ATOMIC AND MOLECULAR DYNAMICS IN INTENSE MID-INFRARED FIELDS

DISSERTATION

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Abstract

In the low optical frequency limit, photoionization processes in atoms and molecules irradiated with intense ultrafast laser fields can be described within the quasi-static tunneling framework. Higher order processes of the photoelectron dynamics were observed and attributed to the recollision of the tunneled electrons. Development of the quantitative rescattering theory laid a foundation for retrieving field-free differential cross section (DCS) from the distribution of rescattered photoelectrons. Due to technological reasons, the majority of strong field physics experiments were carried out at near-infrared wavelengths 0.8 µm or 1 µm. Retrieved DCS’ at these wavelengths were not very accurate since these laser frequencies are high and the systems do not strictly satisfy the quasi-static tunneling condition. Here we present the accurate retrieval of noble gas atom DCS’ from photoelectron distributions under mid-infrared laser radiation. These lower frequency fields not only result in better quasi-static tunneling initial conditions, but also higher photoelectron recollision energies, core penetrating collisions and improved spatial resolutions, suitable for molecular imaging. Bond lengths of nitrogen and oxygen molecules were extracted from the rescattered photoelectron distributions. This method is called laser-induced electron diffraction (LIED). Alternatively, utilizing the broadband nature of recolliding photoelectrons, bond length of the nitrogen molecule was extracted from a Fourier transform of the backscattered photoelectron spectrum along the laser polarization direction. This is the fixed-angle broadband laser-driven electron scattering (FABLES). Both LIED and FABLES rely on well defined recollision geometries, so molecular alignment is needed to generalize both imaging methods for more complex molecules.

Theoretical and experimental evidence shows that the Coulomb potential of the parent
ion can be safely ignored during the high-energy recollisions in LIED and FABLES. However, this is not true for the case of low-energy, small-angle recollisions. Evidence of this is the photoelectron low-energy structure (LES). Soon after the discovery of the LES, theoretical studies attributed its origin to an interplay between the Coulomb field of the parent ion and the electric field of the laser. The type of electron trajectories responsible for the LES are those leading to soft-recollisions, taking place about one and half laser cycles after tunneling ionization. So far, most LES experiments were conducted with multi-cycle pulses where the envelope of the laser electric field is practically constant. Here we present LES measurements with few-cycle laser pulses of various pulse durations. Since in this case the envelope of the laser electric field changes drastically from cycle to cycle and hence during the soft-recollision motion of the LES photoelectrons, changes in the LES peak position as a function of laser pulse duration were expected and observed. Classical trajectory Monte Carlo simulations reproduced experimental data and lead to more insight about the mechanism behind LES. Universal scaling of the LES peak position was also observed, which could be calibrated to obtain \textit{in situ} measurements of few-cycle mid-infrared laser pulses’ duration and carrier-envelope phase offset.
To my parents, my sister and Chi
VITA

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Chapter 1
INTRODUCTION

Atoms and molecules are the building blocks of our world, and their properties determine the behavior of physical, chemical and biological processes. Direct observation of their structure and dynamics calls for imaging techniques with atomic scale spatio-temporal resolution, namely picometers and femtoseconds, respectively. Traditionally, X-ray and electron diffraction have achieved great success in measuring the static structure of matter with sub-picometer resolution. Simultaneous atomic scale temporal resolution has been lacking until recent advancement in X-ray and electron techniques like the invention of free-electron lasers (FELs) [1] and ultrafast electron diffraction (UED) [2]. At the same time, an alternative imaging approach based on laser-ionized bursts of coherent electron wave packets that self-interrogate the parent molecular structure emerged from the strong field physics community, dubbed laser-induced electron diffraction (LIED), the method follows and controls the sub-cycle dynamics of photoelectrons in a femtosecond laser field, and thus it inherently possesses the desired atomic scale temporal resolution. In this chapter, I’ll give a brief summary of conventional imaging techniques like the X-ray and electron imaging followed by an introduction of the ultrafast imaging method using femtosecond mid-infrared wavelength lasers. Different conventions exist for the definition of mid-infrared wavelengths. In this dissertation “mid-infrared” wavelengths refers wavelengths of 1–5 \( \mu \text{m} \), corresponding to photon energy of 0.25–1.1 eV.

Atomic units (a.u.) [3] will be used throughout this dissertation unless specifically stated otherwise. A conversion between a.u. and the International System of Units (SI) is provided.
in Appendix A.

1.1 X-ray and electron diffraction

How nice would it be if we could simply extend the resolving power of an optical microscope to atomic level by using higher magnification objectives?! However, this is prohibited by the diffractive property of visible light. Fortunately, it was our understanding of diffraction that enabled us to capitalize it to our advantage. A target diffracts light most significantly when its size is close to the impinging wavelength of that light. To record the diffraction image of atomic and molecular structures, the required wavelength needs to be on the ångström level, i.e. X-ray wavelengths. After the discovery of X-ray in late nineteenth century, Max von Laue observed X-ray diffraction from crystals in 1912 [4] and William Lawrence Bragg proposed his simple yet powerful $n\lambda = 2d\sin(\theta)$ equation [5] to explain his own X-ray diffraction experiment with his father, William Henry Bragg. These results not only proved the wave nature of X-rays, but also marked the birth of X-ray crystallography. Nowadays imaging crystalline structures can be routinely achieved with atomic level spatial resolution using X-ray crystallography ( [6] and references therein). Despite the great successes of X-ray crystallography, it had two major limitations i) it is restricted by the requirement of growing crystals to sufficient sizes [7], ii) it lacks temporal resolution. These limitations were solved thanks to the modern invention of X-ray free-electron lasers (XFELs) [8]. The high photon flux and high spatial-temporal coherence of XFEL beam made it possible to image nanocrystals or even partially aligned gas-phase molecules [9]. More importantly, the ultra-short duration of XFEL pulses naturally yields atomic scale temporal resolution.

At the same time with the development of X-ray imaging methods, the understanding of diffraction and imaging was further generalized after Louis de Broglie’s wave-particle duality hypothesis in 1924 [10]. From his famous formula $\lambda = h/p$, it was naturally derived that a particle with certain momentum (energy), when projected on a structure with proper size, would diffract just like a wave. In fact, de Broglie’s hypothesis was first verified by
the diffraction of electrons. In 1927, electron diffraction experiments were independently accomplished by Davisson and Germer from a nickle surface [11], Thompson and Reid from a thin foil [12]. From that point on, electron-based imaging methods using varies types of electron microscopes [13] started growing rapidly. Electron beams can be used not only to image crystalline structures. They could also be used for more sensitive study of samples as small as gas molecules due to their stronger interaction with matter than do X-rays, e.g. the cross-section for electron scattering can be about six orders of magnitude larger than that of X-ray scattering [14]. Gas-phase electron diffraction has been used to image the static structure of thousands of systems since Mar and Wierl’s first demonstration in 1930 [15]. Furthermore, recent development of UED in Caltech by Prof. Zewail’s lab made it possible for ultrafast imaging with simultaneous spatial-temporal resolution of 0.01 ångström and 1 picosecond [16] using their third-generation apparatus. Improving the temporal resolution further is extremely challenging because creating electron pulses faster than 100 fs is very difficult due to space-charge effect and dispersion.

1.2 Strong field physics and laser induced electron diffraction

1.2.1 Above threshold ionization (ATI)

With the invention of lasers [17] began a new era of atomic molecular and optical (AMO) physics research thanks to their unique ability to generate electromagnetic (EM) radiation with high spatial and temporal coherence. One great example is the discovery of multiphoton ionization.

Single-photon ionization can occur when the photon energy is larger than the binding potential of the system, the same as Dr. Einstein’s photoelectric effect in 1905. For most atomic or molecular systems, this photon energy is in the ultraviolet (UV) regime. The single-photon ionization rate has a linear dependence on the intensity of the EM field. In 1931, Göppert-Mayer first considered the two-photon transition process [18]. Because of the nonlinear nature of the two photon process, experimental verification was not possible.

1G.P. Thompson, son of J.J. Thompson who discovered the electron in 1897.
until 30 years later when the development of optical masers, or what we call lasers today, allowed researchers to generate intense EM fields [19]. Around the same time emerged the Q-switching technique, which further increased the intensity of EM fields that could be exerted on an atom, and the high-nonlinear process of multiphoton ionization (MPI), or the multiphoton transition from bound state to a continuum state was observed. Early experiments mainly measured the n-photon ionization rate by counting ions, and they could be explained with the lowest-order perturbation theory (LOPT) [20–22]

\[
\Gamma_n = \sigma_n I^n
\] (1.1)

with \( n \) being the minimum number of photons required for ionization, \( I \) the intensity of the field and \( \sigma_n \) the generalized cross section. However, as the laser intensity gets higher, LOPT begins to break because of AC-Stark shifts, i.e. the states involved can no longer be treated as unperturbed since the strong alternating laser field is shifting them dynamically. In 1979, Agostini et.al. [23] observed that in MPI the atom can absorb \( s \) number more photons than the minimum amount required, producing photoelectrons with kinetic energy \( s \) times the photon energy. This process is called the above-threshold ionization (ATI). Despite its non-perturbative nature, perturbation theory was generalized to treat ATI [21, 24]. Explicitly, the ionization rate in Equation 1.1 becomes

\[
\Gamma_{n+s} \propto I^{n+s}
\] (1.2)

and the kinetic energy of the resulting photoelectron takes a similar form with Einstein’s photoelectric effect:

\[
E_{ke} = (n + s)\omega - I_p,
\] (1.3)

where \( s \) is the excess number of photons absorbed, \( I_p \) is the ionization potential of the atom and \( \omega \) is the angular frequency of the field (see Fig. 1.1 for an illustration).

However, investigations of the ATI spectrum with more advanced laser systems and detection schemes soon revealed numerous features that contradicts the perturbative description [25,26]. One example is the discovery of Stark-induced Rydberg resonances which
Figure 1.1: A typical ATI photoelectron spectrum from argon under 0.8 µm laser radiation. Corresponding photon energy is 1.5 eV. Peak laser intensity estimated to be around $1.5 \times 10^{14}$ W/cm$^2$, ionization potential of argon $I_p(Ar) = 15.7$ eV. So here $n = 10$, $s = 1, 2, 3, 4, 5 ...$

involves Stark shifts of the order of the photon energy [27]. In this regime the external field can no longer be treated as a perturbation to the atomic state and theoretical methods like the Floquet theory are needed. With more and more experimental and theoretical studies in the non-perturbative regime were reported ([28] and references therein), the new area of strong field laser physics begun.

Development of the modern Ti:Sapphire laser technology since the 1990s [29] have made it a routine job to generate optical pulses with temporal durations less than 100 femtoseconds. Another advantage that comes with the ultrashort pulse duration is the ability to generate electric field of strength as high as $10^9$ V/cm, enough to rival or even exceed the field that binds electrons to a nucleus. When an atom or molecule is exposed to such strong electric field, the Stark shifts become large compared to the photon energy. An alternative ionization mechanism, optical tunneling ionization, first proposed by Keldysh in 1965 [30], came back onstage and achieved great success.

In the late 1980s strong field investigations extended beyond the early approach of ion and photoelectron measurements. McPherson et.al. [31] and Ferray et.al. [32] reported emission of coherent radiation with frequencies in the vacuum ultraviolet (VUV) and extreme
ultraviolet (XUV) regions, odd harmonics of the laser frequency, from rare gas atoms in intense laser fields. This phenomenon was later called the high-harmonic generation \( G(\text{HHG}) \) process. Major features of the radiation spectrum from HHG was later characterized and explained with a semi-classical model by Schafer \textit{et.al.} [33] and by Corkum [34]. They described HHG and ATI in three steps:

1) An electron is liberated from the ground state of the atom to the continuum via optical tunneling ionization during the laser pulse;

2) The electron gains energy from the intense laser field in the continuum;

3) Some electrons come back to the vicinity of parent target with excess kinetic energy and recollide with it elastically or inelastically.

This three-step model soon became popularly adapted because of its intuitive physical picture and strong predictive power. Refer to Chapter 3 for a more detailed description of this three-step model. Fully quantum-mechanical models of HHG [35, 36] and ATI [37, 38] were also developed with the principle of this recollision picture.

In HHG, one special case of inelastic recollision events, the liberated electron recombines with its parent target and becomes bounded again. The extra energy this electron acquired from the laser field in step 2) is then released in the form of a photon. Taking advantage of the fully coherent nature of this process, molecular orbital information could be retrieved from the emitted photon [39, 40]. What’s more, the coherent emission of XUV photons can also be harnessed to generate attosecond light pulses. For more information about the exciting new area of attosecond physics, see review papers [41–43] and book [44].

The three-step model also showed its power in explaining the long standing puzzle of non-sequential double ionization (NSDI) and non-sequential multiple ionization (NSMI). In the early 1980s, with the help of their more powerful Nd:YAG laser systems, L’Huillier \textit{et.al.} [45] observed formation of multiply charged noble gas ions. Unlike the previous reported study on alkali-earth atoms [46], they found a surprisingly large yield of doubly charged ions [47]. Its explanation was not possible with stepwise removal of electrons. The recollision picture was suggested as a potential mechanism of the NSDI [34] although later experimental evidence suggested it ambiguous [48]. In 2000 Weber \textit{et.al.} [49] and
Moshammer et.al. [50] confirmed the inelastic recollision as the dominate mechanism for NSDI with their momentum distribution measurement of the doubly charged He$^{2+}$ ion. NSDI and NSMI has been reported for all noble gas atoms and some molecules so far. Numerous theoretical and experimental efforts are still underway to decipher the physics of NSDI and NSMI (refer to Becker et.al. [51] for a recent review).

1.2.2 Laser-induced electron diffraction

Competing with the above-mentioned inelastic recollision processes is the elastic rescattering process: the returning electron in step 3) of the three-step model may scatter elastically from its parent target ion, resulting in a diffraction image, like the conventional electron diffraction (CED) that was introduced in section 1.1, except here: a) the diffracting electron comes from the target itself, which makes rescattering a coherent process, but also makes its spatial and spectral distribution more complicated than CED-electrons, and b) the diffraction happens under the influence of the external laser field, so the diffraction image is no longer a simple Fourier transform of the object in the far field as in CED. This process was later called the laser-induced electron diffraction (LIED)$^2$. Since the LIED exploits the intra-cycle dynamics of photoelectrons, its temporal resolution is inherently fraction of a laser cycle, i.e. a few femtoseconds, a temporal resolution very few imaging methods could achieve.

LIED was essentially first observed in atoms when Paulus et. al [53] qualitatively explained the photoelectron angular distribution [54] and plateau behavior [55] in high-order ATI (HATI) from rare gas atoms within the rescattering picture. In their paper, they derived from a classical model [56] that the recollision electron will re-encounter the parent ion with energy ranging from 0 to $3.17U_p$. Here $U_p$ is the cycle-averaged quiver energy of a free electron oscillating in an electromagnetic field. One could calculate with classical mechanics that $U_p$ scales linearly with the intensity of the field (I) and the square of the

$^2$ Although the term LIED was first proposed by Zuo et.al. [52] in 1996, the numerical results in their paper only reflects interferences of direct electron wave packets and no rescattering was involved.
field wavelength ($\lambda^2$), i.e.

\[ U_p \propto I\lambda^2. \]  

(1.4)

Upon backscattering with the parent ion, the electron might gain additional energy from the field and get detected with kinetic energy as high as $10U_p$.

The potential of probing molecular structure with such rescattering has been discussed widely since then ([57], review paper [58] and references therein). However, early proposals of using plateau electrons as imaging tool yielded little actual application, mainly because of the two differences between CED and LIED: a) it is not obvious that the returning electrons in LIED could be represented by an electron wave packet (EWP) similar to the beam of free electrons in CED, and b) since the the rescattering process occurs under the influence of the laser field, there needed to be a procedure to decouple the effect of the laser in LIED. These difficulties were tackled by Chen and Morishita [59–61]. Hinted by a back rescattered ridge (BRR) structure in the two dimensional photoelectron momentum distribution [62], which was achieved from a numerical solution of the time-dependent Schrödinger equation (TDSE) under single-active-electron approximation, they developed the quantitative rescattering theory (QRS) [59]. With QRS, they were able to understand the behavior of the returning electron wave packet and decouple the effect of the laser field in the rescattering process. Moreover, field-free electron elastic scatter differential cross sections (DCS) were extracted for noble gas atoms from LIED. This method was soon confirmed in real laboratory experiments [63–65] (as compared to their numerical TDSE “experiments” in [59–61]). Shortly after that, Chen et al. [60] provided the full details of QRS, generalizing their method to utilizing the whole energy range of recollision electrons instead of using only the ones with highest energy as in BRR [61], established its validity within the single active electron picture, and pointing out QRS’ the potential of using LIED to image molecular structure similar to CED. Experimental efforts immediately followed to apply LIED on molecules [66–70]. While these early results showed great potential of measuring electron elastic scatter DCS on molecular ion, their result were not accurate enough to be applied for molecular imaging and relied on quite complicated theoretical efforts for
interpretation. As addressed by Xu et al. [71], since most of the LIED are performed with Ti:Sapphire lasers, recall relation in Eq. (1.4), the returning electrons have kinetic energies of only 15–50 eV, for peak laser intensities of $1–3 \times 10^{14}$ W/cm$^2$. These energies are much smaller than the hundreds of kilo-electron-volts (keVs) used in CED. Electrons of such energies are typical of those used for probing the valence electrons instead of position of atomic sites in the molecule. Such diffraction images cannot be interpreted without advanced theory.

In CED, a well collimated electron beam with kinetic energies ranging from tens to hundreds of keVs illuminate a randomly distributed ensemble of molecules. The radial distribution of the inter-atomic distances in the molecule can be retrieved from the resulting diffraction image using the so-called independent atom model (IAM) [72–74]. In IAM, a molecule is modeled as a collection of its component atoms fixed in space and the complex scattering amplitude of the molecule is treated as linear combination of atomic scattering amplitudes. This approximation is no longer valid when the scattering process involves the valence electrons or the chemical bonding electrons. In the paper by Xu et al. [71], the authors also pointed out that in principle, there is no need to use electrons with energies as high as hundreds of keVs if measuring at large scattering angle. Calculations showed that for large-angle rescattering (about $40^\circ$ to $180^\circ$), IAM is valid even in a recollision energy range between 100–300 eV. Recalling Eq. (1.4), larger returning electron energy can be achieved by either increasing the intensity or the wavelength of the field. While the increase in field intensity is restricted by the barrier suppression of optical tunneling ionization (see Chapter 3 for more details), the increase in laser wavelength is only limited by the development of laser technology. Nowadays, commercially available optical parametric amplifiers, most pumped by Ti:Sapphire lasers, routinely generate powerful femtosecond laser pulses at mid-infrared (MIR) wavelengths (around 1–2 µm), suitable to induce 100–300 eV recollision electrons for common atomic and molecular targets. In fact, the above theoretical predictions were soon verified experimentally [75] with such MIR systems. In that paper, we used LIED to extract accurate e-ion collision DCSs with dynamic ranges comparable to the ones from CED methods. That demonstrated the power of LIED method.
at mid-infrared wavelengths. Electrons born in mid-infrared wavelength fields may acquire high enough kinetic energies to induce hard collisions with the atomic core and thus the DCS for the atomic cation is the same as that for the neutral, which is a necessity for dynamic molecular imaging, as it signifies that the e-molecule interaction will be dominated by a well-localized, strong short-range \textit{atomic-like} potential while the delocalized, valence electrons are transparent, which also holds good promise for achieving suitable spatial resolutions using LIED. The experimental results also verify that the extracted DCS does not depend on the laser parameters, as predicted by QRS. These results provide essential ingredients needed for deploying LIED for investigating more complex molecules and time-resolved structure retrieval of a molecule under conformal transformation. With this foundation, LIED was first demonstrated in revealing the bond relaxation of O$_2$ molecules following tunneling ionization [76]. It’s worth noting that, in addition to the higher electron return energy, the longer wavelength also works to our advantage in ensuring the validity of the first step of the three-step model, optical tunneling ionization. The lower frequency field is a prerequisite for photoelectron contribution from optical tunneling ionization to dominate over the coexisting multiphoton ionization.

Another ingredient for imaging molecular structures with LIED is the determination of molecular alignment, or the knowledge of direction of inter-atomic axes. As mentioned above, in CED the electron beam sees isotropically distributed molecules. In 1967 Cohen and Fano [77] derived that for randomly distributed molecules, the diffraction image still contain molecular structure information, which is an essential idea behind CED. However, this is not the same for LIED. This is, again, because recollision electrons come from the target cations themselves. In general, the distribution of recollision electrons produced via optical tunneling ionization is not isotropic with respect to the inter-atomic axises in a molecule. Tong and Lin [78] developed a theory in 2002 to treat optical tunneling ionization in some simple molecules including O$_2$ and N$_2$. This theory was a critical tool in the early demonstration of LIED [76]. However, in most cases, this distribution is quite complicated and difficult to calculate. Another approach to achieve a known distribution of molecular axes is to directly fix the molecules in the lab frame via molecular alignment [79]. Since the
Figure 1.2: Low-energy electrons for three gases ionized with constant intensity 2 \(\mu\)m laser pulses. The solid line is from KFR calculation. The shaded area shows the energy region for LES and \(E_H\) denotes the cutoff energy.

Recollision electrons are field driven, they travel along the laser polarization direction which can be well controlled in the lab frame. Once the molecules are also fixed in the lab frame, the scattering geometries are known and a straightforward procedure can be applied to extract the molecular structures from LIED.

Another characteristic of the recollision electrons is their broad energy distributions, ranging from 0 to 3.17U_p. Exploiting this broadband feature of returning electron wave packets, we'll show in this dissertation a new imaging method, fixed-angle broadband laser-induced electron scattering.

1.2.3 The low-energy structure (LES)

In contrast to those recent developments on the study of HATI that was described in the previous section, the low-energy ATI of atoms in intense, long-wavelength laser fields were believed to be well understood decades ago. The theoretical tool is known as the Keldysh-Faisal-Reiss (KFR) strong-field approximation [30, 80, 81], built on the foundation of Keldysh’s optical tunneling ionization proposal, which is also the cornerstone of the first step in the three step model. That is why our report in 2009 on the first experimental observation of the unexpected spike-like feature in low-energy photoelectron spectra at MIR
wavelengths ([82], also [83], see Fig. 1.2) drew significant attention in the community of
strong field physics, especially from theorists. This structure, dubbed low-energy structure
(LES), appears to be a universal feature in all the target atoms and diatomic molecules
studied. Fig. 1.2 shows the low-energy portion of the photoelectron spectrum from Ar,
N\textsubscript{2} and H\textsubscript{2} at constant intensity under 2 µm laser radiation. Shown in the same figure
(green solid line) is the KFR result. Although it matches experimental results well over
a broad range of energies, it completely fails to reproduce the LES. On the other hand,
our TDSE simulation reproduced LES. It was soon suggested that the interaction between
the ionized electron and the Coulomb potential of the parent ion, which is absent in the
KFR formulation, is closely related to the physical origin of the LES. To date, it is widely
accepted that the formation of LES is due to the effect of the Coulomb potential during the
rescattering process of the electron [84,85]. In particular, classical trajectory Monte Carlo
(CTMC) simulation has been a useful tool for revealing such process intuitively [84,86,87],
as Coulomb potential can be easily incorporated and manipulated in CTMC. Extracted
from CTMC, the classical trajectories contributing to the LES are identified as the ones
that go through soft-recollisions with the Coulomb potential, i.e. the LES trajectories pass
by the ionic core with near-zero kinetic energy, so the long-range Coulomb potential is no
longer negligible.

In essence, the LES and HATI fall in the same category of strong field rescattering
processes, except 1) in LES the scattering potential is dominated by the Coulomb potential,
and 2) the soft-recollision event in LES happens roughly one and half laser cycles after the
optical tunneling ionization, while in HATI the recollision event happens about half an laser
cycle after the tunneling ionization event. The longer traveling time in the laser field before
the recollision makes LES photoelectrons more susceptible to pulse amplitude changes than
HATI photoelectrons. As shown in a calculation by Kästner \textit{et al.} [87], by varying the
laser pulse duration and carrier-envelope phase (CEP) of few-cycle lasers, the LES can be
altered. In this dissertation, we’ll show our experimental study of the laser pulse duration
dependence of the LES in few-cycle laser fields.
1.3 Overview of this dissertation

The structure of this dissertation will be as following:

In Chapter 2, the experimental tools involved will be described. This includes laser systems, techniques of generating and characterizing few-cycle mid-infrared laser pulses and measurement methods in the experiment.

In Chapter 3, theoretical and experimental background of LIED will be provided. A new imaging method using the broadband nature of the recollision electron wave packets, fixed-angle broadband laser-induced electron scattering (FABLES), will be introduced. A brief description of molecular alignment will also be supplied, along with some preliminary results of the effect of molecular alignment on FABLES.

In Chapter 4, we’ll describe our experimental, numerical and theoretical study on the pulse duration dependence of the LES. We’ll show the universal pulse duration dependence of the LES peak position. Theoretical analysis of the LES confirms the classical aspect of the returning photoelectrons, which is critical in LIED and FABLES. Further analysis of experimental and numerical results identify the role of longitudinal and transverse component of the Coulomb force in the dynamics of LES photoelectron. Numerical study also reveals the dependence of the LES on the carrier-envelop phase (CEP) of a few-cycle pulse. Then we demonstrate the power of the LES as a potential tool to measure the CEP.

In Chapter 5, a short discussion will be given to summarize the whole dissertation and a future experiment is proposed.
Chapter 2
EXPERIMENTAL APPARATUS

2.1 Laser systems

In Chapter 1, we established that in order for LIED to be suitable for molecular imaging, the driving lasers need to produce ultrafast intense pulses with mid-infrared wavelengths. However, direct generation and amplification of ultrafast intense mid-infrared laser pulses is a challenging job due to the limitation of laser gain materials. An alternative route is to generate tunable mid-infrared pulses with an optical parametric amplifier (OPA). The OPA is pumped by a home-built Ti:Sapphire chirped-pulse amplification (CPA) system.

