

ELECTRON CORRELATION AND FIELD PULSE IONIZATION IN ATOMS

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SYMBOLS

n	principal quantum number
ν	effective principal quantum number
μ	quantum defect
l	angular momentum, azimuthal quantum number
L	total angular momentum, maximum number of angular channels, Lagrangian
m	mass, magnetic quantum number
s	spin
j, m_j	angular momentum of L-S coupling
ω	angular frequency, relative angle between two velocity directions
E	energy, electric field
ϵ	energy
F	electric field, radial wave function
t	time
T	period
e	charge of electron, base of natural logarithm
V	potential, potential energy
r	radial position, radial distance, position vector
ψ, Ψ	wave function
H	Hamiltonian
Y_{lm}	spherical harmonic function
P_l^m	associated Legendre Polynomial
θ	polar angle (with z axis)
ϕ	azimuthal angle (with x axis)
Ω	solid angle

λ	wave length
θ_{12}	the relative angle between two velocity directions
k	wave number $k = 2\pi/\lambda$, arbitrary integer
P	laser power, probability
φ	phase
σ_l	Coulomb phase shift
a_0	Bohr radius
$C_0, c_1, c_2, \dots$	constants
δX	the width (or uncertainty) of physical quantity X
p	momentum, probability
R	radial wave function, radial distance
Z	nuclear charge
Γ_c	Auger core width
S	action
i	imaginary unit, index
$\dot{\omega}_c$	laser frequency chirping
β	asymmetric parameter

ABBREVIATIONS

TDSE	time-dependent Schrödinger equation
TISE	time-independent Schrödinger equation
TDCC	time-dependent close coupling
CTMC	classical trajectory Monte Carlo
SCP	single-cycle pulse
HCP	half-cycle pulse
POL	ponderomotive optical lattice
SOC	spin-orbit coupling
FWHM	full-width at half maximum
PCI	post-collision interaction
PED	photoelectron energy distribution
ICE	isolated core excitation

ABSTRACT

Wang, Xiao PhD, Purdue University, August 2019. Electron Correlation and Field Pulse Ionization in Atoms. Major Professor: Francis Robicheaux.

Quantum mechanics and atomic, molecular, optical (AMO) physics have been widely studied in the past century. This dissertation covers several topics in the field of AMO physics that were the focus of my Ph.D. studies, both theoretical and computational.

The first topic is related to trapping of Rydberg atoms inside an optical trap. The study focuses on the trapping energy and state mixing of Rydberg atoms based on different angular momentum state and spin-orbit coupling of the Rydberg electron.

The second topic is the two-electron correlations in an atom, especially double Rydberg wave packets. We have focused on the rapid autoionization and angular momentum exchanges between the double Rydberg wave packets. Then, the study of two-electron correlation is extended to the post-collision interaction (PCI) in Auger decay and a sequential ionization model. Quantum interference patterns can be found in the final correlated distributions. In the PCI study, quantum calculations and semi-classical calculations are performed to interpret the interference patterns.

The last topic is the ionization behavior of one-electron Rydberg atoms from a terahertz single-cycle pulse. We investigate and compare the different ionization probabilities of a Rydberg electron from an initial stationary state and a wave packet. Also, studies of the ionization behavior are extended to scaled parameters, where all physical parameters of the electron and field pulses are scaled.

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1. INTRODUCTION

1.1 Background

In quantum mechanics, the Schrödinger equation is widely used to study the properties of atomic electrons. One of the most well-known solutions to the Schrödinger equation is that for a hydrogen atom. With the three degrees of freedom of a single electron, the solutions for a hydrogen atom contain three quantum numbers: the principal quantum number n , the azimuthal quantum number ℓ , and the magnetic quantum number m . The principal quantum number describes the energy ¹ of a hydrogen atom which is $E_n = -1/(2n^2)$. The other two quantum numbers describe the angular distribution of the electronic wave function which is a spherical harmonic $Y_{\ell m}$. In the early 20th century, when Pauli introduced the exclusion principle, he stated that electrons should have a “two-valued quantum degree of freedom”. Later in 1925, Uhlenbeck and Goudsmit introduced the 1/2-spin of electrons, which is also the fourth quantum number m_s of the solution.

Coincidentally, eigenenergies of a hydrogen atom treated quantum mechanically are exactly the same as that described with Bohr’s semi-classical model. The Bohr model originates from the solar system with planets orbiting the Sun in nearly spherical orbits. In a Kepler problem, the total energy of a planet can be calculated as its kinetic energy plus the gravitational potential energy with the following formula:

$$E = \frac{1}{2}mv^2 - \frac{GMm}{r}, \quad (1.1)$$

where m is the mass of the planet, v is the velocity, r is the distance between the planet and the Sun, GM is the proportionality constant in the gravitational potential energy. In Kepler’s law of motion, the orbit of a planet is an ellipse with the Sun

¹Atomic units (a.u.) are used to describe quantum systems in the whole dissertation, except Chap. 2, unless specified otherwise. Details about the atomic units can be found in Appendix A.

at one of the two foci. Since the $1/r$ potential is a conservative potential, the total energy of the planet is conserved, which is

$$E = \frac{-GMm}{2a}, \quad (1.2)$$

where a is the length of semi-major axis of the ellipse. The period of this orbit can also be calculated from the Kepler's third law which is

$$T^2 = a^3 \cdot \frac{4\pi^2}{GM}. \quad (1.3)$$

Bohr proposed that the electron in a hydrogen atom can only be in those circular orbits with angular momentum $L = n$, where n is a positive integer and, coincidentally, the principal quantum number we introduced in the previous paragraph. Using appropriate units, we may replace GMm by 1. This is equivalent to saying that the radius ², a , of an electronic circular orbit can only be these discrete values with $a = n^2$. In these orbits, the energy of the electron is also discrete and can be written as

$$E_n = -\frac{1}{2n^2}. \quad (1.4)$$

The orbital period is $T = 2\pi n^3$. The Bohr model and Kepler's solar system give us a first insight into the electron's motion inside a hydrogen atom. Within the Bohr model, the relation of energy, period, and characteristic length scale of an electron in a hydrogen atom with the principal quantum number n can be found in Table 1.1.

The Bohr model is very similar to Kepler's solar system, but it's not a correct description of a hydrogen atom. The main difference of a hydrogen atom from the solar system is the Heisenberg uncertainty principle in quantum mechanics. The uncertainty principle states that the position and momentum of an electron cannot be obtained precisely at the same time, which is

$$\delta x \cdot \delta p \geq \frac{1}{2}. \quad (1.5)$$

²Since circle is a specialization of ellipse, the radius of a circle can also be expressed using the length of semi-major axis in an ellipse.

Table 1.1.
Relations of the physical quantities with the principal quantum number in a hydrogen atom

physical quantities	relation with n
total energy E	$-1/(2n^2)$
orbital period T	$2\pi n^3$
length of semi-major axis a	n^2

In non-relativistic quantum mechanics, this is equivalent to

$$\delta E \cdot \delta t \geq \frac{1}{2}. \quad (1.6)$$

Combining the Eq. (1.6) and Table 1.1 gives the *relative* uncertainty, which is

$$\frac{\delta E}{|E|} \cdot \frac{\delta t}{T} \geq (2\pi n)^{-1}. \quad (1.7)$$

Equation 1.7 shows that the relative uncertainty of an electron decreases as the principal quantum number n increases. Thus, the concept of Rydberg electron can be introduced, which is an electron with a large principal quantum number n .

A Rydberg electron usually has a much longer radiative life time, and larger electric dipole moment than a low-lying electron. Also, a coherent superposition of Rydberg wave packets behaves more classically than a low-lying electron [1, 2].

1.2 Dynamics of two Rydberg electrons

The dynamics of an atom with two electrons is a much harder problem than that of a one-electron atom. The study of correlations between two bound electrons has remained an interesting topic since the development of quantum mechanics in the early 20th century. The Coulomb interaction is a prototype of coupled degrees of freedom in atomic physics. Thus, understanding the correlations between two electrons can help us understand more complicated atoms and molecules. In recent years, numerous experiments have been performed using ultrafast laser pulses to observe, create,

and control different two-electron processes [3–7], where most of the experiments are focused on resonant transitions in low-lying states. In contrast to low-lying states, the novel properties of highly excited Rydberg states make them attractive targets of study. Many experimental and theoretical investigations of Rydberg electrons have been conducted in the past century. We will introduce some of them related to this dissertation.

It is well-known in astronomy that the general three-body problem with the $1/r$ potential and comparable masses is non-integrable and chaotic. It's also hard to find analytic solutions to the Schrödinger equation for a two-electron atom. Various non-perturbative numerical methods have been developed to solve for the wave function of a two-electron atom, including time-dependent close coupling [8], R-matrix [9], multiconfigurational time-dependent Hartree-Fock (MCTDH) [10], complex rotation [11], hyperspherical [12], and other methods [2]. However, most quantum mechanical methods face computational power issues when dealing with highly excited Rydberg electrons due to the large spatial range, long time scale of substantial interactions, and strong mixing among enormous numbers of basis functions.

Early research showed that Rydberg electrons behave more classically than electrons in low-lying states [1,2]. This suggests the use of well-studied classical mechanics to investigate two-electron atoms. The classical trajectory Monte Carlo (CTMC) method will be used in this dissertation.

Since the CTMC method uses classical trajectories of particle-like electrons to study the dynamics, the method gives no phase information of the wave functions. If a method cannot compute the interferences between electronic wave functions, it can give wrong answers on spatial distributions and other physical quantities. In an example of the coherent state of a quantum harmonic oscillator, the localized spatial and momentum distributions also satisfy the classical Hamilton equations. A particle in the coherent state behaves classically, and its motion can be described with the classical Hamilton equations. Similarly, we use Rydberg wave packets with a spread of energies instead of Rydberg states with definite energies in the experimental and

theoretical model. Thus, the CTMC method can give results that well approximate the quantum calculations.

Rydberg states can be superposed to generate spatially localized Rydberg wave packets [13, 14]. Studies of dynamics of a single Rydberg wave packet were started in the 1980s. Some early experimental results are in [14–18], that mainly focused on the generation, detection, and manipulation of these Rydberg wave packets. Several later experiments generated a one electron Rydberg wave packet, and observed time-dependent autoionization of its interaction with the inner ionic core [19, 20]. There are also several studies of interactions between Rydberg wave packets and external electric fields [21, 22]. However, there are only a few experimental studies on the dynamics of double Rydberg wave packets [23–26]. Recently, experiments done by Zhang et al. in Ref. [26] studied the time evolution of two highly excited Rydberg wave packets. Their experimental and numerical results were in good agreement and showed that substantial energy and angular momentum exchanges between the two electrons can happen in just a few Rydberg periods. This motivates us to theoretically study the time-dependent dynamics of two Rydberg wave packets where only a few numerical methods [27, 28] have been introduced, and the dynamics has not been systematically studied before. We will use a grid of points for the radial part of the wave function; the additional electron introduces extra dimensions in the spatial grids. For a one-electron problem with cylindrical symmetry (for example, an atom in an electric field), the spatial grid is two-dimensional including the radial coordinate and the angular channels with different ℓ , since the magnetic quantum number m is conserved. For a two-electron problem with no external fields, the spatial grid is four-dimensional including radial coordinates r_1, r_2 , total angular momentum L , and coupled angular channels $|(\ell_1, \ell_2)L\rangle$. As a special case of $L = 0$, which means $\ell_1 = \ell_2$, the spatial grid would be three-dimensional. The additional dimensions in a finite difference method can greatly increase the memory needed to store wave functions, and the number of steps to propagate the whole wave function. Several numerical studies have been performed with basis expansion techniques and coordinate transformations [27]. A

method [28] based on the time-dependent close coupling method [8] will be used in this dissertation to propagate wave functions and to study dynamics of two Rydberg wave packets.

1.3 Outline of dissertation

This dissertation covers three major topics. In Chap. 2, the energy shift and state mixing of Rydberg atoms in ponderomotive optical traps are studied. In Chap. 3, we focus on the rapid autoionization and angular momentum exchanges between two Rydberg wave packets in an atom. In Chaps. 4 and 5, the dynamics of two Rydberg electrons are extended to the post-collision interaction (PCI) model. Chapter 4 introduces the PCI in a below-threshold photo-excitation followed by Auger decay model, while Chap. 5 introduces the PCI in a sequential photo-ionization model. Finally, in Chap. 6, the ionization behavior of Rydberg atoms and wave packets by scaled terahertz single-cycle pulses are studied. All of these studies are based on theoretical derivations and numerical calculations.

In Chap. 2, we present a degenerate perturbation analysis in the spin-orbit coupled basis for Rydberg atoms in an optical trap. The perturbation matrix is found to be nearly the same for two states with the same total angular momentum j , and orbital angular momentum number l differing by 1. The same perturbation matrices result in the same state-mixing and energy shift. We also study the dependence of state mixing and energy shift on the periodicity and symmetry of the ponderomotive potentials induced by different optical traps. State mixing in a one-dimensional lattice formed with two counter-propagating Gaussian beams is studied and yields a state-dependent trap depth. We also calculate the state-mixing in an optical trap formed by four parallel, separated, and highly focused Gaussian beams.

In Chap. 3, fully quantum and classical calculations on a helium atom with two excited, radially localized Rydberg wave packets are performed. The differences between classical and quantum methods are compared for a wide range of principal

quantum numbers to study the validity of the classical method for low-lying states. The effects of fast terahertz single-cycle pulses on an atomic system with one or two Rydberg wave packets are also studied using classical equations of motion. These results suggest that single-cycle pulses can be used as time-resolved probes to detect motion of the wave packets and to investigate autoionization properties

In Chap. 4, the two-electron correlation model is further extended to the post-collision interaction (PCI) in Auger decay. We focus on the post-collision interaction in Auger processes where the photoelectron energy is near or below the ionization threshold. Time-dependent quantum and classical calculations are performed. When the photoelectron is more deeply bound, interference patterns can be seen in the angular and photoelectron energy distributions. These interference patterns are visible in quantum calculations, but not in purely classical calculations. A semiclassical analysis using the actions from two-path trajectories gives the relative locations of the interference maxima very close to those from the full quantum calculations.

In Chap. 5, the post-collision interaction (PCI) is also studied in the two-electron sequential ionization model. Similar interferences are also found in double continuum wave packets from a two-step time-delayed photoionization of a two-electron atom. Properties of the interferences are studied in detail with respect to laser pulse time widths, laser frequency chirping, and ionization time delay. The effects of these physical quantities on the resulting interferences are discussed.

Finally, in Chap. 6, we focus on the strong field ionization behavior when a one-electron Rydberg atom is exposed to a terahertz single-cycle pulse. Fully three-dimensional time-dependent Schrödinger equation and classical trajectory Monte Carlo calculations are performed. Ionization from stationary eigenstates and Rydberg wave packets are focused, and it is found that the ionization properties can be different for the two cases. All of the pulse parameters and physical quantities are scaled versus the principal quantum number, n . The ionized electron's radial, energy, and angular distributions are investigated for different n , and the quantum results are in-

terpreted using a semiclassical method. The scaling relations of quantum interference amplitudes are discussed.

2. ENERGY SHIFT AND STATE MIXING OF RYDBERG ATOMS IN PONDEROMOTIVE OPTICAL TRAPS

This chapter is directly taken from *J. Phys. B*, **49**, 164005 (2016) [29] with minor differences, where the original draft was written by Xiao Wang.

2.1 Introduction

Laser cooling and trapping of atoms have been important topics in the past couple decades. Optical trapping originates from the idea that neutral atoms can be polarized and have dipole energy in an oscillating electric field causing an energy shift that can be used to manipulate the atoms [30]. Optical trapping has some properties different from other atom traps, such as low trap-induced shifts, highly controllable trap depths. Typical optical trap induced shifts and trap depths are at the MHz level, and the effects caused by optical traps on the atomic internal states are extremely small [31]. These properties make optical trapping a very attractive system in different sub-fields. Optical trapping has been widely used in Bose-Einstein condensates [32], quantum computing [33], and other systems.

Innovative properties emerge when we use Rydberg atoms instead of ground state atoms in an optical trap due to the fact that the size of a Rydberg atom is comparable to the optical lattice period, which is the wavelength of laser beams. Ponderomotive optical traps are based on the fact that an electron oscillates with the same frequency of a highly oscillating electric field, and the time averaged kinetic energy acts as the trapping potential of the atom [34]. Recently, trapping Rydberg atoms based on the ponderomotive force has been studied in several works [34–36]. Most studies are related to a one-dimensional ponderomotive optical lattice formed by two counter-propagating Gaussian beams, since their interference gives a cosine

shape beam intensity and trapping potential. Rydberg atoms in states with different principal quantum numbers n could feel different trapping depths, and the trapping depth in different nS states have been studied in Ref. [37].

Moreover, the angular distribution of the electron in a Rydberg atom also has a significant effect on the ponderomotive energy shift. Trapping properties of Rydberg atoms in high- l states in a one-dimensional lattice have been theoretically studied in Ref. [38]. Also the dependence of trap depth on the angular wavefunction has been experimentally studied in Ref. [36]. The dependence of ground-state atoms on magnetic quantum number m was studied in the late 1980s [39]. However, there has been no systematic theoretical analysis on the energy shift, trap depth and state mixing of Rydberg atoms with low- l in a ponderomotive potential including the effect of spin-orbit coupling. For atoms with small orbital angular momentum l , spin orbit coupling can have significant effects on the angular distribution of electrons. These low- l states with spin-orbit coupling could have different trapping properties compared with nS states.

The state-dependent trap depths of Rydberg atoms provide a new technique that could be used in different systems. The low trap-induced shifts and long coherence times of Rydberg atoms in a ponderomotive optical trap are advantages in different systems such as Bose-Einstein condensates of Rydberg atoms [40], high precision spectroscopy [41, 42], and quantum gate operations [43]. Also, we can change the parameters of the trap to minimize the difference of trap-induced shifts between ground and Rydberg states. This would give a high trapping efficiency when we excite atoms from ground states to Rydberg states [35].

In this chapter, we present a degenerate perturbation analysis of a one-electron Rydberg atom in ponderomotive potentials including the effect of spin-orbit interactions. The method we use here is similar to that in Ref. [38]. We show that the energy shift and state mixing only depend on total angular momentum j , and there is almost no difference for two states with orbital angular momentum $l = j \pm 1/2$. In Sec. 2.2.1, we present the origin of ponderomotive optical trapping, and the method

we used for perturbation analysis. In Sec. 2.2.2, we calculate the perturbation matrix in the degenerate spin-orbit coupled basis with given j . In Secs. 2.2.3, 2.2.4, we study the state mixing under special symmetry and periodicity properties of the potential. In Sec. 2.3, we give the numerical result of our analysis in two specific potentials: a one-dimensional lattice formed by two counter-propagating beams and an optical trap formed by four parallel and separated beams. The SI units are used in this chapter.

2.2 Theoretical analysis of the energy shift and state mixing

2.2.1 Introduction of ponderomotive force and ponderomotive energy

Optical trapping of a Rydberg atom originates from the ponderomotive force. A free electron in a highly oscillating electric field with amplitude E and angular frequency ω oscillates with the frequency of the field. The time averaged kinetic energy is given by

$$V = \frac{e^2 E^2}{4m_e \omega^2}, \quad (2.1)$$

where $-e$ and m_e are the electron charge and mass, respectively. Thus, the time averaged kinetic energy of the electron acts as an effective potential energy for the atom.

Since a Rydberg electron has a large size distribution and spends most of its time far away from the atom nucleus, we can consider it as a quasi-free electron and calculate the spatial average of the ponderomotive potential. The atom nucleus has a much larger mass than the electron, so its ponderomotive energy is far smaller than the electron's and can be neglected here. Suppose the atom is in a space-dependent electric field, then the adiabatic ponderomotive shift can be calculated as [34]

$$V_{\text{ad}}(\mathbf{R}) = \int d^3\mathbf{r} V(\mathbf{r} + \mathbf{R}) |\psi(\mathbf{r})|^2, \quad (2.2)$$

where $\mathbf{R}$ is the coordinate of nucleus, and $\mathbf{r}$ is the electron coordinate relative to the nucleus. $\psi(\mathbf{r})$ is the electron wavefunction in the Rydberg atom. $V(\mathbf{r} + \mathbf{R})$ is the space-dependent ponderomotive shift for a free electron, which is proportional

to the square of electric field amplitude as in Eq. (2.1). The electric-field amplitude $E(\mathbf{r} + \mathbf{R})$ is time-independent as a result of laser-formed standing waves, which leads to a spatial potential $V(\mathbf{r} + \mathbf{R})$. Thus V_{ad} is the spatial average of the free electron ponderomotive energy weighted by the electron distribution in a given state $\psi(\mathbf{r})$. This space dependent potential $V_{\text{ad}}(\mathbf{R})$ can be used as an optical atom trap.

This ponderomotive energy gives an extra potential in the Schrödinger equation and it can couple states together. However, since the energy, V_{ad} , is usually not very large, we need to have degenerate or nearly degenerate states to have substantial mixing. The method we use is based on the degenerate perturbation theory, and we expand the perturbing potential in a degenerate or near degenerate basis. Then we diagonalize the perturbation matrix to study properties of energy shift and state mixing [38].

Suppose we have an atom in a set of degenerate or near degenerate states, e.g. ψ_1, ψ_2 . Then the perturbation matrix can be calculated as

$$V_{\text{ad}}(\mathbf{R}) = \begin{pmatrix} V_{\text{ad},11}(\mathbf{R}) & V_{\text{ad},12}(\mathbf{R}) \\ V_{\text{ad},21}(\mathbf{R}) & V_{\text{ad},22}(\mathbf{R}) \end{pmatrix}, \quad (2.3)$$

where

$$V_{\text{ad},ij}(\mathbf{R}) = \int d^3\mathbf{r} \psi_i^*(\mathbf{r}) V(\mathbf{r} + \mathbf{R}) \psi_j(\mathbf{r}). \quad (2.4)$$

Therefore, state ψ_1, ψ_2 can be coupled by the ponderomotive potential, and their degeneracy could be lifted due to the perturbation of the potential.

2.2.2 Perturbation matrices of atoms in different states

We write the Hamiltonian of a one-electron atom as

$$H = H_0 + H_{\text{SOC}} + V, \quad (2.5)$$

where H_0 is the unperturbed Hamiltonian of the atom, H_{SOC} is the spin-orbit coupling (SOC) correction, and V is the ponderomotive potential. The free electron

ponderomotive shift can be obtained at the MHz level [37], which mainly depends on the power, focal diameter and wavelength of the laser beams used in experiments. For the $n = 50$ state of Rb, the spin-orbit splitting is zero for an s state, 818 MHz for a p state, 92.7 MHz for a d state, and 1.27 MHz for an f state [41, 42]. For Rb 50 S, P, or D Rydberg states, the ponderomotive shifts are approximately 10 MHz as described in Sec. 2.3.1, which is much smaller than the corresponding spin-orbit splitting. In this case, we should consider the ponderomotive potential as a perturbation in the spin-orbit coupled basis. If the spin-orbit splitting is much smaller than the ponderomotive caused coupling between different l 's or j 's, we should consider the ponderomotive perturbation in the basis of pure orbital states.

We start with the atom in an $S_{1/2}$ state; this state is degenerate for $m_j = \pm 1/2$. The angular wavefunctions for these states are

$$\left| l = 0, s = \frac{1}{2}, j = \frac{1}{2}, m_j = +\frac{1}{2} \right\rangle = \left| l = 0, m_l = 0 \right\rangle \left| s = \frac{1}{2}, \uparrow \right\rangle, \quad (2.6)$$

$$\left| l = 0, s = \frac{1}{2}, j = \frac{1}{2}, m_j = -\frac{1}{2} \right\rangle = \left| l = 0, m_l = 0 \right\rangle \left| s = \frac{1}{2}, \downarrow \right\rangle. \quad (2.7)$$

Here $|\uparrow\rangle$ and $|\downarrow\rangle$ denote the electron in the spin-up and spin-down states, respectively. We use the method in Sec. 2.2.1 to calculate the perturbation matrix. These matrix elements can be calculated as

$$V_{m_j, m'_j}(\mathbf{R}) = \langle n, l, j, m_j | V(\mathbf{R}) | n, l, j, m'_j \rangle, \quad (2.8)$$

$$\begin{aligned} V_{\pm\frac{1}{2}, \pm\frac{1}{2}}(\mathbf{R}) &= \left\langle m_j = \pm\frac{1}{2} \left| V(\mathbf{R}) \right| m'_j = \pm\frac{1}{2} \right\rangle, \\ &= \int d^3\mathbf{r} V(\mathbf{r} + \mathbf{R}) |\psi_{n00}(\mathbf{r})|^2 \cdot \langle \uparrow | \uparrow \rangle \text{ or } \langle \downarrow | \downarrow \rangle, \\ &= \int r^2 dr R^2(r) \int d\Omega \left[Y_{00}^*(\theta, \varphi) Y_{00}(\theta, \varphi) \right] V(\mathbf{r}'), \end{aligned} \quad (2.9)$$

$$\begin{aligned} V_{\pm\frac{1}{2}, \mp\frac{1}{2}}(\mathbf{R}) &= \left\langle m_j = \pm\frac{1}{2} \left| V(\mathbf{R}) \right| m'_j = \mp\frac{1}{2} \right\rangle, \\ &= \int d^3\mathbf{r} V(\mathbf{r} + \mathbf{R}) |\psi_{n00}(\mathbf{r})|^2 \cdot \langle \uparrow | \downarrow \rangle \text{ or } \langle \downarrow | \uparrow \rangle, \\ &= 0. \end{aligned} \quad (2.10)$$

Here $R(r)$ is the radial wavefunction of the Rydberg electron, and the $Y_{lm}(\theta, \varphi)$ are spherical harmonics. Note these matrix elements depend on the position of the nucleus, thus the perturbation matrix V is also position-dependent. That means the perturbation matrix has different eigenvalues when the atom is located at different positions in the potential. In Eq. (2.9) and Eq. (2.10), the ponderomotive potential shifts depend on the shape of the electric field in $V(\mathbf{R})$ from Eq. (2.1), on the radial wavefunction $R(r)$, and on the angular distribution of the electron. Rydberg states with the same n and small difference in l have similar radial distributions (e.g. nS, nP, and nD) on the distance scale over which $V(\mathbf{R})$ varies. The radius of their maximum radial distribution are approximately $2(n - \mu_{jl})^2$. The quantum defect μ_{jl} is small compared with the principal quantum number n of Rydberg states, and has a small relative effect on the radial wavefunction.

As a result, the angular part of the integrand of a matrix element V_{m_j, m'_j} will be an important factor in the determination of the coupling between different states. If two matrix elements have the same radial wavefunction and angular integrand, they will have the same integral, which means the same perturbation matrix element. Also, if an angular integrand vanishes, its corresponding element also vanishes. Therefore, it is beneficial to investigate the properties of the angular integrand for different Rydberg states.

For convenience, we can write the angular part of the integrand from the wavefunctions as the matrix element of a new matrix, the angular matrix $\tilde{\rho}$. Extract the angular integrands from the wavefunctions in Eq. (2.9) and Eq. (2.10), the angular matrix elements $\tilde{\rho}_{m_j, m'_j}$ of $S_{1/2}$ state can be written as

$$\tilde{\rho}_{\pm\frac{1}{2}, \pm\frac{1}{2}} = Y_{00}^* Y_{00}, \quad (2.11)$$

$$\tilde{\rho}_{\frac{1}{2}, -\frac{1}{2}} = \tilde{\rho}_{-\frac{1}{2}, \frac{1}{2}}^* = 0, \quad (2.12)$$

which can be written in the more compact form

$$\tilde{\rho} = \begin{pmatrix} Y_{00}^* Y_{00} & 0 \\ 0 & Y_{00}^* Y_{00} \end{pmatrix}. \quad (2.13)$$

We call this matrix the angular matrix of a one-electron system in Rydberg $S_{1/2}$ state.

Similar to the case for an $S_{1/2}$ state, if we consider the atom in a Rydberg $P_{1/2}$ state, we can use Clebsch-Gordan coefficients to convert the spin-orbit coupled basis into an orbital basis (angular part), which is

$$\left| l = 1, s = \frac{1}{2}, j = \frac{1}{2}, m_j = +\frac{1}{2} \right\rangle = -\sqrt{\frac{1}{3}} Y_{10} |\uparrow\rangle + \sqrt{\frac{2}{3}} Y_{11} |\downarrow\rangle, \quad (2.14)$$

$$\left| l = 1, s = \frac{1}{2}, j = \frac{1}{2}, m_j = -\frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} Y_{10} |\downarrow\rangle - \sqrt{\frac{2}{3}} Y_{1,-1} |\uparrow\rangle. \quad (2.15)$$

Matrix elements of the angular matrix of a $P_{1/2}$ state can be written as

$$\tilde{\rho}_{\pm\frac{1}{2}, \pm\frac{1}{2}} = \frac{1}{3} Y_{10}^* Y_{10} + \frac{2}{3} Y_{11}^* Y_{11} = Y_{00}^* Y_{00}, \quad (2.16)$$

$$\tilde{\rho}_{\frac{1}{2}, -\frac{1}{2}} = \tilde{\rho}_{-\frac{1}{2}, \frac{1}{2}}^* = \frac{\sqrt{2}}{3} (Y_{11}^* Y_{10} + Y_{10}^* Y_{1,-1}) = 0, \quad (2.17)$$

which means all matrix elements of the angular matrix of $P_{1/2}$ state are exactly the same as for the $S_{1/2}$ state.

If we have the atom in a Rydberg $P_{1/2}$ state, no matter what shape the ponderomotive potential is, the two states $|m_j = \pm 1/2\rangle$ are never mixed just as for the $S_{1/2}$ case. Each of them is an eigenstate of this system. They also have the same energy shift, which means the ponderomotive potential cannot split the $P_{1/2}$ state.

