

Photoelectron – residual-ion entanglement in streaked shakeup ionization of
helium

by

Hongyu Shi

B.S., South China Normal University, China, 2015

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Physics
College of Arts and Sciences

KANSAS STATE UNIVERSITY
Manhattan, Kansas

2024

Abstract

Streaked photoelectron emission spectra access the correlated dynamics of photoelectrons and residual target electrons with attosecond temporal resolution. We calculated *ab initio* single-ionization spectra for photoemission from helium atoms by co-linearly polarized ultrashort XUV and assisting few-femtosecond IR pulses. Distinguishing direct and shake-up ionization resulting in ground-state and excited ($n = 2, 3$) He^+ residual ions, respectively, we examined the effects of the correlated photoemission dynamics on the photoelectron phase-accumulation as a function of the observable photoelectron detection direction and kinetic energy, and XUV – IR pulse delay. We tracked the dynamical evolution of the residual ion in relative streaked photoemission delays and found dominant contributions for shake-up emission from the residual ion – photoelectron interaction. These are in very good and fair agreement, respectively, for $n = 2$ and $n = 3$ shake-up photoemission along the pulse-polarization directions, with previous experimental and theoretical investigations [M. Ossiander *et al.*, Nature Phys 13, 280–285 (2017)] and reveal a strong photoemission-direction dependence for shake-up ionization due to the coupling between the photoelectron and evolving residual-ion charge distribution in the IR-laser field.

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Nomenclature

- 2D - two dimensional
- 3D - three dimensional
- API - application programming interface
- CG - Clebsch–Gordan (coefficients)
- CLC - Coulomb laser coupling (delay)
- CPU - central processing unit
- CSCO - complete set of commuting operators
- DI - double ionization
- DLC - dipole laser coupling (delay)
- ECS - elastic complex scaling
- EWS - Eisenbud-Wigner-Smith (delay)
- FE - finite element
- FE-DVR - finite-element discrete-variable representation
- FWHM - full-width half-intensity maximum
- GPL - GNU general public license
- He - helium
- HHG - high-order harmonic generation

- IR - infrared (laser)
- JAD - joint angular distribution
- LAPACK - linear algebra package
- NIST - national institute of standards and technology
- OOP - object-oriented programming
- PE - photoelectron
- PWD - photoelectron wave packet delay
- RABITT - reconstruction of attosecond beating by interference of two-photon transitions
- SAE - single active electron (approximation)
- SLISC - scientific library in simple C++
- SSD - streaking spectrum delay
- TAE - two active electron (approximation)
- TDCS - triply differential cross section
- TDPT - time-dependent perturbation theorem
- TDSE - time-dependent Schrödinger equation
- TISE - time-independent Schrödinger equation
- XUV - extreme ultraviolet (laser)

Acknowledgments

The journey to completing this Ph.D. has been demanding, marked by an early transition between research groups and the intricate challenges of the current project. I am deeply grateful for the remarkable people who have supported me along the way.

Dr. Uwe Thumm, my advisor, whom I first met in the Advanced Dynamics course, has been a source of patience and understanding throughout my research. His profound expertise in atomic physics has guided me through countless formidable obstacles that at times seemed insurmountable.

My sincere thanks go to my previous advisors, Dr. Brett DePaola, Dr. Shuting Lei, and Dr. Carlos Trallero-Herrero, for their guidance as I explored various fields of AMO (atomic, molecular, and optical) physics.

I am also indebted to Dr. Jianxiong Li, Dr. Aihua Liu, and Dr. Erfan Saydanzad, who were senior Ph.D. students in our group, Dr. Hung Hoang, Dr. Marcelo Ambrosio, Dr. Francisco Navarrete and Dr. Paul Abanador, who joined us as postdoctoral researchers. Their advice on navigating the Ph.D. process and their insightful discussions about our projects have been invaluable, setting inspiring examples for me to follow.

I am grateful to Dr. Chii-Dong Lin and his postdoc, Dr. Issac Yuen, for their insightful discussions on helium atoms, which were critical to my research. I also thank Dr. Brett Esry for his thought-provoking courses in quantum mechanics and AMO physics and for introducing me to high-performance computing. Other very helpful instructors of my Ph.D. courses include Lado Samushia and Gary Wysin.

My heartfelt appreciation extends to the support staff in the Physics Department, both past and present, particularly Larry McFeeters and Vince Needham for their essential role in maintaining computing resources, and Kim Coy, Kim Elliott, and Peggy Matthews, Cindy Carlyon, Alicia Cribbs, and Peter Nelson for their assistance with administrative matters.

To my friends, Dr. Hanyu Zhang, Dr. Shulei Cao, Dr. Keyu Chen, Dr. Justin Wright, Dr. Xinya Wang, and Dr. Lianjie Xue, thank you for your camaraderie and encouragement throughout this journey.

Finally, my deepest gratitude goes to my wife, Yiping Zhu and my parents. Their unwavering love, understanding, and encouragement have been my anchor, making this journey possible.

Dedication

I dedicate this thesis to my dear wife and parents.

Chapter 1

Introduction

Since Einstein’s groundbreaking work on the photoelectric effect⁶, atomic photoionization was widely regarded as an instantaneous phenomenon. However, after the development of the Schrödinger equation in 1926, physicists found that this is not the case for photoelectron wave packet emission by a short light pulse. Due to technical difficulties, direct observation of electronic dynamics on its natural time scale remained a dream for a long time.⁷ For example, in a seminal theoretical work⁸, Wigner formulated the atomic time delay in the context of elastic particle scattering. However, it is not until the advent of well-controlled ultrashort laser pulse trains and isolated pulses from free electron laser or high-order harmonic generation (HHG) that this delay can be observed experimentally. Two fundamental experimental techniques for this purpose have been performed: attosecond streaking and RABITT (reconstruction of attosecond beating by interference of two-photon transitions).⁹ In this thesis, we focus on the former.

Attosecond ($1 \text{ as} = 10^{-18} \text{ s}$) streaking is an experimental technique to investigate the time-resolved ultrafast electronic dynamics in atoms^{4;10}, molecules^{11–13}, and solids^{14–16}. Attosecond streaking experiments provided the first direct measurement of the oscillating electric field in intense light pulses and confirmed the generation of ultrashort sub-infrared (IR) cycle extreme ultraviolet (XUV) pulses with attosecond duration^{17;18}. In a typical streaking experiment, an ultrashort XUV-pump pulse ionizes the target, emitting photoelectrons

(PEs) into the field of a femtosecond infrared (IR) probe pulse (Fig. 1.1). This allows the recording of photoelectron energy (or momentum) spectra for a set range of time delays τ between the two pulses. The τ -dependent spectra reveal information about the photoemission dynamics with attosecond resolution in time as “streaking traces”, i.e., as an oscillating photoelectron-energy (or momentum) dependence on τ that retraces the temporal profile of the IR streaking pulse with a characteristic *absolute* photoemission time delay relative to the IR-laser carrier electric field. While absolute streaking delays cannot be measured directly for photoemission from gaseous targets¹⁶, dynamical information can be accessed in streaked photoelectron spectra from *relative* streaking delays between the centers of energy of streaking traces that are related to photoemission from two energetically distinct electronic levels¹⁹.

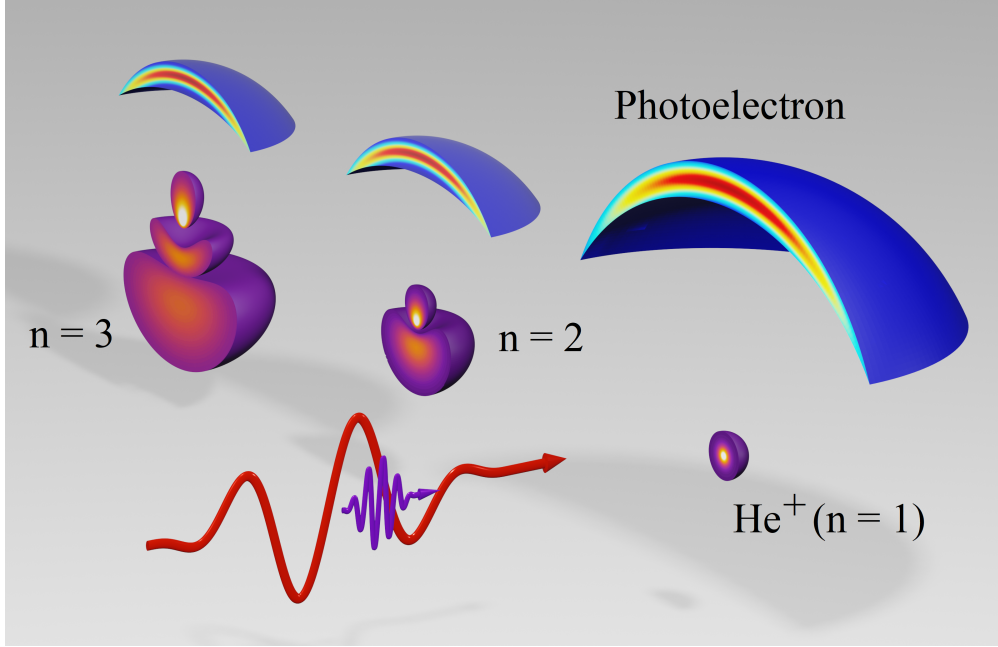


Figure 1.1: *Streaked direct (principal quantum number $n = 1$) and shake-up ($n = 2, 3$) single ionization of helium. Illumination of ground-state helium atoms by ionizing attosecond XUV pulses (purple) and assisting delayed few-femtosecond streaking IR pulses (red) create entangled pairs of photoelectron wave packets and residual He^+ (n) ions. The displayed photoelectron-wave-packet probability densities are calculated ab initio 4 fs after the XUV-pulse center has reached the atomic nucleus for an XUV-IR pulse delay of $-1/4$ IR period. The residual He^+ ($n = 2, 3$) charge densities for the most polarized Stark states and pulse amplitudes and wavelengths are sketched and not to scale.*

Relative streaked photoemission time delays of 21 ± 5 as were measured between photoemission from the $2s$ and $2p$ orbitals of neon by Schultze *et al.*¹⁰ in a milestone experiment that triggered an intense debate about the role of electronic correlation during the single ionization of an atomic target. This debate was fueled by several numerical models for streaked photoemission underestimating the measured relative photoemission time delay by approximately a factor of two, even though the calculations included electronic correlation at various levels of approximation^{9;20–24}.

Accounting for electronic “shake-up” excitation during XUV photoemission from neon atoms, Isinger *et al.*²⁵ compared many-body perturbation theory calculations with measured energy-integrated sideband oscillations in interferometric photoemission spectra. Based on these RABITT experiments, the authors suggested that the discrepancy between the relative streaking time delay of 21 ± 5 as obtained experimentally in Ref.¹⁰ and in previous streaking calculations^{20–23} might be due to shake-up processes. The authors of Ref.²⁵ worded this suggestion very carefully. They pointed out that two of their co-authors²⁴ could not explain the mismatch of streaking experiments and streaking calculations by numerically modeling RABITT spectra, employing a similar theoretical many-body perturbation theory approach as Ref.²⁵ that includes electronic correlation. The authors provide good evidence, based on RABITT spectra, for the importance at the attosecond timescale of shake-up excitation during the photoemission of neon. However, to the best of our knowledge and despite early theoretical testimony for the significance of dynamical electronic correlation on streaked photoemission², the direct theoretical confirmation through streaking calculations of the 21 ± 5 as delay in Ref.¹⁰ is still outstanding.

While the attosecond correlated ionization dynamics for multi-electron targets remains a subject of debate, remarkably, for prototypical helium, Ossiander *et al.*⁴ found measured and calculated relative streaking time delays to agree at the (one) attosecond timescale. In their investigation, ground-state helium is singly ionized, and the dynamical response of the residual He^+ ion is analyzed by comparing direct ionization, resulting in ground-state He^+

($n = 1$) and shake-up ionization to a superposition of He^+ ($n \geq 2$) sub-levels

$$t_s = t_{\text{EWS}} + t_{\text{CLC}} + t_{\text{DLC}} , \quad (1.1)$$

Calculating t_{EWS} and t_{CLC} with attosecond accuracy, the authors were able to isolate a temporal shift due to electronic correlation during $n = 2$ and $n = 3$ shake-up ionization of about six and several tens of attoseconds, respectively.

The Eisenbud-Wigner-Smith (EWS) contribution, t_{EWS} , represents the photoelectron phase accumulation during the ionization of helium atoms in the XUV-pump pulse and includes the short-range part of the electron-electron interaction. It was calculated by direct numerical solution of the bound-continuum transition-matrix element of the two-electron system [cf. Eq. (5.38) below]² using the exterior complex scaling (ECS) method²⁶. While this numerical approach is state-of-the-art for helium, its value for transparently revealing physical details of the correlated dynamics during single ionization of helium is limited.

The delay contributions t_{CLC} and t_{DLC} are due to the simultaneous interaction of the photoelectron with the residual target charge distribution and the IR-laser electric field and are termed “Coulomb-laser coupling (CLC)” and “dipole-laser coupling (DLC)”. The CLC term includes the combined effect of the monopole term of the residual charge distribution and IR-laser²⁷. The DLC term represents the effect of the photoelectron interaction with the dipole-component of the charge distribution of the residual He^+ ion. This term tends to be very small or negligible for direct ionization, but provides an important contribution for shake-up ionization, especially for large photoelectron-detection angles relative to the XUV- and IR-pulse-polarization direction⁴. Applying this scheme to more complex atoms, such as experimentally convenient neon and argon gases^{10;23}, is computationally challenging and requires concessions (most noticeably mean-field approximations), the accuracy of which (at the one attosecond time scale) still needs to be confirmed.

Understanding the physics behind the individual delay contributions in Eq. (1.1) for prototypical helium targets is crucial for the development and scrutiny of dependable attosecond streaking models for many-electron targets. It requires a highly differential study

of streaked photoemission, going beyond the detection of photoelectrons within a small solid angle about the IR- and XUV-pulse-polarization direction, in addition to the reliable modeling of the target electronic response to the incident XUV and IR pulses. For interferometric photoemission from helium, photoelectron-emission-angle-dependent spectra were measured by Heuser *et al.*²⁸. These RABITT experiments detected a striking phase shift of the sideband yields for electron-detection angles that are larger than ≈ 50 degrees relative to the polarization direction, even in the direct emission channel (leaving He^+ in the ground state). A related RABITT study for helium targets was recently carried out by Fuchs *et al.*²⁹, who measured the three-dimensional photoelectron-momentum distribution in coincidence with the residual ions, in order to examine experimentally the dependence of RABITT time delays (i.e., relative phase shifts between sidebands in RABITT spectra) on the photoelectron angular momentum and coupling of continuum states in the assisting IR-laser pulse. Their measured delays of up to 12 as between outgoing *s*- and *d*-wave photoelectrons further emphasize the need for highly differential (angle-resolved) data for the comprehensive analysis of (streaked or interferometric) time-resolved photoemission.

Revisiting the sensitivity of relative streaking delays on the correlated electric photoemission dynamics reported in Ref.⁴ for direct and shake-up streaked photoemission from helium along the polarization direction of the XUV and IR pulse, we carried out *ab initio* calculations for *angle-resolved* direct and ($n = 2, 3$) shake-up photoemission.

This thesis is structured as follows. In Chap. 2 and 3 we review our approach for numerically propagating the time-dependent Schrödinger equation (TDSE) for one and two electrons exposed to external electromagnetic fields and review numerical methods to extract various photoelectron spectra and other observables. In Chap. 4 we discuss the simulated streaked spectra. In Chap. 5, the theoretical delays t_{EWS} and t_{C} in XUV-only ionization are extracted from photoelectron wave packets, while Chap. 6 discusses the IR laser induced Coulomb-laser coupling (CLC) delay. Another laser-induced side effect called dipole laser coupling (DLC) is discussed in Chap. 7. Our summary and conclusions follow in Chap. 8, leaving details of mathematical functions and simulation programs to Appendixes A and B. Throughout this thesis, we use atomic units unless indicated otherwise. With regard to the sign of the

streaking time delays, we follow the convention of² and⁴, denoting delays (advances) with positive (negative) values of time.

Some other notable theoretical works on attosecond streaking and RABITT related to this thesis are as follows.

- A hydrogen attoclock experiment³⁰
- Attosecond delays in RABITT for neon³¹
- Successful RABITT theories for attosecond delay for neon²⁵ and argon³²
- Experimental SiO₂ dielectric transient absorption spectra combined with neon streaking³³
- Polarization effect of initial state in hydrogen streaking³⁴
- RABITT dipole-laser coupling (DLC) delays of molecules³⁵
- Angle-resolved delays of molecule³⁶

Chapter 2

Solving the one-electron time dependent Schrödinger equation (TDSE)

In this chapter, we review numerical algorithms for solving the one-electron time dependent Schrödinger equation (TDSE) on a finite-element discrete-variable representation (FE-DVR) grid, and how we extract various physical observables, such as, e.g., the photoelectron momentum spectra.

2.1 The finite-element discrete-variable representation (FE-DVR) grid

2.1.1 Gauss-Lobatto quadrature

Gauss-Lobatto quadrature is commonly used for numerically calculating integrals using a weighted summation

$$\int_{-1}^1 f(t) dt \approx \sum_{i=1}^N w_i f(t_i) . \quad (2.1)$$

Given the abscissae t_i and the corresponding weights w_i ($i = 1, \dots, N$), when $f(t)$ is a polynomial of order $2N - 3$ or lower ($\sum_{n=0}^{2N-3} c_n t^n$), the above approximation is exact.

The abscissae and weights are symmetrical

$$t_i = -t_{N-i+1}, \quad w_i = w_{N-i+1} , \quad (2.2)$$

where $t_1 = -1$, $t_N = 1$, and t_i ($1 < i < N$) are the zeros of the derivatives of the Legendre polynomials of order $N - 1$, $P'_{N-1}(t)$. The corresponding weights are

$$w_i = \frac{2}{N(N-1)[P'_{N-1}(x_i)]^2} . \quad (2.3)$$

For the same integral linearly stretched over an arbitrary interval $[a, b]$, we define

$$x = \frac{b-a}{2}t + \frac{b+a}{2} \quad (t \in [-1, 1]) \quad (2.4)$$

and

$$g(x) = \frac{2}{b-a}f(t) = \frac{2}{b-a}f\left(\frac{2x-b-a}{b-a}\right) \quad (x \in [a, b]) , \quad (2.5)$$

to obtain

$$\int_a^b g(x) dx = \int_{-1}^1 f(t) dt \approx \sum_i w'_i g(x_i) , \quad (2.6)$$

where

$$w'_i = \frac{b-a}{2} \omega . \quad (2.7)$$

With Mathematica¹, t_i, w_i can be evaluated to arbitrary precision according to:

Listing 2.1: *Gauss-Lobatto implementation*

```

1 NN = 6; (*number of abscissas*)
2 digits = 38; (*numerical precision*)
3 sol = Solve[D[LegendreP[NN - 1, x], x] == 0, x];

```

¹<https://www.wolfram.com/mathematica/>

```

4 sol = Append[sol, {x -> -1}];
5 sol = Append[sol, {x -> 1}];
6 N[sol, digits]
7 w = N[2/(NN (NN - 1) (LegendreP[NN - 1, x])^2) /. sol, digits]

```

We next construct the $(N - 1)$ -order Lagrange interpolation polynomial with respect to the N abscissae:

$$p_n(t) = \begin{cases} \prod_{i=1}^{n-1} \frac{t - t_i}{t_n - t_i} \prod_{i=n+1}^N \frac{t - t_i}{t_n - t_i} & (-1 < t \leq 1) , \\ 0 & (\text{otherwise}) \end{cases} \quad (2.8)$$

satisfying

$$p_n(t_{n'}) = \delta_{n,n'} \quad (n = 1, \dots, N) . \quad (2.9)$$

We note that since the product of any two such polynomials is of order $2N - 2$, (2.1) is not exact here, and the polynomials are only approximate orthogonal, i.e.,

$$\int_{-1}^1 p_i(t) p_j(t) dt \approx \sum_k w_k p_i(t_k) p_j(t_k) = w_i \delta_{ij} \quad (i, j = 1, \dots, N) . \quad (2.10)$$

Taking $N = 6$ for example, this approximation has a relative error of up to 10%. Even for $N = 18$, it is still 3%. However, we will see in the following that the first and second derivative matrices are much more accurate. We find the FE-DVR method to be one of the most efficient tools for solving the two-electron TDSE.³⁷

An equivalent way to construct $p_n(t)$ is to directly use $P'_{N-1}(t)$ with zeros $t_2, t_3 \dots t_{N-1}$. Adding $t_1 = -1$ and $t_N = 1$ as extra zeros, it becomes an N -th order polynomial

$$(1 - t^2) P'_{N-1}(t) . \quad (2.11)$$

We divide this by its tangent line at t_n , forming a limit of type 0/0 at $t = t_n$, and

$$p_n(t) = \frac{(1 - t^2) P'_{N-1}(t)}{[(1 - t^2) P'_{N-1}(t)]'_{t=t_n} (t - t_n)} \quad (n = 1, \dots, N, \quad -1 < t \leq 1) . \quad (2.12)$$

These polynomials agree with (2.8). Finally, we can define our “orthonormalized” basis functions as

$$f_n(t) = \frac{1}{\sqrt{w_n}} p_n(t) \quad (t \in \mathbb{R}) . \quad (2.13)$$

2.1.2 FE-DVR basis polynomials

The flexibility of the FE-DVR method stems from its applicability to any given (possibly unequally spaced) set of FE boundary points. Smaller FEs can be used to represent a faster spatial oscillation of the wave function, such as inside a potential well. We note that it is better for the FE length to change smoothly along the grid, since a sudden change will likely cause larger numerical noise during the propagation, sometimes forming a standing-wave pattern.

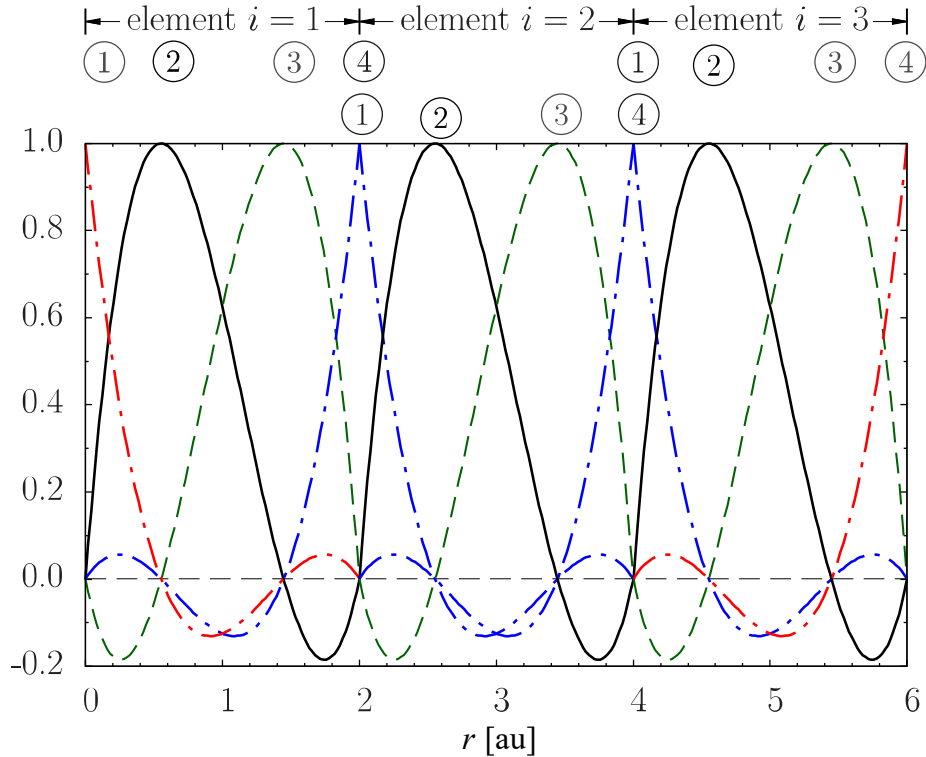


Figure 2.1: Example basis polynomials in (2.16) for an FE-DVR grid (normalized to a maximal value of 1), with $N_G = 4$ abscissae and 3 FEs. The circled numbers indicate the abscissae orders. Polynomial 1 and 4 at the FE boundaries at $x = 2, 4$ form bridge functions. In Application (Figure adapted from¹)

For a 1D FE-DVR grid, we divide the range $[x_{\min}, x_{\max}]$ into N_E finite elements (FE) in the intervals $[x_{i,1}, x_{i+1,1}]$ FE, where we further define N_G Gaussian-Lobatto abscissae. Let x_{ij} ($j = 1 \dots N_G$) denote the abscissae of the i -th FE (including the boundaries). Note that $x_{jN} = x_{j+1,1}$.

We define a set of basis functions $u_{ij}(x)$ each corresponding to an x_{ij} . Let

$$a_i = (x_{i+1,1} - x_{i,1})/2, \quad b_i = (x_{i+1,1} + x_{i,1})/2, \quad (2.14)$$

using $t \in [-1, 1]$ for $f_n(t)$ in (2.13) and linearly mapping $t \in [-1, 1]$ to each of the sub-intervals $x \in [x_{i,1}, x_{i+1,1}]$,

$$x = a_i t + b_i \quad (x_{i1} \leq x \leq x_{iN}). \quad (2.15)$$

Then the global bases can be defined as

$$u_{ij}(x) = \begin{cases} \frac{1}{\sqrt{a_i}} f_j\left(\frac{x - b_i}{a_i}\right) & (1 < j < N_G), \\ \frac{1}{\sqrt{a_i + a_{i+1}}} \left[f_N\left(\frac{x - b_i}{a_i}\right) + f_1\left(\frac{x - b_{i+1}}{a_{i+1}}\right) \right] & (j = N_G). \end{cases} \quad (2.16)$$

Each basis is constructed from one or two polynomials of order $N_G - 1$, and the second case ($j = N_G$) is sometimes called the “bridge function” (Fig. 2.1). The polynomials (2.16) satisfy the approximate orthonormal condition

$$\int_{x_{\min}}^{x_{\max}} u_{ij}(x) u_{i'j'}(x) dx \approx \delta_{ii'} \delta_{jj'}. \quad (2.17)$$

We assume the wave function $\psi(x) = 0$ at both ends of $[x_{\min}, x_{\max}]$ (Dirichlet boundary condition), eliminating the need to define $u_{11}(x)$ and $u_{N_E, N_G}(x)$. The total number of basis

functions and abscissae is $N_E(N_G - 1) - 1$. Rewriting w_i in (2.13) as w_{0i} , yields

$$u_{ij}(x_{i'j'}) = \delta_{ii'}\delta_{jj'} \times \begin{cases} \frac{1}{\sqrt{a_i w_{0j}}} & (1 < j < N_G) , \\ \frac{1}{\sqrt{(a_i + a_{i+1})w_{0N}}} & (j = N_G) . \end{cases} \quad (2.18)$$

For a quadrature at the global interval, we use the global weights

$$w_{ij} = \frac{1}{u_{ij}^2(x_{ij})} = \begin{cases} a_i w_{0j} & (1 < j < N_G) , \\ (a_i + a_{i+1})w_{0N} & (j = N_G) . \end{cases} \quad (2.19)$$

However, for an integral of a few contiguous FE in the middle with nonzero integrand at the boundaries, the weights $a_i w_{0j}$ should still be used for the end points since the bridge function is not needed.

To represent a wave function $\psi(x)$ in $[x_{\min}, x_{\max}]$ in the global bases $u_{ij}(x)$, we define the expansion coefficients as

$$c_{ij} = \frac{\psi(x_{ij})}{u_{ij}(x_{ij})} \approx \int_{x_{\min}}^{x_{\max}} u_{ij}(x) \psi(x) dx . \quad (2.20)$$

For convenience, we use a global index for $u_i(x)$, ordered by their corresponding abscissae x_i .

2.1.3 The second-order derivative matrix

To represent the kinetic energy Hamiltonian of hydrogen and helium TDSE on an FE-DVR grid containing $\partial^2/\partial r^2$, the second-order derivative matrix $\mathbf{D}^{(2)}$ is needed.

Although the basis functions $\{u_i(x)\}$ have discontinuous first derivatives at the FE boundaries, in the global interval $[x_{\min}, x_{\max}]$, we can still assume that the represented wave function

$$\psi(x) = \sum_i c_i u_i(x) \quad (x \in [x_{\min}, x_{\max}]) \quad (2.21)$$

is smooth (specifically at the boundaries of each FE). In the following, we calculate the second derivative matrix $\mathbf{D}^{(2)}$ such that the coefficients of $\psi''(x) = \sum_i c_i'' u_i(x)$ are given exactly by

$$c_i'' = \sum_{i,j} D_{i,j}^{(2)} c_j , \quad (2.22)$$

despite the fact that the functions $u_i(x)$ are not strictly orthonormal. The matrix $\mathbf{D}^{(2)}$ has the overlapped block-diagonal layout shown in Fig. 2.2.

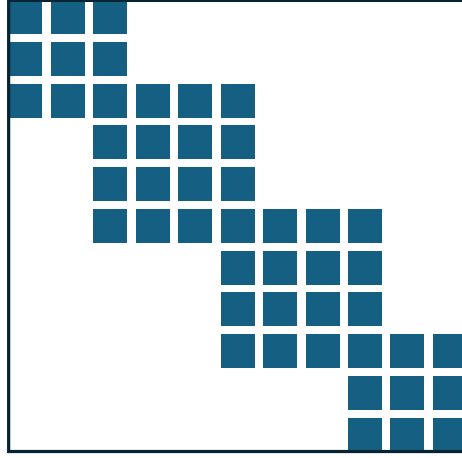


Figure 2.2: The non-zero elements of the second-order derivative matrix $\mathbf{D}^{(2)}$, for $N_F = 4$ FE and $N_G = 4$ Gauss abscissae within each FE. Each block represents one FE, and the first and last FE only have 3 elements due to the boundary conditions. The first derivative matrix $\mathbf{D}$ has the same structure, except that all diagonal elements are 0.

We start by taking the derivative,

$$c_i^{(2)} = \frac{\psi''(x_i)}{u_i(x_i)} = \int_{-\infty}^{+\infty} u_i(x) \frac{d^2}{dx^2} \sum_k c_k u_k(x) dx = \sum_k c_k \int u_i(x) u_k''(x) dx , \quad (2.23)$$

where the boundary points between FEs can be ignored and note that the integrand is of order $2N - 4$. The interval of every integral can be reduced to one or two FEs, so the global weights should not be used anymore. Using

$$\begin{aligned} D_{ij}^{(2)} &= \int u_i(x) u_j''(x) dx \\ &= u_i(x) u_j'(x) \Big|_{x_1}^{x_2} - \int u_i'(x) u_j'(x) dx \quad (\text{non-bridge } u_i) , \end{aligned} \quad (2.24)$$

the first term is canceled out, and $\mathbf{D}^{(2)}$ is a real and symmetric matrix. Since the order of the integrand polynomial is only $2(N-2) < 2N-3$, this integral can be replaced with a weighted sum.