2.1.1 The Ti:Sapphire CPA system

Our home-built Ti:Sapphire system utilizes the standard chirped-pulse amplification (CPA) [88] technique to achieve high laser peak power. The principle of a CPA system is illustrated in Fig. 2.1. The amplification of an ultrashort pulse is limited by optical damaging of the laser gain materials, which can be avoided by temporally stretching and compressing the pulse before and after the amplification stage.

The main components of our Ti:Sapphire CPA are the following:

Oscillator: The ultrashort laser pulses are generated by a commercial oscillator (Venteon by Venteon Laser Technology GmbH, now Laser Quantum) based on Kerr lens mode-locking (review paper [89] and references therein). The oscillator is pumped with a continuous-wave green laser (Millennia by Spectra Physics, now Newport Corporation). The output pulse is 8 fs in duration and 2 nJ in energy. Its bandwidth full width at half maximum
(FWHM) is 200 nm, with a repetition rate of 80 MHz.

Stretcher: The ultrashort laser pulses are subsequently sent through a Martínez type [90] single-grating (1200 grooves/mm by Spectrogon) stretcher [91]. Large positive spectral dispersion is introduced by the stretcher and the pulse duration is stretched to 230 ps. The stretcher is designed to pass 100 nm of bandwidth. For a detailed description of the stretcher layout, refer to page 28 of [92].

Amplifier I: The stretched pulse, also called the seed, is then fed into a regenerative amplifier (regen). A diagram of the regen cavity can be found in [92]. The regen Ti:Sapphire crystal is water-cooled and end-pumped at 1 kHz repetition rate with 8 mJ, 120 ns, 527 nm pulses from a Q-Switched diode-pumped solid state (DPSS) laser, Darwin-527 from Quantronix Corporation (later Continuum Inc., now Amplitude Group). The seed is injected into the regen cavity through a pulse-picker consisting of a Pockels cell (Medox Electro-Optics model 700-KDP) and a thin-film polarizer. The pulse-picker traps 1 pulse
out of every 80,000 seed pulses in the cavity for 10 round trips and releases it. After 10 round trips, which is 20 passes through the population inverted Ti:Sapphire crystal, the pulse is amplified more than a million times and the pulse energy grows to about 1.6 mJ. Thus the repetition rate of the system is effectively reduced to 1 kHz. As a result of gain narrowing and limited bandwidth supported by the regen optics, the spectral FWHM of the pulse becomes 21 nm at the regen output.

**Amplifier II:** The pulse is then amplified further with a *two-pass power amplifier* (power amp). The Ti:Sapphire crystal in power amp is cryogenically cooled in a vacuum chamber and end-pumped at each side with 13.5 mJ, 130 ns, 527 nm pulses from a Q-Switched diode-pumped solid state (DPSS) laser, DM40-527 from Photonics Industries International, Inc. Details of the power amp layout can be found on page 34 of [93]. The pulse energy at power amp output is 9 mJ.

**Compressor:** After two-stage amplifications, the pulse is sent through a Martínez type [90] compressor consisting of two gratings (1500 grooves/mm by Spectrogon). The intentionally mismatched groove density between the compressor gratings and the stretcher grating allows the compressor to compensate both the spectral dispersions introduced by the stretcher and the ones accumulated from the amplifier crystals and other elements in the propagation. The pulse is compressed to around 50 fs in duration after the compressor. The pulse energy at compressor output is 6 mJ, yielding 65% transmission efficiency of the compressor.

A summary of the key parameters in the laser chain can be found in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>pulse energy</th>
<th>$\tau_d$</th>
<th>rep. rate</th>
<th>$\Delta \lambda$</th>
<th>pump power</th>
</tr>
</thead>
<tbody>
<tr>
<td>oscillator</td>
<td>2 nJ</td>
<td>8 fs</td>
<td>80 MHz</td>
<td>200 nm</td>
<td>5 W, CW</td>
</tr>
<tr>
<td>stretcher</td>
<td>1 nJ</td>
<td>230 ps</td>
<td>80 MHz</td>
<td>100 nm</td>
<td>–</td>
</tr>
<tr>
<td>amplifier I</td>
<td>1.6 mJ</td>
<td>230 ps</td>
<td>1 kHz</td>
<td>21 nm</td>
<td>8 mJ, 120 ns</td>
</tr>
<tr>
<td>amplifier II</td>
<td>9 mJ</td>
<td>230 ps</td>
<td>1 kHz</td>
<td>21 nm</td>
<td>27 mJ, 130 ns</td>
</tr>
<tr>
<td>compressor</td>
<td>6 mJ</td>
<td>50 fs</td>
<td>1 kHz</td>
<td>21 nm</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 2.1:** Parameters of the 0.8 $\mu$m laser chain $\tau_d$: pulse duration full width at half maximum (FWHM), $\Delta \lambda$: spectral bandwidth FWHM, rep. rate: repetition rate, CW: continuous wave.
2.1.2 Optical parametric amplifier

The CPA system pumps a beta barium borate (BBO)-based commercial optical parametric amplifier (HE-TOPAS-Prime, Light Conversion Ltd) with 50 fs FWHM pulse duration, 6 mJ pulse energy and center wavelength of 0.8 \( \mu m \). The HE-TOPAS generates a white-light continuum (WLC) by focusing a small portion of the 0.8 \( \mu m \) beam into a sapphire plate. Desired spectrum in the WLC is then parametrically amplified in three stages with three BBO crystals. The HE-TOPAS produces mid-infrared pulses with wavelengths tunable from 1.2 \( \mu m \) to 2.3 \( \mu m \). The pulse energies vary from 0.6 mJ to 1.4 mJ depending on wavelength as shown in Fig. 2.2.

2.1.3 Performance of the laser system

The spatial profile of the 0.8 \( \mu m \) beam was characterized with CCD (charge-coupled device) cameras and the M\(^2\) value was measured to be under 1.1. The temporal profile of
the 0.8 µm beam was characterized with a second harmonic generation, frequency resolved optical gating (SHG-FROG) [94] setup and the FWHM pulse duration was measured to be 50 fs. Details can be found on page 36 of [92].

The spatial and temporal profile of the HE-TOPAS output varies significantly depending on the generated wavelength. Of particular interest in the following part of this dissertation is the 1.8 µm output. A far-field spatial profile of the 1.8 µm beam measurement can be found in Fig. 2.2. The $M^2$ value is of the 1.8 µm beam is measured to be around 1.5. The temporal profile of the 1.8 µm pulse is characterized with a home-built all-reflective second harmonic generation, frequency resolved optical gating (R-SHG-FROG) [94,95]). A diagram of the R-SHG-FROG is shown in Fig. 2.3. The R-SHG-FROG is designed for broadband dispersion-free operation, which are critical conditions for manipulating few-cycle pulses. The beam-splitting in the R-SHG-FROG is achieved via geometrical splitting of the beam, so a spatially uniform input beam is required. Two spatial parts of the beam is focused by a concave spherical mirror with 1 m radius-of-curvature on-to a 10 µm thick type I BBO crystal ($\theta = 20^\circ$). A beam mask is placed in the beam path to minimize the undesired interferences. The motorized mirror reflects the beam in the vertical plane, which minimizes the smearing effect since the two beams cross in the BBO crystal on the horizontal plane. The motorized mirror is mounted on a translation stage actuated by a Thorlabs Z812
actuator controlled by TDC001 controller and the minimum step size it supplies is about 30 nm. This results in a 0.2 fs resolution in optical delay, which is adequate for measuring the 1.8 μm pulse (6 fs in cycle duration). A pinhole with 0.5 mm diameter is placed after the BBO crystal to block the individual arms and pass only the doubled beam resulted from sum frequency generation (SFG). The SFG signal is then coupled into a customized Ocean Optics USB4000 spectrometer (3600 pixels, spectral range 520 – 1200 nm) with an optical fiber. The measured FROG spectrogram was retrieved with Prof. Trebino’s open source Matlab code [96]. Fig. 2.4 shows the temporal characterization of the HE-TOPAS 1.8 μm output. The spectral FWHM of the pulse is 80 nm, enough to support a 60 fs transform-limited Gaussian pulse. However, due to the non-flat spectral phase, the measured temporal FWHM is about 70 fs.
2.2 The few-cycle MIR pulse

There has been several schemes for generating intense few-cycle MIR pulses: An optical parametric chirped pulse amplification system generated 0.74 mJ 15.6 fs pulses at 2.1 μm [97]. Taking advantage of the pulse self-compression by filamentation, 0.27 mJ 17.9 fs pulses at 2.1 μm [98] and 1.5 mJ 19.8 fs pulses at 1.5 μm [99] were produced. 1.2 mJ 17 fs pulses at 1.5 μm [100] were generated by difference frequency generation with few-cycle 0.8 μm followed by optical parametric amplification. 0.4 mJ 13.1 fs pulses at 1.4 μm [101] were produced using spectral broadening in a hollow-core fiber (HCF) and subsequent dispersion compensation with chirped mirrors. 0.4 mJ 11.5 fs pulses at 1.8 μm [102] were generated through spectral broadening in a hollow-core fiber (HCF) followed by pulse compression with fused silica plates.

We adapted the last scheme because of its good stability and straightforward configuration.

2.2.1 Generation and characterization of the few-cycle MIR pulse

Our setup is very similar to the one described in [102]. A schematic diagram of the setup is shown in Fig. 2.5. We took the idler beam at 1.8 μm from the HE-TOPAS and sent it through a 1:2 reflective telescope, expanding the beam diameter from 9 mm to 18
mm. The beam was then focused into a HCF (DURAN Group GmbH) with a $f = 1$ m calcium fluorite (CaF$_2$) lens. The HCF is 1 m long, 6 mm and 0.4 mm in outer and inner diameter, respectively. The beam size at HCF entrance is about 160 $\mu$m in diameter. The energy before and after the fiber is 1 mJ and 0.4 mJ, respectively. The output from HCF is collimated with a 1 m radius-of-curvature concave spherical mirror. The collimated beam is measured to be 10 mm in diameter with a thermal camera (PV320L from Electrophysics). A home-built GaAs-pair polarizer was put into the beam path after collimation. Combining the GaAs-pair polarizer with a half-wave plate before the HCF, the laser intensity can be controlled precisely. After the GaAs-pair polarizer, the pulse energy dropped to about 0.2 mJ. In principle, the pulse energy can be improved by replacing the GaAs-pair polarizer with a single GaAs plate at Brewster angle. But 0.2 mJ of energy was adequate for our early stage of experiments, so we kept the GaAs-pair polarizer for better extinction ratio.

The energy transmission of the HCF is summarized in Table 2.2.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>$\sim 1.8 \mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input energy</td>
<td>$\sim 1$ mJ</td>
</tr>
<tr>
<td>Output energy</td>
<td>$\sim 0.4$ mJ</td>
</tr>
<tr>
<td>Energy after polarizer</td>
<td>$\sim 0.2$ mJ</td>
</tr>
</tbody>
</table>

Table 2.2: Energy transmission of the HCF

With the gas evacuated (pressure $< 1 \times 10^{-3}$ Torr), the HCF acts as a waveguide that cleans up the spatial mode of the HE-TOPAS output, as shown in the lower inset of Fig. 2.2. Measured with our R-SHG-FROG (Fig. 2.4), we did not observe noticeable change in the spectral and temporal profile of the pulse.

A shorter pulse in the temporal domain requires more frequency components in the spectral domain. Broadening of the laser spectrum could be achieved via nonlinear propagation through a gas medium. Taking into consideration the nonlinear response (mainly third order susceptibility $\chi^{(3)}$) of a medium to the strong laser field, the index of refraction can be written as:

$$n(I) = n_0 + n_2 \cdot I \tag{2.1}$$
where $n_0$ is the field-free index of refraction, $n_2$ is the nonlinear index of refraction and $I$ is the intensity of the external field. This phenomenon is called the optical Kerr effect. Typical values of $n_2$ for optical materials are on the order of a few $10^{-16}$ cm$^2$/W. The optical Kerr effect leads to a lot of important phenomena in intense laser fields. For example, the mode-locking mechanism of the Venteon oscillator described in the beginning of this chapter is based on Kerr lensing, which is a result of the combination of optical Kerr effect and radial-dependence of laser intensity.

The optical Kerr effect also leads to a nonlinear phase shift when propagating an intense laser through a medium:

$$\varphi_{NL}(t) = \frac{2\pi}{\lambda} n_2 I(t) \Delta l$$  \hspace{1cm} (2.2)

where $\lambda$ is the wavelength of the laser, the field intensity is time-dependent and $\Delta l$ is the distance of propagation. This self-induced phase shift during propagation is called self-phase modulation (SPM). The integrated peak value of this phase is known as the B integral, $B = \frac{2\pi}{\lambda} \int n_2 I_0 \, dl$, an important parameter to monitor during the transportation of a strong laser beam, e.g. if B integral of the laser beam accumulates to $B \approx \pi$, it will become problematic.

Spectral changes induced by SPM is a direct consequence of the time-dependent nonlinear phase. The temporally varying phase leads to frequency shift across the pulse from its central value $\omega_0$ by:

$$\delta \omega(t) = \frac{\partial \varphi_{NL}}{\partial t}$$  \hspace{1cm} (2.3)

For an unchirped Gaussian pulse, the maximum frequency shift is derived to be $\Delta \omega_{\text{max}}$,

$$\Delta \omega_{\text{max}} = 0.86 \Delta \omega_0 \varphi_{NL}^{\text{max}}$$  \hspace{1cm} (2.4)

where $\Delta \omega_0$ is the $1/e$ half-width in frequency and it shows that the spectral broadening factor is approximately given by the numerical value of the maximum phase shift $\varphi_{NL}^{\text{max}}$.

Filling the HCF with argon gas, more frequency component can be generated after the laser pulse propagates through it due to SPM. The amount of spectral broadening depends on the gas pressure in the HCF since the nonlinear index of refraction $n_2 = 9.73 p \times$
10^{-20}\ \text{cm}^2/\text{W} [104]$, where $p$ is the pressure of argon gas in unit of bar. We measured the pulse spectrum at each gas pressure with a monochromator (HR320 by HORIBA Scientific and InGaAs array G9208 by Hamamatsu). The result is shown in the left and middle panel of Fig. 2.6. We also numerically simulated the spectral broadening with a split-step Fourier method [104], the result is shown in the right panel of Fig. 2.6. It roughly reproduces the major features of the spectral broadening.

The spectrally broadened pulse is still long in duration because of the fast-varying spectral phase. Thanks to the anomalous dispersion introduced by the fused silica (FS) plate ($-63 \text{ fs}^2/\text{mm}$), the spectral phase can be flattened by linear propagation through a FS plate with proper thickness. Carefully choosing the combination of argon gas pressure in the HCF and thickness of the FS plate, the laser pulse duration can be tuned from 70 fs
to 12 fs continuously. In Fig. 2.7 the FROG measurement of a 12 fs pulse is shown. That’s the shortest pulse we achieved with the current setup.

In Fig. 2.8, we show a direct comparison between the uncompressed HE-TOPAS output and a 12 fs pulse after the fiber compressor.

A 12 fs pulse at 1.8 µm only consists two optical cycles. In this case, the amplitude of the electric field varies drastically from cycle to cycle and depends sensitively on the phase of the carrier wave with respect to the envelope, usually called the carrier-envelope phase offset (CEP), as illustrated in the left panel of Fig. 2.9. The relative CEP change can be measured with a f-2f interferometer setup [105]. With sufficient pressure of argon gas in the HCF, the spectrum broadens to more than one octave. Therefore, there is no need for additional white light generating stage in the f-2f setup and each arm of our R-SHG-FROG acts as the f-2f interferometer. For the f-2f measurement, we block the motorized arm in the R-SHG-FROG, take out the pinhole and place a polarizer after the BBO crystal to optimize
the f-2f interference signal. In the top right panel of Fig. 2.9 is shown the f-2f interferogram measured over 160 shots. Each shot integrates three laser pulses (10 ms shutter) and there are 3 seconds between each shot. So the total timespan of this interferogram is about 8 minutes. A fast-Fourier transform of the interferogram shows the CEP fluctuation is about 240 mrad over 8 minutes (lower right panel of Fig. 2.9). So CEP of the 1.8 µm pulse is stable, even though the HE-TOPAS is pumped by a Ti:Sapphire system with random CEP. That’s because as idler of the HE-TOPAS, the 1.8 µm beam is generated by the difference frequency generation process between the pump beam and the signal beam which is generated through white-light continuum generation by the pump beam. From phase relation [106]:

\[ \varphi_I = -\pi/2 + \varphi_P - \varphi_S \]  

(2.5)

where, \( \varphi_I \), \( \varphi_P \) and \( \varphi_S \) are the phase of idler, pump and signal, receptively, since the signal beam is generated by the pump beam, it has the same random phase fluctuation as the pump beam. So the idler phase, as the difference of them, is intrinsically stable (called
passive CEP stabilization).

### 2.2.2 Gaussian beam focusing

To generate ultrahigh laser intensities for our strong field physics studies, the laser beam is focused into the experimental vacuum chamber with a lens or a concave spherical mirror. The experimental ensembles of atoms and molecules in our experiments, effusive gases or molecular beams, are all larger than the dimension of the laser focus. So the interaction volume is defined by the intensity distribution of the laser focus. To properly understand experimental results, the focal volume averaging effect caused by this intensity distribution has to be considered. Following [107], the radial intensity distribution of a propagating Gaussian beam can be derived analytically to be

\[
I(r) = \frac{2P_0}{\pi w^2} e^{-2r^2/w^2} \tag{2.6}
\]
Figure 2.10: Intensity distribution near a Gaussian focus created by focusing a 1.8 µm laser with a $f^\# = 4$ lens. The contour lines are labeled to be where the fractions of peak laser intensity are distributed. In the bottom panel is plotted the Gouy phase shift across the focus. In the right panel is the line out of normalized intensity distribution at the focus.
where $P_0$ is the peak power of the beam and $w$ is the radius of the beam when the intensity is $1/e^2$ times the peak intensity. $w$ as a function of distance to the waist or focus, $z$, can be derived analytically:

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2}$$

where

$$z_R = \frac{\pi w_0^2}{\lambda}$$

is called the Rayleigh range. As shown above, the propagation of a perfect Gaussian beam in a medium can be entirely determined by its waist size $w_0$ and wavelength $\lambda$ in the medium. Here $w_0$ is the laser focus size defined as the radius of the intensity profile at its $1/e^2$ value. Note that there is no need to have a real focus in a medium to use Eqn. 2.7. A Gaussian beam can be diverging or converging in a medium and its propagation can be characterized with a virtual focus outside of the medium. Combining Eqn. 2.6 and 2.7, the cylindrically symmetric three-dimensional intensity distribution at the Gaussian laser focus is known.

The $f$-number of a focusing lens is defined as:

$$f^\# \equiv \frac{f}{D},$$

where $f$ is the focal length of the lens and $D = \pi w$ is the 99% power transmission diameter of the laser beam. The intensity distribution at the beam waist for a 1.8 $\mu$m laser focused with a $f^\# = 4$ lens is calculated and plotted in Fig. 2.10. The intensity profile of a Gaussian beam focus can also be derived analytically. The volume containing field intensities larger than $I_i$ is shown to be [108]:

$$V(I > I_i) = \pi w_0^2 z_R (\frac{4}{3} \beta + \frac{2}{9} \beta^3 - \frac{4}{3} \arctan \beta)$$

where

$$\beta = \sqrt{\frac{I_0}{I_i} - 1}$$

and $I_0 = 2P_0/\pi w_0$ is the peak intensity at the center of the laser focus. Although the mid-infrared beams in the experiment are not ideal Gaussian beams, representing them with the “embedded Gaussian” picture with the $M^2$ parameter is a good enough approximation [109].
Another important feature associated with the laser focus is the Gouy phase shift [110]. As first observed by Gouy in 1890, when an electromagnetic beam propagates through a focus, the field will experience an additional $\pi$ phase shift before and after the focus. As a general property of any focused wave, the Gouy phase shift leads to important phenomena in the focusing of optical range of electromagnetic radiation, e.g., resonate frequencies of laser cavities cannot be properly determined without considering the Gouy phase shift [107]. Phase-matched processes like the HHG are also closely related to the Gouy phase shift. As mentioned earlier, field amplitudes of few-cycle pulses depends sensitively on the CEP. So the Gouy phase shift needs to be considered when propagating a few-cycle pulse through a focus. The Gouy phase shift of a perfect beam is [111,112]:

$$\varphi(z) = -\arctan \left( \frac{z}{z_R(\lambda)} \right), \quad (2.12)$$

which is plotted in the lower panel of Fig. 2.10. Since the Raleigh range $z_R$ depends on the wavelength of the light, different spectral component of the broadband few-cycle pulse will experience different amount of Gouy phase shift. Luckily this chromatic aberration is relatively small for our laser parameters. The Gouy phase shift difference between the smallest and largest frequency component of our 12 fs 1.8 $\mu$m pulse is estimated to be under 200 mrad., within the range of our CEP fluctuation. As stated earlier, our experimental data were collected from the interaction of atoms and molecules in the intensity distribution of a laser focus. CEP averaging effect due to the Gouy phase shift across the focus needs to be properly taken into consideration when analyzing the data.

### 2.3 Measurement systems

Two home-built electron and ion time-of-flight (TOF) spectrometers were used to measure the yields, energies and momenta of electrons and ions produced by photoionization events: the coincidence machine and the cluster machine.

Detailed description of the coincidence machine can be found on page 44 of [92]. Fig. 2.11 is plotted a schematic diagram of the TOF spectrometer in the coincidence machine.
Figure 2.11: Schematic diagram of the coincidence machine MM: gold-coated mu-metal shield, FC: Faraday cage, PH: optional field plate with small hole in the middle for better angular resolution, GR: grounded grid, MCP: Chevron configuration microchannel plates. Different combination of voltages will be applied to field plates 1 through 8 when operating at the different detection modes, P: laser focus.

It sits inside the ultrahigh vacuum chamber (base pressure less than $3 \times 10^{-10}$ Torr). Target gases are delivered into the chamber effusively with a variable leak valve. We restrict the gas pressure to be under $2 \times 10^{-4}$ Torr to maintain good performance of the microchannel plates (MCP) detector. The TOF spectrometer measures the electrons and ions generated by the ultra-strong field at the laser focus in three modes: ion detection, electron detection and coincidence detection. In ion detection mode, singly and multiply charged ions produced at the laser focus are extracted from the interaction region with static field across plate 5 and plate 6. Voltages applied on plates 4, 5 and 6 are arranged under the so-called Wiley-McLaren condition [113] to achieve better resolution. Ions are then focused onto the MCP detector with an electrostatic lens, called the Einzel lens, formed by the different voltages on field plates 1, 2, 3 and the Faraday cage. In electron detection mode, all elements of the spectrometer except the electron side MCP detector will be grounded to create a field-free
flight tube. The interaction region is surrounded by a gold-coated mu-metal cylinder to shield it against external magnetic fields. A grounded grid placed right before the MCP detector prevents electric fields generated by the MCP detector from penetrating into the flight tube. When higher angular resolution is desired, a field plate with small pinhole in the middle is inserted before the grid to restrict the detection solid angle. In coincidence detection mode, since the velocity of electrons are generally much bigger than that of ions, the displacement of ions will be very small when most of the electrons escape to the other side of field plates 1, 2 and 3. The ion extraction voltage will be applied between field plate 3 and 4 impulsively after the electrons escape the interaction region to achieve ion extraction and field-free electron detection simultaneously. Coincidence detection is a powerful tool to study multi-particle correlation. But since the purpose of this dissertation is to study the strong field imaging with electron detection mode, no coincidence data was taken.

The data acquisition system of the coincidence machine is depicted in the upper panel of Fig. 2.12. It measures the travel time of electrons and/or ions from generation to detection with a time-to-digital converter (TDC). Its working principle is similar to a stopwatch. A beam splitter picks off a small fraction of the incoming laser pulse to start the “stopwatch”. It’s detected by the photodiode with 1 ns rise time. The signal pulse from the photodiode is then inverted by a signal inverter, amplified by an ORTEC 574 timing amplifier and discriminated by an ORTEC 473A constant fraction discriminator to provide a NIM pulse\(^3\) for the “start” port of the TDC. The rest of the laser beam passes through the beam splitter and get focused into the vacuum chamber. Electrons and/or ions generated at the laser focus travel through the flight tube to reach the MCP detectors. When high voltage is applied across the MCP, the impact of an ion or electron on its front surface starts a cascade of electrons in the microchannels and generates a shower of millions of electrons at its back face. These electrons are coupled out capacitively to produce a negative signal pulse. The signal pulse then get amplified by the same ORTEC 574 timing amplifier as the start signal, discriminated by an ORTEC 9307 pico-timing discriminator and provides

\(^3\)NIM: the Nuclear Instrumentation Module standard for logic signal, with -16 mA into a 50-Ω load creates a -0.8 V pulse.
Figure 2.12: Data acquisition system of the coincidence machine and timing sequence of the TDC input. Top panel shows schematic of the data acquisition system. BS: beam splitter, PD: fast photodiode (e.g. Thorlabs DET10A with 1 ns rise time), MCP: microchannel plate detector, SI: homemade signal inverter, AMP: ORTEC 574 timing Amplifier, DSC1: ORTEC 473A constant-fraction discriminator, DSC2: ORTEC 9307 pico-timing discriminator, MDX: signal from Pockels cell driver, DG: DG535 digital delay/pulse generator by Stanford Research, TDC: Time-to-Digital Converter (e.g. LeCroy model 4208, LeCroy model 2228A), SRT, STP, EDW, CLR are the “start”, “stop”, “end-of-window” and “clear” channel of the TDC, respectively, CAMAC: Computer Automated Measurement And Control interface. The dashed line illustrates procedure for $t_0$ estimation (see text for details). The bottom panel is an illustration of the timing sequence for TDC input signals. Model 2228A does not take EDW pulses.
a NIM pulse for the “stop” port of the TDC. The time delay between the “start” and “stop” signal is digitized and transferred to the computer via a CAMAC interface (CC32 by Wiener). Two different types of TDCs are used in the experiments, model 4208 TDC and model 2228A TDC by LeCroy. The timing sequence of them is illustrated in the lower panel of Fig. 2.12. Triggered by a signal from the Pockels cell driver, a delay generator (DG535 digital delay/pulse generator by Stanford Research) generates a NIM signal for the “clear” port of the TDCs and prepares them for operation. Both of them are operated in single channel multi-hit mode and they both can register up to eight “stop” signals for every “start” signal, i.e. eight hits per shot. The “start” port on model 4208 and model 2228A are called COMMON and COM START (Common Start), respectively. In eight-hits-per-shot mode, the “stop” signal is delivered into the first channel of them. Model 4208 converts the time difference between the “start” and “stop” signal into a 24 bits signed number with 1 ns resolution which is a total time range of ± 8.3 ms. In our experiment, the “start” is set to be always preceding the “stop” signal so only the positive range is used. Since the repetition rate of the laser is 1 kHz, the time interval between laser pulses is 1 ms. So for model 4208 to function properly, an end-of-window (EDW) is generated by DG535 to trim the data acquisition cycle before the next laser. In fact, the current data acquisition software only receives “stop” signals that comes within 40000 bins, out of the millions of them, after the “start” signal, which is 40 µs in time range, enough to measure the flight time of slow electrons and regular ions. So the data acquisition can be trimmed much earlier than 1 ms. To achieve better resolution, which is crucial for high energy electron measurement, model 2228A will be used. It is a 11-bit TDC with three switchable resolution options: 50, 100 and 250 ps, resulting full time range of 100, 200 and 500 ns, respectively. With better resolution but reduced time range, model 2228A is suitable for fast electron TOF measurements.