Similarly, we find that the angular matrix of the $P_{3/2}$, and $D_{3/2}$ states are the same:

$$\tilde{\rho} = \begin{pmatrix} Y_{11}^* Y_{11} & \sqrt{\frac{2}{3}} Y_{11}^* Y_{10} & \sqrt{\frac{1}{3}} Y_{11}^* Y_{1,-1} & 0 \\ \sqrt{\frac{2}{3}} Y_{11} Y_{10}^* & \frac{1}{3} Y_{11}^* Y_{11} + \frac{2}{3} Y_{10}^* Y_{10} & 0 & \sqrt{\frac{1}{3}} Y_{11}^* Y_{1,-1} \\ \sqrt{\frac{1}{3}} Y_{11} Y_{1,-1}^* & 0 & \frac{1}{3} Y_{11}^* Y_{11} + \frac{2}{3} Y_{10}^* Y_{10} & -\sqrt{\frac{2}{3}} Y_{11}^* Y_{10} \\ 0 & \sqrt{\frac{1}{3}} Y_{11} Y_{1,-1}^* & -\sqrt{\frac{2}{3}} Y_{11} Y_{10}^* & Y_{11}^* Y_{11} \end{pmatrix}. \quad (2.18)$$

Since Eq. (2.18) is an Hermitian matrix, we can use the fact that $Y_{lm}^* = (-1)^m Y_{l,-m}$, and the product of two spherical harmonics can be expanded as a linear combination of spherical harmonics. Then we can re-write the matrix Eq. (2.18) as

$$\tilde{\rho} = \begin{pmatrix} \frac{5Y_{0,0}^* - \sqrt{5}Y_{2,0}^*}{10\sqrt{\pi}} & \frac{Y_{2,-1}^*}{\sqrt{10\pi}} & -\frac{Y_{2,-2}^*}{\sqrt{10\pi}} & 0 \\ -\frac{Y_{2,1}^*}{\sqrt{10\pi}} & \frac{5Y_{0,0}^* + \sqrt{5}Y_{2,0}^*}{10\sqrt{\pi}} & 0 & -\frac{Y_{2,-2}^*}{\sqrt{10\pi}} \\ -\frac{Y_{2,2}^*}{\sqrt{10\pi}} & 0 & \frac{5Y_{0,0}^* + \sqrt{5}Y_{2,0}^*}{10\sqrt{\pi}} & -\frac{Y_{2,-1}^*}{\sqrt{10\pi}} \\ 0 & -\frac{Y_{2,2}^*}{\sqrt{10\pi}} & \frac{Y_{2,1}^*}{\sqrt{10\pi}} & \frac{5Y_{0,0}^* - \sqrt{5}Y_{2,0}^*}{10\sqrt{\pi}} \end{pmatrix}. \quad (2.19)$$

With our definition of the angular matrix element $\tilde{\rho}_{ij}$, we may now calculate the perturbation matrix element in Eq. (2.4) in another way:

$$\begin{aligned} V_{ij}(\mathbf{R}) &= \langle \psi_i | V(\mathbf{R}) | \psi_j \rangle \\ &= \int r^2 dr R^2(r) \int d\Omega \tilde{\rho}_{ij}(\theta, \varphi) V(\mathbf{R} + \mathbf{r}). \end{aligned} \quad (2.20)$$

We first do the radial part integral with the free electron ponderomotive potential $V(\mathbf{R} + \mathbf{r})$ and the radial wavefunction $R(r)$. We have

$$V_{ij}(\mathbf{R}) = \int d\Omega \tilde{\rho}_{ij}(\theta, \varphi) \hat{V}(\mathbf{R}, \theta, \varphi), \quad (2.21)$$

where

$$\hat{V}(\mathbf{R}, \theta, \varphi) = \int r^2 dr R^2(r) V(\mathbf{R} + \mathbf{r}). \quad (2.22)$$

Then we can expand $\tilde{\rho}_{ij}$ and $\hat{V}$ in the spherical harmonic basis and its complex conjugate basis. We have

$$\hat{V}(\mathbf{R}, \theta, \varphi) = \sum_{lm} a_{lm}(\mathbf{R}) Y_{lm}(\theta, \varphi), \quad (2.23)$$

$$\tilde{\rho}_{ij}(\theta, \varphi) = \sum_{l'm'} b_{l'm'} Y_{l'm'}^*(\theta, \varphi). \quad (2.24)$$

Thus Eq. (2.21) can be simplified as

$$V_{ij}(\mathbf{R}) = \int d\Omega \sum_{lm} \sum_{l'm'} a_{lm}(\mathbf{R}) b_{l'm'} Y_{lm}(\theta, \varphi) Y_{l'm'}^*(\theta, \varphi), \quad (2.25)$$

$$= \sum_{lm} a_{lm}(\mathbf{R}) \cdot b_{lm}. \quad (2.26)$$

The last step is based on the orthonormality of the spherical harmonics. In Eq. (2.22), $\widehat{V}$ is the radial averaged free electron ponderomotive potential using the radial wavefunction. Thus $\widehat{V}$ is an angular function and it's nearly independent of quantum number l , m , or m_j . We can find the expression of a_{lm} in Eq. (2.23) using Fourier analysis. We have

$$a_{lm}(\mathbf{R}) = \int d\Omega \widehat{V}(\mathbf{R}, \theta, \varphi) Y_{lm}^*(\theta, \varphi), \quad (2.27)$$

$$= \int d\Omega [Y_{lm}(\theta, \varphi)^*] \int r^2 dr R^2(r) V(\mathbf{R} + \mathbf{r}). \quad (2.28)$$

We name a_{lm} the multipole expansion value of a free electron ponderomotive potential $V(\mathbf{R})$ on the spherical harmonics Y_{lm} in the given radial wavefunction $R(r)$.

For a given potential, we can study its expansion values on different spherical harmonics to study the energy shift and state mixing for an electron in states with different l , m , or m_j . Usually the monopole term a_{00} is several times larger than the other higher order terms because spherical harmonics Y_{00} is always positive in θ and φ , thus there tends to be little cancellation in the integral for the matrix elements. Conversely, higher order spherical harmonics change sign in the integral region, and spherical harmonics with higher l , m flip sign more frequently than those with smaller l , m . Since positive and negative values are somewhat cancelled, the higher order expansion values are usually smaller than the lower order expansion values. Because a_{00} only exists in the diagonal terms with $m_j = m'_j$, the diagonal elements are usually several times larger than the off-diagonal elements. We will study the properties of a_{lm} in potentials with symmetric properties in Sec. 2.2.3.

For an electron in a spin-orbit coupled basis with given j and $l = j - 1/2$, the general expression for the element in the angular matrix, after tracing over the spin, can be written as

$$\tilde{\rho}_{m_j, m'_j}^{(j)} = C_1 C'_1 Y_{j-1/2, m_j-1/2}^* Y_{j-1/2, m'_j-1/2} + C_2 C'_2 Y_{j-1/2, m_j+1/2}^* Y_{j-1/2, m'_j+1/2}. \quad (2.29)$$

The element for j , $l = j + 1/2$ can be written as

$$\tilde{\rho}_{m_j, m'_j}^{(j)} = C_3 C'_3 Y_{j+1/2, m_j-1/2}^* Y_{j+1/2, m'_j-1/2} + C_4 C'_4 Y_{j+1/2, m_j+1/2}^* Y_{j+1/2, m'_j+1/2}. \quad (2.30)$$

These C_i, C'_i symbols are Clebsch-Gordan coefficients. We can expand the product of two spherical harmonics into a linear combination of spherical harmonics, and simplify Eq. (2.29) and Eq. (2.30). They generate the same expansion result (see Appendix Sec. 2.5 for the derivation):

$$\tilde{\rho}_{m_j, m'_j}^{(j)} = \sum_{L=|m_j-m'_j|}^{2j-1} b(m_j, m'_j, L) \times Y_{L, m_j-m'_j}^*, \quad (2.31)$$

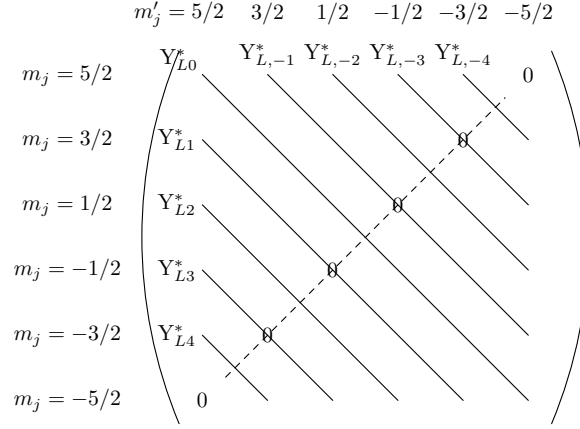
where

$$b(m_j, m'_j, L) = (-1)^{m_j+1/2} \sqrt{\frac{2L+1}{4\pi}} \sqrt{(2j+1+L)(2j-L)} \\ \times \begin{pmatrix} j - \frac{1}{2} & j - \frac{1}{2} & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j & L \\ -m_j & m'_j & m_j - m'_j \end{pmatrix}. \quad (2.32)$$

The brackets in Eq. (2.32) are Wigner 3j-symbol. We name this $b(m_j, m'_j, L)$ the expansion coefficient of an angular matrix element on spherical harmonics $Y_{L, m_j-m'_j}^*$. Note that all of the anti-diagonal matrix elements with $m_j + m'_j = 0$ vanish because of the parity in spherical harmonics. Also note that, according to Eq. (2.32), if $m_j = m'_j$ and $L = 0$, the coefficient multiplying the Y_{00} in the diagonal elements are all $1/\sqrt{4\pi}$. We will use this result for state mixing analysis in Sec. 2.2.4. In Eq. (2.31), the summation index L is in the range $|m_j - m'_j| \leq L \leq 2j - 1$ and L must be an even integer for the expansion coefficient to be non-zero. That means only Y_{00}, Y_{2m}, Y_{4m} , etc terms exist in the angular matrices, and only monopole, quadruple, hexadecapole, etc expansion values of the potential have an effect on the ponderomotive shift.

For example, we can use this analysis for the $D_{5/2}$ state to study the properties of its angular matrix. This is a 6×6 matrix, and we obtain the result in Fig. 2.1, where only diagonal elements contain summation of Y_{L0} terms. The first two off-diagonal lines have $Y_{L, \pm 1}$ terms, while the second two off-diagonal lines have $Y_{L, \pm 2}$ terms, etc. The dashed line in the matrix contains anti-diagonal elements, which are always zero. We will use this figure for symmetry analysis in Sec. 2.2.3.

Angular matrices always have the same form for the two spin-orbit coupled states with the same j , and l differing by 1. In this case, if the energy shift induced by the

Figure 2.1. Angular matrix of $D_{5/2}$ state.

ponderomotive potential is much smaller than that caused by the spin-orbit coupling, the total angular momentum number j determines the eigenvalues and eigenstates of the electron in a ponderomotive potential.

If we consider the atomic Hamiltonian without the spin-orbit coupling term, or if the spin-orbit splitting is much smaller than the ponderomotive shift, the cross terms between different j 's or l 's will be important for obtaining the correct states and energies. If these cross terms are comparable to or larger than the spin-orbit splitting, states between different j 's or l 's have significant mixing. This usually happens for Rydberg states with $l \geq 3$. For example, the natural energy splitting between $50F_{5/2}$ and $50F_{7/2}$ states is 1.27 MHz [42], which is smaller than the cross terms between them (about 5~10 MHz) caused by two Gaussian beams with power 1 W as described in Sec. 2.3.1. For electrons in these states, we need to calculate the perturbation matrix in a larger basis including $j = l \pm 1/2$ and other near degenerate states. This is equivalent to a pure orbital basis since electron spin has no explicit effect on ponderomotive potential. Properties of high- l atoms in ponderomotive potential have been studied in Ref. [38].

2.2.3 Symmetry analysis of the potential shape

We study those special potentials with rotational symmetry properties, and the effect of periodicity on the ponderomotive energy shift. Consider a potential with periodicity in φ , $V(r, \theta, \varphi) = V(r, \theta, \varphi + 2\pi/s)$, s is a positive integer, and $s \geq 2$. We use the conversion relation that $Y_{lm}^* = (-1)^m Y_{l,-m}$. Then we calculate the integral in Eq. (2.27):

$$\begin{aligned}
& \int_0^{2\pi} d\varphi V(\theta, \varphi) Y_{lm}(\theta, \varphi), \\
&= \int_0^{2\pi} d\varphi V(\theta, \varphi) f(\theta) e^{im\varphi}, \\
&= \int_0^{2\pi/s} d\varphi V(\theta, \varphi) f(\theta) \left[e^{im\varphi} + e^{im(\varphi+2\pi\frac{1}{s})} + e^{im(\varphi+2\pi\frac{2}{s})} + \dots + e^{im(\varphi+2\pi\frac{s-1}{s})} \right], \\
&= \begin{cases} \int_0^{2\pi/s} d\varphi V(\theta, \varphi) f(\theta) e^{im\varphi} \frac{1-\exp(2\pi mi)}{1-\exp(2\pi mi/s)} = 0 & \text{when } \exp(2\pi mi/s) \neq 1, \\ \int_0^{2\pi/s} d\varphi V(\theta, \varphi) f(\theta) e^{im\varphi} \cdot s & \text{when } \exp(2\pi mi/s) = 1. \end{cases} \quad (2.33)
\end{aligned}$$

When the common ratio $\exp(2\pi mi/s)$ is not 1 in the geometric summation in Eq. (2.33), m is not a multiple of s , and the integral vanishes. This gives the result that the expansion value a_{lm} in Eq. (2.27) is zero. Based on the fact that $Y_{lm}^* = (-1)^m Y_{l,-m}$, both values $a_{l,\pm m}$ are zero. Conversely, for those m 's which are multiples of s , the expansion values on these spherical harmonics don't vanish (zero is a multiple of any integer s).

For example, if a potential has φ -periodicity that $V(\varphi) = V(\varphi + \pi/2)$, we have $s = 4$. Multipole expansions of the potential with $M = 1, 2, 3, 5, 6, 7, \dots$ vanish, while $M = 0, 4, 8, \dots$ terms are non-zero. Suppose we have an atom in the $P_{3/2}$ or $D_{3/2}$ state. These two states have 4×4 angular matrices which can be found in Eq. (2.19), and the matrix elements consist of Y_{LM} with $|M| \leq 2$. Based on our analysis here, all of these off-diagonal matrix elements vanish for these two states, and only the diagonal elements are non-zero. As a result, $P_{3/2}$ and $D_{3/2}$ states would not mix in this periodic potential at this symmetric position.

Furthermore, suppose we have an atom in the $D_{5/2}$ state with the same periodic potential. In the angular matrix, only diagonal elements and $Y_{L,\pm 4}$ elements are non-zero, and all other elements vanish. Refer to Fig. 2.1, only the elements in the diagonal line and $Y_{L,\pm 4}$ lines have non-zero elements. We will analyse state mixing in this kind of potential in Sec. 2.2.4. Numerical results can be found in Sec. 2.3.3.

There is an interesting limit when $s \rightarrow \infty$, and it means that this potential is cylindrically symmetric and φ -independent. In this case, only the $m = 0$ terms don't vanish. This means, in the angular matrix, only the diagonal terms are non-zero, and the spin-orbit coupled or orbital eigenstates are never mixed in this potential. We can also get this result directly from the fact that cylindrically symmetric potential conserves the magnetic quantum number m . In this kind of potential, we may get the ponderomotive energy shifts directly from calculating the expectation value of the potential in the unperturbed states [36].

Similarly, we study potentials satisfying symmetric properties $V(\theta) = V(\pi - \theta)$, which corresponds to potentials having a mirror symmetry with respect to the x - y plane. We can calculate the integral (let $\theta' = \pi - \theta$)

$$\begin{aligned} \int_0^\pi d\theta \sin(\theta) V(\theta) P_l^m(\cos \theta) &= \int_\pi^0 -d\theta' \sin(\theta') V(\theta') P_l^m(-\cos \theta'), \\ &= \int_0^\pi d\theta' \sin(\theta') V(\theta') P_l^m(\cos \theta') (-1)^{l-m}. \end{aligned} \quad (2.34)$$

Here $P_l^m(\cos \theta)$ is the associated Legendre polynomial. Only even l are allowed in the matrix element expansion, so if m is an odd number, this integral vanishes. Therefore, only expansion values a_{LM} with both L, M even numbers are non-zero.

2.2.4 State mixing analysis based on symmetric potential

Some matrix elements vanish due to the symmetry properties of the potential and parity of the angular wavefunction. That leads to a simpler form of the perturbation matrix, and a simpler result for the state mixing. Generally, if a given potential doesn't have any special symmetry properties, most angular matrix elements are

non-zero. In this case, expansion values a_{L1} exist, which would make state mixing between two adjacent spin-orbit coupled states with $\Delta m_j = 1$, and finally leads to complicated state mixing between almost all states.

We can review the following properties of matrix diagonalization in linear algebra. Suppose we have a diagonal matrix H with diagonal elements $h_{11} \sim h_{nn}$. The eigenstates of this matrix are just n unit vectors. Then we add a perturbation to this matrix by setting $h_{ij} = h_{ji}^* = p$, and let all the other off-diagonal elements remain zero. We can find that only the state i, j are mixed in the new eigenstates. Also, if the off-diagonal term is much smaller than the difference between two corresponding diagonal terms, which means $|p| \ll |h_{ii} - h_{jj}|$, the coupling between state i, j is small. Conversely, if $|p|$ is comparable to $|h_{ii} - h_{jj}|$, the coupling between state i, j gets much stronger.

In the perturbation matrix of $j = 3/2$ states in Eq. (2.19), all coefficients multiplying the Y_{00}^* terms in the diagonal elements are $1/\sqrt{4\pi}$. This is also a general result for the perturbation matrix in all states, and it can be derived from Eq. (2.32). Thus the a_{00} terms are the overall energy shifts for all states, and have no effect on state mixing. Refer to Eq. (2.19), the differences between diagonal terms originate in Y_{20} . Off-diagonal terms consist of $Y_{2,\pm 1}$ and $Y_{2,\pm 2}$. As we discussed in the last paragraph, if expansion values $a_{2,\pm 1}$ or $a_{2,\pm 2}$ are comparable to a_{20} , the coupling between states with $\Delta m_j = 1$, or 2 would be much stronger. Since a_{00} has no effect on the state mixing, the state mixing of a $j = 3/2$ state in a ponderomotive potential turns into analysis and comparison of the quadruple expansions of the potential.

In our perturbation matrix, if a potential has symmetry properties and results in all a_{LM} with odd M vanishes, state mixing only exists between states with $\Delta m_j = 2$, and finally leads to state mixing among all states where Δm_j are even. Consider the 6×6 angular matrix for $D_{5/2}$ state in Fig. 2.1. If all a_{LM} with odd M vanish, the eigenstates would be states that mixed only within the two sets $m_j = 5/2, 1/2, -3/2$, and $m_j = 3/2, -1/2, -5/2$. Each set has 3 different methods of mixing. If we flip all signs of m_j in one mixing, we would get a corresponding mixed eigenstate in the other

set with the same energy shift. As an example, both states $|\phi_1\rangle$, $|\phi_2\rangle$ in Eq. (2.35) and Eq. (2.36) are eigenstates in the ponderomotive potential, and they have the same energy shifts.

$$|\phi_1\rangle = c_1 \left| m_j = \frac{5}{2} \right\rangle + c_2 \left| m_j = \frac{1}{2} \right\rangle + c_3 \left| m_j = -\frac{3}{2} \right\rangle, \quad (2.35)$$

$$|\phi_2\rangle = c_1^* \left| m_j = -\frac{5}{2} \right\rangle + c_2^* \left| m_j = -\frac{1}{2} \right\rangle + c_3^* \left| m_j = \frac{3}{2} \right\rangle. \quad (2.36)$$

Since the angular momentum j_z of these two states have equal magnitudes but opposite signs, they would be split if we apply a small magnetic field B_z . We will study the properties of $|\phi_1\rangle$ instead of $|\phi_2\rangle$ or their linear combinations.

Furthermore, if we consider a potential with only a_{L0} and $a_{L,\pm 4}$ expansion values, non-zero state mixing only exists between $\Delta m_j = 4$ such as the states with $m_j = 5/2, -3/2$, and $m_j = 3/2, -5/2$. States $m_j = \pm 1/2$ are not mixed with any other states in this symmetric potential, and are, thus, eigenstates in the optical trap.

State mixing of an atom in a potential with these symmetry properties can be found in Sec. 2.3.2.

2.3 Specific calculations for two traps

2.3.1 Counter-propagating beams as one-dimensional optical lattice

For an optical trap using two counter-propagating Gaussian beams in the experiment [35], the free electron ponderomotive potential can be written as

$$V(z) = \frac{e^2}{4m_e\omega^2} \times (E_0 e^{ikz} + E_0 e^{-ikz})^2 \quad (2.37)$$

$$= \frac{e^2 E_0^2}{m_e k^2 c^2} \times \cos^2(kz) \quad (2.38)$$

on the beam axis. The beam has a maximum intensity at $z = 0$, and a minimum at $z = \lambda/4$. We put an atom on the axis of the beam, and let the z -axis of the atom be the same with the beam axis. The atom would feel a cylindrically symmetric potential, which means it's φ -independent. Based on our analysis in Sec. 2.2.3, spin-orbit coupled states won't mix in this potential.

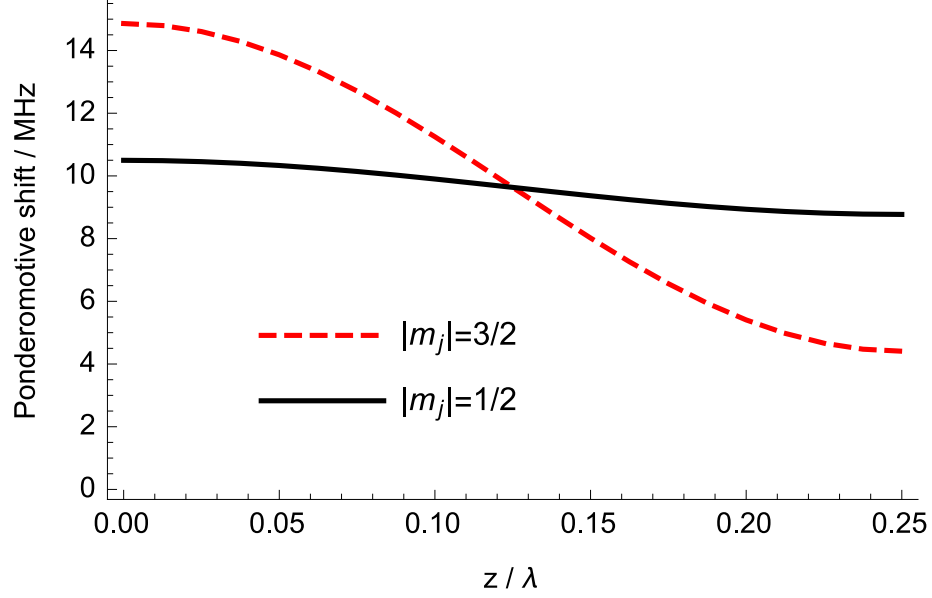


Figure 2.2. Eigenvalues of an atom in $50 D_{3/2}$ state located on the beam axis in a ponderomotive optical lattice. Parameters used in our calculation are: $P = 1.0$ W, $\lambda = 1064$ nm, $\omega_0 = 6.5$ μ m. These parameters correspond to a free electron ponderomotive shift 19.3 MHz at $z = 0$.

We calculate the eigenvalues of a $D_{3/2}$ state when the atom locates on the different positions on the axis. Plot of eigenvalues versus z -position of the atom can be found in Fig. 2.2. Before perturbed by the ponderomotive potential, $D_{3/2}$ has 4 degenerate states which are $m_j = \pm 3/2, \pm 1/2$. After perturbation, we found two different eigenvalues when $z \neq \lambda/8$. The ponderomotive energy partially lifts the degeneracy for $D_{3/2}$ states. States with the same absolute value of m_j are still degenerate. We also find that these two eigenvalues are the same at $z = \lambda/8$, which means a_{20} is zero at this point by comparing with the diagonal elements in Eq. (2.19). Therefore, the degeneracy of $D_{3/2}$ is not lifted at this point, and the state is still four-fold degenerate.

For the atom located at $z = z_0$, the potential can be simplified as

$$V(z, z_0) = V_0 \cos^2 [k(z - z_0)] \quad (2.39)$$

$$= \frac{V_0}{2} \left\{ 1 + \cos [2k(z - z_0)] \right\} \quad (2.40)$$

$$= \frac{V_0}{2} (1 + \cos 2kz_0 \cos 2kz + \sin 2kz_0 \sin 2kz). \quad (2.41)$$

In this expression, the ponderomotive potential consists of three parts. The first part $V_0/2$ is a constant shift, and its expansion in Eq. (2.28) only consists of monopole terms. It's the overall energy shift for all states. The third term $\sin 2kz$ has odd parity, and it vanishes in the integral with all Y_{LM} with even L . In the second term, $\cos 2kz_0$ is the atom position dependent coefficient, and it describes a cosine shape for the energy shift versus atom position z_0 . Also, the spatial average of $V_2 = \cos 2kz$ in a specific eigenstate determines the trap depth in that state.

In Fig. 2.2, states with larger $|m_j|$ have larger trap depth. In those experiments with the atom in a DC electric field polarized perpendicular to the beam axis [36], atoms are in the Stark effect eigenstates with z -axis of the atom perpendicular to the beam axis. We can do similar analysis for the trap depth of atoms in these states with different $|m_j|$, and principal quantum number n . The analytic result is consistent with the experimental observation in Ref. [35].

2.3.2 Symmetric case in a system with four parallel Gaussian beams

A model for trapping atoms using four parallel Gaussian beams has been introduced in Ref. [44]. Each beam is centered at one corner of a square. Two diagonal beams have parallel polarization, and two adjacent beams have perpendicular polarizations. The setup of this system can be found in Fig. 2.3, and Fig. 2 in Ref. [44]. This potential has good symmetries along the z -axis, $y = 0$ line, $y = x$ line, etc. It also has a mirror symmetry with respect to the $z = 0$ plane as described in Sec. 2.2.3. We study the properties of an atom located at these symmetric positions in this section, and located at asymmetric positions in the next section.

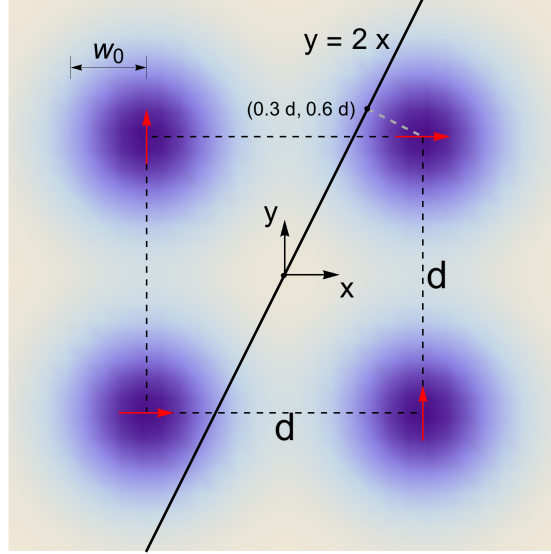


Figure 2.3. Setup of four parallel Gaussian beams system. Red arrows indicate the polarizations of beams. Parameters used in the calculation: $P=5$ mW, $w_0=1.5$ μm , $d=4$ μm , $\lambda=780$ nm, where P is the power of one laser beam, w_0 is the waist of a beam, d is the distance between two adjacent beams, and λ is the wavelength. A free electron has a ponderomotive shift of 12.7 kHz at the center of the square, and 1.94 MHz at the center of one beam.

Suppose the center of a cartesian frame is located at the center of the beam's square, and the z -axis is parallel with the beam axis. The free electron ponderomotive potential has the form

$$V(x, y, z) = \frac{e^2 E_0^2}{4m_e \omega^2} \left[\frac{w_0}{w(z)} \right]^2 \left\{ \left[u \left(x - \frac{d}{2}, y - \frac{d}{2}, z \right) + u \left(x + \frac{d}{2}, y + \frac{d}{2}, z \right) \right]^2 + \left[u \left(x - \frac{d}{2}, y + \frac{d}{2}, z \right) + u \left(x + \frac{d}{2}, y - \frac{d}{2}, z \right) \right]^2 \right\}, \quad (2.42)$$

where

$$u(x, y, z) = \exp \left[-\frac{x^2 + y^2}{w^2(z)} \right] \exp \left[-i \cdot \varphi(x, y, z) \right], \quad (2.43)$$

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R} \right)^2}, \quad (2.44)$$

$$\varphi(x, y, z) = kz + k \frac{x^2 + y^2}{2R(z)} - \eta(z), \quad (2.45)$$

$$R(z) = z \left[1 + \left(\frac{z_R}{z} \right)^2 \right], \quad (2.46)$$

$$\eta(z) = \arctan \left(\frac{z}{z_R} \right), \quad (2.47)$$

$$z_R = \frac{\pi w_0^2}{\lambda}. \quad (2.48)$$

The beam is highly focused so that the distance d is much larger than the beam waist w_0 . This can reduce the effect of interference near $z = 0$ plane. As z increases, the waist size $w(z)$ increases, which increases the interference among these four beams.

