolved micro-ARPES at Stony Brook

At Stony Brook, we have successfully combined a cavity-enhanced HHG source with ToF-MM to produce an advanced beamline that can enable low-fluence time-resolved ARPES at very high data rate. Previously, our group developed an ultra-short table-top HHG source operating at 88 MHz using a resonant cavity enhancement to solve the data-intensity problem of surface photoemission [52]. Using a pulse-preserving monochromator [67], the previous system achieved a nearly synchrotron comparable flux of ~  $10^{11}$  photons per second in a single isolated harmonic to the sample over the broad tuning range of 10 - 40 eV with a spot size of  $58 \times 100 \ \mu\text{m}^2$ , but with ~ 1000 times shorter pulse duration than synchrotron light sources. We observed laser-induced modifications of the photoelectron spectra on Au(111) at the  $10^{-4}$  level in only minutes of integration time using a hemispherical analyzer, demonstrating the feasibility of low-fluence excited-state XUV ARPES experiments nearly free of space-charge effects.

This dissertation presents the work after we further extended our HHG source to the ToF-MM technique at the new 61 MHz repetition rate. It describes highperformance time-resolved ARPES experiments from  $\mu$ m-sized samples in the perturbative excitation regime. To enable such challenging experiments, significant technical advancements are necessary in every component of the instrument and this dissertation describes the required instrumentation and upgrades in detail. Our time-resolved ARPES system consists of a custom-built Yb:fiber frequency comb driver laser, HHG enhancement cavity, subsequent beamline, and ToF-momentum microscope as shown in Fig. 1.1. The upgraded system now delivers a high flux of ~ 10<sup>11</sup> photons per second and a small spot size of 16 × 24  $\mu$ m<sup>2</sup> at the sample, well optimized for performing micro-ARPES measurements. With the upgraded system, we can record ground-state photoemission signals covering the full Brillouin zone in seconds and low-fluence time-reolved ARPES measurements in just a few minutes per delay. This high data rate allows us to systematically explore the large parameter space such as a wide range of fluence, the probe energy, and pump polarization, as shown in our recent measurements in Refs. [25] and [68].



Figure 1.1: The Stony Brook time-resolved ARPES beamline. Time-resolved ARPES experiments are driven by a home-built 80 W, 180 fs Yb:fiber frequency comb operating at a center wavelength  $\lambda_c = 1.03 \ \mu$ m and a repetition rate of 61 MHz. High-order harmonics are generated in a gas jet (GJ) at the focus of a six-mirror enhancement cavity and outcoupled by a sapphire plate at Brewster's angle (BP). A pulse-preserving monochromator, consisting of two toroidal mirrors (TM1 and TM2), a grating, and an exit slit isolates a single harmonic, which is refocused to a sample by a final toroidal mirror (TM3). A ToF-momentum microscope is used for the photoelectron analyzer. This image is courtesy of Sergii Chernov.

This dissertation is organized as follows. Chapter 2 introduces the principles of time-resolved ARPES covering various topics from the basics of ARPES, aspects of time-resolved ARPES, and cavity-enhanced HHG, all relavent to understanding the subsequent chapters. Chapter 3 discusses the critical details of technical optimizations and upgrades on the light source and beamline as well as the performance. Chapter 4 describes the optimization of ToF-MM necessary for performing low-fluence measurements. It addresses what challenges arise from operating a ToF-momentum microscope at a high repetition rate and how the challenges are mitigated in our setup.

The aforementioned optimizations on the instrument have made it possible to study excited-state dynamics in  $\mu$ m domain 2D samples in the perturbative low

fluence regime that previous studies were unable to access. This dissertation particularly focuses on experiments on graphene. Chapter 5 contains the simulations of momentum-space photoelectron distributions by simple tight-binding theory. This chapter also discusses in detail the matrix element effects in photoemission measurements. Chapter 6 presents imaging of initial electron distributions in the nonthermal regime and the details of the subsequent relaxation across a range of fluence. It discusses how electron-electron and electron-phonon couplings play a role on the relaxation. Chapter 7 details data analysis of graphene experiments.

# Chapter 2

# **Time-resolved ARPES**

# 2.1 **Principles of ARPES**

To understand the time-resolved ARPES technique, the general principles of ARPES must be understood first. Many papers and books [9, 10, 69, 70] discuss them in depth. This section follows Refs. [9, 69, 70].

# 2.1.1 $\mathbf{k}_{\parallel}$ determination

When monochromatic light with energy  $h\nu$  greater than the material work function  $\Phi$  (4 - 5 eV for typical metals) impinges on a crystalline solid, electrons absorb that energy, overcoming  $\Phi$  and the binding energy  $E_B$ , and can emit out in different directions with kinetic energies,

$$T = h\nu - (\Phi + |E_B|), \tag{2.1}$$

via the photoelectric effect [11, 12]. The corresponding momenta of these photoelectrons in vacuum are determined by their emission angles  $\theta$  and kinetic energies T as

$$\hbar \mathbf{K} = \hbar \begin{pmatrix} \mathbf{K}_{\parallel} \\ \mathbf{K}_{\perp} \end{pmatrix} = \sqrt{2mT} \cdot \begin{pmatrix} \sin\theta \\ \cos\theta \end{pmatrix}$$
(2.2)

where K are the total wavevectors of the photoelectrons, projected in the planes parallel ( $\mathbf{K}_{\parallel} = \mathbf{K}_x + \mathbf{K}_y$ ) and perpendicular ( $\mathbf{K}_{\perp} = \mathbf{K}_z$ ) to the surface. To derive the energy-momentum dispersion, the crystal momenta  $\hbar \mathbf{k}$  and  $E_B$  of the electrons inside the solid must be retrieved from the photoelectrons' vacuum momenta  $\hbar \mathbf{K}$ and kinetic energies T using proper boundary conditions. However, due to the broken periodic symmetry of the crystal across the surface (i.e. crystal termination), only the in-plane momenta are conserved during a photoemission process. For this reason, the in-plane and out-of-plane momenta,  $\hbar \mathbf{k}_{\parallel}$  and  $\hbar \mathbf{k}_{\perp}$ , are treated separately.

The determination of the in-plane crystal wavevectors  $\mathbf{k}_{\parallel}$  can be done based directly on the detected values of  $\theta$  and T. Due to the in-plane translational symmetry of the crystal, the electron's parallel momenta inside and outside the solid should

match at the surface boundary if the photon momentum is negligible. It then follows that

$$\mathbf{k}_{\parallel} = \mathbf{K}_{\parallel} = \frac{\sqrt{2mT}}{\hbar} \cdot \sin\theta = 0.512 \text{\AA}^{-1} \sqrt{T[\text{eV}]} \cdot \sin\theta.$$
(2.3)

For ARPES experiments conducted in the photon energy range 20 - 100 eV, the photon momentum  $\kappa = 2\pi/\lambda$  is relatively small compared to the typical size of the Brillouin zone  $2\pi/a$  with lattice constant *a* and can be neglected. In this case, the photoelectrons' vacuum momenta  $\mathbf{K}_{\parallel}$  accurately represent the crystal momenta  $\mathbf{k}_{\parallel}$  within the solid and one can construct the energy-momentum dispersion simply by mapping  $E_B$  as a function of  $\mathbf{k}_{\parallel}$  based on measured angles and kinetic energies. For the lower photon energies, their momenta become nontrivial and should be taken into account when writing the momentum conservation statement in Eq. 2.3.

# **2.1.2** $\mathbf{k}_{\perp}$ determination

The determination of the orthogonal crystal wavector  $\mathbf{k}_{\perp}$  becomes important for the complete 3D band mapping of a sample exhibiting substantial  $\mathbf{k}_{\perp}$  dispersion. However,  $\mathbf{k}_{\perp}$  cannot be directly determined from the measurement of  $\mathbf{K}_{\perp}$ (photoelectron's orthogonal wavevector) due to the broken periodicity of the crystal across the surface. To relate  $\mathbf{K}_{\perp}$  and  $\mathbf{k}_{\perp}$ , one must know the final states to which the electrons are photoexcited to inside the solid. Doing so requires the detailed understanding of a photoemission process, which has often been discussed within the context of the Three-Step model [71,72]. The Three-Step model describes photoemission in terms of three successive steps - optical excitation of an electron in the bulk, its propagation to the surface, and its transmission into vacuum (more details follow in Section 2.1.3).

Most often, a nearly free-electron model is used for the final states. This model assumes that after absorbing photons with energy  $h\nu$  in step one, electrons are vertically transitioned to free-electron type final-states with energy,

$$\epsilon_f(\mathbf{k}) = \frac{(\hbar \mathbf{k})^2}{2m} - |V_0| = \frac{\hbar^2 \left(\mathbf{k}_{\parallel}^2 + \mathbf{k}_{\perp}^2\right)}{2m} - |V_0|, \qquad (2.4)$$

where  $V_0$  refers to an energy offset to the true free electron energy  $(\hbar \mathbf{k})^2/2m$ . Commonly known as the inner potential,  $V_0$  is seen as an energy barrier that the electrons must overcome when passing through the surface in the subsequent steps, leading to the discontinuity of the out-of-plane momenta. For those final-state electrons that made it out to the surface without scatterings, their orthogonal crystal wavevectors  $\mathbf{k}_{\perp}$  can be recovered based on the energy conservation before and after exiting the sample,

$$\hbar^2/2m(\mathbf{k}_{\perp}^2) - V_0 = \hbar^2/2m(\mathbf{K}_{\perp}^2).$$
 (2.5)

Using the definition of  $\mathbf{K}_{\perp}$  in Eq. 2.2,  $\mathbf{k}_{\perp}$  takes the form,

$$\mathbf{k}_{\perp} = \sqrt{2m(T\cos^2\theta + V_0)}.$$
(2.6)

The most common way of determining  $V_0$  is from  $h\nu$ -dependent ARPES measrements where the photon energy  $h\nu$  is varied to obtain the periodicity of the  $\mathbf{k}_{\perp}$  dispersion [73,74].

# 2.1.3 The Three-Step model and photoemission cross section

To completely derive the band structure of a solid, one needs to understand photocurrents (photoemission intensities) of energy bands produced in ARPES. The calculation of ARPES photocurrents is usually far more complex as it involves proper treatments for surface/bulk/vacuum effects and interactions. In this regard, the Three-Step model [71, 72] provides a simple description of a photoemission process by breaking it up into three independent steps. Hence, the formulation of ARPES photocurrents is most often discussed within this model.

#### Step 1. Optical excitation of an electron in the solid.

Step 1 is important as it contains all the characteristics of original electronic states necessary for the reconstruction of energy-momentum dispersion. The photocurrent is produced as a result of optical excitation from the N-electron ground state  $\Psi_i^N$  to the N-electron final state  $\Psi_f^N$  by the photon field with energy  $h\nu$ . If the photon field is treated as a small perturbation  $H_{int}$  to the system, the transition probability  $w_{fi}$  for the optical excitation can be approximated by Fermi's Golden Rule:

$$w_{fi} = \frac{2\pi}{\hbar} \left| \left\langle \Psi_f^N \right| H_{int} \left| \Psi_i^N \right\rangle \right|^2 \delta(E_f^N - E_i^N - h\nu).$$
(2.7)

where  $E_i^N$  and  $E_f^N$  denote the initial- and final-state energies, respectively. The delta function is to ensure energy conservation in this step. Eq. 2.7 can be a single step theory if the true final state, i.e. a reversed LEED (Low-Energy Electron Diffraction) state, is provided. The interaction Hamiltonian  $H_{int}$  takes the following form,

$$H_{int} = \frac{1}{2m} (\mathbf{p} + e\mathbf{A})^2 - eU$$
(2.8)

$$\approx \frac{e}{m} \mathbf{p} \cdot \mathbf{A}$$
 (2.9)

where **p** is the electron momentum operator and **A** and *U* are the vector and scalar potentials of the photon field. If one chooses the Weyl gauge U = 0, neglects the term  $\mathbf{A}^2$  for two photon processes ( $\mathbf{A}^2 \ll \mathbf{A}$  in the linear optical regime), and uses the dipole approximation  $\nabla \cdot \mathbf{A} = 0$  (**A** constant over atomic distances, valid in the ultraviolet), then Eq. 2.8 becomes  $[\mathbf{p}, \mathbf{A}] = -i\hbar\nabla \cdot \mathbf{A} = 0$  and simplifies to Eq. 2.9. The dipole approximation does not usually hold for the high photon energy range (i.e. hard X-ray) where photon wavelengths  $\lambda$  becomes comparable to or smaller than atomic dimensions  $a_0$  ( $\mathbf{q} \cdot \mathbf{r} = \frac{2\pi}{\lambda}a_0 \ge 1$  so the higher order terms of the expansion in  $\mathbf{A} = e^{\mathbf{q} \cdot \mathbf{r}}$  become nontrivial).

The transition matrix element  $\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle$  in Eq. 2.7 is a complicated manybody problem and certain approximations about the *N*-electron wavefunctions are necessary for handling this complexity. In the simplest approximation, one can treat electron-electron interactions as a mean field as in the Hartree-Fock theory. In this independent electron approximation, the intial-state (final-state) *N*-electron wavefunctions may be factorized into a single atomic orbital  $\phi_i^k$  ( $\phi_f^k$ ), from (to) which the electron is photoexcited, and the remaining (N-1)-electron wavefunctions  $\Psi_i^{N-1}$  $(\Psi_f^{N-1})$ :

$$\Psi_i^N = \mathcal{A}\phi_i^{\mathbf{k}}\Psi_i^{N-1} \tag{2.10}$$

$$\Psi_f^N = \mathcal{A}\phi_f^{\mathbf{k}}\Psi_f^{N-1} \tag{2.11}$$

where the antisymmetric operator  $\mathcal{A}$  is used to satisfy the Pauli exclusion principle. Note that here  $\phi_i^{\mathbf{k}}$  and  $\phi_f^{\mathbf{k}}$  are taken to be the bulk Bloch states, and are indexed with the same wavevector  $\mathbf{k}$  due to momentum conservation in this step.

In reality, the N-electron system in the final state will try to readjust itself at the instant of photoemission so as to minimize the relaxation energy. In this case, the independent picture no longer holds for the final state, invalidating the factorization in Eq. 2.11. One then needs to invoke an additional approximation, called the *sud*-*den approximation* for justifying Eq. 2.11. In the limit where photoemission occurs instantaneously (no time for interaction between the photoelectron and the remaining system), the escaping photoelectron can be regarded independent, decoupled from the (N-1)-system left behind. The (N-1) electron final-state  $\Psi_f^{N-1}$  can be collapsed into any one of m possible excited states left behind with eigenfunctions  $\Psi_m^{N-1}$  and energy  $E_m^{N-1}$ :

$$\Psi_f^{N-1} = \sum_m a_m \Psi_m^{N-1}.$$
 (2.12)

Equating Eq. 2.10 and 2.12 to 2.7, one can now calculate the total photocurrent  $I(\mathbf{k},T) = \sum_{f,i} w_{fi}$  by summing the transition probabilities  $w_{fi}$  for all possible transitions between the initial and m possible final states:

$$I(\mathbf{k},T) \propto \sum_{f,i} \left| \left\langle \phi_f^{\mathbf{k}} \right| H_{int} \left| \phi_i^{\mathbf{k}} \right\rangle \right|^2 \sum_m \left| \left\langle \Psi_m^{N-1} \right| \Psi_i^{N-1} \right\rangle \left|^2 \delta(T + E_m^{N-1} - E_i^N - h\nu) \right|$$

$$(2.13)$$

$$M_{f,i}^{\mathbf{k}} = \langle \phi_f^{\mathbf{k}} | H_{int} | \phi_i^{\mathbf{k}} \rangle \tag{2.14}$$

$$A^{0}(\mathbf{k}) = \sum_{m} \left| \left\langle \Psi_{m}^{N-1} | \Psi_{i}^{N-1} \right\rangle \right|^{2}$$
(2.15)

where the final-state energy  $E_f^N = T + E_m^{N-1}$  in the  $\delta$  function is rewritten in terms of the kinectic energy of the photoelectron T (referenced to the vacuum level) and

the rest (N - 1) final-state energy  $E_m^{N-1}$ . Under the *sudden approximation*, the *N*-body transition matrix element in Eq. 2.7 has been separated into the simpler one-electron dipole matrix element  $M_{f,i}$  and the spectral function  $A^0(\mathbf{k})$ . These are two essential factors in determining ARPES spectra and more details will be discussed below.

## Step 2. Propagation to the surface.

Following optical excitation in the bulk in step 1, photoexcited final-state electrons travel towards the surface in step 2 under electron scattering events. The electron mean free path plays a crucial role in determining the probability of those photoexcited electrons reaching the surface. Principal scattering mechanisms are electron-phonon and electron-electron scatterings. The electrons, contributing to a background tail of photoemission spectra at lower kinetic energies. The electron mean free path typically follows a kinetic energy dependent "universal curve" in solids [75]. The trend shows a minimum of  $\approx 5$  Å in the kinetic energy range of 20 - 100 eV, the values expected from typical ARPES experiements. Therefore, the vast majority of photoexcited electrons, that made it out to the surface with no energy loss, come from only the top few layers in ARPES, making ARPES a highly surface sensitive technique particularly for the extreme ultraviolet photon energy range used.

## Step 3. Transmission into vacuum

In the last step the photoexcited final-state electrons overcome a potential barrier at the surface and transmit into a free-electron plane wave state in vacuum. During this process the out-of-plane component  $\mathbf{k}_{\perp}$  is not conserved due to this potential step. The total photoemission current is a product of the respective probabilities in the three steps.

#### **Remarks on the Three-Step model.**

Although the Three-Step formalism has been successful in that it gives a simple, intuitive description of the photoemission process, this oversimplified model has a drawback (for detailed discussion, see Ref. [69]). The model barely takes surface effects into account for the photocurrent although it recognizes photoemission as surface, not just bulk, phenomena. First, the final state is treated as a bulk Bloch state, completely neglecting the existence of the surface for the matrix element. Secondly, the model uses the electric dipole approximation  $\nabla \cdot \mathbf{A} = 0$ , but this assumption is generally invalid near the surface, where the gradient of the vector potential  $\mathbf{A}$  changes according to a rapid change in the dielectric constant near the surface-vacuum interface. In some cases, these surface effects are not small and directly impact the photoemission spectra, known as surface photoemission (see Ref. [69] for more details).

Note that a more rigorous approch called the One-Step model [76, 77] also exists, which combines all these three steps into a single coherent step. In certain cases, this One-Step model may be more appropriate and can reproduce the data with a better accuracy. More sophisticated models that take relativistic and many body effects into account have also been developed over the years (see Ref. [69] and references therein).

# 2.1.4 The spectral function

To generalize the photoemission formalism to any kind of systems, even to those exhibiting substantial many-body phenomena, it is important to consider electron interactions more formally. In the context of interacting many-body problems, the most commonly used approach is the Green's function formalism, where manybody interactions are properly accounted for by electron self-energy  $\Sigma(\mathbf{k}, E)$  in Green's functions. In photoemission, the one-electron Green's function  $G(\mathbf{k}, E)$ is a relavent one to use because the equation  $A(\mathbf{k}, E) = -1/\pi \text{Im}G(\mathbf{k}, E)$  directly relates it to the one-electron spectral function  $A(\mathbf{k}, E)$ . For an interacting system,  $G(\mathbf{k}, E)$  is given by

$$G(\mathbf{k}, E) = \frac{1}{E - \epsilon_{\mathbf{k}} - \Sigma(\mathbf{k}, E)},$$
(2.16)

and the corresponding spectral function takes the following form,

$$A(\mathbf{k}, E) = -\frac{1}{\pi} \frac{\Sigma''(\mathbf{k}, E)}{[E - \epsilon_{\mathbf{k}} - \Sigma'(\mathbf{k}, E)]^2 + [\Sigma''(\mathbf{k}, E)]^2}.$$
 (2.17)

Now many-body interactions are introduced in the so-called self-energy,  $\Sigma(\mathbf{k}, E) = \Sigma'(\mathbf{k}, E) + i\Sigma''(\mathbf{k}, E)$ , as a correction to the unperturbed, single-electron energy  $\epsilon_{\mathbf{k}}$ , called the bare band energies.  $A(\mathbf{k}, E)$  here is a Lorentzian in E and the spectral broadening and the renormalized peak position due to the interactions are determined by the imaginary  $\Sigma''$  and real part  $\Sigma'$  of the self-energy, respectively.

In the independent electron approximation,  $\Sigma(\mathbf{k}, E) = 0$  and  $A(\mathbf{k}, E) = -1/\pi$  $\delta(E - \epsilon_{\mathbf{k}})$  and  $A(\mathbf{k}, E)$  consists of a series of sharp lines at the bare band energies  $\epsilon_{\mathbf{k}}$ , that is the single-particle band structure. This approximation is pretty good for ARPES from graphene with the electronic structure well described by band theory. In our work, we excite electrons to energy  $h\nu_{\text{pump}}/2 = +1.2$  eV above the Dirac point by a 2.4 eV pump pulse. Although electron interactions may affect how electrons move in the bands and change the distributions, they are not really expected to modify the electronic structure of graphene. In this case, ARPES measures electrons moving in the bands described by the single-particle band structure.

In the interacting case, which means  $\Psi_m^{N-1}$  has other excited-state contributions in Eq. 2.15,  $A(\mathbf{k}, E)$  consists of the main line dressed with satellite lines. Then,  $A(\mathbf{k}, E)$  encodes not only the single-particle band structure but also the many-body effects.

# 2.1.5 **ARPES** intensity

It is customary to write ARPES intensity in terms of the one-electron spectral function  $A(\mathbf{k}, E)$  in Eq. 2.17 such that many-body interactions are properly accounted for. To carry on,  $A^0(\mathbf{k}) = \sum_m |\langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle|^2$  in Eq. 2.13 needs to be related to  $A(\mathbf{k}, E)$ . In the language of second quantization,  $\langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle$  is represented as  $\langle \Psi_m^{N-1} | c_{\mathbf{k}}^- | \Psi_i^N \rangle$ , where the annihilation operator  $c_{\mathbf{k}}^-$  removes an electron with momentum  $\mathbf{k}$  from N-electron initial-state  $\Psi_i^N$ , resulting in (N-1)-electron initial-state  $\Psi_i^{N-1}$ . In this context,  $A^0(\mathbf{k})$  becomes the single-electron removal spectral function  $A^-(\mathbf{k}, E)$ ,

$$A^{-}(\mathbf{k}, E) = \sum_{m} \left| \left\langle \Psi_{m}^{N-1} \right| c_{\mathbf{k}}^{-} \left| \Psi_{i}^{N} \right\rangle \right|^{2} \delta(E - E_{m}^{N-1} + E_{i}^{N}),$$
(2.18)

relating to the full spectral function by  $A^{-}(\mathbf{k}, E) = A(\mathbf{k}, E)f(E)$  where the Fermi-Dirac function f(E) restricts the state occupation up to  $E_F$ . The standard expression for ground-state ARPES intensity takes the following form,

$$I(\mathbf{k}, E) \propto \sum_{f,i} \left| M_{f,i}^{\mathbf{k}} \right|^2 f(E) A(\mathbf{k}, E).$$
(2.19)

Thus, ARPES measures the single-particle band structure and the associated manybody interactions, determined by  $A(\mathbf{k}, E)$ , with its intensity modulated by the matrix element effects. In the independent-electron approximation, the single-particle spectral function  $A(\mathbf{k}, E)$  becomes a  $\delta$ -function at the Hartree-Fock orbital energy  $\epsilon_{\mathbf{k}}$  and Eq. 2.19 becomes

$$I(\mathbf{k},\varepsilon) \propto \left|\mathbf{M}_{f,i}^{\mathbf{k}}\right|^{2} \delta(\varepsilon - \epsilon_{\mathbf{k}}) f(E).$$
(2.20)

In this limit, ARPES measures the single-particle bare band dispersion with its intensity modulated by the matrix element effect.

# 2.1.6 Matrix element

The photoemission matrix element plays an essential role in determining the ARPES spectra. However, the accurate formulation of the matrix element is generally difficult, mainly due to a difficulty in taking surface effects into account, and thus has been calculated with some levels of approximation as in the Three-Step model. Within the Three-Step model under the independent electron approximation, the matrix element has been introduced earlier as a one electron dipole matrix element,  $\mathbf{M}_{f,i}^{\mathbf{k}} \propto \langle \phi_f^{\mathbf{k}} | \mathbf{A} \cdot \mathbf{p} | \phi_i^{\mathbf{k}} \rangle$  with  $\mathbf{A}$  the vector potential of an incoming photon field and  $\mathbf{p}$  the electron translation momentum. In the electric dipole approximation,  $\mathbf{A}(\mathbf{r}) = \mathbf{A}_0 e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{A}_0(1 + i\mathbf{q}\cdot\mathbf{r} + ...) \approx |\mathbf{A}_0|\hat{\lambda}$  where  $\hat{\lambda}$  is the unit vector along the direction of the light polarization and  $\mathbf{q} = (\omega/c)\hat{n}$  is the wavevector of the light with  $\omega$  the angular frequency, c the speed of light, and  $\hat{n}$  the unit vector along the light propagation direction.

$$\mathbf{M}_{f,i}^{\mathbf{k}} \propto \langle e^{i\mathbf{k}\cdot\mathbf{r}} | \,\hat{\lambda} \cdot \mathbf{p} \, | \phi_i^{\mathbf{k}} \rangle \tag{2.21}$$
This simple approximation actually turns out to be a fair estimate for the matrix element and can be used to interpret ARPES data.