The TOF spectrometer inside the cluster chamber (Fig. 2.13) is essentially half of the one inside the coincidence machine, with similar arrangement of field plates, mu-metal, Faraday cage, grounded grid and MCP detector. By changing the combinations of voltages applied on the field plates and the MCP detector, the cluster TOF operation can be switched between ion detection mode and electron detection mode. It also has two options for the
delivery of target gases. They can be leaked in effusively via a variable leak valve, similar to the coincidence machine. Or, a skimmed atomic/molecular beam (SMB) can be directed to the interaction region from the adjacent source chamber. The SMB is produced by adiabatic gas expansion from a trumpet shaped solenoid valve (the Even-Lavie valve) with an exit diameter of 150 $\mu$m. After passing through a 1 mm diameter skimmer, the pulsed SMB propagates in the TOF chamber and intersects the laser focus with density of about $10^{16}$ particle/cm$^{-3}$, equivalent to room temperature gas density at $10^{-6}$ Torr. An ultra-cold molecular beam can be achieved by applying high backing pressure on the solenoid valve. Only a few rotational levels are populated in the ultra-cold molecular beam, making it an ideal source to study the molecular rotational wavepacket dynamics.

The signal from the cluster TOF detector, coupled out capacitively like the coincidence machine, is read out to the computer by an analog-to-digital converter (Acqiris DC252 digitizer by Agilent). This analog-to-digital converter (ADC) has 10 bits of vertical resolution and 8 GS/s maximum sampling rate, resulting in a temporal resolution of about 125 ps. The ADC is set to operate in sequence acquisition mode. The trigger for the ADC is gener-
ated from a laser pickoff by a fast photodiode with 1 ns rise time (Thorlabs DET10A). The acquisition window after each trigger signal, characterized by the total number of samples and sampling rate, can be varied depending on the operation mode of the TOF (ion mode or electron mode). It can digitize, discriminate and store the whole selected waveform at 1 kHz repetition rate. To save memory, the waveforms are summed up in two ways. The direct-summation mode sums the digitized waveforms directly and the discriminated-summation mode sums them after discriminating at a preset value. At first sight, the direct-summation mode seems like a better mode to work with since it preserves more information about the waveform and is less susceptible to pulse pileup. However, due to the nonlinear MCP pulse height response to electron/ion kinetic energy, the waveforms are distorted and do not represent electron/ion yield directly. So the discriminated-summation mode will be used throughout all experiments in this dissertation.

In ion detection mode, assuming an ion with mass \( m \) and charge \( q \) is born in the interaction region with zero kinetic energy, its travel time from extraction to detection can be shown to be:

\[
t_{\text{TOF}} = p_0 \times \sqrt{\frac{m}{q}} = t_{\text{detection}} - t_0
\]  

where \( p_0 \) is a parameter depends only on the TOF configuration, i.e. the separations and voltages between plates 4, 5, and 6 (see [113] for a detailed derivation), \( t_{\text{detection}} \) is the detected TOF and \( t_0 \) is the internal delay due to optical and/or electrical path differences between the trigger event and signal event. The values of parameters \( p_0 \) and \( t_0 \), and the relation between \( t_{\text{detection}} \) and \( \sqrt{m/q} \), could be calibrated using knowledge of isotope abundances of noble gases. If the ion possesses finite initial velocity \( v_i \) along the spectrometer axis, the TOF peak will be shifted around its static value by a finite amount depending on the value of \( v_i \). If an ion has a finite initial velocity \( v_{i\perp} \) perpendicular to the spectrometer axis, it will get lost before reaching the MCP detector due to the small solid angle of the TOF spectrometers, unless when \( v_{i\perp} \) is small enough, in which case the resolution of the TOF will be degrade due to spatial smearing effect.

Similar to the ion TOF, the electron travel time through the field free flight tube from
the interaction region to the MCP detector is directly related to the detected TOF signal with $t_{\text{TOF}} = t_{\text{detection}} - t_0$. The kinetic energy of this electron is:

$$E_{\text{ke}} = \frac{1}{2}mv^2 = \frac{1}{2}m \left( \frac{l}{t_{\text{TOF}}} \right)^2 = \frac{1}{2}m \left( \frac{l}{t_{\text{detection}} - t_0} \right)^2$$

(2.14)

where $m$ is the electron rest-mass, $v$ and $l$ are the velocity and the travel distance of the electron, respectively. So the conversion between detected TOF $t_{\text{detection}}$ and kinetic energy of the electron is solely determined by $l$ and $t_0$. $l$ is roughly the length of the spectrometer. Estimation of $t_0$ on the coincidence machine TOF can be achieved by splitting the output from the trigger photodiode and feed it also through the amplification chain of the signal, as illustrated with dashed lines in Fig. 2.12. Fine calibration of $l$ and $t_0$ is obtained by measuring the photoelectron ATI spectrum of noble gas atoms in a laser field with the TOF spectrometer. According to Eqn. 1.3, the ATI photoelectron yield forms equally separated peaks in the energy domain, with the separation being the photon energy of the laser. The photon energy is measured with a calibrated USB spectrometer (Ocean Optics USB4000). Final values of $l$ and $t_0$ can be obtained by finely adjusting around the estimated value until all the adjacent ATI peaks are separated equally by the photon energy. When converting photoelectron yields from the time domain to the energy domain, the transformation Jacobian need to be properly taking into account. With relation $E_{\text{ke}} \propto 1/t_{\text{TOF}}^2$, the Jacobian of the transformation from time domain to energy domain is proportional to $E_{\text{ke}}^{-3/2}$.

Performance of the coincidence TOF spectrometer in the low-energy region was calibrated carefully to suit the study of low-energy electrons in the LES [82]. The transfer function of the spectrometer drops gradually to zero below 0.2 eV.
Chapter 3

LIED AND FABLES: EXPERIMENT AND THEORY

As introduced in chapter 1, laser-induced electron diffraction (LIED) probes molecular structures following similar principles as conventional gas-phase electron diffraction (CED). This chapter provides an overview of basic concepts involved in CED, followed by a detailed description of theoretical and experimental aspects involved in LIED and fixed-angle broadband laser-induced electron scattering (FABLES).

3.1 Conventional electron diffraction

CED has been deployed to image molecular structures for more than a century [14,114]. In CED, a collimated electron beam with kinetic energy of hundreds of keVs is illuminated on randomly distributed molecules. The diffracted image is recorded and information of the target molecule is extracted using the independent atom model (IAM). In IAM, it is assumed that the potential of each composite atom in the molecule scatters the incident electron independently. The redistribution of atomic electrons due to molecular binding is neglected. Multiple scattering of the electron inside the molecule is also neglected. So the total scattering amplitude of the electron from the molecule is approximated as linear combination of atomic scattering amplitudes. Assuming the incident electron beam carries momentum $k_0$ along z-axis, the target molecule is constructed with $N$ number of atoms, the location of the $j^{th}$ atom is represented by a vector $R_j$, the orientation of the molecule in the lab frame is described by angle $\Omega$, the amplitude of electron wave that get scattered
to momentum $k = (k, \theta, \phi)$ is:

$$F(q; \Omega) = \sum_j f_j(\theta)e^{iqR_j},$$  \hspace{1cm} (3.1)

where $f_j$ is the complex scattering amplitude of the $j^{th}$ atom and $q = k - k_0$ is the momentum transfer. Considering only elastic scattering $|k_0| = |k|$, the diffraction intensity into angle $(\theta, \phi)$, can be calculated:

$$I(\theta, \phi; \Omega) = F \cdot F^* = \sum_{i,j} f_i \cdot f_j^* e^{iqR_i} e^{-iqR_j}$$

$$= I_A + \sum_{i\neq j} f_i \cdot f_j^* e^{iqR_{ij}} \hspace{1cm} (3.2)$$

where $R_{ij} = R_i - R_j$ is the internuclear separation between the $i^{th}$ atom and the $j^{th}$ atom and $I_A = \sum_i |f_i|^2 = \sum_i \sigma_i$ is the incoherent sum of scattering cross sections from all the atoms in the molecule. The second term in Eqn. 3.2 is the coherent sum of scattering amplitudes, called the molecular interference term (MIT). Structural information of the molecule, $R_{ij}$ is only contained in the MIT. It is usually rectified to a molecular contrast factor (MCF):

$$\zeta \equiv \frac{I}{I_A} - 1 = \frac{1}{I_A} \sum_{i\neq j} f_i \cdot f_j^* e^{iqR_{ij}} \hspace{1cm} (3.3)$$

In CED experiment, the target molecules are usually randomly oriented in space. The diffraction image can be calculated by averaging the diffraction intensity over all molecular alignment angles $\Omega$, which yields MCF:

$$\zeta(q) = \frac{\langle I(\theta) \rangle}{I_A} - 1 = \frac{1}{I_A} \sum_{i\neq j} f_i f_j^* \frac{\sin(qR_{ij})}{qR_{ij}} \hspace{1cm} (3.4)$$

Because of the isotropically distributed sample, the system now possesses cylindrical symmetry. Interestingly, as pointed out by Cohen and Fano [77], the MCF does not vanish for a uniformly distributed ensemble but decays with $1/q$. So it is common to work with a modified MCF, $q \cdot \zeta(q)$, that highlights the $\sin(qR)$ oscillation. The radial distribution

38
function is then obtained by a Fourier (sine) transform of the modified MCF [2],
\[
f(R) = \int_{0}^{q_{max}} q \zeta(q) \sin(qR) \exp(-\alpha q^2) dq
\]  \tag{3.5}
where \( \alpha \) is the damping constant. Artificial high frequency oscillations caused by the sharp cutoff at \( q_{max} \) can be smoothed out by the exponential damping term \( \exp(-\alpha q^2) \). In a typical CED experiment with 30 keV electron beam [2], the momentum transfer range from \( q_{min} = 1.4 \text{ Å}^{-1} \) to \( q_{max} = 17.4 \text{ Å}^{-1} \) for elastic scattering angle \( \theta \) from 0.9° to 11.3°. Due to the rapid drop off of the elastic DCS at larger momentum transfer \( q \), only small scattering angles are usable. Nevertheless, the \( q \)-range is large enough to yield accurate retrieval of molecular radial distributions.

Contrary to the tens-of-keV electron beams in CED, kinetic energies of scattering electrons in LIED is typically on the order of a few hundreds of eVs. Fortunately, by going to large elastic scattering angle, LIED could achieve similar momentum transfer range as CED. For example, for mid-infrared laser systems, returning electron energy of 200 eV can be routinely achieved, of which the momentum transfer range from \( q_{min} = 4 \text{ Å}^{-1} \) to \( q_{max} = 16 \text{ Å}^{-1} \) for elastic scattering angle \( \theta \) from 30° to 180°. However, the scattering electrons in LIED are extracted from the targets by the laser field and scatter under influence of the laser field, so it is not obvious that molecular structures can be extracted from such diffraction. In the following I will present necessary requirements that are imposed on the systems to use LIED as an imaging tool.

### 3.2 Three-step model – the extended version

In Chapter 1, the three-step model was introduced as:

1) An electron is liberated from the ground state of the atom to the continuum via optical tunneling ionization during the laser pulse;

2) The electron gains energy from the intense laser field in the continuum;

3) Depending on the initial condition, the electron might come back to the vicinity of parent target with excess kinetic energy and recollide with it elastically or inelastically.
The elastic recollision events give rise to LIED. Requirements are imposed on all three steps for LIED to be able to image molecular structure.

### 3.2.1 Optical tunneling ionization

**KFR theory**

The first step in LIED is optical tunneling ionization. In 1965, Keldysh originated the theory of optical tunneling ionization [30] based on the experimental observation of exponentially increasing ionization rate with peak laser intensity measured by Damon and Tomlinson [115]. He approximated the ionization process by a DC-tunneling from the initial state to the continuum. The tunneling frequency is \( \omega_t = F / \sqrt{2T_p} \), where \( F \) is the field strength and \( I_p \) is the ionization potential of the initial state. For a laser field which alternates at frequency \( \omega \), Keldysh introduced a parameter which now bears his name:

\[
\gamma = \frac{\omega}{\omega_t} = \sqrt{\frac{I_p}{2U_p}} \quad (3.6)
\]

where \( U_p = F^2 / 4\omega^2 \) is the cycle-averaged quiver energy of a free electron oscillating in this laser field. \( U_p \) is one of the most important quantities in strong field physics and it will appear frequently across the entire dissertation. It’s worth mentioning the different forms of \( U_p \). For a sinusoidal plane wave with vector potential \( A(t) = A_0 \cos(\omega t) \),

\[
U_p = \frac{A_0^2}{4} \quad (3.7)
\]

where \( A_0 \) is the maximum vector potential and note that in this form \( U_p \) does not depend on the field frequency \( \omega \). Another very useful form of \( U_p \) is

\[
U_p[\text{eV}] = 9.3 \cdot \frac{I[10^{14} \text{ W/cm}^2]}{\lambda^2[\mu\text{m}]} \quad (3.8)
\]

where \( I \) is the peak laser intensity divided by \( 10^{14} \text{ W/cm}^2 \) and \( \lambda \) is the wavelength of the laser field in \( \mu\text{m} \).

While perturbation theory describes the strong field ionization process as successive one-photon transitions through virtual states (multiphoton ionization), Keldysh approxi-
mation describes it as direct transition from the atomic ground state to a Volkov state, i.e. neglecting the influence of the Coulomb potential on the final state but taking into account exactly the effect of the laser field. The Keldysh approximation, in spite of many shortcomings, is important especially at low optical frequencies. Together with the work of Faisal [81] and Reiss [80], they are referred to as KFR theory. The KFR formalism starts from

\[ M_p = \lim_{t \to \infty, t' \to -\infty} \langle \psi_p(t) | U(t, t') | \psi_0(t') \rangle. \] (3.9)

\( M_p \) is the transition amplitude of a photoelectron from atomic ground state \( |\psi_0\rangle \) before the laser to final state with momentum \( p, |\psi_p\rangle \). \( U(t, t') \) in Eqn. 3.9 is the time-evolution operator of the Hamiltonian

\[ H(t) = H_0 + H_I(t) + V_a(r), \] (3.10)

where \( H_0 = -\frac{1}{2} \nabla^2, \nabla \equiv \partial/\partial r \), \( H_I(t) \) is the interaction between the laser field and the electron, and \( V_a(r) \) is the atomic potential.

Since \( U(t, t') \) satisfies integral equations (Dyson equations), Eqn. 3.9 can be rewritten as

\[ M_p = -i \lim_{t \to \infty} \int_{-\infty}^{t} d\tau \langle \psi_p(t) | H_I(\tau) | \psi_0(\tau) \rangle. \] (3.11)

The equation above (Eqn. 3.11) is an exact expression of the transition amplitude. However, it’s impractical to calculate Eqn. 3.11 for most systems because of the difficulty to evaluate \( |\psi_p(t)\rangle \) and \( U(t, t') \). Now consider the Hamiltonian of a free electron in the field without the atom, \( H_f(t) = H_0 + H_I(t) \). Its eigenstates of the time-dependent Schrödinger equation are known as the Volkov states and they have analytical forms \( |\psi_p^{(V)}(t)\rangle \). KFR made a crucial simplification to Eqn. 3.11 by approximating the final state \( |\psi_p(t)\rangle \) with the Volkov state \( |\psi_p^{(V)}(t)\rangle \) and neglecting the atomic potential after the interaction. This is the strong-field approximation (SFA). With SFA, the transition amplitude becomes

\[ M_p = -i \int_{-\infty}^{\infty} dt \langle \psi_p^{(V)}(t) | H_I(t) | \psi_0(t) \rangle. \] (3.12)

Note that although the exact formula 3.11 is gauge invariant, as physical process should be,
the SFA transition amplitude in Eqn. 3.12 is gauge dependent due to the approximation. Among the KFR developers, while Keldysh [30] chose the length gauge which led to an intuitive tunneling picture, Faisal [81] and Reiss [80] worked under the velocity gauge which yielded a cleaner result but did not involve tunneling. For a comparison of various forms see [116]. As is pointed out in that paper [116], the Keldysh treatment usually contains one more approximation to the problem, $\omega \ll I_p$, i.e. the photon energy is much less than the binding potential of the system. This dissertation mainly deals with systems with high binding energy ($I_p > 10$ eV) and mid-infrared wavelength ($\hbar \omega \approx 0.6$ eV), so the high multiphoton order requirement is always fulfilled and thus we mainly focus on the length-gauge Keldysh theory. But it should be kept in mind that different forms of the Hamiltonian should yield the same physics. See Appendix B for more information about the velocity gauge and length gauge in strong field physics.

Following Keldysh procedure to treat photoionization of ground state atomic hydrogen in a monochromatic field [30], when the tunneling frequency $\omega_t$ is much smaller than the laser frequency $\omega$ ($\gamma \gg 1$), the ionization rate $w$ is proportional to the intensity $I$ to the power of number of photons absorbed $n$, $w \propto I^n$, which coincides with results from the perturbative multiphoton ionization (MPI) framework. When the tunneling frequency $\omega_t$ is much bigger than the laser frequency $\omega$ ($\gamma \ll 1$), ionization rate $w$ reduces to the DC-tunneling rate by field strength $F$, $w \propto 1/Fe^{-2/3F}$. An illustration of MPI and optical tunneling ionization can be found in Fig. 3.1.
In general, the time-dependent ground state wave function of an atom is expressed as \( |\psi_0(t)\rangle = e^{iI_p t} |\psi_0\rangle \). Within length gauge and dipole approximation, the Volkov states are expressed as (See Appendix B for more details)

\[
|\psi_p^{(V)}(t)\rangle = |p, t\rangle e^{-iS_p(t)},
\]

(3.13)

where

\[
\langle r| p, t \rangle = (2\pi)^{-3/2} e^{i[p + A(t)] \cdot r},
\]

(3.14)

\[
S_p(t) = \frac{1}{2} \int_0^t d\tau [p + A(t)]^2,
\]

(3.15)

and the interaction \( H_I(t) = r \cdot F(t) \). Eqn. 3.12 can be written as

\[
M_p = -i \int_0^{\tau_d} dt \langle p, t | r \cdot F(t) | \psi_0 \rangle e^{i[I_p t + S_p(t)]},
\]

(3.16)

where the laser is turned on at time \( t = 0 \) and ends at time \( t = \tau_d \), vector potential is chosen such that \( A(t) = 0 \) for \( t \leq 0 \) and \( t \geq \tau_d \). The integral 3.16 can be calculated numerically in the current form. For a system that satisfy the tunneling condition \( (\gamma \ll 1) \), the saddle-point approximation could be employed [28] to gain more physical understanding. The stationary phase point \( t_s \) of the integrand in Eqn. 3.16 can be found by solving

\[
\frac{d}{dt} [I_p t + S_p(t)] = I_p + \frac{1}{2} [p + A(t)]^2 = 0.
\]

(3.17)

The integral in Eqn. 3.16 becomes summation over saddle points \( t_s \) [117]

\[
M_p^{(SP)} = -i \sum_s \left\{ \frac{2\pi i}{F(t_s) \cdot [p + A(t_s)]} \right\}^{1/2} \langle p, t_s | r \cdot F(t_s) | \psi_0 \rangle e^{i[I_p t_s + S_p(t_s)]},
\]

(3.18)

Eqn. 3.17 for EM fields, \( A(t) \), with forms more complex than the monochromatic fields usually can not be solved analytically. However, the numerical solutions of it still contain a great deal of physical insight to the problem. It identifies the instants of time which dominates the ionization process and the contribution of each of them can be calculated with Eqn. 3.18. The solution of Eqn. 3.17 is a complex number. The real part of it can be interpreted as the ionization time, \( 0 \leq Re(t_s) < \tau_d \) while the imaginary part can be related
to a tunneling time in the length gauge [118].

The KFR SFA treatment can be extended to molecules, for more details about the molecular strong-field approximation (MSFA) see [119] and references therein.

**PPT and ADK**

After the tunneling proposal by Keldysh and before the above-mentioned KFR’s SFA reach its final form, Perelomov, Popov and Terent’ev (PPT) developed a method to calculate ionization probability by an alternating electric field from three-dimensional atom bounded with a short-range potential in 1966 [120]. Their method was later implemented and extended by Ammosov, Delone and Krainov (ADK) to more complex atomic systems in 1986 [121]. The ionization rate of atomic systems calculated with the simple form ADK formula matches experimental data to their exponential behavior with field intensities, which validates the tunneling assumption.