We can investigate the properties of an atom in the 100 D_{3/2} state and located on the $y = 0$ line in the $z = 0$ plane. The radius of this atom is approximately $2n^2 a_0 \approx 1 \mu\text{m}$, and it is comparable to d . Thus the energy shift and state mixing of this atom could have different properties when it is located at different positions in the potential. We can find from Fig. 2.3 that the potential has good symmetries when the atom is located on the $y = 0$ line in the $z = 0$ plane. When this atom is in the $z = 0$ plane, it feels a potential with $V(z) = V(-z)$. Based on our previous symmetry analysis in Eq. (2.34), all expansion values a_{LM} with odd M vanish. In addition, the atom feels the potential with a mirror symmetry $V(\varphi) = V(-\varphi)$. This kind of symmetric potential guarantees all of the perturbation matrix elements to be real, which leads to a real probability amplitude of the eigenstate in each spin-orbit coupled state. We plot the eigenvalues of the perturbation matrix in Fig. 2.4, and the probability of the corresponding eigenstate in each spin-orbit coupled state in Fig. 2.5.

The eigenvalue versus position curves have similar shapes with the free electron potential, which can be directly calculated from Fig. 2.3 and Eq. (2.42). They have

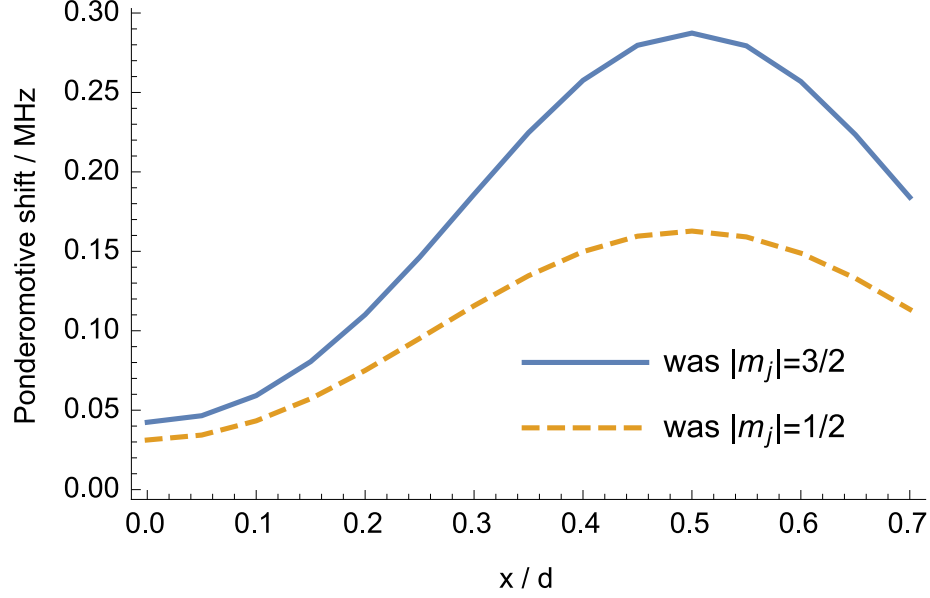


Figure 2.4. Energy shifts of an atom in $100 D_{3/2}$ state located on the $y = 0$ line in the $z = 0$ plane. “Was $|m_j| = 3/2$ ” means that when $x = 0$, the curve corresponds to the unmixed states $|m_j| = 3/2$.

the maximum energy shift at $x = 0.5d$ point. We also do the quadratic fit for this potential near the center $x = y = z = 0$, and the oscillating frequency of an Rb atom is of the order of $3 \sim 10$ kHz in the x - y plane. The exact frequency depends on the wavefunction and the oscillating angle of the atom [44].

In Fig. 2.5, when the atom in a $100 D_{3/2}$ state is located at the center $x = y = z = 0$ position, four m_j states are not mixed, which is because the potential has a $\pi/2$ angle rotational symmetry on φ at the center of the system. This figure shows the probability of the new eigenstates with $m_j = -3/2$ character at $x = 0$ in each SOC state. It gives the state coupling only between $m_j = -3/2$ and $m_j = 1/2$ states. Note that states $m_j = -1/2, 3/2$ have no contribution to this state mixing because expansion values $a_{l,\pm 1}$ and $a_{l,\pm 3}$ vanish due to the property of a mirror symmetric potential described in Eq. (2.34). State mixing only exists between $\Delta m_j = 2$. The state mixing gets stronger with the x -position of the atom, and reaches the maximum

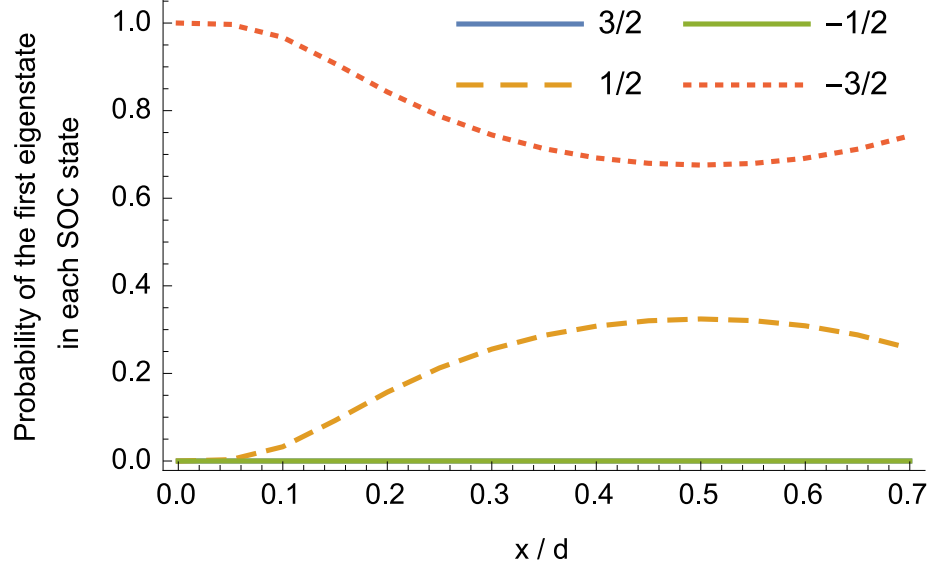


Figure 2.5. State mixing of an atom in $100 D_{3/2}$ state locate on the $y = 0$ line in the $z = 0$ plane. The vertical axis is the probability of the eigenstate in each SOC state m_j .

mixing at $x = 0.5 d$ which is the closest position to the center of two adjacent Gaussian beams on this line.

Based on our analysis in Eq. (2.35) and Eq. (2.36), we can flip the sign of all m_j 's in the first eigenstate, use the complex conjugate of their probability amplitudes as new amplitudes, and then we can get the second eigenstate for this system with the same energy (for convenience, we call the eigenstate in Eq. (2.5) the first eigenstate). There are also two other degenerate eigenstates with different energies from the first and second eigenstates. We can diagonalize a 4×4 perturbation matrix with a_{LM} vanishing for odd M , and get the analytic result for the other two eigenstates. If we write the first eigenstate as $c_1|1/2\rangle + c_2|-3/2\rangle$, the third eigenstate can be written as $c_1|3/2\rangle - c_2|-1/2\rangle$, and the fourth eigenstate can be written as $-c_2^*|1/2\rangle + c_1^*|-3/2\rangle$. Note here the first and the fourth eigenstates have their probabilities of $|1/2\rangle$ and $|-3/2\rangle$ exchanged, so does other two eigenstates.

Similarly, we can investigate the properties of an atom in $100 D_{3/2}$ state and located on the $y = 2x$ line in the $z = 0$ plane. The potential still has z -symmetric

properties, and only states with even Δm_j can mix in the eigenstates. Since the atom is no longer located on the $y = 0$ line, most of the perturbation matrix elements are no longer real numbers. The probability amplitudes of the eigenstates in the spin-orbit coupled states could be complex numbers. We plot eigenvalues in Fig. 2.6, and the probability of the eigenstates in each spin-orbit coupled state is shown in Fig. 2.7.

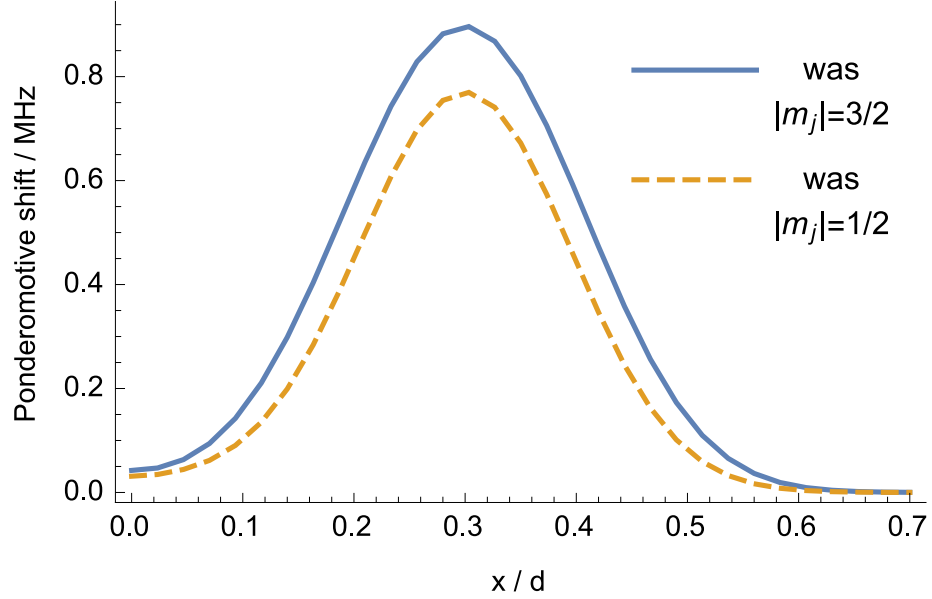


Figure 2.6. Energy shifts of an atom in $100 D_{3/2}$ state located on the $y = 2x$ line in the $z = 0$ plane. “Was $|m_j| = 3/2$ ” means that when $x = 0$, the curve corresponds to the unmixed states $|m_j| = 3/2$.

We can find from Fig. 2.6 that the eigenvalues reach the maximum when the atom is located at $(x, y) = (0.3d, 0.6d)$, which is the closest position to the center of $(d/2, d/2)$ Gaussian beam on this line.. The strongest state mixing of these two states appears at the same position in Fig. 2.7.

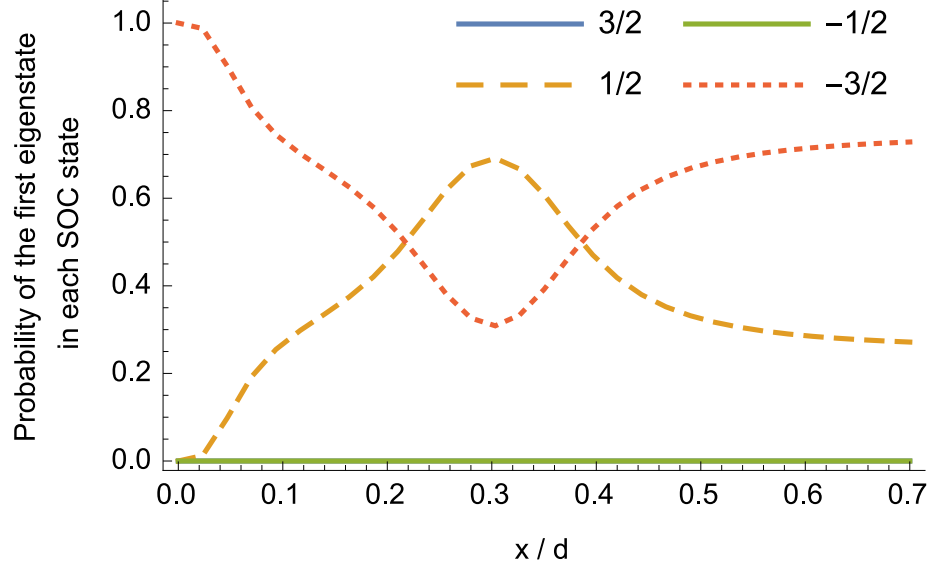


Figure 2.7. State mixing of an atom in 100 $D_{3/2}$ state locate on the $y = 2x$ line in the $z = 0$ plane. The vertical axis is the probability of the eigenstates in each SOC state m_j .

2.3.3 Asymmetric case in a system with four parallel Gaussian beams

As another example, we consider an atom in the state of 100 $D_{5/2}$, but let the atom locate on the line of $y = 2x$ in the $z = 5 \mu\text{m}$ plane. All other parameters of the optical trap remain the same with Sec. 2.3.2.

Since the atom is no longer in the $z = 0$ plane, it doesn't have the mirror symmetry that exists for the $z = 0$ plane. Then the expansion values on Y_{LM} with odd M terms become non-zero on the line of $y = 2x$. Based on our analysis in Sec. 2.2.4, the state coupling with $\Delta m_j = 1$ exists. As $z = 5 \mu\text{m}$ plane is close to the $z = 0$ plane, these odd M expansion values a_{LM} are small compared to the even M expansion values. As a result, the state mixing is mainly between $\Delta m_j = 2$ states, and only has small corrections for the other three states. Our calculated results of the eigenvalues versus the position of the atom can be found in Fig. 2.8, and three plots of the six eigenstates after mixing can be found in Fig. 2.9.

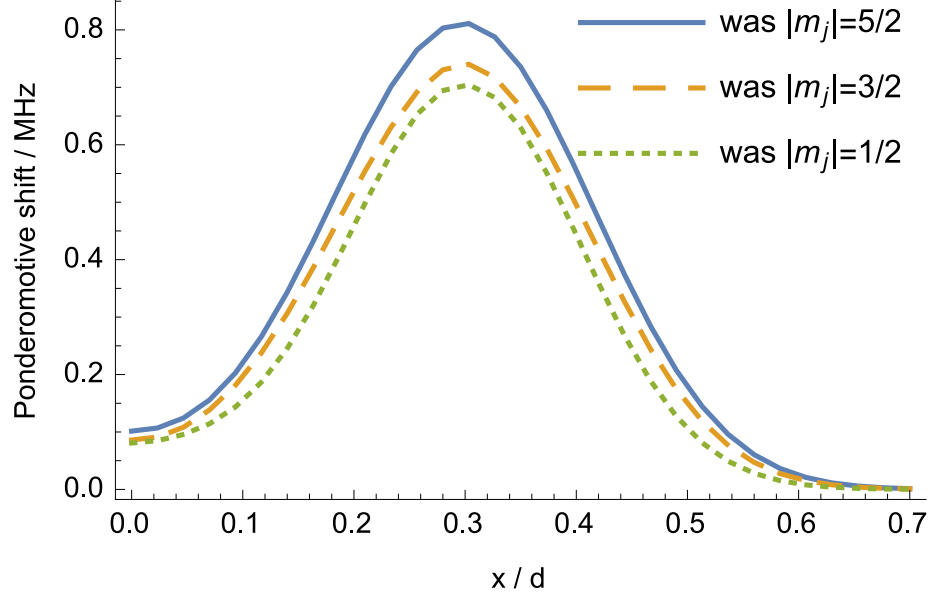


Figure 2.8. Energy shifts of an atom in $100 D_{5/2}$ state located on the $y = 2x$ line in the $z = 5 \mu\text{m}$ plane. “Was $|m_j| = 5/2$ ” means that when $x = 0$, the curve corresponds to the eigenstate mixed between $m_j = \pm 5/2$ and $\mp 3/2$, where $\pm 5/2$ is the main component of this state. “Was $|m_j| = 3/2$ ” means the eigenstate mixed between $\pm 3/2$ and $\mp 5/2$, where $\pm 3/2$ is the main component. “Was $|m_j| = 1/2$ ” means the eigenstate of $\pm 1/2$, and it was not mixed when $x = 0$.

We find that wavefunctions of different eigenstates have substantial difference at different positions in this potential, though their energy shifts are similar between each other.

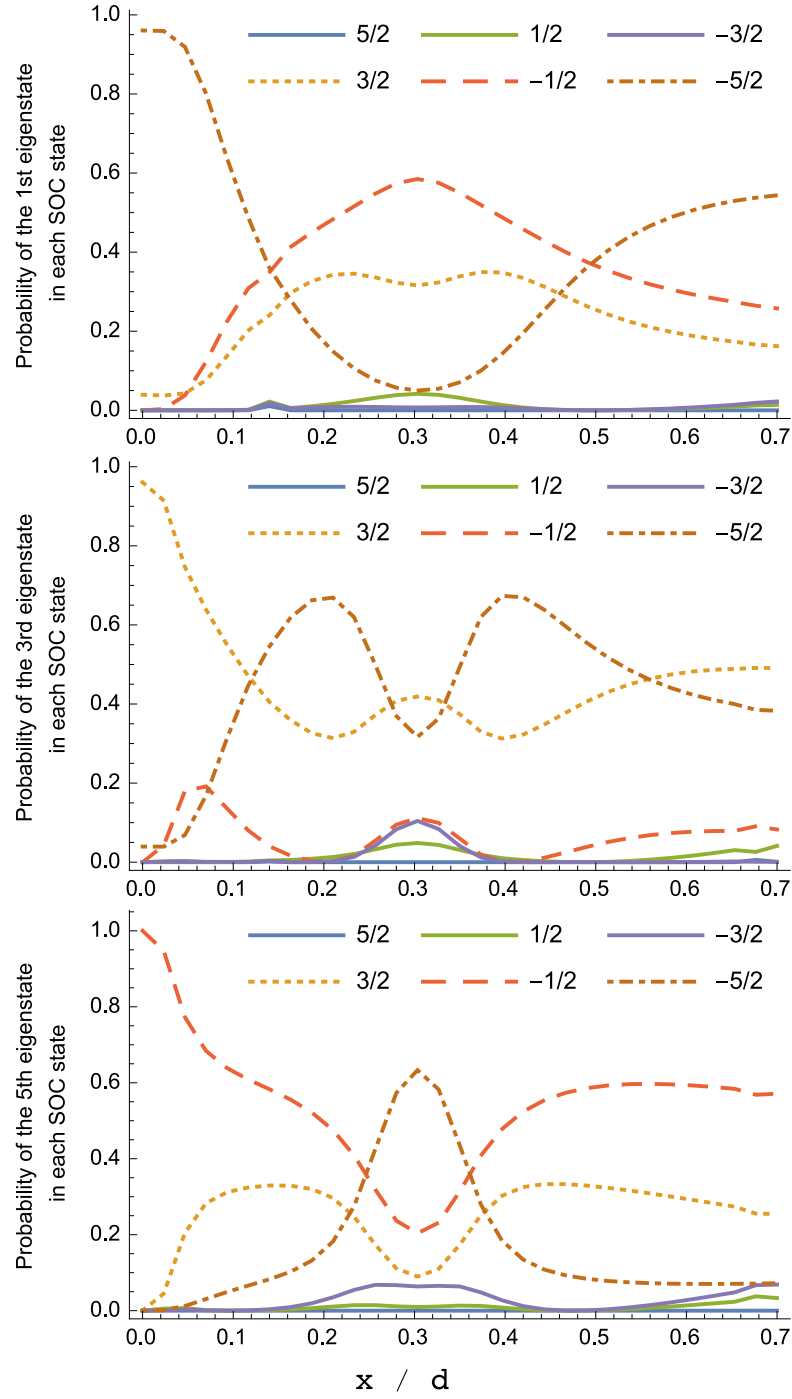


Figure 2.9. State mixing of an atom in $100 D_{5/2}$ state located on the $y = 2x$ line in the $z = 5 \mu\text{m}$ plane. The vertical axis is the probability of the eigenstates in each SOC state m_j . These graphs show the state mixing mainly among the states with $m_j = -\frac{5}{2}, -\frac{1}{2}, \frac{3}{2}$.

2.4 Conclusions

In this chapter, we investigated the effect of the ponderomotive force on a one-electron Rydberg atom. Using the wavefunction of a Rydberg electron, the spatial averaged ponderomotive energy of the Rydberg electron in an oscillating electric field acts as an effective potential energy of the Rydberg atom. This ponderomotive potential can couple degenerate or nearly degenerate states. Under the condition that the ponderomotive shift is much smaller than the spin-orbit coupling energy when $l \leq 3$, the effect of a ponderomotive potential can be analyzed using the degenerate perturbation theory in a spin-orbit coupled basis. We studied the energy shift and state mixing of a one-electron Rydberg atom with given orbital angular momentum l and total angular momentum j in different ponderomotive potentials.

First, we did multipole expansion of a ponderomotive potential. Then we studied matrix elements of a general spherical harmonics in a spin-orbit coupled basis to study the effect of spin-orbit coupled states' wavefunctions on the perturbation matrix. Our derivations showed that the eigenvalues and eigenstates mainly depend on j and n but hardly depend on l . As a result, the $|m_j = \pm 1/2\rangle$ states for $j = 1/2$ are never mixed in a ponderomotive potential.

Some potentials have periodicity or symmetry properties. Under special symmetries, expansion values of some spherical harmonics in a given potential vanish. These zero matrix elements are usually on off-diagonal lines of the perturbation matrix, and lead to a simpler ponderomotive energy shift and state mixing. If the expansion value of a ponderomotive potential in Y_{LM} is zero, there is usually no state mixing between $\Delta m_j = M$ states. This gives a method to study the state mixing between two states by directly calculating the expansion value of the given potential in spherical harmonics. State mixing in this symmetric situation is still valid approximately if the atom is only slightly deviated from the symmetric or periodic position, because the expansion values of the potential in Y_{LM} remain very small even if they are not exactly zero.

We also calculated state mixing and energy shift in a one-dimensional optical lattice formed by two parallel Gaussian beams. Since this potential is cylindrically symmetric, there is no state mixing in this potential. Our result shows that energy shifts of different states are cosine functions versus the atom position on the beam axis. We also analyse the trap depth for states with different angular momentum in this potential, which mainly depends on the polarization direction, $|m|$ or $|m_j|$, and the principal quantum number of the state.

I would like to thank Baochun Yang for helpful discussions in this project. This chapter is based upon work supported by the US National Science Foundation under Grant No. 1404419-PHY.

2.5 Appendix: Proving the equivalence of two angular matrices for $(l = j - 1/2)_j$ and $(l = j + 1/2)_j$ states

Based on our definition of angular matrices in Eq. (2.13), each element is the angular part of the integrand of corresponding perturbation matrix element integral. In our derivation in Eq. (2.24), we expand the angular matrix element $\tilde{\rho}_{m_j, m'_j}$ on a basis of complex conjugate of spherical harmonics:

$$\tilde{\rho}_{m_j, m'_j}(\theta, \varphi) = \sum_{kq} b_{kq}(m_j, m'_j) Y_{kq}^*(\theta, \phi) \quad (2.49)$$

Then we can calculate the matrix element of Y_{kq} in the spin-orbit coupled basis $|l = j \pm \frac{1}{2}, s = \frac{1}{2}, j, m_j\rangle$ to get the coefficient $b_{kq}(m_j, m'_j)$, which is

$$b_{kq}(m_j, m'_j) = \int d\Omega Y_{kq}(\theta, \varphi) \tilde{\rho}_{m_j, m'_j}(\theta, \varphi) \quad (2.50)$$

$$= \langle l, s, j, m_j | Y_{kq} | l, s, j, m'_j \rangle \quad (2.51)$$

Using the Wigner-Eckart theorem [45], we have

$$b_{kq}(m_j, m'_j) = (-1)^{j-m_j} \begin{pmatrix} j & k & j \\ -m_j & q & m'_j \end{pmatrix} \langle l, s, j || Y^{(k)} || l, s, j \rangle \quad (2.52)$$

$$= (-1)^{j-m_j} \begin{pmatrix} j & k & j \\ -m_j & q & m'_j \end{pmatrix} (-1)^{l+s+j+k} (2j+1) \begin{Bmatrix} l & j & s \\ j & l & k \end{Bmatrix} \\ \times \langle l || Y^{(k)} || l \rangle \quad (2.53)$$

$$= (-1)^{2j-m_j+l+s+k} \begin{pmatrix} j & k & j \\ -m_j & q & m'_j \end{pmatrix} (2j+1) \begin{Bmatrix} l & j & s \\ j & l & k \end{Bmatrix} \\ \times (-1)^l \sqrt{\frac{(2l+1)^2(2k+1)}{4\pi}} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \quad (2.54)$$

$$= (-1)^{3/2-m_j+k} \begin{pmatrix} j & k & j \\ -m_j & q & m'_j \end{pmatrix} (2j+1)(2l+1) \begin{Bmatrix} l & j & \frac{1}{2} \\ j & l & k \end{Bmatrix} \\ \times \sqrt{\frac{2k+1}{4\pi}} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \quad (2.55)$$

Here we used the fact that $s = 1/2$, $l = j \pm 1/2$. We must have some restrictions so that the matrix element is non-zero, which are

$$q = m_j - m'_j, \quad (2.56)$$

$$|m_j - m'_j| \leq k \leq 2j, \quad (2.57)$$

$$k \text{ must be an even number}, \quad (2.58)$$

$$\Rightarrow |m_j - m'_j| \leq k \leq 2j - 1. \quad (2.59)$$

The explicitly l -dependent terms of Eq. (2.55) are as follows,

$$c(l) = (2l+1) \begin{Bmatrix} l & j & \frac{1}{2} \\ j & l & k \end{Bmatrix} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}, \quad (2.60)$$

which can be shown to be the same for $l = j \pm 1/2$ [46]. The final form of Eq. (2.55) can be written as

$$b_{kq}(m_j, m'_j) = (-1)^{m_j+1/2} \sqrt{\frac{2k+1}{4\pi}} \sqrt{(2j+k+1)(2j-k)} \\ \times \begin{pmatrix} j - \frac{1}{2} & j - \frac{1}{2} & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j & j & k \\ -m_j & m'_j & m_j - m'_j \end{pmatrix} \quad (2.61)$$

for $l = j \pm 1/2$, where $q = m_j - m'_j$. $b_{kq}(m_j, m'_j)$ are non-zero only when k satisfies the restrictions in Eq. (2.58) and Eq. (2.59).

3. PROBING DOUBLE RYDBERG WAVE PACKETS IN A HELIUM ATOM WITH FAST SINGLE-CYCLE PULSES

This chapter is directly taken from *Phys. Rev. A*, **96**, 043409 (2017) [47] with minor differences, where the original draft was written by Xiao Wang.

3.1 Introduction

The study of correlations between two bound electrons has remained an interesting topic since the development of quantum mechanics in the early 20th century. The basic Coulomb form of the interaction is a prototype of coupled degrees of freedom in atomic physics. Thus, understanding the correlations between two electrons can help us understand more complicated atoms and molecules. In recent years, numerous experiments have been done using ultrafast laser pulses to observe, create, and control different two-electron processes [3–7]. Most of them have been focused on resonant transitions in low-lying states.

In contrast to low-lying states, highly excited Rydberg states have many novel properties. The tiny energy spacing between adjacent Rydberg states makes it easier to generate spatially localized Rydberg wave packets [13,14]. Many experimental and theoretical studies on atoms with a single Rydberg wave packet have been conducted in the past few decades [14–22,48]. However, there are only a few experimental studies of the dynamics of double Rydberg wave packets [23–26,49]. Recently, experiments done by Zhang *et al* in Ref. [26] studied the time evolution of two highly excited Rydberg wave packets. Their experimental and numerical results were in good agreement and showed that substantial energy and angular momentum exchanges between the two electrons can happen in just a few Rydberg periods. This motivates us to study the time-dependent dynamics of double Rydberg wave packets, which has not been

systematically studied before. A numerical method using basis expansion techniques was introduced in Ref. [27]. Another method [28] based on the time-dependent close coupling method [8] will be used in this chapter to study the dynamics of double Rydberg wave packets.

Most quantum mechanical methods face computational power issues when dealing with highly excited Rydberg electrons, due to the wide spatial range, long time scale of substantial interactions, and strong mixing among enormous numbers of basis functions. Early research showed that Rydberg electrons behave more classically than electrons in low-lying states [1, 50]. This suggests the use of well-studied classical mechanics to investigate those two-electron atoms. Classical calculations with a wide range of principal quantum numbers are performed in this chapter, and the results are compared with quantum calculations to study the validity of the classical method.

Experimentalists have been using well-controlled fast THz pulses as a time-resolved probe to study the Rydberg electronic wave function structures at different times as the system evolves [26, 51, 52]. Durations of fast THz pulses can be modified to be shorter than, equal to, or longer than the period of Rydberg electrons, which can yield totally different field-ionization results. Subpicosecond half-cycle pulses (HCP) have been widely used to probe wave function structures of a single Rydberg wave packet since the 1990s [21, 53, 54], but only a few experiments have been done using HCP to study double Rydberg wave packets [26]. The effects of fast THz single-cycle pulses (SCP) on atoms with one valence electron at different bound states have been studied in both theoretical [55–57] and experimental [51] ways. However, there has been no study on the effect of a SCP on an atom with doubly excited Rydberg wave packets. In this chapter, we focus on the use of SCP to obtain wave function structures from double Rydberg wave packets. We can also predict motions of the double Rydberg wave packets from the time-resolved ionization results with SCP.

This chapter is organized as follows. In Sec. 3.2, we introduce the two-step launch model for generating double Rydberg wave packets based on experiments in Ref. [26]. Both fully quantum and classical calculations are performed in order to explore the

differences between them and the validity of classical methods in low-lying states. In Sec. 3.3, we focus on the effect of a fast SCP on an atomic system. The evolution and autoionization of the double Rydberg wave packets are then studied using a SCP. All physical variables and formulas presented in this chapter are in atomic units unless specified otherwise.