The derivative of each basis function can be calculated using the Lagrange polynomial

$$f'_i(t_j) = \frac{1}{\sqrt{w_{0i}}} \times \begin{cases} \frac{t_j - t_1}{t_i - t_1} \frac{t_j - t_2}{t_i - t_2} \cdots \frac{1}{t_i - t_j} \cdots \frac{t_j - t_{i-1}}{t_i - t_{i-1}} \frac{t_j - t_{i+1}}{t_i - t_{i+1}} \cdots \frac{t_j - t_N}{t_i - t_N} & (i \neq j) \\ \frac{1}{t_i - t_1} + \cdots + \frac{1}{t_i - t_{i-1}} + \frac{1}{t_i - t_{i+1}} + \cdots + \frac{1}{t_i - t_N} & (i = j) \end{cases} \quad (2.25)$$

$(i, j = 1, \dots, N) .$

in (2.16). This yields

$$u'_{ij}(x_{ij'}) = \frac{1}{a_i^{3/2}} f'_j(t_{j'}) \quad (1 < j < N) , \quad (2.26)$$

$$u'_{iN}(x_{ij'}) = \frac{1}{a_i \sqrt{a_i + a_{i+1}}} f'_N(t_{j'}) , \quad (2.27)$$

$$u'_{iN}(x_{i+1,j'}) = \frac{1}{a_{i+1} \sqrt{a_i + a_{i+1}}} f'_1(t_{j'}) . \quad (2.28)$$

The bridge functions $u'_{iN}(x)$ are not continuous at x_{iN} . Their left and right derivatives at x_{iN} are $u'_{iN}(x_{iN})$ and $u'_{iN}(x_{i+1,1})$ respectively.

Now we can calculate the matrix elements of the second-order derivative operator

$$D_{(im),(in)}^{(2)} = \begin{cases} - \int_{x_{i1}}^{x_{i+1,N}} u'_{im}(x) u'_{in}(x) dx & (m = n = N) , \\ - \int_{x_{i1}}^{x_{iN}} u'_{im}(x) u'_{in}(x) dx & (\text{otherwise}) . \end{cases} \quad (2.29)$$

This matrix is real and symmetric, and the matrix elements without the bridge function are

$$D_{(im),(in)}^{(2)} = -\frac{1}{a_i^2} \sum_k w_{0k} f'_m(t_k) f'_n(t_k) \quad (1 < m \leq n < N) . \quad (2.30)$$

The matrix elements involving the bridge functions are

$$D_{(im),(iN)}^{(2)} = \frac{-1}{a_i^{3/2} \sqrt{a_i + a_{i+1}}} \sum_k w_{0k} f'_m(t_k) f'_N(t_k) \quad (1 < m < N) , \quad (2.31)$$

$$D_{(iN),(iN)}^{(2)} = \frac{-1}{(a_i + a_{i+1})} \sum_k w_{0k} \left[\frac{1}{a_i} f'_N(t_k)^2 + \frac{1}{a_{i+1}} f'_1(t_k)^2 \right] , \quad (2.32)$$

$$D_{(iN),(i+1,n)}^{(2)} = \frac{-1}{a_{i+1}^{3/2} \sqrt{a_i + a_{i+1}}} \sum_k w_{0k} f'_1(t_k) f'_n(t_k) \quad (1 < n < N) , \quad (2.33)$$

$$D_{(iN),(i+1,N)}^{(2)} = \frac{-1}{a_{i+1} \sqrt{(a_i + a_{i+1})(a_{i+1} + a_{i+2})}} \sum_k w_{0k} f'_1(t_k) f'_N(t_k) . \quad (2.34)$$

2.1.4 The first-order derivative matrix

To represent the external field Hamiltonian of the hydrogen and helium TDSE containing $\partial/\partial r$ on an FE-DVR grid in the velocity gauge, the first-order derivative matrix $\mathbf{D}$ is needed. Similar to second-order derivative, the elements of the first-order derivative matrix $\mathbf{D}$ are

$$D_{(im),(in)} = \frac{u'_{in}(x_{im})}{u_{im}(x_{im})} = \begin{cases} \int_{x_{i1}}^{x_{i+1,N}} u_{im}(x) u'_{in}(x) dx & (m = n = N) \\ \int_{x_{i1}}^{x_{iN}} u_{im}(x) u'_{in}(x) dx & (\text{otherwise}) . \end{cases} \quad (2.35)$$

It can be numerically shown that²⁶

$$f'_i(x_i) = 0 , \quad (2.36)$$

which causes all diagonal elements to vanish.

Similar to the second-order derivative matrix, the matrix elements are

$$D_{(im),(in)} = \frac{\sqrt{w_{0m}}}{a_i} f'_n(t_m) \quad (1 < m \leq n < N) , \quad (2.37)$$

$$D_{(im),(iN)} = \sqrt{\frac{w_{0m}}{a_i(a_i + a_{i+1})}} f'_N(t_m) \quad (1 < m < N) , \quad (2.38)$$

$$D_{(iN),(iN)} = 0 , \quad (2.39)$$

$$D_{(iN),(i+1,n)} = \sqrt{\frac{w_{01}}{(a_i + a_{i+1})a_{i+1}}} f'_n(t_1) \quad (1 < n < N) , \quad (2.40)$$

$$D_{(iN),(i+1,N)} = \sqrt{\frac{w_{01}}{(a_i + a_{i+1})(a_{i+1} + a_{i+2})}} f'_N(t_1) . \quad (2.41)$$

2.2 The TDSE for hydrogen atoms

2.2.1 Coupled equations in spherical coordinates

We solve the TDSE for hydrogen-like atoms in an external linearly polarized electric field,

$$H\Psi = H_0\Psi + H_F(\mathbf{r}, t)\Psi = i\frac{\partial}{\partial t}\Psi , \quad (2.42)$$

where the field-free Hamiltonian is

$$H_0 = -\frac{\nabla^2}{2} + V(r) , \quad (2.43)$$

and in the case of hydrogen,

$$V(r) = -\frac{Z}{r} . \quad (2.44)$$

$H_F(\mathbf{r}, t)$ is the external field interaction operator. In the length gauge, it is given by

$$H_F^{(l)}(\mathbf{r}, t) = \boldsymbol{\mathcal{E}}(t) \cdot \mathbf{r} , \quad (2.45)$$

and in velocity gauge as

$$H_F^{(v)}(\mathbf{r}, t) = \mathbf{A}(t) \cdot \mathbf{p} , \quad (2.46)$$

where $\mathbf{p} = -i\nabla$ is the canonical momentum operator and $\mathbf{A}(t) = -\int^t \mathcal{E}(t') dt'$ the vector potential. Unless indicated otherwise, we use the dipole approximation, assuming the atom is much smaller than the laser wave length, so that $\mathcal{E}(t)$, $\mathbf{A}(t)$ are position independent.

The hydrogen TDSE is usually solved in spherical coordinates, using the partial wave expansion

$$\Psi(\mathbf{r}, t) = \frac{1}{r} \sum_{l,m} \psi_{l,m}(r, t) Y_{l,m}(\hat{\mathbf{r}}) , \quad (2.47)$$

where $Y_{l,m}(\hat{\mathbf{r}}) = Y_{l,m}(\theta, \phi)$ are the spherical harmonics and $\psi_{l,m}(r, t)$ is the scaled radial wave function. Each term in the sum is called a partial wave.

In this thesis, laser pulses are linearly polarized along the z axis unless otherwise indicated. Therefore, Ψ is symmetric about the z axis. Thus only $m = 0$ partial waves are needed, and the z component of angular momentum L_z is conserved,

$$\Psi(\mathbf{r}, t) = \frac{1}{r} \sum_{l'} \psi_{l'}(r, t) Y_{l',0}(\hat{\mathbf{r}}) . \quad (2.48)$$

In the length gauge,

$$H_F^{(l)}(\mathbf{r}, t) = \mathcal{E}(t) r \cos \theta = \sqrt{\frac{4\pi}{3}} \mathcal{E}(t) r \cdot Y_{1,0}(\hat{\mathbf{r}}) . \quad (2.49)$$

Substituting these two equations into (2.42), and projecting each term onto $\langle Y_{l,0}(\hat{\mathbf{r}}) |$, we have a system of coupled equations

$$H_{r0} \psi_l + \mathcal{E}(t) r \sum_{l'=0}^{\infty} F_{l,l'}^{(z)} \psi_{l'} = i \frac{\partial \psi_l}{\partial t} \quad (l = 0, 1, \dots) , \quad (2.50)$$

where H_{r0} is the radial field-free Hamiltonian

$$H_{r0} = -\frac{1}{2m} \frac{d^2}{dr^2} - \frac{Z}{r} + \frac{l(l+1)}{2mr^2} . \quad (2.51)$$

The matrix $\mathbf{F}^{(z)}$ is the angular integration of transition dipole matrix elements

$$\begin{aligned} F_{l,l'}^{(z)} &= \langle Y_{l,0} | \cos \theta | Y_{l',0} \rangle = \sqrt{\frac{4\pi}{3}} \langle Y_{l,0} | Y_{1,0} | Y_{l',0} \rangle \\ &= \sqrt{(2l+1)(2l'+1)} \begin{pmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = \sqrt{\frac{2l+1}{2l'+1}} \begin{bmatrix} l & 1 & l' \\ 0 & 0 & 0 \end{bmatrix}^2, \end{aligned} \quad (2.52)$$

where we used the identity (A.8).

Thus, in the absence of an external electric field, $\mathbf{F}^{(z)} = \mathbf{0}$ each partial wave in (2.50) propagates independently. When the external field is present, the CG coefficients in (2.52) imply the selection rules

$$\Delta l = \pm 1, \quad \Delta m = 0, \quad (2.53)$$

and the latter only applies for z polarized laser pulses. Hence, all elements of the real and symmetric matrix $\mathbf{F}^{(z)}$ are 0, except for the sub-diagonal ones,

$$\mathbf{F}^{(z)} = \begin{pmatrix} 0 & \mathcal{C}_{0m} & 0 & 0 & \dots \\ \mathcal{C}_{0m} & 0 & \mathcal{C}_{1m} & 0 & \dots \\ 0 & \mathcal{C}_{1m} & 0 & \mathcal{C}_{2m} & \dots \\ 0 & 0 & \mathcal{C}_{2m} & 0 & \dots \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix}, \quad (2.54)$$

Therefore

$$\langle Y_{l,m} | \cos \theta | Y_{l',m'} \rangle = \delta_{m,m'} (\delta_{l+1,l'} \mathcal{C}_{l,m} + \delta_{l,l'+1} \mathcal{C}_{l',m'}) , \quad (2.55)$$

where

$$\begin{aligned} \mathcal{C}_{l,m} &= \int Y_{l,m}^*(\hat{\mathbf{r}}) \cos \theta(\hat{\mathbf{r}}) Y_{l+1,m}(\hat{\mathbf{r}}) = \int Y_{l+1,m}^*(\hat{\mathbf{r}}) \cos \theta(\hat{\mathbf{r}}) Y_{l,m}(\hat{\mathbf{r}}) \\ &= \sqrt{\frac{(l+1)^2 - m^2}{(2l+1)(2l+3)}}. \end{aligned} \quad (2.56)$$

2.2.2 Arbitrarily polarized external fields in the length gauge

For possible future applications, we also discuss the formulation for arbitrarily polarized external fields here. For convenience, we use a single number $\lambda = 1, 2, \dots$ to index the ordered list of partial waves of (l, m) ,

$$(0, 0), (1, -1), (1, 0), (1, 1), (2, -2), \dots \quad (2.57)$$

Then (2.47) becomes

$$\Psi(\mathbf{r}, t) = \frac{1}{r} \sum_{\lambda} \psi_{\lambda}(r, t) Y_{\lambda}(\mathbf{r}) . \quad (2.58)$$

The field interaction Hamiltonian in length gauge becomes

$$H_F^{(l)}(\mathbf{r}, t) = \boldsymbol{\mathcal{E}}(t) \cdot \mathbf{r} = \mathcal{E}_x x + \mathcal{E}_y y + \mathcal{E}_z z , \quad (2.59)$$

where x, y, z can be expressed with spherical harmonics,

$$x = \sqrt{\frac{2\pi}{3}} r (Y_{1,-1} - Y_{1,1}) , \quad y = i\sqrt{\frac{2\pi}{3}} r (Y_{1,-1} + Y_{1,1}) , \quad z = \sqrt{\frac{4\pi}{3}} r Y_{1,0} . \quad (2.60)$$

Equation (2.50) then becomes

$$\begin{aligned} H_{r0} \psi_{\lambda}(r, t) + r \sum_{\lambda'} \left[\mathcal{E}_x(t) F_{\lambda, \lambda'}^{(x)} + \mathcal{E}_y(t) F_{\lambda, \lambda'}^{(y)} + \mathcal{E}_z(t) F_{\lambda, \lambda'}^{(z)} \right] \psi_{\lambda'}(r, t) \\ = i \frac{\partial}{\partial t} \psi_{\lambda}(r, t) \quad (\lambda = 0, 1, \dots) . \end{aligned} \quad (2.61)$$

The three coupling matrices are

$$F_{\lambda, \lambda'}^{(x)} = \sqrt{\frac{2\pi}{3}} (\langle Y_{l,m} | Y_{1,-1} | Y_{l',m'} \rangle - \langle Y_{l,m} | Y_{1,1} | Y_{l',m'} \rangle) , \quad (2.62)$$

$$F_{\lambda, \lambda'}^{(y)} = i\sqrt{\frac{2\pi}{3}} (\langle Y_{l,m} | Y_{1,-1} | Y_{l',m'} \rangle + \langle Y_{l,m} | Y_{1,1} | Y_{l',m'} \rangle) , \quad (2.63)$$

$$F_{\lambda,\lambda'}^{(z)} = \langle Y_{l,m} | \cos \theta | Y_{l',m'} \rangle = \sqrt{\frac{4\pi}{3}} \langle Y_{l,m} | Y_{1,0} | Y_{l',m'} \rangle , \quad (2.64)$$

where the integrals can be calculated using (A.8).

2.2.3 Velocity gauge

In the velocity gauge, the wave function Ψ_V differs from the length gauge wave function Ψ_L by only a phase factor³⁸,

$$\Psi_V(\mathbf{r}, t) = \exp \left[-i \mathbf{A}(t) \cdot \mathbf{r} + \frac{i}{2} \int_{-\infty}^t \mathbf{A}(t')^2 dt' \right] \Psi_L(\mathbf{r}, t) . \quad (2.65)$$

In spherical coordinates, this phase difference will change the probability for each partial wave, which might lead to faster convergence. In strong-field approximation, since $\mathbf{A}(t)$ is approximately identical to the photoelectron momentum, this phase factor tends to cancel the phase oscillation of Ψ_L and results in a longer wavelength, reducing the number of partial waves required for convergence (cf. Subsection 2.3.3). We note that in velocity gauge, even when we are only interested in single XUV photon ionization, more than $l = 0, 1$ partial waves are needed for convergence, due to the extra phase factor.

In velocity gauge, for z polarized external fields, the Hamiltonian $H_F^{(v)}$ involves the operator

$$\frac{\partial}{\partial z} = \cos \theta \frac{\partial}{\partial r} - \frac{\sin \theta}{r} \frac{\partial}{\partial \theta} . \quad (2.66)$$

Since the first term couples both partial waves and radial grid points, instead of applying the split-operator-propagation scheme as in³⁹, it is most straightforward to apply $\exp(-iA \frac{\partial}{\partial z})$ to the whole wave function and use the Lanczos algorithm for the wave function propagation (cf. Subsection 2.2.6).

On the FE-DVR grid, $\partial/\partial r$ can be represented with the first-order derivative matrix $\mathbf{D}$ (2.35), and $\cos \theta$ is represented with the partial-wave-coupling matrix $\mathbf{F}^{(z)}$ (2.54). Thus, $\partial/\partial z$ is also represented by a matrix according to (2.66). The matrix for the first term in

(2.66) reads

$$\begin{aligned} & r \left\langle Y_{l,m} \left| \cos \theta \frac{\partial}{\partial r} \right| \frac{\psi_{l',m}}{r} Y_{l',m} \right\rangle \\ &= \frac{d}{dr} \psi_{l',m} \langle Y_{l,m} | \cos \theta | Y_{l',m} \rangle - \frac{\psi_{l',m}}{r} \langle Y_{l,m} | \cos \theta | Y_{l',m} \rangle , \end{aligned} \quad (2.67)$$

and the matrix elements in (2.66) are³⁹

$$G_{l,l'}^{(z)} = \langle Y_{l,m} | \frac{\partial}{\partial z} | Y_{l',m} \rangle = F_{l,l'}^{(z)} \frac{\partial}{\partial r} + \frac{g_{l,l'}^{(z)}}{r} , \quad (2.68)$$

where

$$g_{l,l'}^{(z)} = -\langle Y_{l,m} | \cos \theta + \sin \theta \frac{\partial}{\partial \theta} | Y_{l',m} \rangle = \delta_{l',l+1} l' \mathcal{C}_{l,m} - \delta_{l,l'+1} l \mathcal{C}_{l',m} . \quad (2.69)$$

or

$$\mathbf{g}^{(z)} = \begin{pmatrix} 0 & \mathcal{C}_{0m} & 0 & 0 & \dots \\ -\mathcal{C}_{0m} & 0 & 2\mathcal{C}_{1m} & 0 & \dots \\ 0 & -2\mathcal{C}_{1m} & 0 & 3\mathcal{C}_{2m} & \dots \\ \vdots & 0 & -3\mathcal{C}_{2m} & 0 & \dots \end{pmatrix} . \quad (2.70)$$

Note that this is an antisymmetric real matrix, which, when multiplied by i , becomes Hermitian.

2.2.4 Arbitrarily space-time-dependent potential

If we add to the Hamiltonian in (2.45) an arbitrary space- and time-dependent potential $V'(\mathbf{r}, t)$, it can be used as a single-active-electron (SAE) model that simulates the Coulomb interaction between the photoelectron and oscillating He^+ .

We first need to expand it with spherical harmonics,

$$V'(\mathbf{r}, t) = \sum_{l,m} V'_{l,m}(r, t) Y_{l,m}(\hat{\mathbf{r}}) , \quad (2.71)$$

such that the partial-wave-coupling matrix elements are

$$F'_{\lambda'',\lambda'}(r,t) = \langle Y_{l'',m''} | V'(\mathbf{r},t) | Y_{l',m'} \rangle = \sum_{l,m} V'_{l,m}(r,t) \langle Y_{l'',m''} | Y_{l,m} | Y_{l',m'} \rangle , \quad (2.72)$$

where the integrals can be calculated with (A.8).

For linearly polarized external fields, $m \equiv 0$, and the coupling equation becomes

$$H_0 \psi_l + \mathcal{E}(t) r \sum_{l'=0}^{\infty} F_{l,l'} \psi_{l'} + \sum_{l'=0}^{\infty} F'_{l,l'}(r,t) \psi_{l'} = i \frac{\partial \psi_l}{\partial t} \quad (l = 0, 1, \dots) . \quad (2.73)$$

In the split-operator method below, we found that merging the diagonal elements of $\mathbf{F}'$ to $\mathbf{H}_0$ will result in a smaller numerical propagation error.

2.2.5 The split-operator Crank-Nicolson propagation algorithm

Formally, to propagate the wave function for a time step Δt , we use the propagator

$$\psi(x, t + \Delta t) \approx \exp[-iH(t + \Delta t/2)\Delta t] \psi(x, t) , \quad (2.74)$$

where we assume the Hamiltonian is time independent within each time step Δt . However, directly evaluating the exponential of the Hamiltonian numerically has proven to be inefficient when solving the TDSE for atoms.

The Crank-Nicolson algorithm with the Cayley scheme^{40;41} is a common way to approximate the matrix exponent by solving the linear equation

$$\left(1 + \frac{i}{2} \mathbf{H}_n \Delta t \right) \boldsymbol{\psi}_{n+1} = \left(1 - \frac{i}{2} \mathbf{H}_n \Delta t \right) \boldsymbol{\psi}_n , \quad (2.75)$$

where $\boldsymbol{\psi}_n$ is a column vector of complex coefficients when $\psi(x, t_n)$ is expanded with a finite set of basis functions, in our application, the FE-DVR polynomials [cf. (2.20)]. $\mathbf{H}_n$ is the matrix representation of $H(t + \Delta t/2)$ in the same basis set. In this equation, $\mathbf{H}_n$ and $\boldsymbol{\psi}_n$ are known and $\boldsymbol{\psi}_{n+1}$ has to be solved numerically by a linear equation solver such as, e.g., the

ones in the LAPACK library (cf. Appendix B).

To further reduce the numerical complexity, we can rearrange (2.75) into the form

$$\left(\frac{1}{2} + \frac{i}{4}\mathbf{H}_n\Delta t\right)(\psi_{n+1} + \psi_n) = \psi_n , \quad (2.76)$$

where we can first solve for $\psi_{n+1} + \psi_n$, and subtract ψ_n . This will save the extra matrix-vector multiplication on the right-hand side of (2.75).

The split operator method is commonly applied in addition to the Crank-Nicolson algorithm to further increase efficiency. Instead of using a single matrix $\mathbf{H}_n$ to represent the total Hamiltonian, we can split the propagator in (2.74) in the so-called sandwich form,

$$\psi(t + \Delta t) = e^{-iH_0\frac{\Delta t}{2}} e^{-iH_F\Delta t} e^{-iH_0\frac{\Delta t}{2}} \psi_\lambda(t) + \mathcal{O}(\Delta t^3) , \quad (2.77)$$

where H_0 is the field-free Hamiltonian, and H_F is the external-field interaction in either length or velocity gauge. For hydrogen, $e^{-iH_0\frac{\Delta t}{2}}$ can propagate each partial wave independently, creating an opportunity for CPU parallelism and reducing the matrix size for each partial wave.

2.2.6 The Lanczos algorithm

The Lanczos algorithm is a common propagation algorithm for the FE-DVR grid.^{2;26;37} For each time step and known $|\Psi(t_n)\rangle$ (written as $|\Psi_0\rangle$ below), the K bases of the Krylov subspace

$$\{|\Psi_0\rangle, H|\Psi_0\rangle, \dots, H^{K-1}|\Psi_0\rangle\} \quad (2.78)$$

is orthonormalized with the Gram-Schmidt process to

$$\{|\Psi_0\rangle, |\Psi_1\rangle, |\Psi_2\rangle, \dots, |\Psi_{K-1}\rangle\} . \quad (2.79)$$

This basis set is then used to expand the next wave function $\Psi(t_{n+1})$. The system Hamiltonian H [(2.42) for hydrogen], approximately represented by the matrix $\mathbf{H}$ with

$$H_{ij} = \langle \Psi_i | H | \Psi_j \rangle \quad (i, j = 1, \dots, K) . \quad (2.80)$$

The wave function propagator $\exp(-iH\Delta t)$ can then be approximately represented with

$$\exp(-i\mathbf{H}\Delta t) = 1 + (-i\mathbf{H}\Delta t) + \frac{1}{2!}(-i\mathbf{H}\Delta t)^2 \dots . \quad (2.81)$$

If we diagonalize $\mathbf{H}$ so that

$$\mathbf{H} = \mathbf{P}\mathbf{\Lambda}\mathbf{P}^{-1} , \quad (2.82)$$

where $\mathbf{\Lambda} = \text{diag}(E_1, \dots, E_K)$ is the diagonal matrix of energy eigenvalues. Each eigenvalue corresponds to a column of eigenvector in the unitary matrix $\mathbf{P}$, and (2.81) simplifies to

$$\begin{aligned} \exp(-i\mathbf{H}\Delta t) &= \mathbf{P} \text{diag}(e^{-iE_1\Delta t}, e^{-iE_2\Delta t} \dots e^{-iE_N\Delta t})\mathbf{P}^{-1} \\ &= \sum_{j=0}^{K-1} P_{ij} e^{-iE_j\Delta t} P_{jk}^{-1} = \sum_{j=0}^{K-1} P_{ij} P_{kj} e^{-iE_j\Delta t} . \end{aligned} \quad (2.83)$$

The above derivations have two main approximations: Using $\exp[iH(t_n + \Delta t/2)\Delta t]$ for each time step assumes that the variation of the electric field is negligible within a time step, and using a finite basis set to represent (2.80) introduces a truncation error. With our current application and the time step used (typically 5×10^3 au), the main error comes from the latter and will be quantified below.

The following iterative procedure is followed to construct $\mathbf{H}$ in (2.82) and $|\Psi_i\rangle$ in (2.79) efficiently:

1. Assuming $|\Psi_0\rangle$ is already normalized, then the Gram-Schmidt orthogonalization and normalization of the $H|\Psi_0\rangle$ is

$$|\tilde{\Psi}_1\rangle = (1 - |\Psi_0\rangle\langle\Psi_0|)H|\Psi_0\rangle , \quad |\Psi_1\rangle = |\tilde{\Psi}_1\rangle / \sqrt{\langle\tilde{\Psi}_1|\tilde{\Psi}_1\rangle} . \quad (2.84)$$

From now on we define $\beta_j = \sqrt{\langle \tilde{\Psi}_j | \tilde{\Psi}_j \rangle}$, and it can be proven that

$$\langle \Psi_{j-1} | H | \Psi_j \rangle = \sqrt{\langle \tilde{\Psi}_j | \tilde{\Psi}_j \rangle} = \beta_j . \quad (2.85)$$

2. It can be proven that the Gram-Schmidt orthogonalization of $H^2 |\Psi_0\rangle$ is

$$\begin{aligned} |\tilde{\Psi}_2\rangle &= (1 - |\Psi_1\rangle \langle \Psi_1| - |\Psi_0\rangle \langle \Psi_0|) H |\Psi_1\rangle \\ &= H |\Psi_1\rangle - \alpha_1 |\Psi_1\rangle - \beta_1 |\Psi_0\rangle , \end{aligned} \quad (2.86)$$

where

$$\alpha_i = \langle \Psi_i | H | \Psi_i \rangle . \quad (2.87)$$

Then we normalize it to $|\Psi_2\rangle = |\tilde{\Psi}_2\rangle / \sqrt{\langle \tilde{\Psi}_2 | \tilde{\Psi}_2 \rangle} = |\tilde{\Psi}_2\rangle / \beta_2$.

3. For all the following bases, it can be proven that

$$|\tilde{\Psi}_{j+1}\rangle = H |\Psi_j\rangle - \alpha_j |\Psi_j\rangle - \beta_j |\Psi_{j-1}\rangle , \quad (2.88)$$

which is equivalent to but much simpler than the original orthogonalization

$$|\tilde{\Psi}_{j+1}\rangle = (1 - |\Psi_j\rangle \langle \Psi_j| - \dots - |\Psi_0\rangle \langle \Psi_0|) H^{j+1} |\Psi_0\rangle . \quad (2.89)$$

Finally, $\mathbf{H}$ can be represented by a tridiagonal matrix

$$\mathbf{H} = \begin{pmatrix} \alpha_0 & \beta_1 & & & \\ \beta_1 & \alpha_1 & \beta_2 & & \\ & \beta_2 & \alpha_2 & \ddots & \\ & & \ddots & \ddots & \beta_{K-1} \\ & & & \beta_{K-1} & \alpha_{K-1} \end{pmatrix} , \quad (2.90)$$

which is then directly diagonalized to calculate its matrix exponent. Since the typical order

K needed is around 20, this is much easier to diagonalize than the full Hamiltonian matrix.

The truncation error in the Lanczos algorithm we use to diagonalize $\mathbf{H}$ can be estimated as²⁶

$$\epsilon_{\text{lanc}}^K \approx \frac{\Delta t^K}{K!} \prod_{i=1}^K \beta_i . \quad (2.91)$$

We dynamically adjust K at each propagation time step Δt to satisfy $\epsilon_{\text{lanc}}^{K-1} < 10^{-12}$, rather than using a fixed number of basis states as, e.g., Ref.⁴.

2.3 Hydrogen photoemission spectra

To extract a physical observable from a wave function, we need to project it onto eigenstates of that observable's operator. In the context of photoionization, these eigenstates are (half) scattering states and are the solutions of the operator's eigenvalue equation, subject to certain boundary conditions (e.g., an asymptotic photoelectron momentum vector). In photoionization, the eigenvalue equations are most often the time-independent Schrödinger equation (TISE),

$$H_0 \Psi_E = E \Psi_E , \quad (2.92)$$

where H_0 is the field-free Hamiltonian of the atom, and the energy E is the corresponding eigenvalue.

For non-time-resolved applications, it often suffices to use some form of approximation for the scattering states. However, for time-resolved applications, it is usually important to use exact scattering states that have the correct asymptotic phase.

2.3.1 Plane- and spherical-wave representation of a free electron

For a free electron in 3D, the scattering waves satisfy the TISE (2.92) with $V(\mathbf{r}) = 0$. However, for each given energy E , there is still an infinite number of solutions that form an eigen subspace². To determine an orthonormal basis set in the eigen subspace, further

²An eigen subspace is spanned by all solutions of an eigenvalue equation with the same eigenvalue. It is a subspace of the Hilbert space that any physical wave function of the system lives in.

constraints are required such as the boundary conditions for $r \rightarrow \infty$.

The most common set of solutions are the plane waves

$$\langle \mathbf{r} | \mathbf{k} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r}} , \quad (2.93)$$

satisfying the orthonormality conditions

$$\langle \mathbf{k}' | \mathbf{k} \rangle = \delta(\mathbf{k}' - \mathbf{k}) , \quad (2.94)$$

and the boundary conditions are just the plane waves themselves.

Plane waves also happen to be the eigenstates of the momentum operator $\mathbf{p}$, since $[H_0, \mathbf{p}] = 0$ when $V(\mathbf{r}) = 0$. For both discrete and continuum states, the hydrogen energy eigenstates are degenerate if the fine structures are neglected. Using multiple commuting observable operators to narrow down a unique set of eigenvectors is a common technique when degeneracy is present. Such operators are called a complete set of commuting observables (CSCO). An example of a CSCO is $\{H_0, L^2, L_z\}$ for (non-relativistic) hydrogen-like atoms.