In the simplest case, one can take a free-electron final state with a single plane wave only. The one electron dipole matrix element  $\mathbf{M}_{f,i}^{\mathbf{k}}$  is then written as

$$\mathbf{M}_{f,i}^{\mathbf{k}} \propto (\hat{\lambda} \cdot \mathbf{k}) \langle e^{i\mathbf{k} \cdot \mathbf{r}} | \phi_i^{\mathbf{k}} \rangle.$$
(2.22)

Eq. 2.22 highlights three key factors for intensity modulation. First, the  $\hat{\lambda} \cdot \mathbf{k}$  term in  $\mathbf{M}_{f,i}^{\mathbf{k}}$  selects the directions of outgoing photoelectrons momenta  $\mathbf{k}$  by projecting  $\mathbf{k}$  to the light polarization direction. Second, photon energy  $(h\nu)$  also affects photoemission intensity through a relation  $\hbar^2 |\mathbf{k}|^2 / 2m_e = h\nu - (\Phi + |E_B|)$ , where  $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_z$  and  $h\nu - (\Phi + |E_B|) = T$ , photoelectron's kinetic energies in Eq. 2.1. Lastly, the details of intensity modulation also depends on the initial and final states. For example, in graphene one can take a tight binding, Bloch wavefunction for the initial state (see Chapter 5 for more details). In this case, the overlap integral  $\langle e^{i\mathbf{k}\cdot\mathbf{r}} | \phi_i^{\mathbf{k}} \rangle$ , more precisely the relative phase between two sublattice wavefunctions, leads to interesting interference patterns near the Brillouin zone corners [78]. As a result, signals from some bands are relatively weaker than those from others, and in some cases, they can entirely vanish depending on the polarization and energy of an incident photon field, known as dark corridors [79–82].

While the matrix element helps understand the ARPES spectra, it can also complicate the data analysis in some cases. The reason is that where the matrix element vanishes can coincide with the region of interest where the physics is being studied, obscuring the interpretation of results (see Ref. [68] and Chapter 5). Thus, understanding the matrix element is crucial for discerning the matrix element effects from the actual observables.

# 2.2 General aspects of time-resolved ARPES

Time-resolved ARPES is conducted in a pump-probe scheme where pump pulses excite electrons to unoccupied states and delayed probe pulses track the population of the excited electrons by photoemission. However, adding the ultrashort pump pulse to conventional ARPES typically presents more challenges to the instrumentation of time-resolved ARPES. One must understand not just existing fundamental problems in ARPES, such as space charge, but also many other technical considerations related to light sources (e.g. polarization, photon energy, tunability in both pump and probe pulse, repetition rate, spot size), the system's resolution (e.g. momentum, energy, time), and electron detection schemes. Since many of these factors are related to each other, it is difficult to design a perfect time-resolved ARPES system that meets all these aspects without certain trade-offs. More technical details on the time-resolved ARPES instrumentation can be found in Ref. [70,83,84]. This section discusses key factors relevant to general time-resolved ARPES experiments.

#### 2.2.1 Space charge effect

One of the most fundamental problems in photoemission measurements is the so-called space charge effect. When electrons are emitted from a sample during a short laser period, their mutual Coulomb interactions change each other's trajectories, leading to the redistribution of the electrons in momentum and energy on their way to a detector. This causes broadening and shift of photoelectron spectra, degrading data quality.

Numerous studies [43,44,46,47,85–87] have extensively investigated the space charge effect over a range of kinetic energies and pulse durations. Both shifts and broadening of photoemission spectra are observed to scale with electron density  $\rho \equiv N/D$ , where N and D are the number of electrons generated per pulse and the lateral spot size on the sample, respectively. In terms of the sample current  $I_s$  and the laser repetition rate  $f_r$ , this becomes

$$\Delta E_{b\,(sh)} \propto \left(\frac{N}{D}\right)^x \propto \left(\frac{I_s}{f_r D}\right)^x$$
(2.23)

where  $\Delta E_{b\,(sh)}$  is the energy broadening (b) and shifts (sh) of the photoelectron spectrum. Here, x is an empirical paramter related to kinetic energies and pulse durations. For fs-XUV pulses, both theory and experiment have confirmed  $x \approx 1$  while  $x \approx 0.5$  for ps- or fs-UV pulses [43–47].

Based on the expression in Eq. 2.23, the space charge limits the number of electrons that can be extracted from a sample and thus the number of photons that can be applied to it. Maklar et al. have determined that the number of electrons per pulse should be within 100 - 1000 to limit the resolution to 100 meV for XUV probe pulses, depending on the type of photoelectron analyzer [51]. Their study shows that photoelectron spectra measured with momentum microscopes can experience space charge distortions at much lower photocurrents than conventional hemispherical analyzers. Hellmann et al. have shown in their simulations that to limit the broadening to less than 5 meV, N/D must be less than 3  $\mu$ m<sup>-1</sup> [47]. Spreading the electrons more through space by increasing the spot size D is then a good way of lessening the space charge effect. However, for probing  $\mu$ m-domain samples, as occurring in single crystals or 2D materials prepared by exfoliation, small spot sizes are certainly needed and increasing the spot size may not be desired. A more effective way of mitigating the space charge problem is by increasing repetition rate. However, the repetition rate is usually compromised by other factors such as excited-state decay or detector limitations depending on the analyzer type used [51]. The measurements of space charge characterization and detector limitation using our momentum microscope can be found in Chapter 4.

For time-resolved ARPES, the use of ultrashort pump pulses can intensify the space charge problem via multi-photon photoionization processes [48–50]. The complexity in this case arises from the fact that the space-charge interaction between pump- and probe-induced electrons changes with pump-probe delay, leading to a delay-dependent spectral shift, difficult to separate from the dynamics of interest [48–50]. One must also keep in mind that there is another complexity, called

surface photovoltage, arising from the pump pulses especially in semiconductors. Surface photovoltage refers to illumination-induced changes in the surface potential (or voltage) [88–90] and this shifts photoelectron spectra as a function of pump-probe delay [91–95]. In both cases, the shift depends strongly on laser intensity and thus it is important to keep excitation fluence low enough to minimize the effect.

### 2.2.2 System's resolution

One of the important technical aspects to be considered for the instrumentation of time-resolved ARPES is the system's resolution. From Eq. 2.3, the momentum resolution of the system, neglecting its finite energy resolution, can be expressed as

$$\Delta k_{\parallel} = \sqrt{2mE_k/\hbar^2} \cdot \cos(\theta) \cdot \Delta\theta \tag{2.24}$$

where  $\Delta \theta$  is the angular resolution of a system. It is obvious from this equation that lower photon energy  $h\nu$  and larger emission angle  $\theta$  improve the momentum resolution in general. For this first reason, high-resolution ARPES experiments are often performed using lower energy UV light, for example, to study topological insulators and superconductors. In practice, the momentum resolution of an actual measurement is compromised by sample quality and energy resolution.

The energy resolution of ARPES measurements depends on the energy bandwidth  $\delta E_{h\nu}$  of a probe light and the detector resolution  $\delta E_D$ ,

$$\delta E = \sqrt{(\delta E_{h\nu})^2 + (\delta E_D)^2}.$$
(2.25)

Here, the probe's energy bandwidth is fundamentally limited by its time bandwidth  $\delta t$  via the following Fourier uncertainty relation,

$$\delta E_{h\nu}(\mathrm{eV}) \cdot \delta t(\mathrm{fs}) \ge \hbar 4 \ln 2 = 1.825 \,\mathrm{eV} \cdot \mathrm{fs} \tag{2.26}$$

where  $\delta t$  and  $\delta E_{h\nu}$  are measured at FWHM assuming a Gaussian pulse. Because of this Fourier transform limit, the energy resolution is usually compromised with the time resolution determined by a pump-probe cross relation. The resolution can be further degraded by the space charge effect, as mentioned in the previous section, sample quality, type of photoelectron analyzers [51], or electronic noise/time jitter of the instrument.

#### 2.2.3 Light sources for time-resolved ARPES

The advancement of light sources for time-resolved ARPES has been primarily driven by two motivations, the desire to cover the full Brillouin zone of most condensed-matter systems and the desire to mitigate the space charge effect. Most conventional table-top laser systems for time-resolved ARPES have employed low energy 6 eV probe sources, generated via frequency up-conversion in nonlinear crystals [96–102]. The 6-eV sources are, in general, capable of achieving high resolution as discussed in section 2.2.2, but they have a limited Brillouin zone coverage. According to Eq. 2.3, the maximum parallel momenta of photoelectrons are  $\mathbf{k}_{\parallel,\text{max}} = 0.512 \text{\AA}^{-1} \sin(60^\circ) \sqrt{(h\nu - \Phi - |E_B|)[\text{eV}]}$  assuming  $\theta = 60^\circ$  is within the acceptance angle of the analyzer. The 6-eV probe light yields the maximum accessible momenta  $k_{\parallel}^{max} = 0.54 \text{\AA}^{-1}$  for an electron at the Fermi level ( $E_B = E_F$ ), assuming the work function  $\Phi = 4.5$  eV. It is clear that traditional 6-eV sources probe the electron states near the  $\Gamma$  point located at the the center of the Brillouin zone. In order to cover the full Brillouin zone of most solids, which may extend up to 2.0 Å<sup>-1</sup> [30], it is necessary to employ a higher energy probe light, at minimum in the XUV range.

There are different methods for accessing the extreme ultraviolet spectral region. Synchrotron radiation has been the main choice for XUV ground-state ARPES for many decades. It offers a bright source with tunable parameters, i.e. wavelength, polarization, spot size, which are particularly useful for nano/spin-ARPES. High harmonic generation (HHG) has often been the best choice until now for generating table-top XUV pulses suitable for time-resolved ARPES. However, most HHGbased ARPESsystems have long suffered from severe data-rate restriction imposed by the space charge effect from low repetition rates as discussed in Section 2.2.1. Scientisits have achieved large gains in developing high repetition rate XUV sources suitable for time-resolved photoemission measurements. High repetition rate ultrashort XUV pulses can be generated via single-pass HHG with high-power lasers and tight focusing [54–56] or cavity-enhanced techniques [52, 57]. In this thesis, cavity-enhanced HHG is used for generating high repetition rate XUV pulses and the details of the technique will be discussed below.

# 2.3 Cavity-enhanced high harmonic generation

## 2.3.1 Principles of enhancement cavity

As shown in Fig. 2.1, the typical design of an enhancement cavity is a bow-tie configuration, where the optical path length L is folded with an input coupler (M1) and m high reflectors (HRs). The bow-tie design is useful for generating error signals for feedback loops controlling the cavity length (or laser repetition rate) and laser offset frequency. To understand how input light excites the resonance modes of an enhancement cavity, one can simplify this geometry to a basic Fabry-Perot cavity formed of two lossless mirrors by grouping the HRs into one effective HR, denoted as  $M_m$ . One can then think of its field reflection coefficient  $r_m$  as the effective field reflectivity from the HRs [103].



Figure 2.1: Principles of an optical resonator. A typical bow-tie enhancement cavity shown in a) can be simplified to a basic Fabry-Perot interferometer consisting of two mirrors as shown in b), 1 input coupler (M1) and a group of m high reflectors (HR1 - HRm), denoted as M $_m$ . Cavity transmission is shown in c).

An incident wave with the field amplitude  $E_0$  transmitts through M1 that has the field reflection coefficient  $r_1$  and the field transmission coefficient  $t_1$ . During the first round-trip, the transmitted wave with the field amplitude  $E_0^+ = tE_0$  travels to the right of M1, reflected from  $M_m$ , and reflected back from M1 with the field amplitude  $E_1^+ = E_0^+ r_1 r_m e^{-i\phi}$ . Note that the field amplitude of the reflected wave back from M<sub>1</sub> after each round-trip pass is attenuated by a factor of  $r_1 r_m e^{-i\phi}$  where  $\phi$  is the total round-trip phase shift accumulated by an intracavity pulse. After the  $n^{th}$  pass, the total amplitude of the circulating field,  $E_c$ , is a sum of all these reflected contributions up to  $E_n^+$ :

$$E_c = \sum_{k=0}^{n} E_n^+ = E_0^+ \sum_{k=0}^{n} (r_1 r_m e^{-i\phi})^n = \frac{E_0^+}{1 - r_1 r_m e^{-i\phi}}$$
(2.27)

where the convergent geometric series is used in the last step. The absolute square of  $E_c$  gives the intensity of the internal field:

$$I_c(\phi) = \frac{I_{c,max}}{1 + (\frac{2\mathcal{F}}{\pi})^2 \sin^2(\phi/2)}$$
(2.28)

where  $I_{c,max} = I_0 B$  is the maximum circulating intensity and  $\mathcal{F}$  is the cavity finesse, defined as

$$\mathcal{F} = \pi \frac{\sqrt{r_1 r_m}}{(1 - r_1 r_m)}.$$
(2.29)

The cavity finesse is determined by the cavity losses.

The resonances of the cavity occur when the total round-trip phase accumulated by a circulating light is some integer (q) multiple of  $2\pi$ , i.e.  $\phi_q = q \cdot 2\pi$ . In the abscence of the mirror spectral phase (see section 2.4.1), the resonance condition locates a longitudinal cavity mode at every  $2\pi$ , where the maximum intensity peak  $I_{c,max}$  repeats with a period of  $2\pi$ . The allowed standing wave modes are then given by the familiar Fabry-Perot formula seen from most optics textbooks:

$$\lambda_q = \frac{L}{q}, \qquad v_q = \frac{c}{L}q, \qquad \omega_q = \frac{2\pi c}{L}q \qquad (2.30)$$

The spacing between two adjacent resonance modes is called the free spectral range (FSR),

$$\operatorname{FSR}_{v} = \frac{c}{L}, \qquad \operatorname{FSR}_{\delta\omega} = \frac{2\pi c}{L}.$$
 (2.31)

From Eq. 2.30, one can see that the light can only pass through the cavity if the cavity length is an integer number of the wavelength of the laser light. In terms of frequency, the laser frequency must be an integer multiple of the cavity FSR to resonate the light inside the cavity. Thus, the cavity acts as a frequency discriminating filter with its resonance evenly separated by the FSR for the linear cavity. Note that in practice, cavity mirror dispersion causes the resonance positions not quite integer multiple of  $2\pi$ , but rather adds a small frequency-dependent shift to them (more details are found in section 2.4.1).

The standard expression of circulating field intensity is given by

$$I_c(\omega) = \frac{I_{c,max}}{1 + (\frac{2\mathcal{F}}{\pi})^2 \sin^2(\pi\omega/\text{FSR}_{\delta\omega})}$$
(2.32)

in terms of measurable quantities  $\text{FSR}_{\delta\omega}$  and  $\mathcal{F}$ . The width of a resonance peak can be characterized by finding a frequency  $\omega_{1/2}$  at which  $I_c$  falls to  $I_{c,max}/2$ . This gives  $(2\mathcal{F}/\pi)^2 \sin^2(\pi\omega_{1/2}/\text{FSR}_{\delta\omega}) = 1$ . The small angle approximation  $\sin(\theta) \approx \theta$ gives the expression  $\omega_{1/2} = \text{FSR}_{\delta\omega}/2\mathcal{F}$ . The full width at half-maximum of a cavity linewidth is just a ratio of  $\text{FSR}_{\delta\omega}$  to  $\mathcal{F}$ :

$$\Delta \omega_{\rm fwhm} = \frac{\rm FSR_{\delta\omega}}{\mathcal{F}}.$$
(2.33)

## 2.4 Basics of cavity-comb coupling

The teeth  $v_m$  of an optical frequency comb with repetition rate  $f_r$  and carrierenvelope offset frequency  $f_0^{(\text{comb})}$  are rigorously given by

$$v_m^{(\text{comb})} = m \times f_r + f_0^{(\text{comb})}$$
(2.34)

where m is some integer [104]. In the abscence of mirror dispersion (see next section), the resonance modes of an optical cavity are uniformly spaced by the FSR. The  $n^{\text{th}}$  cavity resonance mode can then be described by a simple formula,

$$v_n^{(\text{cav})} \approx n \times \text{FSR} + f_0^{(\text{cav})}$$
 (2.35)

where  $f_0^{(\text{cav})}$  is an offset frequency between 0 and FSR. Despite the resemblance of two formulas, the cavity  $f_0^{(\text{cav})}$  is not necessarily the same as the comb  $f_0^{(\text{comb})}$ because of the dispersion effects from cavity mirror coatings and the Gouy phase at the cavity focus (see next section). Therefore, by matching the comb repetition rate to the cavity FSR and the comb offset  $f_0^{(\text{comb})}$  to the cavity offset  $f_0^{(\text{cav})}$ , one can simutaneously bring many comb teeth onto resonance, as shown in Fig. 2.2b.

The equivalent time-domain picture for cavity-comb coupling is shown in Fig. 2.2a. The resonace condition is achieved when input pulses from the frequency comb constructively interfere with circulating intracavity pulses. The coupling scheme is described in detail in Chapter 3.3.2.



Figure 2.2: Cavity-comb coupling in both the time and frequency domains. a) In the time-domain picture, input pulses from a frequency comb are constructively interfered with circulating intracavity pulses. b) In the equivalent frequencydomain picture, a large number of frequency comb teeth are simultaneously resonantly enhanced in a large number of cavity modes.

For coupling a frequency comb to an optical cavity, it is more practical to describe an optical frequency comb based on a fixed point analysis [105–108], writing the comb's optical frequency as

$$v_m^{(\text{comb})} = (m - m^*) \times f_r + v_{m^*},$$
(2.36)

where  $m^*$  is an integer indicating a fixed point of the frequency comb that remains stationary to a particular external perturbation. In the fixed point analysis, the comb modes are considered to expand or contract around this fixed point via changes in  $f_r$ . Since a frequency comb has two degrees of freedom, the comb stabilization is typically done via two active feedback loops with two or more actuators. In our laser,

### **2.4.1** Dispersion effects on cavity-comb coupling.

It has been shown in Section 2.3.1 that the resonance of an optical cavity occurs when the total round-trip phase  $\phi$  accumulated by a light wave is an integer multiple of  $2\pi$ ,  $\phi = 2\pi q$  with q an integer. The total round-trip phase shift has three components. First and largest is plane-wave-like propagation the vacuum between the mirrors

$$\phi_{\text{prop}}(\omega) = \frac{2\pi}{\lambda} L_{rt} = \frac{\omega}{c} L_{rt}$$
(2.37)

where c is the speed of light,  $\omega$  is the angular frequency, and  $L_{rt}$  the round trip distance between the mirrors. Second is the round trip Gouy phase,  $\theta_{Gouy}$ , which captures an extra phase shift on the circulating light due to the fact that a focused Gaussian beam is not a plane wave.  $\theta_{Gouy}$  is frequency independent and in the context of cavity-comb coupling, it amount to a pure carrier-envelope offset frequency shift of the circulating intracaviy pulse [109].

The third contribution is the reflection spectral phase of the mirrors. If the mirrors have a combined complex amplitude reflection  $r_{\text{mirror}} \equiv |r|e^{i\phi(\omega)}$ , with all three contributions, the cavity resonance condition becomes

$$\frac{\omega}{c}L_{rt} + \theta_{\text{Gouy}} + \phi(\omega) = 2\pi n . \qquad (2.38)$$

Note that in the absence of the mirror spectral phase, the frequency spacing between adjacent cavity resonances is given by the condition  $(\omega_{n+1}/c)L_{rt} - (\omega_n/c)L_{rt} = 2\pi$  which reduces to the familiar expression for the free spectral range (FSR) of an optical resonator  $\Delta \nu = c/L_{rt}$ , and this is independent of frequency. In general, the mirror phase  $\phi(\omega)$  makes the cavity FSR depend on frequency and this sets the principal limitation on the frequency comb bandwidth that can be simultaneously resonantly enhanced in the cavity [61]. The spectral phase is usually expanded about a central frequency

$$\phi(\omega) = \phi_0 + \phi_1(\omega - \omega_0) + \frac{1}{2}\phi_2(\omega - \omega_0)^2 + \dots$$
 (2.39)

where  $\phi_0$  is the phase shift that would be accumulated by a monochromatic wave at frequency  $\omega_0$ ,  $\phi_1$  is the group delay of a pulse, and  $\phi_2$  is the group-delay dispersion (GDD). In the time-domain picture, the first two terms do not affect the pulse shape but the higher-order terms do. In the frequency-domain picture, it is the GDD and higher order terms that make the cavity FSR frequency dependent.

The GDD distorts the shape of a cavity pulse, both the envelope and the carrier. Consequently the cavity modes are not perfectly spaced by the FSR, rather the FSR changes with the frequencies, leading to comb-cavity mode mismatches. This effect can not be completely compensated by adjusting  $f_r$  and  $f_0^{\text{comb}}$  of a frequency comb, and thus limits the amount of the comb bandwidth coupling into an enhancement cavity. This spectral filtering lowers the peak power circulating inside an enhancement cavity because the pulse is longer and comb-cavity mode walk-offs result in a lower average power. This means that the mirror GDD constrains the design of an femptosecond enhancement-cavity. To maintain high peak power, a lower finesse cavity is often desired since it reduces the spectral filtering as seen from the relation,  $\delta\omega = \frac{\text{FSR}_{\omega}}{\mathcal{F}}$ . For the higher enhancement factor, an over-coupled cavity may be more preferrable over an impedence matched cavity since the buildup of an over-coupled cavity is twice more than that of an impedence matched cavity,  $\approx \mathcal{F}/\pi$ .

# 2.5 High harmonic generation

It generally becomes harder to build lasers below the ultraviolet region because of pump power scaling as  $\lambda^{-4}$  [110]. In a traditional optical pumping scheme, the spontaneous emission rate must exceed the absorption rate to produce a population inversion. The pump power to attain a substantial gain from the population inversion scales with  $\lambda^{-4}$ . This means that lasing at visible 500 nm implies 16 times higher pump power than at the IR 1000 nm. To produce the XUV 10 - 100 nm radiation, the pump power has to increase by at least 4 - 8 orders of magnitude higher than that to generate the IR. For these reasons, commercial ultrafast lasers are widely available in the IR but not many below the UV.

An alternative way of generating the XUV light is to convert the commonly available IR or visible light using nonlinear frequency up-conversion processes. Conventional nonlinear optics is based on perturbation theory where light-matter interaction is treated as a small perturbation to a system. In this case, the atomic polarization density P in a dielectric medium induced by the applied field E can be expanded by the Taylor series around zero E as

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$$
(2.40)

where  $\chi^{(k)}$  is the  $k^{th}$  order susceptibilities [111]. The most familiar nonlinear phenomena seen in ultrafast optics are the second or third harmonic generation where focusing an IR or NIR light onto nonlinear crystals produces a new frequency at two or three times the driving laser frequency [112–114]. The harmonic yield generally decreases following a power law with increasing harmonic order in this perturbative limit.

In order to extend radiation to the XUV range, the field amplitude should increase sufficiently high so that many more higher order terms in Eq. 2.40 become important. However, as the increased field strength becomes comparable to the atomic field that binds electrons to the nucleus of an atom, light-matter interaction is no longer perturbation to a system and the expansion in Eq. 2.40 fails to converge [111], calling for a different model to understand the strong field nonlinear optics.

High harmonic generation (HHG) was first observed in the late 1980's by McPherson et al. [115] and Ferray et al. [116]. When an intense laser was focused onto a noble gas target, the harmonic spectra exhibited a plateau of constant intensities extended into many harmonic orders, instead of the usual exponential fall-off expected from the perturbative nonlinear optics, and then an abrupt cutoff. The experiments of Ferray are much more clearly HHG, showing a much clear plateau/cutoff behaviour due to driving with an infrared laser. The basic phenomena of HHG are now described by the three step model, first proposed by by Kulander et.al [117] and Corkum [118] and later well understood by Lewenstein [119].



**Figure 2.3: Three step model of high-harmonic generation.** The electron bound to its atomic core is tunnel-ionized near the peak of an electric field, gains kinetic energy from motion in the field, and recombines with the parent atom, emitting a high energy photon in the XUV region.

The first step of the thee tree step model is the ionization of an target atom. When a single atom is subject to an intense oscillating electric field, the driving field bends an atomic potential well, leading to the tunneling of an electron through the barrier. The ionization process is characterized by the Keldysh parameter,

$$\gamma = \sqrt{\frac{I_p}{2U_p}} \tag{2.41}$$

where  $I_p$  is the ionization potential of an atom and  $U_p$  is the ponderomotive energy, the time averaged kinemic energy of an electron in the oscillating laser field. The ponderomotive energy is given by

$$U_p = \frac{e^2 E^2}{4m_e \omega^2} \tag{2.42}$$

$$U_p[\text{eV}] = 9.33 \times 10^{-14} I[\text{ W/cm}^2] \lambda^2 [\ \mu\text{m}^2]$$
(2.43)

where  $\omega$ ,  $\lambda$ , E, I are the frequency, wavelength, and amplitude, and intensity of the driving field, and e and m are the electron charge and mass. In Eq. 2.43, all the natural constants are absorbed in the numeric factor [120].

For  $\gamma \gg 1$  ( i.e.  $U_p \ll I_p$ ), the ionization process is described by multiphoton absorption. The applied field is still too weak to distort the atomic potential for the electron tunnelling. The laser field instead imparts the energy of  $N \cdot \hbar \omega$  to the electron in the ground state, supplying enough energy to liberate it to the continuum,  $I_p \leq N \cdot \hbar \omega$ . In the limit  $\gamma \leq 1$ , the so-called strong field regime, the electron tunnelling occurs near the field maximum.

In the second step of the three step model, the freed electron born near the maximum of the driving field gains kinetic energy by acceleration of the field and starts to move in the field away from the parent ion. The motion of the electron is well described by classic Newton's law.

The third step is recombination of the electron. As the field reverses in the next half cycle, it accelerates back to the initial position at the parent ion site. The cut-off energy, maximum photon energy released upon the recombination, is

$$\hbar\omega_{max} = I_p + 3.17U_p. \tag{2.44}$$

It is determined by the ionization potential of a gas medium and the wavelength and intensity of the driving field. The corresponding harmonic spectrum is a rapid fall-off for the low-order harmonics, expected from the perturbation theory, followed by a plateau where the harmonic intensity drops more slowly, and then an abrupt cutoff. Only odd harmonics are present due to the inversion symmetry of atomic gases [121].

# Chapter 3

# Stony Brook Light Source (SBLS) and Beamline

# 3.1 Overview



**Figure 3.1: Stony Brook Light Source and beamline.** TM: toroidal mirror, BP: Brewster plate GJ: gas jet, VPD: vacuum photodiode, PD, IC: input coupler.