3.2 Comparison between fully quantum and classical methods

3.2.1 The two-step launch model

Our theoretical model is motivated by an experiment in Ref. [26], where both valence electrons in Ba are individually excited to Rydberg wave packet type states. The experiment starts with Ba atoms in the ground state, $6s^2$. The atom is excited to a coherent superposition of $5d_{5/2}n_1d$ Rydberg states using two consecutive laser pulses. The first radially localized wave packet is generated as a superposition of n_1 states. Its Rydberg period is about $T_{\text{Ryd1}} = 2\pi\nu_1^3$, where $\nu_1 = n_1 - \mu_1$ is the effective principal quantum number. The ν_1 corresponds to the central binding energy $E_1 = -1^2/2\nu_1^2$, and the μ_1 is the quantum defect. When the first wave packet reaches its outer turning point, the other electron is then excited to a Rydberg wave packet giving n_2gn_1d states. The $\nu_2 = n_2 - \mu_2$ is the effective principal quantum number that corresponds to the central binding energy $E_2 = -2^2/2\nu_2^2$. Central energies and energy widths of the two Rydberg wave packets are controlled by properties of laser pulses used to excite the atom. Dynamics of the double Rydberg wave packets can then be studied.

This experiment can be converted into a theoretical two-step launch model in a helium atom. We focus on an easier case where the angular momenta l_j of both electron at launch are zero. Usually, when the total angular momentum L is on the order of 1 and is much smaller than both principal quantum numbers, the dynamics are insensitive to the total angular momentum L . Calculations with different small L are described in Sec. 3.2.4. Therefore, the first electron is launched as a spherically

symmetric s -wave centered at a negative total energy $E_1 = -1^2/2\nu_1^2$ and a launch time width δt_1 . The δt_1 is a time width parameter that describes a Gaussian shaped electric field amplitude, which is $F_1(t) \propto \exp(-2 \ln 2 t^2 / \delta t_1^2)$. At $t = 0.5 T_{\text{Ryd1}}$, the second electron is also launched as a spherically symmetric s -wave centered at a negative total energy $E_2 = -2^2/2\nu_2^2$ and a launch time width δt_2 . The δt_2 has a similar definition as of δt_1 . In the quantum calculations, the energy width is an automatic result of the duration of the laser pulse that excites each wave packet. In the classical calculations, the energy width is selected to be the same as that in the quantum calculations. To satisfy the uncertainty principle, the FWHM of a Gaussian shaped energy distribution of the Rydberg wave packet satisfies $\delta E_j = 4 \ln 2 / \delta t_j$, where $j = 1, 2$ represent the first and second electron, respectively. We then study the autoionization process of the atom, and angular momenta distributions of the electrons after the second electron's launch.

3.2.2 Quantum approach

For a neutral helium atom with two electrons, the Hamiltonian of this system can be written as

$$H = \frac{\mathbf{p}_1^2}{2} + \frac{\mathbf{p}_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (3.1)$$

where $\mathbf{p}_j$ and $\mathbf{r}_j$ are the momentum and spatial coordinate of the j -th electron, respectively. The main difference of a helium atom's Hamiltonian compared to a hydrogen atom's is the Coulomb interaction term $1/|\mathbf{r}_1 - \mathbf{r}_2|$, which couples the two electrons. In this chapter, a method based on the time-dependent close coupling (TDCC) method is used to propagate the wave function of a helium atom [8, 28].

Expanding the two-electron wave function in a coupled spherical harmonic basis, the wave function can be written as

$$\Psi^{LS}(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l_1, l_2} \frac{R_{l_1, l_2}^{LS}(r_1, r_2, t)}{r_1 r_2} \times \sum_{m_1, m_2} C_{m_1, m_2, 0}^{l_1, l_2, L} Y_{l_1, m_1}(\hat{r}_1) Y_{l_2, m_2}(\hat{r}_2), \quad (3.2)$$

where R_{l_1, l_2}^{LS} is the radial wave function, $C_{m_1, m_2, 0}^{l_1, l_2, L}$ is the Clebsch-Gordan coefficient, Y_{lm} are spherical harmonics, r_1, r_2 represent the spatial coordinates of the two electrons [8]. To reduce the computational requirements, the calculation can be performed with total angular momentum $L = 0$ instead of small non-zero total angular momentum. Additionally, since both Rydberg wave packets are highly localized in phase space and far away from the nucleus, the overlap integral and exchange effect are expected to be small. Singlet and triplet symmetrized calculations will give nearly the same result. With total angular momentum $L = 0$, the wave function only depends on r_1 , r_2 , and the relative angle θ_{12} between $\mathbf{r}_1$ and $\mathbf{r}_2$, [58]. The wave function in Eq. (3.2) with $L = 0$ can be simplified to

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l=0}^{L_{\max}} (-1)^l R_l(r_1, r_2, t) Y_{l0}(\cos \theta_{12}), \quad (3.3)$$

where the $(-1)^l$ term is following the conventions of Refs. [59, 60]. The $L_{\max}$ is the number of angular channels used in the calculation, and it's slightly larger than the maximum allowed angular momentum restricted by the total energy. The goal is to evolve the R_l for all coupled channels with different angular momentum l of one electron.

For the time propagation of the wave function, the split-operator technique is used. The Hamiltonian in Eq. (3.1) can be split into 3 parts, $H_j = p_j^2/2 - 2/r_j$ with $j = 1, 2$ for each electron, and $H_3 = 1/r_{12}$ for the interaction between the two electrons. The unitary propagators of U_1 , U_2 , and U_3 can be taken in various forms at each time step, e.g. Crank-Nicolson, Chebyshev, or leapfrog, etc. The propagators U_1 and U_2 don't couple amplitudes R_l with different angular momentum, and are tridiagonal in r_1 and r_2 , respectively. For the propagator U_3 , the idea from discrete variable representation is used in the calculation [61]. The method is described in Ref. [28] in detail, and we give a brief description here. First, the matrix elements of $\cos \theta_{12}$ in the coupled angular momentum basis $|j\rangle = |(l_j, l_j) L = 0\rangle$ are calculated [59]. Then, the matrix of $\cos \theta_{12}$ is diagonalized, and we can use its eigenstates, eigenvalues and the geometric relation $r_{12} = (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_{12})^{1/2}$ to calculate the matrix element of U_3 in the

coupled angular basis $|j\rangle$. Finally, the U_3 propagator couples all the angular states $|j\rangle$, and the radial amplitudes R_j are propagated to the next time step.

At the final time of the calculation, we can project the calculated wave function onto energy eigenstates of a helium atom to get the energy distribution. Since the total angular momentum of the system is zero, angular momenta of the two electrons have the same magnitude but in the opposite directions. The angular momentum distribution of one electron is calculated using [60]

$$p_{\text{qm}}(l) = \iint dr_1 dr_2 \left| R_l(r_1, r_2, t) \right|^2. \quad (3.4)$$

3.2.3 Classical approach

The three-dimensional classical trajectory Monte Carlo (CTMC) method [21, 28, 62, 63] is used in the calculations as a comparison with the quantum calculation, as a way of interpreting the results, and as a way to obtain results difficult or impossible to converge using quantum calculations. Initial conditions of the electrons are set to obey the quantum uncertainty principle with random Gaussian distributed energies and launch times. Since both electrons are launched as spherically symmetric s -waves, their launch directions are uniformly distributed in all 4π solid angle.

After the initial launches, the system is propagated under Hamilton's equations using a fourth order Runge-Kutta method with adaptive step size [64]. To avoid divergence near the nucleus, a soft core potential $V(r) = -Z/\sqrt{r^2 + a^2}$ is used instead of $V(r) = -Z/r$ for the Coulomb interactions, where a is a soft core parameter. Calculations performed with a ranged from 1.0×10^{-3} to 1.0×10^{-5} give converged results.

At the final time of the calculations, the statistics of energies, angular momenta, and other physical quantities of each electron from all Monte Carlo (MC) runs with different initial conditions give continuous distribution functions. The continuous distribution functions can be discretized and compared to the quantum calculations.

For example, the classical analogy of the probability of the angular momentum at l_c can be calculated as follows

$$p_{\text{cl}}(l_c) = \frac{\text{Number of MC runs with } l_c \leq l < l_c + 1}{\text{Total number of MC runs}}, \quad (3.5)$$

where l is the angular momentum from the classical calculations. The l_c is a non-negative integer, which corresponds to the azimuthal quantum number in the quantum calculations. The $p_{\text{cl}}(l_c)$ is compared to the quantum angular momentum distributions $p_{\text{qm}}(l_c)$, to study the differences between the classical and quantum methods.

3.2.4 Comparisons between quantum and classical methods

To study the validity of the classical methods, we start this subsection with a calculation for $\nu_1 = 23$, $\nu_2 = 38$. The principal quantum numbers are chosen to be neither too large, where the quantum calculations would be hard to converge, nor too small, where the quantum effects can cause huge differences between the quantum and classical calculations. Comparison of angular momentum distributions between quantum and classical methods can be found in Fig. 3.1, with all the corresponding parameters given in the caption. In this calculation, the total angular momentum is set to zero. The results presented here are for the non-ionized part of the wave function, which is only about 30% at the final time of 2 ps. The numerical difference for ionization probabilities between the classical and quantum methods is about 1% at the final time. The final time of this calculation is about one Rydberg period of the first electron. In this time scale, significant interactions between the two electrons can happen. This leads to a large probability of autoionization, and can excite most of the two-electron wave function to high angular momentum states. In the figure, a sharp decrease in angular momentum distribution can be found near $l = 36$, which is the maximum classically allowed angular momentum when both electrons are bound¹.

¹The maximum classically allowed angular momentum l when both electrons are bound can be calculated using energy conservation, which is $0.5v_{1r}^2 + 0.5v_{2r}^2 + l^2/2r_1^2 + l^2/2r_2^2 - 2/r_1 - 2/r_2 + 1/r_{12} =$

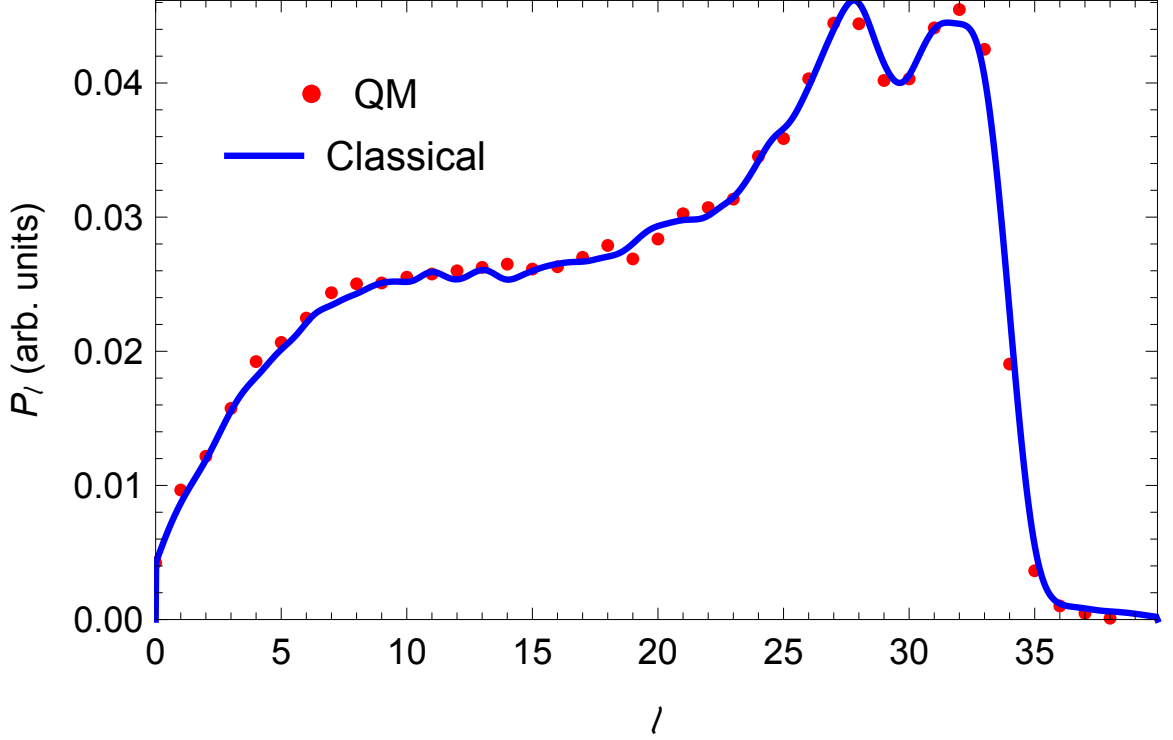


Figure 3.1. Comparison between the quantum and classical methods for the angular momentum distribution. The effective principal quantum numbers are $\nu_1 = 23$, $\nu_2 = 38$, which correspond to central energies $E_1 = -1^2/2\nu_1^2 = -9.45 \times 10^{-4}$, $E_2 = -2^2/2\nu_2^2 = -1.39 \times 10^{-3}$ at launch. Rydberg period of the first electron is $T_{\text{Ryd1}} = 2\pi\nu_1^3 = 7.64 \times 10^4$. The 2nd electron is launched at half of the Rydberg period of the 1st electron after the 1st electron's launch. Launch time widths for the two electrons are $\delta t_1 = 2.17 \times 10^4 = 0.28 T_{\text{Ryd1}}$, $\delta t_2 = 4.28 \times 10^3 = 0.056 T_{\text{Ryd1}}$, which are shorter than a full Rydberg period. The results in the figure are at $t = 8.27 \times 10^4$ a.u. after the 2nd launch, which is about 2 picosecond.

Additionally, classical calculations that the second electron starts at a non-zero angular momentum are performed. The results also match well with the $L = 0$ results, and can be found in Fig. 3.2. The calculations with non-zero total angular momentum

E_{tot} . When the radial velocities $v_{r1} = v_{r2} = 0$, $r_{12} = r_1 + r_2$, and $r_1 = r_2 = -7/(4E_{\text{tot}})$, the l reaches its maximum $7/(4\sqrt{-E_{\text{tot}}})$.

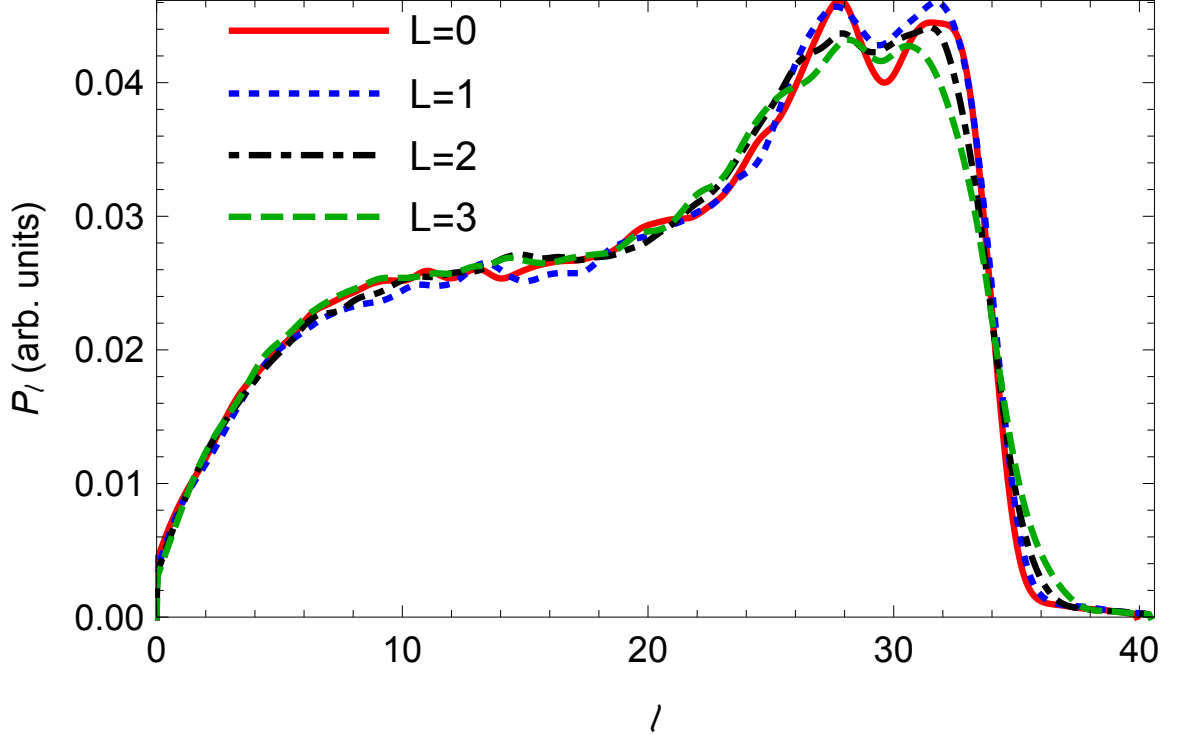


Figure 3.2. Comparison of the angular momentum distributions between classical calculations with total angular momentum $L = 0, 1, 2, 3$. All the parameters are the same as those given in the caption of Fig. 3.1 except for the total angular momentum. Since the total angular momentum is non-zero, the angular momenta of the two electrons have a small difference. The separate angular momentum distributions of the two electrons have no visible differences, thus their distributions are plotted on a single curve as shown in the figure.

strengthen our assumption that the dynamics of Rydberg electrons is insensitive to small non-zero angular momentum.

With the comparison between quantum and classical calculations for highly excited states, the principal quantum number is then lowered, to study the validity of the classical methods at low-lying states. We define a *difference function* to quantita-

tively study the differences between the two methods for different principal quantum numbers. The difference function f_d is defined as

$$f_d = \sum_{l=0}^{L_{\max}} \left| p_{\text{cl}}(l) - p_{\text{qm}}(l) \right|, \quad (3.6)$$

where $L_{\max}$ is the number of coupled angular channels used in the quantum calculations. The $p_{\text{qm}}(l)$ is the probability that the electron has an angular momentum l as defined in Eq. (3.4) in quantum calculations. The $p_{\text{cl}}(l)$ is an analogous probability that the electron has an integer angular momentum l in classical calculations, which is defined in Eq. (3.5). The difference function gives an estimation on the relative error between the two methods at different l . The higher f_d is, the larger differences between the quantum and classical methods are.

Fully scaled calculations with $\nu_1 = 23\zeta$, $\nu_2 = 38\zeta$ have been performed, where $0 < \zeta \leq 1$ is a dimensionless number. The laser time widths are scaled as ζ^3 , since the Rydberg period of an electron and the interval between the two electrons' launches are proportional to cube of their principal quantum numbers. To satisfy the quantum uncertainty principle, the energy widths are scaled as ζ^{-3} in both classical and quantum calculations. Final time of the calculations are also scaled as ζ^3 . Similar to the calculation for $\nu_1, \nu_2 = 23, 38$, the angular momentum distributions used in Eq. (3.6) are only from the non-ionized part of the wave function.

The results of the difference function versus the first electron's principal quantum number ν_1 can be found in Fig. 3.3. In the figure, as the principal quantum number decreases, the difference between the two methods increases. Due to the interference and tunneling effects that only exist in quantum mechanics, the difference between the two methods fluctuates as the energy of the system changes. Also, finite energy spacings in the quantum calculations and finite final time of the calculations may cause additional disagreements between the quantum and classical methods [65, 66]. We use n to denote the principal quantum number of the atomic system. Since the energy spacings between adjacent Rydberg states are also scaled as n^{-3} as energy uncertainties, approximately same number of quantum states are included in a Ryd-

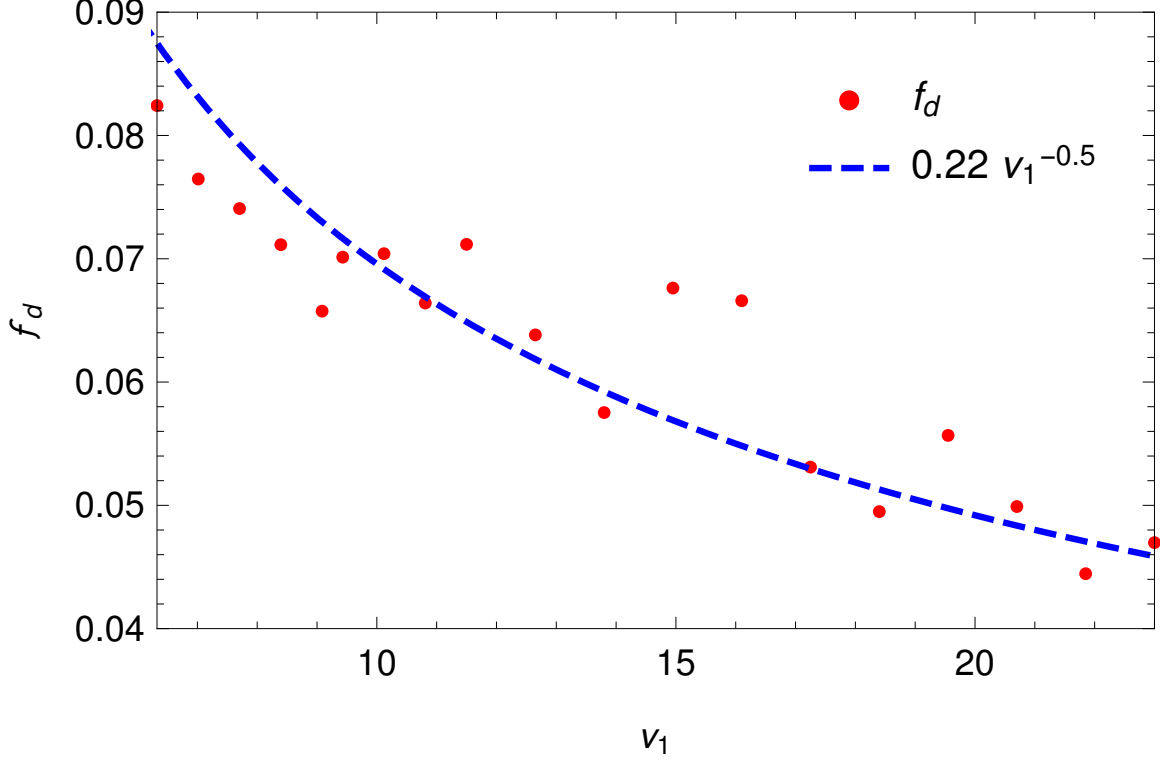


Figure 3.3. The difference function f_d as defined in Eq. (3.6) versus the first electron's principal quantum number ν_1 . In these calculations, the principal quantum numbers of the two electrons satisfy $\nu_1/\nu_2 = 23/38$. The red dots are the numerical results for the f_d , while the blue line is a fit for the numerical results versus ν_1 .

berg wave packet regardless of n . However, as n gets smaller, the discretized energy levels in quantum mechanics may cause totally different behaviors from continuous energies in classical mechanics, which could result in a difference function that scales as power of n . A rough fit of the f_d is also given in the figure, and that indicates the differences between classical and quantum calculations scale as $n^{-1/2}$. There are not many studies on the differences between classical and quantum calculations for different principal quantum numbers in an atomic system. Related studies on the differences in other systems can be found in Refs. [66–68].

3.3 Probing double Rydberg wave packets

Properties of double Rydberg wave packets in an atomic system are well described by classical calculations. To avoid the huge computational effort on mixing of large number of angular momentum states in quantum calculations, all of the following calculations related to single-cycle pulses (SCP) are classical calculations.

3.3.1 The effect of SCP on a one electron atom

We start this subsection with a study of the effect of short SCP on an atomic system with one Rydberg electron. A Rydberg electron is prepared in a classical, elliptical Rydberg orbit with a small angular momentum. The electron has a significant time to be far away from the nucleus, and a relatively short time to be close to the nucleus in its one Rydberg period. The electric field of a SCP in our calculation has the following form

$$F(t) = C_0 F_m \left(\frac{t}{t_w} \right) \exp \left[- \left(\frac{t}{t_w} \right)^2 \right], \quad (3.7)$$

where $C_0 = \sqrt{2e} \approx 2.332$ is a constant to make the maximum field strength be F_m , note that e here is the base of natural logarithms. The t_w is a parameter to characterize the duration of the pulse. In our calculations, a SCP starts at $t = -3.5 t_w$, and ends at $t = +3.5 t_w$. A SCP has a duration $T_{\text{pulse}} = 7.0 t_w$. Durations of the short pulses in the calculations below are much shorter than or equal to one Rydberg period of the electron. Effects of a SCP in these two scenarios can be totally different. Single-cycle pulses are applied to a one-electron atom at different times, and the energy distributions of the electron after the SCP are observed.

We first describe the effect of a SCP with duration much shorter than one Rydberg period. Within the duration of a short SCP, the nucleus-electron interaction can be neglected if the electron is far away from the nucleus. Since the integral of the electric field over time is zero, a short SCP only shifts the position of the electron, and has almost no effect on its kinetic energy. The estimated energy change of the electron

originates from the Coulomb potential energy change. If the electron was close to the nucleus before the SCP, the potential energy change is much higher than that for an electron which was far away from the nucleus. This is equivalent to saying that a short SCP transfers more energy to an atom when an electron is closer to the nucleus at the time of the SCP.

We also study the effect of a SCP with duration equal to one Rydberg period. The electric field of a SCP has maximum amplitude at $t = \pm t_w/\sqrt{2} \approx \pm 0.707 t_w$, which is about half of its duration. If a SCP starts at the time that the electron is close to the nucleus, the electron feels maximum accelerations when it moves to the Rydberg outer turning point. Acceleration from the SCP quickly flips the sign at almost the same time that the electron passes the outer turning point, and reverses its moving direction. This means the SCP can perfectly accelerate the electron during the whole pulse. This is also true if a SCP starts at the time that the electron is close to the outer turning point. However, there is a main difference between these two scenarios. The work done to the electron is the integral of force times displacements. The electron moves much faster when it is close to the nucleus than far away from the nucleus. Using pulses with same strengths, the absolute value of the work done by a SCP is much larger when it starts at the time that the electron is at its outer turning point.

To summarize, a short SCP transfers more energy when the electron is close to the nucleus, while a medium duration SCP transfers more energy when it starts at the time that the electron is far away from the nucleus. An atom can be ionized if the final energy after a SCP is above the ionization threshold. In experiments, a SCP can be used to probe the periodic motion of the Rydberg wave packet in a one electron atom.

3.3.2 Probing double Rydberg wave packets

Within our two-step launch model described in Sec. 3.2.1, dynamics of the double Rydberg wave packets can be divided into two regions based on their initial energies. (i) One wave packet has a much larger Rydberg orbit than the other. This means the two wave packets are usually spatially distinguishable, with an inner wave packet and an outer wave packet. (ii) Two wave packets have similar sized Rydberg orbits. We apply a fast SCP at different times after the electron launches. The SCP can transfer energy to the atomic system. At a long final time, the atom will be singly or doubly ionized. In our following calculations, the double ionization probabilities are very small and can be neglected. We can measure the energy distributions of those singly ionized atoms to study the electronic wave function structures at the start time of the SCP.

A classical calculation with $\nu_1 = 45$, $\nu_2 = 38$ has been performed. This leads to the initial energies $E_{1i} = -2.47 \times 10^{-4}$, $E_{2i} = -1.39 \times 10^{-3}$, and Rydberg periods $T_{\text{Ryd1}} = 13.8$ ps, $T_{\text{Ryd2}} = 2.08$ ps. Before the first wave packet returns to the nucleus ($0.5 T_{\text{Ryd1}} = 6.9$ ps), the second electron is expected to be in its own periodic motion around the nucleus. In this calculation, the first electron is considered as the outer wave packet, while the second electron is the inner wave packet. A short SCP with duration $T_{\text{pulse}} = 0.208$ ps $\approx 0.1 T_{\text{Ryd2}}$, and maximum strength $F_m = 100$ kV/cm is applied at different times (t_{start}) after the second launch. Distributions of the positive ion's final energy, E_+ , can be found in Fig. 3.4. In the figure, most of the energy distributions are lower than E_c , center of the initial total energy shifted by energy widths, which is indicated as the vertical dashed line. For these electrons with $E_+ > E_c$, the atom must have gained energy from the SCP. As our analyses in Sec. 3.3.1, a short SCP transfers more energy to an atom through the inner electron when the electron is close to the nucleus. If the energy transferred to the inner electron is large enough, the inner electron can be directly ripped off from the atom. In this scenario, there will be no further chaotic three-body interactions after the

outer electron returns. The energy of the outer electron after the inner electron being ionized should be approximately $2E_{1i}$, which originates from the changing of ionic core charge from 1 to 2. In Fig. 3.4, when $E_+ > E_c$, the peak of the positive ion's energy is located at $2E_{1i}$.