Starting from the time-dependent Schrödinger equation, PPT derived the cycle-averaged ionization probability in a short range potential from a level with binding energy $I_p$, orbital quantum number $l$ and magnetic quantum number $m$ as [44]:

$$w_{lm}(F, \omega) = |C_\kappa|^2 G_{lm} A_m(\omega, \gamma) I_p \sqrt{\frac{6}{\pi}} \left( \frac{F(1 + \gamma^2)^{1/2}}{2F_0} \right)^{|m|+3/2} \exp\left(-\frac{2F_0}{3F} g(\gamma)\right)$$  \hspace{1cm} (3.19)

where $F$ and $\omega$ are the maximum field strength and angular frequency of the alternating laser field $F(t) = F \cos(\omega t)$, $I_p$ is the ionization potential of the atom, $F_0 = (2I_p)^{3/2}$, $\gamma = \omega F_0^{1/3}/F$ is the Keldysh parameter. The coefficients $G_{lm}$ and $g(\gamma)$ are

$$G_{lm} = \frac{(2l + 1)(l + |m|)}{2|m||m|!(l - |m|)!},$$  \hspace{1cm} (3.20)

$$g(\gamma) = \frac{3}{2\gamma} \left[ \left(1 + \frac{1}{2\gamma^2}\right) \ln(\gamma + \sqrt{\gamma^2 + 1}) - \frac{\sqrt{1 + \gamma^2}}{2\gamma} \right]$$  \hspace{1cm} (3.21)

The term $A_m(\omega, \gamma)$ is evaluated by

$$A_m(\omega, \gamma) = \frac{4}{\sqrt{3\pi}} \frac{1}{|m|!} \frac{\gamma^2}{1 + \gamma^2} \sum_{q \geq \alpha hr} \exp\left[-2\alpha(q - \nu)\right] w_m \left(\sqrt{\beta(q - \nu)}\right)$$  \hspace{1cm} (3.22)
where

\[ \alpha = 2 \left( \frac{1}{\sinh \gamma} - \frac{2 \gamma}{\sqrt{1 + \gamma^2}} \right), \quad (3.23) \]

\[ \nu = \frac{I_p}{\omega} \left( 1 + \frac{1}{2 \gamma^2} \right) = \frac{I_p + U_p}{\omega}, \quad (3.24) \]

\[ \beta = \frac{2 \gamma}{\sqrt{1 + \gamma^2}}, \quad (3.25) \]

\[ w_m(x) = e^{-x^2} \int_0^x e^{y^2} (x^2 - y^2)^{|m|} \, dy = \frac{x^{2|m|+1}}{2} \int_0^1 \frac{e^{-x^2 t}|m|}{\sqrt{1-t}} \, dt \quad (3.26) \]

sums over all integers larger than \( q_{thr} = (I_p + U_p)/\omega \), the minimum number of photon required to lift an electron from ground state to the Volkov state. Formula 3.19 describes the ionization rate in both MPI (\( \gamma \gg 1 \)) and optical tunneling ionization (\( \gamma \ll 1 \)). Under tunneling condition \( \gamma \ll 1 \), it can be shown that \( A_m(\omega, \gamma) \approx 1 \) and \( g(\gamma) \approx 1 \), the ionization rate 3.19 becomes

\[ w_{lm}(F, \omega) = |C_{n^* l^*}|^2 G_{lm} I_p \sqrt{\frac{6}{\pi}} \left( \frac{F}{2F_0} \right)^{|m|+3/2} \exp\left(-\frac{2F_0}{3F}\right) \quad (3.27) \]

The exact value of coefficient \( C_{n^* l^*} \), where \( \kappa = \sqrt{2T_p} \), can be found only in the simplest cases, e.g. for a ground-state hydrogen atom \( C_{H0} = 2 \). For arbitrary atomic levels, Ammosov, Delone and Krainov, known as ADK, derived the constant \( C_{n^* l^*} \) by replacing the principle quantum number and orbital quantum number \( n \) and \( l \) with the effective ones \( n^* \) and \( l^* \) for the asymptotic form the the radial wave function of an electron in a Coulomb potential [121],

\[ |C_{n^* l^*}|^2 = \frac{2^{2n^*}}{n^* \Gamma(n^* + l^* + 1) \Gamma(n^* - l^*)}. \quad (3.28) \]

where the effective principle quantum number \( n^* \equiv Z/\sqrt{2T_p}, Z \) is the asymptotic charge of the atomic residue, the effective orbital quantum number \( l^* = n^* - 1 \). Furthermore, ADK extended PPT theory to treat optical tunneling ionization (\( \gamma \ll 1 \)) of complex atoms and atomic ions. The cycle-averaged tunneling ionization rate is:

\[ w_{ADM} = |C_{n^* l^*}|^2 G_{lm} I_p \sqrt{\frac{6}{\pi}} \left( \frac{2F_0}{F} \right)^{2n^* - |m| - 3/2} \exp\left(-\frac{2F_0}{3F}\right). \quad (3.29) \]

Another useful form of the ADK rate is the instantaneous stationary tunnel ionization rate
at the instant when the field strength is \( F = F(t) \)

\[
w_{ADK}^{\text{(inst.)}} = |C_{n^*l}|^2 G_{lm} I_p \left( \frac{2F_0}{F} \right)^{2n^* - |m| - 1} \exp \left( - \frac{2F_0}{3F} \right).
\] (3.30)

Numerical coefficients for commonly used noble gas atoms can be found in Table 3.1. As evaluated by Ilkove et al. [122], use of the ADK formula Eqn. 3.29 should be restricted to regime where the Keldysh parameter \( \gamma \leq 0.5 \) to avoid significant error.

| E.Config. | \( I_p \) (eV) | \( F_0 \) (a.u.) | \( n^* \) | \( |C_{n^*l}|^2 \) | l, m | \( G_{lm} \) |
|-----------|--------------|----------------|------|----------------|----|-------|
| He \( 1s^2 \) | 24.587 | 2.43 | 0.74 | 4.26 | 0, 0 | 1 |
| Ne \( [He]2s^22p^6 \) | 21.564 | 2.00 | 0.79 | 4.24 | 1, 0 | 3 |
| Ar \( [Ne]3s^23p^6 \) | 15.759, 15.936 (\( J = 3/2, 1/2 \)) | 1.24 | 0.93 | 4.11 | 1, 0 | 3 |
| Kr \( [Ar]3d^{10}4s^24p^6 \) | 13.999, 14.665 (\( J = 3/2, 1/2 \)) | 1.06 | 0.98 | 4.03 | 1, 0 | 3 |
| Xe \( [Kr]4d^{10}5s^25p^6 \) | 12.129, 13.436 (\( J = 3/2, 1/2 \)) | 0.84 | 1.06 | 3.88 | 1, 0 | 3 |

*Table 3.1: ADK parameters for ground state noble gas atoms reproduce from [44]*

The ADK formula represents tunneling ionization rate integrated over all values of the energy and directions of ejected photoelectrons. The tunneling ionization rate for an electron with momentum \( p \) by linearly polarized field can be obtained directly under tunneling condition using adiabatic approximation of quantum mechanics ([123] and references therein):

\[
w(p_\parallel, p_\perp) = w(0) \exp \left[ - \frac{\omega^2}{3} \left( \frac{\kappa}{F} \right)^3 \frac{p_\parallel^2}{F} - \frac{\kappa}{F} p_\perp^2 \right],
\] (3.31)

where \( \omega \) is the frequency of the field, \( \kappa = \sqrt{2I_p} \), \( I_p \) is the ionization potential, \( F \) is the strength of the field, \( p_\parallel \) and \( p_\perp \) are the momentum parallel and perpendicular to field direction, respectively. The exact form of the prefactor \( w(0) \) was obtained by Krainov [124] using KFR S-matrix method and taking into account the Coulomb correction according to semi-classical perturbation theory, up to exponential accuracy:

\[
w(0) \propto \frac{p_\omega^2}{F^{2n^*+1}} \exp \left( - \frac{2\kappa^3}{3F} \right).
\] (3.32)

As pointed out in [123], integrating Eqn. 3.31 would yield ADK formula 3.29, as expected.
The width of photoelectron momentum distribution at 1/e value near the tunnel exit can be derived from Eqn. 3.31

\[ \Delta p_\parallel \approx \sqrt{3 F^3/\omega^2 \kappa^3}, \]  
(3.33)
\[ \Delta p_\perp \approx \sqrt{F/\kappa}. \]  
(3.34)

MO-ADK

The tunneling ionization rate is not only proportional to the penetration probability through the barrier but also proportional to the electron density near the tunnel entrance. The ionization rate of a molecule should depend on the spatial orientation of the molecule with respect to the direction of field since electron charge density distribution in a molecule is not isotropic, contrary to the case of atoms. Evaluation of molecular tunneling ionization rate is a challenging job in general. For the case of diatomic molecules and simple linear triatomic molecules, Tong and Lin [78] developed a method to calculate the tunneling ionization rate with same idea as ADK, which they called molecular-ADK (MO-ADK). They expanded the molecular wave function at large distance where the tunnel occurs to a summation of partial waves

\[ \psi_n^m(r) = \sum_l F_{lm}(r) Y_{lm}(\hat{r}) \]  
(3.35)

where \( Y_{lm}(\hat{r}) \) is the usual spherical harmonics for an electron with principle quantum number \( n \), angular quantum number \( l \) and magnetic quantum number \( m \), quantization axis along internuclear direction. The radial wave function in the asymptotic region can be expressed as

\[ F_{lm}(r \to \infty) \approx C_{lm} r^{3 \kappa - 1} e^{-\kappa r} \]  
(3.36)

where \( \kappa = \sqrt{2I_p} \), \( I_p \) is the ionization potential, \( Z \) is the asymptotic charge as defined in ADK. Then the ionization rate for field direction along the intermolecular distance can be found following the same procedure as [125]. The ionization rate for a molecule with internuclear axis at angle \( \mathbf{R} \) with respect to the field direction is calculated through a
rotation and can be expressed as

$$w(F, R) = \sum_{m'} B^2(m') \frac{1}{\kappa^{2Z/\kappa-1}} \left( \frac{2\kappa^3}{F} \right)^{2Z/\kappa-|m'|-1} e^{-2\kappa^3/3F}$$  \hspace{1cm} (3.37)$$

where

$$B(m') = \sum_l (-1)^{m'} C_{lm'} D_{l,m',m}(R) \sqrt{G_{lm'}/2}$$  \hspace{1cm} (3.38)$$

with $D_{l,m',m}(R)$ being the rotation Wigner D-matrix and $\sqrt{G_{lm'}}$ same as defined in 3.20. In the early MO-ADK paper [78], coefficients $C_{lm}$ were obtained by fitting wave function 3.35 to the ones calculated with other quantum chemistry codes. However, these codes were not suitable to determine the asymptotic behavior of the wave function at large distances. Zhao et al. [126] derived the molecular wave function with good asymptotic behavior by solving the time-independent Schrödinger equation. It’s worth noting that their improved result do not differ much from Tong et al. [78] for the molecule-of-interest in this dissertation, N\textsubscript{2} and O\textsubscript{2}, as shown in Fig. 3.2. They also compared the MO-ADK result with the molecular strong-field ionization (MSFA) result and found general agreement in the relative alignment dependent ionization rate.
3.2.2 Evolution of the tunneled electron

After optical tunneling ionization, the next step in LIED is field acceleration and elastic rescattering. Under strong-field approximation, dynamics of the tunneled electron is governed by the laser field. As introduced in Chapter 1, the alternating electric field drives the photoelectron in an oscillatory motion during which the electron might revisit the proximity of the parent ion. This re-encounter will lead to elastic and inelastic electron rescattering events. High-order ATI (HATI) [54, 55] discovered in the 1990s are results of these elastic rescattering processes. The SFA theory can be extended to an improved version\(^4\) to treat the rescattering events. However, while the improved SFA reproduced experimental HATI spectra for atoms (the agreement is qualitative in general, see [127] and references therein), it became complicated quickly for molecules [119].

Another simple yet powerful approach to understand the HATI spectra is through analyzing the classical motion of the tunneled electron [34, 53]. It considers an electron that tunnels into the field at time \(t_0\). Within the strong-field approximation, influence of the atomic (molecular) potential or atomic (molecular) ion potential is neglected after tunneling ionization. The electrons then undergo oscillatory motion driven by the alternating field. Some of them drift to the detector without subsequent interaction with the parent ion, called the “direct electrons”. Others might revisit the plane of the parent ion and rescatter, called the “rescattering electrons”. For direct electrons and rescattering electrons after rescattering, the canonical momentum of the electron in the field \(p^{(c)} = p - A\) is a constant of motion since the influence of the core potential is neglected. For direct electrons we have

\[
p(t_0) - A(t_0) = p(t_d) - A(t_d),
\]

where \(t_0\) is the time of birth and \(t_d\) is the time of detection. The vector potential at detection can be taken as zero in an experiment, i.e. \(A(t_d) = 0\). Initial momentum of the tunneled electron can also be taken as zero, i.e. \(p(t_0) = 0\), since momentum distribution of the tunneled electron centers at zero (Eqn. 3.33). The detected momentum of this direct\(^4\)

\(^4\)The improved version of SFA is called ISFA or SFA2 by various others, see [127] and references therein.
electron is
\[ p(t_d) = -A(t_0). \] (3.40)

So the detected energy of this direct electron is
\[ E(t_d) = p(t_d)^2/2 = A(t_0)^2/2 \] (3.41)

Assume the field is monochromatic with amplitude \( F(t) = F \sin(\omega t) \), where \( \omega \) is the frequency of the field. The vector potential of the field is \( A(t) = -F/\omega \cos(\omega t) \) and the ponderomotive energy of an electron in this field is \( U_p = F^2/4\omega^2 \). Then we have
\[ E(t_d) = \frac{F^2}{2\omega^2} \cos(\omega t_0)^2 = 2U_p \cos(\omega t_0)^2, \] (3.42)

which means direct electrons are detected with kinetic energy from 0 to \( 2U_p \) depending on the birth phase \( \omega t_0 \).

In the case of rescattering electrons, the time \( t_r \) when they return to the origin can be found by solving equation of motion
\[ \ddot{x}_e = -F \sin(\omega t). \] (3.43)

The initial position of the tunneled electron is often taken to be zero, \( x(t_0) = 0 \), ignoring the small “exit-of-tunnel” offset \( r_0 \approx I_p/F \). The initial momentum is also taken to be zero, \( \dot{x}(t_0) = 0 \), as mentioned earlier. Then the solution is
\[ \dot{x}_e(t) = \frac{F}{\omega} \cos(\omega t) - \frac{F}{\omega} \cos(\omega t_0) \] (3.44)

and
\[ x_e(t) = \frac{F}{\omega^2} \sin(\omega t) - \frac{F}{\omega} \cos(\omega t_0)t - \frac{F}{\omega^2} \sin(\omega t_0) + \frac{F}{\omega} \cos(\omega t_0)t_0, \] (3.45)

with \( x_e(t_0) = 0 \) and \( \dot{x}_e(t_0) = 0 \). The time when the electron returns to the ionic core can be found by setting \( x_e(t_r) = 0 \), which gives
\[ \sin(\omega t_r) - \sin(\omega t_0) = \omega(t_r - t_0) \cos(\omega t_0), \] (3.46)

which can be evaluated numerically to obtain \( t_r(t_0) \) for each \( t_0 \). Another intuitive way to
calculate $t_r(t_0)$ is to work under the non-inertial Kramers-Henneberger (K-H) frame [128] which moves in the lab frame with displacement

$$x_F^{(K-H)}(t) = \frac{F}{\omega^2} \sin(\omega t). \quad (3.47)$$

In the K-H frame, the stationary ion now moves with

$$x_i^{(K-H)} = 0 - x_F^{(K-H)}(t) = -\frac{F}{\omega^2} \sin(\omega t), \quad (3.48)$$

and the electron motion is now

$$x_e^{(K-H)}(t) = x_e(t) - x_F^{(K-H)}(t) = -\frac{F}{\omega} \cos(\omega t_0)t - \frac{F}{\omega^2} \sin(\omega t_0) + \frac{F}{\omega} \cos(\omega t_0) t_0. \quad (3.49)$$

Returning time $t_r$ can be found graphically in the K-H frame as the time when the straight electron trajectory intersects the sinusoidal ion trajectory, as illustrated in the top panel of Fig. 3.3. Then the kinetic momentum of the returning electron in the lab frame is

$$p_r(t_0) = \dot{x}_e(t_r) = \frac{F}{\omega} [\cos(\omega t_r) - \cos(\omega t_0)]. \quad (3.50)$$

So the kinetic energy of the electron at return is

$$E_r(t_0) = \frac{p_r(t_0)^2}{2} = \frac{F^2}{2\omega^2} [\cos(\omega t_r) - \cos(\omega t_0)]^2 \quad \text{[128]}$$

$$= 2U_p [\cos(\omega t_r) - \cos(\omega t_0)]^2. \quad (3.51)$$

Numerical solution of $E_r(t_0)$ is shown in the lower panel of Fig. 3.3. The maximum return energy is $E_r(t_0^{(m)}) = 3.17U_p$, which is reached by electrons born at phase $\omega t_0^{(m)} = 1.88$ radian. Electrons returning with energies below the maximum value have at two degenerate trajectories. For example, degenerate electron trajectories with return energy $E_r(t_0 = 2U_p$ are plotted as $x_e^{(K-H)}(t_0^{(l)}) \rightarrow x_e^{(K-H)}(t_1^{(l)})$ and $x_e^{(K-H)}(t_0^{(s)}) \rightarrow x_e^{(K-H)}(t_1^{(s)})$ in the upper panel of Fig. 3.3 within K-H frame. They are conventionally called the long trajectories and short trajectories according to the time of travel in the field, $t_1^{(l)} - t_0^{(l)} > t_1^{(s)} - t_0^{(s)}$. We’ll discuss more about the degeneracy of the long and short trajectories in the next session. For the following discussion, let’s take the long trajectory as an example without losing generality.
Figure 3.3: Solution of the return time in the K-H frame for electron motion in electric field with field strength $F(t) = F \sin(\omega t)$ (gray line), vector potential $A(t) = A \cos(\omega t)$ (magenta line). The trajectory of ion and electrons in K-H frame are represented in red line and blue lines. $t_0^{(m)}$ and $t_1^{(m)}$ are birth time and return time of electrons with maximum return energy $E_r^{(m)} = 3.17U_p$. $t_0^{(s)}$, $t_1^{(s)}$, and $t_0^{(l)}$, $t_1^{(l)}$ are birth time and return time of two degenerate trajectories with electron return energy $E_r = 2U_p$. The bottom panel shows the relation between electron kinetic energy at return and the phase of birth. The right axis on it shows the corresponding back scatter energy. The green curve in the bottom panel is calculated ADK rate (Eqn. 3.29) for argon ($I_p = 0.58 \text{ a.u.}$) at field strength $F = 0.1 \text{ a.u.}$
Consider only the elastic scattering events of the recolliding electrons from the parent ion\(^5\). Let \(p(t_{r-})\) and \(p(t_{r+})\) be the momentum of the electron at the instant right before and after the elastic rescattering, so \(|p(t_{r-})| = |p(t_{r+})| = p(t_r)\). Canonical momentum of the system is constant of motion before and after recollision,

\[
p(t_{r-}) - A(t_r) = p(t_0) - A(t_0),
\]

\[
p(t_d) - A(t_d) = p(t_{r+}) - A(t_r).
\]

As established previously, \(p(t_0) = 0\) and \(A(t_d) = 0\), so we have

\[
p(t_{r-}) = A(t_r) - A(t_0) \implies p(t_{r-}) = A(t_r) - A(t_0),
\]

\(^5\) The recolliding electron can scatter on the parent ion elastically or inelastically. Here we consider only the elastic scattering events since their cross sections are larger than the inelastic ones in experimental conditions presented through the current dissertation. More details on this in the next session.
and the detected momentum is

\[ p(t_d) = p(t_{r+}) - A(t_r) \]

\[ = \left[ (p(t_r) \cos \theta_r - A(t_r)) \hat{r}_\parallel + p(t_r) \sin \theta_r \hat{r}_\perp \right] \]

\[ = \left\{ [A(t_r) - A(t_0)] \cos \theta_r - A(t_r) \right\} \hat{r}_\parallel + [A(t_r) - A(t_0)] \sin \theta_r \hat{r}_\perp. \]  

(3.52)  

(3.53)

where \( \theta \) is the detected angle, \( \theta_r \) is rescattering angle, \( \hat{r}_\parallel \) and \( \hat{r}_\perp \) are unit vectors parallel and perpendicular to the field polarization direction. In the case of backscattering \( (\theta_r = \pi) \), the detected momentum is only along \( \hat{r}_\parallel \) with amplitude being

\[ p(t_{d_{(bs)}}) = -2A(t_r) + A(t_0). \]

So the detected backscatter energy is

\[ E(t_{d_{(bs)}}) = p(t_{d_{(bs)}})^2/2 = [2A(t_r) - A(t_0)]^2/2 \]

\[ = \sqrt{2U_p} |2 \cos(\omega t_r) - \cos(\omega t_0)|^2 \]  

(3.54)

The maximum detected energy for backscattered electrons is \( E_r(t_{0_{(bs)}}) = 10U_p \), which is reached by electrons born at phase \( \omega t_{0_{(bs)}} = 1.83 \) radian. The relation between \( A(t_r) \), \( p(t_{r-}) \) and \( p(t_{r+}) \) for a general rescatter angle \( \theta_r \) is illustrated in Fig. 3.4. In the two dimensional momentum space, detected momentum of electrons elastically rescattered into different angles at time \( t_r(t_0) \) form a circle with radius \( p_r(t_0) \) displaced from the origin by \( -A_r(t_0) \), as illustrated with red lines in Fig. 3.4. If the recolliding electrons were a plane wave, one would be able to get the elastic scattering differential cross section of the parent ion from the yield along the red circles. However, this is not generally true. Next we’ll address the relation between classical description of the electron trajectories and the quantum nature of the electron wave packet.
3.2.3 The returning electron wave packet

The semi-classical recollision model demonstrated its power in many ways. For example, it successfully explained the cutoff behaviors in HHG and I HATI, the angular structure in HATI and the relation between sequential and non-sequential multiple ionization. Fig. 3.5 shows photoelectron spectra along polarization direction of Ar ($I_p = 15.7$ eV) in laser fields with intensity of $8 \times 10^{13}$ W/cm$^2$ and wavelengths $\lambda = 0.8 \mu m$, $1.3 \mu m$, $2.0 \mu m$, $3.6 \mu m$. Corresponding ponderomotive energies and Keldysh parameter of the systems are also shown on the figure. Fig. 3.5 shows that the photoelectron spectra are becoming more and more classical as Keldysh parameter reduces from $\gamma = 1.3$ with wavelength $\lambda = 0.8 \mu m$ (top solid curve) to $\gamma = 0.3$ with wavelength $\lambda = 3.6 \mu m$ (bottom dotted curve). The photoelectron spectrum from $3.6 \mu m$ laser field shows a smooth curve with distinctive classical $2U_p$ and $10U_p$ cutoffs while the one from $0.8 \mu m$ laser field shows a curve with rich features but
almost no clear cutoff. This indicates that the classical model works best for systems deep in the tunneling regime, especially for systems with Keldysh parameters less than 0.5.

In general, a returning electron can be represented with a wave packet \( W(p_r, \theta_r) \) (cylindrical symmetry), where \( p_r \) and \( \theta_r \) are the returning momentum and rescattering angle of the electron. Since we only deal with core penetrating collisions with small impact parameters, as shown from TDSE and SFA calculations [131], spatial variation of the returning electron wave packet near the target ion can be neglected. The returning wave packet can then be written as \( W(p_r) \). According to the quantitative rescattering theory (QRS), a detected photoelectron spectrum \( D(p, \theta) \) can be factorized as the product of the returning wave packet \( W(p_r) \) and the electron-ion laser-free collision differential cross section (DCS) of the ionic target \( \sigma(p_r, \theta_r) \)

\[
D(p_d, \theta) = W(p_r)\sigma(p_r, \theta_r).
\] (3.55)

The relation between detected momentum \( p_d \), detected angle \( \theta \), rescattering momentum \( p_r \) and rescattering angle \( \theta_r \) can be found in Eqn. 3.52. To experimentally extract the behavior of the returning wave packet \( W(p_r) \), we measure the photoelectron spectra of noble gas atoms in mid-infrared laser fields \( D(p_d, \theta) \) and calculate the field-free electron-ion collision DCS. Experimental details can be found in the next session. Eqn. 3.55 states that \( W(p_r) \) is an overall normalization factor at fixed \( p_r \). Density of the returning electron wave packet as a function of returning momentum, \( W(p_r) \), could be obtained by scanning \( p_r \). In the bottom right panel of Fig. 3.6 is plotted the extracted returning wave packet for different noble gas atoms at various laser parameters. Expressed in \( p_r/A_0 \) units, the returning electron wave packet shows universal scaling:

\[
W(p_r/A_0) \propto (p_r/A_0)^{-2.6\pm0.3}.
\] (3.56)

The returning electron wave packet is independent of laser parameters and target species, which is consistent with the assumptions in QRS. This universality poses significant importance in the LIED imaging framework since it means that, the returning wave packet, although induced by the laser field from the target itself, behaves like an external electron
Figure 3.6: Photoelectron spectrum of argon at 2 \( \mu \text{m} \), extracted differential cross section and returning wave packet Reproduced from [75]. The top panel shows the detected electron yield in two dimensional momentum space. The laser intensity is \( 2 \times 10^{14} \text{ W/cm}^2 \). The bottom left panel shows a series of differential cross sections (DCS’) with 150 eV incident electron obtained with different approaches. The red open circle is the e-Ar\(^+\) DCS extracted from HATI spectra at 2 \( \mu \text{m} \) and \( 2.35 \times 10^{14} \text{ W/cm}^2 \) [75]. The green filled circle is e-Ar DCS from electron gun experiment [130]. The blue line and dashed magenta line are theoretical e-Ar\(^+\) DCS and e-Ar DCS respectively. The bottom right panel shows extracted returning wave packet \( W(p_r) \) in scaled \( p_r/A_0 \) under various conditions (\( A_0 \) is the maximum value of the vector potential at each laser intensity):

<table>
<thead>
<tr>
<th>Target</th>
<th>wavelength in ( \mu \text{m} )</th>
<th>intensity in TW/cm(^2)</th>
<th>( \gamma )</th>
</tr>
</thead>
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<td>red filled circles</td>
<td>Ar 1.7</td>
<td>208</td>
<td>0.37</td>
</tr>
<tr>
<td>green solid squares</td>
<td>Ar 2.0</td>
<td>200</td>
<td>0.32</td>
</tr>
<tr>
<td>blue crosses</td>
<td>Ar 2.0</td>
<td>215</td>
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<td>Ar 2.3</td>
<td>98</td>
<td>0.38</td>
</tr>
<tr>
<td>orange solid inverted triangles</td>
<td>Kr 2.0</td>
<td>180</td>
<td>0.32</td>
</tr>
<tr>
<td>maroon solid right triangles</td>
<td>Kr 2.3</td>
<td>98</td>
<td>0.38</td>
</tr>
<tr>
<td>cyan solid diamonds</td>
<td>Xe 2.0</td>
<td>72</td>
<td>0.41</td>
</tr>
</tbody>
</table>
beam in CED experiment. It’s worth emphasizing again that the Keldysh parameter $\gamma$ in all the systems are below 0.5, which ensures that optical tunneling ionization is the dominating ionization mechanism, a prerequisite for LIED.

Another important conclusion that can be drawn from the above experiments is that the long range Coulomb potential can be neglected for returning electrons with high kinetic energies. In the bottom left panel of Fig. 3.6 is shown the e-Ar$^+$ DCS extracted from experimental HATI spectrum at 2 $\mu$m and $2.35 \times 10^{14}$ W/cm$^2$ (red open circle) [75] and the e-Ar DCS from electron gun experiment (green filled circle) [130] for incident electron beam with 150 eV kinetic energy. The two curves are essentially the same, agreeing the theoretically calculated e-neutral (dashed magenta line) and e-ion (solid blue line) DCS. This is a natural result of hard collisions promoted by the long wavelength laser: the high energy electron penetrates into the short range of the potential, thus the DCS of the atomic cation is the same as that of the neutral. It signifies that the interaction between the electron and molecular ion will be dominated by electron diffraction from the well-localized, strong short-range atomic-like potential while the delocalized, valence electrons will remain transparent, another prerequisite for LIED.

### 3.3 LIED: N$_2$ and O$_2$ results

So far we have established that the returning electron wave packet in mid-infrared laser fields can be used for imaging similar to external electron beams in CED. So we can follow similar procedure as CED to extract molecular structures from LIED.