The layout of the Stony Brook Light Source (SBLS) and beamline is shown in Fig. 3.1. The light source is divided into a Ytterbium (Yb):fiber frequency comb driver laser and cavity-enhanced HHG source. The SBLS driver laser is a home-built 80 W, 180 fs Yb:fiber frequency comb operating at a center wavelength  $\lambda_c$  =1.03  $\mu$ m and a repetition rate of 61 MHz. Fig. 3.2 illustrates the main components of the SBLS driver laser. More details of the laser system can be found in Ref. [122]. The front-end laser system is built with two components—a Yb:fiber mode-locked oscillator producing a 1.03- $\mu$ m seed light at 61MHz and a polarization-maintaining (PM) Yb-doped fiber pre-amplifier (YDFA). This two component system supplies a sufficient amount of steady seed power to the subsequent amplifier system.

The comb is amplified to 80 W average power and 180 fs pulse duration using

linear chirp pulse amplification in a two-stage power amplifier. First, the 1.03- $\mu$ m seed pulse from the YDFA is broadened to several hundred picoseconds in a custom-made fiber stretcher to avoid intensity-dependent nonlinear effects in the subsequent amplifier chain. Our fiber pulse stretcher consists of a 31.9 m single mode fiber with normal second- and third-order dispersion ( $\phi_2 < 0, \phi_3 < 0$ ) and a 11.8 m anomalous third-order dispersion cladding fiber ( $\phi_2 < 0, \phi_3 > 0$ ). These modules are carefully length-controlled to match the higher-order dispersion of our compressors. Next, the stretched, 1.03- $\mu$ m seed pulses are amplified in a 2.5-m long Yb-doped photonic crystal fiber (PCF) with a 31  $\mu$ m mode field diameter (MFD) using a 30 W, 915 nm pump diode laser. The 6.5 W signal then seeds the rod amplifier (a 0.8 m Yb-doped rod-type PCF with a 65  $\mu$ m MFD), which is pumped with a 200 W, 975 nm pump diode. Lastly, the amplified, chirped pulses are compressed to 180 femtoseconds in a transmission grating compressor.



Figure 3.2: Overview of SBLS laser system.

Our HHG source and beamline has been described previously in Ref. [52]. The amplified 80 W,  $1.03-\mu m$  frequency comb laser with a repetition rate of 61 MHz is passively amplified in a six mirror enhancement cavity with a 1 % transmission input coupler and a finesse  $\mathcal{F} > 500$ , providing up to  $\sim 10$  kW circulating average power. High-order XUV harmonics of the amplified IR frequency comb are generated in a gas jet at a cavity focus and reflected from a super-polished sapphire wafer at Brewster's angle for the resonant 1.03  $\mu$ m light. The outcoupled harmonics are separated in a home-built pulse-preserving monochromator, consisting of two toroidal mirrors, a grating, and slit. The harmonics are first collimated by a 350 mm focal length toroidal mirror (TM1) at a 3° grazing angle that forms the first part of a single off-plane grating pulse-preserving monochromator similar to the design described by Frasetto et al [67]. The harmonics strike a motorized grating at a 4° grazing angle and are refocused by a second 350 mm focal length toroidal mirror (TM2) at an adjustable slit. The monochromator grating has 150 grooves/mm and is blazed for optimum diffraction efficiency for  $\lambda = 35$  nm. The XUV harmonics exiting the monochromator are typically monitored using an aluminum coated silicon photodiode (PD). A single selected harmonic exiting from a slit is refocused onto a sample by a last 350 mm focal length toroidal mirror (TM3) at a 3° grazing

angle. This TM3 is electrically floated such that the photocurrent of the electrons ejected from the mirror surface can be used as a passive XUV intensity monitor.

## **3.2 SBLS driver laser**

Cavity enhancement for HHG involves a resonant coupling of a high power frequency comb driver laser to a high-finesse optical cavity to support necessary peak intensity for highly nonlinear HHG processes [60-62]. For these cavityenhancement applications, it is critical to operate mode-locked laser oscillators with low noise [123–125]. This is because our enhancement cavity has the narrow  $\sim 100$ kHz linewidth, determined by the reflectivity of cavity mirrors. Any noise on the comb usually broadens the comb linewidth [105], reducing the cavity-comb coupling. To maximize the cavity-comb coupling, it is then necessary to operate the laser near zero net group delay dispersion (GDD), where the comb linewidth is the narrowest [123]. However, required noise specification can be difficult to fulfill with our mode-locked oscillator based on nonlinear polarization evolution (NPE) [126] for a number of reasons. Firstly, we found that being near zero net cavity GDD in our NPE oscillator is not sufficient to achieve low-noise operation because the details of NPE also affects the noise (e.g., waveplate positions and different modelocked states). Secondly, we learned that the Yb gain fiber used in our oscillator is somewhat prone to photodarkening, which can cause noisy error signals feeding back to the oscillator for laser stabilization. As shown in Appendix A.1, when we observed photodarkening of the gain fiber, it degraded the performance of the NPE oscillator such that we were not able to lock between the cavity and comb. This ultimately led to permanent oscillator failure, motivating us to rebuild the laser cavity.

This section describes upgrades made to the SBLS laser system and the efforts to optimize it to the level of robustness and long-term stabilization. To achieve this goal, we carefully rebuilt the laser cavity and optimized the net cavity GDD for lownoise operation based on the previous lessons that we learned. The upgraded laser system uses a more bulk electro-optic modulator (EOM) for the comb-cavity locking to increase the servo bandwidth. The NPE mode-locked oscillator is upgraded from 83 MHz to 61 MHz with the installation of a YDFA that can boost the seed power from the oscillator. The addition of a YDFA facilitates delivery of sufficient power to the subsequent amplifier chain, minimizing a problem due to intermittent power fluctuation from the NPE oscillator. The main reason for reducing the laser repetition rate is to improve the energy resolution of our time-of-flight momentum microscope (see Chapter 4 for more details). By increasing the time window between the pulses, more time-of-flight bins can be resolved with a given detector time resolution, spreading the energy span through those bins. The repetition rate reduction also makes high-pass filtering of photoelectron energy distributions easier.

#### **3.2.1** Oscillator construction

Our oscillator is a home-built Yb:fiber frequency comb laser passively modelocked based on NPE. The basic layout of our rebuilt oscillator is sketched in Fig. 3.3. The laser cavity consists of a 258 cm fiber section (all non-PM) and a 105 cm free-space section with optical elements. The fiber section provides gain at 1030 nm and the Kerr-effect associated nonlinearity. The free-space optics control polarization for NPE mode locking and compensate total dispersion of the oscillator.

The Yb gain medium is ideal for amplifying a light at 1030 - 1040 nm, where the absorption and emission cross sections are largest [127, 128]. The pump laser is a fiber Bragg grating stabilized diode laser (Oclaro LC96L76P-20R) operating at 976 nm and is driven by Thorlabs's basic current and temperature controllers (LDC210C and TED200C). The pump light, passing through a polarization insensitive isolator (Iso1), is launched into the fiber section of the cavity with a 980nm/1050 nm wavelength division multiplexer (WDM, Thorlabs WD202G-FC). The pump laser's fiber is PM and is just spliced onto the non-PM WDM fiber.

A fiber assembly is made up of a 20.5 cm single-mode Yb-doped gain fiber (YB1200-4/125 from Thorlabs, 4.4  $\mu$ m MFD), the ends of which are spliced onto standard SM980 fibers terminated with anti-reflection coated, angled FC/APC connectors. These end connectors are then plugged into fiber beam collimators (Thorlabs PAF-X-5-C). The specifics of these fiber lengths are described in detail in Fig. A.2 in Appendix A. The most important thing to note is that the fiber length following the gain fiber needs to be longer for easier mode locking. When this section of the fiber was made condiderably shorter, we could not mode-lock the laser at all. The fiber length right after the gain fiber is made to 105.5 cm, long enough to maximize the nonlinear effect for easier NPE mode locking. The relative lengths of other undoped fiber parts do not need to be controlled precisely.

In the free-space section, a pair of diffraction gratings (600 groove/mm, Wasatch photonics 2254-B-21) and a right-angle prism retroreflector (RP, Thorlabs PS908H-C) together constitute a dispersive delay line for compensating total dispersion in the oscillator. The second grating (G2) is mounted on a mechanical translational stage for finding zero dispersion (see Section 3.2.2). The first grating (G1) is glued to a piezo-electric transducer (PZT) to control the comb's carrier-envelope offset frequency for cavity-comb locking. The gratings are aligned parallel to each other at the Littrow angle,

$$2\sin(\alpha) = \lambda/N \quad \Rightarrow \quad \alpha = 18^{\circ} \tag{3.1}$$

where N = 600 groove/mm is the grating pitch,  $\alpha$  is the angle of incidence measured from normal, and  $\lambda = 1030$  nm is the center wavelength. If the grating pair is not aligned in parallel, different spectral components point to different directions in the far field, introducing spatial chirp, which will then reduce mode matching when the beam is launched back into the fiber. The zeroth-order transmitted beam is used for triggering the delay-line detector (DLD) for our momentum microscope (see Chapter 4). The first-order transmitted beam reflects off the retroreflector RP with a lower beam height. This allows the first-order diffracted beam to be clearly separated from the input beam.

Other optical components in the free-space sections are three zeroth-order waveplates used for NPE mode locking and a polarizing beam splitter (PBS) cube as an output coupler reflecting the vertical component out of the cavity. A Faraday isolator (Iso2, Thorlabs IO-3D-1030-VLP) ensures that only the horizontal component of 1030 nm light passes through QWP to the fiber collimator C2.

Our upgraded oscillator uses a commercial EOM (EO-PM-NR-C2 from Thorlabs) with a 45 mm MgO doped LiNbO<sub>3</sub> crystal (GVD = 291.05 fs<sup>2</sup>/mm) and a half-wave voltage of  $V_{\pi}$  = 250 V. The EOM provides 1) phase modulation sidebands and 2) a fast actuation on the oscillator cavity length for cavity-comb locking (see section 3.3.2 for the locking scheme). The previous oscillator used a homebuilt EOM with a 4 mm LiTaO<sub>3</sub> crystal (United Crystal, GVD =224 fs<sup>2</sup>/mm) and a  $V_{\pi}$  = 3 kV [122].

The output spectrum of the current 61-MHz oscillator is shown in the inset of Fig. 3.3. Compared to the previous 83 MHz oscillator, the spectral bandwidth is reduced almost by a factor of 2. This is most likely due to the fact that the current fiber assembly is made much longer by 80 cm and thus has more residual third-order dispersion.



Figure 3.3: Basic layout of the upgraded 61-MHz mode-locked oscillator. QWP = zeroth-order quarter-waveplate, HWP = zeroth-order half-waveplate, PBS = polarizing beamsplitter cube, G1/G2 = grating pair, RP = roof reflecting prism, EOM = electrooptic modulator, Iso = isolator, M = silver mirrors, WDM = wavelength division multiplexer, C1/C2 = fiber beam collimators. The 83-MHz vs. 61-MHz oscillator spectra are compared in the inset.



Figure 3.4: Parallel transmission gratings at the Littrow angle. At the Littrow angle,  $\alpha = \beta$  and the input wavevector  $k_{in}$  is parallel to the diffracted wavevector  $k_{out}$ . To achieve a parallel configuration, as far as possible in the far field, the zeroth-order transmitted and first-order diffracted beams should be level in height  $(\Delta z = 0)$  with a constant spatial separation  $\Delta y$  between the two beams. The grating spacing G can be tuned by  $\Delta G$  for finding net zero dispersion.

## **3.2.2** Net zero-cavity dispersion

In our case, the frequency comb is coupled to a resonant enhancement cavity for generating HHG. For this cavity-enhanced -HHG application, it is important to operate the mode-locked comb oscillator near net zero GDD [123], where optical phase noise is substantially low. This task is particularly important for our upgraded light source because the reduction of repetition rate to 61 MHz leads to a narrower HHG cavity linewidth of  $\sim 100$  kHz. Substantially larger dispersion is now introduced to the current oscillator because of the much longer fiber assembly and more bulk EOM (see Appendix A.3) and therefore the oscillator dispersion must be carefully compensated to achieve a low-noise narrow comb linewidth.

As a starting point, one can calculate the grating spacing for net zero GDD using the material parameters of the oscillator available in literature [129] and set the corresponding spacing. This is described in detail in Appendix A.3. This method generally leaves the cavity close to zero GDD, but the spacing needs to be further fine tuned for true net zero GDD. A better way of achieving net-zero cavity dispersion can be by measuring its actual net GDD *in situ* [130] and compensating accordingly.

In this work, we carefully optimize the oscillator dispersion using the technique reported by Knox [130]. While we insert a knife-edge at incremental steps after a dispersive material (G2) in the oscillator, the corresponding optical spectra (shown in Fig. 3.5a) and pulse trains are monitored simultaneously to measure the center frequencies  $\omega_0$  of the spectra and repetition rates  $f_r$ . Fig. 3.5b plots the group delays  $T_g$  vs.  $\omega_0$ , where  $T_g = 1/f_r$ . The oscillator's net GDD is determined from the slope  $dT_g/d\omega_0$  of a linear fit (solid red). The oscillator dispersion is measured to be +6576 fs<sup>2</sup>/rad. After compensating this normal dispersion by the grating's anomalous dispersion, the measurement is repeated as shown in panel c. The net GDD of the upgraded oscillator is indeed near zero.



Figure 3.5: Net zero GDD measurement of the upgraded mode-locked oscillator. As a knife edge blocks a spectrally dispersed beam step-wise from an indicated direction, the centroid ( $\omega_0$ ) of the measured spectrum in **a**) shifts and the group delay ( $T_g = 1/f_r$ ) changes. The net group delay dispersion (GDD) of the oscillator can be found from a slope  $dT_g/d\omega_0$  as shown in **b**). After the cavity GDD is compensated by the grating pair, the measurement is repeated to ensure the zero GDD as shown in **c**).

## **3.2.3** Performance of upgraded laser system

One good metric for monitoring noise from a frequency comb laser is based on the measurement of a comb tooth linewidth by heterodyne beats between the comb and a quiet laser with a narrow linewidth. For this purpose, a CW Nd:YAG laser (output 1064 nm) is often used in our lab as it has a narrow linewidth less than 1 kHz [131, 132]. Unfortunately, our upgraded oscillator outputs very little light at this wavelength as shown in Fig. 3.3. Instead, we evaluate the performance of the new oscillator and laser system based on an observed linewidth of our enhancement cavity. For coupling a frequency comb laser to an enhancement cavity, the comb linewidth needs to be narrower than the enhancement cavity linewidth determined by the reflectivity of cavity mirrors. If optical noise carried in the driver comb is substantial, it is expected to broaden the observed linewidth when we sweep across the cavity linewidth.

Fig. 3.6a shows the transmission intensity of the intracavity light measured through one of the high reflectors in the HHG cavity. The Lorentzian fit (dotted curve) to this transmission signal results in the linewidth of  $\sim 110$  kHz. For the

given cavity finesse  $\mathcal{F} \sim 500$  and the FSR = 61 MHz, the cavity linewidth is expected to be around  $\delta \omega = \text{FSR}_{\omega}/\mathcal{F} = 120$  kHz. The observed linewidth of ~ 110 kHz is very close to the cavity linewidth determined by the mirrors' power reflectivity, indicating that noise on the comb did not actually broaden the observed cavity linewidth.

We additionally evaluate the performance of our laser locking system based on the quality of a Pound-Drever-Hall (PDH) error signal and the measurement of unity gain bandwidth. The current locking system uses the PDH method [133, 134] and the bulk EOM in the oscillator to lock the laser to the enhancement cavity. As shown in panel b, the quality of the PDH error signal for laser feedback (see section 3.3.2) has been greatly improved compared to that from the previous 83-MHz system (see Appendix A.1). Panel c shows the in-loop signals measured at different servo loop gains when the laser is locked to the cavity. We achieve the unity gain bandwidth of ~ 65 kHz, as indicated by the dotted line, and observe a servo bump at ~ 85 kHz. This is a substantial improvement over the old PZT locking system, where a servo bump occurred at ~ 30 kHz [122]. The careful optimization of zero net laser cavity GDD and the use of the bulk EOM have greatly improved the performance of our laser system with long-term stability. The upgraded oscillator has endured for more than 3 years, much longer than a typical lifetime of about one year for the previous NPE Yb:fiber oscillators used in our lab.



Figure 3.6: Performance of the upgraded mode-locked oscillator based on enhancement cavity-comb locking. a) Oscillator performance based on the linewidth measurement of enhancement cavity transimission shown in the solid line (Lorentzian fit in the dotted line). b) PDH error signal from the enhancement cavity. c) Locking performance based on in-loop PDH error signals at different servo loop gains when the laser is locked to the enhancement cavity.

## 3.2.4 Jin-amp: YDFA

**Construction.** The new 61-MHz oscillator outputs the average power of  $\approx$  45 mW as measured reflecting off of the polarizing beamsplitter cube (PBS). This power should be enough to seed our subsequent amplifier system for power amplification but the power intermittently dropped, which could be an issue for lasing in the subsequent amplifier. This problem has motivated us to build another preamplifier

that can always provide sufficient seed power to the subsequent pre-amplifier. It is an Yb-doped fiber amplifier (YDFA), commonly called Jin-amp in our lab, named after myself, in order to distinguish it from the subsequent amplifiers.

The design of the Jin-amp is shown in Fig. 3.7 and the details of the components are listed in Table A.1 in Appendix A. All the fiber components in the Jin-amp are PM and are fusion sliced to avoid connector damage from backreflections, which is frequently observed in Yb-doped fiber amplifiers. The gain fiber is approximately 3 m long, purchased from nLIGHT (LIEKKI Yb300-6/125-PM). This fiber is rated for its high resistivity to photodarkening which tends to degrade the performance of many Yb-doped fiber lasers and amplifier systems [135–138]. The gain fiber is pumped with a 980-nm pump diode in the forward direction so it copropagates with a 1030-nm seed light via the WDM1. An additional WDM (WDM2) is necessary upstream in the pump line to prevent any amplified spontaneous emissions reflecting back to the pump diode. The 99:1 power splitter is to monitor the input power of the 1030-seed light and is usually used for interlock monitoring.



**Figure 3.7: Schematic layout of a YDFA and output characterization.** The output spectra and the output power of Jin-amp as a function of pump currents are shown in the bottom insets.

**Characterization.** The output of the Jin-amp is characterized in the bottom of Fig. 3.7. The output power of the amplifier and their spectra are measured right after the fiber stretcher before the polarizing beam splitter. The optput power is nearly linear with the pump current within the given range of 0 - 790 mA, producing up to 150 mW maximum. It can in principle produce more if the pump power is increased further. The bandwidth of the output spectrum is substantially reduced compared to the input due to gain narrowing effects in the amplifier [139–141]. This spectral narrowing seems to be independent of the pump current.

The compressed laser pulse after the grating compressors is shown in Fig. 3.8. The autocorrelation is 260 fs and the retrieved pulse width assuming a Gaussian

pulse shape is 260 fs  $\div \sqrt{2}$  = 180 fs.



Figure 3.8: Compressed pulse after installing the YDFA. The autocorrelation is 260 fs and the retrieved pulse width is 260 fs  $\div \sqrt{2} = 180$  fs assuming a Gaussian pulse shape.

## **3.3 HHG cavity and beamline**

Now that our rebuilt Yb:fiber comb driver laser has shown itself to be a reliable high power low noise source, this section presents the efforts of rebuilding and optimizing the HHG source and beamline to be suitable for high-performance time-resolved ARPES measurements on  $\mu$ m region samples. To successfully apply the cavity-enhanced HHG technique to time-resolved micro-ARPES, the system must provide sufficent XUV flux and a small XUV spot size along with a healthy alignment of the beamline. With these technical goals in mind, important upgrades have been made to the system, including rebuilding and realigning the enhancement cavity and subsequent beamline. This work is necessary because of modifications of the enhancement cavity, adapted to the driver laser's repetition rate. Section 3.3.1 describes the enhancement and long-term stability of the light source, it is necessary to match the teeth of the driver comb to the cavity modes via electronic feedback loops. This is discussed in Section 3.4.

## **3.3.1** Femtosecond enhancement cavity

## **Cavity layout**

The layout of our upgraded enhancement cavity is shown in Fig. 3.9. The cavity is folded with six mirrors, five of which are high reflectors (HR) with reflectivity R > 99.95% and one of which is an input coupler (IC) with nominal transmission of 1%. These mirror reflectivities give an over-coupled cavity [142] with a cavity finesse  $\mathcal{F} > 500$  and a power enhancement > 250 without a Brewster plate. All these mirrors are quarter-wave-stack dielectric mirrors for high power management and designed for low GDD at 1030 nm, all purchased from Layertec gmbH.

The cavity focus is formed between two high reflective focusing mirrors with the same radius of curvature R = 15 cm. Harmonics are generated in a gas jet, located near the cavity focus, by flowing a noble gas through a quartz capillary tube with a 50- $\mu$ m inner diameter. Our cavity is operated near the mid-point between the inner and middle of the stability range, where it gives a small focal spot insensitive to thermal distortion of the mirrors [143]. Operating the cavity more towards the edge of the stability region has the advantage of attaining a smaller focal spot. However, this may be undesirable because the thermal induced change in the radius of curvature can push the stability region further toward the edge, which can lead to a divergence of the beam mode and thus a lowered buildup. Although our intracavity beam is somewhat elliptical at the selected region of the stability range, we send in the spherical input beam and still achieve reasonable mode matching between the input and intracavity beams. We use telescope lenses (positive lens with f = +500 mm, negative lens with f = -200 mm ) to mode-match the input beam to the intracavity beam.

A Piezoelectric transducer (PZT) is mounted on mirror HR5 to control the cavity length for the comb-cavity locking described in Section 3.3.2. The leakage beam transmitted through mirror HR4 is used to monitor the cavity performances such as power, buildup factor, and the transverse mode of an intracavity light. The cavity is kept under vacuum to minimize the air dispersion and the XUV absorption in the air.

When operating the enhancement cavity on a daily basis, especially when generating the XUV harmonics, it is important to continuously dose the cavity optics, including all the mirrors and the Brewster plate, with ozone to prevent their degradation from hydrocarbon contamination. It has been demonstrated that the XUV and high peak power IR light can induce the degradation of the cavity optics by photoinduced chemical reaction of the hydrocarbons present on their surfaces [61,144]. Such degradation usually causes the spatial distortion of the intracavity mode, reducing both the cavity's power enhancement and XUV reflectivity. To prevent these effects, we pass pure  $O_2$  gas through a commercial ozone generator (Ozotech Poseidon 220) and flow a generated mixture of ozone and  $O_2$  into 250  $\mu$ m stainless steel capillaries aimed at each cavity optic at a backing pressure of 150 Torr absolute. The gas throughput is roughly 2 Torr-L/s.



Figure 3.9: Layout of 61-MHz enhancement cavity.

#### **XUV outcoupling**

The method to couple the XUV harmonics out of an enhancement cavity is one of the important considerations for designing a time-resolved ARPES system. Several outcoupling methods [52, 145, 146] have been implemented by different groups and this is well reviewed in Ref. [147]. The dielectric grating output coupler [145, 148] can simultaneously couple the harmonics out of the cavity and separate them with only one single optic. This method, however, causes the most distortion of the outcoupled harmonics by introducing significant pulse-front tilt on them, which leads to a temporal broadening of the pulse and an enlarged spot size on a sample. Additionally, a realignment of the cavity is needed when switching to a different harmonic because the harmonics are already well separated in the cavity by the grating. Another outcoupling method of the XUV harmonics is the piercedmirror technique [146], where the harmonics are coupled out of a small hole in the cavity mirror immediately following the HHG medium. While this method can outcouple the higher-order harmonics with lower divergence, it shows poor outcoupling for lower-order harmonics less than 40 eV and introduces intracavity loss.

In our setup, we implement the Brewster outcoupling scheme, where the harmonics are reflected out of the cavity by a thin sapphire wafer placed at Brewster's angle. We use a 250- $\mu$ m thick sapphire wafer placed after the cavity focus at Brewster's angle for 1.03  $\mu$ m. The outcoupled harmonics propagate collinearly with the residual fundamental IR light reflected from the Brewster plate, which can be used as an alignment guide for the rest of the beamline. The p-polarized IR light transmitting through the Brewster plate remains in the cavity for subsequent passes.

Two main concerns with the Brewster plate scheme are thermal and nonlinear effects. The Brewster plate is a dominant contribution to the dispersion of our enhancement cavity (the group-velocity dispersion of sapphire at 1.03  $\mu$ m  $\approx$  30 fs<sup>2</sup>/mm [149]). Although we have previously observed that the distortion of the intracavity nonlinearity limits the power enhancement at high power,  $\sim$  10 kW

intracavity power has been attained with 60 W laser power [150, 151].

Thermal distortion of the Brewster plate is another detrimental effect that degrades the performance of the enhancement cavity. Since several kW power circulates in the cavity, substantial absorption can occur at the Brewster plate, which can impact XUV beam pointing in the subsequent beamline. Stable beam pointing is very critical for time-resolved photoemission measurements, especially on samples with  $\mu$ m-size flakes. To minimize thermal distortion, the Brewster plate is glued to a high emissive anodized aluminum (Al) plate with a high thermal conductive and low outgassing epoxy (two components : 70-3812RNCGR15 and 70-3812CCL16 from Epoxies ETC.). The combined wafer and plate is mounted on a mechanical stage, rigidly fixed to the optical table by a thick, wide copper braid serving as a heat sink. This mounting scheme has provided outcoupling with stable pointing for many hours of continuous operation as long as the cavity-comb lock is maintained.



Figure 3.10: Schematic of Brewster plate mount.

## 3.3.2 Comb-cavity locking scheme

The resonant coupling between a frequency comb driver laser and enhancement cavity involves matching the comb repetition rate  $f_r$  to the cavity FSR (or vice versa) and the comb carrier-envelope offset frequency  $f_0^{(\text{comb})}$  to the cavity offset frequency  $f_0^{(\text{cav})}$ . This is typically achieved by implementing two active feedback loops with actuators. Key elements for each feedback loop are an error signal that measures a deviation of the laser frequency from some reference value, a loop filter that produces a conditioned error signal for feeding back to the laser, and an actuator which changes the laser frequency to a desired setpoint. If a feedback is correctly set up, the laser system automatically adjusts the output frequency according to an error signal. In this work, the frequency comb driver laser is locked to the cavity using a two-point Pound-Drever-Hall (PDH) lock [133, 134] as shown in Fig. 3.11.