To further study our claim that a short SCP transfers energy to an atom when the electron is close to the nucleus, we plot the probability of $E_+ > E_c$ versus t_{start} in Fig. 3.5. The probability indicates direct ionization of the inner electron due to the short SCP. Additionally, we calculate the probability that at least one electron is within a sphere of $R_c = 260$ au centered at the nucleus, when neither electron is autoionized before the pulse. The latter probability, P_c , versus t_{start} is plotted in Fig. 3.5. The R_c is calculated to satisfy

$$\frac{-2}{R_c + \Delta r} - \frac{-2}{R_c} + E_c \geq 0, \quad (3.8)$$

where Δr is the displacement of a free electron due to a SCP. The probabilities of $E_+ > E_c$ and P_c have similar trends and magnitudes on the locations of peaks and troughs. To study the origin of P_c , we calculated the probabilities that each electron is within R_c , indicated with P_{c1} and P_{c2} for the first and second electron, respectively. The plots can be found in Fig. 3.5. Note that, the probability that both electrons are within R_c is less than 0.1% and can be neglected here, which means $P_c \approx P_{c1} + P_{c2}$. The peaks of P_{c2} are located at $t_{\text{start}} \approx 2.0, 4.0, 6.0$ ps, which are multiples of T_{Ryd2} and indicate the inner electron's return to the nucleus. Similarly, the outer electron returns to the nucleus at $t_{\text{start}} \approx 6.9$ ps. Instead of a peak in P_{c1} at 6.9 ps, we can find a small dip on it. This is because at $t_{\text{start}} \approx 7.0$ ps, the inner electron is at its outer turning point. Thus, the repulsion between the inner electron and the returning outer electron shifts the radial positions of the two electrons. Therefore, P_{c1} is slightly lower and P_{c2} is slightly higher at $t_{\text{start}} \approx 7.0$ ps. On the P_{c2} curve at 7.0 ps, the depth of the dip is not as large as that at 5.0 and 8.0 ps. As a result, we have flatter distributions near 7.0 ps on both P_c and $E_+ > E_c$ curves. After 8.0 ps, both curves are mostly flat, indicating a SCP applied after the collisions between the

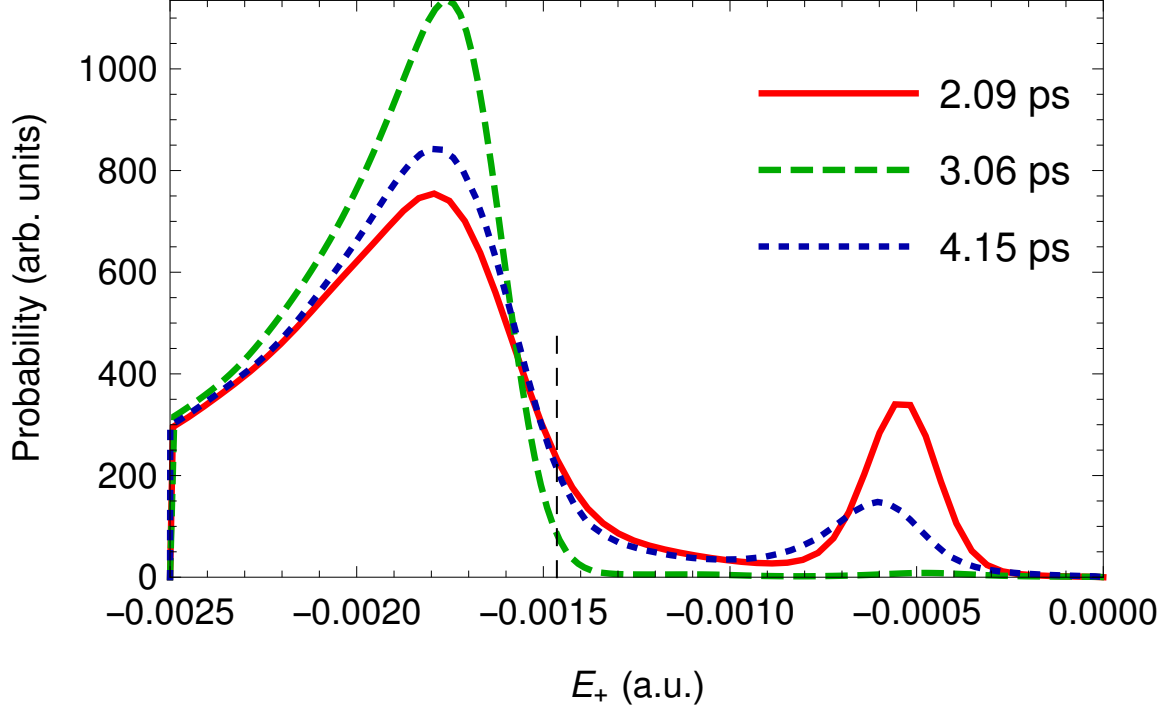


Figure 3.4. Energy distributions of the electron in a singly ionized ion at a long final time, after the effect of a short SCP applied at different time. The principal quantum numbers for the two electrons are $\nu_1 = 45$, $\nu_2 = 38$. The SCP has a maximum strength $F_m = 100$ kV/cm, and a duration $T_{\text{pulse}} = 0.208$ ps. Numbers in the legends indicate the start time of SCP (t_{start}) after the launch of the second electron. The vertical dashed line is plotted at $E_c = -1.46 \times 10^{-3}$. The figure has a cutoff at -0.0025 on the left, but the full energy distributions have long tails to larger binding energies.

two electrons. The probability to find electrons in a small radial range barely changes after collision.

To study the effect of a medium duration SCP, calculations with $\nu_1 = 45$, $\nu_2 = 40$, $T_{\text{pulse}} = 2.43$ ps $\approx 1.0 T_{\text{Ryd2}}$ and $F_m = 5$ kV/cm, have been performed. For this case, the T_{pulse} is smaller than the outer electron's Rydberg period T_{Ryd1} . When the outer electron is far away from the nucleus, the SCP only slightly shifts its position, and has negligible effect on it. We may only consider the effect of the SCP on the

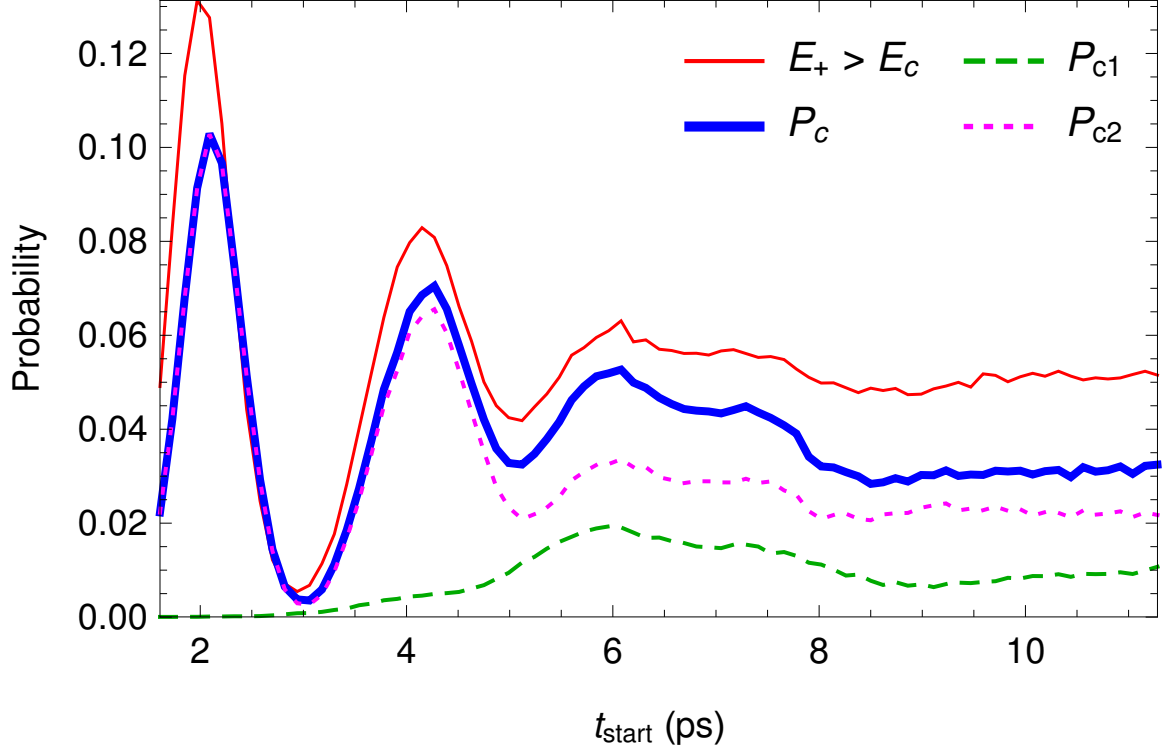


Figure 3.5. Probability results for calculations with $\nu_1 = 45$, $\nu_2 = 38$, $F_m = 100$ kV/cm, $T_{\text{pulse}} = 0.208$ ps. The red thin solid line describes the probability of $E_+ > E_c$, which is the positive ion's final energy higher than -1.46×10^{-3} , with a short SCP applied at different time t_{start} . The blue thick solid line describes the probability that at least one electron is within $R_c = 260$, at different time t_{start} after the second electron's launch, just before the application of a SCP. The green dashed line describes the probability that the first electron is within R_c at different time, while the magenta dotted line describes the probability for the second electron.

inner electron, before the outer electron returns. Energy distributions of the positive ion at a long final time can be found in Fig. 3.6(a), which has the same meaning as described in Fig. 3.4. The probability of $E_+ > E_c$ can be found in Fig. 3.6(b). To have a detailed understanding of the effect of a medium duration SCP, we have performed calculations of a He^+ ion with only one Rydberg wave packet at $\nu_2 = 40$ under the effect of a same medium duration SCP, with $T_{\text{pulse}} = 2.43$ ps and $F_m = 5$ kV/cm,

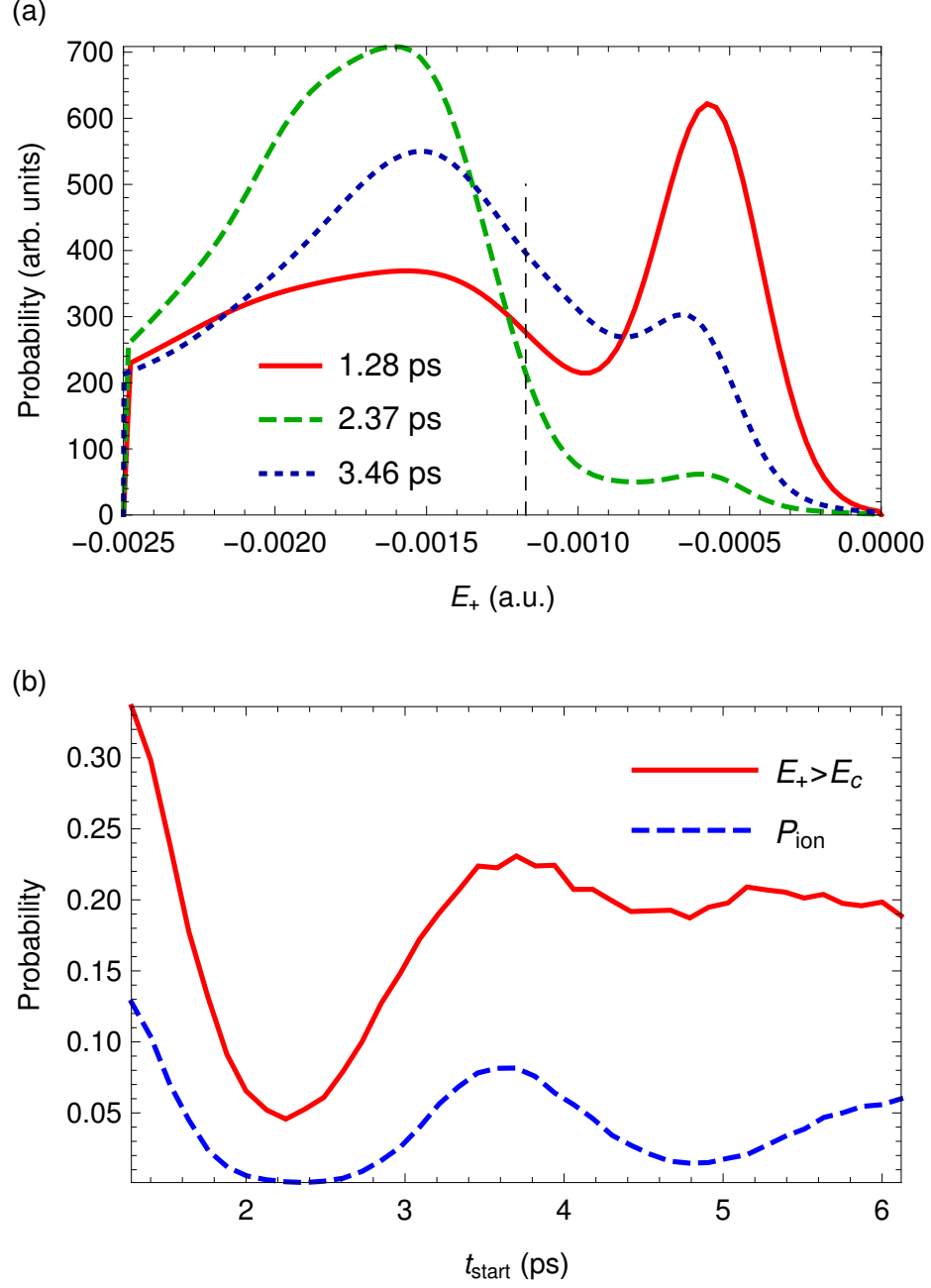


Figure 3.6. Study of the effect of a medium duration SCP with $\nu_1 = 45$, $\nu_2 = 40$, $F_m = 5$ kV/cm, and $T_{\text{pulse}} = 2.43$ ps. Figure (a) describes the same physical quantities as given in the caption of Fig. 3.4. Figure (b) describes the probability of positive ion's energy higher than $E_c = -1.17 \times 10^{-3}$, and the direct ionization probability of a He^+ ion due to a medium duration SCP with same properties. The t_{start} is the start time of a medium duration SCP (see Eq. (3.7) for definition of the start time).

applied at different times. The field induced ionization probability (P_{ion}) of the He^+ is also plotted in Fig. 3.6. At $t_{\text{start}} = 2.4 \text{ ps} \approx 1.0 T_{\text{Ryd2}}$, the electron in He^+ model and the inner electron in the two-electron atom return to the nucleus, and gain the lowest energy transferred from a short SCP. Thus the probabilities of $E_+ > E_c$ and P_{ion} reach their minimum. Similarly, at $t_{\text{start}} = 1.3 \text{ ps} \approx 0.5 T_{\text{Ryd2}}$ and $t_{\text{start}} = 3.5 \text{ ps} \approx 1.5 T_{\text{Ryd2}}$, the electron in He^+ model and the inner electron in the two-electron atom are at their outer turning points, and $E_+ > E_c$, P_{ion} reach their maximum. These two lines have very similar trends, which strengthens our assumption that a medium duration SCP transfers more energy to an atom when it starts at the time that the electron is far away from the nucleus.

These calculations show that single-cycle pulses with a short duration and a medium duration behave oppositely on the energy transfer to a Rydberg electron. Experimentally, a SCP can be used to probe the wave function structures of the inner wave packet, by transferring energy to the atom through the inner electron while the inner electron is located at different positions.

3.3.3 Atoms with similar sized double Rydberg wave packets

In the previous subsection, we studied the effect of a SCP on a two-electron atom with the size of one Rydberg wave packet much larger than the other's. Here we focus on those scenarios that the two Rydberg wave packets have similar sizes. A classical calculation with $\nu_1 = 34$, $\nu_2 = 40$ has been performed. The single-cycle pulses have durations $T_{\text{pulse}} = 0.1 T_{\text{Ryd2}} = 0.243 \text{ ps}$, and maximum strengths $F_m = 100 \text{ kV/cm}$. The $E_c = -1.42 \times 10^{-3}$ is center of the initial total energy shifted by energy widths. The probability of $E_+ > E_c$, versus different start time of the SCP is plotted in Fig. 3.7. The probabilities to find electrons within $R_c = 300 \text{ au}$, P_c , P_{c1} , P_{c2} , as introduced in the previous subsection can also be found in Fig. 3.7. In the figure, similar trends between $E_+ > E_c$ and P_c can be found, which is because a short SCP transfers more energy to an electron when it's close to the nucleus. The peak of P_{c1}

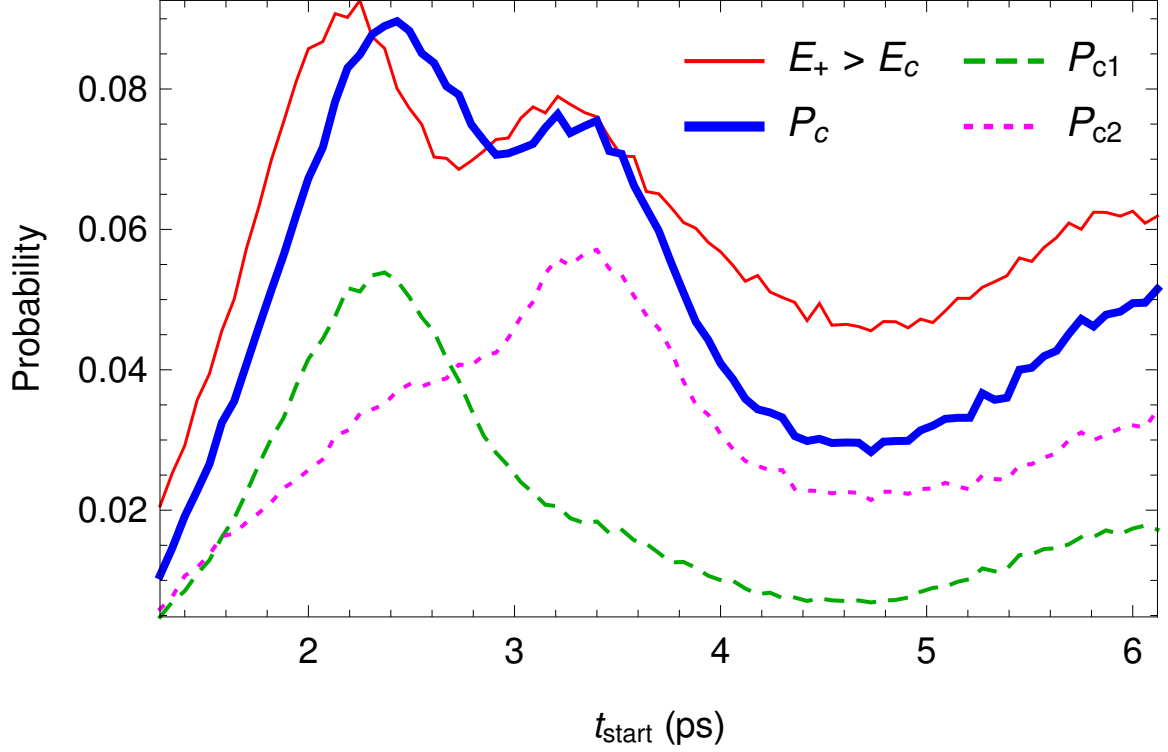


Figure 3.7. The curves have the same meaning as introduced in the caption of Fig. 3.5. Parameters used in the plot are $\nu_1 = 34$, $\nu_2 = 40$, $F_m = 100$ kV/cm, $T_{\text{pulse}} = 0.243$ ps, $E_c = -1.42 \times 10^{-3}$, and $R_c = 300$.

is located at $t_{R1} = 2.4$ ps, which indicates the first electron's return to the nucleus. Similarly, the second electron returns to the nucleus at $t_{R2} = 3.4$ ps. These return times are neither a full nor a half Rydberg period related to their initial energies. Due to the correlations between the two electrons, their energies, angular momenta, and Rydberg periods are changed.

After the two electrons return to the nucleus, respectively, they will be in Rydberg orbits with new periods. The new periods are approximately $2t_{R1}$ and t_{R2} for the two electrons, which can be deduced from the peaks and troughs on the P_{c1} and P_{c2} curves in Fig. 3.7. The first electron arrives at its new outer turning point at about $2t_{R1} = 4.8$ ps, while the second electron arrives at its new outer turning point at about $1.5t_{R2} = 5.1$ ps. As can be seen in Fig. 3.7, at $t_{\text{start}} \approx 4.8$ ps, the probabilities

to find either electron inside R_c are at minimum. The energy transferred from a short SCP and the probability of $E_+ > E_c$ are also at local minimum.

Experimentally, a short SCP can be used to probe an atom with two similar sized Rydberg wave packets. Usually, the first two peaks of the probability of $E_+ > E_c$ indicate the return times of the two electrons. After that, the two electrons will be in new Rydberg periods which are related to their first return times to the nucleus.

3.4 Conclusions

Inspired by a previous experiment in Ref. [26], and various numerical methods for solving two-electron atoms developed in the past few years, we studied dynamics of two Rydberg wave packets in a helium atom. We first briefly introduced the helium model with two-step launches, where the first electron was excited to a radially localized Rydberg wave packet using laser pulses with tunable parameters. When the first electron reached its outer turning point, the other electron was then excited to a Rydberg wave packet using laser pulses with different properties. As studied in Ref. [26], energy and angular momentum exchanges between the two electrons can happen quickly, leading to rapid autoionization.

We then performed both quantum and classical calculations to show the validity of the classical methods when dealing with Rydberg wave packets, comparing to an accurate quantum method. The classical and quantum methods were in good agreement at high principal quantum numbers. The numerical differences between the two methods at lower principal quantum numbers were also quantitatively studied.

Furthermore, we introduced the effects of a fast single-cycle pulse on an atom with one Rydberg electron. Detailed analyses showed that, a short duration single-cycle pulse transfers more energy to an atom when the electron is closer to the nucleus, while a medium duration single-cycle pulse transfers more energy when it starts at the time that the electron is further away from the nucleus. With these results, we studied the effects of a single-cycle pulse on an atom with double Rydberg wave

packets. A short single-cycle pulse is applied to an atomic system with distinguishable wave packets at different time, and the energy distribution of the positive ion at a long final time is measured. The probability that significant energy is transferred to the atom has a very similar trend as the probability that at least one electron is located in a small region very close to the nucleus. We also compared the results of a single-cycle pulse acting on an atom with double wave packets of significantly different sizes, and on a positive ion with only the inner wave packet. The results have very similar trends which verify our assumptions that a fast single-cycle pulse only has small effects on the outer electron. Moreover, we studied the case that the two Rydberg wave packets have similar sizes. From the time-dependent probabilities that each electron is close to the nucleus, we found out the return times of the two electrons. Due to the correlations between the two electrons, return times of the two electrons are different from their initial Rydberg periods. The new Rydberg periods after both electrons return to the nucleus are related to their return times. Experimentally, a fast single-cycle pulse can be applied at these times that an electron is close to the nucleus, and a large amount of energy will be transferred to the atom. Further novel autoionization behaviors after the effects of single-cycle pulses remain open questions to be studied in both theoretical and experimental ways.

I would like to thank Dr. Baochun Yang for helpful discussions. This chapter is based upon work supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Award No. DE-SC0012193. This research was supported in part through computational resources provided by Information Technology at Purdue University, West Lafayette, Indiana.

4. INTERFERENCE PATTERNS FROM POST-COLLISION INTERACTION IN BELOW-THRESHOLD PHOTOEXCITATION AUGER PROCESSES

This chapter is directly taken from *Phys. Rev. A*, **98**, 013421 (2018) [69] with minor differences, where the original draft was written by Xiao Wang.

4.1 Introduction

In Auger processes, the Coulomb interaction between the outgoing photoelectron and the Auger electron emitted later is known as post-collision interaction (PCI) [70–76]. Typically, the energy of the Auger electron is much higher than the energy of the photoelectron, thus the fast Auger electron will pass the slow photoelectron a short time after the core decays. The effective charge of the ionic core that the photoelectron experiences suddenly changes from +1 to +2. Energy and angular momentum exchange between the two electrons can happen in the PCI due to the repulsive Coulomb interaction between them, and, in some cases, the ionized photoelectron can be recaptured to bound states with different energies or angular momenta [77–82].

The PCI has been extensively studied both theoretically and experimentally in the past few decades. Several early semiclassical theories considered extreme cases, where the energy of one electron is much greater than the other, like the Barker-Berry model [83], the Niehaus formula [84], and other derivations [75, 85, 86]. Later, many stationary quantal theories were developed, including [72–74, 87, 88], which gave similar PCI energy shifts but in a wider range of two electron energies. Detailed

analysis of the angular momentum exchange in PCI can be found in Refs. [89–92]. Several time-dependent studies of PCI were developed in recent years [60, 91, 93–96]. Experimentally, the effect of PCI in a near-threshold photoionization has also been widely studied [76–82, 97–100], while several studies mainly focused on angular correlation in the double continuum [101, 102]

When the incident photon energy is much below the ionization threshold for an inner-shell electron, researchers study the resonant Auger process where the photon can excite an inner-shell electron to an excited bound state above the valence shell. There are also many studies of the resonant Auger process which has been thoroughly reviewed [71]. Intuitively thinking, with a high density of states, the PCI with slightly below-threshold photoexcitation and slightly above-threshold photoionization should behave similarly. However, our calculations show differences in the angular and photoelectron energy distributions (PED). This is partly due to the fact that a highly excited bound electron will return after it reaches its outer turning point, but a positive energy electron will not. Thus, the outgoing fast Auger electron could meet the photoelectron in a shorter distance and an earlier time, and the interaction between the two electrons would be stronger.

For the PED in an above-threshold photoionization, angular correlations have been investigated in experiments [25, 103, 104], and in theories [60, 91, 101, 102, 105]. There has not been studies focused on the PED in below-threshold photoexcitations, where the photoelectron gains enough energy to be ionized due to the PCI. In this chapter, we focus on the PED in below-threshold photoexcitation Auger process at different initial conditions, including photoelectron energy and Auger width. Interference patterns can be found in the PED. Properties of the interference patterns in PED at different initial conditions are studied, and also analyzed from a semiclassical approach. Both a quantum method, by solving two-electron time-dependent Schrödinger equations, and a classical method, by solving Hamilton’s equations, are used in this chapter to study the PCI effect across the ionization thresholds. Our

method is based on [28, 47, 91, 105], with extensions to negative photoelectron energies.

This chapter is structured as follows: in Sec. 4.2, a model of the Auger process and the quantum and classical numerical methods used in this chapter are briefly introduced. In Sec. 4.3, the results from both quantum and classical calculations are presented and compared. Also in Sec. 4.3, the PED is studied for different photoelectron energies across the threshold, and for different Auger widths. Atomic units are used unless specified otherwise.

4.2 Numerical methods

Instead of a full model considering all electrons in an atom, we consider only the photoelectron and the Auger electron in our calculations. This approximation can be made because significant interactions between the two electrons mostly happen outside the ionic core. Therefore, the detailed shell structure is less important and can be interpreted as a simple model potential.

Additionally, we limit our calculations with total angular momentum L being 0, as well as the initial angular momentum for each electron. This approximation can greatly reduce the number of coupled angular channels in the calculation. From Ref. [90] and our analyses in Sec. 4.3, the angular momentum exchange between the two electrons are fairly weak. Also, since the electron-electron interactions mostly occur far from the ionic core, we assume that the results from the $L = 0$ approximation will not significantly misinterpret the essence of energy and angular momentum exchange in the PCI. For the cases with non-zero angular momentum, brief discussions are given at the end of Sec. 4.3.3.

4.2.1 Quantum methods

The dynamics of the emitted photoelectron before the Auger core decays can be described by the following time-independent inhomogeneous Schrödinger equation [91, 105]:

$$\left(E_1 + i\frac{\Gamma_c}{2} - H_a\right) F_1(\mathbf{r}_1) = D\phi_g(\mathbf{r}_1), \quad (4.1)$$

where $E_1 = E - E_c$ is the incident photon energy minus binding energy of the Auger core, and E_1 is also the photoelectron energy above the ionization threshold. Γ_c is the Auger core width, and $H_a = \mathbf{p}_1^2/2 + V(\mathbf{r}_1)$ is the Hamiltonian for the photoelectron. The imaginary $i\Gamma_c/2$ is applied to the Auger core energy E_c to calculate the wave function of the photoelectron before the Auger core decays. While Ref. [105] gives the mathematical reason for this positive imaginary term, the qualitative reason is that it leads to a finite spatial extent for $F_1(\mathbf{r}_1)$ even when E_1 is positive, which reflects that the part of the wave function representing a photoelectron with **no** Auger electron should have a finite extent in r_1 . The $D\phi_g$ is the dipole operator acting on the ground state wave function of the inner-shell photoelectron. With the approximations we proposed at the beginning of this section, the $D\phi_g$ can be chosen as any short range function as long as: (1) it is not orthogonal to the continuum wave function of the photoelectron F_1 and, (2) it has the correct angular momentum. For the potentials in our problem, we may use a model potential that has an asymptotic form of $-Z/r$ as $r \rightarrow \infty$:

$$V(r) = -\frac{Z + (Z_t - Z)e^{-r/r_a}}{r}, \quad (4.2)$$

where Z_t , r_a are adjustable parameters that represent the properties of the model potential or, different atomic structures. We may also use a Coulomb potential with $V(r) = -Z/r$ as a simplified model. Here in H_a , we have $Z = 1$ in the potential for the photoelectron.

After the Auger core decays, the dynamics of the two electron system can be described by the following time-dependent Schrödinger equation [91, 105]:

$$\left(i\frac{\partial}{\partial t} + E_1 + E_2 - H\right) \Lambda(\mathbf{r}_1, \mathbf{r}_2, t) = S(t)F_1(\mathbf{r}_1)F_2(\mathbf{r}_2), \quad (4.3)$$

$$H = \frac{\mathbf{p}_1^2}{2} + \frac{\mathbf{p}_2^2}{2} + V(\mathbf{r}_1) + V(\mathbf{r}_2) + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4.4)$$

where H is the full two-electron Hamiltonian with $Z = 2$ in the potentials for both electrons. E_2 is the energy of the Auger electron above the ionization threshold. F_2 is a short range function that represents the source term for the Auger electron, and it is not orthogonal to the Coulomb eigenstate at E_2 . $S(t)$ is a step-like function that acts as the source term for the Auger decays, and we choose $S(t) = 1/(1 + \exp[10\{1 - 5t/t_f\}])$ in our calculations [105], where t_f is the final time of the calculation that all physical quantities are stable.

The whole two-electron wave function $\Lambda(\mathbf{r}_1, \mathbf{r}_2, t)$ is represented on a three-dimensional mesh:

$$\Lambda(\mathbf{r}_1, \mathbf{r}_2, t) = \sum_{l=0}^{L_{\max}} (-1)^l R_l(r_1, r_2, t) Y_{l0}(\cos \theta_{12}), \quad (4.5)$$

where the $Y_{l0}(\cos \theta_{12})$ are the spherical harmonics on the relative angle between $\mathbf{r}_1$, $\mathbf{r}_2$, and the phase factor follows the convention in [60, 106]. $L_{\max}$ is the maximum number of coupled angular channels in the calculations, chosen to give converged results. In the radial dimension, a square root mesh is used which provides more grid points near the origin. For the time propagation of the wave function, the split operator method and the implicit Crank-Nicolson method are used. When dealing with the $1/r_{12}$ operator, the discrete variable representation is used for the coupling between different angular momenta. Further details of the numerical calculations can be found in Ref. [28].