When solving the TISE (2.92) in spherical coordinates by separation of variables, we have the set of scattering states in spherical form

$$\langle \mathbf{r} | s_{l,m}(k) \rangle = \frac{1}{r} u_{l,m}(r) Y_{l,m}(\hat{\mathbf{r}}) , \quad (2.95)$$

with the orthonormality conditions

$$\begin{aligned} & \langle s_{l,m}(k) | s_{l',m'}(k') \rangle \\ &= \int_0^\infty \left[\frac{1}{r} u_{l,m}(k, r) Y_{l,m}(\hat{\mathbf{r}}) \right]^* \left[\frac{1}{r} u_{l',m'}(k', r) Y_{l',m'}(\hat{\mathbf{r}}) \right] r^2 dr d\Omega \\ &= \int_0^\infty u_{l,m}^*(k, r) u_{l',m'}(k', r) dr \int Y_{l',m'}(\hat{\mathbf{r}}) Y_{l,m}(\hat{\mathbf{r}}) d\Omega \\ &= \delta_{l,l'} \delta_{m,m'} \delta(k - k') , \end{aligned} \quad (2.96)$$

and

$$\int_0^\infty u_{l,m}^*(k, r) u_{l,m}(k', r) dr = \delta(k - k') . \quad (2.97)$$

For $V(r) = 0$, the radial wave functions are

$$u_{l,m}(k, r) = \sqrt{\frac{2}{\pi}} kr j_l(kr) , \quad (2.98)$$

where j_l are the spherical Bessel functions of the first kind. The asymptotic form is

$$u_{l,m}(k, r) \xrightarrow{r \rightarrow \infty} \sqrt{\frac{2}{\pi}} \sin\left(kr - \frac{l\pi}{2}\right) . \quad (2.99)$$

Since both $|\mathbf{k}\rangle$ and $|s_{l,m}(k)\rangle$ are the orthonormal bases of the same eigen subspace, they are related by a unitary transform

$$|\mathbf{k}\rangle = \sum_{l,m} \frac{i^l}{k} Y_{l,m}^*(\hat{\mathbf{k}}) |s_{l,m}(k)\rangle , \quad (2.100)$$

i.e.,

$$\frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}} = \sqrt{\frac{2}{\pi}} \sum_{l=0}^{\infty} i^l j_l(kr) \sum_{m=-l}^l Y_{l,m}^*(\hat{\mathbf{k}}) Y_{l,m}(\hat{\mathbf{r}}) . \quad (2.101)$$

2.3.2 The Fourier transform in spherical coordinates

The Fourier transform of an arbitrary one-particle 3D wave function

$$\psi(\mathbf{r}) = \frac{1}{r} \sum_{l,m} u_{l,m}(r) Y_{l,m}(\hat{\mathbf{r}}) \quad (2.102)$$

is obtained by projection onto plane waves (2.101), resulting in the wave function in momentum space

$$g(\mathbf{k}) = \langle \mathbf{k} | \psi \rangle = \frac{1}{(2\pi)^{3/2}} \int \psi(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r = \frac{1}{k} \sum_{l,m} g_{l,m}(k) Y_{l,m}(\hat{\mathbf{k}}) , \quad (2.103)$$

where

$$g_{l,m}(k) = \sqrt{\frac{2}{\pi}} i^{-l} \int_0^{+\infty} u_{l,m}(r) k r j_l(kr) dr . \quad (2.104)$$

The reverse Fourier transform is

$$|\psi\rangle = \int g_{l,m}(k) |\mathbf{k}\rangle d^3k , \quad (2.105)$$

and the momentum spectrum of $\psi(\mathbf{r})$ (at a given instant t)

$$P(\mathbf{k}) = |g(\mathbf{k})|^2 . \quad (2.106)$$

However, for the exact photoemission momentum spectra, this method requires the wave function $|\psi\rangle$ at $t \rightarrow +\infty$, even if the external laser field only has a finite duration. This is because the field-free Hamiltonian H_0 of an atom does not commute with the momentum operator $\mathbf{p}$. Instead of $\langle \mathbf{k} |$, for hydrogen-like atoms, the wave function must be projected onto the Coulomb waves. The latter yields the accurate asymptotic momentum spectra if the projection is done after the end of the external field.

2.3.3 Coulomb spherical waves

The Coulomb spherical waves are the exact scattering states of hydrogen-like atoms. They are the solutions to the TISE (2.92) with the Coulomb potential,

$$H_0 \Psi = -\frac{\nabla^2}{2} \Psi - \frac{Z}{r} \Psi = E \Psi \quad (E > 0) . \quad (2.107)$$

After separation of variables in spherical coordinates, the radial Schrödinger equation reads (let $E = k^2/2$ and $k > 0$)

$$-\frac{1}{2} \frac{d^2 \psi_l}{dr^2} + \left[-\frac{Z}{r} + \frac{l(l+1)}{2r^2} \right] \psi_l = \frac{k^2}{2} \psi_l , \quad (2.108)$$

which simplifies to

$$\frac{d^2 u_l}{d\rho^2} + \left[1 - \frac{2\eta}{\rho} - \frac{l(l+1)}{\rho^2} \right] u_l = 0 \quad (2.109)$$

after substituting $\rho = kr$, and defining the **Sommerfeld parameter**

$$\eta = -\frac{Z}{k} . \quad (2.110)$$

This is a second-order homogeneous ordinary differential equation, the two linearly independent solutions of which are the **Coulomb function of the first kind** $F_l(\eta, \rho)$ and the second kind $G_l(\eta, \rho)$. In our study η, l are real parameters, so F_l, G_l are real functions. $G_l(\eta, \rho)$ is not relevant for this thesis, since it is singular at $r = 0$ and therefore not physical.

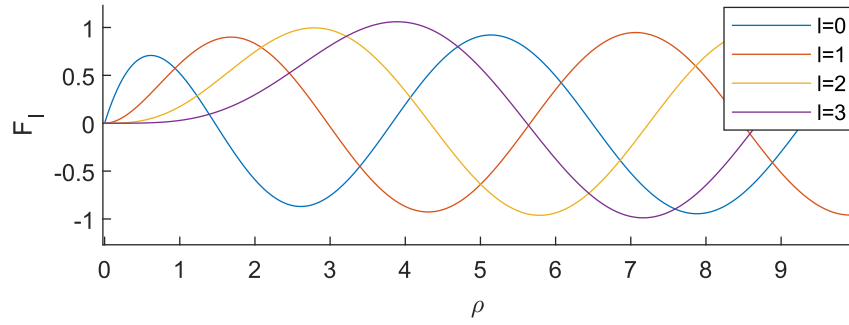


Figure 2.3: *Coulomb functions of the first kind ($Z = 1, k = 1$)*

The definition of F_l is (the choice of upper or lower signs is arbitrary)

$$F_l(\eta, \rho) = A_l(\eta) \rho^{l+1} e^{\mp i\rho} M(l+1 \mp i\eta, 2l+2, \pm 2i\rho) , \quad (2.111)$$

where the normalization coefficient is

$$A_l(\eta) = \frac{2^l e^{-\pi\eta/2} |\Gamma(l+1+i\eta)|}{(2l+1)!} . \quad (2.112)$$

$M(a, b, z)$ is the **Kummer M function**. It is also called the confluent hypergeometric function of the first kind and denoted as ${}_1F_1(a; b; z)$.

For convenience or verification purpose in our numerical calculation, F_l can also be defined

with the Whittaker M function in a more compact form

$$F_l(\eta, \rho) = \left(\frac{\mp i}{2} \right)^{l+1} A_l(\eta) M_{\pm i\eta, l+\frac{1}{2}}(\pm 2i\rho) , \quad (2.113)$$

where the Whittaker M function relates to the Kummer M function as

$$M_{\kappa, \mu}(z) = e^{-z/2} z^{\mu+1/2} M(\mu - \kappa + 1/2, 1 + 2\mu, z) . \quad (2.114)$$

We note that the symbols for the two functions are distinguished by their subscripts and number of arguments.

The asymptotic form of F_l is

$$F_l(\eta, \rho) \xrightarrow{\rho \rightarrow \infty} \sin \left[\rho - \frac{\pi l}{2} - \eta \ln(2\rho) + \sigma_l(\eta) \right] , \quad (2.115)$$

where

$$\sigma_l(\eta) = \arg[\Gamma(l+1+i\eta)] \quad (2.116)$$

is the **Coulomb phase shift** and $\arg$ is the complex angle in polar representation. The short range limit is

$$\lim_{r \rightarrow 0} F_l(\eta, \rho) = A_l(\eta) r^{l+1} + \mathcal{O}(r^{l+2}) , \quad (2.117)$$

and

$$\left. \frac{dF_l(\eta, \rho)}{d\rho} \right|_{\rho=0} = \begin{cases} A_0(\eta) & (l=0) \\ 0 & (l>0) \end{cases} . \quad (2.118)$$

F_l satisfies the radial orthonormal condition (2.97),

$$\int_0^\infty \sqrt{\frac{2}{\pi}} F_l\left(-\frac{Z}{k'}, k'r\right) \cdot \sqrt{\frac{2}{\pi}} F_l\left(-\frac{Z}{k}, kr\right) dr = \delta(k - k') \quad (k, k' > 0) . \quad (2.119)$$

Thus, we can construct the complete set of orthonormal Coulomb spherical waves as

$$\langle \mathbf{r} | C_{l,m}(k) \rangle = \frac{1}{r} \sqrt{\frac{2}{\pi}} F_l(\eta, kr) Y_{l,m}(\hat{\mathbf{r}}) , \quad (2.120)$$

satisfying

$$\langle C_{l',m'}(k') | C_{l,m}(k) \rangle = \delta_{l,l'} \delta_{m,m'} \delta(k - k') . \quad (2.121)$$

2.3.4 Coulomb plane waves

For a given asymptotic momentum vector $\mathbf{k}$, Coulomb plane waves can have two kinds of boundary conditions. We use the superscript $(-)$ to denote outgoing plane wave with incoming spherical wave, and $(+)$ for outgoing spherical wave and incoming plane wave.³⁸

$$\langle \mathbf{r} | C^{(\pm)}(\mathbf{k}) \rangle \xrightarrow{kr \mp \mathbf{k} \cdot \mathbf{r} \rightarrow +\infty} \frac{1}{(2\pi)^{3/2}} \left\{ e^{i\mathbf{k} \cdot \mathbf{r} \pm i\eta \ln(kr \mp \mathbf{k} \cdot \mathbf{r})} + f^{(\pm)}(\hat{\mathbf{k}}) \frac{\exp[\pm ikr \mp i\eta \ln(2kr)]}{r} \right\} . \quad (2.122)$$

Using parabolic coordinate, the solution can be expressed with the confluent hypergeometric function of the first kind ${}_1F_1$,

$$\langle \mathbf{r} | C^{(\pm)}(\mathbf{k}) \rangle = \frac{1}{(2\pi)^{3/2}} \Gamma(1 \pm i\eta) e^{-\pi\eta/2} e^{i\mathbf{k} \cdot \mathbf{r}} {}_1F_1(\mp i\eta; 1; \pm ikr - i\mathbf{k} \cdot \mathbf{r}) . \quad (2.123)$$

It is orthonormalized according to

$$\langle C^{(\pm)}(\mathbf{k}) | C^{(\pm)}(\mathbf{k}') \rangle = \delta(\mathbf{k} - \mathbf{k}') . \quad (2.124)$$

The cross section of an example Coulomb plane wave is shown in Fig. 2.4.

2.3.5 Projection onto Coulomb plane waves

Since Coulomb plane waves are eigenstates of the field-free Hamiltonian H_0 with asymptotic momentum $\mathbf{k}$, once the external field ends, we can immediately project the wave function $\psi(\mathbf{r}, t)$ onto them to obtain photoelectron momentum spectra.

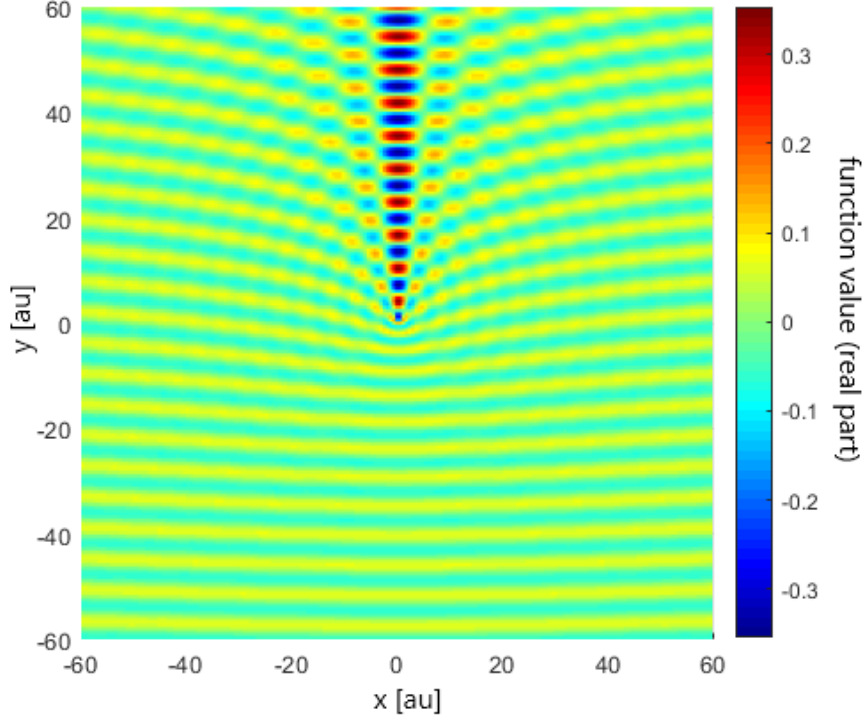


Figure 2.4: The real part of $\langle \mathbf{r} | C^{(-)}(\mathbf{k}) \rangle$ in the x - y plane for $Z = 5$, $\mathbf{k} = -\hat{\mathbf{y}}$, $\eta = -5$. For $y \rightarrow -\infty$ it becomes a plane wave.

Coulomb plane waves and spherical waves are related by the transform

$$|C^{(\pm)}(\mathbf{k})\rangle = \sum_{l,m} a_{l,m}^{(\pm)}(\mathbf{k}) |C_{l,m}(k)\rangle , \quad (2.125)$$

where

$$a_{l,m}^{(\pm)}(\mathbf{k}) = \frac{i^l}{k} e^{\pm i\sigma_l} Y_{l,m}^*(\hat{\mathbf{k}}) . \quad (2.126)$$

Plugging in (2.120) leads to

$$\langle \mathbf{r} | C^{(\pm)}(\mathbf{k}) \rangle = \sqrt{\frac{2}{\pi}} \sum_{l,m} \frac{i^l}{rk} e^{\pm i\sigma_l(\eta)} F_l(\eta, kr) Y_{l,m}^*(\hat{\mathbf{k}}) Y_{l,m}(\hat{\mathbf{r}}) . \quad (2.127)$$

In spherical coordinates, this allows us to project any wave function

$$\psi(\mathbf{r}, t) = \frac{1}{r} \sum_{l,m} u_{l,m}(r, t) Y_{l,m}(\hat{\mathbf{k}}) \quad (2.128)$$

onto Coulomb plane waves to obtain

$$\langle C^{(\pm)}(\mathbf{k})|\psi(t)\rangle = \frac{1}{k} \sum_{l,m} g_{l,m}^{(\pm)}(k) Y_{l,m}(\hat{\mathbf{k}}) , \quad (2.129)$$

with

$$g_{l,m}^{(\pm)}(k) = \sqrt{\frac{2}{\pi}} \mathrm{i}^{-l} \mathrm{e}^{\mp \mathrm{i} \sigma_l} \int_0^\infty F_l(\eta, kr) u_{l,m}(r) \mathrm{d}r . \quad (2.130)$$

(2.129) is used to calculate the simulated hydrogen spectra in this thesis, which in turn defines the CLC delay in Chap. 6.

Chapter 3

Solving the two-electron time-dependent Schrödinger equation

3.1 The TDSE for helium

We describe the single ionization of ground-state para-helium atoms by ultrashort XUV pulses with and without assisting phase-coherent delayed (or advanced) IR-laser pulses by solving the TDSE in full dimensionality,

$$H\Psi = i\frac{\partial}{\partial t}\Psi . \quad (3.1)$$

The Hamiltonian

$$H = \sum_{i=1,2} (H_i + H_{Fi}) + V_{12} \quad (i = 1, 2) \quad (3.2)$$

consists of the single-electron Hamilton operators for the interaction of each electron with the atomic nucleus, H_i , the electronic correlation, V_{12} , and the electron—external-field-interaction terms, H_{Fi} .

$$H_i = -\frac{\nabla_i^2}{2} + V(r_i) \quad (i = 1, 2) , \quad (3.3)$$

where $V(r_i) = Z/r_i$ and $Z = 2$ for helium,

$$V_{12}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} , \quad (3.4)$$

and

$$H_{Fi} = \begin{cases} \mathcal{E}(t) \cdot z_i & \text{(length gauge)} \\ -iA(t) \cdot \frac{\partial}{\partial z_i} & \text{(velocity gauge)} \end{cases} \quad (i = 1, 2) . \quad (3.5)$$

The electron position vectors, $\mathbf{r}_i$, $i = 1, 2$, are chosen so that the atomic nucleus coincides with the origin of our coordinate system. The external electromagnetic-field pulses are assumed to be linearly polarized along the quantization (z) axis with cosine-squared electric-field envelopes of pulse length T ,

$$\begin{aligned} \mathcal{E}(t) &= \mathcal{E}_{\text{XUV}}(t - \tau) + \mathcal{E}_{\text{IR}}(t) , \\ \mathcal{E}_j(t) &= \mathcal{E}_{j,0} \sin(\omega_j t) \cos(\pi t/T_j)^2 , \quad j = \text{XUV, IR}, \end{aligned} \quad (3.6)$$

and corresponding vector potential $A(t) = -\int_{-\infty}^t dt' \mathcal{E}(t')$. The delay (advance) of the center of the IR pulse with respect to the center of the XUV pulse is designated by $\tau < 0$ ($\tau > 0$).

Assuming initial helium ground state in singlet-spin configuration (para-helium) and neglecting spin – orbital angular coupling as well as spin flips in the external electromagnetic fields, the total spin of the two-electron system during streaked photoemission is preserved, and the spatial part of the two-electron wave function remains symmetric with respect to electron exchange. According to our choice of the quantization direction along the XUV and IR pulse polarization direction, symmetry imposes that M remain zero throughout the ionization process. We therefore will not keep track of M in this thesis.

We solve the TDSE (3.1) using a finite-element discrete-variable representation (FE-DVR) of the partial-wave radial wave functions $\psi_\lambda(r_1, r_2, t)$ on a 2D adaptive rectangular numerical grid for the radial coordinates (r_1, r_2) . For details of our implementation of the FE-DVR method, we refer to Ref. ⁴², references therein, and Chap. 2 and App. B of the present work.

3.1.1 Length gauge

Expressing the electron interactions with the XUV and IR pulse (3.5) in the length gauge, we time-propagate the radial TDSE (3.13) using the split-operator Crank-Nicolson technique⁴¹ with equidistant time steps Δt ,

$$\psi_\lambda(t + \Delta t) = e^{-iH\Delta t}\psi_\lambda(t) = e^{-iH_0\frac{\Delta t}{2}}e^{-iH_{\text{int}}\Delta t}e^{-iH_0\frac{\Delta t}{2}}\psi_\lambda(t) + \mathcal{O}(\Delta t^3) . \quad (3.7)$$

This scheme assumes that the time dependence of H is negligible during each time step. In all applications in this thesis, we ascertain numerical convergence by selecting sufficiently small time steps so that the accumulation of numerical errors in each time step is irrelevant.

The advantageous choice of $H_0 = H_1 + H_2$ allows the factorization of the propagation along the radial coordinates,

$$e^{-iH_0\frac{\Delta t}{2}} = e^{-iH_1\frac{\Delta t}{2}}e^{-iH_2\frac{\Delta t}{2}}, \quad (3.8)$$

since H_1 and H_2 commute. In the length gauge, the interaction operator $H_{\text{int}} = H_{F1} + H_{F2} + V_{12}$ in the position representation does not contain derivatives. It thus couples all partial waves separately at any given point of the 2D numerical grid (without the need for error-susceptible finite differencing). The split-operator method is therefore particularly suitable for length-gauge calculation. For all exponentiations we use the Cayley form of the time-evolution operator⁴⁰,

$$e^{-iH\Delta t} = \left(1 + \frac{i}{2}H\Delta t\right)^{-1} \left(1 - \frac{i}{2}H\Delta t\right) . \quad (3.9)$$

3.1.2 Velocity gauge

For applications in this thesis, we employ both the length and velocity form of H_{Fi} [cf. Eq. (3.5)], in order to assess the numerical convergence of our photoelectron-momentum distribution and temporal shifts. While formally quantum mechanics is gauge invariant,

approximations introduced in the modeling and the progression of numerical errors tend to affect the accuracy of length- and velocity-gauge calculations unequally. Their comparison is therefore a common tool for assessing the accuracy of numerical models. In particular, as pointed out by Cormier and Lambropoulos⁴³ for the numerical computation of photoemission spectra for strong-field ionization based on partial-wave expansions, the rate of convergence in length and velocity gauge calculations with the number of included partial waves tends to be different. For above-threshold ionization of hydrogen atoms, the authors obtained converged spectra including 10 partial waves in velocity-gauge calculations, while requiring in excess of 200 partial waves in the length gauge. The physical reason for the very different rate of convergence is a more effective inclusion of the external-field-driven electronic quiver-motion in velocity-gauge final photoelectron states in terms of the canonical photoelectron momentum, $\mathbf{k} - \mathbf{A}(t)$. In contrast, the same anisotropic dynamics requires a large number of partial waves in the length gauge, where the final-state description hinges on the (time-independent) kinematic photoelectron momentum $\mathbf{k}$.

While this convergence comparison appears to clearly favor the velocity gauge, the split-operator scheme outlined above in part offsets its advantageous inclusion of the canonical photoelectron momentum due to the appearance of the differential operator $\partial/\partial z_i$ in Eq. (3.5). In contrast to the length gauge and represented in spherical coordinates, the electron-external-field interaction H_{Fi} now involves the coupling of two-electron partial waves at adjacent grid points that are addressed in the finite-difference implementation of the $\partial/\partial z_i$ operator on the (r_1, r_2) grid. For this reason, we abandon the split-operator propagation scheme when working in the velocity gauge and, instead, use a Lanczos algorithm² with an adaptive number of Krylov basis states to keep the numerical error below a set threshold. Please refer to Sec. 2.2.6 for details.

3.2 Coupled radial equations

3.2.1 Partial-wave expansion

In our applications to photoionization by linearly polarized light, the magnetic quantum number of the spinless two-electron system, $M = 0$, is preserved and will be omitted below. The relevant set of quantum numbers needed to specify a partial wave, $\lambda = \{l_1, l_2, L\}$, thus comprises the individual angular-momentum quantum numbers l_i according to H_i , $i = 1, 2$, and the total angular-momentum quantum number L . Expanding the two-electron wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \mathcal{S} \frac{1}{r_1 r_2} \sum_{\lambda} \psi_{\lambda}(r_1, r_2, t) \mathcal{Y}_{\lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \quad (3.10)$$

in terms of real-valued generalized spherical harmonics (A.18). Here the symmetrization operator is defined as

$$\mathcal{S}f(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[f(\mathbf{r}_1, \mathbf{r}_2) + f(\mathbf{r}_2, \mathbf{r}_1)] , \quad (3.11)$$

and the wave function is normalized as

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3r_1 d^3r_2 = 1 . \quad (3.12)$$

We express the TDSE (3.1) as the set of coupled equations for the radial partial waves ψ_{λ} ⁴⁴

$$\sum_{\lambda'} H_{\lambda, \lambda'} \psi_{\lambda'} = i \frac{\partial}{\partial t} \psi_{\lambda} , \quad (3.13)$$

with (r_1, r_2) -dependent angular coupling matrix elements

$$H_{\lambda, \lambda'} = \langle \mathcal{Y}_{\lambda} | H | \mathcal{Y}_{\lambda'} \rangle . \quad (3.14)$$

The coupling of partial waves by H_i is described by the matrix elements

$$\begin{aligned}\langle \mathcal{Y}_\lambda | H_i | \mathcal{Y}_{\lambda'} \rangle &= \delta_{\lambda, \lambda'} \left(K_{ri} + \frac{L_i^2}{2r_i^2} - \frac{2}{r_i} \right) \\ &= \delta_{\lambda, \lambda'} \left(-\frac{1}{2m} \frac{\partial^2}{\partial r_i^2} + \frac{l_i^2}{2mr_i^2} - \frac{2}{r_i} \right) \quad (i = 1, 2) ,\end{aligned}\tag{3.15}$$

where $\langle \mathcal{Y}_\lambda | L_i^2 | \mathcal{Y}_\lambda \rangle = l_i^2$, because $|\mathcal{Y}_\lambda\rangle$ is the eigenfunction of two-electron angular momentum L^2 and L_z . The other three terms V_{12}, H_{F1}, H_{F2} also couple partial waves and are introduced below.

3.2.2 The two-electron interaction term

In the TDSE for helium, the e-e interaction potential is

$$\begin{aligned}V_{12} = \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} &= 4\pi \sum_{l=0}^{\infty} \frac{1}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} \sum_{m=-l}^l Y_{l,m}^*(\hat{\mathbf{r}}_1) Y_{l,m}(\hat{\mathbf{r}}_2) \\ &= 4\pi \sum_{l=0}^{\infty} \frac{(-1)^l}{\sqrt{2l+1}} \frac{r_{<}^l}{r_{>}^{l+1}} \mathcal{Y}_{l,l}^{0,0}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) ,\end{aligned}\tag{3.16}$$

where

$$\mathcal{Y}_{l,l}^{0,0}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \frac{(-1)^l}{\sqrt{2l+1}} \sum_{m=-l}^l Y_{l,m}^*(\hat{\mathbf{r}}_1) Y_{l,m}(\hat{\mathbf{r}}_2) .\tag{3.17}$$

The partial wave coupling matrix for each term is

$$\begin{aligned}
& \left\langle \mathcal{Y}_{l_1 l_2}^{LM} \left| Y_{lm}^*(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2) \right| \mathcal{Y}_{l'_1 l'_2}^{L'M'} \right\rangle \\
&= \sum_{m'_1, m'_2} \sum_{m_1, m_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & M' \end{bmatrix} \times \\
& \quad \iint Y_{l_1 m_1}^*(\hat{\mathbf{r}}_1) Y_{l_2 m_2}^*(\hat{\mathbf{r}}_2) Y_{lm}^*(\hat{\mathbf{r}}_1) Y_{lm}(\hat{\mathbf{r}}_2) Y_{l'_1 m'_1}(\hat{\mathbf{r}}_1) Y_{l'_2 m'_2}(\hat{\mathbf{r}}_2) d\Omega_1 d\Omega_2 \\
&= \frac{2l+1}{4\pi} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \sum_{m'_1, m'_2} \sum_{m_1, m_2} (-1)^{m_1+m_2+m} \times \\
& \quad \begin{pmatrix} l_1 & l & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l'_1 \\ -m_1 & -m & m'_1 \end{pmatrix} \begin{pmatrix} l_2 & l & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l & l'_2 \\ -m_2 & m & m'_2 \end{pmatrix} \times \\
& \quad \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & M' \end{bmatrix} . \tag{3.18}
\end{aligned}$$

With regard to the summation over m in (3.17), the selection rule for the 3j symbol requires that only one term in the sum be non-zero, hence

$$\begin{aligned}
& \left\langle \mathcal{Y}_{l_1 l_2}^{LM} \left| \mathcal{Y}_{l, l}^{0,0} \right| \mathcal{Y}_{l'_1 l'_2}^{L'M'} \right\rangle = \\
& \delta_{M, M'} (-1)^l \frac{\sqrt{2l+1}}{4\pi} \sqrt{(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)} \times \\
& \quad \sum_{m'_1, m'_2} \sum_{m_1, m_2} (-1)^{m'_1+m_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m'_1 & m'_2 & M \end{bmatrix} \begin{pmatrix} l_1 & l & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \times \\
& \quad \begin{pmatrix} l_1 & l & l'_1 \\ -m_1 & m_1 - m'_1 & m'_1 \end{pmatrix} \begin{pmatrix} l_2 & l & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l & l'_2 \\ -m_2 & m_2 - m'_2 & m'_2 \end{pmatrix} . \tag{3.19}
\end{aligned}$$

Note that the summations are subject to the restrictions

$$m_1 + m_2 = m'_1 + m'_2 = M , \quad |m'_1 - m_1| \leq l , \quad |m'_2 - m_2| \leq l . \tag{3.20}$$

This can be further simplified¹ with the Wigner 9j symbol

$$\begin{aligned} \langle \mathcal{Y}_{l_1 l_2}^{LM} | \mathcal{Y}_l^{00} | \mathcal{Y}_{l'_1 l'_2}^{L'M'} \rangle &= \frac{2l+1}{4\pi} \delta_{L,L'} \delta_{M,M'} \sqrt{(2l'_1+1)(2l'_2+1)(2L+1)} \times \\ &\quad \begin{bmatrix} l & l'_1 & l_1 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} l & l'_2 & l_2 \\ 0 & 0 & 0 \end{bmatrix} \begin{Bmatrix} l & l'_1 & l_1 \\ l & l'_2 & l_2 \\ 0 & L & L \end{Bmatrix}. \end{aligned} \quad (3.21)$$

Note also that when $M = M'$, the result is M independent.

3.2.3 The Poisson integral

From the previous discussion of the FE-DVR grid, it might seem natural to calculate $\langle u_i u_j | r_{<}^l / r_{>}^l | u_{i'} u_{j'} \rangle$ with the Gauss-Lobatto quadrature. However, this is not accurate, since $r_{<}^l / r_{>}^l$ has a sharp ridge at $r_1 = r_2$. A solution has been proposed by Eq. 68 of²⁶, derived with the Poisson integral method, as

$$\langle u_i u_j | \frac{r_{<}^l}{r_{>}^{l+1}} | u_{i'} u_{j'} \rangle = \delta_{i,i'} \delta_{j,j'} \left[\frac{2l+1}{r_i r_j \sqrt{\omega_i \omega_j}} (2\mathbf{T}_l)_{i,j}^{-1} + \frac{r_i^l r_j^l}{r_{max}^{2l+1}} \right], \quad (3.22)$$

where $\mathbf{T}_l$ is the kinetic energy operator for a single electron, with matrix representation

$$\begin{aligned} (T_l)_{ij} &= \langle u_i | \left[-\frac{1}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)}{2mr} \right] | u_j \rangle \\ &= -\frac{1}{2m} \langle u_i | \frac{d^2}{dr^2} | u_j \rangle + \delta_{i,j} \frac{l(l+1)}{2mr_i^2}. \end{aligned} \quad (3.23)$$

and $r_{max} = \max\{r_{1,max}, r_{2,max}\}$ is the length of the long side of the radial grid.