#### 3.3.1 Molecular contrast factor

Recall the CED procedure introduced in the beginning of this chapter. For simplification, consider a homo-nuclear diatomic molecule that is fixed in space at alignment angle $\theta_a$ with respect to the returning electrons (Fig. 3.7). The total scattering intensity in equation Eqn. 3.2 is reduced to:

$$\sigma_M = 2\sigma_A + \sigma_A(e^{iq\cdot R} + e^{-iq\cdot R}),$$  \hspace{1cm} (3.57)
where $\sigma_A$ is the differential cross section of each atomic site, $R$ is the internuclear separation vector and $q = p'_r - p_r$ is the momentum transfer with $p_r$ and $p'_r$ being the momentum of the recollision electron right before and after rescattering, respectively. For elastic rescattering, $|p_r| = |p'_r| = p_r$. The MCF is now

$$\zeta = \frac{\sigma_M}{2\sigma_A} - 1 = \frac{1}{2} (e^{iqR} + e^{-iqR}) \cos[qR \sin(\theta_r/2 - \theta_a)] \quad (3.58)$$

where $\theta_r$ is the rescattering angle. Using relation $q = 2p_r \sin(\theta_r/2)$, the MCF can also be written as

$$\zeta = \cos[2p_r R \sin(\theta_r/2) \sin(\theta_r/2 - \theta_a)]. \quad (3.59)$$

For molecules aligned parallel to the laser field, $\theta_a = 0$ and $\zeta \sim \cos[2p_r R \sin^2(\theta_r/2)]$. For molecules aligned perpendicularly to the laser field, $\theta_a = \pi/2$ and $\zeta \sim \cos[p_r R \sin(\theta_r)]$. For molecular ensemble with arbitrary alignment distribution, the MCF is averaged over all angles weighted by the alignment distribution function

$$\langle \zeta \rangle(p_r, \theta_r) = \int_0^{\pi} \sin\theta_a d\theta_a \zeta(p_r, \theta_r, \theta_a) N(\theta_a), \quad (3.60)$$

where $N(\theta_a)$ is the normalized alignment distribution function seen by the returning electron and $\int_0^{\pi} \sin\theta_a d\theta_a N(\theta_a) = 1$. For uniform distribution, $N(\theta_a) = 1/2$, Eqn. 3.60 gives $\zeta \propto \sin(qR)/qR$, same as Eqn. 3.4. However, since LIED returning electrons come from tunneling ionization of the molecule, even for an ensemble of randomly aligned molecules, $N(\theta_a)$ is not uniform. Instead, it is determined by the alignment dependent ionization rate. Ignoring the small rotation of the molecule from tunneling ionization to recollision,
the distribution function can be treated as the alignment dependent tunneling ionization rate of the molecule. Depending on the shape of the molecular orbital, it can be quite far from uniform. For example, according to MO-ADK (molecular-ADK, introduced earlier in this chapter), the ionization rate of N$_2$ at $\theta_a = 0$ can be more than ten times larger than at $\theta_a = \pi/2$ (Fig. 3.2). The alignment dependent molecular tunneling ionization rate of simple diatomic molecules can be calculated with MO-ADK. For a more general treatment, molecular alignment is needed, which will be presented later this chapter.

### 3.3.2 LIED: N$_2$ and O$_2$ results

For proof-of-principle experiments, we performed LIED measurements on unaligned N$_2$ and O$_2$ [76]. Since alignment dependent ionization rate $N(\theta_a)$ of N$_2$ and O$_2$ can be calculated reliably with MO-ADK, the integral in Eqn. 3.60 can be evaluated to get $\langle \zeta \rangle (p_r, \theta_r)$. Follow convention of CED and write MCF as a function of momentum transfer $q$ at fixed returning momentum $p_r$, $\langle \zeta \rangle (q)$, one have

$$\langle \zeta \rangle (q) = \frac{\bar{\sigma}_{M}^{(exp.)}(q)}{2\sigma_{A}^{(the.)}(q)} - 1,$$

(3.61)

where $q = 2p_r \sin(\theta_r/2)$. Experimental molecular DCS $\bar{\sigma}_{M}^{(exp.)}(q)$ is retrieved from electron momentum distribution by tracing the elastic rescatter circle at fixed return momentum $p_r$ with QRS principle, $I(p_d) = W(p_r)\sigma_{M}^{(exp.)}(q)$, the same as before. Atomic DCS $\sigma_{A}^{(the.)}(q)$ comes from theoretical calculations with Yukawa potential $V(r) = Ze^{-\alpha r}/r$. Parameters are $Z = 7$, $\alpha = 1.695$ for nitrogen and $Z = 8$, $\alpha = 1.720$ for oxygen. A generic algorithm is utilized to find internuclear distance $R$ [71]. The fitness function is defined as

$$\chi^2(R, \beta) = \sum_i \left[ \frac{\sigma_{M}^{(exp.)}(q_i)}{2\sigma_{A}^{(the.)}(q_i)} - \frac{\sigma_{M}^{(the.)}(q_i)}{2\sigma_{A}^{(the.)}(q_i)} \right]^2,$$

(3.62)

where $q$ has been discretized in to $q_i$ and $\beta$ is the normalization constant since the experimental DCS is not absolute. The search range of $R$ is restricted to [0.95 Å, 1.60Å] for computational efficiency.

The results are plotted in Fig. 3.8. In the left columns a), c) and e) are results for N$_2$. 60
Figure 3.8: LIED for unaligned $N_2$ and $O_2$ molecules Reproduced from [76]. a)-d) are MCF extracted from experimental data under various conditions in comparison with theoretical predictions. a) $N_2$ data taken with $I = 2.6 \times 10^{14}$ W/cm$^2$, $\lambda = 2.0$ $\mu$m, $\gamma = 0.28$ and fixed at $p_r = 2.97$ a.u. b) $N_2$ data take with $I = 2.9 \times 10^{14}$ W/cm$^2$, $\lambda = 2.3$ $\mu$m, $\gamma = 0.23$ and fixed at $p_r = 4.11$ a.u. c) $O_2$ data take with $I = 1.3 \times 10^{14}$ W/cm$^2$, $\lambda = 2.0$ $\mu$m, $\gamma = 0.36$ and fixed at $p_r = 2.91$ a.u. d) $O_2$ data take with $I = 1.3 \times 10^{14}$ W/cm$^2$, $\lambda = 2.3$ $\mu$m, $\gamma = 0.29$ and fixed at $p_r = 2.97$ a.u. The scattered points are experimental data with error bars coming from the Poisson statistics. The solid red lines and dotted gray lines are theoretical calculations using retrieved internuclear distances and equilibrium internuclear distances respectively. The magenta and orange dash-dotted lines in a) and b) are theoretical calculations using internuclear distance deviated from the retrieved value by -5 and +5 pm, respectively. e) and f) illustrates the retrieved internuclear distance as a function of the delay between ionization and recollision. The green diamond, blue circle and yellow square represent data taken with 1.7 $\mu$m, 2.0 $\mu$m and 2.3 $\mu$m lasers in corresponding order. The error bars are IAM deviations coming from experimental uncertainties. The red solid line represent the evolution of the vibrational wave packet and its associated full-width at half maximum from equilibrium distance of neutral molecules (solid gray line) to molecular ions (dashed gray line). The X symbol in f) depicts result from [57].
The top two panels a) and c) are experimental and theoretical MCF with 2.0 µm and 2.3 µm pulses, respectively (see figure caption for details). Panel c) demonstrates the sensitivity of the MCF to the change of $R$. The bottom panel e) is the retrieved internuclear distance with 1.7 µm, 2.0 µm and 2.3 µm pulses. The results are 1.15 Å, 1.14 Å and 1.12 Å in corresponding order. They agree well with the theoretical equilibrium distance of N$_2$ (1.10 Å) and N$_2^+$ (1.12 Å).

In the right columns b), d) and f) are results for O$_2$. The same as before, top two panels b) and d) are experimental and theoretical MCF with 2.0 µm and 2.3 µm pulses, respectively (see figure caption for details). The bottom panel f) is the retrieved internuclear distance with 1.7 µm, 2.0 µm and 2.3 µm pulses. The results are 1.10 Å, 1.11 Å and 1.02 Å in corresponding order. They are all closer to the theoretical equilibrium distance of molecular ion O$_2^+$ (1.10 Å) and consistently deviated from the neutral O$_2$ (1.21 Å). The reason of this deviation lies in the LIED process. The returning electron was promoted into the continuum through optical tunnel ionization at time $t_0$. If the ionization is rapid, Franck-Condon principle can be employed to evaluate the subsequent evolution of the vibrational wave packet. When the tunneled electron returns to rescatter with the parent ion, it probes the new internuclear distance at time of recollision $t_r$. The time difference between $t_r$ and $t_0$ is about 4 to 6 fs depending on the wavelength. The HOMO of N$_2$ is a bonding $\sigma_a$ orbital and removal of the $\sigma_a$ electron results in a small change in the equilibrium internuclear distance while the HOMO of O$_2$ is an anti-bonding $\pi_a$ orbital and ionization leads to large equilibrium internuclear distance change. The evolution of the O$_2^+$ vibrational wave packet from O$_2$ equilibrium distance is plotted with solid red line in panel f) of Fig. 3.8 with the dashed red lines representing the FWHM width of the vibrational wave packet. The measured internuclear distances can be mapped on the Franck-Condon curve within experimental error. It illustrates that the LIED is capable of imaging sub-Ångström structural changes of gas-phase molecules with femtosecond time resolution.
3.4 FABLES

Using LIED, one can extract the internuclear distance of molecules from the oscillation of molecular interference term with momentum transfer \( q \) for fixed electron return momentum scattered into different angles, which is the same principle as CED. However, the returning electron wave packet is different than the CED electron beam since it’s composed of broadband spectral contents. Recall relation \( q = 2p_r \sin(\theta_r/2) \) between momentum transfer \( q \), returning momentum \( p_r \) and rescattering angle \( \theta_r \), momentum transfer range \( q^{(\min)} \) to \( q^{(\max)} \) can be achieved by going through different rescattering angle at fixed return momentum \( 2p_r \sin(\theta_r^{(\min)}/2) \) to \( 2p_r \sin(\theta_r^{(\max)}/2) \) or going through different returning momentum at fixed rescattering angle \( 2p_r^{(\min)} \sin(\theta_r/2) \) to \( 2p_r^{(\min)} \sin(\theta_r/2) \). The former is the principle of LIED and the latter gives rise to fixed-angle broadband laser-driven electron scattering (FABLES) which I’ll introduce in the following.

To get largest range of momentum transfer, it’s most desirable to fix the rescattering angle at \( \pi \), i.e. detect backscattering electrons. Then the available momentum transfer ranges from \( q^{(\min)} = 2p_r^{(\min)} \) to \( q^{(\max)} = 2p_r^{(\max)} \). It was calculated in section 3.2.2 that the returning electron energy \( E_r \) range from 0 to 3.17\( U_p \). However, for detected energy \( E_d \) below 2\( U_p \), the photoelectron yield is dominated by direct electrons. So we limit the minimum returning electron energy range to \( E_r^{(\min)} = 0.8U_p \) for which the detected backscatter energy range is \( E_d = 3U_p \), away from the region where direct electrons are contributing. The corresponding momentum transfer range is from \( q^{(\min)} = 2\sqrt{2} \times 0.8U_p \) to \( q^{(\max)} = 2\sqrt{2} \times 3.17U_p \). For a noble gas atom in mid-infrared laser fields, typical ponderomotive energy can be \( U_p = 100 \text{ eV} \). The corresponding momentum transfer range is then \([9.1 \text{ Å}^{-1}, 18 \text{ Å}^{-1}]\), which is comparable to the momentum transfer range of CED and LIED experiments introduced in the beginning of this chapter.

3.4.1 FABLES: \( \text{N}_2 \) and \( \text{O}_2 \) results

Fig. 3.9 shows the backscattered photoelectron energy distributions for unaligned nitrogen and oxygen molecules measured using 2 \( \mu \text{m} \) and 2.5 \( \mu \text{m} \) laser pulses at constant
Figure 3.9: High-resolution photoelectron energy distributions along the laser polarization. Reproduced from [132]. In the top left panel: photoelectron spectrum of nitrogen and argon recorded at a wavelength of 2.0 μm and an intensity of $2.7 \times 10^{14}$ W/cm$^2$. The error bars indicate the $\sqrt{N}$ Poisson statistical fluctuations for each time bin, $N$ being the number of detected electrons in the bin. The vertical dashed line marks the $2U_p$ energy, electrons below this are direct. Above it, the long plateau corresponds to photoelectrons that are backscattered following ionization. The plateaus are a direct illustration of the broadband nature of the returning electron wave packet. In the top right panel: photoelectron spectrum of oxygen and krypton at a wavelength of 2.5 μm and an intensity of $1.3 \times 10^{14}$ W/cm$^2$. In the bottom left and middle panel are shown the calculated atomic DCS for Ar/N and Kr/O pairs. In the bottom right panel is shown additional experimental data at $3 \times 10^{14}$ W/cm$^2$, 2.3 μm, in which the vertical dashed blue arrows denote the position of the interference minimum. Note that the DCS for N and O atoms is multiplied by a factor of two, representative of the molecular species.
ponderomotive energy \(U_p = 100 \text{ eV}\). According to QRS, the detected photoelectron distribution can be expressed as \(I(p_d) = W(p_r)\sigma(q)\). Behavior of the returning electron wave packet as a function of recollision momentum has been extracted in section 3.2.3. It is, although featureless, not monotonic. So the photoelectron spectrum of each molecule is accompanied by its corresponding atomic partner with similar ionization potential (Ar/N\(_2\) and Kr/O\(_2\)) to retrieve the returning electron wave packet [39]. Given the small magnitude of the expected interference signal, the rescattered plateaus (energies greater than the dashed black lines) were recorded with 1 – 3\% statistical fluctuations. For each atom-molecule pair, the spectra were normalized such that the direct electrons overlap. For both pairs, the direct electron distributions show remarkable agreement, confirming the assertion that in the strong field limit, the ionization rate and hence the electron wave packet spectral densities depend mainly on the value of the ionization potential [39].

A closer inspection of the Ar-N\(_2\) plateaus (top left panel of Fig. 3.9) reveals a distinct modulation present in nitrogen but not in argon. As shown in the bottom panel of Fig. 3.9, at high collision energies, electron-atom backscattering DCS is monotonically decaying and structureless. Consequently, the modulation must be attributed to the intramolecular term, which is produced by interfering backscattered waves emanating from each atomic core, analogous to the two-center effect observed in high harmonic generation [133], valence/core-shell photo-ionization spectrum [134,135] and ion impact electron ionization spectrum [136] from a diatomic molecule. In the bottom right panel of Fig. 3.9 is plotted the photoelectron spectrum of Ar-N\(_2\) with mid-infrared laser of 2.3 \(\mu\text{m}\) wavelength, it also shows interference minimums. Thus, the N\(_2\) structure is encoded in the interference patterns. On the other hand, the plateau of O\(_2\) (top right panel of Fig. 3.9) reveals no modulation.

The same as LIED, recollision geometries of unaligned molecules are determined by the angle dependent ionization rate \(N(\theta_a)\). As mentioned before, \(N(\theta_a)\) of N\(_2\) and O\(_2\) can be reliably calculated with MO-ADK. They are plotted in polar coordinates in top left and bottom left panel of Fig. 3.10, together with their HOMOs and ball-and-stick model molecules. Molecular DCS’ of N\(_2\) and O\(_2\) can then be calculated through weighted averaging, \(\bar{\sigma}_M = \int \sin(\theta_a) d\theta_a \sigma_M(\theta_a) N(\theta_a)\). The results are shown in top right and bottom
Figure 3.10: Effect of the ionization rate as a function of molecular alignment angle on the elastic backscattering differential cross-sections Reproduced from [132]. For a randomly distributed N$_2$/O$_2$ gas, the ionization rate maximizes when the molecule is aligned so that the laser polarization axis is parallel to the lobes of the electron cloud of the highest-occupied molecular orbital (HOMO). The HOMOs of N$_2$ and O$_2$ have different symmetries, $\sigma$ and $\pi$, respectively, which are depicted in top left panel and bottom left panel by the color density plots, as well as their associated molecules in the ball-and-stick model.
Figure 3.11: FABLES-bond length retrieval and Fourier transform. Reproduced from [132]. In the left panel: the intramolecular interference fringes extracted from the nitrogen plateau data at 2.0 µm (light blue open circles) and 2.3 µm (dark blue solid squares). The error bars represent the standard deviations of the two data sets, which are calculated from measurement errors of their corresponding photoelectron energy distribution by assuming that the theoretical atomic DCS is exact. In the right panel: the mean internuclear distance function obtained by Fourier Transform of the data in the left panel. The dash-dotted and dotted lines are the FT of the theoretical DCS spanning the same momentum transfer range as the experiments at 2.0 µm and 2.3 µm, respectively. The vertical arrow in the right panel denotes the known N$_2$ equilibrium distance, $R_{eq}$. Our retrieved bond lengths deviate from $R_{eq}$ by 0.01 Å.

For reference, the corresponding incoherent atomic DCS for each molecule is also shown (dashed lines). For nitrogen, a clear ($\pm 20\%$) modulation is observed, whereas for oxygen the modulation is $\pm 3\%$, both results are consistent with the experiment.

Structural information can be retrieved from the molecular interferences in N$_2$ following the same procedure as LIED or CED. The first step is to rectify the measured ensemble-averaged molecular DCS to its MCF following Eqn. 3.61. The MCFs extracted from the nitrogen distributions at 2.0 and 2.3 µm as a function of the momentum transfer $q$ is plotted in the left panel of Fig. 3.11. Following CED inversion procedure, a Fourier transform extracts from the momentum space interferogram the real-space structural information, as illustrated in the power spectra plotted in the right panel of Fig. 3.11. The internuclear distance functions retrieved from the experimental data peak at nearly the same position, 1.09 and 1.11 Å for 2.0 and 2.3 µm experiments, respectively. In comparison, the nitrogen equilibrium distance, $R_{eq}$, is 1.10 Å. It is worth noting that as the electron return time varies
with rescattering energies, for example, the returning electron wave packet is chirped, the extracted distances here are the average length of the nitrogen bond over the temporal slit defined by the energy range used in the analysis (roughly a quarter of the 6-7 fs laser cycle). Also plotted in the right panel of Fig. 3.11 is the FT result for the theoretical DCS, covering the same $q$ range as the 2.0-$\mu$m and 2.3-$\mu$m data, respectively. The agreement with the experiment is excellent. We emphasize that the FT power spectrum strength is strongly affected by the modulation depth. As seen in the plot on the right panel of Fig. 3.11, the FT width of the internuclear distance peak is determined by the range of momentum transfer $q$, that is, a larger $q$ range results in a narrower peak in space. One technical challenge for applying FABLES to large molecules is maintaining a sufficiently large value of $q$ over a broad range for resolving different bonds. In principle, longer wavelength drivers (>5 $\mu$m) can fulfill this requirement.

### 3.5 Molecular alignment

So far we have established that the recollision geometry is important when applying LIED or FABLES to retrieve molecular structure. Although alignment dependent molecular tunneling ionization rate of simple diatomic molecules can be calculated with MO-ADK, molecular alignment is needed to generalize LIED and FABLES for more complex molecular systems. Molecular alignment can achieved through the interaction with a laser field\(^6\). One requirement on molecular alignment for LIED and FABLES is that it need to be in a field-free environment so that the electron recollision dynamics won’t be modified. The method to obtain field-free molecular alignment is called non-adiabatic alignment or impulsive alignment.

#### 3.5.1 Molecular alignment: theory

In order to understand the impulsive alignment, we take a look at the Hamiltonian that describes a molecule interacting with an intense laser pulse. The state of a molecule can be described by its rovibronic (rotational-vibrational-electronic) wave function \([137]\). For a

\(^6\)For more general categories of molecular alignment see \([79]\).
molecule in its rovibronic ground state, the separation of rotational levels are the smallest among all the rotational, vibrational and electronic levels. For example, for a N\textsubscript{2} molecule sitting at its rovibronic ground state \cite{138}, the first excited rotational level is about 0.001 eV away while the first exited vibrational level and electronic level are about 0.3 and 6.2 eV away, respectively. When considering the interaction of a molecule with a laser field, if the laser intensity is strong enough to induce rotational transitions yet too weak to couple vibrational and electronic states, the Hamiltonian can be written as \cite{139}

\[
H = BJ^2 + V_\mu(\theta) + V_\alpha(\theta)
\]  

(3.63)

where \(J^2\) is the squared angular momentum operator, B the rotational constant, \(\theta\) the polar angle between the molecular axis and the laser field. For a permanent dipole moment \(\mu\) along the internuclear axis and polarizability components \(\alpha_\parallel\) and \(\alpha_\perp\) parallel and perpendicular to the axis \cite{140}, the interaction potentials are

\[
V_\mu(\theta) = -\mu \epsilon \cos \theta
\]  

(3.64a)

\[
V_\alpha(\theta) = -\frac{1}{2}\epsilon^2(\alpha_\parallel \cos^2 \theta + \alpha_\perp \sin^2 \theta)
\]  

(3.64b)

where \(\epsilon(t) = \epsilon_0 f(t) \cos(\omega t)\) is the electric field strength of the laser with frequency \(\omega\), envelope \(f(t)\) and peak field strength \(\epsilon_0\). For a molecule without a permanent dipole moment \footnote{In fact, even for a molecule with a dipole moment \(\mu\), \(V_\mu\) interaction will be mostly averaged out since the laser lasts several cycles \cite{139}. So the permanent dipole moment is not important in impulsive alignment}, the Hamiltonian is

\[
H(t) = BJ^2 - \frac{1}{2}\epsilon^2(t)[(\alpha_\parallel - \alpha_\perp) \cos^2 \theta + \alpha_\perp],
\]  

(3.65)

and the corresponding time-dependent Schrödinger equation is

\[
\frac{i}{\partial t} \frac{\partial \psi(t)}{\partial t} = H(t)\psi(t)
\]  

(3.66)

The solution of Equation (3.66) can be expanded in a series of field-free rotor wave
functions $|JM\rangle \equiv Y_{JM}$,

$$\psi(\Delta \omega(t)) = \sum_J d_J(\Delta \omega(t))|J, M\rangle,$$

(3.67)

where

$$\Delta \omega(t) = \frac{\epsilon^2(t)(\alpha_\parallel - \alpha_\perp)}{2B}$$

(3.68)

is the dimensionless interaction parameter. In interaction representation, the time-dependent expansion coefficients, $d_J(\Delta \omega(t))$ can be found by solving differential equation:

$$i\frac{d_d J(\Delta \omega(t))}{B} = d_J(\Delta \omega(t))[(J, M | J^2 | J, M) - \alpha_\perp \epsilon^2(t)/2B]$$

$$- \sum_{J'} d_{J'}(\Delta \omega(t))\langle J, M | \Delta \omega(t) \cos^2 \theta | J', M \rangle$$

(3.69)

The only non-vanishing matrix elements are the ones with $J' = J, J \pm 2$. So Equation (3.69) becomes tridiagonal form

$$i\frac{d_d J(\Delta \omega(t))}{B} = d_J(\Delta \omega(t))[(J, M | J^2 | J, M) - \alpha_\perp / (\alpha_\parallel - \alpha_\perp) \Delta \omega(t)]$$

$$- \Delta \omega(t)d_{J-2}(\Delta \omega(t))\langle J, M | \cos^2 \theta | J - 2, M \rangle$$

$$- \Delta \omega(t)d_{J}(\Delta \omega(t))\langle J, M | \cos^2 \theta | J, M \rangle$$

$$- \Delta \omega(t)d_{J+2}(\Delta \omega(t))\langle J, M | \cos^2 \theta | J + 2, M \rangle.$$ 

(3.70)

After the laser pulse is gone, the evolution of the rotational wave packet is solely determined by the complex expansion coefficients $d_J$'s. A good parameter to represent the degree of alignment for a linear molecule is the expectation value of $\cos^2 \theta$,

$$\langle \cos^2 \theta \rangle = \sum_{J, J'} d^*_{JM}d_{J'M}\langle J, M | \cos^2 \theta | J', M \rangle$$

(3.71)

### 3.5.2 Impulsive alignment of $\text{N}_2$: simulation and experiment

In an experiment, we start from an ensemble of molecules with finite rotational temperature $T$. According to Boltzmann statistics, the equilibrium population at each rotational level is

$$I(J) \propto g_N(2J + 1) \exp[-BJ(J + 1)/k_B T]$$

(3.72)
Figure 3.12: Simulation of \( \langle \cos^2 \theta \rangle \) at different initial temperatures and laser intensities In the left panel is shown the maximum achievable value of \( \langle \cos^2 \theta \rangle \) at different initial temperatures (in Kelvin) and laser intensities. In the top right panel is shown the evolution of \( \langle \cos^2 \theta \rangle \) from 0 to 10 ps at initial temperature 10 K, laser intensity \( 1 \times 10^{13} \) W/cm\(^2\) (solid blue line) and initial temperature 10 K, laser intensity \( 4 \times 10^{13} \) W/cm\(^2\) (solid red line). It is zoomed in on the bottom right panel.

where \( g_N \) is to account for the nuclear spin degeneracy [137], e.g. for \(^{14}\)N\(_2\), \( g_N = 2 \), \( J \) even and \( g_N = 1 \), \( J \) odd. Averaging over the thermal ensemble, we can get the experimentally measured expectation value of the alignment cosine,

\[
\langle \langle \cos^2 \theta \rangle \rangle = \sum_J g_N(2J + 1) \exp[-BJ(J + 1)/k_BT] \sum_{M=-J}^{M=J} \langle \cos^2 \theta \rangle_{J,M}.
\]

Note that \( \langle \langle \cos^2 \theta \rangle \rangle \) is time-dependent.