It can be seen from Eq. (4.3) that the two-electron wave function Λ has an increasing probability from the source term for Auger decay. At the final time of the calculation, physical quantities should be extracted as their time derivatives normalized by the probability increasing rate of Λ [107]. This can be understood that the

probability to find the system in a given channel is equal to the *rate* that electrons go into the channel divided by the norm increasing *rate* of the whole two-electron wave function. For example, the probability that the two electrons having energy ϵ_1 , ϵ_2 and angular momentum l_1 , l_2 , respectively, can be calculated as:

$$P(\epsilon_1, \epsilon_2, l_1, l_2) = \frac{\frac{d}{dt} \left| \langle f_{\epsilon_1 l_1} f_{\epsilon_2 l_2} | \Lambda(t) \rangle \right|^2}{\frac{d}{dt} \left| \langle \Lambda(t) | \Lambda(t) \rangle \right|^2}, \quad (4.6)$$

where the Coulomb wave function f_{ℓ} should be energy normalized for a continuum eigenstate, and unity normalized for a bound eigenstate.

4.2.2 Classical methods

It has been shown in many previous studies, e.g. Ref. [2], that a highly excited Rydberg electron or a continuum electron often can be approximated as a classical particle. We can use the much faster and more efficient classical-trajectory Monte Carlo method to understand the system in a totally different approach. The classical method can also give intuitive interpretations to the PCI.

In every Monte Carlo trajectory, a photoelectron is emitted near the origin at $t_1 = 0$ [91]. The energy of the photoelectron satisfies a normal distribution centered at E_1 with standard deviation $\sigma = \Gamma_c/2\sqrt{2\ln 2}$. The initial angular momentum and angular distribution should satisfy those given in $D\phi_g(\mathbf{r}_1)$. After a delay time of t_2 , which satisfies an exponential distribution $\Gamma_c \exp(-\Gamma_c t)$, the Auger electron is emitted near the origin. The energy of the Auger electron is the difference of the photoelectron energy from the total incident photon energy. The initial angular momentum and angular distribution of the Auger electron are the same as those from $F_2(\mathbf{r}_2)$. With these initial conditions, we can propagate the classical system using Hamilton's equations, and extract the physical quantities as a statistical distribution at the final time of the calculation. Further details can be found in [28, 47, 91]

4.3 Results and discussions

In Sec. 4.3.1, we report results from calculations using quantum and classical methods to show the validity of these methods with model potentials and negative energy photoelectrons. In Sec. 4.3.2 and Sec. 4.3.3, calculations are performed in pure Coulomb potentials, and we mainly focus on the quantum results of PED and the semiclassical interpretations. All calculations performed in this section have zero total angular momentum, and zero initial angular momentum for both electron.

4.3.1 Comparisons between quantum and classical methods

We first perform calculations using a model potential as given in Eq. (4.2) with $r_a = 1.0$, $Z_t = 6.0$. In this model potential with nuclear charge $Z = 1$, the quantum defects for Rydberg states with different angular momentum are approximately $\delta_s = 1.27$, $\delta_p = 0.97$, $\delta_d = 0.19$, $\delta_f = 0.008$. For $Z = 2$, the quantum defects are $\delta_s = 0.88$, $\delta_p = 0.70$, $\delta_d = 0.35$, $\delta_f = 0.06$. In the calculation, we have the Auger core width $\Gamma_c = 0.003$ a.u. ≈ 82 meV and Auger electron energy $E_2 = 2.0$ a.u. ≈ 54 eV. The photoelectron energy is set to be $E_1 = -6.0 \times 10^{-3}$ a.u., below the threshold, where the Rydberg spacing is much smaller than the Auger width. Also, for simplicity of the calculation, the initial angular momentum for both electrons is set to be zero.

The energy and state distributions for the photoelectron after PCI are plotted in Fig. 4.1, from both quantum and classical calculations. Since there is no quantization for a classical system, the classical energy distribution is a continuous function, and it has a similar distorted shape to those calculations for an above-threshold Auger process [60, 90, 91]. On the other hand, the quantum system is quantized and the photoelectron can only be in discrete eigenstates. The probabilities to find the photoelectron in different states are given in the figure. The overall envelope of the quantum state distribution qualitatively agrees with the classical energy distribution. Using the Niehaus formula [84], the maximum of the photoelectron energy distribution is located at -0.0157 , while our classical calculation gives -0.0167 . The initial

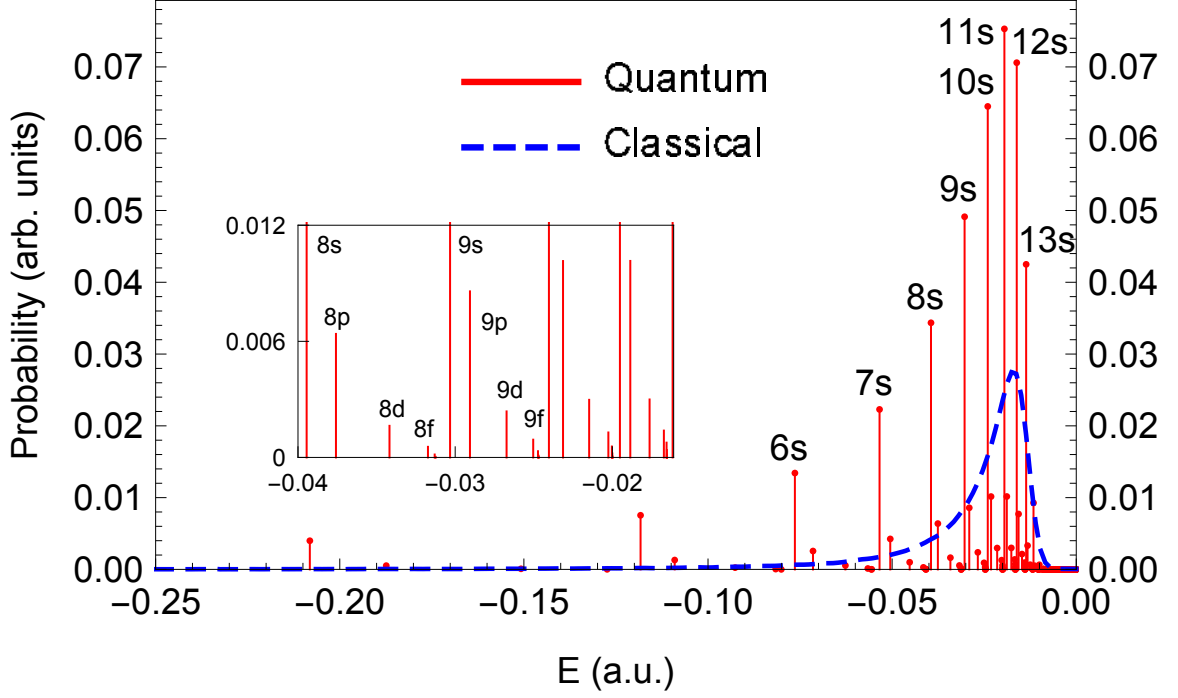


Figure 4.1. Photoelectron energy distributions after PCI from both quantum and classical calculations. The initial photoelectron energy is $E_1 = -6.0 \times 10^{-3}$ a.u., below the threshold. Auger electron energy is $E_2 = 2.0$ a.u. above the threshold, and the Auger width is $\Gamma_c = 3.0 \times 10^{-3}$ a.u. The inset figure is a magnification of quantum results at high density of Rydberg state.

energy $E_1 = -6.0 \times 10^{-3}$ a.u. is close to the resonant state of $10s$ of $Z = 1$. After the PCI, the photoelectron is shaken-up to those $11s$, $12s$, $13s$ states of $Z = 2$, although the photoelectron loses energy in the PCI. The ionization probabilities from both quantum and classical calculations are about 0.5%.

Refs. [89–92] discussed the angular momentum exchange and angular distribution between the two electrons due to the PCI. For our calculations of the angular momentum distributions, the ns peaks have much higher probabilities than other non-zero angular momentum peaks. Our quantum calculations show that about 82% of the photoelectron wave function after PCI is in s orbitals. We also count the probability that the classical angular momentum is within $0 \leq l < 1$, and the result is 78%.

These calculations show that the angular momentum exchange during the PCI with these initial parameters is fairly weak but non-trivial, and most of the wave function tends to keep its initial angular momentum.

4.3.2 The photoelectron angular and energy distributions

To further study the energy and angular momentum exchange during the PCI for near-threshold photoionizations (or photoexcitations), we perform multiple quantum calculations at different photoelectron launch energies across the threshold. The following calculations are performed with Auger electron energy $E_2 = 2.0$ a.u. and Auger width $\Gamma_c = 0.003$ a.u. The photoelectron energies are varied. The initial angular momentum for both electrons are set to be zero to simplify the calculations. All of the following calculations are performed in a pure Coulomb potential. Although we don't show model potential calculations, they give very similar results.

In PCI with the photoelectron energy near the threshold, the vast majority of the photoelectron wave function loses energy due to the change of nuclear charge from +1 to +2 when the Auger electron leaves the atom. However, when the outgoing angles of the two electrons are nearly the same, the early ejected photoelectron may be strongly repelled by the Auger electron. As a result, the photoelectron gains energy, and its momentum direction is also changed from its initial outgoing direction. Therefore, we study the correlation of the photoelectron energy (E_{1f}) versus the relative angle between momentum of the two outgoing electrons (θ_{12}). Both values are achieved at a long final time when they are already stable. We focus on the angular and photoelectron energy distributions (PED) of the wave functions in the double continuum.

In Fig. 4.2, the PED from *quantum* calculations are plotted for different initial photoelectron energies E_1 . When E_1 is well above the threshold at 0.07 a.u., most of the photoelectron wave functions have a lower energy but still remains ionized, and the angular distribution is nearly spherically symmetric other than for those $\cos \theta_{12}$

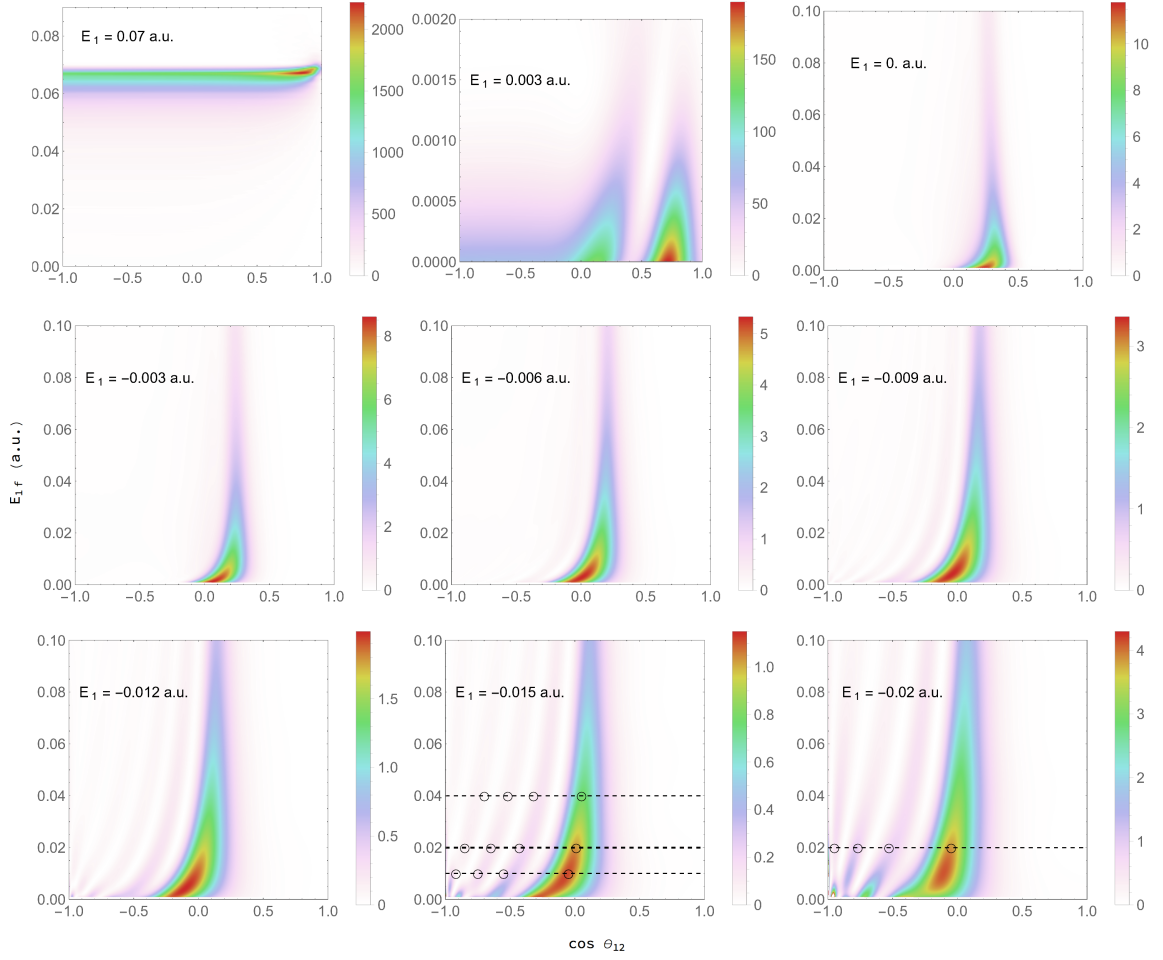


Figure 4.2. Quantum results of the angular ($\cos \theta_{12}$) and photoelectron energy (E_{1f}) distributions (PED) at different initial photoelectron energy E_1 . The initial Auger electron energy is $E_2 = 2.0$ a.u., and Auger width is $\Gamma_c = 0.003$ a.u. The photoelectron energy E_1 is given at the top left of each subfigure. Note that, the E_{1f} and PED scales are different in different subfigures. All calculations are performed at the same initial intensity in the source terms. Among different subfigures, the PED number is proportional to their absolute count of detections due to the same initial photon intensities. The dashed horizontal lines in the subfigures of $E_1 = -0.015$ and -0.02 a.u. are plotted at $E_{1f} = 0.01, 0.02$, and 0.04 a.u. The small circles are the corresponding classical maxima presented later in the text.

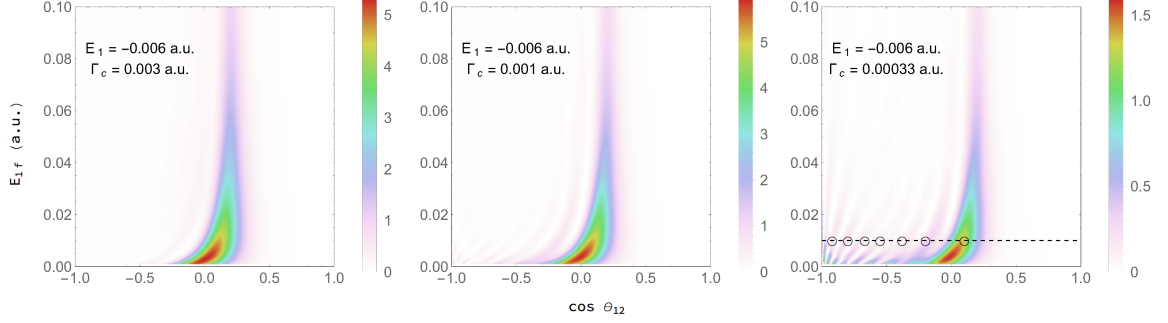


Figure 4.3. Quantum results of the PED at $E_1 = -0.006$ a.u., and different Γ_c . The Γ_c is given at the top left of each subfigure. The initial Auger electron energy is $E_2 = 2.0$ a.u. Other properties are the same as those given in the caption of Fig. 4.2. The dashed horizontal line in the subfigure of $\Gamma_c = 3.3 \times 10^{-4}$ a.u. is plotted at $E_{1f} = 0.01$ a.u. The small circles are the corresponding classical maxima presented later in the text.

near 1 [25, 105]. When E_1 is slightly above the threshold at 0.003 a.u., two local maxima can be found in the figure. The right peak originates from those positive energy, outgoing photoelectrons being closely passed by a late emitted fast Auger electron at a large distance away from the nucleus. The photoelectron is then pushed aside to a slightly larger angle, and still remains in the continuum. Photoelectrons in the left peak near $\cos \theta_{12} = 0$ are due to the repulsion from an early emitted Auger electron just after the photoionization. The strong repulsion may directly push the photoelectron to a much larger angle than the previous scenario. Detailed analyses can be found in [91].

As the photoelectron energy E_1 decreases and goes below the threshold, the absolute value of the PED also decreases. This is partly due to the fact that, as E_1 gets lower, the Rydberg spacings become greater than the Auger width, and the initial photoabsorptions at non-resonant energies are much weaker. The abnormal increase in the PED for $E_1 = -0.02$ a.u. is because -0.02 a.u. is an eigenenergy of a pure Coulomb potential with $n = 5$ and $Z = 1$. With the same intensity in the

initial source terms, the resonant photoabsorption at -0.02 a.u. causes higher counts in the double continuum. The ionization probabilities barely decrease to 0.4% for $E_1 = -0.02$ a.u., comparing to the 0.5% for $E_1 = -0.006$ a.u.

Comparing the subfigures for $E_1 = 0.003$ a.u. and $E_1 = 0$ a.u., the “right” peak disappears, and the “left” peak grows. This indicates a nearly zero probability for an outgoing photoelectron being closely scattered by an Auger electron *at a large distance* and still remain positive energy, as those scenarios described earlier for the $E_1 = 0.003$ a.u. Another interesting feature in Fig. 4.2 is that, as the E_1 decreases, interference patterns start to appear in the distributions. However, those interference patterns do not exist in classical calculations with the same parameters, which indicates that those patterns are quantum effects. The subfigure for $E_1 = -0.02$ a.u. also illustrates that resonance in the initial photoelectron excitation has no significant effect in those final interference patterns.

To study the interference patterns at different initial conditions, we perform several quantum calculations with the same E_1 at -0.006 a.u. but different Γ_c . The resulting PED can be seen in Fig. 4.3. The interference pattern is barely visible at $\Gamma_c = 0.003$ a.u., but is very clear at $\Gamma_c = 3.3 \times 10^{-4}$ a.u. A smaller Γ_c gives well-resolved energy spectrum in the photoabsorption, and that leads to better-resolved interference patterns in the PED. Another feature is that the oscillations in the interference pattern are much faster than that of $E_1 = -0.015$ a.u. or -0.02 a.u. This can be interpreted using our semiclassical approach introduced in the next subsection. Further estimations and numerical calculations show that, when the photoelectron energy satisfies $E_1 < -0.5 \Gamma_c^{2/3}$, the interference pattern starts to be visible. This is also the energy, E_1 , that the Rydberg spacings $\sim n^{-3}$ equals the Auger width, and states with different principal quantum number n are resolved by the photoexcitation photon and the Auger decay rate.

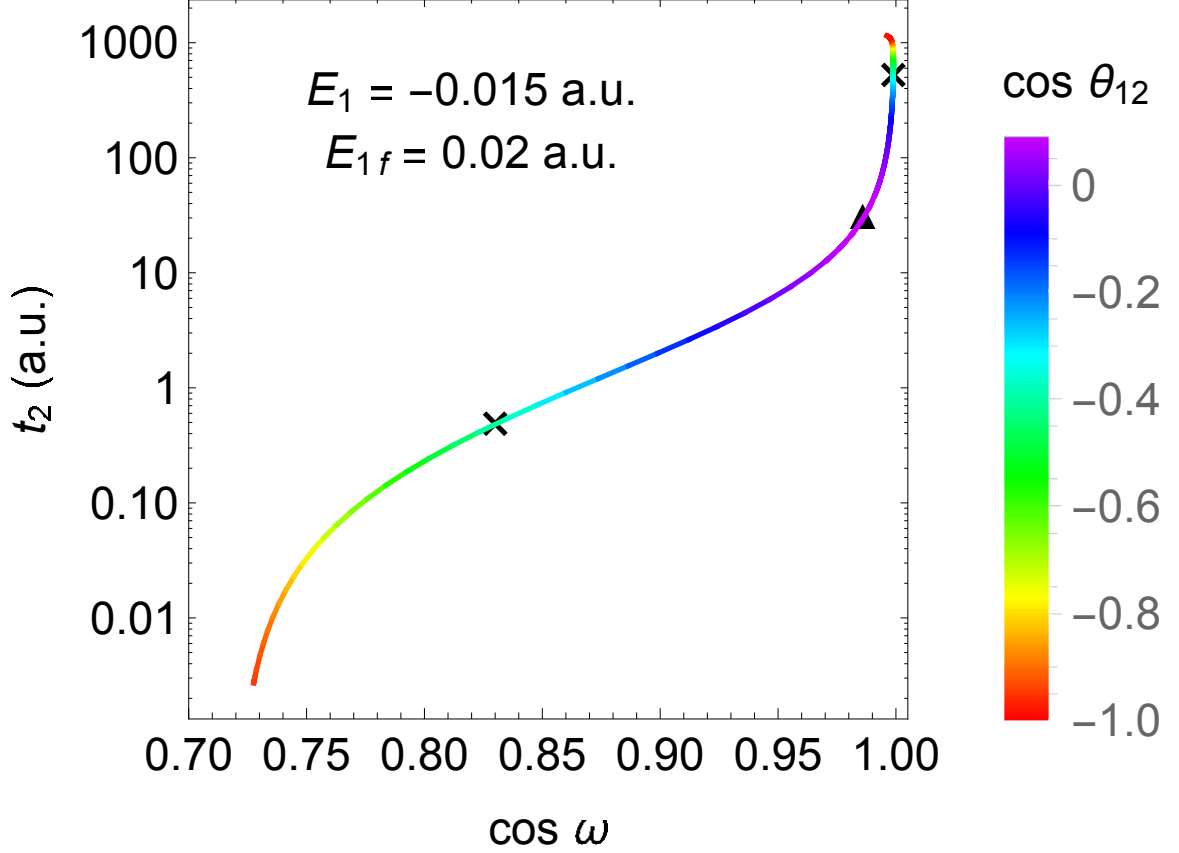


Figure 4.4. The relation of t_2 versus $\cos \omega$ with a fixed $E_{1f} = 0.02$ a.u. The $\cos \theta_{12}$ value, which is the angle difference in the asymptotic momentum of the two continuum electrons, is marked with different colors. The ω is the angle difference between the launch directions of the two electrons, and t_2 is the time of Auger decay after launch of the photoelectron. Two X's are plotted at (0.83, 0.45) and (0.9989, 630), which both give $\cos \theta_{12} = -0.4$. The triangle is plotted at (0.987, 32.8), which is the transition point that distinguishes the two paths, and is also the initial condition to achieve the classically maximum allowed $\cos \theta_{12} = 0.108$.

4.3.3 Semiclassical interpretations of the interference patterns in PED

Interference in quantum systems often results from two paths leading to the same final state. Since the quantum and classical calculations give similar results for a below-threshold photoexcitation Auger process as presented in Sec. 4.3.1, multiple

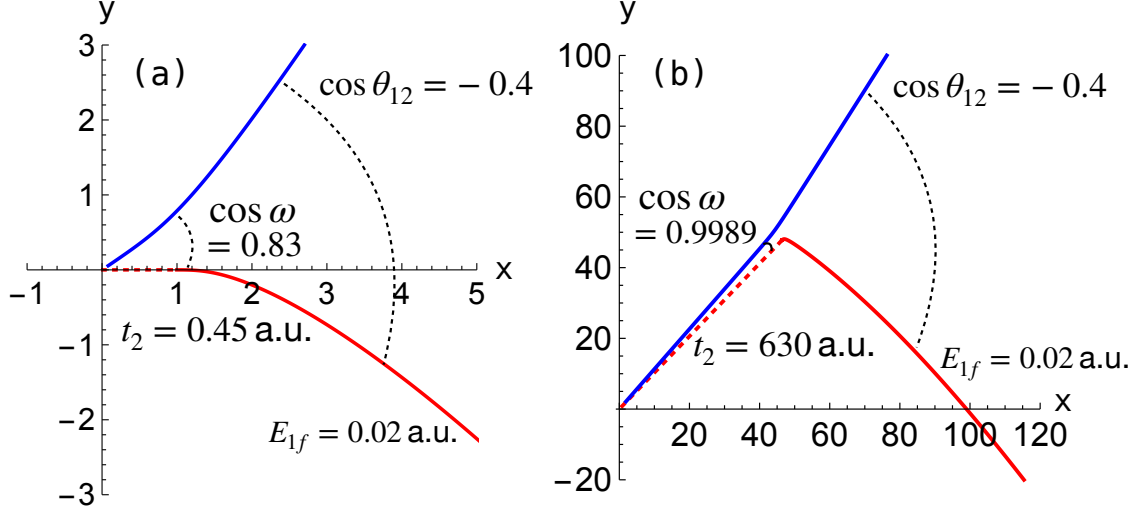


Figure 4.5. Illustrations for the two classical trajectories with final angle $\cos \theta_{12} = -0.4$ and photoelectron energy $E_{1f} = 0.02$ a.u. The nucleus is located at the origin. The red and blue lines are trajectories for photoelectron and Auger electron, respectively. The dashed red lines are photoelectron trajectories before the Auger decay. The figure (a) refers to an early Auger decay, and the figure (b) refers to a late Auger decay.

classical calculations are performed to qualitatively study the quantum interference patterns. We trace back those classical trajectories that give specific E_{1f} and $\cos \theta_{12}$ at the final time, and study their spatial trajectories and initial launch variables. With fixed initial energies for the photoelectron and Auger electron, only two variables may affect the final values of E_{1f} and $\cos \theta_{12}$: the Auger decay time t_2 after the photoelectron excitation, and the initial launch angle difference ω between the two electrons.

In classical trajectories, there exists a mapping from the initial pair $(\cos \omega, t_2)$ to the final pair $(\cos \theta_{12}, E_{1f})$. For example, when $E_1 = -0.015$ a.u., $E_{1f} = 0.02$ a.u., the function of $\cos \theta_{12} \sim (\cos \omega, t_2)$ is given in Fig. 4.4. Note that, for initial angle $\cos \omega < 0.7$, it is nearly impossible for the photoelectron to gain enough energy and become ionized. On this curve, to achieve $\cos \theta_{12} = -0.4$, which is close to a quantum

constructive interference region in Fig. 4.2, there are two classical trajectories with totally different initial values. Illustrations for the two trajectories are given in Fig. 4.5. The first trajectory has $\cos\omega = 0.83$, $t_2 = 0.45$ a.u., and the second trajectory has $\cos\omega = 0.9989$, $t_2 = 630$ a.u. In the first trajectory, the photoelectron is directly pushed out by the early emitted Auger electron. For the second trajectory, we have $t_2 > 0.5 T_{\text{Ryd1}} \approx 604$ a.u. The Auger decay happens when the photoelectron is just starting to return to the nucleus, and the emitted angle of the Auger electron is very close to that of photoelectron. The returning photoelectron is then scattered by the outgoing Auger electron, gains energy, and gets ionized from the atom in a different direction from its initial launch direction. Since there are two totally different paths that can reach the same final region in the double continuum, quantum interferences exist, and interference patterns can be found in the PED figure.