#### **Generation of PDH error signal**

The PDH error signal is generated in the following way [134]. The phase of the incident laser beam is modulated with an EOM in the oscillator, driven by a 2-MHz

sine wave output from a local oscillator (LO). This phase-modulated incident beam has two symmetric sidebands,  $\omega_c \pm \Omega$ , around the carrier frequency  $\omega_c$ . The beam reflecting from the cavity is a coherent sum of a promptly reflected beam, which has never passed through the input coupler (IC), and a small fraction of the intracavity beam that leaks through the IC. This reflected beam is dispersed with a diffraction grating and two different portions of the spectrum,  $\lambda_1$  and  $\lambda_2$ , are sent to two 100-MHz bandwidth photodiodes (PDs) to set two separate feedback loops. Each PD detects the reflected power containing many terms: DC terms,  $\Omega$  terms arising from an interference between the carrier and two sidebands, and  $2\Omega$  terms resulting from two sidebands interfering with each other. This PD signal is demodulated with  $\Omega' = 2$  MHz sine wave using a double balanced mixer. To extract the phase of the reflected carrier, only  $\sin(\Omega t)$  and  $\cos(\Omega t)$  terms matter. When we mix the modulated  $\sin(\Omega t)$  term with the demodulation  $\sin(\Omega' t)$  wave, the mixer outputs the cosine signals at both the difference  $(\Omega - \Omega')$  and the sum  $(\Omega + \Omega')$  frequencies. For  $\Omega = \Omega'$ , these two output signals become a DC and  $2\Omega$  signal, respectively. The high frequency term is eliminated with a low-pass filter (LPF) to isolate the DC term, which is our error signal. The product of the other  $\cos(\Omega t)$  term and  $\sin(\Omega' t)$ results in the vanishing DC signal and naturally eliminate this  $\cos(\Omega t)$  part after the LPF.

## $f_r$ locking

The locking scheme between the comb  $f_r$  and the cavity FSR is indicated in the blue solid and dashed arrows in Fig. 3.11. We use a commercial PI<sup>2</sup>D type controller (D2-123 Vescent Photonics) as a loop filter to servo the error signal on the oscillator EOM for a fast control of the laser  $f_r$  (see the blue solid arrows). The PDH error signal is an input to the loop filter and the fast output servo signal is amplified in a high-voltage (HV) amplifier (HVA200 from Thorlabs). The amplified signal is combined with a 2-MHz sine wave in a bias tee, which provides two frequency modulation sidebands on the carrier and a high voltage feedback signal to the EOM. For a long term stabilization of the  $f_r$  locking, it is necessary to use another actuator that can correct a slow drift of the cavity FSR due to low frequency mechanical perturbations. As shown in the blue dashed arrows, the integrated servo signal from the auxilary output port of the same loop filter feeds back to a PZT mounted on one of the cavity mirrors, HR5, to control the length of the cavity. If the PZT is out of travel range, we manually adjust a picomotor to bring it back near a resonance and lock the cavity to the comb.

#### Locking comb breathing mode

Once the above  $f_r$  locking is accomplished, the slow comb breathing mode needs to be controlled in order to match the comb  $f_0^{(\text{comb})}$  to the cavity  $f_0^{(\text{cav})}$  for a maximum comb-cavity coupling [152]. This is accomplished via a separate servo

loop using a home-built integrator (see Ref. [151] for the details of the integrator). The schematic is shown in the red portion of Fig. 3.11. The output signal is amplified in an HV amplifier and then sent to the PZT grating actuator in the oscillator. This comb breathing is usually a slow process, observed on a minute time scale. We can correct this drift manually without the active feedback, or we can also lock using the integrator.



**Figure 3.11: Two-point Pound-Drever-Hall locking scheme.** Two active feedback loops are implemented to lock a driver frequency comb to an enhancement cavity. The comb's repetition rate is locked to the cavity FSR via a fast oscillator EOM as shown in the blue portion. The comb carrier-envelope offset frequency is matched to the cavity offset frequency using a grating PZT in the oscillator as shown in the red portion.

# **3.4** Performance of HHG light source and beamline

## 3.4.1 The XUV spot size

To measure the XUV spot size at the sample, we record the photoelectron image from a silicon substrate with photoemission electron microscopy (PEEM, see Chapter4 for more details). The experimental setup is shown in Fig. 3.12b. Harmonics generated in argon at a cavity focus are outcoupled, collimated by a first toroidal mirror TM1 (f = 350 mm), and refocused by a second toroidal mirror TM2 (f = 350 mm) at a slit. The 21st harmonic exiting the slit plane is 1:1 imaged to the sample plane with a last toroidal mirror TM3 (f = 350 mm). Fig. 3.12a shows the image of the 21st harmonic beam along with the vertical and horizontal lineouts through the image centroid. The data indicates an elliptical beam with a 24  $\mu$ m FWHM in the horizontal and a 16  $\mu$ m FWHM in the vertical dimension. This beam size is comparable to what is used in synchrotron [153]. In general, a small spot size is useful for measuring inhomogeneous samples with  $\mu$ m size domains. It also requires less pump power for achieving a given fluence of time-resolved ARPES measurements.



Figure 3.12: The XUV spot size measurement. a) The PEEM image of the 21st harmonic from argon measured on a silicon substrate at the sample plane. b) The experimental setup. The cavity focal plane, where harmonics are generated, is imaged to the slit plane with two 350 mm focal length toroidal mirrors TM1 and TM2 and the exit slit plane of the monochromator is 1:1 imaged to the sample plane using another toroidal mirror TM3 (f = 350 mm). The photoelectron image is recorded using real-space PEEM (see Chapter 4).

## 3.4.2 The XUV flux

Fig. 3.13 shows a typical XUV harmonic spectrum from argon from the upgraded 61 MHz light source. The XUV flux is recorded using an aluminum coated silicon photodiode (PD in Fig. 3.1) right after the exit slit while rotating the grating in the pulse-preserving monochromator. The measured spectral widths in Fig. 3.13 are determined by the low resolving power of the monochromator and do not reflect the intrinsic harmonic linewidths. The XUV flux of  $\sim 10^{11}$  photons per second ( $\gamma$ /s) is generated in the range of photon energies from 20 to 40 eV. The flux is not corrected for the monochromator efficiency nor Brewster plate reflectivity and therefore  $\sim 10^{11} \gamma$ /s over a broad tuning range is expected to be delivered to a sample in the time-resolved ARPES endstation.

In Fig. 3.13, the argon harmonic spectra from the previous 88 MHz vs. upgraded 61 MHz light source are also compared at different intracavity average powers. When comparing the two spectra (navy solid and light blue dashed curves) at 8 kW average power, the 88 MHz source has barely produced HHG while the 61 MHz source has produced a flux of more than  $10^{11} \gamma$ /s. Clearly, we can now generate HHG at lower average power from the 61 MHz light source. Despite the lower repetition rate, the light source still generates similar average harmonic flux when compared to the 88 MHz system at 10 kW average power.



**Figure 3.13: Optimized XUV harmonic spectrum in argon from the upgraded 61 MHz light source.** For comparison, the harmonic spectra from the 88 MHz previous light source are plotted together at different intracavity average powers.

# Chapter 4

# **Optimization of ToF-Momentum Microscopy for High-performance Time-resolved ARPES**

# 4.1 Introduction

Time- and angle-resolved photoelectron spectroscopy (Time-resolved ARPES) based on high harmonic generation (HHG) has become an essential tool for studying excited-state dynamics with the full Brillouin zone coverage. However, most time-resolved XUV ARPES studies have been previously limited to the high-fluence regime due to severe data rate limitation imposed by space charge issues. In photoemission measurements, space charging, arising from the mutual Coulomb interaction of photoelectrons emitted from a sample, causes spectral broadening and shift [43–47], limiting the XUV flux that can be applied to the sample. To avoid this detrimental effect, XUV photoemission measurements have been performed with several orders of magnitude lower data rate, precluding the study of the intrinsic dynamics of excited states in weakly excited systems.

Recently, HHG-based time-resolved ARPES has achieved large gains in coping with such data-rate problems. MHz HHG systems, achieved either via single pass HHG with tight focusing [54] or cavity-enhanced HHG [52], has now implemented the new technique of time-of-flight momentum microscopy (ToF-MM) [63, 64] for photoelectron analyzers. ToF-MM enables simultaneous detection of the full 3D  $(k_x, k_y, E)$  distribution of photoelectrons emitted from the full  $2\pi$  solid angle, dramatically increased data rate by several orders of magniude higher than conventional hemispherical analyzers. ToF-MM can also select photoemission signals from micron-size regions of interest on the sample via selectable field apertures in the front end of the electron microscope, enabling micro-ARPES from inhomogeneous samples. A powerful combination of a MHz XUV source and ToF-MM has indeed enabled breakthroughs in time-resolved ARPES studies in the previously inaccessible low-fluence limit [25, 54, 68].

Applying ToF-MM to intensity-demanding problems of time-resolved XUV

photoemission is very promising [25, 54, 65, 66, 68, 154] for studying low-fluence electron dynamics across the full Brillouin zone. However, there are also major challenges arising from detector limitations and space charge, as discussed by Maklar et al. [51]. In our setup, we combine a cavity-enhanced HHG source and ToF-MM operating at 61 MHz and record data with a 3D time- and position-resolving delay-line detector based on microchannel plates (MCPs). When working at such a high repetition rate, the immediate challenge arises from detector saturation. With our 61 MHz repetition rate, 1 electron per pulse can produce 60 million photoelectrons per second, far more than what the MCPs can typically handle, which is at most  $10^7$  electrons per second. Additionally, the high repetition rate can further limit detector energy resolution. We have only a 16-ns time window  $(1/f_r)$  between the pulses and 200-ps detector resolution ( $\Delta T$ ) gives only 80 resolved ToF bins. For the full energy range of  $E_{\text{range}} = 20 \text{ eV}$  of photoelectrons emitted from the sample, for example, this yields the detector resolution of  $\Delta E = E_{\text{range}} \Delta T / (1/f_r)$ = 240 meV. The only way of gaining the resolution in this case is to narrow the energy span. Thus, both of these constraints make electron filtering essential in our setup.

Electron filtering is critically important for high quality time-resolved ARPES measurements with high dynamic range as needed to study samples under perturbative excitation. In the ToF-MM method, the strong accelerating extractor field of typically several kV/mm at the sample effectively pulls all photoelectrons, even unimportant secondary ones, into the microscope column. The corresponding valence band distribution contains a substantial amount of secondary low-energy electrons. If the full distribution is incident on the detector, it does not only saturate the detector but also degrades the photoemission signal of interest. For the goal of studying electron (not hole) dynamics, only electrons above  $E_F$  matter and the suppression of all other electrons below is not expected to change the physics of interest. Thus, by rejecting most of the valence band signal, one can attain high dynamic range of a time-resolved measurement while mitigating detector saturation.

To address these detector limitations, we implement a simple high-pass filter (HPF) scheme using a retarding field between two parallel grids. The scheme and optimization of the HPF grids is discussed in section 4.3. Once the HPF configuration is optimized, we study how the HPF affects real- and momentum-space resolution, which is detailed in section 4.4. Once the detector limitations have been resolved by high-pass filtering electrons, the space charge issue remains a challenge. We discuss the space charge characterization in section 4.5.

# 4.2 Overview of ToF-momentum microscope

The schematic cross-section of the ToF-momentum microscope with electron trajectories is shown in Fig. 4.1a. The front end of the microscope is a photoemission electron microscope, where the sample, extractor, and focus lens together form a cathode lens. The strong accelerating extractor field of typically several kV/mm at the sample pulls all emitted photoelectrons into the microscope column. The

microscope can operate either in real-space or momentum-space imaging modes. Momentum-space images are formed on the back focal plane (BFP) of the objective. Real-space images are formed later in the zoom optics on the field aperture plane, where a group of nine selectable field apertures from a few  $\mu$ m to a few mm is located. By inserting one of these apertures, photoemission signals can be selected from a  $\mu$ m-sized region of interest on the sample, enabling micro-ARPES. A "contrast" aperture placed in the backfocal plane of the objective lens allows for image adjustment and aberration correction when working in the real-space imaging mode. For a given operational mode, the subsequent imaging of either the back focal plane or the real-space plane via the projection optics transfer the image to the detector with a desired magnification. ToF energy discrimination of photoelectrons occurs in the 0.9 m ToF-drift section.

We use the 3D time- and position-resolving delay-line detector (DLD from Surface Concepts) based on microchannel plates (MCP) for electron detection and use 61-MHz pulses from our mode-locked oscillator (the zeroth-order transmitted beam from the first grating) for triggering the DLD, which takes only up to 8 MHz. To divide the repetition rate down, we first convert the 61-MHz optical signal to an electrical signal using a fast photodiode (EOT 3000) with rise time < 175 ps and a 30 GHz RF amplifier, and feed it into SRS DG645 pulse generator, the divided output of which then triggers the DLD.



**Figure 4.1: a)** Schematic view of our ToF momentum microscope with electron high-pass filter, illustrating a momentum-space image formed on the back focal plane of the objective. The full photoelectron signal, illustrated in **b**), is cut by the full high-pass filter, leaving only a few eV near the Fermi level in **c**).

# 4.3 High-pass filter (HPF) scheme

In our setup, we implement a simple PHF scheme based on two parallel grids with a net transmission of 56 %. Fig. 4.2 shows the layout of our HPF grids. The

HPF grids are placed 2 mm away from the MCP and the space between the grids are 3 mm. The first and second grids are called ToF grid and HPF grid, respectively, and HPF grid is a place for applying a retarding voltage. Retarding voltage  $V_{\rm HPF}$  is set relative to sample voltage  $V_{\rm s}$  such that only electrons with kinetic energies greater than the potential difference  $V_{\rm HPF} - V_{\rm s}$  can pass through a potential energy barrier. The MCP voltage is typically set at 200 V where electron quantum efficiency is maximized.

We have previously experimented the optimum HPF setup using different grid configurations and different types of grids and have learned a few important lessons. The results are shown in Appendix B.1. First, when the two grids were at the end of the ToF tube, microlensing [155] was found to limit momentum resolution significantly. Mesh holes in the grids disturb incoming electric field lines and this acts as local diverging lens. We thus placed the grids closer to the MCP in order to optimize the microlensing effect. Although the wires in the second grid can still act as a diverging lens in this optimized geometry, the propagation distance from the second grid to the detector is very short, which is expected to minimize the microlensing effect. We also learned that the first grid is not optimal for HPF because it stretches the electron pulse substantially (see Fig. B.1b in Appendix). We have thus arrived at this optimal geometry shown in Fig. 4.2.

The HPF suppresses signal below its cutoff energy by more than a factor of  $3 \times 10^3$  as shown in Fig. 4.1c, limited by dark MCP counts and background signal intensity. The HPF allows us to cut away strong valence band signal and concentrate on the  $\sim 4 \text{ eV}$  wide energy region from < 1 eV below to 3 eV above the top of the valence band structure, comprising only about 1 % of total photocurrent. In what follows, we discuss to what extent the optimized HPF configuration affects real-space and momentum-space resolutions.



Figure 4.2: Optimized geometry of the grid-based high pass filter.

# 4.4 HPF performance

## 4.4.1 Spatial resolution

We optimize real-space resolution on a chessboard sample consisting of knownsized rectangles using a Xenon-Mercury (Xe-Hg) lamp. An Xe-Hg lamp has the advantage of providing high imaging contrast and uniform illumination on the entire sample. However, the lamp has limited energy bandwidth and is therefore unable to produce a wide range of photoelectron's kinetic energies like actual measurements with XUV photons. We thus scan sample (SA) voltage relative to HPF voltage to produce the wide energy range of photoelectrons emitted from the sample. We also perform an additional experiment where HPF voltage is instead scanned referenced to SA for producing a similar range of energies in order to study the chromatic abberation effect.

The real-space images of the chessboard sample at selective kinetic energies of electrons for SA and HPF scans are shown in Fig. 4.3a and d, respectively. The momentum integrated electron counts vs. kinetic energies are plotted in panel b. In this figure, the cutting edge of HPF is about 1 eV wide. To study how our HPF affects spatial resolution, we make lineouts on the 10  $\mu$ m×10  $\mu$ m squares (the yellow lines) and fit the rising edges with an error function. Corresponding resolutions on both sample and detector (DLD) planes are shown in Fig. 4.3b. The resolution on the sample plane is approximately 4 - 5  $\mu$ m at the higher energies > 1 eV and becomes worse near the cutoff. Especially for SA scan the resolution near the cutoff is worse by almost a factor of two compared to HPF scan. When SA voltage is scanned, photoelectrons travelling toward HPF with different kinetic energies experience chromatic abberation. This abberation effect seems to be more pronounced near the cutoff, also as seen from comparing panels a and d, and this may be the reason for more degraded resolution when SA voltage is scanned.



Figure 4.3: Spatial resolution. Real-space images of a chessboard sample at selective kinetic energies **a**) when sample (SA) voltage changes relative to high-pass filter (HPF) voltage (referred to as SA scan) and **d**) when HPF voltage changes relative to SA voltage (referred to as HPF scan). Energies  $E - E_{HPF}$  represent the kinetic energies of photoelectrons at HPF. **b**) Momentum integrated electron counts vs. kinetic energies. **c**) Real-space resolution on both sample and detector (DLD) planes. The resolution  $\delta x$  is determined from fitting the sharpness of lineouts on the 10  $\mu m \times 10 \mu m$  squares (the yellow lines) by an error function.

## 4.4.2 Momentum-space resolution

We optimize momentum-space resolution on Au(111) with a momentum grid inserted in the backfocal (Fourier) plane using an XUV probe light with  $h\nu = 25$  eV. The resolution is determined from the sharpness of a momentum grid line along the direction indicated by a yellow line in the momentum-space images shown in panels c - e. The images in panels c - e represent a surface state in Au(111) and are obtained by integrating 350 meV below  $E_F$  as shown in panel b. The momentum resolution is within  $\approx 0.06$  Å<sup>-1</sup> and it becomes slightly worse near the cutoff. Ironically, the resolution well below the cutoff improves far more, almost by a factor of 2, in stark contrast to the real-space resolution in Fig. 4.3. We do not know the origin of this anomalous effect and more investigation is needed.

In summary, our grid-based HPF scheme in Fig. 4.2 shows good suppression of secondary low-energy electrons. However, it degrades the spatial and momentum-space resolution to some extent, especially near the cutoff.



**Figure 4.4: Momentum-space resolution.** Momentum space measurements are done on Au(111) with the 25 eV XUV probe light with the momentum-space grid (k-grid) inserted onto the Fourier plane. **a)** Momentum resolution ( $\delta$ k) on the k-grid edge (marked in yellow in panel c - e) by fitting an error function. Errorbars are from 1- $\sigma$  confidence interval of fits. **b)** Energy-momentum cut along  $\overline{M} - \overline{\Gamma} - \overline{M}$ . **c) - e)** Selective momentum-space images at different E - E<sub>HPF</sub> by integrating the energy window of 350 meV (marked as dotted lines of panel b) near E<sub>F</sub>.

# 4.5 Space charge characterization

Now that the detector limitations have been mitigated, the problem of space charge remains. As discussed previously [51, 156], ARPES spectra recorded with ToF-MM can experience space charge distortions at much lower photocurrents than conventional hemispherical analyzers. Fig. 4.5 quantifies space-charge induced energy shifts and broadening measured using the Fermi edge of Au(111) at the  $\Gamma$ point. By performing measurements with and without an insertable attenuator, we can discriminate between the space charge effect and photon energy shifts due to operating our HHG source with different driving laser intensity. Remarkably we observe a notable energy shift of  $\approx 50$  meV already at 10 photoelectrons/pulse. In turn, this suggests that large statistical noise on this number would cause an additional energy broadening  $B_{Poiss} = (dS/dN)\Delta N$ , where dS/dN is the energy shift per extracted electron and  $\Delta N = \sqrt{N}$  is the Poisson noise. Taking the value of dS/dN from our data, in Fig. 4.5b, we compare the expected  $B_{Poiss}$  with total measured space charge broadening  $B_{sp.charge} = \sqrt{(B_{full}^2 - B_{atten}^2)}$ . We conclude that by measuring the number of electrons emitted every light pulse, one could, in principle, significantly reduce energy broadening by correcting for the space charge shift on a shot-by shot basis.



Figure 4.5: Space charge characterization. Fermi edge shift and broadening measured at room temperature at  $\Gamma$  on Au(111) with full and attenuated probe flux and at different initial XUV source intensities.
# Chapter 5

# **Pseudospin Distributions of Photoexcited Electrons in Graphene by Tight-binding Simulations**

# 5.1 Introduction

The electronic band structure of graphene is often modeled by a simple tightbinding model. A tight-binding model is based on an assumption that electrons are "tightly" bound to their own atomic cores but only weakly perturbed by interaction with nearby atoms. For those crystals with weakly interacting atoms, the electronic wavefunctions can be represented with a relatively small number of localized atomic wavefunctions [3], i.e. those corresponding to the atomic orbitals in the unit cell, via the so-called linear combination of atomic orbitals (LCAO), and also commonly known as the Hückel model in chemistry. Such tight-binding LCAO is particularly useful for graphene since it yields a simple analytic formula [157, 158], making the band structure of this  $sp^2$  covalent bonded material even simpler to calculate. Despite this simplicity, the model reproduces the  $\pi$  energy bands near the Brillouin zone corners (K points) surprisingly close to an *ab-initio* study with only the first nearest-neighbor interaction accounted for [159].

Motivated by this merit, the analytic tight-binding approach is often implemented to study the optical selection rules in doped/undoped graphenes [1, 160– 163], and also other graphene derivatives such as carbon nanotubes [164]. According to a theory, phtoexcitation of electrons from the valence band to the conduction band creates a strong pseudospin polarization around the K points via the k-depencence of the optical matrix element [1]. How this initial pseudospin anisotropy relaxes both in time and energy has been the subject of previous pumpprobe experiments. However, these initial pseudospin polarized electrons are only expected to be seen in the nonthermal electron distributions within the lifetime of  $\approx 50$  fs with low fluence where electron-phonon scattering is dominant [160]. Thus, the direct observation of this nonthermalized momentum anisotropy has always been challenging in optical and time-resolved ARPES experiments.

In our work, with a combination of a high-repetition rate XUV light source and time of flight momentum microscope, we have been able to directly resolve the nonthermal electron distributions for neutral graphene under low fluence with strong pseudospin polarization persisting through a few optical phonon scattering events. The experimental results have been shown in Chapter 6 and also published in Ref. [68]. We have also simulated initial momentum distributions of pseudospinpolarized electrons across the full Brillouin zone by simple-tight binding theory, resulting in excellent agrement with experiment. The central aim of this chapter is thus to provide the simulation details and to ultimately help understand our data. Our simulations incorporate the analytic expressions of the band structure and both optical and photoemission matrix elements using Ref. [1] and [78]. The photoemission matrix element is essential in modeling the time-resolved ARPES signals as it can strongly modulate photoemission intensity, even completely suppressing it in some cases with the so-called "dark corridors" [79]. For studying the pumpinduced momentum anisotropy, this photemission matrix element effect must be distingushed from the pure optical effect.

This chapter is organized as follows. Following a brief overview of graphene's lattice structure in Section 5.2.1, the band structure is calculated next in Section 5.2.2. The photoemission matrix element and the optical pump matrix element are discussed in sections 5.2.4 and 5.2.3 respectively. Lastly, Section 5.3 combines all three ingredients, i.e. the band structure, the photoemission matrix element, and optical matrix element, to simulate initial pseudospin distributions in the conduction band. The simulated images are compared to the experimental images for both the valence band and the conduction band.

# 5.2 Microscopic simulation details

#### 5.2.1 Lattice structure

Graphene lattice is shown in Fig. 5.1. Graphene is a single-atomic layer of carbon atoms arranged in a 2D honeycomb lattice. By convention, the honeycomb lattice is considered a non-Bravais lattice [2] because the orientations of any two adjacent lattice points are not equivalent, i.e. for points 1 and 2 in Fig. 5.1a, the page has to be rotated by 180° to match their orientations. Instead, the honeycomb lattice is usually represented as a 2D triangular Bravais lattice with a two-atom basis. The unit cell, shown in a shaded parallelogram, contains two carbon atoms A and B, each of which forms sublattices A and B. In this way, the two-atom basis unit cell can tile the entire honeycomb lattice without void or overlap when it is translated by the lattice vectors  $\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$  where  $n_1$  and  $n_2$  are integers and  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are two primitive lattice vectors. Here the vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are defined for sublattice A as

$$\mathbf{a}_1 = \frac{\sqrt{3}}{2}a\hat{x} - \frac{1}{2}a\hat{y}, \qquad \mathbf{a}_2 = \frac{\sqrt{3}}{2}a\hat{x} + \frac{1}{2}a\hat{y}$$
 (5.1)

with the lattice constant  $a = |\mathbf{a}_1| = |\mathbf{a}_2| = 2.46$  Å [165]. The positions of the two atoms 1 and 2 in the unit cell are specified by the position vectors,

$$\boldsymbol{\tau}_1 = 0, \qquad \boldsymbol{\tau}_2 = a_0 \hat{x}. \tag{5.2}$$

The vectors  $\delta_j$  directly connect atom 1 in sublattice A to the three nearest neighboring sublattice B atoms:

$$\boldsymbol{\delta}_{1} = -\frac{1}{2}a_{0}\hat{x} + \frac{\sqrt{3}}{2}a_{0}\hat{y}, \qquad \boldsymbol{\delta}_{2} = a_{0}\hat{x}, \qquad \boldsymbol{\delta}_{3} = -\frac{1}{2}a_{0}\hat{x} - \frac{\sqrt{3}}{2}a_{0}\hat{y} \qquad (5.3)$$

where  $a_0$  is the length of the connecting vector  $|\delta_j| = a/\sqrt{3}$ , equal to the C-C bond length.