3.2.4 External-field interactions in the length gauge

The length-gauge external-field-interaction term H_{Fi} in the TDSE (3.1) contributes to the matrix element in Eq. (3.13) and is given by the top Eq. (3.5) with

$$z_i = r_i \cos \theta_i = 2\sqrt{\frac{\pi}{3}} r_i Y_{1,0}(\hat{\mathbf{r}}_i) \quad (i = 1, 2). \quad (3.24)$$

The angular part of the partial-wave coupling matrix elements for $i = 1$ becomes

$$\begin{aligned} & F_{\lambda,\lambda'}^{(1)} \\ &= \langle \mathcal{Y}_{l_1 l_2}^{LM} | \cos \theta_1 | \mathcal{Y}_{l'_1 l'_2}^{L'M'} \rangle = 2\sqrt{\frac{\pi}{3}} \sum_{m'_1, m'_2} \sum_{m_1, m_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l_2 & L' \\ m'_1 & m'_2 & M' \end{bmatrix} \times \\ & \quad \iint Y_{l_1 m_1}^*(\hat{\mathbf{r}}_1) Y_{l_2 m_2}^*(\hat{\mathbf{r}}_2) Y_{10}(\hat{\mathbf{r}}_1) Y_{l'_1 m'_1}(\hat{\mathbf{r}}_1) Y_{l'_2 m'_2}(\hat{\mathbf{r}}_2) d\Omega_1 d\Omega_2 \\ &= 2\sqrt{\frac{\pi}{3}} \delta_{l_2, l'_2} \sum_{m_1, m_2, m'_1} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m'_1 & m_2 & M' \end{bmatrix} \times \\ & \quad \int Y_{l_1 m_1}^*(\hat{\mathbf{r}}_1) Y_{10}(\hat{\mathbf{r}}_1) Y_{l'_1 m'_1}(\hat{\mathbf{r}}_1) d\Omega_1 \\ &= \delta_{l_2, l'_2} \sqrt{(2l_1 + 1)(2l'_1 + 1)} \sum_{m_1, m_2, m'_1} (-1)^{m_1} \times \\ & \quad \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l_2 & L' \\ m'_1 & m_2 & M' \end{bmatrix} \begin{pmatrix} l_1 & 1 & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & 1 & l'_1 \\ -m_1 & 0 & m'_1 \end{pmatrix} \\ &= \delta_{l_2, l'_2} \delta_{M, M'} \sqrt{(2l_1 + 1)(2l'_1 + 1)} \sum_{m_1, m_2} (-1)^{m_1} \times \\ & \quad \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l'_1 & l_2 & L' \\ m_1 & m_2 & M \end{bmatrix} \begin{pmatrix} l_1 & 1 & l'_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & 1 & l'_1 \\ -m_1 & 0 & m_1 \end{pmatrix}, \quad (3.25) \end{aligned}$$

where the curly brackets denote the Wigner 9j symbols. The last step used the property of 3j symbols that $m_1 + m_2 + m_3 = 0$ and the property of CG coefficients that $m_1 + m_2 = M$. The two delta functions show that the field action for the first electron will not affect the angular momentum of the second. In the final sum for m_1, m_2 , $m_1 + m_2 = M$ is required

and $|m_1| < \min\{l_1, l'_1\}$. Similarly, for the second electron,

$$\begin{aligned} \left\langle \mathcal{Y}_{l_1 l_2}^{LM} \left| \cos \theta_2 \right| \mathcal{Y}_{l'_1 l'_2}^{L'M'} \right\rangle &= \delta_{l_1, l'_1} \delta_{M, M'} \sqrt{(2l_2 + 1)(2l'_2 + 1)} \sum_{m_1, m_2} (-1)^{m_2} \times \\ &\begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \begin{bmatrix} l_1 & l'_2 & L' \\ m_1 & m_2 & M \end{bmatrix} \begin{pmatrix} l_2 & 1 & l'_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & 1 & l'_2 \\ -m_2 & 0 & m_2 \end{pmatrix}. \end{aligned} \quad (3.26)$$

Using Wigner 9j symbols, the dipole-coupling matrix elements can be written as

$$\begin{aligned} F_{\lambda, \lambda'}^{(i)} &= \langle \mathcal{Y}_\lambda | \cos \theta_i | \mathcal{Y}_{\lambda'} \rangle = \sqrt{9(2l'_1 + 1)(2l'_2 + 1)(2L' + 1)/(4\pi)^2} \begin{bmatrix} \delta_{i,1} & l'_1 & l_1 \\ 0 & 0 & 0 \end{bmatrix} \\ &\times \begin{bmatrix} \delta_{i,2} & l'_2 & l_2 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 & L' & L \\ 0 & 0 & 0 \end{bmatrix} \left\{ \begin{matrix} \delta_{i,1} & l'_1 & l_1 \\ \delta_{i,2} & l'_2 & l_2 \\ 1 & L' & L \end{matrix} \right\} \quad (i = 1, 2). \end{aligned} \quad (3.27)$$

3.2.5 External-field interactions in the velocity gauge

Similar to hydrogen in (2.68), the field-coupling matrix elements for electron i are

$$G_{\lambda, \lambda'}^{(i)} = F_{\lambda, \lambda'}^{(i)} \frac{\partial}{\partial r_i} + \frac{g_{\lambda, \lambda'}^{(i)}}{r_i}, \quad (3.28)$$

where $F_{\lambda, \lambda'}^{(z1)}$ is defined in (3.25). The matrix element in the second term is

$$g_{\lambda, \lambda'}^{(i)} = - \langle \mathcal{Y}_\lambda | \cos \theta_i + \sin \theta_i \frac{\partial}{\partial \theta_i} | \mathcal{Y}_{\lambda'} \rangle. \quad (3.29)$$

When $M \equiv 0$, we have

$$\begin{aligned}
g_{\lambda,\lambda'}^{(1)} &= \delta_{l_2,l'_2} \sum_{m_1,m_2,m'_1} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & 0 \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m'_1 & m_2 & 0 \end{bmatrix} \times \\
&\quad \int Y_{l_1 m_1}^*(\hat{\mathbf{r}}_1) F^{(vz1)}(\hat{\mathbf{r}}_1) Y_{l'_1 m'_1}(\hat{\mathbf{r}}_1) d\Omega_1 \\
&= \delta_{l_2,l'_2} \sum_{m_1} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & -m_1 & 0 \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m_1 & -m_1 & 0 \end{bmatrix} \times \\
&\quad (\delta_{l'_1,l_1+1} l'_1 \mathcal{C}_{l_1,m_1} - \delta_{l_1,l'_1+1} l_1 \mathcal{C}_{l'_1,m_1}) ,
\end{aligned} \tag{3.30}$$

where $\mathcal{C}_{l,m}$ is defined in (2.56). Similarly,

$$\begin{aligned}
g_{\lambda,\lambda'}^{(2)} &= \delta_{l_1,l'_1} \sum_{m_1,m_2,m'_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & 0 \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ m_1 & m'_2 & 0 \end{bmatrix} \times \\
&\quad \int Y_{l_2 m_2}^*(\hat{\mathbf{r}}_2) F^{(vz2)}(\hat{\mathbf{r}}_2) Y_{l'_2 m'_2}(\hat{\mathbf{r}}_2) d\Omega_1 \\
&= \delta_{l_1,l'_1} \sum_{m_2} \begin{bmatrix} l_1 & l_2 & L \\ -m_2 & m_2 & 0 \end{bmatrix} \begin{bmatrix} l'_1 & l'_2 & L' \\ -m_2 & m_2 & 0 \end{bmatrix} \times \\
&\quad (\delta_{l'_2,l_2+1} l'_2 \mathcal{C}_{l_2,m_2} - \delta_{l_2,l'_2+1} l_2 \mathcal{C}_{l'_2,m_2}) .
\end{aligned} \tag{3.31}$$

3.3 Symmetry, selection rules, and optimizations of the helium wave function

3.3.1 Exchange symmetry

In this thesis, we assume that the two electrons are in the singlet spin configuration, so their spatial wave functions are symmetric under particle exchange (para-helium).

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1) . \tag{3.32}$$

Combined with (3.10) and (A.20), this gives us the requirement for radial wave functions

$$\psi_{l_1, l_2}^{L, M}(r_1, r_2) = (-1)^{l_1 + l_2 - L} \psi_{l_2, l_1}^{L, M}(r_2, r_1) . \quad (3.33)$$

For para-helium, $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric with respect to electron exchange, thus (3.33) eliminates about half of the partial waves in Eq. (3.10) for a square (r_1, r_2) grid, allowing us to keep only those for $l_1 \leq l_2$. This simplification is compromised for the rectangular (non-quadratic) grids we used for the single ionization in streaking, where r_1 and r_2 have different spatial ranges, and l_1 and l_2 require different maximal values for numerical convergence.

3.3.2 Selection rules

The symmetry properties of the Clebsch-Gordan and Wigner 9j coefficients imply that Eq. (3.14) couples partial waves with the same oddity of $l_1 + l_2 - L$ ⁴².

Therefore, since the initial ground state of para-helium ($L = 0$, $l_1 = l_2$) has even $l_1 + l_2 - L$, partial waves with odd $l_1 + l_2 - L$ are not excited during the field-driven evolution of $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$. This reduces the number of partial waves that need to be retained in (3.14) to achieve numerical convergence.

3.3.3 Adaptive grid with optional sliding window

We propagate the radial wave function on an adaptive (r_1, r_2) grid, which we determine during the numerical calculation by adding a “detector region” outside the complex absorber potentials at the outer grid boundaries of r_1 and r_2 ⁴⁵ (Fig. 3.1). When the wave-function probability density in the detector region on either side reaches a threshold (typically 5×10^{-9}), the length of that side is automatically extended, keeping the existing grid points, grid spacing and basis polynomials unchanged. For single ionization, one radial coordinate has a fixed length and no detector region is needed along its grid direction. In our applications, we found that this technique can accelerate the numerical throughput for single-ionization 2 to 3 times. For XUV energy larger than 100 eV, after the single-ionization wave packet

has separated from the no-ionization wave packet, the minimum value of r_2 can also be automatically increased by using another detector region, so that the range of r_2 only includes the single-ionization wave packet.

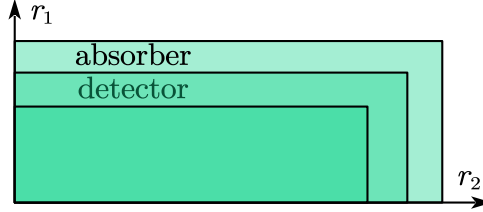


Figure 3.1: *2D radial grid layout for every partial waves in Eq. (3.10).*

3.4 Partial-wave convergence

For potential future optimization¹, we performed trial calculations to determine which partial waves (l_1, l_2, L) should be included to calculate converged photoelectron yields and streaking time delays. These test runs with predetermined limits for incremental relative changes in photoelectron yield allow us to find, separately for each L , a minimal range of l_1, l_2 values (Fig. 3.2). This is an improvement over the previous implementation of our two-electron code^{2;44} that uses for all values of L the same $l_{1,max}$ and $l_{2,max}$ values. When partial-waves calculations do not converge, one indicator is that the photoelectron wave packet becomes distorted (Fig. 3.3).

3.5 Single-ionization photoemission spectra of helium

In this thesis, we only use para-helium, which is the most abundant form of helium under lab conditions. It has an anti-symmetric singlet spin and a symmetric spatial wave function. Some frequently used data are listed below.

- **Ground state energy:** -2.9037244 au (-79.014366 eV)²

¹Since this optimization is not extensively tested, we have not applied it for the simulations in this thesis yet.

²For energy levels of helium, cf. ^{46;47}.

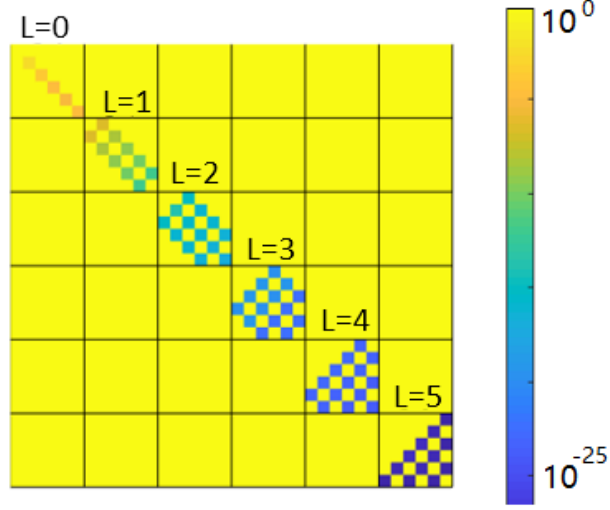


Figure 3.2: Distribution of partial-wave probabilities in a typical streaking simulation. Each large square represents a different L , and each small grid for the total probability of a partial wave (l_1, l_2, L) .

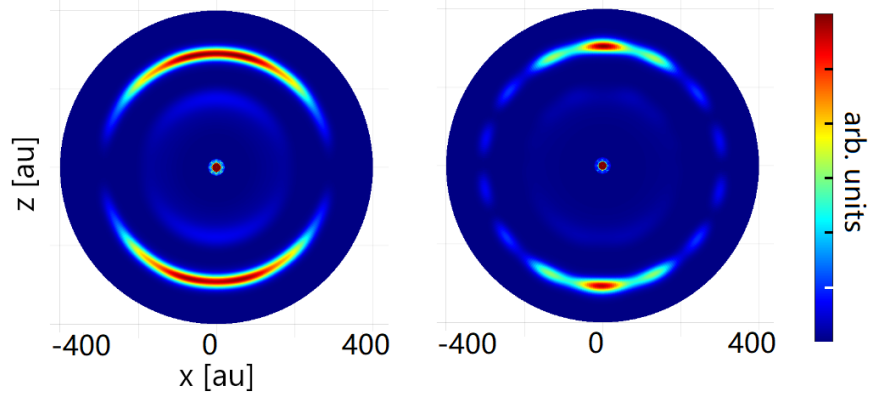


Figure 3.3: Cross section of the single-electron spacial distribution 3.39 fs after ionization, using the partial wave configuration $(l_{1,max}, l_{2,max}, L_{max}) = (5, 8, 8)$ with a total of 132 partial waves. Left: converged photoelectron wave packet, using the velocity gauge and Lanczos algorithm; Right: non-converged photoelectron wave packet, using the length gauge with the Crank-Nicolson and split operator algorithm.

- **Direct** ($n=1$) single-ionization potential: 0.9037244 au (24.591594eV)
- **Shake-up** ($n=2$) single-ionization potential: 2.4037244 au (65.408673eV)
- **Shake-up** ($n=3$) single-ionization potential: 2.68150218 au (72.967391eV)

3.5.1 Radial position distribution

One useful quantity for following the progress of numerical TDSE propagations is the two-electron radial probability distribution

$$P(r_1, r_2) = 2 \iint |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 r_1^2 r_2^2 d\Omega_1 d\Omega_2 . \quad (3.34)$$

For example, $\int_a^b \int_c^d P(r_1, r_2) dr_1 dr_2$ is the probability of finding one electron within the radius interval $[a, b]$ and another electron within $[c, d]$. The factor of 2 is due to symmetrization. The same factor applies for other two-electron distributions in this thesis.

Let λ denote the combined quantum numbers (l_1, l_2, L) , then the normalization condition reads

$$\begin{aligned} & \iint P(r_1, r_2) dr_1 dr_2 \\ &= 2 \iiint \left| \frac{1}{r_1 r_2} \sum_{\lambda} \psi_{\lambda}(r_1, r_2) \mathcal{Y}_{\lambda}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \right|^2 d\Omega_1 d\Omega_2 r_1^2 r_2^2 dr_1 dr_2 \\ &= 2 \iint \sum_{\lambda} |\psi_{\lambda}(r_1, r_2)|^2 dr_1 dr_2 = 2 . \end{aligned} \quad (3.35)$$

Hence, P can be expressed in terms of partial waves as

$$P(r_1, r_2) = 2 \sum_{\lambda} |\psi_{\lambda}(r_1, r_2)|^2 . \quad (3.36)$$

A typical example of this distribution on a rectangular grid is shown in Fig. 3.4.

3.5.2 Exact scattering states for single ionization

In order to accurately calculate the phase of the transition element, we need to calculate the exact photoelectron states for single ionization of helium. They are the solutions of the TISE,

$$H_0 \Psi = E \Psi , \quad H_0 = H_1 + H_2 + V_{12} , \quad (3.37)$$

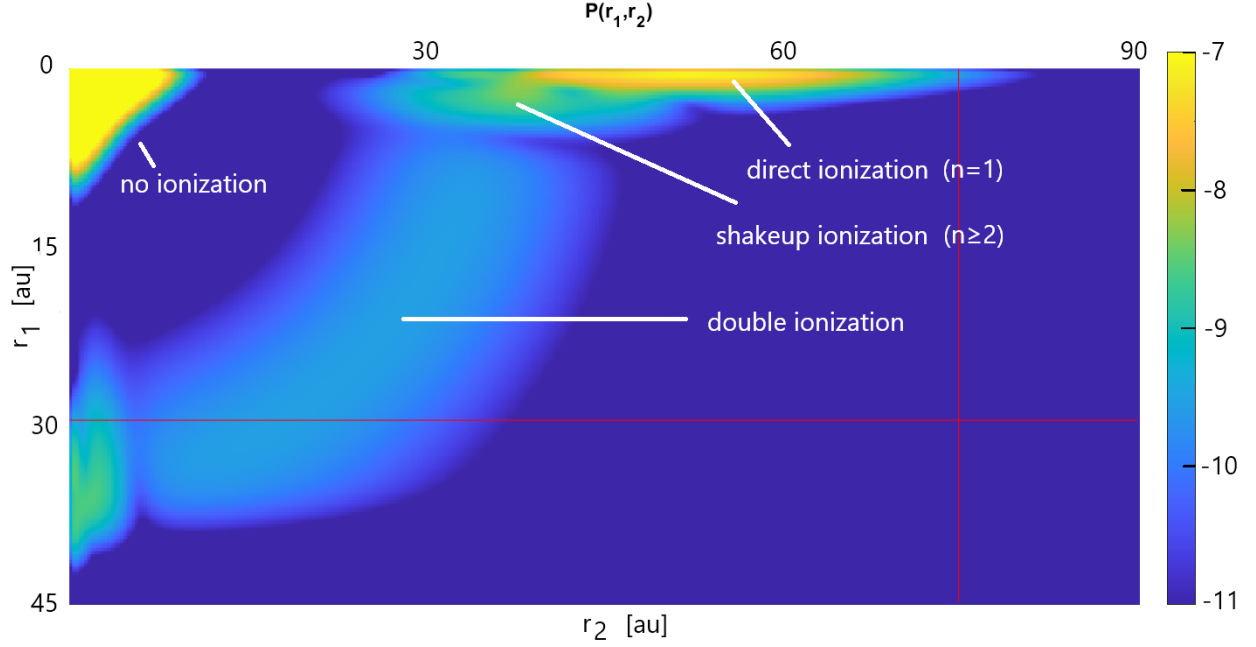


Figure 3.4: Two-electron radial distribution with XUV photon energy of 110 eV and $t = 20.71$ au after the peak of the XUV pulse. A rectangular grid is used, with red lines marking the boundaries of the virtual absorbers. Note that although symmetry $P(r_1, r_2) = P(r_2, r_1)$ holds, the wave packets on the short side of the rectangular grid is mostly absorbed.

with energy eigenvalue $E = -Z^2/n_1^2 + k_2^2/2$. Depending on the chosen boundary condition, Ψ can be expressed in different forms. For example, states with a given total angular momentum L , $\mathcal{S}|n_1, \lambda, k_2\rangle$, are mathematically simpler and easier to solve numerically. The asymptotic product basis $\mathcal{S}|n_1, l_1, m_1, \mathbf{k}_2\rangle$ is physically well known and is used to calculate the EWS time delay. We stress that to extract the asymptotic phase required by the time delay calculation, it is important to use the exact scattering state like $\mathcal{S}|n_1, l_1, m_1, \mathbf{k}_2\rangle$ instead of the tensor product state like $\mathcal{S}|n_1, l_1, m_1\rangle|\mathbf{k}_2\rangle$ as an approximation. The latter can only be used for phase-insensitive calculations such as the streaked spectra.

Without external field interactions, the total energy E and the total angular momentum L of the two-electron system are conserved. Since H_0 commutes with the two-electron orbital angular momentum operator L^2 . The two operators thus have a common set of complete and orthonormal eigenstates in the single-ionization continuum (exact scattering states). We

expand these eigenstates in the basis of generalized spherical harmonics [Eq. (A.18)],

$$\langle \mathbf{r}_1, \mathbf{r}_2 | n_1, \lambda, k_2 \rangle = \frac{1}{r_1 r_2} \sum_{l'_1, l'_2} \psi_{\lambda', n_1, k_2}(r_1, r_2) \mathcal{Y}_{\lambda'}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) , \quad (3.38)$$

where $\lambda' = \{l'_1, l'_2, L\}$. Since the TISE is a real valued partial differential equation, (3.38) is a real valued function. This expansion is analogous to expanding the exact helium ground state with different partial waves (not just approximately $|1s\rangle|1s\rangle$). (3.39) tells us only the $\lambda' = \lambda$ term in the sum has incoming and outgoing wave, all other terms represent short range e-e interaction.

We note that n_1, l_1, l_2, k_2 in (3.38) are not eigenvalues of $|n_1, \lambda, k_2\rangle$ since their operators do not commute with H_0 or L^2 . Instead, they are specified in terms of the following boundary condition³⁸

$$\begin{aligned} \psi_{\lambda', n_1, k_2}(r_1, r_2) &\xrightarrow{r_2 \rightarrow \infty} \delta_{\lambda', \lambda} \delta_{l_2, l'_2} r_1 R_{n_1, l_1}^{(Z=2)}(r_1) \\ &\times \sqrt{\frac{2}{\pi}} \sin \left[k_2 r_2 - \frac{\pi l_2}{2} + \frac{1}{k_2} \ln(2k_2 r_2) + \sigma_{l_2} + \delta_{n_1}^\lambda(k_2) \right] . \end{aligned} \quad (3.39)$$

They depend on the radial wave function, $R_{n, l}^{(Z=2)}$, of the residual He^+ ion in the bound state $\psi_{n, l, m}^{(Z=2)}(\mathbf{r})$ and the energy-dependent Coulomb phase shift,

$$\sigma_l(\eta) = \arg[\Gamma(l + 1 + i\eta)] , \quad (3.40)$$

with Sommerfeld parameter $\eta = -Z/k$. The sin factor in Eq. (3.39) derives from the asymptotic form of the Coulomb function of the first kind, $F_l(kr)$, and includes the additional energy-dependent phase $\delta_n^\lambda(k)$ due to the short-range electronic interaction during the emission process.

We stress that to extract the asymptotic phase required by the time delay calculation, it is important to use the exact scattering state like $\mathcal{S} |n_1, l_1, m_1, \mathbf{k}_2\rangle$ instead of the tensor product state like $\mathcal{S} |n_1, l_1, m_1\rangle |\mathbf{k}_2\rangle$ as an approximation. The latter can only be used for phase-insensitive calculations such as the streaked spectra.

To provide the partial wave contributions of emitted electrons with asymptotic momentum magnitude k_2 in angular momentum states $|l_2, m_2\rangle$, we decouple the outgoing spherical wave part of $|n_1, \lambda, k_2\rangle$ in (3.38) with the unitary transformation

$$\begin{aligned} |n_1, l_1, m_1, l_2, k_2\rangle &= |n_1, l_1, m_1, l_2, -m_1, k_2\rangle \\ &= i \sum_L \begin{bmatrix} l_1 & l_2 & L \\ m_1 & -m_1 & 0 \end{bmatrix} e^{-i\delta_{n_1}^\lambda} |n_1, \lambda, k_2\rangle , \end{aligned} \quad (3.41)$$

where the first equation indicates that we will drop the redundant quantum number $m_2 = -m_1$ from now on. This allows us to compose entangled two-electron states with asymptotic momentum vector $\mathbf{k}_2$ by combining these partial waves into asymptotic plane-wave states,

$$|n_1, l_1, m_1, \mathbf{k}_2\rangle = \sum_{l_2} \frac{i^{l_2}}{k_2} e^{-i\sigma_{l_2}} Y_{l_2, -m_1}^*(\hat{\mathbf{k}}_2) |n_1, l_1, m_1, l_2, k_2\rangle , \quad (3.42)$$

where l_1 relates to the bound electron and l_2 to the photoelectron. To simplify the notation, we drop subscripts and the symmetrization operator from now on and refer to the symmetrized scattering states as

$$|n, l, m, \mathbf{k}\rangle = \mathcal{S} |n_1, l_1, m_1, \mathbf{k}_2\rangle , \quad (3.43)$$

$$|n, \lambda, k\rangle = \mathcal{S} |n_1, \lambda, k_2\rangle . \quad (3.44)$$

3.5.3 Product and total-angular-momentum representations of the wave function

For some applications in this chapter, we expand the two-electron wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ in (3.10) with another angular basis set:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_1 r_2} \sum_{l_1, m_1, l_2, m_2} \psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) Y_{l_1, m_1}(\hat{\mathbf{r}}_1) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) . \quad (3.45)$$

The advantage of this expansion is that it decouples the two electrons in the summation, so $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ can easily be projected onto the subspace of the bound states $|n, l, m\rangle$ of the He^+ .

Using (3.10) and (A.18), for each pair of (l_1, l_2) , we have the unitary transform

$$\psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) = \sum_{L, M} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \psi_{l_1, l_2}^{L, M}(r_1, r_2) . \quad (3.46)$$

For the linearly polarized electric field in this thesis, we are restricted to $M \equiv 0$ and $m_1 + m_2 = 0$.

3.5.4 Single-electron position distribution

The probability density of a single electron located at $\mathbf{r}_2$ is

$$P(\mathbf{r}_2) = 2 \int |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 d^3 r_1 . \quad (3.47)$$

Defining

$$\psi_{l_1, m_1}(r_1, \mathbf{r}_2) = \frac{1}{r_2} \sum_{l_2, m_2} \psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) , \quad (3.48)$$

(3.45) becomes

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{r_1} \sum_{l_1, m_1} \psi_{l_1, m_1}(r_1, \mathbf{r}_2) Y_{l_1, m_1}(\hat{\mathbf{r}}_1) , \quad (3.49)$$

and the single-electron probability can be written as

$$\begin{aligned} P(\mathbf{r}_2) &= 2 \sum_{l_1, m_1} \int |\psi_{l_1, m_1}(r_1, \mathbf{r}_2)|^2 dr_1 \\ &= \frac{2}{r_2^2} \sum_{l_1, m_1} \int \left| \sum_{l_2, m_2} \psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) \right|^2 dr_1 . \end{aligned} \quad (3.50)$$

An example plot is shown in Fig. 3.5.

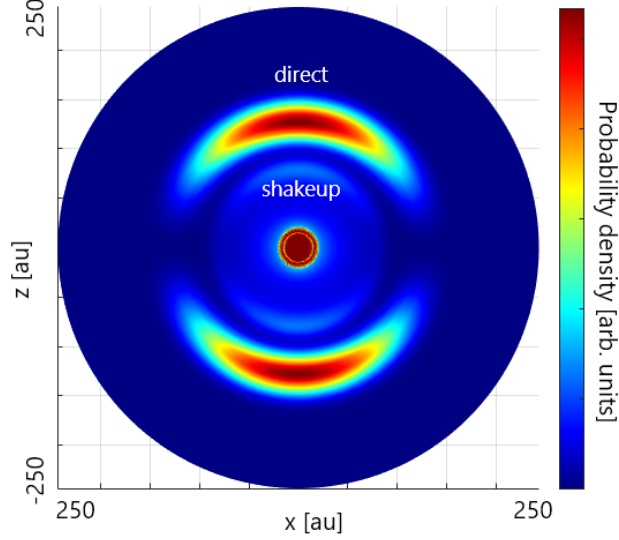


Figure 3.5: *Single-electron position distribution in the x - z cross section, with an XUV photon energy of 90 eV and $t = 39.3$ au after the peak of the XUV pulse.*

3.5.5 Photoelectron momentum spectra for single ionization

In order to calculate the probability density of asymptotic momentum of the photoelectron, we can first project the final wave function onto a spherical Coulomb wave, resulting in a single-electron wave function

$$\langle \mathbf{r}_1 | \langle C_{l_2, m_2}(k_2) | \Psi \rangle = \frac{1}{r_1} \sum_{l_1, m_1} \psi_{l_1, m_1}(r_1) \cdot Y_{l_1, m_1}(\hat{\mathbf{r}}_1) , \quad (3.51)$$

where

$$\psi_{l_1, m_1}(r_1) = \int_{r_{2, min}}^{+\infty} \sqrt{\frac{2}{\pi}} F_{l_2}(\eta_2, k_2 r_2) \psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) dr_2 . \quad (3.52)$$

The Coulomb function $|C_{l, m}(k)\rangle$ is defined in (2.120) and $\psi_{l_1, l_2}^{m_1, m_2}$ is defined in (3.46).

Applying the basis transform (2.125) to (3.51) yields the wave function projection onto a Coulomb plane wave

$$\langle \mathbf{r}_1 | \langle C^{(-)}(\mathbf{k}_2) | \Psi \rangle = \sum_{l_2, m_2} \frac{i^{-l_2}}{k_2} e^{i\sigma_{l_2}} Y_{l_2, m_2}(\hat{\mathbf{k}}_2) \langle \mathbf{r}_1 | \langle C_{l_2, m_2}(k_2) | \Psi \rangle . \quad (3.53)$$

Substitution of (3.51) into (3.53) yields the photoelectron asymptotic momentum distribution

$$\begin{aligned}
P(\mathbf{k}) &= 2 \int_0^{r_{1,max}} |\langle \mathbf{r}_1 | \langle C^{(-)}(\mathbf{k}_2) | \Psi \rangle|^2 d^3 r_1 \\
&= \sum_{l_1, m_1} \int_0^{r_{1,max}} \left| \sum_{l_2, m_2} \frac{i^{-l_2}}{k_2} e^{-i\sigma_{l_2}} Y_{l_2, m_2}(\hat{\mathbf{k}}_2) \cdot \psi_{l_1, m_1}(r_1) \right|^2 dr_1 .
\end{aligned} \tag{3.54}$$

Note that this distribution combines all channels and should be used for the streaking trace simulation. For channel-specific momentum distribution, cf. Eq. (3.62).

3.5.6 Photoelectron position distribution in a given (n, l) channel of single ionization

The normalized He^+ bound state is the hydrogenic wave function

$$\phi_{n,l,m}(\mathbf{r}) = R_{n,l}^{(Z=2)}(r) Y_{l,m}(\hat{\mathbf{r}}) , \tag{3.55}$$

and projecting the two-electron wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ onto it for the first electron, we have

$$\begin{aligned}
\psi^{(n_1, l_1, m_1)}(\mathbf{r}_2) &= \langle \mathbf{r}_2 | \langle n_1, l_1, m_1 | \Psi \rangle \\
&= \int \phi_{n_1, l_1, m_1}^{(Z=2)}(\mathbf{r}_1) \Psi(\mathbf{r}_1, \mathbf{r}_2, t) \cdot r_1^2 d\Omega_1 dr_1 \\
&= \int R_{n_1, l_1}(r_1) Y_{l_1, m_1}(\hat{\mathbf{r}}_1) \left[\frac{1}{r_1 r_2} \sum_{l'_1, m'_1, l_2, m_2} \psi_{l'_1, l_2}^{m'_1, m_2}(r_1, r_2) Y_{l'_1, m'_1}(\hat{\mathbf{r}}_1) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) \right] r_1^2 dr_1 d\Omega_1 \\
&= \frac{1}{r_2} \sum_{l_2, m_2} \psi_{l_2, m_2}^{(n_1, l_1, m_1)}(r_2) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) ,
\end{aligned} \tag{3.56}$$

where

$$\psi_{l_2, m_2}^{(n_1, l_1, m_1)}(r_2) = \int r_1 R_{n_1, l_1}(r_1) \psi_{l_1, l_2}^{m_1, m_2}(r_1, r_2) dr_1 . \tag{3.57}$$

The photoelectron position distribution after symmetrization is

$$P_{n,l,m}(\mathbf{r}) = 2 |\psi^{(n,l,m)}(\mathbf{r})|^2 . \tag{3.58}$$

We can also define the averaged probability distribution

$$P_{n,l}(\mathbf{r}) = \sum_m P_{n,l,m}(\mathbf{r}) , \quad P_n(\mathbf{r}) = \sum_l P_{n,l}(\mathbf{r}) . \quad (3.59)$$

Now we can analyze the photoelectron wave packet based on these position distributions for any given direction and calculate their trajectories, e.g. in Section 5.4.2.