We also use a semiclassical idea to analyze the quantum interference pattern as presented in Fig. 4.2. We consider the two classical paths that go to the same final region in $\cos\theta_{12}$ and E_{1f} , and accumulate their classical actions as the time integral of their respective Lagrangians from the launch of photoelectrons to a large fixed final time. For example, in the problem with $E_1 = -0.015$ a.u., $E_2 = 2.0$ a.u. and $\Gamma_c = 0.003$ a.u., we consider the thick horizontal dashed line of $E_{1f} = 0.02$ a.u. in the PED plot given in Fig. 4.2. The relation of $\cos\theta_{12}$ versus initial value $(\cos\omega, t_2)$ pairs are given in Fig. 4.4. Since the photoelectron is in a periodic Rydberg motion before Auger decay, we may only consider cases that the t_2 is less than one Rydberg period. For the first path with small t_2 and small $\cos\omega$, the $\cos\theta_{12}$ increases as $\cos\omega$ and t_2 increase until reaching the classically maximum allowed $\cos\theta_{12} = 0.108$ at this energy, where $\cos\omega = 0.987$ and $t_2 = 32.8$. Beyond this point, the $\cos\theta_{12}$ decreases as the t_2 increases, which gives the mapping of the second path. We then calculate the semiclassical actions S accumulated from the two paths, and δS as the action difference. The phases φ , which are the actions modulo 2π , versus $\cos\theta_{12}$ are given in Fig. 4.6. Comparing to the quantum results in Fig. 4.2, where the global maximum for $E_{1f} = 0.02$ a.u. is achieved at around $\cos\theta_{12} = 0$, the classical action difference

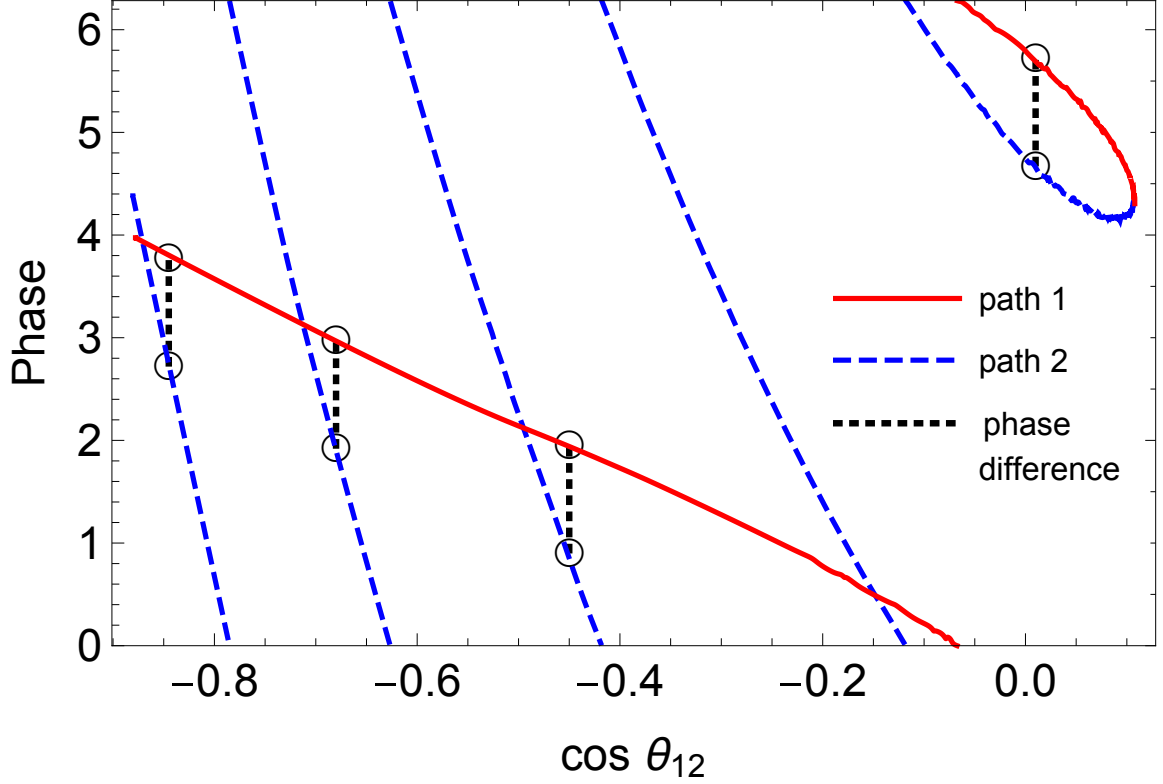


Figure 4.6. The classical phases from the two paths versus different final value of $\cos \theta_{12}$, at the same final energy of $E_{1f} = 0.02$ a.u. The action difference reaches a local maximum around $\cos \theta_{12} = 0$, and $\delta S = 1.05$, which is plotted in black dotted line. The $(\cos \theta_{12}, E_{1f}) = (0, 0.02)$ is a constructive interference point as presented in Fig. 4.2. All other three black dotted lines represent the same phase differences $\delta\varphi = 1.05$, and are plotted at $\cos \theta_{12} = -0.45$, -0.67 , -0.85 , respectively.

$\delta S = 1.05$ can be found at this angle. We then find those classical paths having action differences $\delta S = 1.05 \pm k \cdot 2\pi$, where k is an integer. The classical paths with final angles of $\cos \theta_{12} = -0.45$, -0.67 , and -0.85 have phase differences $\delta\varphi = 1.05$ modulo 2π , and these $\cos \theta_{12}$ values are approximately the same constructive interference angles as those presented in Fig. 4.2. Similarly, classical maxima are also calculated at several other E_{1f} values and different initial conditions, and their locations can be found in Fig. 4.2 and Fig. 4.3.

In Fig. 4.3, the locations of interference maxima do not change with Auger width Γ_c , and the interference patterns are better resolved when the Γ_c gets smaller. This can be understood that the Γ_c only controls the distributions of the Auger decay time t_2 , but not the actual electronic dynamics. With a smaller Γ_c , the t_2 has a higher probability to be a large value, which could result in more trajectories of those extreme conditions in $\cos \theta_{12}$ or E_{1f} . On the other hand, the interference intensities oscillate much faster in Fig. 4.3 with $E_1 = -0.006$ a.u. than that in Fig. 4.2 with $E_1 = -0.015$ a.u. The fast change in the relative interference phase comes from the rapid increase in the semiclassical action in the second path, where the returning photoelectron is scattered by the fast outgoing Auger electron. In the second path, the Auger electron is emitted a long time after excitation of the photoelectron. Considering the Bohr-Sommerfeld quantization condition, the photoelectron accumulates more action with a higher initial energy. Thus, the semiclassical phases would be more sensitive to the launch time t_2 and final angle $\cos \theta_{12}$.

Further studies of this model can be extended to non-zero initial angular momentum. We know that the interference patterns are constructed from two paths, and one crucial path is at small ω and large t_2 . For non-zero angular momentum, the initial angular distributions of the photoelectron and Auger electron are polarized. If they have the same polarization angle, there will be a higher chance that the initial angle difference ω is a small value, and the interference patterns would be brighter and easier to observe in experiment. Furthermore, since our calculations are performed with zero angular momentum using pure Coulomb potential or simple model potential, study of non-zero angular momentum in a sophisticated model potential could be an interesting topic. A non-negligible ionic core could twist the motion of electrons at small distance near the nucleus, thus the dynamics of the first path would be affected. The exact interference patterns might be different in different atoms.

4.4 Conclusions

In this chapter, we performed quantum calculations and classical calculations to numerically study the Auger process and the post-collision interaction. Both methods are time-dependent calculations, which can help us better understand the time-resolved dynamics of the Auger process. We mainly focused on those photoexcitation and photoionization scenarios in which the excited (or ionized) photoelectron energy is near the ionization threshold. An initial calculation demonstrated the effectiveness of our classical method when describing a quantum model with negative photoelectron energy and model potential. The numerical results showed that the angular momentum exchange during the post-collision interaction is fairly weak [89–92]. To further study the interaction between the two electrons during the post-collision interaction, we focused on the correlation of angular and photoelectron energy distribution. We decreased the initial energy of the photoelectron, and checked the PED at different initial photoelectron energies and Auger core widths. Interestingly, when the initial energy of the photoelectron is low enough, interference patterns can be found in the PED. We studied the mappings between initial values of launch time and angles and final values of energies and angles in the interference region. We found that there are two paths with different initial conditions that can contribute to the same final region in the double continuum. We used a semiclassical treatment to calculate the classical actions as the time integral of the Lagrangian of the system, and calculated the phase difference of the two paths. Along a given line in the PED correlation figure, our semiclassical treatment gave the relative locations of the interference maxima, which are nearly the same as those from quantum calculations. Finally, we briefly discussed our model with non-zero initial angular momentum, and proposed further studies on those interference patterns in different atomic systems.

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5. ANGULAR INTERFERENCES OF SEQUENTIALLY IONIZED DOUBLE CONTINUUM WAVE PACKETS

This chapter is directly taken from *Phys. Rev. A*, **98**, 053407 (2018) [108] with minor differences, where the original draft was written by Xiao Wang.

5.1 Introduction

The correlations between two electrons in an atom remain an interesting and difficult topic for many years. The Coulomb interaction between the two electrons acts as the most important factor of the coupled degree of freedom in a complex atomic or molecular system. In order to understand the basic interaction between the two electrons, many theoretical and experimental studies have been conducted.

One of the most basic ideas is to study laser induced photoionization of a helium atom. Experimentally, laser induced photoionization has been presented in many previous works [109–116]. Theoretically, many calculations have also been successfully performed [3, 117–121]. Some studies focus on the intrinsic correlations between the two electrons, for example, how the two electrons are ionized or excited by one photon. On the other hand, several authors conducted experiments on probing the two-electron dynamics in an atom [23, 26, 122], using sequential two-step laser excitations. In their experiments, barium atoms are prepared in the ground state. First, two consecutive laser pulses excite one of the valence electrons to a coherent Rydberg wave packet. After a short time delay, the other valence electron is also excited to a coherent Rydberg wave packet, possibly with different energy, utilizing the isolated core excitation (ICE) technique [17, 123–125]. Due to the rapid interactions between the two electrons, fast autoionizations can occur in less than one Rydberg period. Time delay of the second excitation gives control over the strength of interaction

between the two electrons. Time-resolved observations on the fraction of singly or doubly charged ions act as a probe of the strong interactions between the two electrons. Theoretical calculations on this two-step launch model were performed in a previous study [47] and focused on probing the autoionization of the double Rydberg wave packets.

Another possible way to study the two electron correlation is through the post-collision interaction (PCI) in a laser-induced Auger process. Many theoretical and experimental studies have been performed in the past decades, e.g. Refs. [71, 72] and references therein. In our previous work [69], we focused on the post-collision interaction in below-threshold photoexcitation Auger processes. Interferences in the distribution of photoelectron energy and relative angle between the two ionized electrons were found. The quantum interferences make visible some of the phase properties of the double continuum wave function. The interference originates from two different classical paths that evolve to the same final energy and relative angle. Properties of this interference were studied using classical trajectories and the classical actions. The semiclassical interference maxima reproduced those from quantum calculations.

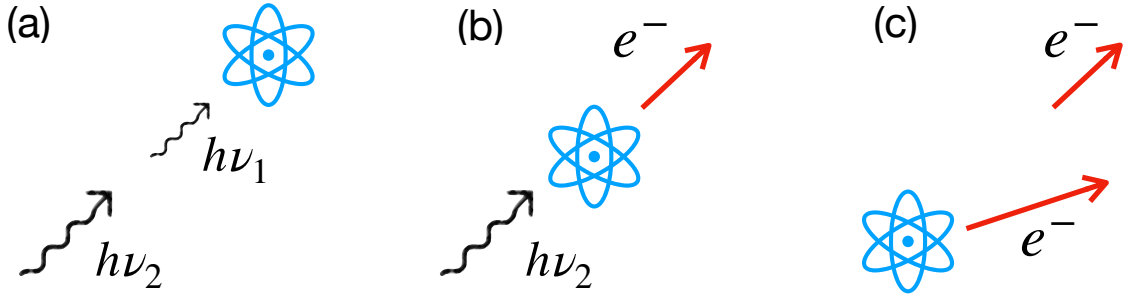


Figure 5.1. Cartoon of the two-step ionization model.

Similar to the photoexcitation Auger decay model, simulations also find interferences in the two-step ionization model. In this chapter, fully quantum calculations on a two-electron atom are performed, see Fig. 5.1(a). The first electron is ionized to a

spherically symmetric coherent wave packet in the continuum, see Fig. 5.1(b). After a short time delay, the second electron is ionized to a spherically symmetric coherent wave packet with energy higher than the first wave packet, see Fig. 5.1(c). After the second electron fully passes the first electron, correlations of the first electron's final energy and the relative angle between the two electrons are evaluated. Effects from properties of the ionization laser pulses on final energy and angle are studied, including time widths and frequency chirpings of the laser pulses. The effects of the variable time delay between the two-step laser ionizations are also investigated. All of the above quantum calculations are interpreted using semiclassical techniques, and detailed analyses are presented on the properties of the interference patterns. Finally, the differences between the two-step ionization model and the photoexcitation Auger decay model are discussed in detail.

This chapter is structured as follows. In Sec. 5.2, the quantum and classical models used in this chapter are briefly introduced. In Sec. 5.3, properties of the interference patterns with different initial conditions are presented. In Sec. 5.4, discussions of the two models are given. Atomic units are used throughout the chapter unless specified otherwise.

5.2 Methods

The two-electron atomic model used in this project has been introduced previously in Refs. [47, 69]. Related experiments have been performed in Ref. [26]. The basic idea of the theoretical model is presented in this section. To reduce the complexity of calculations, both electrons are launched into spherically symmetric radial wave packets, which means their initial angular momentum just after launch is set to zero.

An atom with two active valence electrons, e.g. Ba, is prepared in its ground state. Experimentally, two consecutive short laser pulses are used to excite (or ionize) one of the valence electrons to a coherent radial wave packet. The dynamics of the outgoing

ionized electronic wave packet can be described using the following time-dependent inhomogeneous Schrödinger equation [28]:

$$\left[i \frac{\partial}{\partial t} - (H_1 - E_1) \right] R_1(r_1, t) = S_1(r_1) G_1(t). \quad (5.1)$$

The $H_1 = p_1^2/2 + V(r)$ is the Hamiltonian of the first outgoing electron. Although the Coulomb potential $V(r) = -Z/r$ is used in our calculations, model potentials give very similar results since significant interactions between the two electrons occur away from the nucleus. The potential for the first electron is $Z = 1$, before the second electron is ionized. R_1 is the time-dependent radial wave function of the wave packet. E_1 is the central energy of the wave packet. S_1 is source term of the first electron before laser ionization, and it has a small radial extent. The

$$G_1(t) = \exp \left[-2 \ln(2) t^2 / t_{w,1}^2 - i \dot{\omega}_{c,1} t^2 / 2 \right] \quad (5.2)$$

is a source term reflecting properties of the laser pulse electric-field used to ionize the first wave packet. $t_{w,1}$ is the FWHM of the laser pulse, and $\dot{\omega}_{c,1}$ represents the frequency chirping.

After a variable time delay t_d , the other valence electron is exposed to a laser pulse with different frequency from the previous excitation, and being excited to another radial wave packet. The dynamics of double wave packets can be calculated using the following time-dependent Schrödinger equation [28]:

$$\left[i \frac{\partial}{\partial t} - (H - E_1 - E_2) \right] \Psi(r_1, r_2, t) = R_1(r_1, t) S_2(r_2) G_2(t). \quad (5.3)$$

The $H = p_1^2/2 + p_2^2/2 + V(r_1) + V(r_2) + 1/r_{12}$ is the full Hamiltonian of the two-electron three-body Coulomb system, and E_1, E_2 are the central energies of the two electronic wave packets, respectively. Here $Z = 2$ is used in the Coulomb potential term $V(r)$. Ψ is the full two-electron wave function, while R_1 is the radial wave function calculated from Eq. (5.1). S_2 is the source term with a small radial extent, and

$$G_2(t) = \exp \left[-2 \ln(2) (t - t_d)^2 / t_{w,2}^2 - i \dot{\omega}_{c,2} (t - t_d)^2 / 2 \right] \quad (5.4)$$

is a source term reflecting properties of the laser pulse electric-field used to ionize the second wave packet. Similarly, $t_{w,2}$ is the FWHM of the second laser pulse, and $\dot{\omega}_{c,2}$ is the frequency chirping. The phase of the second laser pulse relative to the first laser pulse only gives an overall phase shift of the two-electron wave function Ψ , and has no physical impact to the system.

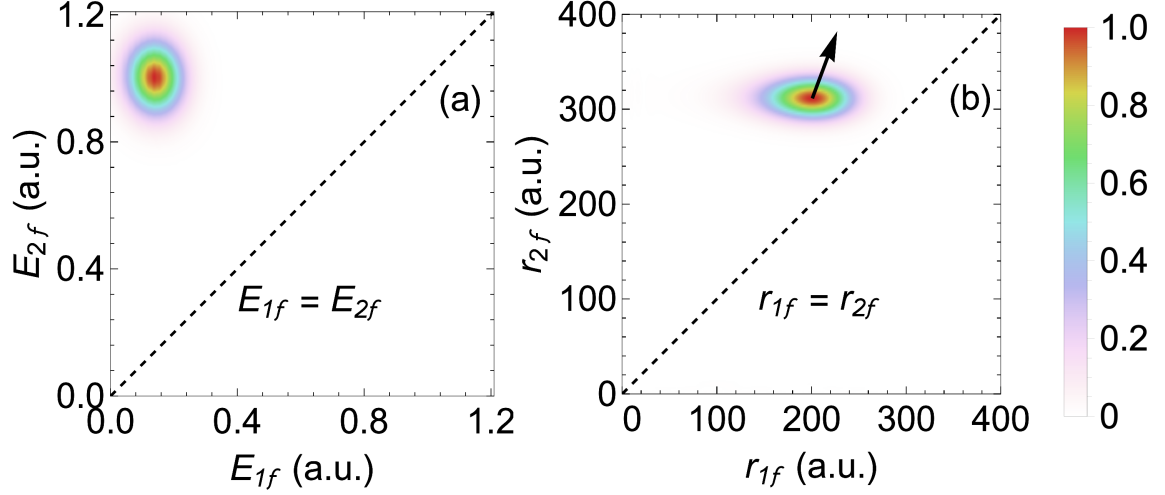


Figure 5.2. Final energy and radial distributions from a quantum calculation with initial parameters given in the caption of Fig. 5.4. The results are non-symmetrized. The final time of the calculation is set to 215 a.u. after the center of the second laser pulse; at this time, the second wave packet has fully passed the first wave packet in position space. The black arrow in figure (b) indicates the moving direction of the wave packet in position space. The separation between the two electrons only gets larger at later times.

It can be seen in Eq. (5.1) and (5.3) that the two-electron wave function is non-symmetrized whereas the actual spatial function should be symmetric or anti-symmetric under exchange, depending on the spin coupling. However, all of the calculations below are for cases where the two electrons' energies have relatively large differences which makes them essentially distinguishable. To illustrate this, the final energy and radial distributions from an example quantum calculation are

presented in Fig. 5.2. In neither the energy nor the position representations do the wave functions have overlap with their symmetrized counterpart. Non-symmetrized, symmetrized, or anti-symmetrized wave functions yield nearly identical results in the physical quantities shown in later sections. All results presented in this chapter are from non-symmetrized wave functions.

In the expressions for laser pulses in Eq. (5.2) and (5.4), the possibility for a substantial chirp has been included for additional control of the two-electron wave functions. There are two important consequences from the chirp. Firstly, the chirping introduces an energy-dependent phase into the two-electron wave function. For a positive chirping $\dot{\omega}_c$, low energy electrons are emitted early; for a negative chirping $\dot{\omega}_c$, fast electrons are emitted early. Because of the energy exchange between the two electrons, these relative energy-dependent phases are important. Secondly, when there is frequency chirping, the energy width of the electrons are larger than the minimum from the uncertainty principle. For example, the FWHM of energy distributions are

$$\delta E_j = \left(\frac{4 \ln 2}{t_{w,j}} \right) \sqrt{1 + \left(\frac{\dot{\omega}_{c,j} t_{w,j}^2}{4 \ln 2} \right)^2}, \quad (5.5)$$

where $j = 1, 2$ represent the first and the second electron. When $\dot{\omega}_c t_w^2 = \pm 4\sqrt{3} \ln 2 \approx \pm 4.802$, the energy width, δE , is doubled from the minimum width without chirping. This provides a tool to study the effect of laser time width or energy width only, without changing the other.

The wave function Ψ is expanded in a spherical harmonic basis and propagated using the time-dependent close coupling method [8, 28] with an implicit time propagator. The final time of the calculation is chosen such that the second electron's radial wave function fully passes the first electron's. The first electron's energy and the relative angle between the two electrons are evaluated at the final time.

This two-step launch model can also be simulated using the classical trajectory Monte Carlo method [28, 91]. The ionization (launch) times of the electrons are randomly sampled from the quantum source term $|G_{1,2}(t)|^2$ for each electron. The initial

energies are sampled from the Fourier transform of the corresponding launch time distributions. The classical energies E_j satisfy the following Gaussian distribution:

$$E_j \sim \exp \left(-4 \ln 2 \cdot \left[E - \tilde{E}_j(t) \right]^2 / \delta E_j^2 \right), \quad (5.6)$$

where $j = 1, 2$ represent the first and the second electron. The $\delta E_j = 4 \ln 2 / t_{w,j}$ is the FWHM of the Gaussian energy distribution *without chirping*. To simulate the frequency chirping, the central energy $\tilde{E}_j(t) = \tilde{E}_j(0) + \dot{\omega}_{c,j}t$ is time-dependent, where $\tilde{E}_j(0)$ is the corresponding laser central energy, and $\dot{\omega}_{c,j}$ is the frequency chirping.

5.3 Results

The first calculation is performed with the following initial variables and properties. Each electron's angular momentum just after launch is set to be zero. The initial energies for the two electrons are $E_1 = 0.15$ a.u., $E_2 = 1.0$ a.u. The laser time widths are $t_{w,1} = 40.0$ a.u., $t_{w,2} = 15.0$ a.u., and there is no frequency chirping. The second electron's launch time delay is $t_d = 120.0$ a.u. At the final time, the relative angle $\cos \theta$ is defined as the angle between the two electrons' asymptotic momentum at infinity.

Correlation between the first electron's final energy and the relative angle can be found in Fig. 5.3. Since the launch angular momenta for each of the two electrons are zero, the relative angle $\cos \theta$ has a flat distribution from -1 to 1 *if* there are no interactions between the two electrons. The interactions between the two electrons are nearly negligible at large relative angle (i.e. small $\cos \theta$), and the distribution presented in Fig. 5.3 is nearly flat in these regions. However, at a small relative angle (i.e. large $\cos \theta$), when the second electron passes the first electron, the strong repulsion between the two electrons push them away from each other. Thus, nearly no probability can be found at $\cos \theta_f > 0.95$, and electrons initially emitted at these relative angles are pushed aside to larger final angles, i.e. smaller $\cos \theta$. That makes the relative angle distribution have a local maximum near $\cos \theta_f \approx 0.87$ and $E_{1f} \approx 0.15$ a.u. Also, most

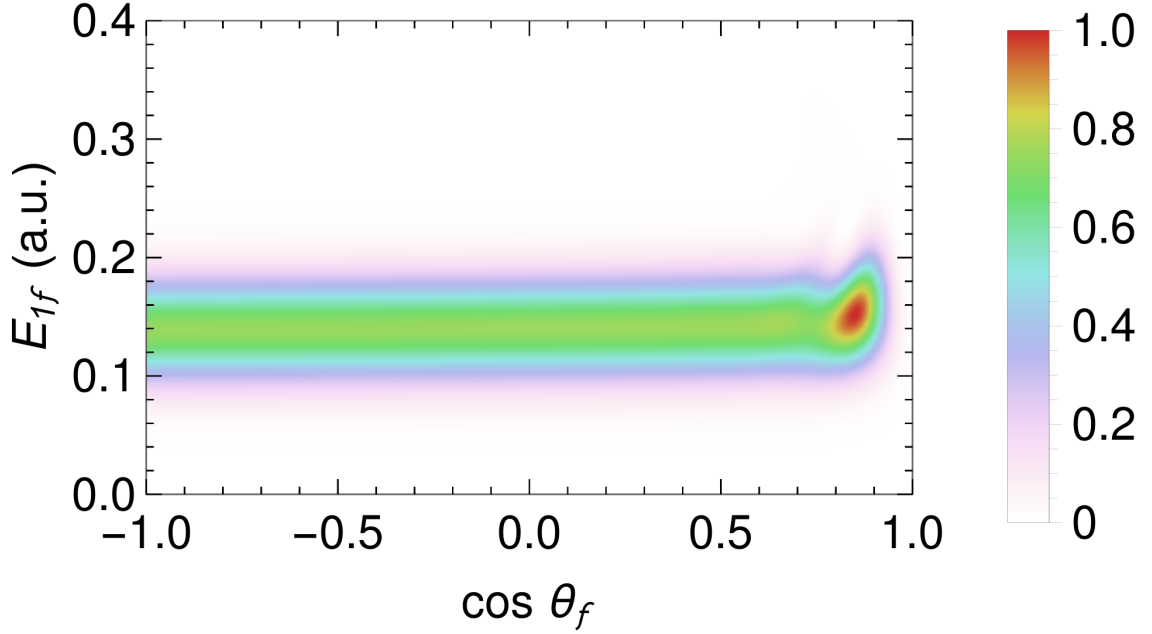


Figure 5.3. Distribution of the first electron's final energy versus the final relative angle between the two electrons. The distribution is from quantum calculations. The second electron's final energy is integrated over in the distribution. The initial energies for the electrons are $E_1 = 0.15$ a.u., $E_2 = 1.0$ a.u. The laser widths are $t_{w,1} = 40.0$ a.u., $t_{w,2} = 15.0$ a.u. There is no frequency chirping. The second electron is launched at $t_d = 120.0$ a.u. after the first electron.

of those electrons pushed aside gain energy from the strong repulsions, and they can be found in a small tail near $\cos \theta_f \approx 0.9$ and $E_{1f} > 0.18$ a.u.

In Fig. 5.3, another small tail can be found near $\cos \theta \approx 0.75$ and $E_{1f} > 0.18$ a.u. which is barely visible. To study the properties of this small tail, quantum calculations are performed with only the first electron's energy width doubled. From the quantum uncertainty principle, this can be achieved by halving the first electron's launch time width $t_{w,1}$ without introducing any frequency chirping. The distribution of the first electron's energy and the relative angle can be found in Fig. 5.4. Similar to Fig. 5.3, the strong repulsion between the two electrons, when they pass close to each other,

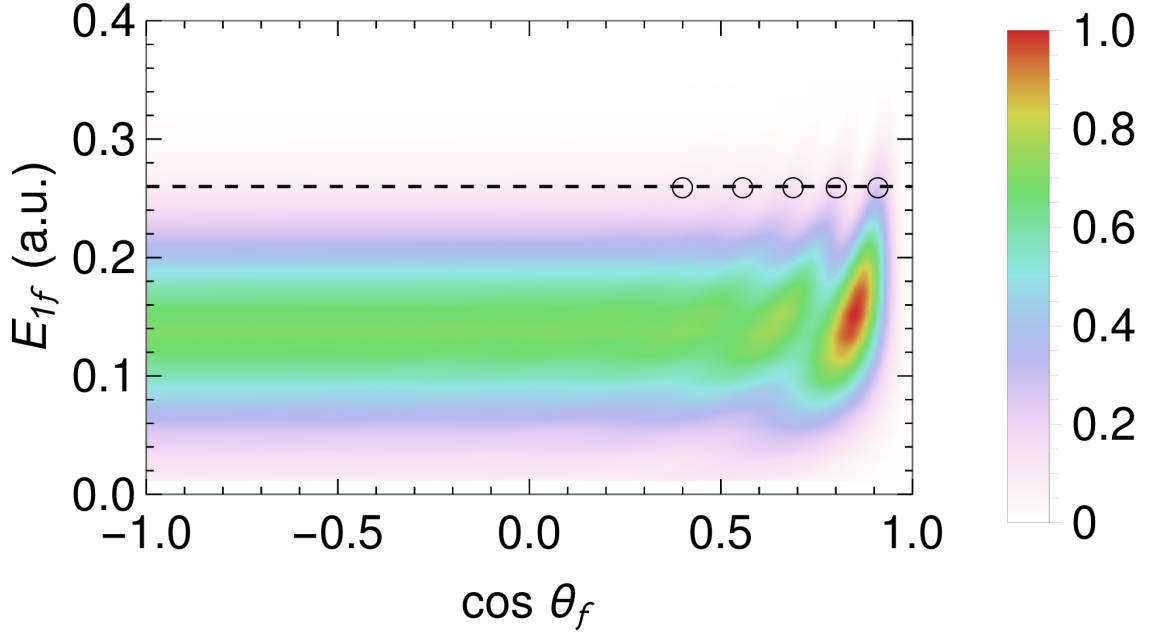


Figure 5.4. Distributions of the first electron's final energy versus the final relative angle from quantum calculations. The first electron's launch time width is $t_{w,1} = 20$ a.u., all other parameters are the same as those given in the caption of Fig. 5.3. The dashed line is at $E_{1f} = 0.26$ a.u., while the circles are at the semiclassical interference maxima described later in the text.

introduce the vacancy at $\cos \theta_f > 0.95$, the local maximum near $\cos \theta_f \approx 0.87$ and $E_{1f} \approx 0.15$ a.u., and the first tail near $\cos \theta_f \approx 0.9$ and $E_{1f} > 0.18$ a.u. Importantly, a second and a third tail near $\cos \theta_f \approx 0.8$ and 0.7 also are found. The alternations between high and low distributions with respect to $\cos \theta_f$ are indications of quantum interferences.