The initial rotational temperature is an important quantity since it sets the lower limit to the number of rotational states that can be populated. Impulsive alignment simulations for \( \text{N}_2 \) was carried out by solving differential equation Eqn. 3.70. The polarizability components parallel and perpendicular to the field direction for \( \text{N}_2 \) are \( \alpha_\parallel = 1.094 \) Å\(^3\) and \( \alpha_\perp = 0.373 \).
Å³, respectively. Calculated maximum ensemble averaged $\langle \cos^2 \theta \rangle$ as a function of initial rotational temperature $T$ and laser intensity $I$ is plotted in the left panel of Fig. 3.12. It shows that molecules with lower rotational temperatures are easier to align. For given initial temperature, maximum $\langle \langle \cos^2 \theta \rangle \rangle$ increases with increasing laser intensity. However, the increase of laser intensity is limited by two factors. First, the ensemble will get ionized when the laser intensity is too high. Second, even before ionization becomes a problem, the laser intensity can become high enough to pump the rotational wave packet to very high $J$ states and the time duration that the molecules stay aligned will decrease. In the top right panel of Fig. 3.12 is plotted the temporal evolution of $\langle \langle \cos^2 \theta \rangle \rangle$ for initial rotational temperature 10 K with laser intensities $1 \times 10^{13}$ W/cm² and $4 \times 10^{13}$ W/cm². It shows that $\langle \langle \cos^2 \theta \rangle \rangle$ reaches maximum value around half revival time 4 ps and full revival time 8 ps. At higher laser intensity ($4 \times 10^{13}$ W/cm²), although the maximum value of $\langle \langle \cos^2 \theta \rangle \rangle$ is increased from 0.6 to 0.8, its oscillation becomes more rapid due to the higher $J$ states. The plot is zoomed in around half revival in the bottom right panel. The time it takes for the rotational wave packet to evolve from alignment to anti-alignment is 600 fs for laser intensity $1 \times 10^{13}$ W/cm² while the value is 200 fs for laser intensity $4 \times 10^{13}$ W/cm². The same is true for molecular ensembles that starts from high initial rotational temperatures. For example, laser pulses with intensity of $7 \times 10^{13}$ W/cm² can align room temperature N₂ to $\langle \langle \cos^2 \theta \rangle \rangle = 0.58$, however, due to the high level of $J$ states, the time it takes for the rotational wave packet to evolve from alignment to anti-alignment around half revival is only about 120 fs in that case. In conclusion, the key to get high degree of good-behaving molecular alignment is to start from molecules with low initial rotational temperature and apply appropriate laser intensity.

The experimental setup for N₂ impulsive alignment is sketched in the top panel of Fig. 3.13. A cold molecular beam was produced by supersonic expansion through an E-A-Lavie (E-L) valve. The E-L valve has a trumpet shaped opening with exit diameter of 150 μm and is backed with 16 bar of N₂ gas. The cold molecular beam is skimmed with a skimmer before it intersects the laser. It is hard to evaluate the temperature of a skimmed molecular beam because degree of reheating by the skimmer happens depends sensitively on
Figure 3.13: Impulsive alignment of N$_2$: simulation versus experiment. In the top panel is shown the experimental setup. In the middle panel is plotted the temporal evolution of the ensemble averaged expectation value of $\cos^2 \theta$ from simulation (solid red line) and experiment (solid blue line). In the bottom left panel is plotted the initial rotational $J$-state distribution of the ensemble from simulation. In the bottom right panel is shown the power spectra from Fourier transform of the time dependent the ensemble averaged expectation value of $\cos^2 \theta$ in units of $J$. The solid red line is from the simulation data and the dashed blue line is from experimental data.
its wall thickness and opening diameter [141]. Roughly, temperature of the molecular beam should be bellow 20 K. Coherently evolving rotational wave packet is produced by a linearly polarized 50 fs, 800 nm pulse from the depleted pump of the TOPAS. This pulse is called the pump. The molecular alignment is probed by a linearly polarized 50 fs, 2.3 μm pulse from the signal of the TOPAS. This pulse is called the probe. A delay stage was placed in the pump beam path with capability to change the delay between pump and probe in fine steps. The pump and probe are combined before the chamber with a dichroic mirror. Polarization of the pump and probe are controlled individually with half waveplates before combination.

In the middle panel of Fig. 3.13 is plotted the ion yield as a function of pump-probe delay (solid blue line). Polarization of the pump and probe are chosen to be parallel to each other and positive delay means pump comes before probe. On the same plot is also plotted the evolution of $\langle \cos^2 \theta \rangle$ for a molecular ensemble with initial temperature 11 K pumped by a 65 fs laser pulse of intensity $1.2 \times 10^{13}$ W/cm$^2$ at time zero. Since the ionization rate of N$_2$ is peaked along internuclear axis, the evolution of ionization rate in the parallel direction agrees with the evolution of $\langle \cos^2 \theta \rangle$. A quantitative assessment of the agreement degree was shown in the bottom right panel. It shows the good agreement of the Fourier transform (FT) power spectra of the experimental data (dashed blue line) and the simulation (solid red line). The x scale on the FT power spectra is the beating frequency of coherent vibrational wave packets. Beating frequency between $J$ state is $J'(J' + 1) - J(J + 1) = 4J + 6$ since $J' = J + 2$. In the bottom left panel is plotted the Boltzmann distribution for initial temperature 11 K, comparing it with the FT power spectra one concludes that the laser pulse effectively aligned the molecule without pumping the vibrational wave packet to too high vibrational levels. The maximum degree of alignment is $\langle \cos^2 \theta \rangle_{\text{max}} = 0.63$.

This method of impulsive alignment can be applied to any molecules with non-zero polarizability to achieve field-free alignment.

### 3.5.3 LIED and FABLES with aligned molecules

With the impulsive alignment, LIED procedure can be carried out to image molecular structure of complex molecules. Preliminary results has been reported by Pullen et.al. [142]
In the left panel: IAM-calculated backscattering elastic electron-ion differential cross sections for a cis-$S_2O_2$ molecule aligned with respect to the lasers linear polarization along its S=O bond (green), and S=S bond (black). For each case, the molecule is allowed to rotate freely around the aligned axis. As expected, the fringe separation is inversely proportional with the bond length. In the right panel: Fourier transform-retrieved normalized power spectra from the two DCS in the left panel. The dashed vertical lines indicate the lengths of S=O and S=S bonds. When the S=S bond is aligned, the internuclear vector between two oxygen nuclei is also aligned, resulting in the secondary peak above 3 Å. The dashed vertical lines indicate the position of the known real distances. Utilizing molecular alignment, one can envision the result in the right panel as forming the basis of molecular tomography.

from ICFO-Institut de Ciencies Fotoniques. They successfully measured the C-C and C-H bond length in aligned $C_2H_2$ molecule with a 160 kHz mid-infrared few-cycle laser.

**FABLES with aligned molecules: a Gedanken experiment**

In comparison to LIED, FABLES offers two significant advantages. First, the dominant, atomic part of the energy-dependent differential cross section for backscattering geometry displays a simple smooth, Rutherford-like dependence. This allows one to easily extract the useful interference term via a simple rectification. Second, bond retrieval is straightforward, the procedure necessitating only a 1D Fourier transformation. Combining with molecular alignment, the two advantages enumerated above make FABLES well suited for molecular tomographic reconstruction. In the following Gedanken experiment is proposed, to illustrate the principle of molecular tomographic reconstruction.

The experiment consists of recording a series of FABLES spectra for a molecule aligned
along the polarization axis of a linearly polarized copropagating femtosecond aligning pump pulse. The angle between the FABLES axis and the molecular alignment axis can be varied by rotating the polarization axis of the alignment pulse. The tomographic reconstruction is performed for a disulfur dioxide molecule, cis-S$_2$O$_2$, a planar molecule with C$_{2v}$ symmetry. The SO dimer has a strong S=O bond of 1.467 Å and a weak S=S bond of 2.023 Å [143]. In the left panel of Fig. 3.14, backscattered energy-dependent DCS are calculated for the two cases in which each bond is aligned parallel with the FABLES axis (depicted in red). The molecules are allowed to rotate freely along the aligning axis. As expected, the oscillatory behavior in the DCS due to internuclear interferences is clearly visible. Furthermore, the interference spacing observed is inversely proportional to the length of the aligned bond. After rectification, the interference signals were Fourier transformed and the resulting power spectra are displayed in the right panel of Fig. 3.14. Just as was observed in the case of N$_2$, only the bond parallel to the FABLES axis is visible. Therefore, a series of one-dimensional FABLES spectra recorded at different, controlled angles between the FABLES axis and the alignment axis constitutes the basis of molecular tomography. Compared to the previously reported high-harmonic generation tomographic reconstruction [39] in which the molecular orbital was reconstructed, FABLES is a complementary method, as it reconstructs the location of individual atoms. Thus, laser-driven femtosecond tomography has the potential to become an important tool in molecular dynamics, as it appears capable as imaging both electrons [39] and nuclei (FABLES).

**FABLES with aligned molecules: preliminary result on N$_2$**

Preliminary results of FABLES with aligned molecules were obtained for N$_2$. The experimental setup is the same as impulsive alignment experiment (top panel of Fig. 3.13). A series of backscattered photoelectron FABLES spectra were taken at different alignment angles. There are two way to change the alignment angle of the impulsively aligned molecular ensemble. The rotational wave packet evolves from alignment to anti-alignment in a few hundreds of femtoseconds near half revival. With the probe fixed parallel to the alignment pump pulse, different molecular angle could be probed by scanning the delay near half re-
Figure 3.15: Illustration of two ways to change molecular alignment angle

The probe pulse polarization direction is kept horizontal, illustrated with the direction of its electric field in the figure. In the top row, different angles (0°, 45° and 90°) between probe pulse and the angle of the molecular axis is achieved by changing the delay between pump and probe pulse around half revival from alignment to anti-alignment. In the bottom row, it is done by directly changing the angle between pump and probe pulse with half waveplates while the delay is kept at maximum alignment.

vival. This is illustrated in the top row of Fig. 3.15. The system always have cylindrical symmetry in this case. It is also the scheme proposed in the Gedanken experiment in the last section. The molecular angle can also be rotated directly by changing the angle between of linearly polarized pump and probe pulse with delay fixed at maximum alignment. This scheme is illustrated in the bottom row of Fig. 3.15. In this case, the system no longer posses cylindrical symmetry.

In Fig. 3.16 is shown the experimental data obtained with the direct-rotation scheme together with numerical simulation from the first delay-rotation scheme. The laser wavelength is 2.3 µm and estimated ponderomotive energy of the experiment is $U_p = 100$ eV. Experimentally extracted MCF agrees well with numerical simulation of N$_2$ molecule with bond length of 1.10 Å, the same as FABLES result in [132]. However, the MCF at different alignment angles 0° (red circle), 45° (blue circle) and 90° (yellow circle) do not show conclusive differences. This is mainly due to inadequate degree of alignment and insufficient experimental signal.
Figure 3.16: Preliminary results of FABLES with aligned $N_2$ molecules. In the top left panel is experimental results at alignment angle $0^\circ$ (red circle), $45^\circ$ (blue circle) and $90^\circ$ (yellow circle). The numerical simulation with bond length of $R = 1.10 \, \text{Å}$ is plotted in solid lines. The molecular axis distribution is the product of the MO-ADK rate and alignment ensemble with $\langle \langle \cos^2 \theta \rangle \rangle = 0.46$. Solid purple, green and cyan line represent simulation for $0^\circ$, $90^\circ$ and random alignment. In the top right panel and bottom right panel is shown the molecular axis distributions for $0^\circ$ and $90^\circ$ alignment, respectively. The solid gold, red and blue line represent molecular axis angular distribution calculated with MO-ADK, alignment ensemble and the product of the two, in corresponding order. In the lower left panel is plotted the integral weighting function $N(\theta) \sin \theta$ as a function of angle for different alignment direction.
Working towards the goal of molecular tomography with FABLES, two improvements can be made to the current system. First, the degree of molecular alignment can be improved. It can be done by using pump pulses with better spatial profile and controllable temporal profile. For example, an ideal pulse shaper in frequency domain could improve the alignment \( \langle \cos^2 \theta \rangle \) from 0.58 to 0.73 [144], or multiple pump pulses repetitively “kicking” the rotational wave packet around revivals could improve the alignment \( \langle \cos^2 \theta \rangle \) from 0.4 to 0.68 [145]. Second, the signal strength in the experiment can be improved by using higher repetition rate laser systems, or denser molecular beams.

### 3.6 The trajectory degeneracy

According to the semi-classical model, the electron trajectories have degeneracy at recollision. The degenerated trajectories are characterized into two groups: the “long” and “short” trajectory, according to the electrons’ travel time. So far we have treated the returning electrons as if they are following the long trajectory. In this section we’ll justify the long trajectory approximation.

The spectral density of the recollision electron wave packet is determined by two factors: the initial density and the subsequent wave packet spread during its propagation in the continuum. The initial density of the electron wave packet is determined by the tunneling ionization rate. As introduced in chapter 3, the tunneling ionization rate can be calculated with the ADK formula 3.30. For example, for an Argon atom, \( n^* = 0.93, |m| = 0, I_p = 0.5772 \) a.u. and \( F_0 = (2I_p)^{3/2} = 1.24 \) a.u., Eqn. 3.30 yields

\[
w_{Ar}^{ADK}(t_0) \propto \frac{1}{|F(t_0)|^{0.86}} \exp \left( -\frac{0.83}{F(t_0)} \right),
\]

where \( t_0 \) is the time of tunnel ionization and \( F(t_0) \) is the strength of electric field at time \( t_0 \). The liberated electron wave packet will oscillate back and forth driven by the laser field. The evolution of the electron wave packet is complicated and for an accurate treatment one has to solve the TDSE. However, to make an order-of-magnitude estimation, let’s regard the wave packet as superpositions of Gaussian wave packets. The spread of Gaussian wave

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Figure 3.17: Semiclassical calculation of the returning trajectories and spectral density

In the top left panel is the return energy, backscattered energy and returning electron density as a function of return time in units of optical period. The calculation is for monochromatic field and energy is divided by $U_p$. In the top right panel is the detected backscatter energy as a function of return energy in unit of $U_p$ for the first return long trajectory, the second return short trajectory and the third return long trajectory. In the bottom left panel is plotted the spectral density of the returning electron wave packet with ADK rate and spectral dispersion included. “1L”, “1S”, “2L”, “2S”, “3L” and “3S” represent first return long trajectory, first return short trajectory, second return long trajectory, second return short trajectory, third return long trajectory and third return short trajectory, respectively. In the bottom right panel is plotted the returning electron wave packet spectral density for each trajectory divided by the spectral density of first return long trajectory. See text for details.
packets can be found following standard quantum mechanics treatment. The evolution of the probability distribution of a Gaussian wave packet starting from initial width $\sigma_0$ can be expressed as \[146\]

$$
\rho(x,t) = \frac{1}{\sqrt{2\pi\sigma_t^2}} \exp\left[ -\frac{(x - kt)^2}{2\sigma_t^2} \right],
$$

where $\sigma_t^2 = \sigma_0^2 + t^2/4\sigma_0^2$ and $k$ is the wave vector. The travel time of recollision electrons in mid-infrared laser field is much bigger than $\sigma_0^2$, so $\sigma_t^2 \propto t^2$. The on-axis evolution of the electron wave packet density is

$$
\rho(t) \propto 1/t. \tag{3.75}
$$

For an electron wave packet liberated from ground state of an argon atom at time $t_0$ and returns to it at time $t_r$, the on-axis probability density at recollision is

$$
W(t_0) \propto w_{ADK}(t_0) \times \rho(t_r - t_0)
\propto \frac{|F(t_0)|^{-0.86}}{t_r(t_0) - t_0} \exp\left( -\frac{2.48}{3F(t_0)} \right). \tag{3.76}
$$

In the semiclassical model, the electron recollision momentum $p_r$ at the return time $t_r$ is determined by the birth time $t_0$. So the electron probability density $W(t_0)$ in Eqn. 3.76 can be transformed into spectral density of the returning electron wave packet $W(p_r)$ by applying Jacobian $dt_0/dp_r$

$$
W(p_r) = \frac{dt_0}{dp_r} W(t_0) = \lim_{\Delta p_r \to 0} \frac{\Delta t_0}{\Delta p_r} W(t_0)
\propto \lim_{\Delta p_r \to 0} \frac{\Delta t_0}{\Delta p_r(t_0)} \frac{|F(t_0)|^{-0.86}}{t_r(t_0) - t_0} \exp\left( -\frac{0.83}{F(t_0)} \right), \tag{3.77}
$$

which can only be calculated numerically since there is no analytical expression of $p_r(t_0)$ and $t_r(t_0)$. The numerically calculated returning electron spectral density in a monochromatic laser field with intensity $2 \times 10^{14}$ W/cm$^2$ (maximum field strength $F_{\text{max}} = 0.0756$ a.u.) and wavelength 1.8 $\mu$m is plotted in the lower left panel of Fig. 3.17 with “1L” representing long trajectory and “1S” representing short trajectory. The ratio between them is plotted in blue line on the lower right panel of Fig. 3.17. It shows that below $p_r/A_0 = 1.2$, the spectral density of short trajectory is less than 30% of the long due to the exponential drop
The degeneracy of backscattered multiple return trajectories

Detected backscattered energy of electrons following trajectories “1L”, “2S” and “3L” are all $6U_p$. Of tunneling ionization rate. That corresponds to return energy of $2.9U_p$ or backscattered energy of $9.7U_p$. Below this regime we treat the returning electron wave packet as following the long trajectory.

Some of the long trajectory electrons might revisit the plane of parent ion multiple times depending on the birth phase. The return energy as a function of return time for every return is plotted in the top left panel of Fig. 3.17. An illustration of this multiple return degeneracy is plotted in Fig. 3.18. If an electron is detected along the laser polarization axis with kinetic energy of $6U_p$, it might come from electrons following trajectory “1L”, “2S” or “3L”. Those three trajectories all arise from similar birth phase space, so their tunneling ionization rates are similar. But since the travel time of trajectories are increasing, $(t_r - t_0)^{1L} < (t_r - t_0)^{2S} < (t_r - t_0)^{3L}$. Their spectral densities are decreasing due to wave packet spreading, $W(p_r)^{1L} > W(p_r)^{2S} > W(p_r)^{3L}$. In general, as showed in the lower right panel of Fig. 3.17, the spectral density from the second return short trajectory is about $40\% \sim 60\%$ of that from the first return long trajectory and the spectral density from the third return long trajectory is about $30\% \sim 36\%$ of that from the first return long trajectory. Fortunately, although the spectral density from the second return short
trajectories is relatively high, the highest detected backscattered energy it can reach is about $7U_p$. One can avoid contamination from the second return by working with backscattered energy above $7U_p$.

In summary, working within backscattered energy range from $7U_p$ to $9.7U_p$, one can minimize contamination from the degenerated short trajectories and higher-order return trajectories. In this regime, spectral density from first return long trajectories dominates over that from all other trajectories by three times or more and therefore is the most ideal regime to work in for LIED and FABLES.
Chapter 4
THE LOW-ENERGY STRUCTURE: ANOTHER PIECE OF THE PUZZLE

As established in the last chapter, the above-threshold ionization (ATI) and high-order ATI (HATI) photoelectron spectra from systems deep in the tunneling regime ($\gamma \lesssim 0.5$) are well understood with the Keldysh-Faisal-Reis (KFR) $[30, 80, 81]$ strong-field approximation (SFA) or the semi-classical model (SCM). Such photoelectron spectra have signature cutoffs at $2U_p$ for direct electrons and $10U_p$ for backscattered electrons (see Fig. 4.1 left panel inset). Given the success of the SCM in explaining a wealth of experiments $[34, 53, 147]$, the strong field ionization process was believed to be well understood and even used to extract information about the target structure in the ultra-fast time scale, i.e. LIED and FABLES, as discussed in chapter 3. Thus, the observation $[82, 83]$ of new structures in the low end of the electron energy spectrum came as a puzzle since, although reproduced by numerical solutions of the time-dependent Schrödinger equation, it appeared to diverge from the semi-classical model.

4.1 The LES: a universal structure

The low-energy structures (LES) appear as spike-like peaks at a value that corresponds to a few percent of $U_p$ in the photoelectron spectra. In the left panel of Fig. 4.1 is plotted the low-energy region of the photoelectron spectra from argon (black dash-dotted line), nitrogen molecule (red dashed line) and hydrogen molecule (blue dotted line) produced by $1.5 \times 10^{14}$ W/cm$^2$, 2.0 $\mu$m pulses together with theoretical simulation result obtained by
Figure 4.1: Characteristics of the low-energy structure (LES) Reproduced from [82]. In the left panel: the low-energy region of the photoelectron spectra from argon (black dash-dotted line), nitrogen molecule (red dashed line) and hydrogen molecule (blue dotted line) produced by $1.5 \times 10^{14}$ W/cm$^2$, 2.0 $\mu$m pulses. The black dashed line labeled $E_H$ defines the cutoff position of the LES. The green solid line is calculation result using KFR. Inset: The entire photoelectron energy distribution exhibits the well-documented behavior of the “direct” and “rescattered” electrons. For comparison, the theoretical result is adjusted to match the normalized experimental distributions at 15 eV. In the top right panel: the LES in xenon for constant ponderomotive energy ($U_p \sim 19$ eV) or constant Keldysh parameter ($\gamma \sim 0.56$). In the bottom right panel: the LES region in xenon for linearly (LP) and circularly (CP) polarized 2.0 $\mu$m pulses for a peak vector potential of 1.8 atomic units.
KFR. The results are zoomed out to full energy range in the inset with logarithm y-scale. In the full range plot, the first-order KFR calculation neglects rescattering and consequently is not expected to reproduce the rescattered plateau. However, within the energy region of direct electrons, where KFR was believed to be valid, it shows a strong deviation from the measured distributions in the shaded region. Thus the LES is called an “ionization surprise” by Faisal [148]. It is a universal feature in the tunneling regime regardless of the laser parameters and target nature. Although the LES energy cutoff does change with laser parameters, it seemed to depend only on the ponderomotive energy, as shown in the top right panel of Fig. 4.1, in the case of xenon irradiated with 1.7 µm, 2.0 µm and 2.3 µm laser pulses. The intensities at different wavelengths were adjusted such that they have same ponderomotive energy $U_p = 19$ eV. The LES of all three systems behave similarly and have the same cutoff at 2 eV.

In the lower right panel of Fig. 4.1 was plotted the LES with circularly polarized light and linearly polarized light. The fact that the LES disappears in circularly polarized field suggests that its origin could be related to rescattering effects, even though rescattering was usually only taking into consideration for high energy plateau region of the photoelectron spectrum.

Shortly after the experimental observation of the LES was reported, classical and quantum mechanical theories incorporating the Coulomb potential of the parent ion has been developed to study the LES. By now it is recognized that the LES is the consequence of two effects: the soft recolliding trajectories and the influence of the parent ion Coulomb potential, which is neglected in the SCM [84, 86, 87, 127, 147, 149]. In the top left panel of Fig. 4.2 is plotted the longitudinal displacement of three classical electron trajectories that return to the proximity of the parent ion. The solid magenta line illustrates photoelectrons that return to the neighborhood of parent ion and pass through without interaction. They are detected with drift energy from 0 to $2U_p$. The solid gold line signifies a photoelectron that backscatters (represented with a star) upon return and drifts to the other side of interaction region with relatively high kinetic energy (up to $10U_p$). The green line illustrates a soft recolliding trajectory. The electron passes through the neighborhood of parent ion.
Figure 4.2: Classical return trajectories and the corresponding detection energies. In the top left panel is plotted the three categories of classical trajectories that return to the plane of the parent ion. In the lower left panel is plotted the return energy (solid blue line) and detected direct drift energy (solid red line) as a function of return phase. The “direct-through” trajectories passes through the plane of parent ion directly without any interaction and drifts towards the detector with drift energy from 0 to \(2U_p\). The “hard-recollision” trajectories rescatters with short range potential at high momentum (gold star) and drifts to the detector with kinetic energy up to \(10U_p\). The “soft-recollision” trajectories passes through the plane of parent ion upon first return and comes back to the proximity of the parent ion with small kinetic energy (green dot). Then it drifts to the detector with small kinetic energy. The position of their return phases are illustrated with dashed lines in the lower left panel. In the right panel is enumerated a series of classical trajectories at different birth phase with (top right panel) and without (lower right panel) Coulomb potential. The one with Coulomb potential clearly shows signature of trajectories bunched together.
twice during its oscillatory motion. Its velocity is close to zero at second encounter, represented with a green dot in the top left panel. From lower left panel, one can see that the return energy of this trajectory is around zero and the drift energy is about $0.1U_p$, agreeing with the experimentally observed LES cutoff. A series of classical trajectories near the soft-recollision condition with and without Coulomb potential are plotted on the top right and bottom right panel of Fig. 4.2, respectively. The Coulomb force at the soft-recollision acts to make these trajectories independent of the initial phase and thus increase the detected photoelectron yield within a narrow energy range (notice the contrast between top right and bottom right panel of Fig. 4.2).

According to the classical model, the interaction that is responsible for the formation of LES happens about one and half optical cycles after the instant of tunnel ionization. Consequently, the LES should depend on the laser pulse duration, which has been investigated theoretically [86, 87]. Experimental verification, however, was difficult since the tunneling condition require tunable pulse durations in the mid-infrared spectral region. As described in chapter 2, our duration-tunable mid-infrared laser system made it possible the direct verification of pulse duration dependence study of the LES. In the following I’ll present our first experimental study of the pulse duration dependence of the LES. I’ll show that this dependence is universal and link it to the cycle-to-cycle change of the laser field at which the soft recollision occurs. I’ll then introduce a semi-analytical approach based on the soft recollision mechanism. Taking into account the effect of the ionic Coulomb potential during the soft recollision and averaging over the focal volume, theoretical results agree with the experimental data. Combined with the classical trajectory Monte Carlo (CTMC) simulation, the role of Coulomb force can be identified to be the dominating factor in creating the LES.
Figure 4.3: Schematic setup of the LES pulse duration study The idler output from TOPAS at 1.8 \( \mu \)m is expanded with telescope T1-T2. It then passes through a half waveplate and get focused into argon-filled hollow core fiber (HCF). Output from HCF is collimated with concave spherical mirror and passes through GaAs pair at Brewster angle. It is then delivered to the split-mirror SHG FROG or TOF for experiment with flip mirror (F-M). Identical fused silica windows are placed before diagnoses and experiment to compensate for dispersion.
Figure 4.4: Photoelectron spectra of krypton with 13 fs, 17 fs, 27 fs and 38 fs pulses at constant intensity $1 \times 10^{14}$ W/cm$^2$ and wavelength 1.8 $\mu$m. The intensity was kept constant by adjusting the waveplate such that the $2U_p$ and $10U_p$ position at different pulse duration remain constant. The fluctuation of photoelectron yield between $2U_p$ and $10U_p$ is due to lack of signal. There is sufficient photoelectron yield in the LES since it’s orders of magnitude larger.