3.5.7 Channel-distinguished momentum distribution

We project the final wave function onto the product state of a bound state and a spherical Coulomb wave (2.120)

$$\langle C_{l_2,m_2}(k_2) | \langle \phi_{n_1,l_1,m_1} | \Psi \rangle = \sqrt{\frac{2}{\pi}} \iint r_1 R_{n_1,l_1}(r_1) F_{l_2}(\eta_2, k_2 r_2) \psi_{l_1,l_2}^{m_1,m_2}(r_1, r_2) dr_1 dr_2 , \quad (3.60)$$

where $|C_{l,m}(k)\rangle$ is defined in (2.120) and $\phi_{n,l,m}$ in (3.55). With (2.125), we can replace the Coulomb spherical wave with a Coulomb plane wave

$$\langle C^{(-)}(\mathbf{k}_2) | \langle \phi_{n_1,l_1,m_1} | \Psi \rangle = \sum_{l_2,m_2} \frac{i^{-l_2}}{k_2} e^{i\sigma_{l_2}} Y_{l_2,m_2}(\hat{\mathbf{k}}_2) \langle C_{l_2,m_2}(k_2) | \langle \phi_{n_1,l_1,m_1} | \Psi \rangle , \quad (3.61)$$

which can be further calculated with (3.56). Finally, the (n, l, m) channel-distinguished photoelectron momentum spectrum is

$$P_{n,l,m}(\mathbf{k}) = 2 \left| \langle C^{(-)}(\mathbf{k}_2) | \langle \phi_{n_1,l_1,m_1} | \Psi \rangle \right|^2 . \quad (3.62)$$

We can also define averaged momentum spectra as

$$P_{n,l}(\mathbf{k}) = \sum_m P_{n,l,m}(\mathbf{k}) , \quad P_n(\mathbf{k}) = \sum_l P_{n,l}(\mathbf{k}) . \quad (3.63)$$

Note that the infinite sum $\sum_{n=1}^{\infty} P_n(\mathbf{k})$ is equivalent to (3.54), but in reality there will be a truncation error.

3.6 Double-ionization photoemission spectra of helium

3.6.1 Double-ionization momentum and energy spectra

To calculate the double-ionization momentum spectra $P(\mathbf{k}_1, \mathbf{k}_2)$ at $t \rightarrow \infty$, the exact scattering waves of double ionization $|\mathbf{k}_1, \mathbf{k}_2\rangle$ are required so that the total wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ can be projected onto them once all the external field has vanished. However, these states do not have a well-known analytical expression¹. For simplicity, we choose to use a symmetrized product of single-electron Coulomb plane waves (2.125).

The symmetrized scattering state is

$$\begin{aligned} \langle \mathbf{r}_1, \mathbf{r}_2 | C^{(-)}(\mathbf{k}_1, \mathbf{k}_2) \rangle &= \mathcal{S} [\langle \mathbf{r}_1 | C^{(-)}(\mathbf{k}_1) \rangle \langle \mathbf{r}_2 | C^{(-)}(\mathbf{k}_2) \rangle] \\ &= \frac{2}{\pi} \mathcal{S} \sum_{l_1, m_1} \sum_{l_2, m_2} \frac{i^{l_1+l_2}}{r_1 r_2 k_1 k_2} e^{-i[\sigma_{l_1}(\eta_1) + \sigma_{l_2}(\eta_2)]} F_{l_1}(\eta_1, k_1 r_1) F_{l_2}(\eta_2, k_2 r_2) \\ &\quad \times Y_{l_1, m_1}^*(\hat{\mathbf{k}}_1) Y_{l_2, m_2}^*(\hat{\mathbf{k}}_2) Y_{l_1, m_1}(\hat{\mathbf{r}}_1) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) . \end{aligned} \quad (3.64)$$

The full two-electron wave function is

$$\begin{aligned} \Psi(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{L, M, l_1, l_2} \frac{1}{r_1 r_2} \psi_{l_1, l_2}^{L, M}(r_1, r_2) \mathcal{Y}_{l_1, l_2}^{L, M}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\ &= \sum_{L, M, l_1, l_2} \frac{1}{r_1 r_2} \psi_{l_1, l_2}^{L, M}(r_1, r_2) \sum_{m_1, m_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} Y_{l_1, m_1}(\hat{\mathbf{r}}_1) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) . \end{aligned} \quad (3.65)$$

Projection onto the product states (3.64) yields

$$\langle C^{(-)}(\mathbf{k}_1, \mathbf{k}_2) | \Psi \rangle = \frac{2\sqrt{2}}{\pi k_1 k_2} f(k_1, k_2, \hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) , \quad (3.66)$$

where

$$f(k_1, k_2, \hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) = \sum_{L, M, l_1, l_2} (-i)^{l_1+l_2} e^{i[\sigma_{l_1}(\eta_1) + \sigma_{l_2}(\eta_2)]} I_{l_1, l_2}^{L, M}(k_1, k_2) \mathcal{Y}_{l_1, l_2}^{L, M}(\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) , \quad (3.67)$$

and

$$I_{l_1, l_2}^{L, M}(k_1, k_2) = \int_0^\infty \int_0^\infty F_{l_1}(\eta_1, k_1 r_1) F_{l_2}(\eta_2, k_2 r_2) \psi_{l_1, l_2}^{L, M}(r_1, r_2) dr_1 dr_2 . \quad (3.68)$$

The two-electron momentum distribution follows as

$$P(\mathbf{k}_1, \mathbf{k}_2) = \left| \langle C^{(-)}(\mathbf{k}_1, \mathbf{k}_2) | \Psi \rangle \right|^2 , \quad (3.69)$$

with the normalization condition

$$\frac{1}{2} \int P(\mathbf{k}_1, \mathbf{k}_2) d^3 k_1 d^3 k_2 = 1 . \quad (3.70)$$

The distribution of the magnitudes of momenta is

$$P(k_1, k_2) = k_1^2 k_2^2 \int P(\mathbf{k}_1, \mathbf{k}_2) d\Omega_{k_1} d\Omega_{k_2} . \quad (3.71)$$

Plugging in (3.69) yields

$$P(k_1, k_2) = \frac{8}{\pi^2} \sum_{L, M, l_1, l_2} \left| I_{l_1, l_2}^{L, M}(k_1, k_2) \right|^2 , \quad (3.72)$$

and the energy distribution

$$P(E_1, E_2) = \frac{1}{k_1 k_2} P(k_1, k_2) . \quad (3.73)$$

The total probability of double ionization is then

$$P_{DI} = \frac{1}{2} \int P(k_1, k_2) dk_1 dk_2 . \quad (3.74)$$

3.6.2 Double-ionization cross section

Now we can calculate the single-frequency double-ionization cross section $\sigma_i(\omega)$ from the initial bound state $|i\rangle$. Let $\bar{E}$ denote the mean energy absorbed from the XUV pulse by one

atom due to double ionization, then

$$\frac{d\bar{E}}{d\omega} = \sigma_i(\omega)s(\omega) , \quad (3.75)$$

where $s(\omega)$ is the laser pulse energy per unit area per unit angular frequency.

Thus the total energy absorption for double ionization becomes

$$\begin{aligned} \bar{E} &= \frac{1}{2} \iint \sigma_i s(\omega) d\omega \\ &= \iint \sigma_i \frac{s(\omega(k_1, k_2))}{\pi m} dk_1 dk_2 \\ &= \iint \frac{\partial^2 \sigma_i}{\partial \Omega_1 \partial \Omega_2} \frac{s(\omega(k_1, k_2))}{\pi m} d\Omega_1 d\Omega_2 dk_1 dk_2 , \end{aligned} \quad (3.76)$$

where

$$\omega(k_1, k_2) = \frac{k_1^2 + k_2^2}{2m} + I_0 , \quad (3.77)$$

and the identity $\int \dots d[\pi(k_1^2 + k_2^2)/4] = \int \dots dk_1 dk_2$ is used.

On the other hand, the average energy absorption for each double ionization is

$$\begin{aligned} \bar{E} &= \frac{1}{2} \iint \omega(k_1, k_2) P(\mathbf{k}_1, \mathbf{k}_2) k_1^2 k_2^2 dk_1 dk_2 d\Omega_1 d\Omega_2 \\ &= \frac{1}{2} \iint \omega(k_1, k_2) P(k_1, k_2) dk_1 dk_2 . \end{aligned} \quad (3.78)$$

Comparing to (3.76), the doubly differential cross section is

$$\frac{\partial^2 \sigma_i}{\partial \Omega_1 \partial \Omega_2} = \frac{\pi m \omega}{2s(\omega)} \langle k_1^2 k_2^2 P(\mathbf{k}_1, \mathbf{k}_2) \rangle . \quad (3.79)$$

Here, $\langle \dots \rangle$ means taking the mean value in the quarter circle of the (k_1, k_2) plane, defined by (3.77). The total cross section is

$$\sigma_i(\omega) = \frac{\pi m \omega}{2s(\omega)} \langle P(k_1, k_2) \rangle . \quad (3.80)$$

For an XUV pulse with a narrow energy bandwidth, they simplify to

$$\frac{\partial^2 \sigma_i}{\partial \Omega_1 \partial \Omega_2} \propto \int P(\mathbf{k}_1, \mathbf{k}_2) k_1^2 k_2^2 dk_1 dk_2 \quad (3.81)$$

and

$$\sigma_i(\omega) \propto P_{DI} . \quad (3.82)$$

3.6.3 Joint angular distributions

The joint angular distribution (JAD)⁴² is discussed in detail in¹. Here, it is used mainly as a test to validate our TDSE solver. It is defined as

$$\begin{aligned} P_{JAD}(\hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) &= \int_0^\infty \int_0^\infty P(\mathbf{k}_1, \mathbf{k}_2) k_1^2 k_2^2 \delta(k_1 - k_2 + \Delta k) dk_1 dk_2 \\ &= \frac{8}{\pi^2} \int_0^\infty \int_0^\infty \left| f(k_1, k_2, \hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) \right|^2 \delta(k_1 - k_2 + \Delta k) dk_1 dk_2 \\ &= \frac{8}{\pi^2} \int_0^\infty \left| f(k_1, k_1 + \Delta k, \hat{\mathbf{k}}_1, \hat{\mathbf{k}}_2) \right|^2 dk_1 . \end{aligned} \quad (3.83)$$

The energy sharing between the two electrons is often quantified by the parameter

$$\varepsilon = \frac{\min \{E_1, E_2\}}{E_1 + E_2} \quad (0 < \varepsilon \leq 0.5) . \quad (3.84)$$

On the plane of a fixed azimuthal angle ϕ and for a fixed ε , this function can be shown as a density plot of θ_1 and θ_2 , as shown in Fig. 3.6.

3.6.4 Triply differential cross sections

Similar to the doubly differential cross section (3.81), we can define the triply differential cross section (TDCS)¹ as

$$\frac{\partial^3 \sigma}{\partial E_1 \partial \Omega_1 \partial \Omega_2} = \frac{k_1}{n} \int P(\mathbf{k}_1, \mathbf{k}_2) k_2^2 dk_2 , \quad (3.85)$$

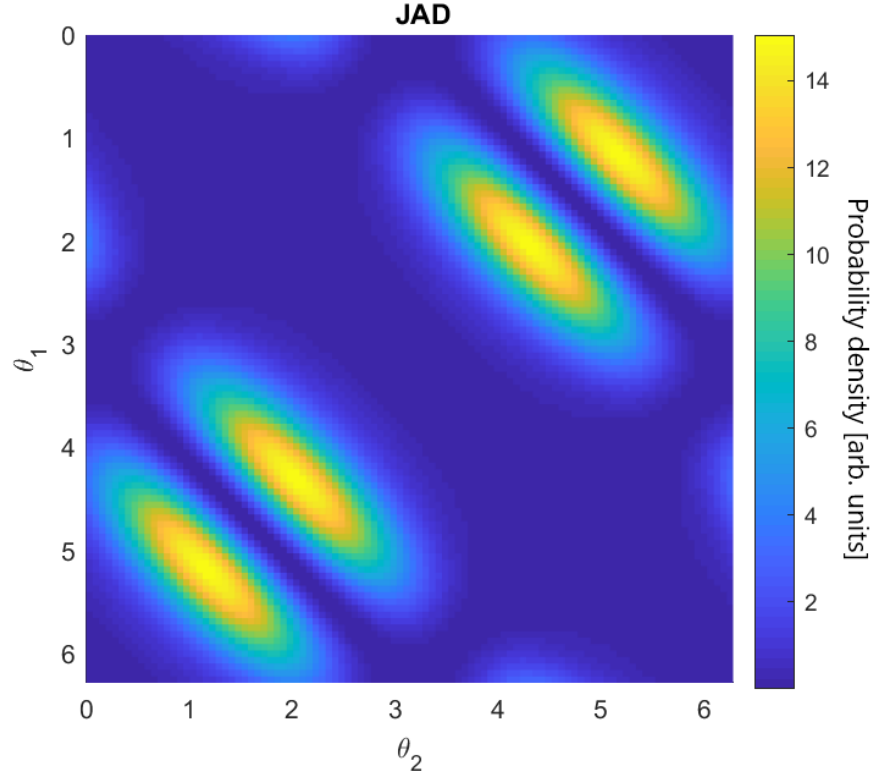


Figure 3.6: *Joint angular momentum with the same parameters as Figure 4.8 (a) of¹: XUV photon energy 90 eV at equal energy sharing. The XUV pulse has a peak intensity of 10^{14} W/cm² and a pulse lengths of 1 fs.*

where n is the photon density.

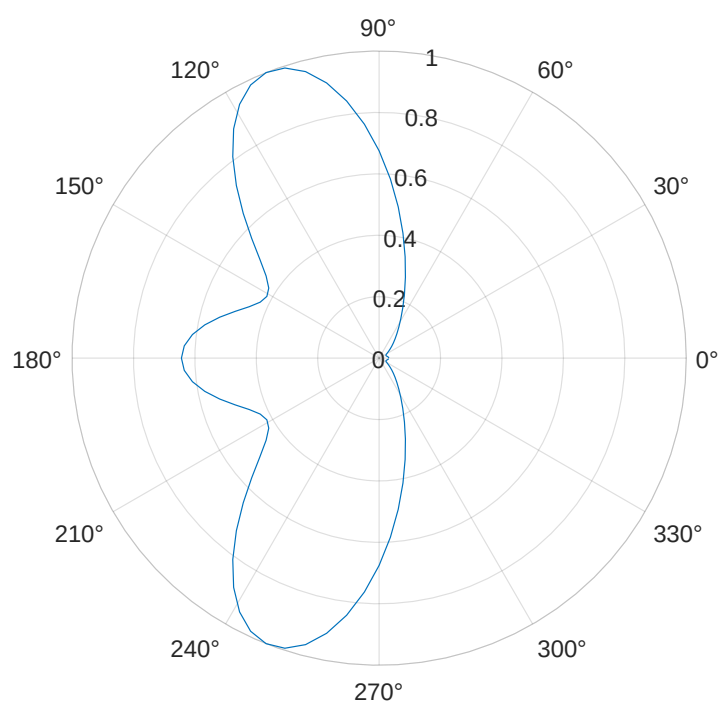


Figure 3.7: *An example triply differential cross section plot for $\epsilon = 0.5$ in arb. units.*

Chapter 4

One- and two-electron *ab initio* streaking simulations

4.1 Streaked photoemission from helium

Following⁴, we assume an IR streaking pulse with a Full-Width Half-Intensity Maximum (FWHM) of 3 fs and a peak intensity of 4×10^{11} W/cm². The XUV pulse has a photon energy of 90 eV, FWHM of 200 as, and peak intensity of 10^{12} W/cm². We use 40 equally spaced XUV-IR-pulse delays for a delay range of 2 IR periods, calculate the center of photoelectron momenta within an infinitely narrow detection cone, and fit to the IR-pulse vector potential to extract the streaking delays according to Eq. (4.1). Figure 4.1 shows our corresponding calculated streaked photoemission spectrum. The streaking traces for the direct and $n = 2$ shake-up emission are clearly separated.

Absolute streaking delays t_s for direct and $n = 2, 3$ shake-up emission extracted from the spectrum in Fig. 4.1 are shown in Fig. 4.2, together with delays for XUV photon energies of 100 and 110 eV. The dependence of t_s on the XUV-pulse photon energy and photoelectron-detection angle for emission is complex, owing to the three distinct terms in Eq. (1.1) and different He⁺ (n, l, m) sub-channels. We therefore separately examine the contributions to t_s in the following subsections. The most prominent feature, a rapid decrease of t_s with

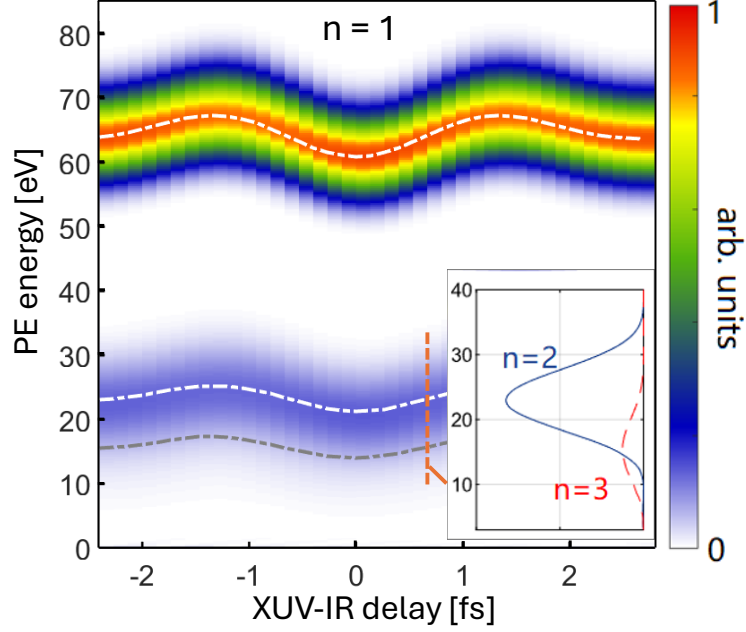


Figure 4.1: Streaked photoemission spectra for ground-state para-helium for a photon energy of 90 eV XUV. The centers of energy for direct ($n = 1$) and $n = 2$ shake-up emission are shown as white dash-dotted lines. The gray dash-dotted line is the center of energy for $n = 3$ shake-up emission. The inset shows line-outs at $\tau = T_{\text{IR}}/4 = 0.6671$ fs of the $n = 2$ and $n = 3$ shake-up emission yields.

photoelectron-detection angle, is primarily due to the $1/\cos\theta$ factor in the DLC term [cf. Eqs. (1.1) and (7.11)].

4.2 Streaked photoemission delays

Absolute and relative streaking time delays

The delay t_{XUV} is not directly measurable with current experimental techniques, but contributes to the observable photoemission delay in streaked photoelectron spectroscopy, where a probe pulse with an adjustable delay relative to the XUV-pump pulse is introduced^{17;19}. The probe pulse, usually in the IR spectral range, maps temporal shifts in the photoemission process to observable shifts in asymptotic photoelectron momenta. Recorded as a function of the pump-probe delay τ , streaked photoelectron spectra allow the extraction of *relative* streaking time delays Δt_s by comparing the temporal offset between energetically separa-

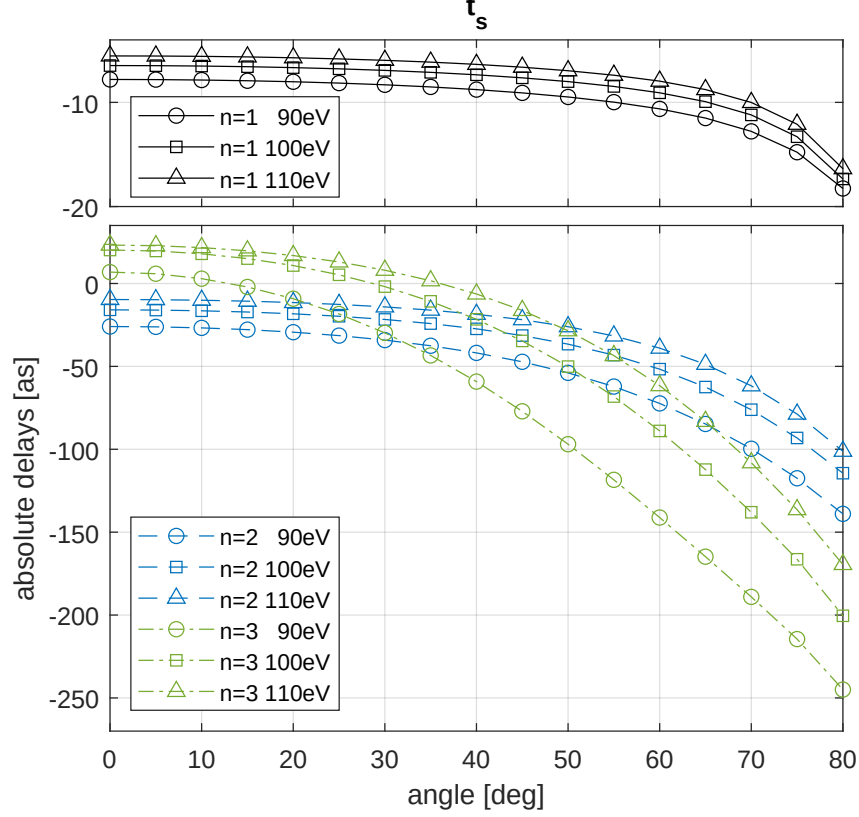


Figure 4.2: *Electron-emission-angle-dependent absolute direct ($n = 1$) and shake-up ($n = 2$) streaking delays t_s for XUV photon energies of 90, 100, and 110 eV.*

ble oscillatory photoemission yields (streaking traces). This method for deriving relative streaked photoemission time delays has been applied to electron emission from different atoms⁴⁸, different initial electronic levels in the same target¹⁰, and to identify temporal shifts between direct and shake-up photoemission⁴. Differences of absolute streaking delays are experimental observables.

Absolute streaking time delays t_s for streaked photoemission from a specific electronic state relate temporal photoemission shifts to the phase of the probe-pulse electric field $\mathcal{E}_{\text{IR}}(t)$. Numerical modeling allows the calculation of absolute delays in two distinct schemes, as either “streaked spectral delays (SSDs)” or “photoelectron wave-packet delays (PWDs)”. We refer to SSDs as delays that are extracted from streaked photoelectron spectra by fitting

the center of momentum of a given streaking trace

$$p_f(\tau) = -aA_{\text{IR}}(\tau + t_s) + b \quad (a, b > 0) \quad (4.1)$$

to the IR vector potential $A_{\text{IR}} = -\int_{-\infty}^t dt' \mathcal{E}_{\text{IR}}(t')$. In contrast, we name delays that are extracted from the wave-packet displacement on a numerical grid using (5.33) and (5.44) in XUV-only ionization as PWDs (cf. Chap. 5). The accuracy of the SSD t_s relies only on the accuracy of the XUV-IR-delay-dependent photoelectron-momentum spectrum and does not require the calculation of phase derivatives. For peak intensities between 10^8 - 10^{12} W/cm², streaking delays and their numerical fitting accuracy are largely independent of the IR-probe-pulse intensity^{3;27}.

In classical particle streaking models, SSD and PWD can still be defined. t_s and t_{XUV} in Eq. (5.34) are SSDs and PWDs, respectively. They are both equal to t_{EWS} and are thus identical for short-range potentials if the photoelectron is assumed to be emitted at time $\tau + t_s$ with a fixed initial momentum and subsequently only affected by the IR field.

However, in reality, the photoelectron also feels the long-range Coulomb force from the residual ionic core. In such cases, SSD and PWD are no longer equal either classically or quantum mechanically. The well-known phase derivative method [cf. Eq. 5.6] only applies to PWD but not SSD. In *ab initio* simulation, the SSD convergence relies only on the convergence of the momentum spectrum for each τ and does not require the calculation of the phase derivatives.

Equation (1.1) tells us that SSD t_s incorporates contributions induced by τ -dependent momentum shifts induced by the probe pulse, in particular the Coulomb- and dipole-laser shifts t_{CLC} and t_{DLC} , in addition to the probe-independent shift t_{EWS} . For direct photoemission, the short-range PWD contribution t_{EWS} to t_{XUV} in Eq. (5.34) merges into t_s when a sufficiently weak delayed IR probe pulse is added. In contrast, the long-range Coulomb delay t_{C} , being sensitive to the phase accumulation along the entire photoelectron trajectory, is affected by the probe-laser field and transformed into the Coulomb-laser-coupling delay t_{CLC} ^{27;49}.

Although t_{CLC} can be roughly seen as t_C “distorted” by the IR field, it is important to note that t_{CLC} is only an SSD while t_C is only a PWD. The convergence of t_{CLC} (with respect to the detector distance) requires only the momentum spectrum for each τ to converge. In contrast, t_C , being only a PWD, depends on the phase derivative. Thus, the fact that t_C does not converge, in contrast to t_{CLC} , is not contradictory, due to their different nature. In contrast, since t_{EWS} is short-range¹ and almost instantaneous, it appears identically in both SSD and PWD.³

We have verified that t_{CLC} depends on the photoelectron-energy and -detection direction. For emission along the XUV- and IR-pulse-polarization direction, it is identical for direct and shake-up ionization. In Chap. 6 below, we show that the CLC delay can be different for hydrogen and helium for large emission angles, i.e., identical for direct and shake-up ionization channels. We note that for peak intensities between $10^8 - 10^{12}$ W/cm², streaking delays and their numerical fitting accuracy are largely independent of the IR-probe-pulse intensity^{3;27}.

For shake-up ionization, the probe-laser pulse causes an additional dipole-laser-coupling temporal shift t_{DLC} ², even if the probe-pulse intensity is kept sufficiently low to make the quasi-static Stark effect in the ground-state-helium entrance channel negligible (as is the case in typical streaking experiments). This delay contribution has no counterpart in t_{XUV} . In the exit channel the probe-laser mixes degenerate and nearly degenerate states of the residual ion, causing the formation of quasi-static He⁺ Stark hybrid states with dipole moment $\mathbf{d}^n(\mathbf{k})$ as linear combinations of excited He⁺ states with opposite parity. The formation of the residual dipole affects the energy of the two-electron system in the probe-laser electric field and, in turn, the final photoelectron-momentum and streaking delay^{2;3;34}.

¹This means that the photoelectron obtains the EWS delay right after its separation from the He⁺ wave function, instead of accumulating the delay on its trajectory out (cf. Section. 5.1).

Chapter 5

XUV only time delays

5.1 XUV-only photoelectron wave-packet delay

We first define what it means to say that two wave packets have a certain relative time delay (PWD). Let $|\mathbf{k}\rangle$ be a complete set of exact single-ionization scattering states of a generic quantum system, with asymptotic momentum $\mathbf{k}$ and energy $E(k) = k^2/2$. The time-dependent field-free evolution of a *reference* wave packet can be described as

$$|\psi_r(t)\rangle \equiv \int C_r(\mathbf{k}) |\mathbf{k}\rangle e^{-iEt} d\mathbf{k} . \quad (5.1)$$

Another wave packet with a constant relative time delay of Δt can then be defined as

$$|\psi(t)\rangle \equiv |\psi_r(t - \Delta t)\rangle = \int C(\mathbf{k}) |\mathbf{k}\rangle e^{-iEt} d\mathbf{k} , \quad (5.2)$$

with

$$C(\mathbf{k}) = e^{iE\Delta t} C_r(\mathbf{k}) . \quad (5.3)$$

This defines the photoelectron wave-packet delay (PWD) Δt . Thus, given $C(\mathbf{k})$ and $C_r(\mathbf{k})$, the relative delay at a given asymptotic momentum is

$$\Delta t(\mathbf{k}) = \frac{\partial}{\partial E}(\arg C - \arg C_r) = \frac{1}{k} \frac{\partial}{\partial k}(\arg C - \arg C_r) . \quad (5.4)$$

We note that we have not imposed any condition on the potential energy $V(\mathbf{r})$ or the shape of the wave function, which means that for any $V(\mathbf{r})$, no matter how irregular the shape and movement of $|\psi_r(t)\rangle$ are, $|\psi(t)\rangle$ will always have a well-defined and constant Δt . On the other hand, if the two wave packets moves in a smooth enough $V(\mathbf{r})$ landscape and are sufficiently localized, then the classical trajectories of their mean positions are related by

$$\mathbf{r}(t) = \mathbf{r}_r(t - \Delta t) . \quad (5.5)$$

If (5.3) is only approximately satisfied within the bandwidth of a wave packet, (5.4) can still be approximately applied. Unless otherwise stated, we choose the reference wave packet with $\arg C_r(\mathbf{k}) \equiv 0$, so that

$$\Delta t(\mathbf{k}) = \frac{\partial}{\partial E} \arg C . \quad (5.6)$$

In the limit that the wave packet bandwidth is infinitesimal, this equation defines the PWD for a single photoelectron energy and emission direction.

In summary, the concept of PWD relates the trajectory delay (5.5) to the energy derivative of phase-shift (5.4). Note that the above derivation does not apply to streaking, where an additional IR field is present.

5.2 Photoelectron wave-packet delays in 1D

We choose a reference wave packet as a free wave packet in 1D

$$\psi_r(x, t) = \int A_r(k) e^{i(kx - Et)} dk , \quad (5.7)$$

where $A_r(k)$ is a real and even function about a center of momentum k_r , then according to the properties of the Fourier transform, $|\psi_r(x, 0)|^2$ is an even wave packet centered at exactly $x = 0$, despite its shape. According to Ehrenfest theorem, the center of wave packet $x_r = \langle \psi_r | x | \psi_r \rangle$ moves with the exact trajectory

$$x_r = k_r t . \quad (5.8)$$

For a 1D particle in a short-range potential $V(x)$ satisfying

$$V(x) = \begin{cases} +\infty & (x < 0) \\ 0 & (x > a) , \end{cases} \quad (5.9)$$

the exact scattering wave (eigenstate of the TISE) has the form

$$\psi_k(x) = \begin{cases} \sqrt{\frac{\pi}{2}} \sin[kx + \delta(k)] & (x > a) \\ 0 & (x < 0) . \end{cases} \quad (5.10)$$

Note that this is a real function corresponding to a standing wave because it is a combination of the incoming and outgoing part of the form $\exp(\pm ikx)$.

Now we use an XUV laser pulse

$$\mathcal{E}(t) = \mathcal{E}_0(t) \sin(\omega t) \quad (5.11)$$

to ionize a bound state $|n\rangle$ of the potential well, where the envelope $\mathcal{E}_0(t)$ is a real and even function. Applying the first-order time-dependent perturbation theorem (TDPT), after the pulse, the photoelectron wave packet will be

$$\psi(x, t) = \int A(k) \psi_k(x) e^{-iEt} dk , \quad (5.12)$$

where

$$A(k) = -i\sqrt{2\pi} \langle \psi_k | x | n \rangle \tilde{\mathcal{E}}(-\omega) \quad (5.13)$$

and $\omega = k^2/2 - E_n$. The Fourier transform of $\mathcal{E}(t)$,

$$\tilde{\mathcal{E}}(\omega) = \frac{1}{\sqrt{2\pi}} \int \mathcal{E}(t) e^{-i\omega t} dt , \quad (5.14)$$

is an odd and pure imaginary function. Since $\langle \psi_k | x | n \rangle$ is a real function, $A(k)$ and $\psi(x, 0)$ are also real functions.