Figure 5.1: Graphene lattice. a) Direct-space honeycomb lattice composed of two inverted triangular sublattices A and B. The unit cell, indicated by a shaded parallelogram, contains two atoms A and B. Vectors  $\mathbf{a}_1$  and  $\mathbf{a}_2$  are the primitive lattice vectors defined for sublattice A. Point 1 in sublattice A is connected to the nearest neighboring B atoms by vectors  $\delta_j$  with j = 1, 2, 3. b) Reciprocal-space lattice showing the reciprocal lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$  and the first Brillouin zone (shaded light blue) with high symmetry points  $\Gamma$  at the origin, K at the corners of the Brillouin zone, and M the mid point between neighboring Ks.

Reciprocal lattice vectors  $\mathbf{b}_1$  and  $\mathbf{b}_2$  satisfying  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$  are given by

$$\mathbf{b}_1 = \frac{2\pi}{a} \left[ \frac{\sqrt{3}}{3} \hat{x} - \hat{y} \right], \qquad \mathbf{b}_2 = \frac{2\pi}{a} \left[ \frac{\sqrt{3}}{3} \hat{x} + \hat{y} \right]. \tag{5.4}$$

The magnitude of the reciprocal lattice vectors is  $|\mathbf{b}_1| = |\mathbf{b}_2| = 4\pi/(\sqrt{3}a)$ .

#### 5.2.2 Band structure

The calculation of a band structure is in principle a matrix eigenvalue problem for electrons moving in a periodic crystal potential. Within the Hartree mean-field approximation, these electrons behave independently, each of which obeys a oneelectron Schrödinger equation with the one-electron Hamiltonian of the form,

$$\mathbf{H}(\mathbf{r}) = \mathbf{H}_{at} + \mathbf{U}(\mathbf{r}). \tag{5.5}$$

The potential  $\mathbf{U}(\mathbf{r})$  has the periodic symmetry of the underlying Bravais lattice,  $\mathbf{U}(\mathbf{r} + \mathbf{R}) = \mathbf{U}(\mathbf{r})$  for all lattice vectors  $\mathbf{R}$  [2, 3]. In the tight-binding limit, the crystal Hamiltonian  $\mathbf{H}(\mathbf{r})$  at each lattice point can be approximated by the localized atomic Hamiltonian  $\mathbf{H}_{at}$ , provided  $\mathbf{U}(\mathbf{r}) \rightarrow 0$  as  $\mathbf{r} \rightarrow 0$ .

Because of the translational symmetry and periodicity of the Bravais crystals, the solution  $\Psi(\mathbf{r})$  to the one-electron Hamiltonian **H** in Eq. 5.5 should satisfy Bloch's theorem,  $|\Psi(\mathbf{r} + \mathbf{R})\rangle = e^{i\mathbf{k}\cdot\mathbf{R}} |\Psi(\mathbf{r})\rangle$ . To preserve this Bloch condition for graphene, we construct two sublattice basis functions via N linear superpositions of carbon's  $2p_z$ -atomic orbitals  $\phi(\mathbf{r} - \mathbf{R}_{\mu})$ ,

$$|\Phi_{A}^{\mathbf{k}}(\mathbf{r})\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_{A}}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_{A}} |\phi(\mathbf{r}-\mathbf{R}_{A})\rangle$$
(5.6)

$$|\Phi_B^{\mathbf{k}}(\mathbf{r})\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}_B}^{N} e^{i\mathbf{k}\cdot\mathbf{R}_B} |\phi(\mathbf{r}-\mathbf{R}_B)\rangle$$
(5.7)

where  $\mathbf{R}_{\mu}$  refers to the lattice vectors for sublattices  $\mu = A$  or B. Then, the electron wavefunction  $\Psi(\mathbf{r})$  is a linear combination of these two Bloch sums weighed by tight-binding coefficients  $C_{\mu}^{\lambda}(\mathbf{k})$ ,

$$|\Psi^{\lambda \mathbf{k}}(\mathbf{r})\rangle = C_A^{\lambda}(\mathbf{k}) |\Phi_A^{\mathbf{k}}(\mathbf{r})\rangle + C_B^{\lambda}(\mathbf{k}) |\Phi_B^{\mathbf{k}}(\mathbf{r})\rangle$$
(5.8)

where the electronic states with different energies are distinguished by the additional index  $\lambda$ .

With the form of  $\Psi^{\lambda \mathbf{k}}(\mathbf{r})$  in Eq. 5.8, the Schrödinger equation  $\mathbf{H} |\Psi^{\lambda \mathbf{k}}(\mathbf{r})\rangle = \mathcal{E}_{\mathbf{k}}^{\lambda} |\Psi^{\lambda \mathbf{k}}(\mathbf{r})\rangle$  can be solved analytically to determine the band structure  $\mathcal{E}_{\mathbf{k}}^{\lambda}$ . In order to do so, one can multiply both sides of the the Schrödinger equation by the complex conjugates of two sublattice basis functions  $\langle \Phi_{A}^{\mathbf{k}} |$  and  $\langle \Phi_{B}^{\mathbf{k}} |$  to obtain the following matrix equation,

$$\begin{bmatrix} \mathbf{H}_{AA} & \mathbf{H}_{AB} \\ \mathbf{H}_{BA} & \mathbf{H}_{BB} \end{bmatrix} \begin{pmatrix} C_A^{\lambda}(\mathbf{k}) \\ C_B^{\lambda}(\mathbf{k}) \end{pmatrix} = \mathcal{E}_{\mathbf{k}}^{\lambda} \begin{bmatrix} \mathbf{S}_{AA} & \mathbf{S}_{AB} \\ \mathbf{S}_{BA} & \mathbf{S}_{BB} \end{bmatrix} \begin{pmatrix} C_A^{\lambda}(\mathbf{k}) \\ C_B^{\lambda}(\mathbf{k}) \end{pmatrix}.$$
 (5.9)

The transfer integral matrix elements  $\mathbf{H}_{mn} = \langle \Phi_m^{\mathbf{k}} | \mathbf{H} | \Phi_n^{\mathbf{k}} \rangle$  and the overlap integral matrix elements  $\mathbf{S}_{mn} = \langle \Phi_m^{\mathbf{k}} | \Phi_n^{\mathbf{k}} \rangle$  can be determined by taking only the first nearest-neighboring interaction into account, which is the most dominant contribution to the matrix elements in the tight-binding formalism. Since the two sublattices A and B are chemically equivalent, by symmetry, it follows that

$$\mathbf{H}_{AA} = \mathbf{H}_{BB}, \mathbf{H}_{AB} = \mathbf{H}_{BA}^*, \mathbf{S}_{AA} = \mathbf{S}_{BB}, \mathbf{S}_{AB} = \mathbf{S}_{BA}^*.$$
(5.10)

An off-diagonal element of the transfer integral matrix  $\mathbf{H}_{AB}$ , describing hopping between A and B sublattice, is defined as

$$\mathbf{H}_{AB} = \langle \Phi_A^{\mathbf{k}}(\mathbf{r}) | \mathbf{H} | \Phi_B^{\mathbf{k}}(\mathbf{r}) \rangle$$
(5.11)

$$= \frac{1}{N} \sum_{\mathbf{R}_A} \sum_{\mathbf{R}_B} e^{i\mathbf{k}\cdot(\mathbf{R}_B - \mathbf{R}_A)} \langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \mathbf{H} | \phi_B(\mathbf{r} - \mathbf{R}_B) \rangle.$$
(5.12)

For a fixed lattice point  $\mathbf{R}_A$ , the A atom has three nearest neighboring B atoms positioned at  $\mathbf{R}_{B,l} = \mathbf{R}_A + \boldsymbol{\delta}_l$  with l = 1...3. Eq. 5.12 is then simplified to

$$\mathbf{H}_{AB} \approx \frac{1}{N} \sum_{\mathbf{R}_{A}} \sum_{l=1}^{3} e^{i\mathbf{k} \cdot (\mathbf{R}_{B,l} - \mathbf{R}_{A})} \langle \phi_{A}(\mathbf{r} - \mathbf{R}_{A}) | \mathbf{H} | \phi_{B}(\mathbf{r} - \mathbf{R}_{B,l}) \rangle = \gamma_{0} f(\mathbf{k}) \quad (5.13)$$

$$f(\mathbf{k}) = \sum_{l=1}^{3} e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{l}} = \sqrt{1 + 4\cos(\frac{\sqrt{3}a_{0}k_{y}}{2})\cos(\frac{3a_{0}k_{x}}{2}) + 4\cos^{2}(\frac{\sqrt{3}a_{0}k_{y}}{2})} \quad (5.14)$$

where the nearest-neighbor hopping integral is denoted as  $\gamma_0 = \langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \mathbf{H} | \phi_B(\mathbf{r} - \mathbf{R}_{B,l}) \rangle$ . For the diagonal transfer matrix element  $\mathbf{H}_{AA}$ ,

$$\mathbf{H}_{AA} = \frac{1}{N} \sum_{\mathbf{R}_A} \sum_{\mathbf{R}'_A} e^{i\mathbf{k} \cdot (\mathbf{R}'_A - \mathbf{R}_A)} \langle \phi_A(\mathbf{r} - \mathbf{R}_A) | \mathbf{H} | \phi_A(\mathbf{r} - \mathbf{R}'_A) \rangle, \qquad (5.15)$$

if only the nearest-neighbor interaction is considered, the same-site ( $\mathbf{R}'_A = \mathbf{R}_A$ ) exchange integral contributes most, in which case Eq. 5.15 becomes  $\epsilon_0$  the energy of an electron in the  $2p_z$  atomic state,

$$\mathbf{H}_{AA} \approx \frac{1}{N} \epsilon_0 \sum_{\mathbf{R}}^{N} \langle \phi(\mathbf{r} - \mathbf{R}_A) | \phi(\mathbf{r} - \mathbf{R}_A) \rangle = \epsilon_0, \qquad (5.16)$$

if one uses  $\mathbf{H}\phi = \epsilon_0 \phi$  and the normalization of the atomic orbital  $\langle \phi | \phi \rangle = 1$ . Since  $\epsilon_0$  is a k-independent constant value, it may be set to zero matching the zero energy, the Fermi level, of neutral graphene.

Putting the results together, the general expression for graphene's tight-binding Hamiltonian with the nearest-neighbor approximation takes the form,

$$\mathbf{H} = \begin{bmatrix} \epsilon_0 & \gamma_0 f(\mathbf{k}) \\ \gamma_0^* f^*(\mathbf{k}) & \epsilon_0 \end{bmatrix}.$$
 (5.17)

The overlap matrix elements  $S_{AA}$  and  $S_{AB}$  can be calculated in a similar way to the transfer matrix elements. The resulting overlap matrix S is given by

$$\mathbf{S} = \begin{bmatrix} 1 & s_0 f(\mathbf{k}) \\ s_0^* f^*(\mathbf{k}) & 1 \end{bmatrix}$$
(5.18)

with the nearest-neighbor overlap integral  $s_0 = \langle \phi(\mathbf{r} - \mathbf{R}_A) | \phi(\mathbf{r} - \mathbf{R}_{B,l}) \rangle$ . Solving the secular equation  $\mathbf{H} - \mathcal{E}_{\mathbf{k}}^{\lambda} \mathbf{S} = 0$  results in two energy eigenvalues,

$$\mathcal{E}_{\mathbf{k}}^{\pm} = \frac{\epsilon_0 \pm \gamma_0 |f(\mathbf{k})|}{1 \pm s_0 |f(\mathbf{k})|},\tag{5.19}$$

for the conduction (+) and valence (-) band. The tight-binding coefficients are given by

$$C_{A}^{\pm}(\mathbf{k}) = \pm \frac{f(\mathbf{k})}{|f(\mathbf{k})|} C_{B}^{\pm}(\mathbf{k}), C_{B}^{\pm}(\mathbf{k}) = \frac{1}{\sqrt{2(1 \pm s_{0}|f(\mathbf{k})|)}}.$$
 (5.20)

Note that the values of  $\gamma_0$  and  $s_0$  cannot be determined by the tight-binding model but can be calculated numerically using an alternative computational method such as density-functional theory. The range of  $\gamma_0$  is typically from -3.0 to -2.5 eV and that of  $s_0$  is from 0.06 to 0.13 eV [158,159]. In this work,  $\epsilon_0 = 0$ ,  $\gamma_0 \approx$  -2.8 eV, and  $s_0 \approx 0.1$  are used, quoted from Ref. [1].

The resulting 2D band structure  $\mathcal{E}_{\mathbf{k}}^{\pm}$  near the boundary of the first Brillouin zone is shown in Fig. 5.2a. The most prominent feature of the band structure is that  $\pi$ and  $\pi^*$  bands cross at six corners of the Brillouin zone, known as the K points and also "valleys" using semiconductor physics nomenclature. A cut through  $K_-$ ,  $\Gamma$ , and  $K_+$  points in the band structure is also shown in Fig. 5.2b for different values of  $s_0$ . Non-zero overlap parameter  $s_0$  breaks symmetry between the conduction and valence band particularly near the  $\Gamma$  point.



Figure 5.2: Band structure of graphene by tight-binding model. a) 3D energy spectrum near the vicinity of the first Brillouin zone according to Eq. 5.19 with  $\gamma_0 = -2.8 \text{ eV}$  and  $s_0 = 0.1 \text{ eV}$ . b) The band dispersion cutting through the  $k_y$  axis intersecting points,  $K_-$ ,  $\Gamma$ , and  $K_+$ , of the band structure in panel a with  $s_0 = 0.1$  and  $s_0 = 0$ . The cut is shown as the dotted line in the inset.

#### **5.2.3** Probe matrix element

The standard expression of ARPES intensity has been discussed in Chapter 2.1.5. Within the independent electron approximation, the single-particle spectral function becomes a bare band dispersion, that is a  $\delta$ -function at the Hartree-Fock orbital energy  $\epsilon_{\mathbf{k}}$ . Using the calculated tight-binding band structure  $\mathcal{E}_{TB}(\mathbf{k})$  in Eq. 5.19, the ground-state ARPES intensity is written in the following form [69],

$$I(\mathbf{k},\varepsilon) \propto \left|\mathbf{M}_{f,i}^{\mathbf{k}}\right|^{2} \delta(\varepsilon - \epsilon_{\mathbf{k}}),$$
(5.21)

$$\mathbf{M}_{f,i}^{\mathbf{k}} = e/m \left\langle \phi_f^{\mathbf{k}} \right| \mathbf{A} \cdot \mathbf{p} \left| \phi_i^{\mathbf{k}} \right\rangle.$$
(5.22)

Commonly known as the photoemission or probe matrix element, the one-electron dipole matrix element  $\mathbf{M}_{f,i}^{\mathbf{k}}$  connects the one-electron initial state  $\phi_i^{\mathbf{k}}$  and the one-electron final state  $\phi_i^{\mathbf{k}}$  through a perturbative Hamiltonian  $\mathbf{H}_{int} \approx \mathbf{A} \cdot \mathbf{p}$  where  $\mathbf{A}$  is the vector potential of an incident photon field and  $\mathbf{p}$  is the electron's translational momentum. Within the electric dipole approximation, the vector potential  $\mathbf{A}$  becomes  $\mathbf{A}(\mathbf{r}) = \mathbf{A}_0 e^{i\mathbf{q}\cdot\mathbf{r}} = \mathbf{A}_0(1 + i\mathbf{q}\cdot\mathbf{r} + ...) \approx |\mathbf{A}_0|\hat{\lambda}$  where  $\hat{\lambda}$  is the unit vector along the direction of the light polarization and  $\mathbf{q} = (\omega/c)\hat{n}$  is the wavevector of the light with  $\omega$  the angular frequency, c the speed of light, and  $\hat{n}$  the unit vector along the light propagation direction. If one assumes the free electron final state with one single plane wave only, the matrix element is further simplified to

$$\mathbf{M}_{f,i}^{\mathbf{k}} \propto \langle e^{i\mathbf{k}\cdot\mathbf{r}} | \,\hat{\lambda} \cdot \mathbf{p} | \phi_i^{\mathbf{k}} \rangle \\
\propto (\hat{\lambda} \cdot \mathbf{k}) \langle e^{i\mathbf{k}\cdot\mathbf{r}} | \phi_i^{\mathbf{k}} \rangle.$$
(5.23)

Thus, the matrix element projects outgoing photoelectrons in the direction of a light polarization via  $\hat{\lambda} \cdot \mathbf{k}$ , and the details of intensity modulation in k-space depends on the overlap of the outgoing free-electron plane wave and the initial state,  $\langle e^{i\mathbf{k}\cdot\mathbf{r}}|\phi_i^{\mathbf{k}}\rangle$ . In what follows, the matrix element for graphene will be denoted  $\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})$  with the band index  $\lambda$ .

The photoemission matrix element for graphene has been previously modeled by Shirley *et al.* using the dipole approximation within the tight-binding picture [78]. Following Eq.5.6 - 5.8, the tight-binding wavefunctions of graphene take the form

$$\Psi^{\lambda \mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}} \sum_{\mu}^{A,B} C^{\lambda}_{\mu}(\mathbf{k})\phi_{\mu}(\mathbf{r} - (\boldsymbol{\tau}_{\mu} + \mathbf{R}))$$
(5.24)

where the  $\mu$ th atomic orbital  $\phi_{\mu}$  at lattice site **R** in the unit cell is specified by the position vector of the atom  $\tau_{\mu}$ . Substituting Eq. 5.24 into Eq. 5.23 for the initial state  $\phi_i^{\mathbf{k}}$ , the matrix element  $\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})$ , can be explicitly written as

$$\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k}) \propto (\mathbf{k} \cdot \hat{\lambda}) \sum_{\mu}^{A,B} C_{\mu}^{\lambda}(\mathbf{k}) \mathrm{e}^{-i\mathbf{k}\cdot\boldsymbol{\tau}_{\mu}} \tilde{f}_{\mu}(|\mathbf{k}|) Y_{\mu}(\hat{\mathbf{k}})$$
(5.25)

$$\propto (\mathbf{k} \cdot \hat{\lambda}) C_B^{\lambda}(\mathbf{k}) \mathrm{e}^{i\mathbf{k} \cdot \boldsymbol{\tau}_B} \left[ \frac{C_A^{\lambda}(\mathbf{k})}{C_B^{\lambda}(\mathbf{k})} \mathrm{e}^{-i\mathbf{k}(\boldsymbol{\tau}_A - \boldsymbol{\tau}_B)} + 1 \right] \tilde{f}(|\mathbf{k}|) Y(\hat{k}) \quad (5.26)$$

where  $\tilde{f}_{\mu}(|\mathbf{k}|)$  and  $Y_{\mu}(\hat{\mathbf{k}})$  are the respective Fourier transforms of the radial and angular components of the  $\mu$ th orbital function,  $\phi_{\mu}(\mathbf{x}) \approx f_{\mu}(|\mathbf{x}|)Y_{\mu}(\hat{\mathbf{x}})$ . Since the unit cell contains two identical carbon atoms,  $\tilde{f}_{A}(|\mathbf{k}|)Y_{A}(\hat{k}) = \tilde{f}_{B}(|\mathbf{k}|)Y_{B}(\hat{k}) \equiv$  $\tilde{f}(|\mathbf{k}|)Y(\hat{k})$  is used in Eq. 5.26. For calculating ARPES intensity, only the square of the matrix element  $|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})^{2}|$  matters, written as

$$\left|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})\right|^{2} \propto \left|\left(\mathbf{k}\cdot\hat{\lambda}\right)\right|^{2} \left|\frac{C_{A}^{\lambda}(\mathbf{k})}{C_{B}^{\lambda}(\mathbf{k})}e^{-i\mathbf{k}\cdot(\boldsymbol{\tau}_{A}-\boldsymbol{\tau}_{B})}+1\right|^{2} \left|\tilde{f}_{\mu}(|\mathbf{k}|)Y_{\mu}(\hat{k})\right|^{2}$$
(5.27)

where the constant terms  $|C_B^{\lambda}(\mathbf{k})|^2$  and  $|e^{i\mathbf{k}\cdot\boldsymbol{\tau}_B}|^2$  in Eq. 5.26 are absorbed into a proportionality sign.

We now consider each squared factor in Eq. 5.27 in more detail and discuss its implication for the photoelectron distributions. First,  $\mathbf{k} \cdot \hat{\lambda}$  projects the photoelectron's total crystal momentum,  $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_z$ , in the polarization direction  $\hat{\lambda}$  of an incident field. For our case of the *p*-polarized probe light impinging on the sample at angle  $\theta \approx 48^{\circ}$  as shown in Fig. 5.3a,  $\mathbf{k} \cdot \hat{\lambda}$  is given by

$$\mathbf{k} \cdot \hat{\lambda} = (k_x, k_y, k_z) \cdot (\lambda_x, 0, \lambda_z)$$
(5.28)

$$\propto k_x(\cos\theta) + k_z(\sin\theta) \tag{5.29}$$

where the out-of-plane component  $k_z$  is determined by a relation  $\hbar^2 |\mathbf{k}|^2 / 2m_e = h\nu_{XUV} - W - \varepsilon$  with  $W \approx 5$  eV the work function and  $h\nu_{XUV} = 30$  eV. Because of this polarization factor  $\mathbf{k} \cdot \hat{\lambda}$ , an asymmetry is expected in the photoelectron angular distributions.

Next, we follow the work by Podolsky and Pauling [166] to evaluate the Fourier transform of the atomic wavefunction  $\tilde{f}(|\mathbf{k}|)Y(\hat{k})$  in the third factor. For carbon's  $2p_z$  orbital, the  $\tilde{f}$  function is unimportant because it is just a constant, angle-independent prefactor. Only the Y function contributes to the photoelectron angular distributions through an angle-dependent term  $P_l^m(\cos\Theta)$ , the associated Legendre polynomial of degree l and order m. In this case  $\tilde{f}(|\mathbf{k}|)Y(\hat{k})$  is just simplified to

$$\tilde{f}(|\mathbf{k}|)Y(\hat{k}) \propto P_l^m(\cos\Theta) \propto \cos\Theta$$
 (5.30)

with  $\Theta = \sin^{-1}(\mathbf{k}_{\parallel}/\mathbf{k})$  (see Fig. 5.3a for photoemission geometry).

Lastly, the second squared term in Eq. 5.27 leads to interesting interference effects. We refer to this interference factor as  $|\xi(\mathbf{k})|^2$ ,

$$|\xi(\mathbf{k})|^2 \equiv \left| \frac{C_A^{\lambda}(\mathbf{k})}{C_B^{\lambda}(\mathbf{k})} \mathrm{e}^{-i\mathbf{k}\cdot(\boldsymbol{\tau}_A - \boldsymbol{\tau}_B)} + 1 \right|^2.$$
(5.31)

Note that the modulation of  $|\xi(\mathbf{k})|^2$  arises from two effects. First, the ratio  $C_A^{\lambda}(\mathbf{k})/C_B^{\lambda}(\mathbf{k})$  in Eq. 5.31 indicates the relative phase between two sublattice wavefunctions, given by

$$\frac{C_A^{\lambda}(\mathbf{k})}{C_B^{\lambda}(\mathbf{k})} = -\frac{H_{AB}(\mathbf{k})}{|H_{AB}(\mathbf{k})|}$$
(5.32)

$$H_{AB} = t \left[ 1 + e^{2\pi i \beta_1(\mathbf{k})} + e^{2\pi i \beta_2(\mathbf{k})} \right],$$
 (5.33)

where  $\beta_1$  and  $\beta_2$  are specified by the electron's crystal momentum **k** through the notation  $\mathbf{k} = \beta_1 \mathbf{b_1} + \beta_2 \mathbf{b_2}$  with  $\beta_1 = 2/3$  and  $\beta_2 = 1/3$  for the *K*-points of the Brillouin zone. Secondly, the exponent of  $e^{-i\mathbf{k}\cdot(\boldsymbol{\tau}_A-\boldsymbol{\tau}_B)}$  in Eq. 5.31 involves a difference between two atomic positions in the unit cell,

$$\boldsymbol{\tau}_A - \boldsymbol{\tau}_B = a_0 \hat{x} \tag{5.34}$$

(see Eq. 5.2). This is equivalent to the path length difference between two photoelectrons on sublattices A and B to the detector in ARPES measurements. Combining Eq. 5.32 - 5.34, the final expression for  $|\xi|^2$  takes the following form,

$$\left|\xi(\beta_{1}(\mathbf{k}),\beta_{2}(\mathbf{k}))\right|^{2} = \left| \left[ \frac{1 + e^{-2\pi i\beta_{1}(\mathbf{k})} + e^{-2\pi i\beta_{2}(\mathbf{k})}}{|1 + e^{-2\pi i\beta_{1}(\mathbf{k})} + e^{-2\pi i\beta_{2}(\mathbf{k})}|} \right] e^{[2\pi i(\beta_{1}(\mathbf{k}) + \beta_{2}(\mathbf{k}))]/3} + 1 \right|^{2}.$$
(5.35)

We see that  $|\xi|^2$  varies with k near the corners of the Brillouin zone.

With the explicit forms of the three squared terms given in Eq.5.29, 5.30, and 5.35, one can simulate  $|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})|^2$  in Eq. 5.27. The simulated results for  $|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})|^2$  are shown in Fig. 5.3b and 5.3c at energy slices  $E - E_F = \pm 1.2$  eV. These are the valence and conduction band energies, where we expect optical transition from the valence band at  $-h\nu_{\text{pump}}/2 = -1.2$  eV to the conduction band at  $+h\nu_{\text{pump}}/2 = +1.2$  eV in our time-resolved ARPES experiment with  $h\nu_{\text{pump}} = 2.4$  eV. The interference effects via  $|\xi(\beta_1(\mathbf{k}), \beta_2(\mathbf{k}))|^2$  are clearly evident in both images as well as a left-right symmetry due to the polarization factor  $\mathbf{k} \cdot \hat{\lambda}$ . At the energy  $E - E_F = -1.2$  eV,  $|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})|^2$  vanishes completely in the outer part of the Fermi surface near each K point due to a destructive interference between two photoelectrons emitted from two chemically equivalent sublattices. This trend is reverse for the energy  $E - E_F = +1.2$  eV.



Figure 5.3: Probe matrix element. a) Photoemission geometry. Our *p*-polarized probe light with  $h\nu_{\text{probe}} = 30 \text{ eV}$  impinges on the sample at angle  $\theta = 48^{\circ}$  measured normal to the sample plane. The square of the probe matrix element  $|\mathbf{M}_{\text{probe}}^{\lambda}(\mathbf{k})|^2$  for b) the conduction band ( $\lambda = c$ ) at  $E - E_F = +1.2 \text{ eV}$  and c) the valence band ( $\lambda = v$ ) at  $E - E_F = -1.2 \text{ eV}$ .