4.2 Dependence of LES on the laser pulse duration

4.2.1 Experiment

The schematic diagram of the experimental setup is shown in Fig. 4.3. The laser system was described in chapter 2. A beta barium borate (BBO)-based commercial optical parametric amplifier (HE-TOPAS, Light Conversion Ltd) is pumped by a home-built Titanium:Sapphire-based chirped pulse amplification (CPA) system with 60 fs FWHM pulse duration, 6 mJ pulse energy and center wavelength of 0.8 $\mu$m. The 1 mJ, 75 fs (FWHM) idler from the TOPAS with a central wavelength of 1.8 $\mu$m is focused into a 1 m long, 400 $\mu$m diameter, argon-filled hollow core fiber (HCF). The 1.8 $\mu$m pulse is spectrally-broadened by self-phase modulation inside the fiber. The amount of broadening is controlled by adjusting the gas pressure between 0 and 30 psi, ranging from about 0.08 $\mu$m up to 0.4 $\mu$m, enough to support a laser pulse with FWHM duration down to two optical cycles at 1.8 $\mu$m.
Figure 4.5: The LES in laser fields with different pulse duration (a), (b) and (c) are detected photoelectron spectrum for 27.4 fs pulse, 16.9 fs pulse and 12.7 fs pulse, respectively. The cartoon in the inset are the illustrated field at each pulse duration. The fitted LES peak position are 1.21 eV, 1.07 eV and 0.74 eV in the three cases. The VLES is absent in our spectrum because of the rapid decrease below 0.3 eV due to the electron spectrometer’s transfer function.
(12 fs). The spectrally broadened pulses then pass through fused silica windows (FS) with thicknesses from 1.5 to 3 mm to compensate for the spectral dispersion introduced by the Ar gas in the HCF, the 1.5 mm thick CaF$_2$ exit window of the HCF, the propagation in air and the entrance CaF$_2$ window to the experiment chamber [150]. A pair of GaAs plates at Brewster angle clean up the polarization after the beam collimation. Combining the GaAs plates with a half-wave plate before the HCF, the laser intensity can be controlled precisely to maintain a constant field strength when doing experiment at different pulse durations by adjusting the pulse energy while monitoring the $2U_p$ and $10U_p$ points in the photoelectron spectrum. The pulse is focused into the coincidence TOF chamber with a spherical mirror to minimize spectral dispersion and chromatic aberration. For more details about the laser measurement system, refer to chapter 2. At each pulse duration, photoelectron spectrum within ±1° to the laser polarization direction were measured. Argon and krypton gases are fed into the TOF chamber through a leak valve. The peak intensity of the field is kept constant (within ±10%) at different pulse durations. In Fig. 4.4 the photoelectron spectra of krypton with 13 fs, 17 fs, 27 fs and 38 fs pulses at constant intensity $1 \times 10^{14}$ W/cm$^2$ is plotted. One can see the clear characteristic classical $2U_p$ and $10U_p$ positions on all spectra and they are kept constant at different pulse durations. Fig. 4.5 shows the photoelectron spectra zoomed into the low-energy region for 13 fs, 17 fs and 27 fs pulses. A polynomial fitting algorithm was used to find the peak position of the LES. In Fig. 4.5 it shows that the LES peak position moves to lower energy in laser field with shorter pulse duration.

The extracted LES peak positions normalized to the ponderomotive energy is plotted in Fig. 4.6. Measurements for argon and krypton at other laser intensities and pulse durations are also shown. The LES peak position behavior versus pulse duration clearly appears to be universal: the peak energy shifts to higher values for longer pulses regardless of the intensity and atomic species.

4.2.2 Classical trajectory Monte Carlo simulation

Because of the success of CTMC method in analyzing the physics behind the LES [83, 84, 86, 87], we employ this intuitive method to investigate the effect of the laser pulse
Figure 4.6: LES peak energy positions at wavelength 1.8 \( \mu \text{m} \) as a function of laser pulse length in terms of optical cycles normalized to the peak ponderomotive energy \( U_p = \frac{F_0^2}{(2\omega)^2} \). Data is for krypton (\( U_p = 20 \text{ eV}, \text{ green and 25 eV}, \text{ blue} \) and argon (31 eV, black and 55 eV, red). Circles are from experiment, triangles are from a numerical classical calculation as in [87] and lines are analytical results, see text. Theoretical results are focus averaged and reduced by 15\% to match the experiment. The star is adapted from the experiment Blaga et al. [82] for Argon with \( U_p = 35.6 \text{ eV} \).

Figure 4.7: Initial condition space responsible for the LES for 2 and 5 cycle pulses from CTMC simulation. Cyan represents initial condition phase space of LES in 2-cycle laser field and red is for 5-cycle case. Grey area represent initial condition space responsible for photoelectrons detected \( \pm 0.1 \text{ eV} \) next to the peak LES position.
Figure 4.8: Initial condition phase space for the LES electrons with corresponding ADK rate. Vertical lines L, M and N represent positions with constant birth phase, see text for more details.

duration on the LES. In CTMC, the electronic wave packet emerged from tunnel ionization is mimicked by an ensemble of classical particles whose initial conditions are specified by the instant of ionization $t_0$, initial momentum $(p_{0\perp}, p_{0\parallel})$ and initial position. The initial conditions are distributed according to the ADK rate [121]

$$w(p_{0\perp}, t_0) \propto \exp\left(-\frac{2(2I_p)^{3/2}}{3F(t_0)}\right)\exp\left(-\frac{\sqrt{2I_p}p_{0\perp}^2}{F(t_0)}\right)$$

(4.1)

where $F(t_0)$ is the instantaneous field strength at $t = t_0$ and $I_p$ is the ionization potential. The equation above is the same as Eqn. 3.31 introduced in chapter 3. Here we assume the initial longitudinal momentum $p_{0\parallel} = 0$. A common way to mimic the distribution is to generate an uniform random distribution on the sample space $(p_{0\perp}, t_0)$ and calculate the weight of each point by $2\pi p_{0\perp} w(p_{0\perp}, t_0)$. The initial position is at the tunneling exit [151].

The subsequent motions of the electrons are modeled by Newton’s equation of motion

$$\frac{d^2 r}{dt^2} = -\frac{\partial A}{\partial t} - \nabla V(r),$$

where $A(t)$ is the vector potential of the laser field and $V(r)$
**is the Coulomb potential of the ion core.** In our simulation, $V(r) = 1/r$ and $A(t)$ has a cosine squared envelope. The pulse duration in terms of optical cycles $n$ is defined by the full width at half maximum (FWHM) of the pulse intensity. The electrons are propagated until the end of the pulse $t = t_f$, the asymptotic momenta are determined analytically from $r(t_f)$ and $p(t_f)$ [152]. Notice that the electrons with final energy $E = p(t_f)^2/2 - 1/r(t_f) < 0$ do not contribute to the photoelectron spectrum. The electrons with emission angle close to the laser polarization are collected and are sorted into bins according to their asymptotic kinetic energies, the photo-electron spectrum is then given by the weighted sum of the number of electrons in each energy bin.

Since we are studying only the low-energy electrons detected along the laser polarization, full simulations with sampling over the entire sample space ($p_{0\perp}, t_0$) would be inefficient since many of the particles would fall outside the range of interest. In order to suppress the computations on the irrelevant trajectories, we first perform simulation with a small ensemble ($\sim 10^6$ trajectories) under an uniform sampling within the ranges $t_0 \in (-t_f, t_f)$ and $p_{0\perp} \in (0, 0.35)$ a.u.. Thus we could identify the regions in the sample space which actually contribute. Then we perform simulation again with a more intensive sampling.
Low energy part of photoelectron spectra from CTMC simulation after focal volume averaging under different pulse durations are plotted in Fig. 4.9. Peak positions of the LES are plotted with black triangles in Fig. 4.6. They are normalized to the ponderomotive energy $U_p$ of the each specific conditions, the same as the experimental results. Both experiment and simulation show the same trend of increasing LES peak position with longer laser pulse duration for all of the pulse energies and target atom species. This behavior agrees with the predictions by Kästner et al. [87] and Lemell et al. [86].

Since the CTMC simulation reproduces the experimental data well, more understanding of the LES can be achieved by analyzing the electrons’ classical motion from CTMC simulation. As described earlier, in the CTMC simulation, the electron’s trajectory is determined by the equation of motion and it’s initial conditions. In this “experiment”, the two most important initial conditions are the phase of field at the moment of the electron formation ($\phi_0 = \omega t_0$) and the initial transverse momentum of the electron ($p_{\perp 0}$). In Fig. 4.7 is plotted $\phi_0$ and $p_{\perp 0}$ of the electrons that are in the LES for 2-cycle pulses and 5-cycle pulses, extracted from the CTMC simulation. The chaotic points on the lower left part of the plot are the initial conditions that lead to trajectories contributing to the low-energy part of the LES after relatively complex motions. Those only account for a few percent of the total population in the LES ([84]). So we’ll neglect them from here on. The gray areas are representing initial conditions of the photo-electrons detected near the peak of the LES. Overall, the birth phases of the photoelectrons in the peak of the LES are getting closer to zero (the peak of the field) as the pulse duration gets shorter. As the birth phase gets closer to zero the LES peak position will also be closer to zero, i.e. smaller initial vector potential leads to smaller drift momentum. So for shorter laser pulses, the detected LES peak position will be smaller. For any individual pulse duration, the initial condition phase space (IC) that is responsible for the LES occur at where the slope of the shape changes, as is pointed out by Liu et.al. ([84]). In Fig. 4.8 we plotted the ADK rate within the IC for LES. We picked three lines L, M and N with constant phase. The ADK ionization rate $w(p_{\perp 0}, \phi_0)$ is largest along L, smaller along M and smallest among N. However, due
to the slope change in the shape, the phase space is largest per unit $\phi$ along N. And this leads to the largest the integrated rate $\int_p w(p_{0,\perp}, \phi_N) dp$ along line N ($L \sim 0.88 \times 10^{-8}$, $M \sim 1.38 \times 10^{-8}$ and $N \sim 1.45 \times 10^{-8}$). For phases larger than N, although they have comparable phase space per unit $\phi$, their ADK rate drops. So in the detected photo-electron spectrum, we now have a peak that originates from IC around N, where the slop of the phase space just increased. In Fig. 4.7 we can see that this slope change is earlier for shorter pulses, which will lead to smaller detected energy of the LES peak positions.

To study the dynamics of the LES electrons, we extracted two typical classical trajectories from the simulation: in Fig. 4.10(a) we plotted two trajectories solved with initial conditions A and B near the LES peak position from Fig. 4.7. Those trajectories are the ones born with a finite initial transverse momentum and revisit the neighborhood of the parent ions (orange area in Fig. 4.10(a)) two or three times as the periodic field pulls them away from the parent ions. Each time the electron comes close to the ionic core, it gets a kick in transverse direction towards the core (Fig. 4.10(c) and 4.10(d)). This Coulomb interaction is maximized when the electron can get close enough to the proximity of the ionic core, which correspond to area I and II in Fig. 4.10. As the laser pulse gets shorter, the field amplitude drops faster after the peak of the pulse envelop (Fig. 4.10(b)). So at the biggest birth phase in Fig. 4.7, the field strength of the longer pulse (red line) after one and half cycles is still strong enough to pull back the photo-electrons that are born in a phase further away from the peak of the field close enough to the ionic core to get transverse Coulomb focusing. Thus on-axis electron population get enhanced to form the LES peak. In the case of shorter pulses (blue line), the electric field one and half cycles later is only strong enough to pull back the electrons that are born closer to the peak of the field.

**Role of longitudinal and transverse component of the Coulomb force**

From the intuitive classical argument, one might think that transverse Coulomb focusing is the dominating mechanism behind LES. To study the role of longitudinal trajectory bunching and transverse Coulomb focusing in the formation of LES, we did CTMC simulations with longitudinal component of the Coulomb force turned off and transverse com-
Figure 4.10: Two typical LES trajectories in 2-cycle and 5-cycle laser field. The corresponding initial conditions are A and B in figure 4.7. Panel (a) classical motion of the electron from IC A (blue line) and IC B (red line). The area in orange indicates when the electron gets closest to the ionic core, it feels most Coulomb force from the parent ion. This happens at first and second soft recollision (I and II respectively). Panel (b) strength of the field vs. time. Panel (c) transverse displacement vs. time. (d) transverse momentum vs. time. (e) longitudinal momentum vs. time. In the gray inset of (e) is the asymptotic limit of the longitudinal momentum, in which the electron from 5-cycle-pulse condition is detected with larger momentum.
Figure 4.11: Low-energy photoelectron distribution in full Coulomb field, longitudinal Coulomb field and transverse Coulomb field from CTMC simulation. The red dashed line represents the $0.1U_p$ position.
Figure 4.12: Low-energy photoelectron spectra at different angles in full Coulomb field, longitudinal Coulomb field and transverse Coulomb field from CTMC simulation. The red dotted line is the $0.1U_p$ position.
Figure 4.13: Angular distribution of the LES from in N₂ experimental result reproduced from [92]. The laser intensity is $2.6 \times 10^{14}$ W/cm² and wavelength is 2.0 µm. It’s zoomed in to $p_{\parallel} = 0$ to $\sqrt{0.1} U_{p}$. In the bottom panel is shown line outs from the top panel, to be compared with Fig. 4.12.
ponent turned off. The results are plotted in Fig. 4.11 and 4.12. The CTMC simulations are done with 2 \( \mu \)m laser pulses at \( 7.5 \times 10^{13} \) W/cm\(^2\). The pulses are 4 cycles long with a sine square envelop. The carrier-envelope phase is set to zero. The initial transverse momentum distribution follows ADK and initial longitudinal momentum is set to zero as before. As shown in Fig. 4.11, although there is always a peak near detected energy of 0.1\( U_p \), the LES peak position in the full Coulomb field and in Coulomb field only along longitudinal direction falls below 0.1\( U_p \) while the LES peak position in Coulomb field only along transverse direction is larger than 0.1\( U_p \). Line-outs of Fig. 4.11 at different detection angles are plotted in Fig. 4.12. It clearly shows that the longitudinal Coulomb field leads to the same LES peak position as the case of full Coulomb field. However, in this case the most prominent peak is not along the polarization axis but slightly off-axis.

In general, if one switches off the transverse or longitudinal Coulomb potential, the probability for any interaction with the ion significantly decreases, so that both the peak and the background are weak. Switching off the Coulomb force in one direction changes the physical problem qualitatively and one should be careful to draw general conclusions from this. Here it shows that both transverse and longitudinal effect are important in shaping the overall spectrum, and neither of them was able to reproduce the LES peak by itself. If the transverse Coulomb focusing were the only mechanism. As it’s just a redistribution of photoelectrons, the LES should vanish when summing over all detection angles. In Fig. 4.14

![Figure 4.14: Photoelectron spectrum integrated over all transverse momentum: comparison between experimental data and CTMC simulation](image)
is plotted the photoelectron yield as a function of longitudinal momentum. If the Coulomb only affected the distribution in the transverse direction, the resulting curve would have been smooth. However, due to the interaction of the Coulomb potential with the photoelectrons in longitudinal direction, the integrated curve still shows a peak in the LES position. So the role of longitudinal component of the Coulomb force is just as important as the transverse component of the Coulomb force, if not more.

4.2.3 Analytical approach

The experimental and CTMC numerical simulation results (Fig. 4.6) indicate that the LES position depends (i) sensitively on the pulse length, but (ii) only weakly on the target and laser parameters, once the trivial dependence on $U_p$ is factored out, and (iii) that the CEP-averaged experimental results agree quite well with our classical numerical calculation, laser focus averaged over a Gaussian pulse profile but at fixed zero CEP (triangles). The experimental conditions and numerical parameters can be found in the caption of Fig. 4.6. That the CEP-fixed numerical results agree with the experimental ones, which can be interpreted as an average over the CEP due to the Gouy phase shift along the Gaussian laser focus is not obvious, in particular considering the pronounced CEP dependence of the LES for short pulses [86,87].

The expression for our analytical results (solid lines in Fig. 4.6) will directly explain and illustrate (i)-(iii). Although easily generalizable to higher order LES recollisions and the VLES, we restrict ourselves here for the sake of clarity to the principal LES peak. To this end we consider a free electron moving in one dimension in a time-dependent vector potential $A(t)$

$$H = \frac{(p - A(t))^2}{2}. \quad (4.2)$$

Hamilton’s equations produce a constant drift momentum which assumes the value $p_d = A(t_0)$ if we demand that the velocity $\dot{x}(t_0) = 0$ (tunneling condition). Integration of $\dot{x}(t) = p_d - A(t)$ in time from $t_0$ to the recollision time $t^* = t_0 + \Delta t$ gives

$$x(t^*) = p_d \Delta t + \int_{t_0}^{t^*} dt \, A(t_0 + t). \quad (4.3)$$
For a soft recollision leading to the LES as observed in the experiment, \( \Delta t = 3\pi/\omega \). This follows from the fact that both tunneling and recollision occur when the vector potential \( A(t) \) vanishes [149]. According to Eqn. (4.3) the recollision condition \( x(t^* ) = 0 \) requires a particular drift momentum which can be interpreted as the average of the time-dependent vector potential over \( \Delta t \), the time it takes the electron from the tunnel exit to the soft recollision,

\[
p = -\frac{1}{\Delta t} \int_{0}^{\Delta t} dt A(t_0 + t).
\]  

Equation (4.4) predicts a reduction of the LES peak momenta for finite pulse length by the factor \( \zeta(n, \phi) \) compared to a monochromatic field (\( \zeta = 1 \)) and a pronounced dependence on the CEP \( \phi \) as illustrated in Fig. 4.15. However, since the experimental signal comes from the whole focal volume with Gouy phase shift of \( \pi \) across it, Eqn. 4.6b needs to be averaged over all CEP to reproduce experimental data. The \( \zeta(n, \phi) \) for \( \phi = \pm \pi/2 \) almost symmetrically bracket the central curve for zero CEP which is easily seen from a
Taylor expansion of Eq. (4.6b) about $\phi = 0$, since the quadratic term is already suppressed by a factor $(n\pi)^2$. This suggests, that up to a small correction proportional to $n^{-2}$, CEP averaging $\bar{\zeta}(n) = \frac{1}{\pi} \int_{-\pi/2}^{+\pi/2} \, d\phi \zeta(n, \phi)$ will give the zero CEP result $\bar{\zeta}(n) \approx \zeta(n, 0)$,

$$\bar{p}(n) \approx p_\infty \bar{\zeta}(n) = \frac{p_\infty}{2} \left(1 + e^{-c(3/n)^2}\right)$$  \hspace{1cm} (4.7)$$

for the CEP-averaged LES momenta, indistinguishable from exact CEP averaging (grey line in Fig. 4.15) for $n \geq 2$.

The laser properties enter Eqn. (4.7) only as an overall scale. Hence, the LES dependence $\bar{\zeta}(n)$ on the pulse length Eqn. (4.7) is universal in the sense that the ratio of the LES position for two different pulse lengths $p(n)/p(n') = \bar{\zeta}(n)/\bar{\zeta}(n')$ does neither depend on properties of the light nor of the target. Remarkably, this property of the LES time dependence is largely preserved even under modifications of the target (Coulomb) potential and the experimentally necessary laser focus averaging which we will introduce now.

Firstly, in the numerical calculation all LES peaks appear slightly red-shifted compared to (4.7), since the electron suffers a small momentum reduction before finally leaving the (attractive) potential. This momentum change along the laser polarization can be expressed
\[ \delta p = - \int_0^\infty dt \frac{d}{dz} V(\vec{r}) \bigg|_{\vec{r}(t)} = -c_{3D} \left( \frac{\omega^3}{F} \right)^{\frac{1}{5}} \] (4.8)

with \( \vec{r}_s(t) = \{ \rho, z \} = \{ \rho_s, z_s + \frac{F}{2} [t-t_s]^2 \} \), the soft-recollision trajectory without potential, and the soft collision at \( \{ \rho_s, z_s \} = (2\omega^2)^{1/5} \{ 2.723, -1.521 \} \) for a 3D Coulomb potential with the value \( c_{3D} = 0.073 \) of the integral Eqn. (4.8) [149]. The resulting LES momentum redshift \( \delta p/p_\infty \) amounts to about 3% for the laser parameters considered here and agrees very well with the classical numerical result (not shown).

In our experiment the photoelectrons come from the full Gaussian focus, so volume averaging is also required. Since we are interested here only in the position of the LES peak, it is sufficient to consider ionization from the center half-cycle. The ionization rate is given by the static field expression

\[ P(\vec{F}) = \frac{4}{|\vec{F}|} \exp(-2/3|\vec{F}|). \]

\( \vec{F} \) is the reduced field strength \( \vec{F} = F/[2I_p]^{3/2} \) with the instantaneous field \( F \) and the ionization potential \( I_p \).

Using the volume intensity distribution in a Gaussian focus introduced in chapter 2, with \( I_0 = F_0^2 \) the maximal intensity at the center, \( \eta \equiv F/F_0 \) and \( \tilde{F}_0 = F_0/(I_p)^{3/2} \), the ionization rate per field strength reads

\[ P_{\tilde{F}_0}(\eta) \propto \exp \left[ -\frac{2}{3\tilde{F}_0 \eta} \right] \frac{4\eta^2}{\eta^5} \sqrt{1 - \eta^2}. \] (4.9)

The focal-averaged LES-peak positions are obtained by integration \( \bar{p} \propto \eta \) from Eqn. (4.7) with the weight Eqn. (4.9) between 0 and 1. Realizing that for relevant parameters \( \tilde{F}_0 < 1/10 \) one can expand Eqn. (4.9) about \( \eta = 1 \), the averaging can be done analytically to give

\[ P(n) = \bar{p}(n)/C_{av} \text{ where} \]

\[ C_{av} = 1 + \frac{9}{4} \frac{F_0}{(2I_p)^{3/2}}, \] (4.10)

which gives another reduction \( 1/C_{av} \) of the LES momentum of about 10% for the laser parameters and targets considered here.

The \( F^{1/5} \)-dependence of \( \delta p \) is too weak for a significant averaging effect. At first sight, \( \delta p \) and the focal averaging seem to destroy the universality of the pulse length dependence of the LES with additional dependence on laser and target \( (I_p) \) properties, respectively. Taking advantage of the fast convergence of Eqn. (4.7) with \( n \) to \( p_\infty \) and the fact that \( \delta p \) is
a small correction to \( p(n) \), it turns out that the universality of the LES pulse dependence is preserved since, to a good approximation, the \( \delta p \)-shifted and focus-averaged LES momentum assumes the original form Eqn. (4.7) with \( p_\infty \) replaced by \( p_{\text{eff}}^\infty \),

\[
p_{\text{LES}}(n) = \left( \frac{p_\infty}{C_{\text{av}}} + \delta p \right) \bar{\zeta}(n) \equiv p_{\text{eff}}^\infty \bar{\zeta}(n).
\]  

(4.11)

This is the final expression for the LES position, shown as energy \( p_{\text{LES}}^2(n)/(2U_p) \) with solid lines in Fig. 4.6. Note, that the corrections due to the potential \( \delta p \) and focus averaging \( C_{\text{av}} \) reduce the LES position in energy by about 25\% compared to the “pure” result (4.7). The product form Eqn. (4.11) restores the universal pulse length dependence \( \bar{\zeta}(n) \) of the LES and shows how the laser parameters and the binding energy of the electron influence the LES. Expanding Eqn. (4.11) in \( \omega \) for fixed Keldysh parameter \( \gamma = \sqrt{I_p/2U_p} \),

\[
p_{\text{LES}}(n) = p_\infty \bar{\zeta}(n) \left( 1 - \frac{9}{16\gamma^3 U_p} - \frac{3\pi c_{3D}}{2^{11/5} 5 p^{3/5}} \right),
\]  

(4.12)

shows that in addition to the strong-field nature of the LES, it is also a phenomenon unique with the long wavelength laser field.

In summary, the completely analytical formulation in good agreement with the numerical and experimental results shows that the pulse length dependence is universal since all residual dependences on the laser properties and the target can be cast into a factor of proportionality which describes the position of the LES for long pulses with analytical target dependence and laser focus averaging also included.

4.3 Discussion and outlook

4.3.1 TDSE result

Ultimately, the microscopic world is quantum mechanical. Everything about it is contained in the time-dependent Schrödinger equation (TDSE). However, analytical solutions are only possible for a handful of quantum mechanical systems. Luckily, with the help of powerful modern supercomputers, “brutal force” numerical solution of the TDSE is possible. But even for the fast developing modern supercomputers, numerical treatment of
Figure 4.16: TDSE calculation result of the LES pulse duration dependence for a hydrogen atom in laser field with intensity of $1 \times 10^{14}$ W/cm$^2$, wavelength of 1.8 µm and cosine squared temporal profile with duration of 4, 8 and 12 cycles.

the full quantum mechanical system is still too computationally demanding. Therefore, the numerical TDSE is often carried out under the single-active-electron approximation (SAE). The SAE-TDSE solution provides useful benchmarks against the experiment and other theoretical calculations. In Fig. 4.16 is plotted the low-energy part of photoelectron spectrum calculated with Prof. Dieter Bauer’s open-source SAE-TDSE code Qprop [153]. Photoelectrons are produced from a hydrogen atom by laser field with intensity of $1 \times 10^{14}$ W/cm$^2$, wavelength of 1.8 µm and cosine squared temporal profile with duration of 4, 8 and 12 cycles. The SAE-TDSE contains all essential ingredients of the quantum mechanical system: ground state and excited states of the atom, the long range Coulomb potential and the full description of the electron wave packet. In principle, one needs to calculate contributions from the full volume of the Gaussian focus to compare with the experiment. However, the computational demands grow quickly with increasing laser wavelength. So we have not yet completed the focal-volume averaged TDSE result. Despite the rich features in the photoelectron spectra due to the single intensity, one can clearly identify the LES in Fig. 4.16. The LES peak position decreases from $0.07U_p$ to $0.02U_p$ when the pulse duration decrease from 12 to 4 cycles, qualitatively consistent with experimental and theoretical results earlier this chapter.
4.3.2 CEP effect of LES

The universal pulse duration dependence of the LES peak position provides further evidence of its soft recollision origin. The mechanism suggests that LES should depend sensitively on the carrier-envelope phase (CEP) of few-cycle pulses. However, due to the Gouy phase shift across the focal volume, the CEP dependence of LES is averaged out. In principle, one can measure the CEP dependence by restricting signal from a small portion of the focal volume through inserting a slit between the interaction area and the detector [112] or using combination of thin atomic/molecular beam targets and slow focusing geometry [154].