If we split (5.12) into an outgoing and incoming wave packet, the incoming wave packet will vanish, while the outgoing wave reads

$$\psi(x, t) = \frac{1}{2i} \sqrt{\frac{\pi}{2}} \int [e^{i\delta(k)} A(k)] e^{i(kx - Et)} dk \quad (x > a) . \quad (5.15)$$

If we define the reference wave packet as

$$\psi_r(x, t) = \frac{1}{2i} \sqrt{\frac{\pi}{2}} \int A(k) e^{i(kx - Et)} dk , \quad (5.16)$$

then the relative delay from (5.6) is

$$\Delta t(E) = \frac{\partial}{\partial E} \arg e^{i\delta} = \frac{\partial \delta}{\partial E} . \quad (5.17)$$

Note that this is only accurate if the wave packet energy spectrum is narrow enough, so that the variation of $\Delta t(E)$ is negligible within the spectrum. In other words, we require the peak of $A(k)$ to be sharp enough. Using the stationary wave argument, when real-valued $A(k)$ is narrow, the reference wave packet $\psi_r(x, t)$ has the mean position trajectory as

$$x_r = kt , \quad (5.18)$$

and the photoelectron wave packet will have the trajectory

$$x = k(t - \Delta t) . \quad (5.19)$$

5.3 XUV-only delays for hydrogen

We now extend the 1D calculation to more realistic hydrogen ionization, with the same laser pulse (5.11). With the first order time-dependent perturbation theorem, the wave packet can be expanded with the Coulomb plane waves

$$|\psi\rangle = \int A(\mathbf{k}) |C^{(-)}(\mathbf{k})\rangle d^3k , \quad (5.20)$$

with

$$A(k) = -i\sqrt{2\pi} \langle C^{(-)}(\mathbf{k}) | z | n, l, m \rangle \tilde{\mathcal{E}}(-\omega) , \quad (5.21)$$

Using the reference pulse

$$|\psi_r\rangle = \int |A(\mathbf{k})| |C^{(-)}(\mathbf{k})\rangle d^3k , \quad (5.22)$$

the delay of $|\psi\rangle$ relative to $|\psi_r\rangle$ is

$$t_{\text{EWS}}^{\text{H}_{nlm}}(\mathbf{k}) = \frac{\partial}{\partial E} \arg \langle C^{(-)}(\mathbf{k}) | z | n, l, m \rangle = \frac{\partial}{\partial E} \arg \langle C^{(-)}(\mathbf{k}) | \cos \theta | n, l, m \rangle . \quad (5.23)$$

Note that the accuracy of this delay also depends on the sharp-energy-spectrum assumption.

Using (2.125), the matrix element becomes

$$\langle C^{(-)}(\mathbf{k}) | \cos \theta | n, l, m \rangle = \sum_{l', m'} a_{l', m'}^{(-)}(\mathbf{k})^* \langle C_{l', m'}(k) | \cos \theta | n, l, m \rangle , \quad (5.24)$$

where

$$a_{l, m}^{(-)}(\mathbf{k})^* = \frac{i^{-l}}{k} e^{i\sigma_l} Y_{l, m}(\hat{\mathbf{k}}) . \quad (5.25)$$

We can thus see that the energy-dependent Coulomb phase $\sigma_l(k)$ (2.116) is the origin of the EWS delay (5.23).

The angular integral on the right is (2.55), which has the selection rule $l' - l = \pm 1$, and the radial integral is a real number, since the radial parts of $|n, l, m\rangle$ and (2.120) are both real functions. In the simple case of ionization from the hydrogen ground state, only the $l' = 1$ term contributes to the EWS delay, which simplifies to

$$t_{\text{EWS}}^{\text{H}_{100}}(k) = \left. \frac{\partial \sigma_{l=1}}{\partial E} \right|_{E=k^2/2}, \quad (5.26)$$

and is angle independent due to the selection rule.

However, unlike a short-range potential, the reference wave packet (5.22) does not move at a constant velocity, but has a delay that's caused by the long-range phase accumulation of $|C_{l',m'}(k)\rangle$ in the first term of (2.122) due to the Coulomb potential

$$\delta_l = -\eta \ln(2kr) . \quad (5.27)$$

Thus, comparing to another reference wave packet $|\psi_{r0}\rangle$ that moves as $r_c = kt$, there is another r -dependent delay

$$t_{\text{C}}(k, r) = \frac{\partial \delta_l}{\partial E} = \frac{1}{k} \frac{\partial \delta_l}{\partial k} = \frac{1}{k^3} [1 - \ln(2kr)] , \quad (5.28)$$

which does not converge with the detector distance r . To keep the contribution of the EWS delay to the absolute XUV delay (5.34) in perspective, we note that for direct emission by 90 eV XUV pulses the non-convergent Coulomb delay amounts to $t_{\text{C}} = -53.8, -57.0, -59.1$ as at detector distances $r_2 = 0.5, 2, 5$ m, respectively. The negative long-range Coulomb delay thus constitutes an advance that dominates the EWS delay.

Thus the total delay of XUV-only ionization of a hydrogen atom becomes

$$t_{\text{XUV}}^{\text{H}_{nlm}} = t_{\text{EWS}}^{\text{H}_{nlm}} + t_{\text{C}} . \quad (5.29)$$

We note that the terms $t_{\text{XUV}}^{\text{H}_{nlm}}$ and t_{C} are, by definition, PWD only and do not directly contribute to the total SSD (1.1), which converges with the detector distance. The term $t_{\text{EWS}}^{\text{H}_{nlm}}$, however, contributes to both PWD and SSD due to its short range nature.

Since both the Coulomb spherical and plane waves are complete sets, we can apply the perturbation theorem again with the Coulomb spherical wave. The wave packet will be

$$|\psi\rangle = \sum_{l,m} \int B_{l,m}(k) |C_{l,m}(k)\rangle d^3k , \quad (5.30)$$

where

$$B_{l,m}(k) = -i\sqrt{2\pi} \langle C_{l,m}(k) | z | n, l, m \rangle \tilde{\mathcal{E}}(-\omega) , \quad (5.31)$$

is a real function and does not have an energy-dependent phase.

The radial part of the Coulomb spherical wave has the asymptotic form (2.115), which is a real function that combines the incoming and outgoing spherical waves. The reference wave packet ($|j_{l,m}(k)\rangle$ are the Bessel spherical waves)

$$|\psi_{r0}\rangle = \sum_{l,m} \int B_{l,m}(k) |j_{l,m}(k)\rangle d^3k \quad (5.32)$$

moves like $r_c = kt$, the two extra terms in (2.115) and leads to the same delay in (5.29).

If we follow the trajectories of the center of the wave packet, r_c , then for large enough t we will have the asymptotic trajectory

$$r_c(\mathbf{k}, t) = \dot{r}_c(\mathbf{k}, t_\infty) [(t - \tau) - (t_{\text{EWS}}^{\text{H}_{nlm}}(\mathbf{k}) + t_{\text{C}}(k, r_c))] . \quad (5.33)$$

5.4 XUV-only delays for helium

Exposure of helium to just the XUV-pump pulse releases a photoelectron wave packet whose center is displaced relative to a fictitious free electron that starts to move at the atomic nucleus with constant final photoelectron velocity at the instant when the center of the

XUV pulse coincides with the atomic center. This “XUV-pulse-only” photoemission delay,

$$t_{\text{XUV}}(\mathbf{k}) = t_{\text{EWS}}(\mathbf{k}) + t_{\text{C}}(k, r) , \quad (5.34)$$

consists of the EWS delay t_{EWS} and the Coulomb delay

$$t_{\text{C}}(k, r) = \frac{1}{k^3} [1 - \ln(2kr)] . \quad (5.35)$$

The EWS delay corresponds to the phase accumulation during the absorption of XUV radiation and release of the photoelectron^{8;50}. The Coulomb delay accounts for the ongoing phase accumulations of the photoelectron in the long-range $-1/r$ Coulomb potential of the residual He^+ ion. It is identical for all atoms and does not converge as the photoelectron propagates to the detector.

$$P_{\gamma}(\mathbf{r}_2) = 2 \left| \frac{1}{r_2} \psi_{\gamma}(r_2) Y_{l_2, m_2}(\hat{\mathbf{r}}_2) \right|^2 , \quad (5.36)$$

and the radial distribution is

$$P_{\gamma}(r_2) = \int P_{\gamma}(\mathbf{r}_2) r_2^2 d\Omega_2 = 2 |\psi_{\gamma}(r_2)|^2 . \quad (5.37)$$

5.4.1 XUV dipole transitions

In first-order time-dependent perturbation theory, the photoemission yield and photoelectron phase information are calculated based on dipole transition matrix elements. For photoemission by an XUV pulse $\mathcal{E}_{\text{XUV}}(t)$ from the initial helium ground state, $|i\rangle$, into asymptotic spherical waves (3.41) and plane waves with momentum $\mathbf{k}$ (3.42), the dipole-matrix elements are, respectively,

$$M_s = \langle n, l_1, m, l_2, k | (z_1 + z_2) | i \rangle , \quad (5.38)$$

$$M_p = \langle n, l, m, \mathbf{k} | (z_1 + z_2) | i \rangle$$

and depend on the energy-dependent phase δ_n^{λ} .

For single-photon ionization from the helium ground state, dipole selection rules restrict accessible final-state quantum numbers to $L = 1$, $M = m_1 + m_2 = 0$ and odd $l_1 + l_2$. Thus, for direct ionization, the only accessible final configuration is $(n, l_1, m, l_2) = (1, 0, 0, 1)$. In contrast, for $n = 2$ shake-up ionization, the five channels $(2, 0, 0, 1)$, $(2, 1, 0, 0)$, $(2, 1, 0, 2)$, $(2, 1, \pm 1, 2)$ can be reached. Similarly, $n = 3$ shake-up ionization allows the 13 final configurations $(3, 0, 0, 1)$, $(3, 1, 0, 0)$, $(3, 1, 0, 2)$, $(3, 1, \pm 1, 2)$, $(3, 2, 0, 1)$, $(3, 2, \pm 1, 1)$, $(3, 2, 0, 3)$, $(3, 2, \pm 1, 3)$, $(3, 2, \pm 2, 3)$. In general, the number of dipole-accessible final channels is $2n(n - 1) + 1$.

5.4.2 The Eisenbud-Wigner-Smith (EWS) delay

The EWS delay carries element-specific information on the electronic correlation dynamics during the photo-release. It can be interpreted as the group delay experiences by the photoelectron wave packet relative to a hypothetical reference wave packet [19;25;50](#). It excludes the long-range Coulomb delay t_C and can be calculated numerically as the energy derivative of the phase of the dipole-matrix element for entangled spherical-partial-wave and plane-wave final photoelectron states, respectively,

$$\begin{aligned} t_{\text{EWS}}^{n,l_1,m,l_2}(k) &= \frac{\partial}{\partial E} \arg M_s , \\ t_{\text{EWS}}^{n,l,m}(\mathbf{k}) &= \frac{\partial}{\partial E} \arg M_p . \end{aligned} \tag{5.39}$$

As a measure for the net delay for direct or shake-up ionization to a specific He^+ sub-shell, we define the weighted average of Eq. [\(5.39\)](#):

$$t_{\text{EWS}}^{n,l}(\mathbf{k}) = \frac{\sum_m |M_p|^2 t_{\text{EWS}}^{n,l,m}(\mathbf{k})}{\sum_m |M_p|^2} . \tag{5.40}$$

Similarly, we average over $\{l, m\}$ to define $t_{\text{EWS}}^n(\mathbf{k})$. Since the $|n, l, m, \mathbf{k}\rangle$ basis is orthonormal, photoelectron wave packets from different sub-shell do no interfere.

Instead of calculating matrix elements that yield the delays in first-order perturbation theory [cf. Eq. [\(5.39\)](#)], we can retrieve *absolute* delays for ionization by the XUV-pulse

directly from the (non-perturbative) two-electron wave function (3.10), based on the numerically calculated radial partial-wave functions $\psi_\lambda(r_1, r_2, t)$. This approach is particularly well suited for our applications in this thesis, which are based on the numerical propagation of partial-wave functions (cf. Chap. 3). Projection of the numerically propagated wave function (3.10) on residual hydrogenic He^+ states $\phi_{n,l,m}^{(Z=2)}(\mathbf{r})$, provides the photoelectron probability density for direct ($n = 1$) and shake-up ($n > 1$) ionization $\phi_{n,l,m}^{(Z=2)}(\mathbf{r})$,

$$P_{n,l,m}(\mathbf{r}, t) = 2 \left| \int \phi_{n,l,m}^{(Z=2)}(\mathbf{r}') \Psi(\mathbf{r}', \mathbf{r}, t) (r')^2 d\Omega' dr' \right|^2, \quad (5.41)$$

where the factor of 2 is due to symmetrization of $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ (cf., Section 3.5.6).

Assuming photoelectrons are detected within the detector solid angle Ω_{det} centered around the direction $\hat{\mathbf{k}}$, the mean photoelectron distances from the atomic nucleus are now given by integrating Ω over Ω_{det} as

$$r_c^{n,l}(\mathbf{k}, t) = \frac{\sum_m \int_{\Omega_{\text{det}}} r P_{n,l,m}(\mathbf{r}, t) r^2 d\Omega dr}{\sum_m \int_{\Omega_{\text{det}}} P_{n,l}(\mathbf{r}, t) r^2 d\Omega dr}. \quad (5.42)$$

Similarly, we average over $\{l, m\}$ to define

$$r_c^n(\mathbf{k}, t) = \frac{\sum_{l,m} \int_{\Omega_{\text{det}}} r P_{n,l,m}(\mathbf{r}, t) r^2 d\Omega dr}{\sum_{l,m} \int_{\Omega_{\text{det}}} P_{n,l}(\mathbf{r}, t) r^2 d\Omega dr}. \quad (5.43)$$

Omitting the integration over Ω corresponds to an infinitely high photoelectron-detection resolution. Fitting the averaged radial photoelectron displacements at times after which

- the photoelectron wave packet has separated from the charge distribution of the residual ion and
- the photoelectron velocity $\dot{r}_c^\alpha(\mathbf{k}, t)$ has converged to the asymptotic velocity $\dot{r}_c^\alpha(\mathbf{k}, t_\infty)$ within a preset tolerance

according to

$$r_c^\alpha(\mathbf{k}, t) = \dot{r}_c^\alpha(\mathbf{k}, t_\infty)[(t - \tau) - (t_{\text{EWS}}^\alpha(\mathbf{k}) + t_c(k_f, r_c))], \quad (5.44)$$

$$\alpha = \{n, l, m\}, \{n, l\}, n,$$

we find the EWS delays t_{EWS}^α relative to the center of the XUV-pulse electric field.

5.4.3 XUV-only delays from TDSE

Figure 5.1 shows the EWS time delay, t_{EWS} , extracted from the photoelectron wave packet according to Eqs. (5.42) and (5.44), for direct ionization ($n = 1$) and all (n, l) shake-up sub-channels of the ionic L and M shells. These results were calculated for emission along the XUV-pulse polarization and XUV photon energies of 90, 100, 110, and 120 eV. Lines in between the small markers are added to guide the eye. For direct (black line) and $2s$ shake-up (red dashed line) our results in Fig. 5.1 (a) agree with the phase-derivative calculation of Pazourek *et al.*² according to Eqs. (5.39) and (5.40). For shake-up emission to He^+ ($2p$) our results still agree with Ref.² with attosecond accuracy and show small discrepancies only at the sub-attosecond level. Generally, in the absence of resonances, EWS delays tend to decrease in absolute value for increasing XUV photon energy, due to the decreasing time left for strong photoelectron interactions. This trend is followed for direct, $2p$ -, and $3p$ -shake-up emission. At the sub-attosecond time scale, the onset for this expected decrease is not reached for $2s$ -shake-up emission for XUV photon energy up to 120 eV.

Figure 5.2 extends the sub-shell-resolved EWS delays, shown in Fig. 5.1 for emission along the XUV-polarization axis, to arbitrary photoelectron-detection directions for XUV photon energies of 90, 100, and 110 eV. For $3p$ and $3d$ shake-up emission, this graph clearly shows the expected decrease in magnitude of the EWS delay for increasing XUV photon energy and a more pronounced dependence on the photoelectron-detection direction in comparison to $2p$ shake-up emission. Noticeable are also the general increase of the delay magnitude with the principal and angular momentum quantum numbers of the residual shake-up He^+ shake-up state, in compliance with the larger extent of the residual charge distributions. The delays for $1s$, $2s$, $3s$ shake-up emission are angle-independent, shown in Fig. 5.1, and are not

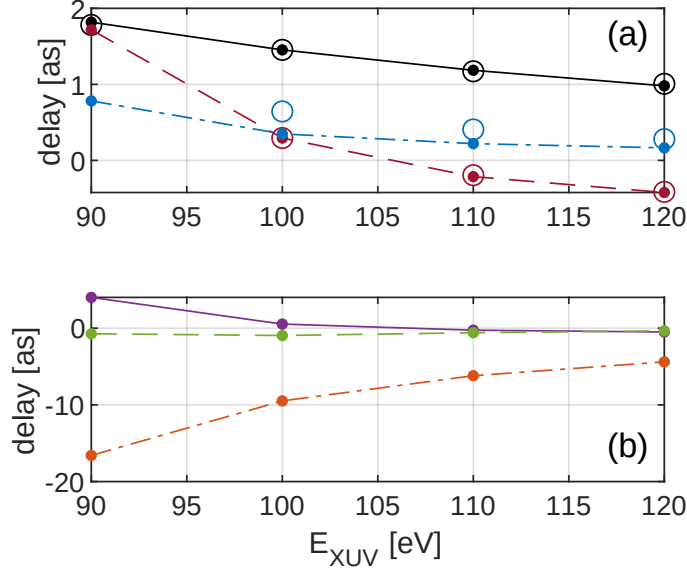


Figure 5.1: Absolute (n, l) sub-channel-resolved EWS delays t_{EWS} for emission along the XUV-polarization direction and XUV-photon energies of 90, 100, 110, and 120 eV. (a) Direct (black line), He^+ (2s) (red dashed line), and He^+ (2p) (blue dash-dotted line) shake-up emission. Open circles show corresponding numerical results of Pazourek et al.² (b) 3s (purple line), 3p (green dashed line), and 3d (orange dash-dotted line) shake-up emission.

uplicated in this graph.

Averaging the EWS photoemission delays for $n = 2$ and 3 according to Eqs. (5.43) and (5.44) results in the emission-angle-dependent absolute sub-shell averaged delays displayed in Fig. 5.3, in addition to the angle-independent delays for direct XUV photoemission. The angular dependence is most pronounced for shake-up emission at the lowest XUV photon energy (90 eV). In comparison with the sub-shell-resolved delays in Fig. 5.2, the angular dependence of the sub-shell-averaged delays in Fig. 5.3 tends to follow more closely the 3p than the 3d delays. The less uniform angle dependence of the sub-shell-averaged delays for different photon energies, in particular, the crossing of $n = 3$ delays in Fig. 5.3, is a result of the sub-shell and XUV-photon-energy- and angle-dependent emission probabilities $P_{n,l,m}(\mathbf{r}_2, t)$ employed as weights in Eq. (5.43).

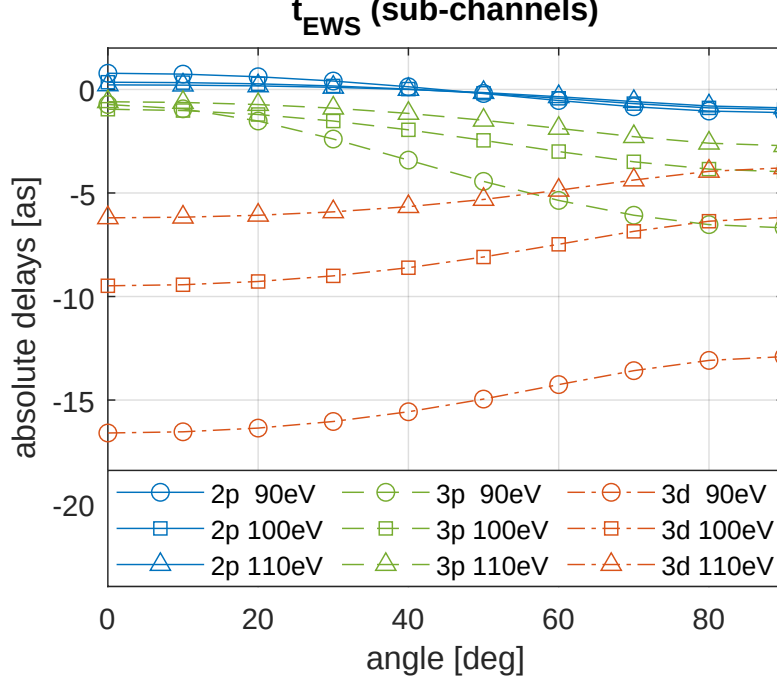


Figure 5.2: *Electron-emission-angle-dependent absolute EWS delays t_{EWS} for XUV photon energies of 90, 100, and 110 eV and specific He^+ (n, l) shake-up sub-shells.*

5.5 Residual multipole analysis

To investigate the role of photoelectron-ion interaction in the XUV-only setting, we use a more intuitive way to calculate the time-dependent electric dipole moment in this subsection.

During photoemission, the electronic probability density of the residual He^+ ion keeps evolving while interacting with the photoelectron. A sufficiently long time after the photo-release by the XUV pulse, the photoelectron wave-function overlap with the charge distribution of the residual electron is small enough for the conditional electronic probability density,

$$P^{\text{He}^+}(\mathbf{r}, t) = \frac{|\Psi(\mathbf{r}, \mathbf{r}_{\text{PE}}, t)|^2}{\int |\Psi(\mathbf{r}', \mathbf{r}_{\text{PE}}, t)|^2 d^3r'} , \quad (5.45)$$

to be associated with the residual ion's electronic charge density, where the photoelectron is assumed as a classical particle located at the maximum of the photoelectron wave-packet probability, $\mathbf{r}_{\text{PE}}$.

The multipole expansion of the electronic potential energy V^{He^+} corresponding to the

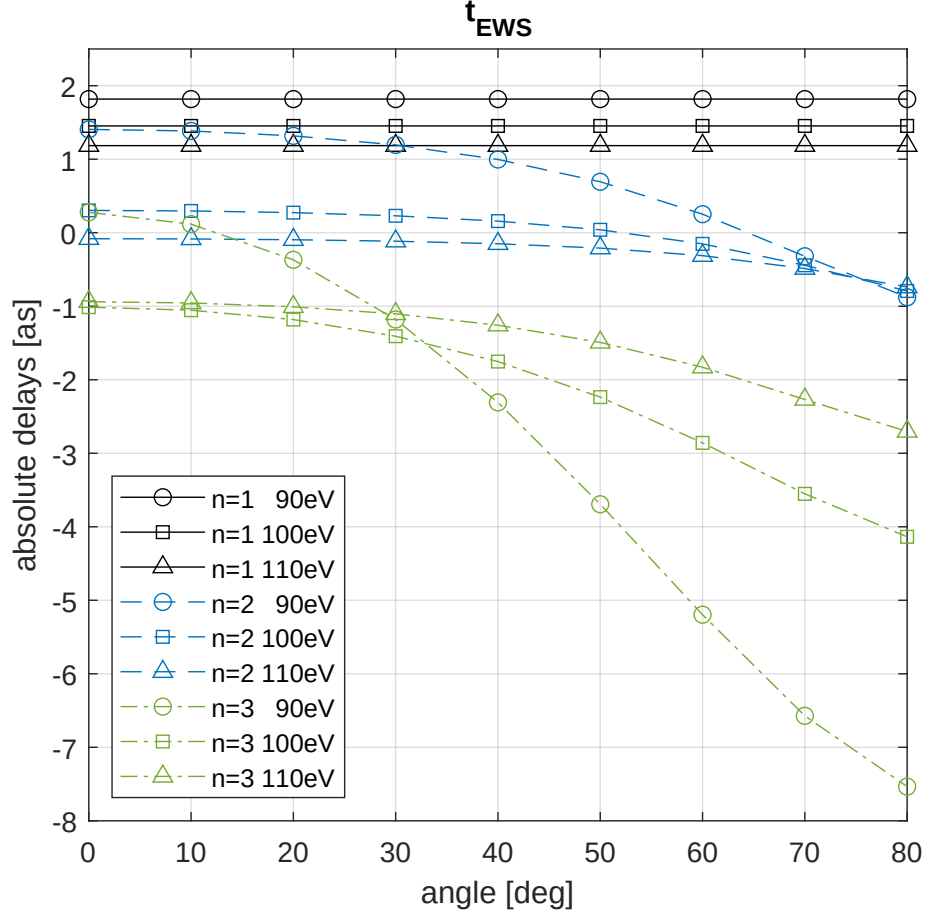


Figure 5.3: *Electron-emission-angle-dependent absolute EWS delays t_{EWS} for direct ($n = 1$) and $n = 2, 3$ shake-up emission for XUV photon energies of 90, 100, and 110 eV. The shake-up delays are averaged over (l, m) sub shells according to Eq. (5.43).*

charge density P^{He^+} , assumed to be confirmed within a volume of radius $a < r_{\text{PE}}$, results in

$$V^{\text{He}^+}(\mathbf{r}, t) = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{1}{r^{l+1}} C_{l,m}(t) Y_{l,m}(\hat{\mathbf{r}}) \quad (r > a) , \quad (5.46)$$

$$C_{l,m}(t) = \frac{-4\pi}{(2l+1)} \int_{r \leq a} r^l Y_{l,m}^*(\hat{\mathbf{r}}) P^{\text{He}^+}(\mathbf{r}, t) d^3r . \quad (5.47)$$

Using individual terms of this expansion as effective potentials in separate SAE calculations allows the quantitative comparison of the effects of given multipole orders on photoelectron spectra and streaking time delays. Performing such simplified one-electron calculations for the parameters of the present work, we found dominant monopole and dipole interactions,

while quadrupole and higher multipole orders are negligible.

A few snapshots of the residual charge-density evolution are shown in Fig. 5.4 for the ionization of para-helium in 90 eV, 10^{12} W/cm² XUV pulses with a FWHM of 200 as (no IR pulse is present). We assumed emission along the XUV-polarization direction (more specifically, the $+z$ axis), such that only multipole terms with $m = 0$ are present. The color-coded graphs show residual charge distributions $P^{\text{He}^+}(\mathbf{r}, t)$ for increasing classical photoelectron distances r_{PE} from the atomic nucleus. Residual probability densities for direct and shake-up emission are displayed in Figs. 5.4 (a) and (c), respectively. The corresponding coefficients $C_{1,0}(t)$ of the dipole term in the multipole expansion (5.46) for direct and shake-up emission are shown in Figs. 5.4 (c) and (d), respectively.

The oscillation period of the contribution for direct emission in Fig. 5.4 (b) is about 88 as, corresponding to an energy of 47 eV, close to the energy difference between the undistorted K and L shells of He^+ , 40.8 eV. We therefore attribute these small-amplitude oscillations to weak quantum beats of the He^+ ground state against transiently populated $n = 2$ levels. The rapid decay of these beats as the photoelectron moves away from the residual ion illustrates the noticeable presence of electronic entanglement, even for direct emission and photoelectron distances way outside the residual charge distribution.

For shake-up ionization, the composition and evolution of the residual charge cloud are more complex than for direct emission [Fig. 5.4 (d)]. Now, the dipole term starts oscillating with a period of about 120 as (35 eV). 0.7 fs after the ionization, the oscillation period changes to 530 as (7.8 eV). These two quantum-beat frequencies are close to undistorted K- to L-shell and L- to M-shell excitation energies of He^+ , respectively. As expected, the oscillation amplitude for shake-up emission in Fig. 5.4 (d) is significantly larger than for direct emission in Fig. 5.4 (b). In addition, the oscillations for shake-up ionization persist long after those for direct emission have decayed. These findings are in agreement with an intuitively expected stronger correlation of the photoelectron with electronically excited He^+ .

This analysis gives us an intuitive physical picture of the photoelectron - ion interaction. However, the classical trajectory and single-active-electron (SAE) simulations we performed

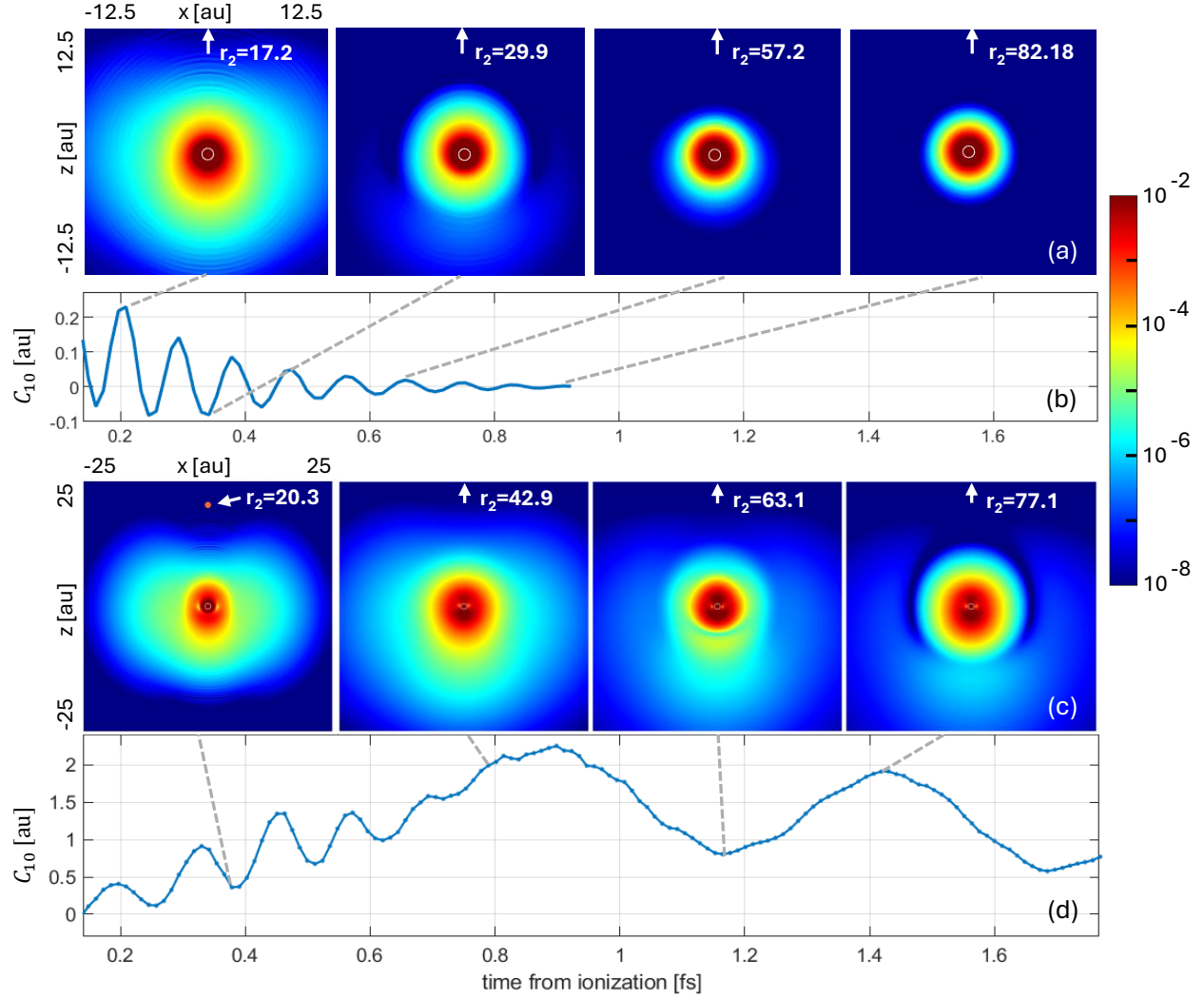


Figure 5.4: Evolution of the residual He^+ electronic charge distribution after photoionization of helium by 90 eV, 10^{12} W/cm^2 XUV pulses with a FWHM of 200 as for (a) direct and (c) shake-up emission. (b) and (d): Corresponding dipole coefficients $C_{1,0}(t)$ in the multipole expansion of the residual-ion potential energy [Eq. (5.46)]. The distance from the nucleus of the (assumed classical) photoelectron, r_{PE} , is given in au and pointed to by white arrows.

based on this model do not agree and do not provide a comprehensive physical interpretation for the EWS delays in Fig. 5.3. We thus argue that a large part of the EWS delay is due to electronic entanglement before the separation of the photoelectron wave packet from the ionic core, which has no classical representation.