#### 5.2.4 Pump matrix element

This section details the optical matrix element following from Ref. [1] and [167]. Within the dipole approximation, the interband optical matrix element between two electronic states is given by [164, 168]

$$\mathbf{M}_{\mathbf{k},\mathbf{k}'}^{\lambda,\lambda'} = \langle \Psi_{\mathbf{k}}^{\lambda}(\mathbf{r}) | \nabla_{\mathbf{r}} | \Psi_{\mathbf{k}'}^{\lambda'}(\mathbf{r}) \rangle$$
(5.36)

where the band index  $\lambda'$  and the wavevector k' characterize states in the valence band,  $\lambda$  and k characterize states in the conduction band, and  $\nabla_{\mathbf{r}}$  is related to the linear momentum operator via  $\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}$ . This optical matrix element can be determined analytically using the tight-binding wavefunctions defined in Eq.5.6 -5.8,

$$\mathbf{M}_{\mathbf{k},\mathbf{k}'}^{\lambda,\lambda'} = \frac{1}{N} \sum_{\mu,\mathbf{R}_{\mu}}^{A,B} \sum_{\mu',\mathbf{R}'_{\mu}}^{A,B} C_{\mu}^{\lambda*}(\mathbf{k}) C_{\mu'}^{\lambda'}(\mathbf{k}') e^{-i(\mathbf{k}\cdot\mathbf{R}_{\mu}-\mathbf{k}'\cdot\mathbf{R}_{\mu'})} \left\langle \phi(\mathbf{r}-\mathbf{R}_{\mu}) \right| \nabla_{\mathbf{r}} \left| \phi(\mathbf{r}-\mathbf{R}_{\mu'}) \right\rangle.$$
(5.37)

For a direct transition  $(\mathbf{k} = \mathbf{k}')$ , the nearest-neighbor interaction simplifies Eq. 5.37 to

$$\mathbf{M}_{\mathbf{k},\mathbf{k}}^{\lambda,\lambda'} = m \sum_{l=1}^{3} \frac{\boldsymbol{\delta}_{l}}{|\boldsymbol{\delta}_{l}|} \left[ C_{A}^{\lambda*}(\mathbf{k}) C_{B}^{\lambda'}(\mathbf{k}) e^{i\mathbf{k}\cdot\boldsymbol{\delta}_{l}} - C_{B}^{\lambda*}(\mathbf{k}) C_{A}^{\lambda'}(\mathbf{k}) e^{-i\mathbf{k}\cdot\boldsymbol{\delta}_{l}} \right]$$
(5.38)

where  $m = \langle \phi(\mathbf{r} + |\boldsymbol{\delta}_1|\hat{x}) | \partial_x | \phi(\mathbf{r}) \rangle \approx 3 \text{ nm}^{-1}$  is used. With  $C_A^{\lambda}(\mathbf{k})$  and  $C_B^{\lambda}(\mathbf{k})$  given in Eq. 5.20, the optical matrix element in Eq. 5.38 can be explicitly evaluated as

$$\mathbf{M}_{\text{pump}}^{c,v}(\mathbf{k}) \equiv \mathbf{M}_{\mathbf{k},\mathbf{k}}^{\lambda,\lambda'} = \frac{1}{\sqrt{1 - s_0^2 |e(\mathbf{k})|^2}} \frac{m}{|e(\mathbf{k})|} \mathcal{R}\left[e^*(\mathbf{k}) \sum_{l=1}^3 e^{i\mathbf{k}\cdot\boldsymbol{\delta}_l} \frac{\boldsymbol{\delta}_l}{|\boldsymbol{\delta}_l|}\right].$$
 (5.39)

From here on, we change the notation from  $\mathbf{M}_{\mathbf{k},\mathbf{k}}^{\lambda,\lambda'}$  to  $\mathbf{M}_{pump}^{c,v}(\mathbf{k})$  to distinguish it from the probe matrix element.

Fig. 5.4 shows x and y components of  $|\mathbf{M}_{pump}^{c,v}(\mathbf{k})|^2$  in the first Brillouin zone. Both components are minimum near the six zone corners along the polarization directions of pump pulses and maximum perpendicular to them. No optical transition is expected at the  $\Gamma$  point since both x and y components vanish there.



**Figure 5.4: Optical matrix element. a)** x and **b)** y component of the optical matrix element square  $|\mathbf{M}_{pump}^{c,v}(\mathbf{k})|^2$  between the valence (v) and conduction (c) band.

# 5.3 **Results and discussion**

#### 5.3.1 Valence-band pseudospin distributions

Fig. 5.6 compares the experimental photoelectron distribution for states near  $E - E_F = -1.2$  eV to a tight-binding model,

$$I(\mathbf{k}_{\parallel}) \propto \int_{-1.21 \text{ eV}}^{-1.16 \text{ eV}} d\varepsilon \left[ \delta(\varepsilon - \mathcal{E}_{\text{TB}}(\mathbf{k}_{\parallel})) \times |\mathbf{M}_{\text{probe}}^{v}(\mathbf{k}_{\parallel}, \mathbf{k}_{z})|^{2} \right] * h(\mathbf{k}_{\parallel}) .$$
(5.40)

Here  $\mathcal{E}_{\text{TB}}(\mathbf{k})$  is the band structure given by Eq. 5.19 and  $\mathbf{M}_{\text{probe}}^{v}(\mathbf{k}_{\parallel}, \mathbf{k}_{z})$  is the probe matrix element between the valence-band initial states and the single plane-wave final states with wave vector  $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_{z}$  determined by energy conservation relation  $\hbar^{2}|\mathbf{k}|^{2}/2m_{e} = h\nu_{\text{XUV}} - W - \varepsilon$ , with  $W \approx 5$  eV the work function and  $h\nu_{\text{XUV}} = 30$  eV. The function  $h(\mathbf{k}_{\parallel})$  used for convolution is a 2D Gaussian of  $\approx 0.1$ 

 $Å^{-1}$  FWHM reflecting the momentum resolution of our measurements. This is determined from the size of our observed Dirac point in the momentum space images as illustrated in Fig. 5.5 (this also effectively captures the energy resolution). The simulated distribution is shown in Fig. 5.6c, together with the experimental distribution in Fig. 5.6d. In Fig. 5.6d, two key experimental observations arise from the matrix element effect; a left-right asymmetry in the Brillouin zone due to the ppolarized probe XUV light and a partial suppression of intensity around each zone corner due to the k-dependence of the probe matrix element. Originally modelled by Shirley et al. [78], a simple interference between two photoelectrons emitted from two chemically equivalent sublattices is known to suppress part of  $\pi$ -band distributions of graphene around the Brillouin zone corners, leading to a strong momentum anisotropy known as "dark corridors" [79]. Although dark corridors have been previously seen several times in ARPES for graphene [80-82], it was Gierz et al. [79] who extensively investigated the effects of dark corridors with changing light polarizations and photon energies. While our present tight-binding model predicts zero intensity at these dark corridors along the  $\Gamma$ -K directions around the six K points for  $h\nu_{\rm XUV} = 30$  eV, in reality the observed dark corridors are not as pronounced as expected, especially for K1, K4, K5, and K6. Gierz et al. attribute these residual signals to AB sublattice symmetry breaking due to spin-orbit coupling [79], which may be weak in graphene [169].

We also quantitatively compare the experiment and theory by plotting normalized photoemission intensity vs. angle  $\theta$  around K. Only the result of K2 is shown in Fig. 5.6b. Overall, the experiment is in good agreement with the simulation for K2, and also for K3. Somewhat worse agreement with the simulation is seen for the rest of the valleys, K1, K4, K5 and K6, when photoelectron final-state momenta are further away from the light polarization vector. For these valleys, the dark corridor positions are instead perpendicular to the  $\Gamma K$  with our 30-eV photon and the TB approximation with the single-plane wave final state does not explain our data. Multiple plane-wave basis or different final state assumption may be needed to improve the calculation as seen from the work by Gierz *et al.* [79].



Figure 5.5: Momentum resolution applied to tight-binding (TB) simulation. Photoelectron momentum distribution near  $E - E_F = 0$  eV for **a**) experiment (Expt) and **b**) tight-binding model (TB). The vertical (red) and horizontal (blue) lines going through the center of the images are shown as the dashed lines for experiment and a solid line for TB. Comparison of **c**) the horizontal (blue) and **d**) the vertical (red) lineouts between experiment and TB.



Figure 5.6: Comparison between experiment (Expt) and the tight-binding (TB) model for the valence band. a) Schematic of a photoemission process in graphene Dirac cone illustrating that a probe pulse (*p*-polarized 30 eV) ejects electrons from energy  $E - E_F = -1.2$  eV to the continuum. b) Photoemission intensity vs. angle  $\theta$  around K2, constructed via integrating the data in c and d in an ROI referenced to the center of K2 while the images are rotated clockwise by  $\theta$  starting from the dark corridor position indicated by the green line in c. c) Experimental and d) simulated momentum distribution of valence band electrons ( $E - E_F = -1.2$  eV) in the whole Brillouin zone.

#### 5.3.2 Photoexcited conduction-band pseudospin distribution

We consider a pump-probe measurement at time zero where a linearly polarized 2.4-eV pump pulse takes electrons to  $h\nu_{pump}/2 = +1.2$  eV and a probe pulse simultaneously tracks those photoexcited electrons by a photoemission process as illustrated in Fig. 5.7a. The momentum-space distributions of these initially excited photoelectrons can be modeled similarly to the ground-state photoelectron distributions in Eq. 5.40,

$$I_{t0}(\mathbf{k}_{\parallel}) \propto \int_{1.05 \text{ eV}}^{1.2 \text{ eV}} d\varepsilon \left[ \delta(\varepsilon - \mathcal{E}_{\text{TB}}(\mathbf{k}_{\parallel})) \times |\mathbf{M}_{\text{pump}}^{c,v}(\mathbf{k}_{\parallel})|^{2} \times |\mathbf{M}_{\text{probe}}^{c}(\mathbf{k}_{\parallel},\mathbf{k}_{z})|^{2} \right] * h(\mathbf{k}_{\parallel}) , \qquad (5.41)$$

with  $\mathbf{M}_{\text{pump}}^{c,v}(\mathbf{k}_{\parallel})$  denoting the optical matrix element between the valence (v) and conduction (c) band, given by Eq. 5.39. The simulated distributions for *y*- and *x*-polarized excitation are shown in Fig. 5.7b and 5.7c, together with the corresponding experimental distributions in Fig. 5.7d and 5.7e measured with the excitation fluence 45  $\mu$ J/cm<sup>2</sup>. The angular distributions are now additionally affected by

the **k**-dependent optical matrix element [1], imposing the nodes (gray dotted lines) parallel to the pump polarization directions as seen in panel d and e. The photoemission matrix element effects are also clearly seen in the images as expected, a left-right asymmetry and the p-polarized probe XUV light.

For quantitative comparison, normalized photoelectron intensities vs.  $\theta$  around K3 for y- and x-excitation are plotted in Fig. 5.7f and g respectively. We also show a similar comparison for K2 in Fig. 6.7. Similar to the ground state result in Fig. 5.6, remarkable agreement is found for K2 and K3, but larger discrepencies are observed for K1, K4, K5 and K6. Such inconsistencies are likely due to the reduced accuracy of modeling the photoemission matrix element (not pump matrix element) with only the single plane wave for the final state since we observe similar discrepencies for the ground states. Note that the pump matrix element here does not take any scattering processes into account. For K2 and K3, such excellent quantitative agreement with tight-binding theory indicates that these initial pseudospin polarized electrons have undergone minimal scattering events in our experiment.



Figure 5.7: Comparison between experiment (Expt) and the tight-binding (TB) model for the conduction band. a) Schematic of a time-resolved photoemission process on graphene Dirac cone. A linearly polarized 2.4-eV pump pulse excites electrons to  $E - E_F = 1.2$  eV and a 30-eV *p*-polarized probe pulse ejects them to the continuum. The simulated momentum-space distributions of electrons between 1.05 and 1.21 eV at pump-probe delay  $\Delta t = 0$  for b) y- and d) x-polarized pump excitation. The observed momentum-space distributions are shown in panels d and e. Comparison of photoemission intensity vs. angle  $\theta$  around K3 between the experiment and the TB model for f) y- and g) x-polarized pump excitation. The directions of pump and probe polarizations are indicated by the gray dashed lines and purple arrow, respectively in the simulated images. The position of  $\theta = 0$  is colored in red, indicated by the solid lines in panels b and c, and the dotted lines in panels f and g. For better visualization, the optical nodes are not indicated on the observed images.

# Chapter 6

# Ultrafast Pseudospin Relaxation in Graphene

## 6.1 Introduction

The gapless, conical band structure of graphene is the origin of many exotic optical and electronic phenomena that can be harnessed for applications in optoelectronic devices. The broadband absorption [170] arising from the band linearity makes graphene suitable for optical sensors [171, 172] or photodetectors [173] in the near-IR to visible range and graphene is now routinely used in technologies such as saturable absorbers in passively mode-locked lasers [174–180]. The ultrafast optical response of graphene is due to carrier relaxation mediated by different scattering processes which lead to rapid thermalization of excited electrons. Electron-electron (e-e) scattering is very efficient in graphene due to the gapless band structure and high carrier mobility, and also electron-phonon (e-ph) coupling between high-energy electrons and graphene's optical phonons is calculated to be exceptionally large [1]. The microscopic details of excited carrier relaxation in graphene are thus both of fundamental interest and are important for the design of graphene-based devices, and have been the subject of a substantial body of previous work.

Also proposed for use in graphene devices is an additional quantum number labeling Bloch wave functions in graphene termed lattice pseudospin [181, 182]. The lattice pseudospin  $\phi$  refers to the relative phase of the Bloch wave function on the two equivalent carbon sublattices A and B in its honeycomb lattice via  $\psi = \frac{1}{\sqrt{2}} \left[ \psi_A \pm e^{i\phi} \psi_B \right] e^{i\mathbf{k}\cdot\mathbf{r}}$ . Here the upper sign is for the conduction band, the lower sign is for the valence band, and **k** is the crystal momentum. The angle  $\phi$ also corresponds to the angular position of Bloch states around the K points in the Brillouin zone, with the pseudospin orientation parallel to the relative crystal momentum ( $\mathbf{k} - K$ ) in the conduction band and antiparallel in the valence band [3].

Photoexcitation of electrons from the valence to the conduction band creates pseudospin polarization via the k-dependence (and thus  $\phi$ -dependence) of the optical matrix elements [1]. Theoretical work has predicted that nonthermal electron

distributions with strong lattice pseudospin polarization, i.e. the excited electrons of most interest for next-generation graphene-based optoelectronic devices, should be observable in pump/probe experiments in neutral (i.e. undoped) graphene with low excitation fluence, with lifetimes of a few tens of femtoseconds [1, 160–162]. Pseudospin dynamics in graphene have been previously studied using polarization resolved optical spectroscopy [183-189] and also using time- and angle-resolved photoemission (time-resolved ARPES) [190, 191]. However, this previous work has been limited in scope. The optical experiments have been performed with sufficient sensitivity to access the low-fluence regime, where e-ph scattering is expected to be the dominant relaxation mechanism. However these optical measurements have probed only limited energy ranges of the excited electron distribution, either at the initial excitation energy in degenerate pump/probe measurements or much higher or much lower energies in a few cases. Furthermore, the optical observables involve drastic integrations over the momentum-space electron distributions, and require a priori assumption of strict pseudospin selection rules for interpretation in terms of the electron dynamics around the Dirac cone.

Time-resolved ARPES experiments can measure the full excited electron distrubutions directly in momentum space and do not rely on any assumptions regarding selection rules. There have been a number of previous time-resolved ARPES studies on graphene and graphite [37, 38, 40, 190–195], with two studies addressing pseudospin polarization [190, 191]. However, this previous time-resolved APRES work has been predominantly conducted at very high excitation fluence in the  $\sim$ mJ / cm<sup>2</sup> regime and/or on either heavily doped graphene or graphite, both of which have a large density of states (DoS) at the Fermi level  $E_F$ . Both non-zero DoS at  $E_F$  and strong pumping lead to the dominance of e-e scattering and very rapid thermalization of the electron distribution, and the data have been mostly well-described in terms of evolving Fermi-Dirac distributions characterized by time-dependent temperatures [37, 191–193, 196].

In this work, we report time-resolved APRES imaging of electrons excited with 2.4 eV ( $\lambda = 517$  nm) photons in high-quality neutral graphene samples produced via exfoliation. A series of pump/probe measurements with high dynamic range and variable pump polarization are enabled by a unique high-performance instrument for time-resolved ARPES incorporating ultrashort extreme ultraviolet (XUV) pulses at 61 MHz repetition rate [25, 52, 150] with time-of-flight momentum microscopy [63, 64]. High dynamic range enables us to observe pronounced nonthermal distributions with strong lattice pseudospin polarization. For energies near the  $h\nu_{pump}/2 = 1.2$  eV level populated by the pump pulse, at low excitation fluence the observed photoelectron signals are in remarkably good agreement with a simple model based on tight-binding theory accounting for the pump and probe optical matrix elements but with no consideration of e-e or e-ph scattering. In the full distribution, pseudospin polarization is still visible down to 0.8 eV above the Dirac point, or multiple optical phonon energies below 1.2 eV, indicating the persistence of lattice pseudospin through multiple optical phonon scatterings. With increasing excitation fluence we observe that increased e-e scattering leads to more rapid thermalization and reduced pseudospin polarization, although we do observe

up-scattered electrons to retain a degree of polarization, as previously predicted by theory [161]. To our knowledge, this is the first report of excited-state ARPES measurements in neutral graphene, and also the first to vary the excitation fluence over a range where e-e scattering vs. e-ph scattering are expected to be comparable [160, 163].

## 6.2 Experiment

#### 6.2.1 Set-up

Our overall experimental scheme for time-resolved ARPES is summarized in Fig. 6.1. Visible ( $h\nu_{pump} = 2.4 \text{ eV}$ ) pump pulses with variable polarization and *p*-polarized XUV (20 - 30 eV) probe pulses impinge on the sample at 48 degrees. The pump-probe experiements are driven by a home-built Yb:fiber frequency comb laser [122] operating at 61.3 MHz repetition rate with a 185-fs IR pulse centered at 1035 nm (more details can be found in Chapter 3). 1  $\mu$ J of this IR driver is passively amplified in an enhancement cavity (a finesse of  $\mathcal{F} > 500$ ) by constructively interfering with intracavity pulses. High harmonic generation in gas (Argon or Krypton) takes place at the cavity focus, where the peak intensity on the order of  $10^{14}$ W/cm<sup>2</sup> is reached (see Chapter 3 and Ref. [52, 150]). The XUV harmonics ranging from 10 to 40 eV are out-coupled by a sapphire Brewster plate. A time-preserving grating monochromator selects a single harmonic, which is then focused on a sample. Our cavity-enhanced high harmonic generation (CE-HHG) source and subsequent beamline are described in Chapter 3 (also see references [52, 150]). Photoelectrons are collected with a custom time-of-flight momentum microscope similar to that described by Medjanik et al. [63]. Real-space photoelectron microscopy (PEEM) images of two graphene samples are shown in Fig. 6.1b and c (see Section 6.2.2 for details on the samples). We select photoelectrons emerging from the graphene sample using a small aperture in a real-space image plane of the momentum microscope, and also high-pass filter the energy distribution (EDC) as described in Chapter 4. The XUV probe beam is  $24 \times 16 \ \mu m^2$  FWHM on the sample, and the pump beam size is set to be at least three times as large such that the recorded sample area is uniformly pumped. All measurements are performed at a base pressure of  $\sim 5 \times 10^{-10}$  Torr and with the sample held at room temperature.

We determine time-zero (delay where pump and probe pulses maximally overlap on the sample) and instrument response function (IRF = cross-correlation between pump and probe) using both the graphene signal itself as shown in the right panel of Fig. 6.4, and also complementary pump-probe experiments on polycrystalline gold (see Chapter 7.6 for more details). The IRF is well-described as a Gaussian width of  $\approx 200$  fs FWHM. Here we report measurements with incident pump fluences between 45 and 207  $\mu$ J/cm<sup>2</sup>. We correct for small time-dependent surface photovoltage shifts (due to excitation of the silicon substrate) less than 40 meV via observing shifts in the Dirac point (see Chapter 7.5), and overall determine the position of the Dirac point with an uncertainty of 50 meV (see Chapter 7.4). From comparing ground state signals to those expected from a Fermi-Dirac distribution at 300 K, we estimate the energy resolution of these experiments to be approximately 250 meV FWHM.



Figure 6.1: Experiment overview. a) Linearly polarized pump pulses (green) promote electrons to 1.2 eV above the Dirac point ( $E_D$ ) and a time-delayed XUV probe pulse ejects them into the continuum. b) and c) Real space-PEEM images of two graphene samples. The dashed lines show the region of the hBN support. The scale bars in the two images are 10  $\mu$ m.

#### 6.2.2 Samples

Samples studied in this work are neutral monolayer graphene stacked on a buffer layer of hexagonal boron nitride (hBN) on a silicon (Si) substrate. We repeated our experiments on several graphene samples and over a range of XUV photon energies, with the key results reported here reproducing across several samples and a range of conditions. The main difference observed between different samples is the background level (noise floor) observed in the photoelectron spectra, with higher background precluding clear observation of non-thermal distributions in experiments with lower excitation fluence. We present here data recorded from two samples, denoted as Gr1 and Gr2 in Fig. 6.2. Both samples are prepared by a mechanical exfoliation and their fabrication procedures are described below. The main time-resolved ARPES data is collected using a pump pulse with  $h\nu_{pump} = 2.4$  eV and an extreme ultraviolet (XUV) probe pulse with  $h\nu_{probe}$  = 30 eV for Gr1 and with  $h\nu_{probe}$  = 22.8 eV for Gr2 unless otherwise noted. The flake size of Gr1 is  $\approx$ 10  $\mu$ m × 40  $\mu$ m. The actual flake size of Gr2 is  $\approx$  20  $\mu$ m × 30  $\mu$ m but the usable area (indicated in yellow in Fig. 6.2d) is  $\approx 10 \ \mu m \times 10 \ \mu m$  due to multiple cracks inside.



Figure 6.2: Graphene samples studied in this work. Real space-PEEM images of **a**) Gr1 and **b**) Gr2 measured with  $h\nu_{pump} = 4.75$  eV. **c**) is an optical microscope image of Gr1, and **d**) is a scanning electron microscope (SEM) image of Gr2. The blue and gray dashed lines outline graphene and hBN, respectively. For Gr2, we measure photoelectrons only from the smaller region marked in yellow to avoid cracks in the large flake. The scale bars in all the images are 10  $\mu$ m.

#### 6.2.3 Fabrication

Gr1: The Gr1 sample was fabricated by the Kawakami group at Ohio State University, following the similar procedure described previously for WS2 [25]. Monolayer graphene flakes are exfoliated from Kish graphite and hexagonal boron nitride (hBN) flakes are exfoliated from hBN purchased from HQ Graphene, each onto separate SiO<sub>2</sub>(300 nm)/Si substrates (figures 6.3a and 6.3b). Next, a dry transfer method is used to stack the Gr1/hBN heterostructure. A polydimethylsiloxane (PDMS) hemisphere is first made on a clean glass slide and then covered by a thin film of polycarbonate (PC). This PDMS/PC stamp is then used to pick up the monolayer Gr1 flake from the SiO<sub>2</sub>/Si substrate (Fig. 6.3c). The pick-up procedure is to lower the PDMS/PC stamp and heat the sample stage to 70° C, and when the target flake is fully covered by PC film, shut down the heating and slowly detach the PDMS/PC from the sample stage; the Gr1 flake is picked up by the PDMS/PC stamp after separation. Then, the PDMS/PC/Gr1 is used to further pick up the bottom hBN flake ( $\sim 10-20$  nm thickness) by the same procedure (Fig. 6.3d). The PDMS/PC/Gr1/hBN is then transferred onto a pre-patterned gold-grid-marked Si substrate with good alignment by heating the sample stage to 170° C and slowly lifting up the PDMS stamp; the PC/Gr1/hBN remains on the Si substrate. The PC film is then dissolved in chloroform.



Figure 6.3: Sample fabrication procedure for monolayer graphene (Gr1). Optical microscope images of a) the exfoliated monolayer graphene (Gr) flake, b) the hBN, c) the Gr picked up on the PDMS/PC stamp, d) the PDMS/PC/Gr with the picked up bottom hBN flake, and e) the Gr/hBN on the target Si substrate. The blue dashed line outlines the Gr. Part of the Gr is draped directly onto Si substrate to prevent sample charging. The scale bars in all the images are 10  $\mu$ m.

**Gr2.** The Gr2 sample was fabricated by the Du group at Stony Brook University. First hBN flakes are exfoliated onto a Si substrate. For graphene exfoliation, we first spin-coat a SiO<sub>2</sub> substrate with a very thin layer of polypropylene carbonate PPC (~10nm). The substrate is slightly warmed up to ~40° C, and the Gr2 flake is exfoliated on top of the PPC using the standard scotch tape method. The PPC layer greatly enhanced the adhesion of the surface, allowing large graphene flakes to be exfoliated. The thickness of the PPC layer is sufficiently small that the color contrast of graphene is similar to that on a bare SiO<sub>2</sub> substrate, allowing easy identification. We next use PDMS to pick up graphene: PDMS is pressed onto the target graphene flake at ~45° C. Then temperature is increased to ~60° C, at which point PPC loses its adhesion, and PDMS is slowly separated from the substrate at 60° C, to pick up graphene. Finally, to drop the Gr2 flake onto a target hBN flake, PDMS/Gr2 is pressed down onto hBN at ~80° C. Then the temperature is raised to ~140° C, at which point we separate PDMS from the hBN flake, with graphene transferred onto the hBN flake.