CTMC simulations were carried out to study the CEP dependence of the LES numerically. The results are shown in Fig. 4.17. The parameters are: $\lambda = 1.8\mu m$, $I_p = 15.7$ eV (Ar) and intensity $= 1 \times 10^{14}$ W/cm$^2$. The plot in the top panel of Fig. 4.17 shows that the peak position and height of the LES depends sensitively on the CEP of the few-cycle pulse. This makes LES a potential tool for CEP measurement.

CEP measurement is critical since the field of few-cycle laser pulses depend drastically on its CEP. One of the most popular CEP characterization method is utilizing the f-2f interferogram [105] as introduced in chapter 3. However, the f-2f scheme can only measure the relative CEP change but is not able to determine the absolute value of CEP. One of the most successful methods in determining the absolute CEP of a few-cycle pulse is the stereo-ATI [155]. In a stereo-ATI measurement, the plateau of xenon photoelectron spectrum under 0.8 $\mu$m laser radiation along both sides of the polarization direction are recorded. The HATI photoelectron yield on the plateau at each side are asymmetric. The asymmetry depends on the CEP of the few-cycle pulse. Choosing two different energy regions on the plateau and characterizing the asymmetry in photoelectron yield, one can get the absolute CEP value. For more details about the stereo-ATI, refer to [155] and [156]. So far, the stereo-ATI is successfully applied to measure CEP of 0.8 $\mu$m lasers. In principle, it could be extended to measure the CEP of few-cycle mid-infrared laser pulses. However, the photoelectron plateau yield drops fast with laser wavelength ($\propto \lambda^{-4}$). Combined with the fact that
Figure 4.17: CEP dependence of the LES calculated with CTMC simulation In the top panel is plotted the evolution of LES as a function of CEP. In the bottom panel is plotted asymmetry of LES yield (blue) and LES peak position (red) as a function of CEP. See text for details.
intensity achieved with most few-cycle mid-infrared lasers are lower than 0.8 µm lasers, one would struggle with signal level when applying stereo-ATI to mid-infrared pulses. In contrast, the LES photoelectron yield is usually more than four order of magnitude higher than plateau yield at mid-infrared wavelengths. So it would be advantageous to utilize the CEP dependence of the LES for absolute CEP measurement of few-cycle mid-infrared laser pulses.

To measure absolute CEP of a few-cycle mid-infrared pulse, define the asymmetry parameter similar to stereo-ATI:

\[ A_H = \frac{H_L - H_R}{H_L + H_R}, \]  

(4.13)

where \( H_L \) and \( H_R \) are integrated photoelectron counts in energy range [0.8, 1.2] eV from the left and right side detector, respectively. Numerical simulation result of the asymmetry parameter as a function of CEP is plotted with blue lines in the bottom panel of Fig. 4.17. Our simulation shows that as long as the integration energy window is within the LES, asymmetry parameter \( A_H \) does not depend on window position. It also shows that the asymmetry parameter \( A_H \) has a two-fold degeneracy at given value. To lift this degeneracy, we turn to the asymmetry of the LES peak position, which is defined as

\[ A_P = \frac{P_L - P_R}{P_L + P_R}, \]  

(4.14)

where \( P_L \) and \( P_R \) are the LES peak position from the left and right side detectors, respectively. Simulation result of \( A_P \) is plotted with red lines in the bottom panel of Fig. 4.17. It shows that \( A_P \) is positive for CEP range 0–\( \pi \) and negative for CEP range \( \pi \)–2\( \pi \). Combining parameters \( A_H \) and \( A_P \), the absolute CEP of a few-cycle laser pulse can be determined. At given intensity, there is a one-to-one correspondence of the LES peak position to the CEP of the few-cycle pulse. We do not propose to use the LES peak position as LES measurement parameter because of two reasons. First, as a function of CEP, the LES not only changes peak position, but also changes shape. For example, at CEP around \( \pi \), the LES shows two peaks with comparable height which makes it hard to define the LES peak position (notice the sharp jump of \( A_P \) around that value). Second, the asymmetry parameters are
less susceptible to laser intensity fluctuations.

In summary, the CEP of few-cycle laser pulses can be measured reliably with stereo photoelectron LES measurements. Combined with the universal scaling of CEP averaged LES peak position, the temporal behavior of a few-cycle mid-infrared laser pulse (pulse duration and CEP) can be completely characterized.
Chapter 5
DISCUSSION AND OUTLOOK

So far we have shown that the strong-field processes deep in the tunneling regime \((\gamma \lesssim 0.5)\) can be quantitatively described within the semi-classical model. In chapter 3 it was shown that the HATI spectra can be deciphered under the recollision picture to extract molecular structures with LIED and FABLES. In chapter 4, the LES is attributed to the soft recollision of the tunneled photoelectron. The semiclassical model reproduced quantitatively the LES peak position as a function of laser pulse duration.

5.1 Role of wavelength in LIED and FABLES

It has been emphasized throughout this dissertation that the semiclassical model should only be applied to strong-field systems with Keldysh parameter \(\gamma < 1\). It is most favorable to work with systems deep in the tunneling regime (typically \(\gamma \lesssim 0.5\)) so that one can get quantitatively accurate result in LIED and FABLES. As a function of laser field strength \(F\) and laser wavelength \(\lambda\), the Keldysh parameter is

\[
\gamma = \frac{2\pi c \sqrt{2I_p}}{\lambda F}
\]  

(5.1)

where \(c\) is the speed of light \((c = 137 \text{ a.u.})\) and \(I_p\) is the ionization potential of the atom/molecule. For a given atom/molecule \((I_p\) fixed), one can decrease \(\gamma\) by increasing laser wavelength \(\lambda\) or laser field strength \(F\). As is illustrated in Fig. 3.1, the barrier formed by the atom/molecule and the laser field will be suppressed more and more as the laser field strength increases. When the laser field strength is high enough such that the
Table 5.1: Minimum laser wavelength required for LIED for different molecules.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>N₂</th>
<th>O₂</th>
<th>CO₂</th>
<th>NO</th>
<th>N₂O</th>
<th>C₂H₂</th>
<th>C₆₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iₚ (eV)</td>
<td>15.6</td>
<td>12.1</td>
<td>13.8</td>
<td>9.3</td>
<td>12.9</td>
<td>11.4</td>
<td>7.6</td>
</tr>
<tr>
<td>λₘᵟₗ (µm)</td>
<td>1.2</td>
<td>1.7</td>
<td>1.4</td>
<td>2.6</td>
<td>1.6</td>
<td>1.9</td>
<td>3.5</td>
</tr>
<tr>
<td>λ₁₀₀ (µm)</td>
<td>1.2</td>
<td>2.0</td>
<td>1.6</td>
<td>3.4</td>
<td>1.8</td>
<td>2.3</td>
<td>5.3</td>
</tr>
</tbody>
</table>

Ionization potential data Iₚ is taken from NIST website. λₘᵟₗ is the wavelength required to get γ = 0.5 at OTBI intensity. λ₁₀₀ is the wavelength required to get 3Uₚ = 100 eV at OTBI intensity.

ground state of the atom/molecule is above the top of the barrier, the ionization process should no longer be described with optical tunneling ionization, but with the over-the-barrier ionization (OTBI) mechanism instead. Photoelectron dynamics in the OTBI is complex and cannot be described with the semiclassical model [157]. Consequently, the we should limit the laser intensity below the OTBI intensity. The OTBI field strength can be estimated by

\[ F_{\text{OTBI}} = \left( \frac{I_p}{2} \right)^2. \]  

(5.2)

Substituting it into Eqn. 5.1, one get the smallest γ achievable for an atom/molecule with ionization potential Iₚ with laser wavelength λ

\[ \gamma(\text{OTBI}) = \frac{8\pi c \sqrt{2}}{\lambda I_p^{3/2}}. \]

(5.3)

For imaging purposes, one would wish to ensure that γ(OTBI) ≤ 0.5, which requires

\[ \lambda \gtrsim \frac{16\pi c \sqrt{2}}{\left( \frac{I_p^{3/2}}{9739} \right)} = 9739/I_p^{3/2}. \]

(5.4)

Estimations of the minimum laser wavelength to meet the deep-tunneling condition for typical molecules are presented in table 5.1, they are all beyond the typical Ti:Sapphire wavelength 0.8 µm.

Another important requirement of molecular imaging with LIED and FABLES is for the recollision electrons to have core-penetrating kinetic energy. As introduced in chapter 3, the maximum LIED returning electron energy is \( E_r^{\text{max}} \sim 3U_p \). As a function of laser
wavelength $\lambda$ and field strength $F$, the ponderomotive energy $U_p$ is

$$U_p = \frac{F^2\lambda^2}{16\pi^2c^2}. \quad (5.5)$$

Again, the field strength has to stay below the OTBI value, so the maximum return energy one can achieve for fixed $I_p$ and $\lambda$ is

$$U_p^{\text{max}} = \frac{I_p^4\lambda^2}{256\pi^2c^2}. \quad (5.6)$$

For high-energy recollision, one demands $3U_p^{\text{max}} > 100$ eV. So the laser wavelength need to satisfy $\lambda > \lambda_{100}$, where

$$\lambda_{100} = \frac{4\pi c \sqrt{100/27.2/3}}{(I_p/2)^2} = \frac{7623}{I_p^2} \quad (5.7)$$

is the minimum laser wavelength required to ensure $3U_p = 100$ eV. $\lambda_{100}$ values for some typical molecules are presented in table 5.1.

### 5.2 Event rate of rescattered electrons in LIED and FABLES

Mid-infrared laser wavelengths are necessary for molecular imaging with LIED and FABLES. However, the longer the wavelength, the longer the electrons will travel from birth to recollision, thus suffering more wave packet dispersion. Also, the scattering cross section usually drops exponentially with increasing electron energy. So with longer laser wavelengths also comes the disadvantage of lower rescattered signal yield. It was demonstrated experimentally that the ratio of direct electron yield ($< 2U_p$) and backscattered electron yield ($> 2U_p$) scales roughly as $\lambda^{-4}$ [129]. So the most ideal wavelength to use for LIED and FABLES should be larger than the values calculated with Eqn. 5.4 and 5.4 but not by too much such that the signal level becomes too low.

Along laser polarization direction, the ratio between number of rescattered electrons and total electron yield is usually less than $10^{-4}$ at mid-infrared wavelengths. So LIED and FABLES were not possible without the high event rate created by high repetition rate laser systems (kHz).
Our LIED photoelectron angular distributions are measured with a TOF spectrometer one-angle-at-a-time by rotating the laser polarization with a half-wave plate. This scanning approach requires long data acquisition time and is susceptible to instabilities of experimental conditions, e.g. the intensity fluctuations of mid-infrared laser pulses produced by nonlinear processes. Other ways to measure photoelectron angular distribution includes velocity-map imaging (VMI) \[158\] and reaction microscope (ReMi) \[159\]. Although they used to be limited to detecting electrons with energy less than 100 eV, LIED has motivated new development of VMI with 350 eV maximum detection energy \[160\] and ReMi with 600 eV maximum detection energy \[161\]. With more engineering improvements, keV electron detection should be within reach. However, although TOF’s are less efficient compared to VMI’s and ReMi’s in angular distribution measurement, they offer superior signal-to-noise ratio. The signal-to-noise ratio in our TOF systems are typically better than \(10^{-6}\) while typical number for VMI’s and ReMi’s is about \(10^{-4}\) or \(10^{-5}\). The signal-to-noise is crucial for LIED experiments since it determines the vertical dynamic range of the measured photoelectron distribution.

Improvements can be made to increase the data acquisition speed in LIED with TOF. One way is by using multiple TOFs simultaneously to detect several angles at a time. For example, the AMO division in SLAC Linac Coherent Light Source operates with five electron TOF’s simultaneously. Implementing similar designs for LIED experiment could significantly reduce the acquisition time. Another way to increase the event rate is by increasing the laser repetition rate event further. For example, a powerful optical parametric chirped pulse amplification laser system built by Prof. J. Biegert et.al. \[162\] could generate mid-infrared laser pulses at 160 kHz repetition rate.

### 5.3 Pump-probe measurement with LIED and FABLES

The power of LIED and FABLES lies in their unprecedented temporal resolution. Although ultimately below one optical cycle, the temporal resolution is deteriorated by the multiple-cycle duration of laser pulses \[76\]. This multi-cycle smearing effect could be solved
straightforwardly by using laser pulses with few-cycle duration and controlled CEP. The hollow-core fiber based pulse compression scheme in our lab can produce laser pulses down to two optical cycles in FWHM. With a two-cycle pulse, the tunneling ionization rate from adjacent half cycles are only less than 10% of that from the center cycle. Then the temporal resolution is better than an optical-cycle within the peak of the pulse envelop. Another advantage comes with the few-cycle driving laser is that contribution from multiple returns will be greatly suppressed, further enhancing the ability of LIED.

The characterization of few-cycle pulses is a challenging job, especially the determination of the absolute CEP. Fortunately, LIED and FABLES work under the tunneling condition, in which the LES can be calibrated for pulse duration and CEP measurements.

With the fully characterized few-cycle mid-infrared laser pulses, LIED and FABLES can be implemented to image molecular transformations in real time. In the following we’ll propose a typical procedure for such an experiment.

Nitrous oxide (N$_2$O) is an important greenhouse gas and its photo-dynamics is of great interest to chemists and physicists. Under 0.2 µm radiation, N$_2$O photo-dissociates into an oxygen atom in excited state and a nitrogen molecule in its electronic ground state. This makes it a suitable system for real-time dynamical imaging. The required minimum wavelengths for tunneling condition and hard-collision condition is listed in table 5.1. The two-cycle 1.8 µm pulses from our fiber compressor are ideal source to study this process. N$_2$O is a linear molecule with polarizability $\alpha_\parallel = 2.880$ Å$^3$ along laser polarization direction and $\alpha_\perp = 0.373$ Å$^3$ perpendicular to laser polarization direction. So the alignment is even easier than N$_2$ molecule.

All three output from the TOPAS will be used in the experiment. Schematic diagram of the proposed experiment is shown in Fig. 5.1. In step 0, the depleted 0.8 µm pump will be converted to 0.2 µm with fourth frequency generation to produce the wavelength needed to initiate N$_2$O single photon dissociation. The signal at 1.4 µm will be used to align the N$_2$O molecules impulsively. A beam stacking scheme can be implemented if higher degree of alignment is needed. The idler at 1.8 µm will be sent through the hollow-core fiber based pulse compressor to generate the two-cycle pulse for LIED or FABLES measurement. In
Figure 5.1: proposal for a pump-probe measurement of $\text{N}_2\text{O}$ dissociation. Green pulse train: 1.4 $\mu$m alignment pulse, blue pulse: 0.2 $\mu$m dissociation pulse, orange pulse: LIED/FABLES pulse. See text for details.
step 1, the 1.4 µm alignment pulse is focused onto the rotationally cooled N₂O molecular beam and initiates a rotational wave packet. Assuming initial temperature 10 K and laser intensity $2 \times 10^{13}$ W/cm², our simulations show that the $\langle \cos^2 \theta \rangle$ can be as high as 0.82 at half revival time, which is about 20 ps after the alignment pulse. Furthermore, the aligned wave packet lasts more than 100 fs. In step 2, the 0.2 µm pulse incidents on the aligned molecular ensemble at maximum alignment and pumps the N₂O molecule to a dissociative state. It then fragments into ground state N₂ and excited state O⁺ on the femtosecond timescale. In step 3, the few-cycle 1.8 µm pulse incidents onto the dissociating N₂O molecule and photoelectron distribution can be taken at different delay to observe the dissociation process in real time with LIED or FABLES.

So far all preliminary demonstration of imaging methods LIED and FABLES have been finished. A controlled experimental like the one proposed above will directly reveal the power of LIED/FABLES in ultrafast imaging.
Bibliography


[102] Bruno E. Schmidt, Pierre Bejot, Mathieu Giguere, Andrew D. Shiner, Carlos Trallero-Herrero, Eric Bisson, Jeroˆme Kasparyan, Jean-Pierre Wolf, David M. Villeneuve,


## Appendix A

### ATOMIC UNITS SYSTEM

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>SI value</th>
<th>SI unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>elementary charge</td>
<td>e</td>
<td>$1.602176565(35) \times 10^{-19}$</td>
<td>C</td>
</tr>
<tr>
<td>reduced Planck Constant</td>
<td>h</td>
<td>$1.054571726(47) \times 10^{-34}$</td>
<td>J·s</td>
</tr>
<tr>
<td>electron rest mass</td>
<td>$m_e$</td>
<td>$9.10938291(40) \times 10^{-31}$</td>
<td>kg</td>
</tr>
<tr>
<td>atomic unit of vacuum permittivity</td>
<td>$4\pi\varepsilon_0$</td>
<td>$1.112650056053618 \times 10^{-10}$</td>
<td>F/m</td>
</tr>
</tbody>
</table>

**Table A.1:** Defining values in atomic units

Using the above definition, it can be derived:

Length: $a_0 = \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} = \frac{\hbar}{\alpha m_e c} = 0.52917721092(17) \times 10^{-10}$ m (Bohr radius)

Time: $\tau_0 = \frac{(4\pi \varepsilon_0)^2 \hbar^3}{m_e e^4} = \frac{\hbar}{\alpha^2 m_e c^2} = 2.418884326502(12) \times 10^{-17}$ s

Velocity: $v_B = \frac{4\pi \varepsilon_0 \hbar}{4\pi \varepsilon_0 h} = \alpha c = 2.18769126379(71) \times 10^6$ m/s = $a_0/\tau_0$

Energy: $E_h = \frac{m_e e^4}{(4\pi \varepsilon_0)^2 \hbar^2} = \alpha^2 m_e c^2 = 4.35974434(19) \times 10^{-18}$ J = $m_e v_B^2$

Some other units can be derived as:

Momentum: $p_0 = \hbar/a_0 = 1.992851740(88) \times 10^{-24}$ kg·m/s

Angular frequency: $\omega_0 = 2\pi/\tau_0 = 2.597555095 \times 10^{17}$ rad/s

Electric potential $V_0 = E_h/e = 27.21138505(60)$ V

Electric field: $F_0 = E_h/ea_0 = 5.14220652(11) \times 10^{11}$ V/m

And the atomic unit of electric field intensity is conventionally defined as the field...
intensity when field strength is one atomic unit:

Electric field intensity: \( I_0 = \frac{1}{2} \epsilon_0 c F_0^2 = 3.5094452 \times 10^{20} \text{ W/m}^2 (\times 10^{16} \text{ W/cm}^2) \)
Appendix B

**Velocity gauge and length gauge in strong-field physics**

The electric field \( \mathbf{F} \) and magnetic field \( \mathbf{B} \) can be calculated from scalar potential \( \phi \) and vector potential \( \mathbf{A} \) by

\[
\mathbf{F} = -\nabla \phi - \frac{\partial}{\partial t} \mathbf{A} \tag{B.1}
\]

\[
\mathbf{B} = -\nabla \times \mathbf{A} \tag{B.2}
\]

\( \mathbf{F} \) and \( \mathbf{B} \) are unchanged under substitutions \( \phi \to \phi - \partial \chi / \partial t, \mathbf{A} \to \mathbf{A} + \nabla \chi \) where \( \chi \) is any scalar field. This is the gauge invariance. The Hamiltonian of an electron in a electromagnetic field is

\[
H = \frac{1}{2} (\mathbf{p} + \mathbf{A})^2 - \phi \tag{B.3}
\]

where \( \mathbf{p} = \nabla / i \) is the canonical momentum, the mechanical momentum \( \mathbf{p}_m = \mathbf{p} + \mathbf{A} \). The time-dependent Schrödinger equation (TDSE) can be proven to be “form invariant” under a gauge transformation. The TDSE with Hamiltonian B.3 is

\[
i \frac{\partial}{\partial t} \psi = \left[ \frac{1}{2} (\mathbf{p} + \mathbf{A})^2 - \phi \right] \psi. \tag{B.4}
\]

Replacing \( \psi \) by \( \psi = e^{ix} \psi' \), Eqn. B.4 can be transformed to

\[
i \frac{\partial}{\partial t} \psi' = \left[ \frac{1}{2} (\mathbf{p} + \mathbf{A}')^2 - \phi' \right] \psi', \tag{B.5}
\]

where \( \phi' = \phi - \partial \chi / \partial t, \mathbf{A}' = \mathbf{A} + \nabla \chi \) is the gauge transformation relation.
In velocity gauge under dipole approximation $\phi^{(V)} = 0$ and $A^{(V)}(t)|_{r=0}$, 

\[ H^{(V)} = \frac{1}{2}(p + A^{(V)})^2. \]  

(B.6)

Gauge transformation function from velocity gauge to length gauge is $\chi = -r \cdot A^{(V)}$, so

\[ \phi^{(L)} = \phi^{(V)} - \partial \chi / \partial t = r \cdot \partial A^{(V)} / \partial t = -r \cdot F, \]  

(B.7)

\[ A^{(L)} = A^{(V)} + \nabla \chi = A^{(V)} - \nabla (r \cdot A^{(V)}) = 0. \]  

(B.8)

So the Hamiltonian in length gauge is

\[ H^{(L)} = \frac{1}{2}p^2 + r \cdot F \]  

(B.9)

To achieve an exact solution of the Volkov state, consider the TDSE of an electron in a EM field under velocity gauge

\[ i \frac{\partial}{\partial t} \psi = \frac{1}{2}(p + A^{(V)})^2 \psi. \]  

(B.10)

By applying Fourier transform in space for the above TDSE and solving the wave equations in momentum space, one could find the Volkov state in space representation to be:

\[ \psi (r,t) = \frac{1}{(2\pi)^{3/2}} e^{ip \cdot r} e^{-i \int_0^t d\tau (p + A(\tau))^2} \]  

(B.11)

Transforming to length gauge, the Volkov state is then:

\[ \psi (r,t) = \frac{1}{(2\pi)^{3/2}} e^{i(p+A(t)) \cdot r} e^{-i \int_0^t d\tau (p + A(\tau))^2} \]  

(B.12)

Direct derivation from the length gauge TDSE is more complicated, see tutorial [163] for details.
# Appendix C
## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADC</td>
<td>Analogy-to-digital converter</td>
</tr>
<tr>
<td>ADK</td>
<td>Ammosov, Delone and Krainov theory</td>
</tr>
<tr>
<td>ATI</td>
<td>Above threshold ionization</td>
</tr>
<tr>
<td>CED</td>
<td>Conventional electron diffraction</td>
</tr>
<tr>
<td>CEP</td>
<td>Carrier-envelop phase</td>
</tr>
<tr>
<td>CPA</td>
<td>Chirped pulse amplification</td>
</tr>
<tr>
<td>CTMC</td>
<td>Classical-trajectory Monte Carlo simulation</td>
</tr>
<tr>
<td>DCS</td>
<td>Differential cross section</td>
</tr>
<tr>
<td>FABLES</td>
<td>Fixed-angle broadband laser-driven electron scattering</td>
</tr>
<tr>
<td>FROG</td>
<td>Frequency-resolved optical gating</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HATI</td>
<td>High-order above threshold ionization</td>
</tr>
<tr>
<td>HCF</td>
<td>Hollow-core fiber</td>
</tr>
<tr>
<td>HHG</td>
<td>High harmonic generation</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Ionization potential</td>
</tr>
<tr>
<td>IAM</td>
<td>Independent atom model</td>
</tr>
<tr>
<td>KFR</td>
<td>Keldysh-Faisal-Reiss theory</td>
</tr>
<tr>
<td>KH frame</td>
<td>Kramers-Henneberger frame</td>
</tr>
<tr>
<td>LES</td>
<td>The low-energy structure</td>
</tr>
<tr>
<td>LIED</td>
<td>Laser-induced electron diffraction</td>
</tr>
<tr>
<td>MCF</td>
<td>Molecular contrast factor</td>
</tr>
<tr>
<td>MCP</td>
<td>Microchannel plates</td>
</tr>
<tr>
<td>MIR</td>
<td>Mid-infrared (for this document $\lambda = 5 \mu m$)</td>
</tr>
<tr>
<td>MO-ADK</td>
<td>Molecular-ADK, molecular tunneling theory developed by XM Tong and CD Lin</td>
</tr>
<tr>
<td>OPA</td>
<td>Optical parametric amplifier</td>
</tr>
<tr>
<td>PPT</td>
<td>Perelomov, Popov and Terent’ev theory</td>
</tr>
<tr>
<td>QRS</td>
<td>Quantitative rescattering theory</td>
</tr>
<tr>
<td>SFA</td>
<td>Strong-field approximation</td>
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<tr>
<td>SHG</td>
<td>Second-harmonic generation</td>
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<tr>
<td>TDC</td>
<td>Time-to-digital converter</td>
</tr>
<tr>
<td>TDSE</td>
<td>Time-dependent Schrödinger equation</td>
</tr>
<tr>
<td>TOF</td>
<td>Time-of-flight</td>
</tr>
<tr>
<td>$U_p$</td>
<td>Ponderomotive potential (cycle averaged quiver energy of a particle in laser field)</td>
</tr>
</tbody>
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