Chapter 6

Coulomb laser coupling (CLC) delay

6.0.1 CLC delays for hydrogen

For short range delays, adding the IR probe field results in an SSD that is the same as the PWD, e.g. the t_{EWS} delay for both hydrogen and helium. However, this identity breaks down when the long-range Coulomb potential of the residual ion brings some side-effects to the streaking spectra, adding the CLC and DLC correction terms in this and the next chapter.

We note that the CLC and DLC terms are both SSD-only and do not have direct counterparts in PWD. It might be tempting to think that after the IR field has ended, we can still plot the wave packet trajectories and extract their PWD delays, but these delays are irrelevant to this thesis and have not been measured experimentally to our knowledge.

The CLC delay is largely a classical and long-range effect and is found to agree within ~ 1 as for quantum and classical-trajectory Monte Carlo calculations³. For emission along the XUV- and IR-pulse-polarization directions it does not noticeably depend on the target electronic structure and is approximately identical for hydrogen and helium². We assume its long-range classical behavior to apply for any final photoelectron-momentum direction $\hat{\mathbf{k}}$ (i.e., for any photoelectron detection angle θ) and calculate it *ab initio*, following Refs.^{2,3}, according to

$$t_{\text{CLC}}(\mathbf{k}) = t_{\text{s}}^{\text{H}_{100}}(\mathbf{k}) - t_{\text{EWS}}^{\text{H}_{100}}(k) , \quad (6.1)$$

based on $t_s^{\text{H}_{100}}(\mathbf{k})$ defined in (5.26).

Figure 6.1 shows the CLC delay for hydrogen as a function of the photoelectron-detection angle for the final photoelectron energies between 17.03 and 85.41 eV, as given by Eq. (6.1). As expected, $|t_{\text{CLC}}|$ decreases with increasing XUV photon energy (or asymptotic photoelectron kinetic energy) since faster photoelectrons leave the Coulomb potential tail faster.

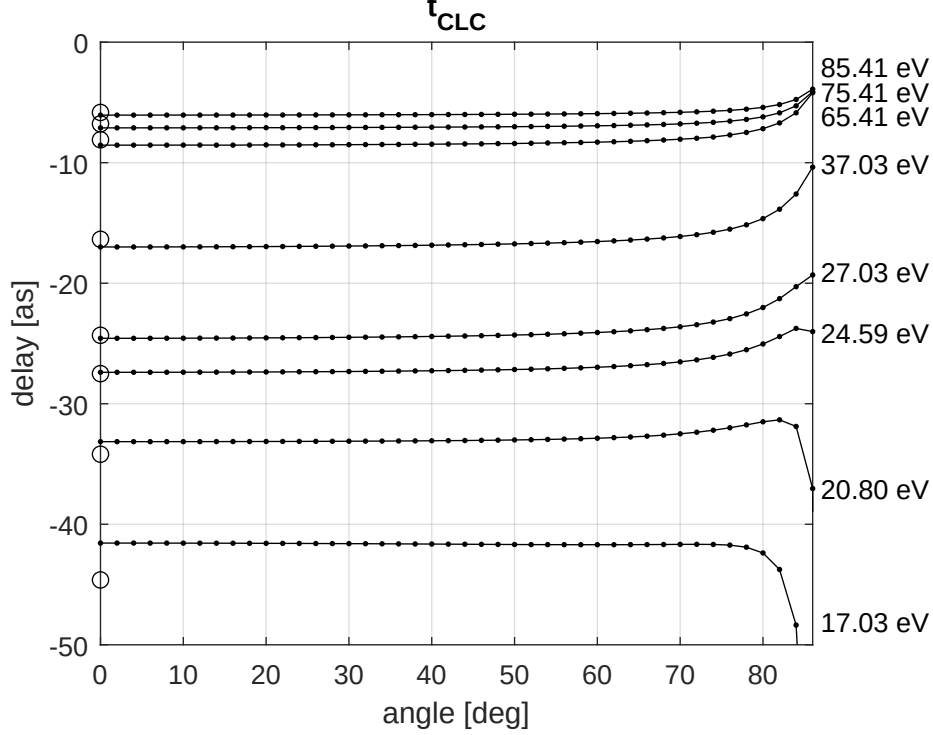


Figure 6.1: *CLC delays for hydrogen as functions of the photoelectron-detection direction for final photoelectron energies between 17.03 and 85.41 eV (dots). Circles show delays calculated in Ref. ³ for photoemission along the XUV- and IR-pulse-polarization direction.*

6.0.2 Classical trajectory CLC calculation

To investigate the angular dependence for photoelectron emission at large angles in Fig. 6.1, we extended the classical calculation for emission along the XUV-pulse-polarization direction in Ref. ³ and performed an angle-resolved classical-trajectory simulation. We assume instant absorption of a single XUV photon with energy E_{XUV} to provide photoelectrons at aligned

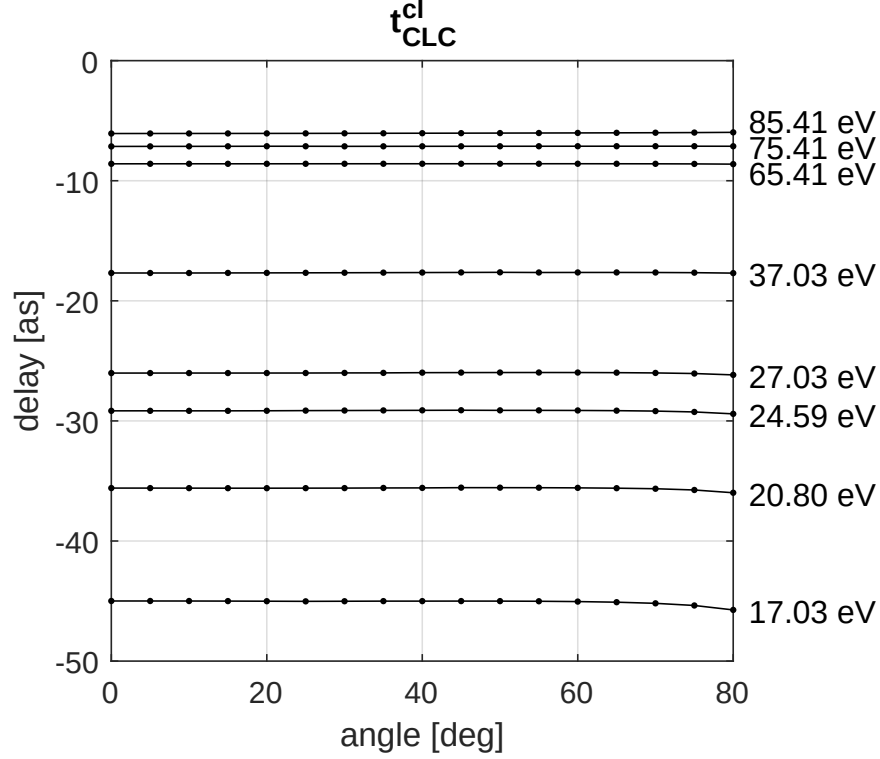


Figure 6.2: *Classical CLC delay, with the same parameters as in Fig. 6.1.*

initial positions and momenta, $\mathbf{k}_0 \propto \mathbf{r}_0$, with total energy

$$E_{\text{PE}} = E_{\text{XUV}} + E_{100}^{(Z)} = \frac{\mathbf{k}_0^2}{2} - \frac{Z}{r_0}, \quad (6.2)$$

where $E_{100}^{(Z)}$ is the ground-state energy of a hydrogen-like atom. Without the IR field, this energy is conserved, resulting in a final kinetic energy of $E_{\text{PE}} = \mathbf{k}_f^2/2$. Note that for a given k_f , this equation gives k_0 as a function of r_0 .

After applying the same IR field that we use for helium streaking with different XUV-IR delays, we can calculate the classical hydrogen streaking trace and extract the classical streaking delay $t_s^{\text{H}_{100}, \text{cl}}$ for the detector direction $\hat{\mathbf{k}}_f$.

For our parameters, $t_{\text{CLC}}^{\text{cl}}$ is sensitive to $\mathbf{r}_0$ (resulting in a few attoseconds of variation). We determine $r_0 = 0.55$ au, such that the classically calculated CLC delay, $t_{\text{CLC}}^{\text{cl}}$, largely matches the results in Fig. 6.1 at zero degrees, and apply this value to all energies considered in this figure.

To obtain the classical streaking trace for each fixed $\hat{\mathbf{k}}_f$, for each given τ , determining the correct classical trajectory becomes the well-known boundary value problem when solving the ordinary differential equation numerically, and the direction $\hat{\mathbf{r}}_0$ in the x - z plane can be determined by the shooting method. Note that although the angle between $\hat{\mathbf{k}}_0$ and $\hat{\mathbf{k}}_f$ is very small (below $\sim 1^\circ$), we cannot assume that $\hat{\mathbf{k}}_f = \hat{\mathbf{k}}_0$ since it would lead to a large relative error for $t_{\text{CLC}}^{\text{cl}}$. The shooting method plays a key role in the classical CLC delay calculation.

Propagating classical photoelectron trajectories starting at $(\mathbf{r}_0, \mathbf{k}_0)$ in the IR field for a range of XUV–IR pulse delays τ , we obtain the τ -dependent asymptotic photoelectron momenta, that is, the classical streaking traces, from which we extract the classical streaking delay $t_s^{\text{H}_{100}, \text{cl}}$. Substitution into Eq. (6.1) now yields delays $t_{\text{CLC}}^{\text{cl}}$ that are *independent* of the photoelectron detection direction, suggesting that the angle dependence of t_{CLC} in Fig. 6.1 is a quantum-mechanical effect.

Chapter 7

Dipole - laser coupling delay

During single ionization in the streaking process, exposure of the residual He^+ dipole to the electric field of the IR streaking pulse results in an energy shift that affects the entangled photoelectron-residual-ion system and results in the DLC contribution t_{DLC} to the streaking delay in Eq. (1.1). The effect of t_{DLC} on photoelectron emission along the XUV-polarization direction has been discussed in². In this chapter, we examine $t_{\text{DLC}}(\mathbf{k})$ for arbitrary photoelectron detection directions $\hat{\mathbf{k}}$.

7.1 Entangled residual Stark states

To describe the formation of quasi-static residual Stark states during shake-up ionization, we unitarily transform the scattering states $|n, l, m, \mathbf{k}\rangle$ (3.42) to Stark scattering states with the same (n, m) quantum numbers and total energy $-Z^2/n^2 + k^2/2$,

$$|n, \alpha, m, \mathbf{k}\rangle = \sum_l C_{\alpha, l}^{n, m} |n, l, m, \mathbf{k}\rangle , \quad (7.1)$$

where α denotes the Stark quantum numbers³⁸. Technically, both $|n, \alpha, m, \mathbf{k}\rangle$ and $|n, l, m, \mathbf{k}\rangle$ are exact scattering states (3.43) and are used as single continuum bases to expand the wave function in single-ionization channels. However, in this section, they can also be approximated with the product states of the ionic bound states and the Coulomb plane waves (2.125)

provided the wave function propagation time is long enough to make the results converge.

The unitary transform matrices $\{C_{\alpha,l}^{n,m}\}$ for the $n = 2, 3$ shells of He^+ are listed in Tabs. 7.1. They can be calculated by diagonalizing z in each degenerate subspace spanned by all states $\{|n, l, m\rangle\}$ for fixed n, m ³⁸. The subspaces with $n = 2, m = \pm 1$ and $n = 3, m = \pm 2$ are non-degenerate and have zero polarization with the Stark quantum number $\alpha = 0$. We note that in general, the values in the table scale with $1/Z$.

Table 7.1: *Stark states for $n = 2, m = 0$*

$d_z^{(n,\alpha,m)}$	$ n, l, m\rangle$	$ 2, 0, 0\rangle$	$ 2, 1, 0\rangle$
	$ n, \alpha, m\rangle$		
$3/2$	$ 2, 1, 0\rangle$	$1/\sqrt{2}$	$1/\sqrt{2}$
$-3/2$	$ 2, -1, 0\rangle$	$1/\sqrt{2}$	$-1/\sqrt{2}$

Table 7.2: *Stark states for $n = 3, m = 0$*

$d_z^{(n,\alpha,m)}$	$ n, l, m\rangle$	$ 3, 0, 0\rangle$	$ 3, 1, 0\rangle$	$ 3, 2, 0\rangle$
	$ n, \alpha, m\rangle$			
$9/2$	$ 3, 1, 0\rangle$	$1/\sqrt{3}$	$1/\sqrt{2}$	$1/\sqrt{6}$
0	$ 3, 0, 0\rangle$	$1/\sqrt{3}$	0	$-\sqrt{2/3}$
$-9/2$	$ 3, -1, 0\rangle$	$1/\sqrt{3}$	$-1/\sqrt{2}$	$1/\sqrt{6}$

Table 7.3: *Stark states for $n = 3, m = \pm 1$*

$d_z^{(n,\alpha,m)}$	$ n, l, m\rangle$	$ 3, 1, \pm 1\rangle$	$ 3, 2, \pm 1\rangle$
	$ n, \alpha, m\rangle$		
$9/4$	$ 3, 1, \pm 1\rangle$	$1/\sqrt{2}$	$1/\sqrt{2}$
$-9/4$	$ 3, -1, \pm 1\rangle$	$1/\sqrt{2}$	$-1/\sqrt{2}$

The He^+ electric dipole moment eigenvalues of the Stark bases are oriented along the

polarization direction (always along z axes),

$$\mathbf{d}^{(n,\alpha,m)} = -\langle n, \alpha, m | z | n, \alpha, m \rangle \hat{\mathbf{z}} . \quad (7.2)$$

After shake-up ionization by the XUV pulse, assuming $|\Psi(t^*)\rangle$ as the helium wave function after the pulse has vanished, we define the projection coefficients

$$c_{n,\alpha,m}(\mathbf{k}) = \langle n, \alpha, m, \mathbf{k} | \Psi(t^*) \rangle . \quad (7.3)$$

Further, we represent the asymptotic (photoelectron far away) residual He^+ ion wave function with fixed $n, \mathbf{k}$ will be a superposition of degenerate Stark states

$$|\psi_{\text{He}^+}^{(n)}(\mathbf{k})\rangle = e^{-i\frac{k^2}{2}(t-t^*)} \mathcal{N} \sum_{\alpha,m} c_{n,\alpha,m}(\mathbf{k}) |n, \alpha, m\rangle , \quad (7.4)$$

with the normalization constant $\mathcal{N} = (\sum_{\alpha,m} |c_{n,\alpha,m}|^2)^{-1/2}$. Note that both $c_{n,\alpha,m}(\mathbf{k})$ and $|\psi_{\text{He}^+}^{(n)}(\mathbf{k})\rangle$ depend on t or t^* only up to a phase factor.

For photoemission along the XUV-pulse-polarization direction ($\hat{\mathbf{k}} = \hat{\mathbf{z}}$), only $m = 0$ terms contribute in Eq. (7.4). Thus, $|\psi_{\text{He}^+}^{(n)}(\mathbf{k})\rangle$ is rotationally symmetrical about the z axis and its dipole moment,

$$\mathbf{d}^{(n)}(\mathbf{k}) = -\langle \psi_{\text{He}^+}^{(n)}(\mathbf{k}) | \mathbf{r} | \psi_{\text{He}^+}^{(n)}(\mathbf{k}) \rangle , \quad (7.5)$$

aligned with $\hat{\mathbf{k}}$. In contrast, for photoelectron-detection directions $\hat{\mathbf{k}}$ that are not aligned with $\hat{\mathbf{z}}$, the combination of terms with $m \neq 0$ results in electric dipole vectors (7.5) that generally do not align with $\hat{\mathbf{z}}$. In this thesis, only the z -component of this dipole is needed, which simplifies to

$$\begin{aligned} d_z^{(n)}(\mathbf{k}) &= -\langle \psi_{\text{He}^+}^{(n)}(\mathbf{k}) | z | \psi_{\text{He}^+}^{(n)}(\mathbf{k}) \rangle , \\ &= \mathcal{N}^2 \sum_{\alpha,m} |c_{n,\alpha,m}(\mathbf{k})|^2 d_z^{(n,\alpha,m)} . \end{aligned} \quad (7.6)$$

In XUV-only single ionization, due to energy conservation, all sub-channel wave packets with the same n have approximately the same center of momentum, despite the different EWS

time delays they might have.

7.2 The angle resolved DLC model

In streaking, a sufficiently weak, quasi-static IR-streaking electric field does not noticeably distort the electronic structure of the initial He atom and residual ion. We assume that the above perturbation theory yields approximately the same coefficients in (7.3), and the above energy conservation still holds. The interaction of the IR with the XUV-pulse-generated dipole yields the momentum shift for the photoelectron for each (n, α, m) sub-channel

$$\Delta k^{(n, \alpha, m)} \approx \frac{-\Delta E_1^{(n, \alpha, m)}}{k} = \frac{d_{n, \alpha, m} \mathcal{E}_{\text{IR}}(\tau)}{k} = -\frac{d_{n, \alpha, m}}{k} \frac{dA_{\text{IR}}}{d\tau}, \quad (7.7)$$

where $k = \sqrt{2(\omega_{\text{XUV}} - I_p)}$ is the classical XUV-only final photoelectron momentum, and applies for ionization in any photoemission direction $\hat{\mathbf{k}}$.

Since photoelectron wave packets from each sub-channel do not interfere, the combined n channel's photoelectron momentum shift is the probability-weighted average

$$\Delta k^{(n)}(\mathbf{k}) = \mathcal{N}^2 \sum_{\alpha, m} |c_{n, \alpha, m}(\mathbf{k})|^2 \Delta k^{(n, \alpha, m)} = \frac{\mathcal{E}_{\text{IR}}}{k} d_z^{(n)}(\mathbf{k}). \quad (7.8)$$

At large photoelectron – He⁺ distances, the photoelectron has accumulated the EWS phase shift, and the photoelectron-momentum shift in the oscillating IR field can be approximated as³,

$$\mathbf{k}_f(\tau) \approx (k + \Delta k^{(n)})\hat{\mathbf{k}} - \mathbf{A}_{\text{IR}}(\tau + t_{\text{EWS}}). \quad (7.9)$$

Denoting the polar angle of $\mathbf{k}_f$ and $\mathbf{k}$ as θ_f and θ , respectively, and defining $\gamma = \theta_f - \theta$,

projection of Eq. (7.9) onto $\hat{\mathbf{k}}_f$ yields

$$\begin{aligned}
& k_f(\tau) \\
&= k \cos \gamma - \cos \theta_f \left[A_{\text{IR}}(\tau + t_{\text{EWS}}) + t_{\text{DLC}} \frac{dA_{\text{IR}}(\tau + t_{\text{EWS}})}{d\tau} \right] \\
&\approx k \cos \gamma - \cos \theta_f \cdot A_{\text{IR}}(\tau + t_{\text{EWS}} + t_{\text{DLC}}) ,
\end{aligned} \tag{7.10}$$

where

$$t_{\text{DLC}}(\mathbf{k}) = \frac{\cos \gamma}{\cos \theta_f} \frac{d_z^{(n)}(\mathbf{k})}{k} \approx \frac{d_z^{(n)}(\mathbf{k})}{k \cos \theta} . \tag{7.11}$$

For the peak intensity of the IR pulse considered in this thesis, γ is less than 1.6° , making it negligible in Eq. (7.11). The approximation in Eq. (7.10) is supported by our typical delays t_{DLC} being less than 5% of the IR period. We note that an alternative approximation is to treat $A_{\text{IR}}(\tau)$ as sinusoidal⁴, which results in

$$t_{\text{DLC}}(\mathbf{k}) \approx \frac{1}{\omega_{\text{IR}}} \tan^{-1} \left[\omega_{\text{IR}} \frac{d_z^{(n)}(\mathbf{k})}{k \cos \theta} \right] . \tag{7.12}$$

Applying Eq. (7.11), we calculate the coefficients $c_{n,\alpha,m}(\mathbf{k})$ according to Eq. (7.3) by using the expansion (7.1) of the Stark scattering states and project the numerically propagated two-electron wave function onto the symmetrized product states $\mathcal{S} |n_1, l_1, m_1\rangle |\mathbf{k}_2\rangle$ as in (3.61). For the XUV-pulse parameters considered in this thesis, we find that the ratios of the complex-valued coefficients $c_{n,\alpha,m}(\mathbf{k})$ remain approximately constant over the spectral profile of the photoelectron wave packet. This allows us to evaluate these coefficients at the central photoelectron momentum $k = \sqrt{2(\omega_{\text{XUV}} - I_p^{(n)})}$. Figure 7.1 illustrates this proportionate change for the example of $n = 2$ shake-up emission.

The approximate DLC delays t_{DLC} for $n = 2$ and $n = 3$ shake-up ionization of para-helium and XUV pulses with photon energies of 90, 100, and 110 eV show a striking photoelectron-detection-direction dependence at large angles that is easily traced to the $1/\cos \theta$ factor in the dipole model given by Eq. (7.11) (Fig. 7.2). Within this model, direct photoemission has no DLC delay, since $d_z^{(0)} = 0$. The sign change for the shake-up emission at $\theta \approx 40^\circ$

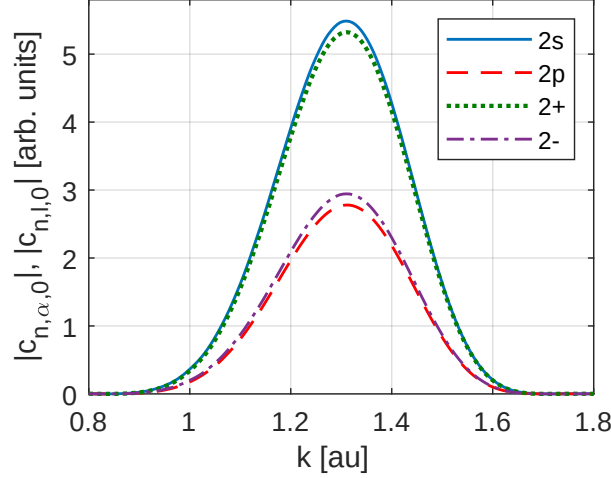


Figure 7.1: Absolute values of the probability amplitudes of scattering states for $n = 2$ shake-up emission from helium as a function of the photoelectron momentum magnitude k . The probability amplitudes are represented in the Stark basis according to Eq. (7.3). Labels “ $2^\pm$ ” indicate Stark states with quantum numbers $\alpha = \pm 1$ of the residual He^+ ion. Hydrogenic states are labeled as “ $2s$ ” and “ $2p$ ”.

indicates a change in the orientation of the residual dipole at larger angles.

Table 7.4: Comparison of our *ab initio* calculated and modeled DLC delays for emission along the XUV- and IR-pulse-polarization direction with the correlation delays of Ossiander et al.⁴ derived from measured streaking delays. This table complements Fig. 7.2.

n	$\hbar\omega_{\text{XUV}}$ [eV]	<i>ab initio</i> [as]	DLC model [as]	Ossiander et al. ⁴ [as]
2	90	1.4	7.3	7.8
2	100	2.5	6.7	6.55
2	110	3.9	5.9	5.6
3	90	48.4	38.1	45.9
3	100	44.8	34.0	37.7
3	110	40.2	29.8	32.2

We validate the results of the DLC model in Fig. 7.2 by computing the streaking, EWS, and CLC delays *ab initio*. The *ab initio* DLC delays shown in Fig. 7.3 are obtained from

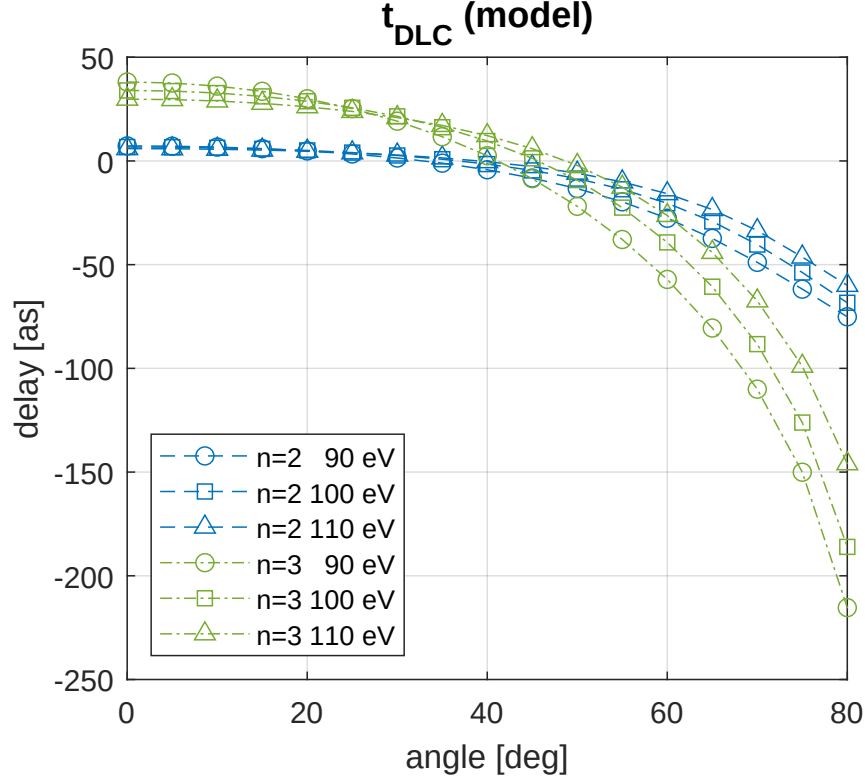


Figure 7.2: Model DLC delays according to Eq. (7.11) for $n = 2$ and $n = 3$ shake-up ionization of helium and XUV pulses with photon energies of 90, 100, and 110 eV as functions of the photoelectron-detection direction. For a comparison with results for emission along the XUV-polarization direction of Ossiander et al.⁴ see Tab. 7.4.

Eqs. (1.1) and (6.1) as

$$\begin{aligned}
 t_{\text{DLC}}(\mathbf{k}) &= t_s(\mathbf{k}) - t_{\text{EWS}}(\mathbf{k}) - t_{\text{CLC}}(\mathbf{k}) \\
 &= t_s(\mathbf{k}) - t_s^{\text{H}_{100}}(\mathbf{k}) - [t_{\text{EWS}}(\mathbf{k}) - t_{\text{EWS}}^{\text{H}_{100}}(\mathbf{k})] ,
 \end{aligned}
 \tag{7.13}$$

in good overall agreement with the model DLC delays for shake-up emission in Fig. 7.2. For most angles, this agreement is better than 10 as. It becomes worse at large angles near $\theta = 90^\circ$, possibly due to a combination of the model assumptions leading to Eq. (7.11) and small numerical signal-to-noise ratios (very small yields) at large detection angles. As seen in Tab. 7.4, for the special case of photoelectron emission along the XUV-polarization direction (0°), our DLC-model delays are in good quantitative agreement with the correlation delays derived from measured streaking delays in Fig. S10 of the supplementary material of Ref.⁴.

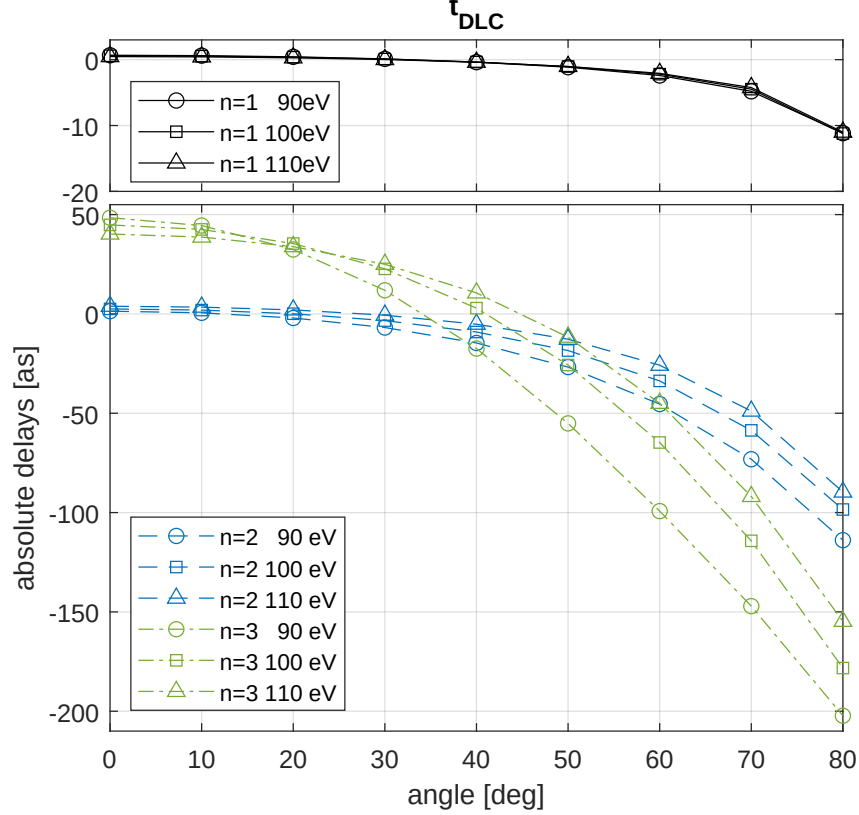


Figure 7.3: *Ab initio angle- and energy-resolved absolute DLC delays for direct ($n = 1$) and $n = 2, 3$ shake-up ionization of helium for XUV-pulse photon energies of 90, 100, and 110 eV as functions of the photoelectron-detection direction.*

The DLC model does not explain the angle dependence of the *ab initio* DLC delay for direct emission shown in the upper graph of Fig. 7.3. In addition, on the attosecond time scale, it is in variance with our *ab initio* calculated delays (Tab. 7.4). A possible cause for this variation is that the approximate calculation of t_{CLC} for hydrogen according to Eq. (6.1) does not accurately represent the CLC delay for helium. On the other hand, accurately calculating the CLC delay for direct photoemission from helium according to

$$t_{\text{CLC}}^{\text{He}}(\mathbf{k}) = t_s^{n=1}(\mathbf{k}) - t_{\text{EWS}}^{n=1}(k) , \quad (7.14)$$

as for the $n = 1$ curves in Fig. 7.3, would merely illustrate the difference of the two definitions, $t_{\text{CLC}}^{\text{He}} - t_{\text{CLC}}$, instead of a deviation from the physically intuitive DLC model (7.11).

7.3 Polarization of the residual ion by IR field

In this thesis, we have assumed that the IR field is weak enough so that it does not distort the initial state before XUV ionization². After ionization, in addition to the XUV photoionization dynamics generating polarized residual He^+ ions, the electric field of the IR streaking pulse contributes to the polarization of the residual ion and may thereby affect angle-dependent shake-up photoemission yields and streaking delays. In this section, we investigate this effect and show that, for the assumed IR-pulse intensity in the present work, the effect of the residual-ion polarization by the streaking pulse can be neglected.