# 6.3 Results

#### 6.3.1 General overview of fluence-dependent dynamics

Fig. 6.4 shows the general overview of electron relaxation dynamics for the excitation fluence range of 45 - 207  $\mu$ J/cm<sup>2</sup>. The left panels show the full electron distribution for all electrons above the Dirac point as a function of pump-probe delay as a false color plot, along with the electron distribution curves (EDC) at

selected pump/probe delays. For all three fluences, most of the electrons initially excited to the energy  $h\nu_{pump}/2 = +1.2$  eV above  $E_D$  have already scattered out of their initial distributions at delays even before time zero, where the pump and probe pulses maximally overlap. The electrons relaxing down to the energy region  $\leq 0.8$  eV seem to decay very fast on a time scale much shorter than our temporal resolution of  $\approx 200$  fs. Despite this limitation in the dynamics, these electrons seem to have not yet thermalized in the EDC, showing a substantial deviation from a Fermi-Dirac distribution upon visual inspection. This non-thermal feature is most prominent for 45  $\mu$ J/cm<sup>2</sup> and smeared out more for 132 and 237  $\mu$ J/cm<sup>2</sup>. Also noticeable in the distributions are incressed electron populations by up-scattering with increasing excitation fluence. In the following, we look into the details of these non-thermal signatures.



Figure 6.4: General overview of electron relaxation dynamics across a range of excitation fluence. Left panels show time-dependence of momentum integrated electron distributions, with data from the unexcited sample at  $\Delta t = -1$  ps subtracted, represented as a false color map for **a**) 45  $\mu$ J/cm<sup>2</sup>, **b**) 132  $\mu$ J/cm<sup>2</sup>, **c**) 207  $\mu$ J/cm<sup>2</sup>. Middle panels are electron distribution curves at selective time delays, i.e. vertical lineouts from the left panels without the negative delay signal subtracted. The right panels show the integrated signal for all electrons above the Dirac point (black circles) along with fits (blue curves) with double-exponentials convolved with a Gaussian IRF (see Chapter 7.6 for more details). The IRF is shown in the figure as the gray shaded curves.

#### 6.3.2 Non-thermal electron distributions

Fig. 6.5 shows momentum-integrated EDCs on a logarithmic scale for three different fluences: 45, 132, and 207  $\mu$ J/cm<sup>2</sup>. For comparison, thermal signals expected from Fermi-Dirac distributions at different temperatures are shown by the

dashed lines. The thermal signals are constructed via the product of the Fermi function  $\langle n(E) \rangle = (e^{(E-E_F)/k_BT} + 1)^{-1}$  with the DoS and photoemission matrix elements derived from tight-binding theory, all convolved with a Gaussian of 250 meV FWHM to account for the instrumental energy resolution. The kinks in the thermal signals at  $E = E_F$  are due to the zero in the DoS at the Dirac point. At delays ( $\Delta t$ ) longer than our IRF width, i.e. delays where the pump and probe pulses no longer overlap significantly, the spectra are well described with the simulated thermal signals with temperatures consistent with previous work [192, 196]. Note that it is expected that the temperature does not scale linearly with the fluence due to both the non-constant graphene DoS and the onset of saturated absorption in this fluence regime [179]. For all fluences, the momentum- and energy-integrated signal for all electrons above the Dirac point is fit well by a biexponential decay with  $\tau_1 \approx 200$  fs and  $\tau_2 = 1 - 3$  ps depending on fluence, as shown in the right panels of Fig. 6.4 (more details can be found in Chapter 7.6).

However, near  $\Delta t = 0$ , significant population is observed above 0.8 eV that cannot be described by a Fermi-Dirac distribution. The behavior we observe in the EDC agrees qualitatively with that predicted by Winzer et al. [160], who performed density-matrix/Bloch equation simulations of electron dynamics in graphene at different excitation fluences. At low fluence, electrons relax by emitting optical phonons in discrete steps and the EDC shows a plateau behavior with a steep drop-off at  $h\nu_{pump}/2$ , with few electrons above this initial excitation energy. At higher fluence, electron-electron scattering is dominant and the distribution is smoother with a tail extending to higher energies well above  $h\nu_{pump}/2$ . We note that the non-thermal distributions we observe here on a logarithmic scale, and their very fast relaxation, are qualitatively different than previous reports using much larger pump fluences in doped graphene [38, 193, 197].



**Figure 6.5:** Energy distribution curves (EDC, solid lines) at selected time delays for a) 45  $\mu$ J/cm<sup>2</sup>, b) 132  $\mu$ J/cm<sup>2</sup>, and c) 207  $\mu$ J/cm<sup>2</sup>. Simulated thermal distributions at different temperatures (dashed) are shown for comparison. The experimental data are at time delays  $\Delta t = -1$  ps in black,  $\Delta t = 0$  fs in blue,  $\Delta t = 200$  fs in red, and  $\Delta t = 500$  fs in green. The vertical dotted lines in gray represent Dirac points  $E - E_F = 0$  and  $E - E_F = h\nu_{pump}/2 = 1.2$  eV for the direct excitation energy. The noise floor of the measurement at high energies is seen in the negative delay data (black curves).

#### 6.3.3 Initial pseudospin polarization

Fig. 6.6 shows the photoelectron momentum distributions for electrons between 1.05 and 1.21 eV above the Dirac point, i.e. within one optical phonon of the initial excitation at  $h\nu_{pump}/2$ , with the in-plane component of the excitation electric field polarized in the x and y directions. For this data the excitation fluence is 45  $\mu$ J/cm<sup>2</sup> and the pump and probe pulses are maximally overlapped ( $\Delta t = 0$ ). Nodes, illustrated by the white dashed lines, are clearly observed along the pump polarization directions, as expected from the optical matrix element pseudospin selection rules [1]. Also visible are the so-called dark corridors along the  $\Gamma K$ -direction and a left-right asymmetry in the images due to the k-dependence of the photoemission matrix element and the p-polarization of the XUV light [78,79] (see Chapter 5.2.3 for more detail). Note that for K1 and K4 the dark corridor is not as prominent and similar behavior of the missing dark corridor is also observed in photoemission signals from the valence band as shown in Fig. 5.6. In what follows, we do not include data from the K5 and K6 regions in our analysis due to the low statistics in these regions.



Figure 6.6: Polarization-dependent initial pseudospin anisotropy. a) The 3Dband structure at  $\Delta t = 0$ . Momentum distributions for electrons between 1.05 and 1.21 eV above the Dirac point at  $\Delta t = 0$  are shown for b) y- and c) x-polarized pump excitation. The excitation fluence is 45  $\mu$ J/cm<sup>2</sup>, and the directions of pump and probe polarization are indicated by the white and the magenta dotted lines, respectively. The intensity near the  $\Gamma$  point is an artifact of the detector.

### 6.3.4 Comparison of nascent pseudospin distributions to tightbinding theory

In Fig. 6.7 we compare the observed photoelectron distribution recorded at 45  $\mu$ J/cm<sup>2</sup> excitation fluence to a simple model

$$I_{t0}(\mathbf{k}_{\parallel}) \propto \int_{1.05 \text{ eV}}^{1.2 \text{ eV}} d\varepsilon \left[ \delta(\varepsilon - \mathcal{E}_{\text{TB}}(\mathbf{k}_{\parallel})) \times |\mathbf{M}_{\text{pump}}^{c,v}(\mathbf{k}_{\parallel})|^2 \times |\mathbf{M}_{\text{probe}}^{c}(\mathbf{k}_{\parallel}, \mathbf{k}_z)|^2 \right] * h(\mathbf{k}_{\parallel}) , \qquad (6.1)$$

where  $\mathcal{E}_{\text{TB}}(\mathbf{k}_{\parallel})$  is the band dispersion,  $\mathbf{M}_{\text{pump}}^{c,v}(\mathbf{k}_{\parallel})$  is the optical matrix element between the valence band (v) and conduction band (c), and  $\mathbf{M}_{\text{probe}}^{c}(\mathbf{k}_{\parallel}, \mathbf{k}_{z})$  is the probe matrix element between the conduction band states and plane wave final states with wave vector  $\mathbf{k} = \mathbf{k}_{\parallel} + \mathbf{k}_{z}$  determined by a relation  $\hbar^{2}|\mathbf{k}|^{2}/2m_{e} = h\nu_{\text{XUV}} - W - \varepsilon$ , with  $W \approx 5$  eV the work function and  $h\nu_{\text{XUV}} = 30$  eV. Both matrix elements are derived from tight-binding theory [1, 78]. More simulation details can be found in Chapter 5. The function  $h(\mathbf{k})$  used for convolution is a 2D Gaussian of 0.11 Å<sup>-1</sup> FWHM, determined from the size of our observed Dirac point in the momentum space images as shown in Fig. 5.5. This Gaussian width reflects the momentum resolution of our measurements, and also effectively captures the energy resolution. The simulated distributions for *y*-polarized and *x*-polarized light are shown in Fig.6.7b and 6.7d respectively, for the region labeled  $K^{2}$  in Fig. 6.6, alongside zoomed-in images of the momentum-space photoelectron distributions from the experiment. In Fig. 6.7e and 6.7f we compare theory and experiment quantitatively by plotting the intensity vs. angle around K. Remarkable agreement is seen with only a single overall scaling parameter applied to the theoretical curves to match with the experiment, indicating that these electrons have undergone minimal scattering processes that alter their pseudospin polarization. Similar results are observed for K3 as shown in Fig. 5.7f and g.



Figure 6.7: Comparison to tight-binding (TB) theory for K2. a) and c) K2 Momentum distribution spectra for electrons from 1.05 to 1.21 eV above the Dirac point for  $\Delta t = 0$  for y- and x-polarized excitation, respectively. b) and d) Photoemission momentum maps predicted by the TB model according to Eq. 6.1. Inset in panel d is Eq. 6.1 without the pump matrix element illustrating the so-called "dark corridor" and how the signals would look in the absence of pseudospin polarization. Comparison of angle-resolved intensities between the TB model and the experiment for e) y-polarization and f) x-polarization. The pump polarization direction is indicated by the white dotted lines in the top panels. The assigned pump nodes are denoted by the thin magenta lines in the top panels and by magenta dotted lines in the bottom panels.

Theory/experiment comparisons for K1, K3, and K4 are also presented in Fig. 6.8. For the initial momentum distributions across the full Brillouin zone, see Fig. 5.7. In Fig. 6.8 worse agreement with the simple tight-binding model is observed, mainly because the "dark corridor" due to the probe matrix element is not as prominent in the experiment as it is in theory. Similar behavior of the missing dark corridor for K1 and K4 is also observed in photoemission signals from the valence band in Fig. 5.6, indicating that our model based on tight-binding wavefunctions for graphene and a single-plane wave final state does not work as well for these valleys when the photoelectron final-state momenta are further away from the light polarization vector. Subtleties of modeling the dark corridor have been previously discussed by Gierz et al. [79].



Figure 6.8: Comparison to tight-binding (TB) theory for K1, K3, and K4. a) - d) K1. e) - h) K3. i) - l)K4. Polarization directions are indicated by the white dashed lines. Experimental data is in panels a, c, e, g, i, and k and theory is in panels b, d, f, h, i, and l.

#### 6.3.5 Pseudospin relaxation

To investigate the dynamics of the momentum anisotropy we performed measurements with pump polarization alternating between x and y directions. The detailed data analysis can be found in Chapter 7.7. Fig. 6.9b shows the photoelectron signals vs. pump-probe delay, recorded in selected regions of interest (ROI) oriented 90 degrees to the nodes created by y-polarized pump pulses. An example ROI for K2 is shown in Fig. 6.9a. ROI transient signals with x-polarized and y-polarized pump pulses are labelled  $N_x$  and  $N_y$  respectively. Figure 6.9c shows their difference  $\Delta N = N_y - N_x$ . Using the same ROI while alternating the excitation polarization between x and y each pump/probe scan ensures that both datasets share the same probe matrix element and also any systematics due to detector response inhomogeneity, as shown in Fig. 7.10, enabling careful comparison of the intensities within the ROI. The ROI signals are integrated over all energies of the non-thermal distribution, i.e. 0.8 eV and above based on Fig. 6.5, and the shaded gray Gaussian is the temporal IRF. As seen in Fig. 6.9b and 6.9c, both the excited population  $(N_x \text{ or } N_y)$  and the anisotropy  $\Delta N$  closely follow the 200 fs instrument response, indicating very fast relaxation.

Although we cannot recover anisotropy relaxation times from the pump/probe traces, significant information about the dynamics comes from analyzing the energy dependence of the anisotropy. Since electrons are initially promoted to energy 1.2 eV above the Dirac point by the pump pulse, electrons observed away from this energy get there via either e-e or e-ph scattering. Fig. 6.9d shows the energy dependence of the normalized anisotropy  $A \equiv (N_y - N_x)/(N_x + N_y)$  at  $\Delta t = 0$ 

for different excitation fluences. The maximum anisotropy is always observed at the initial excitation energy corresponding to the gray energy bin of Fig. 6.9d, and reduced anistoropy is observed at all other energies populated by scattering. The energy binning of 160 meV is chosen to correspond to the lowest optical phonon energy in graphene [40, 198] such that the points in Fig. 6.9 are spaced by approximately one optical phonon energy. With smaller binning the overall shape of the curve remains the same as shown in Fig. 7.12, but the statistical error is larger due to the reduced electron counts in each bin. As predicted by theory, at low fluence where e-ph coupling is the main relaxation mechanism, relaxation of the pseudospin polarization via e-ph interactions is very efficient [161]. The low fluence data in Fig. 6.9d show that the observed momentum anisotropy of the electrons approximately halves for each optical phonon emitted.

In contrast, e-e scattering is expected to better preserve the momentum anisotropy due to pseudospin dependence of the e-e interaction  $V \propto 1 + e^{i(\phi_f - \phi_i)}$ , which favors collinear scattering  $\phi_f = \phi_i$  [1, 161]. At higher fluences, where e-e scattering dominates, we do observe that the anisotropy of relaxed electrons is comparable to what we observe at 1.2 eV, however we also observe that the anisotropy is overall reduced with increasing fluence as shown in Fig. 6.9c, indicating significant non-collinear scattering [160, 187, 191]. The same degree of anisotropy is observed for electrons at energies above 1.2 eV, which appear with significant population for our two higher fluences. These electrons are expected to be upscattered only via e-e scattering since the initial optical phonon population at room temperature is small [160].



**Figure 6.9:** Pseudospin Relaxation. a) ROI illustration for K2. Data are recorded with y-polarized (left) and x-polarized (right) pump pulse. Data from similar ROIs in all the valleys are combined to produce the transient signals  $N_y$  and  $N_x$  integrated over all energies > 0.8 eV. b  $N_y$  (blue) and  $N_x$  (red) vs. pump-probe delay. c) The difference  $\Delta N = N_y - N_x$  (black) and the IRF (shaded gray). Both the populations and the anisotropy track the IRF, indicating relaxation much faster than the 200fs IRF. d Normalized anisotropy A vs. energy for different fluences. At higher fluences anisotropy is overall reduced but persists through more scattering events. More details in text.

# **Chapter 7 Graphene Data Calibration**

As important as technical optimizations are, data analysis is also an essential task for the instrumentation of time-resolved APRES. This becomes increasingly important as most high-performance time-resolved APRES systems have now integrated time of flight momentum microscopy (ToF-MM) for photoelectron detection to mitigate data-rate problems. With the provision of simultaneous detection of the full ( $k_x$ ,  $k_y$ , E) photoelectron distribution with  $2\pi$  collection efficiency, ToF-MM combined with a high repetition rate HHG source can record time-resolved APRES measurements at multiple megabytes per second. This capability creates opportunites to explore other experimental parameters such as a range of pump fluence, pump polarization, pump/probe photon energies, or spin polarizations, which is often needed to extract meaningful physics. However, the resulting data at the end of measurements are an enormously large volume of multidimensional datasets, posing an immediate challenge for data processing.

When working with such large data, a challenge usually arises from navigating large, multidimensional space via a series of systematic procedures. Desired outcomes must be ultimately reduced to manageable 1D/2D arrays for practical comparison. By doing so, systematic errors can possibly occur and a critical task is, therefore, to keep the data consistency by applying the same systematic procedures. This way the outcomes are unbiased and fair comparisons can be made between different experimental parameters. This being our goal, we check our systematics throughout the work and validate our analysis procedures as best we can. This chapter provides the details of important systematic checks for graphene data reported in Chapter 6 along with data analysis procedures. For all of the data presented in this work, neither symmetrization nor noise-filtering have been applied, only normalization, shear correction, and background subtraction have been applied.

# 7.1 Momentum and energy calibration

Raw ARPES data collected by ToF-MM are 3D-array boxels, N(x, y, E) where x and y are given in pixels and E in time of flight. To completely access the band structure  $\mathcal{E}(k_x, k_y, E)$  of a material, momentum and energy coordinates must be

calibrated at the plane of the electron detector. A common procedure for energy calibration in electron microscopes is to correlate the change of sample potential with the shift of an electron spectrum [199]. Another option is to simply use the known distance between two peaks, i.e spin-orbit splitting, if present. Monolayer graphene we study here does not display such spectral features and we determine the scaling of energy by scanning sample voltage in a controlled manner. We perform a control experiment on the same graphene sample used for the tr-ARPES measurements using the identical microscope setup. While scanning sample voltage across a range of  $\approx 2.5$  V (large enough to cover the whole energy axis), we record the shift of an energy point, such as near the onset of the Fermi edge, in the observed electron spectrum. We usually choose a tracking point sufficiently far from our high-pass filter (HPF) cut-off so that it remains uncut by the HPF throughout the measurement. We then fit the applied sample voltages against the corresponding ToF slices to get a scaling factor in eV per ToF slice.

The momentum axes can be calibrated based on the Brillouin zone size of a material. For graphene the first Brillouin zone is a hexagon, the sides of which are all equal to  $4\pi/(3a) = 1.7028$  Å<sup>-1</sup> with the lattice constant a = 2.46 Å (see Fig. 5.1). To convert x and y coordinates of raw data to Å<sup>-1</sup>, a momentum distribution at the Fermi energy is used to obtain an average length of all hexagon sides in pixels.

# 7.2 Data normalization



Figure 7.1: Drift of total electron counts during a typical tr-ARPES measurement.

Fig. 7.1 shows the drift of total electron counts during a typical time-resolved APRES measurement. In general, the electron signal can fluctuate in time due to systematic drifts such as a change in the XUV beam pointing to a  $\mu$ m-scale sample, a change in the XUV harmonic flux due to a fluctuation of driver laser power or a HHG gas medium, or other perturbation. In our case, where the XUV beam is  $24 \times 16 \ \mu\text{m}^2$  FWHM, the fluctuation is mainly due to the difficulty in pointing the small XUV beam to a 10- $\mu$ m scale graphene sample. To correct such drift, each raw data cube at a given pump-probe delay t,  $N_t(k_x, k_y, E)$ , is normalized by the total electron count in that delay so that all data cubes have the same valence band

signal:

$$S_t = \frac{N_t(k_x, k_y, E)}{\int \int \int N_t(k_x, k_y, E) dE dk_x dk_y}$$
(7.1)

This normalization scheme is expected to correct any systematic drift since the fluctuation is, in principle, captured in the drift of the total counts.

## 7.3 Correction of image shear

Fig. 7.2 describes the standard procedure for correcting image shear in our ARPES data. In panel a, the energy-momentum dispersion at K1 valley is shown for a cut normal to the  $\Gamma K$ -direction together with momentum distribution curves at different energies. In the figure two  $\pi$ -bands disperse asymmetrically downward in energy, and the Dirac point  $(E - E_F = 0 \text{ eV})$  is not aligned with the mid-points (red dots on MDC) between two bands. In an ideal case, the Dirac point must go through the center of a Dirac cone at all energies. To correct such distortion in our time-resolved ARPES data, a simple affine transformation, called an image translation, is employed with a bilinear interpolation. The translation operation shifts each point (x, y) of the image given at a  $z_k$  energy slice,  $S_{z_k}(x, y)$ , by a translation vector  $T_{z_k} = [T_x T_y]_{z_k}$ . To determine the x- and y-components of the translation vector, the center coordinates  $(x_c, y_c)_{z_k}$  of the images are fitted with a line in x and y separately to get the slopes dx/dz and dy/dz. The respective vector components are  $T_{x,z_k} = dx/dz(z_k - z_0)$  and  $T_{y,z_k} = dy/dz(z_k - z_0)$  where  $E_F$  slice is used as a reference pivot point  $z_0$ . The same translation operators are applied to all other delays for a given Dirac cone. This procedure is done for all six Dirac cones independently.

It is optimal to determine the slopes from as large an energy range as possible either using the conduction or valence band since it yields a longer leverage arm. A searching algorithm for finding the center points becomes much easier to automate if one uses strong valence band images, but this is not always the case when we use an aggressive high pass-filter (HPF) setup to mitigate the detector saturation. In some cases, we only pass several hundred meV below  $E_F$ , not leaving enough energy range in the valence band for the determination of the slopes. We therefore use two different procedures to find the center points depending on the HPF setup. For aggressive HPF setups, the procedure is based on the conduction band as demonstrated in Fig. 7.3. The measurements are usually performed with pump polarization alternating between x and y directions to ensure that for a given ROI each pump-probe scan shares the same probe matrix element and detector background (see Section 7.7). Since time-resolved conduction-band signals are several orders of magnitude smaller than valence-band signals, we combine x- and y-excitation datasets near  $\Delta t \approx 0$  to enhance the photoemission intensity. For the energy range near the Dirac point, such as  $e^3$ , the images are circular disks and their center points are determined from their centroid positions. For the higher energy range, labeled e1 and e2, where trigonal image distortion is observed, we manually find the center points by extrapolating two optical nodes (dotted lines) to the center of the images where the Dirac point is expected to be. According to the pseudospin optical selection rule [1], the nodes are generated parallel to the field directions of x- and y-excitations traversing the Dirac point (see Figs. 5.7, 6.7, and 6.8).

For the HPF setup passing > 1 eV below  $E_F$  or for low fluence data that usually have poorer statistics in the conduction band, we use the valence-band images to find the center points as shown in Fig. 7.2. Near the vicinity of the Dirac point (E - E) $E_F \lesssim 0.4 \text{ eV}$ ), the Dirac cones are still circular, but usually collapsed into blurred disks due to our energy and momentum resolutions (see Section 7.4). Also, the dark corridors [79], partial suppression of angular intensity due to the probe matrix element, are not well resolved (the details of dark corridors can be found in Chapter 5.2.3 and 5.3.1). We thus calculate the centroid positions of those disks for E - E $E_F \lesssim 0.4$  eV. Beyond  $E - E_F > 0.4$  eV, we make horizontal and vertical lineouts through the void region of the images near the middle. The center coordinates are determined from equidistant points, indicated by red solid lines in panel b, between two peaks in the lineouts. In the presence of the dark corridor, the lineouts still show appreciable peaks because their intensities are never completely suppressed to zero in our setup as shown in Fig. 5.6. We check the accuracy of this procedure by applying it to the shear absent, tight-binding simulated data according to Eq. 5.40. The center point found by this lineout procedure only differs by  $\approx 0.028$  Å<sup>-1</sup> (1 pixel in this data) relative to the Dirac point.



**Figure 7.2: Image shear correction based on the ground states. a)** The Brillouin zone and energy-momentum dispersion along a cut (blue line) through K1 valley parallel to the  $\Gamma K$ -direction. Momentum distribution curves (white curves) at selective energies are plotted together with the mid-points (red dots) between two peaks, illustrating that a Dirac point shifts with energy due to image shear. b) Demonstration of finding a Dirac point by a lineout procedure. A theoretical Dirac point, which must go through the center of momentum-space images at all energies (here near -1.2 eV shown), is determined from the mid-points (red lines) between two peaks in horizontal and vertical lineouts (white curves) of the images. c) Checking the accuracy of the lineout procedure on the shear absent data obtained by a tight binding model according to Eq. 5.40. The center of the simulated image determined by the same lineout procedure in panel b is where the two mid-points intersect, deviating from a true Dirac point (magenta) of the simulated data by  $\approx 0.027$  Å<sup>-1</sup>, corresponding to 1 pixel in this data.



Figure 7.3: Image shear correction based on the excited states. a) Extraction of Dirac cone centers  $(x_i, y_i)$  by extrapolating two optical nodes, which are expected to pass through a Dirac point according to an optical selection rule [1]. b) Denotation of  $K^2$  valley processed. c) Determination of slopes in x and y by line fit. The x-and y-coordinates of the center points are fitted with a line to obtain slopes dx/de and dy/de which are used to determine the translation vectors for image translation in order to align the center points with energy.

## **7.4** $E_F$ calibration

In neutral graphene, the position of the Fermi level  $(E_F)$  coincides with a Dirac point  $(E_D)$ , where the two vertices of the conduction and valence band meet with vanishing density of states. However, finite energy and momentum resolutions in our experiments typically smear  $E_D$  in momentum space, showing it as a blurred disk. This usually makes it difficult to determine where the two bands exactly intersect. One way of determining  $E_D$  is to look for an energy corresponding to zero density of states on electron distribution curves (EDCs). Since pump excitation  $\hbar \nu_{pump}$  takes electrons from energy  $-\hbar \nu_{pump}/2$  to  $+\hbar \nu_{pump}/2$ , electron depletion together with electron population shapes EDCs symmetrically about  $E_D$  and at different pump-probe delays EDCs cross at this mid-point. In our case, we do not observe electron depletion on EDCs making it difficult to determine  $E_D$  this way. Another way of determining  $E_D$  is by fitting EDCs with a Fermi-Dirac function but in some cases our HPF cuts the valence band substantially, reducing the accuracy of actual  $E_D$  determination. In this work we find an energy slice corresponding to the smallest waist from MDCs and designate  $E_D$  (equivalently  $E_F$ ) at that slice.

Fig. 7.4 illustrates the overall procedure of finding  $E_D$ . The  $\pi$ -band dispersion of K1 valley along the  $\Gamma K$ -direction (cut shown in panel a) is shown in panel b and MDCs are shown in panel c. We fit a range of MDCs plotted just near  $E_D$  with a single Gaussian function (energy window shown in the magenta line in panel b). Resultant Gaussian width  $\sigma_{MDC}$  vs. energy is plotted in panel d and the minimum in energy is called  $E_D$  here.

As a check,  $E_D$  is also determined from a crossing point of two downward dispersing bands as shown in panel c. MDCs are selected from a larger energy
window, indicated by the white line in panel b, to ensure that two bands are clearly separated and fitted with a double Gaussian function. Two band maxima for the left and right branches are fitted with a line separately. Where the two lines intersect is 45 meV higher than  $E_D$  determined by the skinniest MDC linewidth described in panel d. We calibrate  $E_F$  by the skinniest MDC linewidth in this work and use this deviation as an uncertainity in the position of  $E_D$ . This procedure is inevitable in some cases where we have to implement an aggressive high-pass filter setup to suppress the valence band signals for less detector saturation. This only leaves less than 1 eV below the  $E_F$ , in which case two branches do not clearly disperse downward in energy.

Fig. 7.5 compares the positions of  $E_F$  for different Dirac cones estimated from the skinniest MDC linewidth. For a better visualization, each curve is offset by a constant. The positions of  $E_F$  in these Dirac cones coincide with each other within the 1- $\sigma$  errorbar of the fit. The minimum value in  $\sigma_{MDC}$  at  $E_F$  is  $\approx 0.04$ Å<sup>-1</sup>, reflecting the overall resolution of our measurement, contributed from both momentum and energy resolutions.



Figure 7.4: Comparison of two calibration methods for the Fermi level  $(E_F)$ in graphene experiments. a) Demonstration of the momentum cut and the  $k_x$ integration range for b) the ARPES spectrum of K1 valley. c) Extraction of the band crossing point at  $E_F$  by fitting the two band positions in the MDCs. The MDCs in gray diamonds are horizontal lineouts from the energy window indicated by the white line in b). The fits by a double-Gaussian function are indicated by solid lines. d)  $E_F$  calibration by the skinniest MDC linewidth. A small range of MDCs near  $E_F$  (the magenta window in b) are fitted with a single Gaussian to determine the linewidth  $\sigma_{MDC}$ . The values of  $\sigma_{MDC}$  are fitted with a polynomial to find a minimum in energy to determine  $E_F$ . The shaded area in light purple is  $1-\sigma$ errorbar associated with the fit.



Figure 7.5: Checking  $E_F$  of other Dirac cones. The positions of  $E_F$  are estimated from the calibration by the skinniest MDC linewidth described in Fig. 7.4. Each curve is offset by a constant, 0.015 Å<sup>-1</sup> × (valley index - 1), for a better visualization.

### 7.5 Surface photovoltage shift

When light illuminates on a semiconductor, electrons and holes move according to the induced-field gradient in the space charge region on the surface. This changes the surface potential, which tends to flatten the intrinsic band bending of a semiconductor. Such light-induced potential difference is called surface photovoltage (SPV) [88]. SPV is found to increase logarithmically with laser intensity [89, 90]. For pump-probe experiments, where a probe pulse is delayed with respect to a pump pulse, SPV changes with pump-probe delay, complicating the dynamics of interest under consideration. If photoemission is employed as a probe, as in time-resolved ARPES, this transient effect adds another level of complexity to measurements. The added potential is thought as bias in the material's workfunction (a difference between the vacuum and Fermi level), which shifts the photoelectron spectrum as a function of time [91–95]. This SPV-related shift may be difficult to separate from a shift due to pump-induced space charges via multi-photon photoionization process [48, 49].

To check SPV shift in our data, the position of  $E_F$ , calibrated by the skinniest MDC linewidth in Section 7.4, is plotted as a function of pump-probe delays in Fig. 7.6. In Fig. 7.6, the SPV effect is most pronounced near  $\Delta t \approx 0$  fs and becomes less noticeable for longer delays. The maximum shift of  $\approx +40$  meV (2.5 ToF slices) is estimated between  $\pm$  500 and 0 fs. The lesser shift of  $\approx +20$  meV (1 ToF slice) is observed beyond 600 fs. In our case, where we use a 2.4-eV pump pulse, SPV is due to the Si substrate underneath the graphene sample, not due to hBN buffer layer (bandgap of  $\approx 6$  eV).



Figure 7.6: Surface photovoltage shift in the Fermi energy of neutral graphene measured as a function of pump-probe delay. The Fermi energy  $(E_F)$  is estimated at all time delays using the calibration method described in Fig. 7.4d to measure the transient shift. For neutral graphene stacked on a buffer layer of hBN on a Si substrate (see Chapter 6.2.2), the  $E_F$  shift is from excitation in the Si substrate underneath graphene. The position of  $E_F$  in the y-axis is referenced to the last delay point.

# 7.6 Extraction of instrument response function and time zero

Fig. 7.7 demonstrates the extraction of the instrument response function and time zero from graphene experiments. Our overall time-resolved ARPES scheme is summarized in panel a, where visible pump pulses ( $h\nu = 2.4 \text{ eV}$ ) with x- or y-polarization excite electrons to 1.2 eV above the Dirac point and time-delayed XUV (20 - 30 eV) probe pulses with *p*-polarization eject them to the continuum. Panel c shows the electron distribution for all electrons above the Dirac point vs. a pump-probe delay, recorded from combining ROI integrated signals from K1 - K4valleys (ROIs shown in panel b). The transient signal integrated for all electrons above the Dirac point is shown in panel d. We determine the instrument response function (IRF = cross-correlation between pump and probe) and time zero by fitting this transient signal with a bi-exponential decay convolved with a Gaussian IRF. In the fit, time zero and the Gaussian width are set as free fit parameters. The biexponential decay is motivated by previous work on doped graphene [37, 192] and this method of extracting the IRF is analogous to other efforts that have fit the fast rising edge of the signals with an error function [191]. The fit gives a Gaussian width of 196 fs at FWHM.



Figure 7.7: Extraction of instrument response function (IRF) and time zero (t0) from graphene experiments. a) Experimental scheme. b) ROI illustration for momentum integration. An ROI, shown in the yellow dotted box for K1, encloses the entire momentum distribution of excited electrons in the conduction band. Similar ROIs are applied to K2 to K4. c) Time dependence of momentum-integrated electron distribution produced from combining K1 - K4, represented as a false color map. d) Transient signal integrated all above the Dirac point and its fit. The energy integration range is indicated by the white line in panel c and the fit is a convolution of a bi-exponential decay and Gaussian IRF (purple shaded area).

We further verify this procedure for determining the IRF and time zero by repeating pump-probe measurements on polycrystalline gold (Au). We deposit a thin Au film in close proximity to a graphene sample, following a similar procedure for Gr2 in Chapter 6.2.3). Both samples, supported on the same Si substrate, sit nearly on the equivalent sample plane such that any path length difference does not need to be accounted for. Fig. 7.8 compares the IRF and time zeros from these two measurements. For graphene shown in the right panels, time zero is determined by fitting the transient signal of all excited states, similar to Fig. 7.7. For Au in the left panels, a Gaussian response is observed for the highest energy electrons, the lifetime of which is typically short on the order of 10 fs [200,201]. Excellent agreement is found between the two methods, validating our method of extracting the two temporal parameters by fitting graphene's total transient signal. Nevertheless, ths 230-fs IRF does not agree with a196-fs IRF reported in Fig. 7.7. Note that these two measurements are conducted one and a half years apart, during which time the laser pulse duration may have changed due to changes in the Yb:fiber oscillator or nonlinear broadening after the Jin amp (see Chapter 3).



Figure 7.8: Checking the extraction of temporal parameters on polycrystalline gold (Au). Complimentary pump-probe experiments are performed on a graphene flake and a thin Au film ( $\approx 10 - 20$  nm) deposited close to graphene on the same Si substrate. Time-dependent photoelectron distributions represented as a false colormap for **a**) Au and **b**) graphene. Extraction of time zero (t0) and IRF from pumpprobe measurments for **c**) Au and **d**) graphene. For graphene, temporal parameters are determined by fitting the total integrated signal of all excited electrons above the Dirac point with a model described in Fig. 7.7. For Au, where high-energy electrons are expected to have a short lifetime of  $\approx 10$  fs, the transient signal is fitted with a single Gaussian response function. The energy integration windows are indicated by the white arrows in panels a and b.

We also check the drift of time zero in our measurement as shown in Fig. 7.9. This measurement contains a total of 77 scans collected over the integration time of  $\approx 3$  hours. The data is subdivided into blocks of 10 scans and time-zero values from 8 blocks are determined by a similar procedure in Fig. 7.7. We observe the drift of 20 fs at most, much less than our 200-fs time resolution. The main goal of this work is to study nonthermal distributions of pseudospin-polarized electrons (more details found in Chapter 6), following optical excitation. While the dynamics of this momentum anisotropy is typically on the order of  $\approx 50 - 100$  fs [1,161,186], we cannot recover this fast relaxation time with our 200-fs IRF and instead put an emphasis on the energy dependence of momentum anisotropy near time zero (see Chapter 6.3.5). For this purpose, a 20-fs drift may not be an issue.



Figure 7.9: Checking time-zero drift during a tr-ARPES measurement. A total of 77 scans is divided into subsets of 10 scans and the values of time zero  $(t_0)$  are extracted by the similar procedure described in Fig. 7.7. The errorbar is  $1-\sigma$  uncertainty of the fit. The zero in the y-axis refers to the global  $t_0$  from a combined 77 scans.

## 7.7 Metrics for extracting pseudospin anisotropy: 2box vs. 1-box analysis

This section details two metrics for measuring momentum-space pseudospin anisotropy. This is the main subject in Chapter 6, where we have initially observed strong momentum-space pseudospin polarization of electrons around the K points excited by x- and y-polarized pump pulses (see Fig.6.6). The nodes are clearly visible along the pump field directions as expected from the optical pseudospin selection rules [1]. The goal is to study how these initial pseudospin-polarized electrons relax both in time and energy across a range of excitation fluence based on a metric that measures the magnitude of the anisotropy. However, it may be difficult to separate this pure optical matrix element effect from the probe matrix element effect during a photoemission measurement since the probe matrix element also plays an important role in the angular distribution [78, 79] (see Chapter 5.2.3 for more details). Thus, a successful metric must be able to subtract this momentum anisotropy induced by k-dependent probe matrix element in addition to accounting for any residual anisotropy from detector inhomogeneity. In the following, we discuss two paradigms of measuring the pseudospin anisotropy based on integration in different regions of interest.

#### 7.7.1 2-box analysis

Fig. 7.10 describes the extraction of momentum anisotropy by 2-box analysis. Example ROIs are shown in the left of panel a for K2 valley for energy 1.05 - 1.21 eV near  $\Delta t = 0$  fs excited by y-polarized pump pulses. For comparison, the unpumped momentum distribution at  $\Delta t = -1$  ps (-1 ps prior to pump excitation) is shown in the right of panel a with similar ROIs. For 2-box analysis, two selected regions of interest (ROI) are oriented perpendicular to each other around the Dirac point, one enclosing a pure optical node (not dark corridor) and the other oriented 90° to the node, usually where the signal is intense. In panel a, these two components are labeled v and h, and respective net integrated signals over these ROIs are labeled  $N_h^{\text{sub}}$  and  $N_v^{\text{sub}}$  with the following definition,

$$N_{\text{ROI}}^{\text{sub}}(e,t) = \int_{\text{ROI}} dk_{\parallel} S_t(k_{\parallel},e) - S_{t_{bg}}(k_{\parallel},e)$$
(7.2)

where ROI = h or v, and  $t_{bg}$  refers to a pump-probe delay before the pump arrival, taken as  $\Delta t = -1$  ps. Here,  $N_{\text{ROI}}^{\text{sub}}(e, t)$  are transient signals as a function of energy e and pump-probe delay t.

We now define the background-subtracted momentum anisotropy as

$$A(e,t) = N_h^{\rm sub}(e,t) - N_v^{\rm sub}(e,t).$$
(7.3)

We also define the normalized anisotropy for a particular pump-probe delay  $t_i$  as

$$A(E;t_j) = \pm \frac{N_h^{\text{sub}}(E;t_j) - N_v^{\text{sub}}(E;t_j)}{N_h^{\text{sub}}(E;t_j) + N_v^{\text{sub}}(E;t_j)}$$
(7.4)

where E represents the binned energy axis and the  $\pm$  sign ensures A > 0 with + denoting x- and - denoting y-polarization. Note that  $A(E; t_j)$  is normalized by the sum to account for a fluctuation of the counts due to the source drift. Eq. 7.4 represents the energy spectrum of the anisotropy for an arbitrary delay  $t_j$ , bounded between  $0 \le A(E; t_j) \le 1$ , where the maximum of 1 describes highly anisotropic pseudospin alignment and the minimum of 0 describes complete isotropization.

Fig. 7.10d shows the energy dependence of momentum anisotropy near  $\Delta t = 0$  with the energy binning of 160 meV. The maximum anisotropy is observed at the initial excitation  $h\nu_{pump}/2$  indicated by the gray shaded region in Fig. 7.10d and it washes out by scattering into other energies. For comparison, the momentum anisotropy at -1 ps is also plotted in the magenta curve together with the anisotropy of the probe matrix element in the green curve, following the similar analysis in Eq. 7.4. Even though pump and probe pulses don't overlap at -1 ps, some residual aniostropy is observed in the background due to inhomogeneous detection of electrons emitted from outside the graphene flake or the detector inhomogeneity. Also, k-dependent probe matrix element contributes to the anisotropy, which may not be easily separated from the pure optical effect in 2-box analysis. Because of these flaws, we do not proceed with 2-box analysis to study momentum anisotropy.



Figure 7.10: Extraction of pseudospin anisotropy via 2-box anaysis. a) Left: illustration of example ROIs on the momentum-space image of K2 valley near  $\Delta t = 0$  measured with a 2.4-eV pump pulse polarized along y-excitation. Right: same as the left panel except  $\Delta t = -1$  ps, showing that inhomogeneous detector response can produce a residual anisotropy in background. b) Valleys processed for this figure. K2 and K3 are combined to produce anisotropy A in panel d. c) Tightbinding simulated image for K2 valley according to Eq. 5.40. Even without the pump matrix element, some anisotropy is still expected from the angle dependence of the probe matrix element. d) The energy spectrum of normalized, backgroundsubtracted pseudospin anisotropy A according to Eq. 7.4.  $\Delta t = 0$  is indicated by navy,  $\Delta t = -1$  ps by magenta, and the probe matrix element by green.

#### 7.7.2 1-box analysis

Fig. 7.11 describes the extraction of momentum anisotropy by 1-box analysis. To carefully extract optically induced momentum anisotropy, transient signals are recorded in the same ROI oriented either parallel or perpendicular to a node while pump polarization is alternated between x- and y-directions for each pump-probe delay. Example ROIs for K2 is shown in panel a for the energy 1.05 - 1.21 eV near  $\Delta t = 0$ , measured by y-polarization in the left and x-polarization in the right. Corresponding net ROI transient signals are labeled  $N_x^{sub}$  and  $N_y^{sub}$ , each following the definition from Eq. 7.2 with ROI = x or y indicating pump polarization instead.

In 1-box analysis, momentum anisotropy is defined as

$$A(e,t) = N_x^{\text{sub}}(e,t) - N_y^{\text{sub}}(e,t).$$
(7.5)

With this definition, it is possible to track the dynamics of the anisotropy using integration for a selected region of interest in energy (see Fig. 6.9b). Normalized

anisotropy for an arbitrary pump-probe delay  $t_i$  is defined as

$$A(E;t_j) = \pm \frac{N_x^{sub}(E;t_j) - N_y^{sub}(E;t_j)}{N_x^{sub}(E;t_j) + N_y^{sub}(E;t_j)}.$$
(7.6)

where ROI signals are typically binned by E = 160 meV, corresponding to the optical phonon energy in graphene [40, 198].

Fig. 7.11c shows the energy dependence of the anisotropy near  $\Delta t = 0$  binned by 160 meV. Similar to the results obtained by 2-box analysis, the anisotropy is maximum at the initial excitation, indicated by the gray shaded region, and is reduced at all other energies by scattering processes. This metric completely cancels out the anisotropy from the probe matrix element regardless of the pump excitation. As shown in the magenta dotted line in Fig. 7.11c, it also effectively subtracts off the residual anisotropy persistant in the background for 2-box analysis.

We also measured the anisotropy in Eq, 7.6 with smaller energy bins of 80 meV as shown in Fig. 7.12. The smaller binning does not change the overall shape of the curve. The statistical errors in those smaller bins are larger due to lower electron counts.



Figure 7.11: Extraction of pseudospin anisotropy via 1-box anaysis. Example ROI illustrated on momentum distribution of K2 valley a) near  $\Delta t = 0$  and b) at  $\Delta t = -1$  ps. Data are measured with y-polarized (left panels) and x-polarized (right panels) pump pulses. c) Normalized anisotropy near  $\Delta t = 0$  processed from K2 and K3 valleys combined. This 1-box analysis effectively cancels out residual anisotropy in background.



Figure 7.12: Anisotropy measured with smaller energy bin. a) Anisotropy parameter (A) vs. energy with 80 meV bins. a) Anisotropy parameter (A) vs. energy with 160 meV bins.

#### 7.7.3 Poisson error bars

The error bars on the momentum anisotropy parameters, shown in Fig. 7.10d, Fig. 7.11c, and Fig. 7.12, are based on Poisson statistics. The validation of the Poisson error bars in our measurements will follow in the next section. For 2-box analysis, for example, the background-subtracted normalized anisotropy A in Eq.7.4 at  $\Delta t = 0$  is explicitly written as

$$A(E; \Delta t = 0) = \pm \frac{(N_h - N_h^0) - (N_v - N_v^0)}{(N_h - N_h^0) + (N_v - N_v^0)}$$
(7.7)

where  $N_h$  and  $N_v$  are the photoelectron signals before background subtraction recorded in the horizontal (*h*) and vertical (*v*) ROIs at  $\Delta t = 0$ , and  $N_h^0$  and  $N_v^0$ are the signals at  $\Delta t = -1$  ps when pump and probe pulses no longer overlap (see Fig. 7.10 for ROI demonstration). Since the quantity of interest A is calculated from four variables  $N_h$ ,  $N_h^0$ ,  $N_v$ , and  $N_v^0$ , one can propagate the error via Eq. 7.7,

$$\left(\delta A\right)^{2} = \left(\frac{\partial A}{\partial N_{h}}\right)^{2} \left(\delta N_{h}\right)^{2} + \left(\frac{\partial A}{\partial N_{h}^{0}}\right)^{2} \left(\delta N_{h}^{0}\right)^{2} + \left(\frac{\partial A}{\partial N_{v}}\right)^{2} \left(\delta N_{v}^{0}\right)^{2} + \left(\frac{\partial A}{\partial N_{v}^{0}}\right)^{2} \left(\delta N_{v}^{0}\right)^{2}$$

$$+ \left(\frac{\partial A}{\partial N_{v}^{0}}\right)^{2} \left(\delta N_{v}^{0}\right)^{2}$$

$$(7.8)$$

$$\delta A_{,2\text{box}} = \sqrt{\left(\delta A\right)^2} \tag{7.9}$$

Here,  $\delta N_h$ ,  $\delta N_h^0$ ,  $\delta N_v$ , and  $\delta N_v^0$  are independent errors calculated based on the Poisson noise, e.g.  $\delta N_h = \sqrt{N_h}$ . A similar procedure is used to calculate error bars for 1 box-analysis.

#### 7.7.4 Error analysis

To check the validity of Poisson error bars reported on the normalized momentum anisotropy, we confirm that fluctuations in the measurements are solely due to Poisson statistics, not due to systematic drifts such as a fluctuation of laser intensity. For this task, we divide a long accumulated measurement into several subsets and check if Poisson statisites actually represent the fluctuations in these repeated measurements. Fig. 7.13a (same plot as in Fig. 7.10d) shows the anisotropy parameters at  $\Delta t = 0$  processed from a total of 77 scans. In panel b, we test the confidence of one Poisson errorbar for the energy 1.21 - 1.05 eV, where it has less statisites, by comparing the size of the error bars (blue error bars) derived from Poisson statistics to the standard deviation  $\sigma_A$  (red error bar) of the data points in 8 subdivided measurements. It is clear that most of the data points are scattered within the range of  $\sigma_A$  without a constant offset nor general trend, confirming that the fluctuations in these measurements are indeed due to the Poisson noise, not due to systematic errors.



Figure 7.13: Checking the validity of Poisson error bars for pseudospin anisotropy. a) Background-subtracted pseudospin anisotropy A from 2-box analysis presented in Fig. 7.10 and the Poisson errorbars  $\delta_{A,2box}$  according to Eq. 7.9. b) Comparison of the Poisson error bars vs. the standard deviation of 8 subdivided measurements for the energy 1.21 - 1.05 eV to check if Poisson statistics actually capture the fluctuations in the measurements. A total of 77 scans is subdivided into 8 subsets. The error bars in 8 subsets predicted by Poisson statistics in Eq. 7.9 are shown in blue and the standard deviation of 8 data points is shown in the red error bar.

## **Appendix A**

# **Upgrades to Stony-Brook Light Source**

#### A.1 Instability issues in previous 83-MHz oscillator

After a six month-lifetime, the previous 83-MHz oscillator began to underperform. Noisy error signals were frequently observed and the laser unmode-locked itself sometimes, preventing from coupling the frequency comb laser to the enhancement cavity for high harmonic generation. One quick metric to help diagnose the source of such noise can be checking the RF frequency components of the laser light. In the absence of any noise, only signal expected is at the laser repetition rate and its harmonics. Fig. A.1 a) shows the RF spectra of the seed light measured at two different times. Even when the error signal seemed relatively quiet in b), a nontrivial signal at 8 MHz was observed as shown in the blue trace in a). This 8-MHz signal was persistent even upon different mode-lock states.

When noise was drastically increased in the error signal as in Fig. A.1 c), the spectrum shown in the red trace of a) was observed. When this happened, the laser would just not mode-lock even at different operation states, which could be a sign of the degraded gain fiber. We were confident to conclude that the problem stems from the oscillator, not from the HHG cavity, so we proceeded to install a new fiber assembly with a fresh gain fiber.



**Figure A.1: Instability issues in the previous 83-MHz oscillator.** a) The RF spectrum of the oscillator light measured at two different times. The blue trace was measured when the quiet error signal was observed in b). The red trace was measured when the noisy error signal was observed in c). The black trace is background.

## A.2 Details on the oscillator fiber assembly



**Figure A.2:** Layout of the new 61-MHz Yb:fiber oscillator (top) and the length specification on the fiber assembly (bottom).

# A.3 Cavity dispersion compensation with a grating pair

The longer fiber and other components of the new 61 MHz oscillator have more dispersion compared to the previous 83-MHz version. The new EOM (LiNbO<sub>3</sub>, 45 mm, GVD =  $291.05 \text{ fs}^2/\text{mm}$ ) is 11 time longer than the previous EOM (LiTaO<sub>3</sub>, 4 mm, GVD = $224 \text{ fs}^2/\text{mm}$ ). This EOM shortens the rep-rate by 1.22 MHz in free space but introduces an additional group delay dispersion (GDD) of  $+1.22 \times 10^4$  fs<sup>2</sup> to the oscillator. Additional dispersion from the fiber length change can be caculated using Ref. [129], where the dispersion parameter D is expressed in ps/nm·km. The D value of a HI-1060 type fiber (from Corning) found from Ref. [129] is  $D \approx$ -40 ps/nm·km at 1030 nm. The group velocity dispersion  $\beta_2$  can be found from a relation  $D = -2\pi c\beta_2/\lambda^2$ . The additional GDD of  $+1.78 \times 10^4$  fs<sup>2</sup> is introduced to the laser from an extra fiber length of 80 cm. Summing both contributions, the additional net GDD is  $GDD_{extra} = +3 \times 10^4 \text{ fs}^2$ . The positive sign indicates the GDD<sub>extra</sub> of the oscillator is normal dispersion. The grating separation needs to be adjusted in such a way that the amount of GDD<sub>extra</sub> is cancelled by the anomalous dispersion of gratings. This method generally leaves the cavity close to zero GDD, but the spacing needs to be further fine tuned for true net zero GDD. A better way of achieving net-zero cavity dispersion can be by measuring its actual net GDD in situ [130] and compensating accordingly. This is described in Chapter 3.2.2.

## A.4 Details of Jin-amp components

Components	Details
Iso	Isolator, SN18037663
Pol	In-line polarizer, SN1402771
90/10	90/10 power splitter, SN9047310
Gain	nLight Liekki, Yb300-6/125-PM
Pump-diode	3SP Technologies, 1999CHP
DC	Pump-diode controller, Thorlabs, LDC200C
TC	Temperature controller, Thorlabs, TLD200C

Table A.1: Details of Jin-amp components.

## **Appendix B**

# **Optimization of Momentum Microscopy**

#### **B.1** Optimization of high pass filter performance

Fig. B.1 shows the performance of non-optimal high pass filter (HPF) configuration. In this configuration, the two grids are 1 cm apart and the second grid (HPF grid) is placed 1 cm away from the MCP. We try to optimize this configuration by applying the retarding voltage on three elements, the two grids and the MCP front. In Fig. B.1a, the two grids are set to 100 V, the same as the ToF tube voltage, and the MCP front = 3 V is used as HPF. This scheme shows the sharp cutoff of the energy momentum dispersion in the bottom right panel, but is generally unwanted mainly because running the MCP front with a lower voltage can drop electron detection efficiency. Fig. B.1 b) illustrates ToF grid acting as a high-pass filter (ToF grid = HPF grid = 3 V and ToF = 200 V). While this setup shows reasonable momentum resolution in the bottom left panel, it stretches the electron pulse substantially, overlapping with the lower energy side of the previous pulse. Thus, using the ToF grid as HPF is not ideal and it must be set to higher or equal to the ToF voltage as in Fig. B.1c. When the HPF grid is used as high-pass filter in Fig. B.1c, momentum resolution becomes worse due to microlensing issue. We therefore put the grids closer to the MCP as shown in Fig. 4.2.



Figure B.1: The performance of non-optimal high-pass filter (HPF) configuration. HPF scheme with a) the MCP front b) the ToF grid c) the HPF grid. In the bottom figures, the momentum-space images of the Dirac point in HOPG (highly oriented pyrolytic graphite) are shown in the left and energy-momentum cuts along  $K-\Gamma-K$  in the right.

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