For hydrogen atoms, this effect was previously investigated by Baggesen and Madsen³⁴, who pointed out that the polarization of a target atom by the streaking IR-pulse may influence the angle-dependence of streaked photoemission yields and delays. They showed that, for sufficiently strong IR streaking fields, the asymptotic energy of the streaked photoelectron acquires an additional phase shift relative to the IR vector potential $A_{\text{IR}}(t)$, due to the fact that the dipole-laser coupling is proportional to the IR electric field $\mathcal{E}_{\text{IR}}(t)$ and thus phase-shifted by 90° .

To quantify the distortion of the residual ion He^+ by the streaking field, we calculate its static polarizability³⁸,

$$\begin{aligned}\beta_{n,l,0} &= \beta_{n,l,0}^b + \beta_{n,l,0}^c \\ &= 2 \sum_{n',l'}^{n' \neq n} \frac{|\langle n', l', 0 | z | n, l, 0 \rangle|^2}{E_{n'}^{(0)} - E_n^{(0)}} + 2 \sum_{l'} \int_0^\infty dk \frac{|\langle k, l', 0 | z | n, l, 0 \rangle|^2}{k^2/2 - E_n^{(0)}}.\end{aligned}\quad (7.15)$$

The polarizability β for hydrogen-like atoms is defined with the electric dipole distortion in a static field with $\Delta d = \beta \mathcal{E}$, and can be calculated with the second-order time-independent perturbation theorem ($Z = 2$ for He)

$$\beta = -\frac{2E_n^2}{\mathcal{E}^2}, \quad (7.16)$$

based on virtual excitations to hydrogenic bound states, $\{|n, l, m\rangle\}$, $(\beta_{n,l,0}^b)$ and spherical

partial-wave continuum states, $|k, l', m\rangle$, $(\beta_{n,l,0}^c)$ for the nuclear charge $Z = 2$. Our numerical values for the lowest four states of He^+ are in close agreement with the scaled theoretical values in Refs. ^{5;51} (Tab. 7.5). The literature values in Tab. 7.5 are calculated for hydrogen atoms and multiplied by $1/16$ to account for the scaling $\beta_{n,l,0} \propto 1/Z^4$ ^{38;51}.

Table 7.5: Ab initio *static polarizabilities of He^+ in au according to Eq. (7.15) in comparison with calculations by Baye⁵. $\bar{m}$ indicates values averaged over m within an (n, l) sub-shell.*

n, l, m	$\beta_{n,lm}^b$	$\beta_{n,l,m}^c$	$\beta_{n,l,m}$	$\beta_{n,l,m}$ ⁵
1, 0, 0	0.2287	0.0520	0.2807	0.2812
2, 0, 0	6.917	0.571	7.488	7.500
2, 1, 0	12.98	0.508	13.49	
2, 1, ± 1	9.391	0.351	9.742	
2, 1, $\bar{m}$	10.59	0.403	10.99	11.00
3, 0, 0	60.94	2.231	63.17	63.28
3, 1, 0	98.50	2.646	101.2	
3, 1, ± 1	69.08	1.702	70.78	
3, 1, $\bar{m}$	78.89	2.017	80.91	81.00
3, 2, 0	145.3	1.445	146.7	
3, 2, ± 1	130.3	1.248	131.5	
3, 2, ± 2	85.24	0.759	86.00	
3, 2, $\bar{m}$	115.3	1.092	116.4	116.4

For the IR-pulse peak intensity assumed in this work of $4 \times 10^{11} \text{W}/\text{cm}^2$, corresponding to a peak-electric-field strength of $\mathcal{E}_{\text{IR},0} = 3.4 \times 10^{-3} \text{ au}$, the distortion of the electric dipole moment of the He^+ ground state is

$$\Delta d_{1,0,0,\text{max}} = 2 \mathcal{E}_{\text{IR},0} \beta_{1,0,0} = 1.9 \times 10^{-3}, \quad (7.17)$$

where the factor of two derives from the maximal variation of the IR electric field over one IR oscillation period. For the $n = 2$ shell of He^+ , the largest dipole polarizability is $\beta_{2,1,0} = 13.49$, resulting in

$$\Delta d_{2,1,0,\text{max}} = 2\mathcal{E}_{\text{IR},0}\beta_{2,1,0} \approx 9.2 \times 10^{-2} . \quad (7.18)$$

The maximal IR-pulse-induced dipole in the $n = 2$ shell is thus about 50 times larger than that for the ground state, and the distortion of the He^+ ground state may be neglected compared with the distortion of excited He^+ states by the streaking IR field.

At the same time, the maximal IR-pulse-induced dipole in the $n = 2$ shell in Eq. (7.18) is about 16 times smaller than the dipole moment of 1.5 of the XUV-pulse-excited $n = 2$ Stark states according to Tab. 7.1. This is consistent with the numerical example in Fig. 5.4, where the maximal dipole coefficient for $n = 2$ shake-up emission exceeds the maximal dipole coefficient for direct emission by an order of magnitude. The distortion by the IR streaking pulse of the XUV-photoemission-produced residual dipole is thus a small correction. This difference is less pronounced for the $n = 3$ shake-up excitation. Here, the XUV-photoemission-produced residual-dipole moment is 4.5 (cf., Tabs. 7.2 and 7.3), exceeding 6.5 times the IR-pulse-induced dipole distortion,

$$\Delta d_{3,1,0,\text{max}} = 2\mathcal{E}_{\text{IR},0}\beta_{3,1,0} \approx 0.69 . \quad (7.19)$$

These comparisons indicate that, for shake-up ionization into the K and L shells of He^+ , the distortion of the XUV-produced dipole by the IR pulse is negligible, while for $n = 3$ shake-up ionization further scrutiny is needed in this regard.

We note that once the IR distortion of He^+ becomes relevant, the distinction of three separate delay contributions to the streaking delay in Eq. (1.1) breaks down, and the EWS term needs to be modified to account for the influence of the IR-pulse during photoemission for small XUV – IR pulse delays. In the present work, the fact that the three contributions in Eq. (1.1) correctly add up to the streaking delay, provides further evidence that the IR-pulse

distortion of He^+ is negligible. Furthermore, the classical trajectory analysis in Sec. 6.0.2, excluding the IR-pulse distortion of the residual ion, agrees for emission angles below $\approx 60^\circ$ with the quantum result and further supports the very minor role of the IR distortion of the residual ion in the present work.

This analysis of the distortion of the residual ion by the IR pulse may provide a reference for future streaking-pulse parameters that break the non-distorting dipole assumption. For a discussion of the IR-pulse distortion of helium in the entrance channel, we refer to². For the description of relative streaking delays, the IR-pulse distortion of the neutral helium target affects direct and shake-up channels equally, and thus tends to cancel in the calculation of relative streaking delays.

Chapter 8

Summary

In this thesis, we confirmed the results of previous theoretical and experimental investigations for streaked direct and shake-up photoemission from helium atoms along the IR- and XUV-pulse linear polarization. We performed *ab initio* and model calculations and extended these earlier investigations to arbitrary photoelectron detection directions, scrutinizing EWS, CLC and DLC contributions for direct and He^+ ($n = 2, 3$) shake-up ionization.

For large photoelectron detection angles, we found that CLC delays become angle dependent and tracked this dependence as a purely quantum-mechanical effect that cannot be explained with classical-trajectory simulations. For shake-up ionization, we find dominant contributions to the streaking delay due to DLC. Confirming a physically intuitive model for the DLC effect, we validated the model predictions for the DLC delay against *ab initio* calculations over a wide range of photoelectron detection angles.

Distinguishing the production of polarized residual He^+ ions due to the XUV-photoemission dynamics and possible contributions from its time-dependent polarization by the oscillating IR pulse, we estimated the IR-pulse-induced polarization contribution. Our model DLC calculations without including the IR distortion of the XUV-pulse-generated dipole agreeing with the DLC-delay contribution derived from *ab initio* calculations provide evidence that the IR pulse distortion of the residual dipole is negligible.

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Appendix A

Mathematical functions

In this appendix, we review the mathematical functions relevant to this thesis.

A.1 Clebsch–Gordan and Wigner coefficients

The Clebsch–Gordan (CG) coefficients couple two single-electron angular momentum eigenstates $|l_i, m_i\rangle$ ($i = 1, 2$) to form an eigen state of $|L, M\rangle$ of the total angular momentum³⁸.

$$|L, M\rangle = \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} |l_1, m_1\rangle |l_2, m_2\rangle . \quad (\text{A.1})$$

A direct expression for the Clebsch–Gordan coefficients is

$$\begin{aligned}
& \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} \\
&= \sqrt{\frac{(2L+1)(L+l_1-l_2)!(L-l_1+l_2)!(l_1+l_2-L)!}{(l_1+l_2+L+1)!}} \\
&\times \sqrt{(L+M)!(L-M)!(l_1-m_1)!(l_1+m_1)!(l_2-m_2)!(l_2+m_2)!} \\
&\times \sum_{k=k_{min}}^{k_{max}} \frac{(-1)^k}{k!(l_1+l_2-L-k)!(l_1-m_1-k)!(l_2+m_2-k)!} \\
&\times \frac{1}{(L-l_2+m_1+k)!(L-l_1-m_2+k)!} ,
\end{aligned} \tag{A.2}$$

where the range of the sum is chosen such that every factorial in the expression takes a non-negative number, i.e.

$$\begin{aligned}
k_{min} &= \max\{0, \quad l_2 - m_1 - L, \quad l_1 + m_2 - L\} , \\
k_{max} &= \min\{l_1 + l_2 - L, \quad l_1 - m_1, \quad l_2 + m_2\} .
\end{aligned} \tag{A.3}$$

Some common selection rules, i.e. the necessary conditions for non-zero CG coefficients, are

$$|l_1 - l_2| \leq L \leq l_1 + l_2 . \tag{A.4}$$

$$m_1 + m_2 = M , \tag{A.5}$$

$$-L \leq M \leq L , \quad -l_1 \leq m_1 \leq l_1 , \quad -l_2 \leq m_2 \leq l_2 . \tag{A.6}$$

The 3j coefficients are closely related to the CG coefficients

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \begin{bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & -m_3 \end{bmatrix} . \tag{A.7}$$

The CG or 3j coefficients can be used to express the integral of three spherical harmonics³⁸

$$\begin{aligned} & \int Y_{l_1 m_1}^*(\hat{\mathbf{r}}) Y_{l_2 m_2}(\hat{\mathbf{r}}) Y_{l_3 m_3}(\hat{\mathbf{r}}) d\Omega \\ &= (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix}. \end{aligned} \quad (\text{A.8})$$

For $l_2 = 1$ and $m_2 = 0$, we have

$$\begin{aligned} \begin{pmatrix} l+1 & 1 & l \\ -m & 0 & m \end{pmatrix} &= \begin{pmatrix} l & 1 & l+1 \\ -m & 0 & m \end{pmatrix} \\ &= -(-1)^{l-m} \sqrt{\frac{(l+1)^2 - m^2}{(l+1)(2l+1)(2l+3)}}. \end{aligned} \quad (\text{A.9})$$

Compared to the CG coefficients, the 3j coefficients better display symmetries for:

1. Column exchange

$$\begin{aligned} \begin{pmatrix} j_3 & j_2 & j_1 \\ m_3 & m_2 & m_1 \end{pmatrix} &= \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \\ &= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \end{aligned} \quad (\text{A.10})$$

2. Column rotation

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix}, \quad (\text{A.11})$$

3. Second-row inversion

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}. \quad (\text{A.12})$$

A.2 Generalized spherical harmonics

We first review the ordinary spherical harmonic function $Y_{l,m}(\hat{\mathbf{r}})$. In spherical coordinates, the kinetic energy Hamiltonian $-\nabla^2/(2m)$ contains the Laplacian operator, which can be separated into radial and angular parts

$$\begin{aligned}\nabla^2 &= \nabla_r^2 + \frac{\nabla_\Omega^2}{r^2} \\ &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 u}{\partial \phi^2} .\end{aligned}\tag{A.13}$$

It contains the single-electron angular momentum operator

$$L^2 = L_x^2 + L_y^2 + L_z^2 = -\nabla_\Omega^2 = -\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 u}{\partial \phi^2} ,\tag{A.14}$$

where the single-electron z component angular momentum operator is

$$L_z = -i \frac{\partial}{\partial \phi} .\tag{A.15}$$

The spherical harmonics is thus the simultaneous eigenvector of the L^2 and L_z ,

$$\nabla_\Omega^2 Y_{l,m}(\hat{\mathbf{r}}) = -l(l+1) Y_{l,m}(\hat{\mathbf{r}}) ,\tag{A.16}$$

$$\frac{\partial}{\partial \phi} Y_{l,m}(\hat{\mathbf{r}}) = im Y_{l,m}(\hat{\mathbf{r}}) ,\tag{A.17}$$

and represents the eigenvector $|l, m\rangle$ in spherical coordinates.

The generalized spherical harmonics function (with $M = 0$) is defined in terms of the spherical harmonics and Clebsch–Gordan coefficients

$$\mathcal{Y}_{l_1, l_2}^{L, M}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_1, m_2} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & m_2 & M \end{bmatrix} Y_{l_1 m_1}(\hat{\mathbf{r}}_1) Y_{l_2 m_2}(\hat{\mathbf{r}}_2) .\tag{A.18}$$

In this thesis, we have $M = m_1 + m_2 = 0$, thus

$$\mathcal{Y}_\lambda(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = \sum_{m_1 = -\min\{l_1, l_2\}}^{\min\{l_1, l_2\}} \begin{bmatrix} l_1 & l_2 & L \\ m_1 & -m_1 & 0 \end{bmatrix} Y_{l_1, m_1}(\hat{\mathbf{r}}_1) Y_{l_2, -m_1}(\hat{\mathbf{r}}_2) , \quad (\text{A.19})$$

where $\min\{l_1, l_2\}$ denotes the smaller value of l_1, l_2 .

Spherical harmonics satisfy the symmetry relation

$$\mathcal{Y}_\lambda(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) = (-1)^{l_1 + l_2 - L} \mathcal{Y}_\lambda(\hat{\mathbf{r}}_2, \hat{\mathbf{r}}_1) , \quad (\text{A.20})$$

Appendix B

Description of the FE-DVR TDSE computer program

We implement our TDSE solver, named FEDVR-TDSE, with C++ language (C++11 or later), as a command-line program for Linux operating systems. Both 1- and 2-electron targets in linearly polarized electric fields are supported. The program includes options for wave-function analysis. Some plotting and analysis scripts that are not performance-critical are implemented with Matlab®.

B.1 The SLISC library and dependencies

We maintain our open-source general-purpose C++ utilities with a separate library named Scientific Library in Simple C++ (SLISC) for the FEDVR-TDSE and future projects. SLISC includes basic dense and sparse matrix classes, common algorithms such as sorting, linear algebra, numerical quadrature, partial differential equation solvers, special function evaluation, quad-precision (128-bit floating point) calculations, file input/output, exception handling, etc.

SLISC provides high-level wrappers for some third-party libraries, such as LAPACK (NIST version or [Intel oneAPI®](#) version) for linear algebra, [Arb](#) for high-precision spe-

cial function evaluations, [Arpack++2](#) for large eigenvalue problems, [MPLAPACK](#) for quad-precision linear algebra, and a few code snippets adapted from Numerical Recipes (3rd edition)⁴⁰. There are about 68,500 lines of code (not including 3rd-party libraries and code generation).

SLISC provides a text file format with extension `.matt` (`t` for “text”) to store multiple named multidimensional arrays in a single file. To store large matrices and save disk space, it also provides a binary file format with the extension `.matb` (`b` for “binary”) with the same functionality, and the file size is only about 1/3 of `matt` files on average. C++ and Matlab functions are provided to read or write to these files. For detailed documentation and the latest source code, visit the GitHub repository SLISC¹ (GPL-3 licensed).

B.2 The FEDVR-TDSE program

The FEDVR-TDSE program is highly modular, using modern C++ features such as object-oriented programming (OOP), template meta-programming, and code generation techniques, with efficient memory and threading control. This makes it easy to continuously add new features to meet the needs of future research projects. Currently, the FEDVR-TDSE program might be provided on request.

The `H_prop` folder contains the one-electron TDSE program, and the parameters of the input file `params.inp` are explained below. Unless otherwise stated, atomic units are used.

- `out_dir`: The output directory of a TDSE propagation, two subdirectories will be created: `prop/` will contain the parameter files `params.matb`, the data file (e.g. the grid definition, electric field in each step) `data.matb` and the wave function files `Psi<index>.matb`
- `Nth`: The number of OpenMP threads. Use `[0]` for default (usually the number of logical CPUs available).

¹<https://github.com/MacroUniverse/SLISC>

- `write_step`: Write wave function every `write_step` steps to `<out_dir>/prop/Psi<index>.matb`.
- `print_step`: Print a one-line report to the terminal every `print_step` steps, including current time of the TDSE, whether various thresholds are met, etc.
- `gauge`: Length or velocity gauge. Use a single letter `[l]` for the length gauge and `[v]` for the velocity gauge.
- `r_algo`, `pw_algo`: Propagation algorithms for the radial direction and partial wave coupling. All options except `[L]` use the split operator method, different options can be used for different parts of the split operator.
 - `[k]` (for `r_algo`): Using the Expokit package⁵². This is mainly used to compare with our previous program in¹.
 - `[d]` (for either): Matrix exponential by diagonalization.
 - `[c]` (for either): Crank-Nicolson algorithm as described in Section 2.2.5.
 - `[n]` (for `pw_algo`): Crank-Nicolson algorithm with $e^{-iH_F\Delta t/2}e^{-iH_F\Delta t/2}$ for partial wave coupling propagation. Used to compare with `[c]`.
 - `[L]` (for both): Lanczos algorithm without split operator.
- `imag_time`: Imaginary time method to solve the ground state, `[0]`: off, `[1]`: on.
- `tmin`, `tmax`, `Nt`: The time points for the TDSE are $t_{\min}$, $t_{\min} + \Delta t$, $t_{\min} + 2\Delta t$, $\dots$, $t_{\max}$, with $\Delta t = (t_{\max} - t_{\min})/(N_t - 1)$ and a total of N_t grid points.
- `Npw`: The number of partial waves ($l = 0, 1, \dots, N_{pw} - 1$).
- `YYYY`: The number of partial waves in (2.72), for time-dependent multipole potential in Section 2.2.4. The list of (l, m) needs to be specified in a separate file `C1m.txt`, use `[0]` to turn off.
- `NkryR`, `NkryF`: Number of Krylov bases for radial/field prop (for `algorithm = [k|l]`), set both to the same for `L` algorithm.

- `pw_thresh`, `grid_thresh`, `f_thresh`: Probability threshold for radial/field propagation. In length gauge, electric field with an absolute value smaller than `f_thresh` will be ignored. In velocity gauge, A vector potential with an absolute value smaller than `f_thresh` will be ignored. Zero values will always be ignored.
- `grid_file`: Each line is an FE boundary. There are $N_{\text{FE}} + 1$ boundaries.
- `Ngs`, `Nfe`: Number of Gaussian points and FE.
- `absorbW`, `absorbA`: Absorber width and strength.
- `eff_pot` : Effective potential for SAE approximation
 - `eff_pot_a`, `eff_pot_b`, `eff_pot_V0`, `eff_pot_N`, `eff_pot_Z`
 - `[H]`: Hydrogen.
 - `[He]`: Helium SAE model using Tong-Lin potential⁵³, with the same ionization potential as ground-state helium.
 - `[HeSU]`: SAE model for helium $n = 2$ shake-up ionization, with the same ionization potential, by scaling the screening potential of `[He]`.
 - `[HeSU2]`: The same as `[HeSU]` , but by modifying the parameter a_3 of the Tong-Lin potential.
 - `[yukawa]`: Yukawa potential $-Z \exp(-ar)/r$, with parameters `eff_pot_Z` and `eff_pot_a`.
- `n_init`, `l_init`, `r_init`: Set initial state to the bound state `(n_init, l_init)` of the chosen effective potential, by solving TISE eigen problem with a spherical box with radius `r_init`.
- `field_file`: Path to the custom electric field file. The first column is time and the second column is the z -polarized field strength. The provided data points will be spline-interpolated for each time point. Use `[none]` to generate an electric field of the XUV and IR pulses with the following parameters.

- `I_xuv`: XUV pulse peak intensity (w/cm^2), use `[0]` to turn off.
- `eV_xuv`: XUV photon center of energy (eV).
- `shape_xuv`: XUV pulse shape, `[s]` for $\sin^2$ profile, `[g]` for Gaussian profile.
- `cyc_xuv`: The number of cycles of total duration when `shape_xuv = [s]`. The number of cycles of the FWHM when `shape_xuv = [g]`.
- `I_ir`: Peak intensity (w/cm^2) of the IR pulse, use `[0]` to turn off.
- `lambda_ir`: Center of wavelength (nm) of the IR pulse.
- `cyc_ir`: The number of cycles of total duration. The IR pulse always has a $\sin^2$ profile.
- `xuv_shift`: The shifts between the center of the XUV and IR pulses. A positive value denotes the delay of the XUV pulse.

The `H_analysis` folder contains the hydrogen wave function analysis program. The input file parameters are as follows:

- `in_path`: The wave function files should be in `<in_path>/<test_num>/prop/` where `<test_num>` is optional.
- `out_path`: `<out_path>/<test_num>/analysis/` where `<test_num>` is optional.
- `test_num_start`, `test_num_end`, `test_num_step`: Select the sub-folders `<test_num>` to analyze wave functions. `<test_num>` is from `test_num_start` to `test_num_end`, with a step size of `test_num_step`.
- `sis_start`, `sis_end`, `sis_step`: The wave function indices `<index>` to calculate the single-ionization momentum spectra (2.129). The indices are from `sis_start` to `sis_end`, with a step size of `sis_step`.
- `kmin`, `kmax`, `Nk`: The momenta in the spectra to calculate.

- `cut_r0`: Cut the wave function around the nucleus within a radius of `cut_r0` before projection to reduce noise.
- `Z`: The nucleus charge. The value should always be `[-1]` for atoms.
- `P_pw_start`, `P_pw_end`, `P_pw_step`: The wave function indices `<index>` to calculate the probability of each partial wave.

The `He_prop` folder contains the TDSE solver for the two-electron atoms. The input file parameters are as follows:

- `out_dir`: (same)
- `Nth`: The number of OpenMP threads. Use `[0]` for default (usually the number of logical CPUs available). For the `[L]` algorithm, if `Nth` is more than the free CPU number, the performance might be lower.
- `write_step`, `print_step`, `gauge`: (same)
- `r_algo`, `pw_algo`: radial/partial-wave prop algorithm
 - `[k]`: Expokit package⁵²
 - `[l]`: Lanczos algorithm with split operator
 - `[L]`: Lanczos with non-split operator
 - `[d]`: Matrix exponential by diagonalization
 - `[c]`: Crank-Nicolson (recommended for length gauge)
 - `[n]`: (for `pw_algo`): Crank-Nicolson algorithm with $e^{-iH_F\Delta t/2}e^{-iH_F\Delta t/2}$ for propagation of partial-wave coupling. Used to compare with `[c]`.
 - `[C]`: Crank-Nicolson (non-split operator) with bi-conjugate linear solver that supports quad precision scalar.
- `save_mem`: (only applies for `[L]` or `[C]` algorithm) Use `[0]` to pre-calculate all partial wave coupling matrices for each r_1, r_2 grid point. Use `[1]` to recalculate them for each Hamiltonian action (which could even be faster).

- `box_L`, `box_Nn1`, `box_Nn2`: Solve helium eigenstates in a spherical box with total momentum `box_L` and `box_Nn1*box_Nn2` hydrogenic product bases for each partial wave. Use `[-1]` to turn off.
- `imag_time`: (same)
- `tmin`, `tmax`, `Nt`: (same)
- `Nkry1`, `Nkry2`, `Nkry3`: Krylov basis for each split operator. It only applies for `algorithm` is `[k]`, `[l]`, or `[L]`. For `[L]` the 3 values must be the same.
- `[kry_err_max]`: Lanczos algorithm error bound for early termination (use `[0]` to turn off). This is actually $\epsilon_{\text{lanc}}^{K-1}$ in (2.91) to save time.
- `r_thresh`, `grid_thresh`, `f_thresh`: Probability threshold for radial and partial wave propagation for split-operator algorithms, and for field or vector potential. When $|\psi_\lambda|^2$ is less than `r_thresh` or $\sum_\lambda |\psi_\lambda(r_1, r_2)|^2$ is less than `grid_thresh`, the corresponding propagation is skipped. Use `[-1]` to skip checking and propagate anyway (causing more noise for the `[k]`, `[l]`, `[L]` algorithm).
- `lconfig_file`: User partial wave configuration, use `[none]` to disable, and use `l1_max`, `l2_max`, `L_max` to generate.
- `Npw_file`: Number of partial waves to truncate in `lconfig_file`, use `[0]` to include all partial waves.
- `l1_max`, `l2_max`, `L_max`: Maximum value for (l_1, l_2, L) .
- `pw_select` is `[o|e|a]` to select only the partial waves with odd/even/all values of `l1+l2-L`. Use `[-1]` to disable.
- `grid_file`: The path of the file of the FE grid points for r_1 and r_2 . There must be at least `max(Nfe1, Nfe2)+1` points in the file. See `He_grid` for the files used in this thesis.
- `fe1start`, `Nfe1`: The range of finite elements for r_1 .

- `fe2start`, `Nfe2`: The range of finite elements for r_2 . For the sliding window method, `fe2start` is non-zero.
- `Ngs`: The number of Gaussian points.
- `absorbW1`, `absorbA1`: The absorber parameters for r_1 .
- `absorbW2`, `absorbA2`: The absorber parameters for r_2 .
- `check_dt_step`: (almost obsolete, applies for `[c]` algorithm only) Check numerical error caused by Δt every `check_dt_step` steps, use `[0]` to turn off the variable time step.
- `auto_grid_mode`:
 - `[n]` Turn off auto-grid completely.
 - `[d]` Use the following parameters to automatically resize the grid based on the virtual detector region:
 - * `detecW1`, `detecW2`: Regions at the end of r_1 , r_2 to monitor wave function probability (use `[0]` to turn off each side)
 - * `check_grid_step`: Check the grid size every `check_grid_step` time steps.
 - * `threshP1`, `threshP2`: Probability threshold to increase grid size.
 - `[x]` (only applies when `field_file = [none]`) Use a classical trajectory plus the wave packet spreading ($\sim \sqrt{t}$) to predict the needed grid size as a function of time.
 - * `auto_grid_n_sigma`: (for `auto_grid_mode = [x]`) The number of `sigma_x` of current photoelectron to determine grid size.
 - * `auto_grid_r_extra`: The extra grid length required to accommodate the photoelectron time advance and other effects.
- `incW1`, `incW2`: Increments to r_1, r_2 each time the criteria are met.

- `Nfe_max1`, `Nfe_max2`: Max FE numbers for r_1 and r_2 .
- `eff_pot_a`, `eff_pot_b`, `eff_pot_V0`, `eff_pot_N`: Effective potential, for the two-active electron (TAE) approximation, set `eff_pot_a = [0]` to turn off.
- `init_file`: Initial wave function file (only applies for `imag_time = [0]`), use `[none]` for a toy function
- `resume_file`: Which `Psi<index>.matb` file to resume. Use `[none]` to run from the beginning, `[auto]` to detect the latest, or use a file path to specify a file
- `resume_ind`: Which wave function `<index>` to use, use `[-1]` to auto detect.
- `force_resume_grid`: Use a truncated or extended grid for assumed propagation. The existing grid points should not be changed.
- `field_file`: (same)
- `I_xuv`, `eV_xuv`, `shape_xuv`: (same)
- `as_xuv_FWHM`: The FWHM of the XUV pulse in attoseconds.
- `I_ir` , `lambda_ir`: (same)
- `fs_ir_full_width`: The full width of the IR pulse (always has a $\sin^2$ profile) in femtoseconds.
- `xuv_shift`: (same)

The `He_analysis` folder contains the helium wave function analysis program. The input file parameters are as follows:

- `Nth`: (same)
- `grid_type`: The shape of the (r_1, r_2) grid, `[s]` for square grid, `[r]` for rectangular grid.

- `in_path`: Path to wave functions (where `Psi<index>.matb` are).
- `out_path`: Output path for analysis data files.
- `P12_start`, `P12_end`, `P12_step`: Calculate the radial probability distribution $P(r_1, r_2)$ (3.34) and total probability of each partial wave (`P_pw`). For wave functions `<index>` starting from `P12_start`, no larger than `P12_end`, and a step size of `P12_step`. Set `P12_end < P12_start` to turn off (same below for all `*_start`, `*_end`, `*_step`).
- `Imat_start`, `Imat_end`, `Imat_step`: Calculate $I_\lambda(k_1, k_2) = \langle F_{l_1}(k_1) | \langle F_{l_2}(k_2) | \Psi_\lambda(r_1, r_2) \rangle$ (3.68) for double-ionization momentum spectrum. Also calculates $P(k_1, k_2)$ and total ionization rate (3.72) .
- `Imat_kmin`, `Imat_kmax`, `Imat_Nk`: The discrete values of k for the output of $I_\lambda(k_1, k_2)$.
- `jad_start`, `jad_end`, `jad_step`: Calculate the joint angular distribution spectrum (JAD) (3.83).
- `jad_kmin`, `jad_kmax`, `jad_Nk`: The momentum magnitudes for the JAD spectrum.
- `tdcs_start`, `tdcs_end`, `tdcs_step`: Calculate the triple differential cross section (TDCS) (3.85).
- `tdcs_th1` [deg], `tdcs_k1`: Specify the angle and magnitude of momentum $\mathbf{k}_1$ for TDCS.
- `tdcs_k2min`, `tdcs_k2max`, `tdcs_Nk2`: The range of k_2 for TDCS.
- `sis_start`, `sis_end`, `sis_step`: For single-ionization momentum spectrum (3.62).
 - `sis_kmin`, `sis_kmax`, `sis_Nk`: (same)
 - `Nn1`: The number of n 's for the ionic bound states, not applicable for TAE approximation.
 - `sis_r0`: Cut the wave function around the nucleus within a radius of `sis_r0` before projection to Coulomb plane waves to reduce noise.

- The following parameters are used to solve the ionic bound states in the TAE effective potential.
 - * `bound_r0`: Use a spherical box with radius `bound_r0`, use `[0]` to turn off and use He^+ bound states.
 - * `l_max`: Maximum l of bound states.
 - * `Nbound`: The number of lowest ionic bound states. Note that bound state energy will depend on both n and l .
- `single_prob1_start`, `single_prob1_end`, `single_prob1_step`, `Nth1`, `ph1` [deg]: Calculate the probability distribution $P(\mathbf{r}_1)$ (3.50) for a plane across the z axis, with `Nth1` polar angles and the azimuthal angle `ph1`.
- `single_prob2_start`, `single_prob2_end`, `single_prob2_step`, `Nth2`, `ph2` [deg]: Calculate $P(\mathbf{r}_2)$ (3.50). The maximum radius will be different than $P(\mathbf{r}_1)$ if a rectangular grid is used.
- `dipole_r_start`, `dipole_r_end`, `dipole_r_step`: Calculate the probability distribution $P(\mathbf{r}_1)$ for many fixed $\mathbf{r}_2$ (5.45), where
 - `dipole_r_th2` [deg], `dipole_r_ph2` [deg]: The direction of $\mathbf{r}_2$.
 - `dipole_r_r2min`, `dipole_r_r2max`, `dipole_r_ir2_step`: The magnitudes of r_2 .