To study the properties of these interference patterns, the semiclassical method described in Ref. [69] is used to analyze these classical trajectories. For example, there are two totally different trajectories with final $\cos \theta_f = 0.91$ and $E_{1f} = 0.26$ a.u. in Fig. 5.4. Illustrations of the two trajectories are given in Fig. 5.5. The first trajectory, as shown in Fig. 5.5(a), has a larger initial angle between the two electrons'

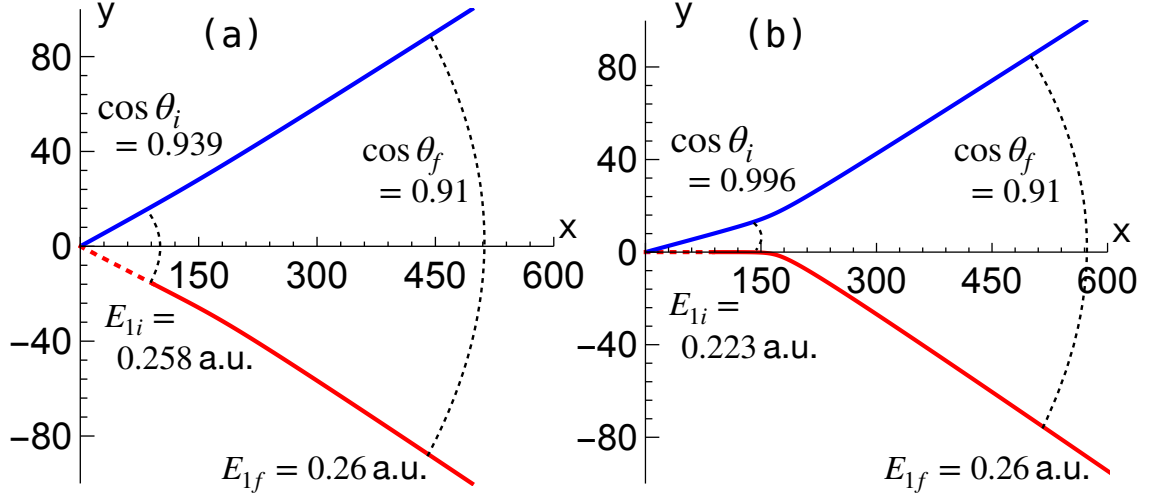


Figure 5.5. Illustrations of the two classical trajectories that result in the same final energy and final angle of the first electron. The first electron is indicated by the red line, and the second electron is indicated by the blue line. The dashed red line indicates the motion of the first electron before the second electron is emitted. The launch time delay of the second electron is 120 a.u. The second electron has an initial energy of 1.0 a.u. The figure (a) indicates trajectories with larger initial angle and weaker interaction between the two electrons, while the figure (b) indicates trajectories with smaller initial angle and stronger interaction. The final angle looks larger than $\cos \theta_f = 0.91$ because the x -scale is much larger than the y -scale in the figure.

launch directions. The Coulomb interaction between the two electrons in this case is relatively weak. The final energies and angle is nearly the same as their initial values. The second trajectory, as shown in Fig. 5.5(b), has a smaller initial launch angle. Since the second electron has a much higher energy than the first electron, intense Coulomb interaction will happen after the late-launched second electron catches up to the early-launched first electron. As can be found from the labels in the figure (b), the first electron gains energy in this process, and gets repelled to a larger final angle. In order for the two trajectories to evolve to the same final energy, the early-emitted electron from the second path must have a much lower energy than the expected final

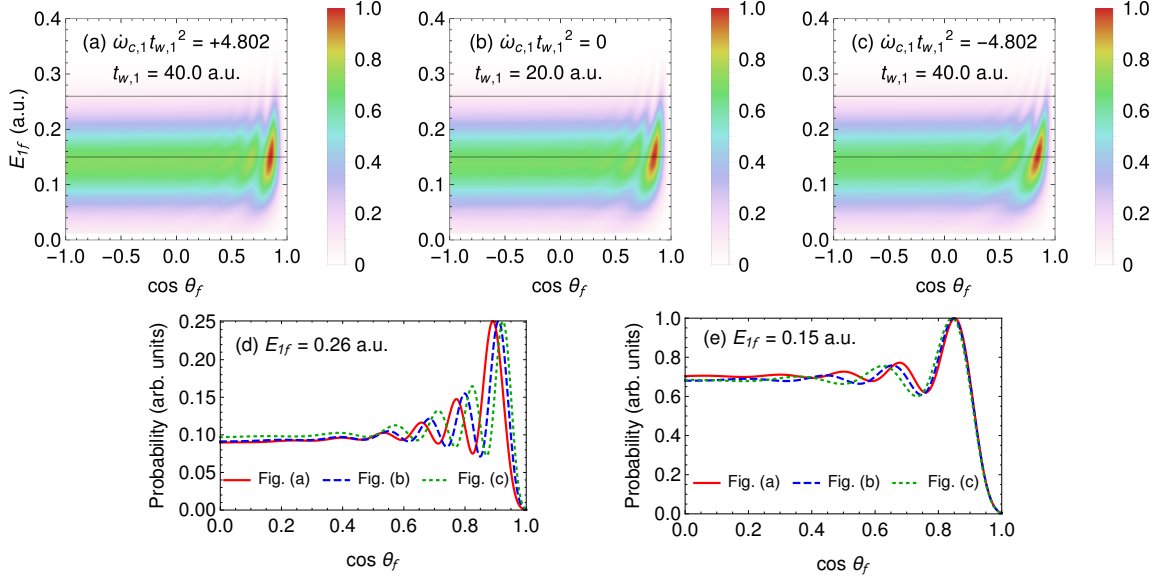


Figure 5.6. Comparisons of the first electron's final energy and the relative angle from three quantum calculations are given in (a), (b), and (c). FWHM and frequency chirping properties of the first laser pulse are given in the figure. All other quantities are the same as those given in the caption of Fig. 5.3. Note that the probability densities are in arbitrary units. Solid lines in the first three figures are plotted at $E_{1f} = 0.26$ a.u. or 0.15 a.u., corresponding to the respective horizontal slices at energies E_{1f} presented in subfigures (d) and (e).

energy. This requires the early-emitted electron be ionized from a laser with a wider energy width, which explains why the interference pattern is stronger in Fig. 5.4 than in Fig. 5.3.

When two classical paths have the same final energy and relative angle, quantum interferences may appear [69]. A semiclassical technique is used to calculate the action of the two paths. Note that when the final state is in the momentum representation, an extra phase, $-\mathbf{p}_{1f} \cdot \mathbf{r}_{1f} - \mathbf{p}_{2f} \cdot \mathbf{r}_{2f}$, from Fourier transform of the wave function, is added to the total classical action [126–128]. The $\mathbf{p}_f$ and $\mathbf{r}_f$ represent the vector momentum and position of the two electrons at a fixed final time. The phase difference between the two paths are used to find the semiclassical interference maxima. For calculations

in Fig. 5.4, the first interference maximum angle is aligned for the semiclassical and quantum calculations, e.g. the $\cos \theta_f = 0.91$ at $E_{1f} = 0.26$ a.u. Then, the rest of the interference maxima are found at semiclassical phase difference of 2π from the first interference maximum, e.g. the $\cos \theta_f = 0.80$ at $E_{1f} = 0.26$ a.u. matched fairly well with the quantum result. The semiclassically calculated interference maxima are marked as circles in Fig. 5.4.

From calculations in Fig. 5.3 to calculations in Fig. 5.4, not only the energy width is doubled, the first electron's launch time width is also halved. In order to study properties of the interference patterns, three quantum calculations are designed with the same energy width but different time widths. This can be achieved by introducing frequency chirping as mentioned in Sec. 5.2 and Eq. (5.5). Correlations of the final energy and the relative angle can be found in Fig. 5.6. For calculations shown in Fig. 5.6(a) and (c), the first electron's launch time widths are $t_{w,1} = 40$ a.u., and frequency chirpings $\dot{\omega}_{c,1}t_{w,1}^2 \approx \pm 4.802$ are added. Note that the opposite signs in frequency chirping result in a different energy vs launch time distribution for the first electron. As a comparison, the Fig. 5.6(b) has the same parameters as those in Fig. 5.4, where its doubled energy width is directly due to the halved time width without frequency chirping. The interference patterns exist in all three calculations, but with slightly different inclines in the distributions of the relative angle. These results verify that the first electron's energy width, but not the launch time width, makes the interference patterns stronger in Fig. 5.4 than that in Fig. 5.3.

To study the detailed effects of frequency chirpings in Fig. 5.6(a-c), the two horizontal slices at $E_{1f} = 0.26$ and 0.15 a.u. are given in subfigures Fig. 5.6(d) and (e). At high final energy $E_{1f} = 0.26$ a.u., as chirping $\dot{\omega}_c$ goes more negative, the interference maxima shift to higher $\cos \theta_f$. At low final energy $E_{1f} = 0.15$ a.u., the maxima shift to lower $\cos \theta_f$ as $\dot{\omega}_c$ increases. This can be qualitatively explained that with negative chirping, e.g. in Fig. 5.6(c), the first electron emitted at an earlier time has higher average energy. Thus, its scattering from the second electron happens at a much further distance from the nucleus, and it is harder for the first electron to be scattered

into a larger final angle. As a result, for higher E_{1f} , the rightmost angle $\cos \theta_f$ is larger. With negative chirping, the first electron emitted at a later time has lower average energy, and it is more likely to be scattered to larger final angle (i.e. smaller $\cos \theta_f$). The frequency chirpings affect the inclinations of the interference patterns but not the strength of them.

All of the above quantum calculations are performed with the delay time of the second launch being $t_d = 120$ a.u. Quantum calculations with the delay time being $t_d = 200$ a.u. are performed. The energy and angle correlation results can be found in Fig. 5.7. One interesting result for $t_d = 200$ a.u. is that the interference patterns are more dense than those of $t_d = 120$ a.u. in the upper right interference region, with respect to the final angle $\cos \theta_f$. This can be qualitatively understood that in order to get the same final angle and same final energy, with the first electron being further away from the nucleus, the scattering should be more intense and the first electron gains more energy in this process. To reach the same final energy, the first electron's initial energy has to be much lower, and E_{1i} decreases much faster versus θ_f . Before the second electron is launched, the lower E_{1i} is, the slower action is accumulated. Then the final total action changes faster as a function of the final angle. Faster oscillations are found in the interference amplitudes with respect to the final angle, with a longer launch delay time.

5.4 Comparisons between double wave packets and Auger decay model

As discussed in a previous chapter [69], quantum interferences also exist in the photoexcitation Auger decay model with post-collision interaction. Different classical trajectories were found that lead to the interferences in the Auger decay model. However, there are several key differences between the Auger decay model and the double wave packets model, and they lead to different interference properties.

The first major difference is the energy widths of the electrons in the two models. In the present double wave packets model, energy widths of the electrons are directly

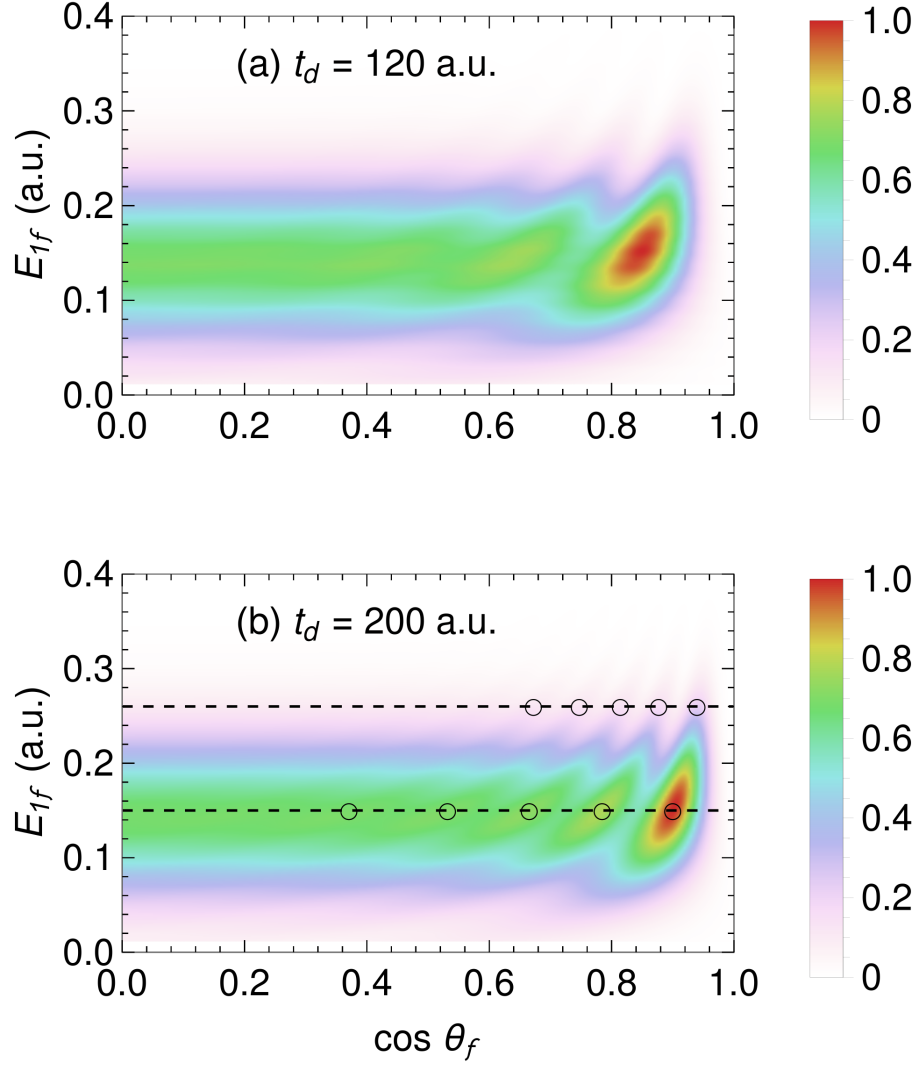


Figure 5.7. Distributions of the first electron's final energy versus the final relative angle. The two electrons' launch time widths are $t_{w,1} = 20.0$ a.u. and $t_{w,2} = 15.0$ a.u. There is no frequency chirping. The delay times of the second electron's launch t_d are given in the figure labels. All other parameters are the same as those given in the caption of Fig. 5.3. Dashed lines in (b) are plotted at $E_{1f} = 0.26$ a.u. and $E_{1f} = 0.15$ a.u. while circles are at the semiclassical interference maxima. Note that the $\cos \theta_f$ range is from 0 to 1.0 in the figure.

controlled by the properties of the laser pulses used to ionize the electrons, and the energy widths can be comparable to the absolute energy of the ionized electrons. In the Auger decay model, the photoelectron's energy width only depends on the lifetime of the inner shell vacancy. This depends on the actual atom considered in the Auger decay. It is often of the order of magnitude around 100 meV [71], which is about 3.7×10^{-3} a.u. That is usually smaller than the absolute energy of the photoelectron, but comparable to the Rydberg spacings. Based on energy conservation, the Auger electron's energy width is the bandwidth of the laser pulse minus the Auger core width. Considering the very high energy of a typical Auger electron, its energy width usually has negligible effect on the final state of the photoelectron.

In the present double wave packets model, the interferences are achieved partly by relatively large energy exchange when the two electrons are launched into small relative angles. However, for the Auger decay model with a positive energy photoelectron, the photoelectron can still be scattered by the later-emitted fast Auger electron in the two paths as presented in Fig. 5.5, but the photoelectron will not have the same final energies in the two paths. Interferences with the present two-step launch mechanics thus do not exist in the above-threshold Auger decay model.

The second major difference is the controllable launch time delay between the two electrons. In the Auger decay model, the delay time between the two launches satisfies an exponential distribution. The interference occurs when the Auger core width is equal to or smaller than the adjacent Rydberg spacings of the photoelectron. Locations and oscillations of the interference amplitudes, with respect to the relative angle $\cos \theta_f$, mostly depend on the photoelectron energy, but not the Auger core width [69]. The smaller Auger core width only makes the interference patterns brighter. In the present two-step launch model, the delay time is a single tunable value. Locations and oscillations of the interferences mainly depend on this delay time between the two launches. The first electron's larger energy width makes the interference pattern brighter.

As discussed in the final paragraph in Sec. 5.3, in the present two-step launch model, the main difference in total action accumulation is from the the first electron before the second electron emission. This is also true for the below-threshold Auger decay model. In the Auger decay model, the action accumulated by the photoelectron before the Auger decay significantly affects the final interference patterns. For fixed initial and final photoelectron energies, the Auger decay times of the two paths only depend on the final relative angle. Thus the action accumulation differences and oscillations of the interference patterns, with respect to the final relative angle, mainly depend on the initial photoelectron energy, but not the Auger core width.

Last, the tilting direction of the interference patterns with respect to the final angle are studied for the two models. For results presented in the two models, in the correlation of the first electron's final energy and the relative angle, along an interference ridge, both $\cos \theta_f$ and E_{1f} go higher or lower, in the same numerical direction. This can be understood that for electrons with higher energy, the scattering usually happens at a far distance from the nucleus. It is then harder for the first electron to be scattered into a larger final angle, or smaller $\cos \theta_f$, because the second electron has to be aimed at a very narrow angle relative to the first electron's. As an interesting example presented in Fig. 5.6(a), due to the laser frequency chirping, the first electron with lower energy is emitted earlier while higher energy is emitted later. With a reasonable delay time, the first electron's wave function can have a very narrow radial width while scattered by the second electron. This causes the final interference pattern be nearly vertical on the $\cos \theta_f$ scale.

5.5 Conclusions

In this chapter, the interferences in the two-step launch double wave packets model were presented. The two-step launch model contains sequentially ionized double wave packets using laser pulses. The two wave packets can have different energies or different energy widths due to the properties of the laser pulses. The delay time

between the ionizations of the double wave packets is also tunable in an experiment. Numerical calculations are performed using both quantum and classical methods. The angular momentum of both electrons is set to zero just after launch. At the final time of the calculations, the distribution of the first electron's energy versus the relative angle between the two electrons is studied. At large final relative angle, the distribution is mostly flat, and the final angle is nearly the same as their initial angle. In these regions, the final energies are also nearly the same as their initial energies. However, due to the repulsion between the two electrons, the two electrons initially launched into very close directions are repelled to larger final relative angles. The first electron gains energy in this process. In these two different scenarios, there are two sets of trajectories that start with different initial energies and angles but result in the same final energy and relative angle. Semiclassical action is used to analyze the two different trajectories and locations of quantum interference maxima. Properties of the quantum interferences are studied in detail with respect to different initial physical parameters, including laser pulse width, laser frequency chirping, and time delay between the two-step ionizations.

Furthermore, the present double wave packet model and the below threshold photoexcitation Auger decay model [69] are compared. Differences in the physical model are discussed, including the fixed tunable delay time between the two-step ionizations in the double wave packet model, versus the exponentially distributed Auger core decay time after photoexcitation. Effects of the initial energy distributions of the two electrons in these two models are also studied. Further studies of these two models can focus on the non-zero initial angular momentum of the two electrons, and novel interference patterns may be discovered.

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6. IONIZATION FROM RYDBERG ATOMS AND WAVE PACKETS BY SCALED TERAHERTZ SINGLE-CYCLE PULSES

This chapter is directly taken from *Phys. Rev. A*, **99**, 033418 (2019) [129] with minor differences, where the original draft was written by Xiao Wang.

6.1 Introduction

Strong field ionization is a tool commonly used to study and probe atomic and molecular structure. In contrast to deeply bound electrons, Rydberg electrons have many novel properties, such as weak binding energy, high density of states, long period, large dipole moment, etc. The similar frequencies between terahertz radiation and Rydberg orbits makes terahertz field pulses an alternative tool to study properties of Rydberg electrons.

Strong terahertz radiation was used in many experiments studying field ionization [51, 130–135]. However, strong terahertz single-cycle pulses have only become widely used in the past few years. Strong terahertz single-cycle pulses are usually generated by optical rectification in non-linear crystals [136, 137]. In most cases, the single-cycle pulses are non-symmetric in the time-domain. The effects of asymmetry in field ionization was studied theoretically in Ref. [55, 56]. The field strength of terahertz single-cycle pulses can be up to 1 MV/cm [138]. A 1 picosecond duration is approximately the same as the Rydberg period with principal quantum number $n \sim 20$, which makes the terahertz single-cycle pulse an effective tool to probe and study the periodic motion of Rydberg electrons.

Time-resolved studies of the spatial distributions of Rydberg wave packets have been conducted extensively. Many different optical tools have been used, such as ultraviolet laser pulses [139–141], half-cycle pulses [53, 54, 142], single-cycle pulses [47, 52], microwaves [143–145], and others. Compared with the other methods, the ionization properties of single-cycle pulses on Rydberg wave packets have not been widely studied. When a single-cycle pulse duration is much shorter than a Rydberg period, previous studies showed that the threshold field amplitude for ionization from a stationary Rydberg state is proportional to $(n/t_w)^2$ [55, 56], where n is the principal quantum number and t_w is proportional to the pulse duration. The ionization mechanism is described as displacement ionization. In this chapter, ionization of Rydberg wave packets using single-cycle pulses with durations shorter or equal to one Rydberg period are studied.

For field pulse ionization due to a long pulse, the scaling relations of ionization thresholds versus the principal quantum number n have been studied before. Different ionization thresholds can be found in different ionization regimes [146]. For ionization due to a single-cycle pulse, only a few studies have been conducted, including experimental [51] and theoretical studies [55, 56, 147, 148]. These studies focused on the ionization probability versus initial pulse parameters or initial state nl of the Rydberg electron. The distributions and scaling relations of a single variable physical quantity, such as ionization probability, ionized electron's angular distribution, energy distribution, etc, are presented in several previous studies [51, 55]. There have been no studies on the scaling relations for correlated two-dimensional distributions from single-cycle pulse ionizations in Rydberg atoms. It is well known that classical calculations scale perfectly for different n , but quantum calculations do not scale due to the restrictions from the uncertainty principle. In this chapter, comparisons between quantum and classical calculations are studied, including correlated distributions for two physical quantities, at different scaled n states and scaled pulse parameters. Additionally, scaled ionization results for Rydberg wave packets due to a single-cycle pulse are first discussed in this chapter.

This chapter is structured as follows. Section 6.2 gives a brief introduction to the quantum and classical methods used in our calculations. Section 6.3 introduces the scaling relations for pulse parameters and all physical quantities. The quantum and classical results in different conditions are compared. Also, the scaled properties of ionization and quantum interference are studied. Section 6.4 introduces the type of Rydberg wave packets used in this chapter, and the scaled ionization properties from short and medium duration single-cycle pulses are investigated. Atomic units are used throughout the chapter unless specified otherwise.

6.2 Methods

6.2.1 Quantum methods

With a linearly polarized laser pulse in the dipole approximation, a hydrogenic atomic system follows the time-dependent Schrödinger equation:

$$i\frac{\partial\psi}{\partial t} = \left(-\frac{1}{2}\nabla^2 - \frac{1}{r} + F(t) \cdot z\right)\psi, \quad (6.1)$$

where $F(t)$ is the time-dependent strength of the electric field. The full three-dimensional wave function is expanded on a spherical harmonic basis:

$$\psi(r, \theta, \phi, t) = \sum_{l=0}^{l_{\max}} \frac{R_l(r, t)}{r} Y_{l0}(\theta, \phi). \quad (6.2)$$

The Y_{lm} are spherical harmonics, and the cylindrical symmetry of $m = 0$ is assumed in the present work. The $l_{\max}$ is the number of angular channels needed to converge all of the physical quantities in the calculations. The radial wave functions can be propagated using various methods. Split operator and Crank-Nicolson methods are used in our calculations. For the radial wave functions, a square-root mesh with Numerov approximation is adopted. Further details on the wave function propagation can be found in Ref. [28].

For the single-cycle laser pulse, two different forms are used in our calculations. The first form was introduced in Ref. [148]. It is used in this chapter to reinterpret some results from Ref. [148]. The pulse is expressed as

$$F(t) = \begin{cases} -F_m \sin(\omega t), & \text{if } -T < t < 0 \\ -F_m \beta \sin(\beta \omega t), & \text{if } 0 < t < T/\beta \\ 0, & \text{otherwise.} \end{cases} \quad (6.3)$$

The F_m is the peak intensity and T is the duration of the first half cycle, $T = \pi/\omega$, and β is a factor representing the asymmetry of the pulse. In the calculations, the pulse starts at $t_i = -T$, and ends at $t_f = T/\beta$.

The second form was used in Ref. [56], which is a symmetric, Gaussian-like single-cycle pulse. It is expressed as

$$F(t) = -C_0 F_m \left(\frac{t}{t_w} \right) \exp \left[- \left(\frac{t}{t_w} \right)^2 - 0.1 \left(\frac{t}{t_w} \right)^4 \right], \quad (6.4)$$

where $C_0 = \sqrt{(\sqrt{35} + 5)/5} \exp[(\sqrt{35} - 4)/4] \approx 2.385$ is a constant that makes the maximum field amplitude to be F_m [56]. The fourth-power term in the exponent is used to shorten the Gaussian tail of the electric field without significantly affecting the properties of a single-cycle pulse. The t_w is a scale of time width of the laser pulse. The electronic wave function is propagated from $t_i = -3.5 t_w$ to $t_f = +3.5 t_w$, which gives well converged results. The second form of the Gaussian-like single-cycle pulse is mainly used in the rest of the chapter, due to its smooth expression and no discontinuities in the time domain. Although this chapter is based on these two specific pulse types, the results can be generalized to other pulses with similar asymmetry, duration, and strength.

The energy and angular distributions of the ionized electrons are the focus of this chapter. At the final time of the calculations, the continuum part of the wave function is expanded using energy normalized Coulomb eigenstates. The probability amplitude at a positive energy ϵ and angular momentum l can be calculated as

$$a_{el} = \int dr R_l(r, t = t_f) f_{el}(r), \quad (6.5)$$

where $f_{\epsilon l}$ is the energy normalized regular Coulomb wave function [149]. The energy distributions for ionized electrons can be calculated as

$$\frac{dP}{d\epsilon} = \sum_{l=0}^{l_{\max}} |a_{\epsilon l}|^2. \quad (6.6)$$

The angular distribution for the ionized part of the electron wave functions at a given energy can be calculated as

$$\frac{d^2 P}{d \cos \theta d\epsilon} = 2\pi \left| \sum_{l=0}^{l_{\max}} a_{\epsilon l} e^{i\sigma_l} Y_{l0}(\cos \theta) \right|^2, \quad (6.7)$$

where σ_l is the Coulomb phase shift [149]. Note that the cylindrical symmetry of $m = 0$ is assumed in our calculations. The integration of Eq. (6.7) at all positive energies gives the full angular distributions at infinity. The emission angle θ is the polar angle from the field polarization axis.

The radial distributions and the emission angle, just after the pulse is turned off, are also studied in this chapter. They are mainly used to compare the results from quantum and classical calculations. The radial distribution of ionized electrons at a given emission angle can be calculated as

$$\frac{d^2 P}{d \cos \theta dr} = 2\pi \left| \sum_{l=0}^{l_{\max}} \int d\epsilon a_{\epsilon l} f_{\epsilon l}(r) Y_{l0}(\cos \theta) \right|^2, \quad (6.8)$$

and the radial distribution averaged over all angles is calculated as

$$\frac{dP}{dr} = \sum_{l=0}^{l_{\max}} \left| \int d\epsilon a_{\epsilon l} f_{\epsilon l}(r) \right|^2. \quad (6.9)$$

6.2.2 Classical methods

For the strong field ionization problem, the classical trajectory Monte Carlo method is used [56]. Specifically, consider a quantum problem starting from a stationary Rydberg eigenstate at $|nl\rangle$. By using the microcanonical ensemble treatment [150],

the initial energies and angular momenta of the electrons in classical calculations are set to be $E_{\text{cl}} = -0.5/n_{\text{cl}}^2$, where

$$[(n-1)(n-\frac{1}{2})n]^{1/3} < n_{\text{cl}} \leq [n(n+\frac{1}{2})(n+1)]^{1/3}, \text{ and} \quad (6.10)$$

$$l^2 - \frac{1}{4} < l_{\text{cl}}^2 \leq (l+1)^2 - \frac{1}{4}, \text{ when } l \neq 0, n. \quad (6.11)$$

For $l = 0$ or n , the simple lower or upper bound at 0 or n are used. At a large n and non-zero l , the above two inequalities go to the following approximations:

$$n - 0.5 < n_{\text{cl}} \leq n + 0.5, \quad (6.12)$$

$$l < l_{\text{cl}} \leq l + 1, \quad (6.13)$$

where the classical quantities n_{cl} , l_{cl}^2 are uniformly distributed in the given ranges, not the classical energy $-1/2n_{\text{cl}}^2$. Comparing with n_{cl} being a single value fixed at n , this microcanonical ensemble treatment gives better agreement between quantum and classical calculations in some critical cases, which will be shown in Sec. 6.3.2.

In order to simulate the radial distribution from a stationary quantum state, all the trajectories start the classical propagations from their respective classical outer turning point at a random time $t_{\text{init}} = t_{\text{turn-on}} - \alpha T_{\text{Ryd}}$ [56]. Here, $t_{\text{turn-on}}$ is the turn-on time of the single-cycle pulse. For example, $t_{\text{turn-on}} = -T$ for single-cycle pulse in Eq. (6.3), and $t_{\text{turn-on}} = -3.5 t_w$ for single-cycle pulse in Eq. (6.4). α is a uniformly distributed random number between 0 and 1 to simulate the initial radial distribution from a full Rydberg period. The initial angular distribution of the electrons at t_{init} follows $|Y_{l0}(\cos \theta)|^2$. The initial velocity direction of the electron is randomly selected as long as it's perpendicular to the position vector, and the magnitude of velocity is chosen to satisfy the initial angular momentum l_{cl} from the microcanonical ensemble in Eq. (6.13). The initial direction of the velocity vector can be randomly chosen on the tangential plane because the ionization probability from our numerical calculations does not depend strongly on the velocity directions. Then, the electron is propagated only considering the pure Coulomb potential $1/r$ until $t_{\text{turn-on}}$, when the single-cycle pulse electric field turns on. Next the electron trajectory is calculated from both the

$1/r$ potential and the single-cycle pulse potential until the pulse turn-off time. To achieve the final angular distribution, the electrons are then propagated to a long fixed final time t_f , when its momentum direction is nearly converged. The statistics of the electrons' final energy and final velocity angle give classical distributions which are compared to those from quantum calculations.

Additionally, the classical trajectory Monte Carlo method can be extended to a semiclassical version, which is known as the quantum trajectory Monte Carlo [126]. In this method, the actions for the classical trajectories are calculated. If there is more than one classical path that can go into the same final region, e.g. position or momentum, the amplitudes of the paths are added coherently using the classical actions as the phase factor. The initial electronic states in our calculations are Rydberg states in their position representations. If the final state is in the momentum representation, e.g. when energy versus angle distribution is studied, an extra factor of $-\mathbf{p}_f \cdot \mathbf{r}_f$ needs to be added to the phase [126]. This is due to the Fourier transform of the wave function to another representation.

6.3 Scaling relations

In this section, the scaling behavior of single-cycle pulse ionization with respect to the principal quantum n is studied: we show quantum and classical results for different n but with the field parameters scaled. Specifically, the physical quantities are scaled as follows

$$\begin{aligned} r &\propto n^2, \quad t \propto n^3, \quad p \text{ (momentum)} \propto n^{-1}, \\ E \text{ (energy)} &\propto n^{-2}, \quad F_m \propto n^{-4}, \end{aligned} \tag{6.14}$$

and other unit-less quantities are not scaled, such as angle or ionization probability. The nuclear and electronic charges are not scaled. For example, if $F_m = 500$ kV/cm is used at $n = 15$, then the scaled field strength at $n = 30$ can be calculated as $500 \text{ kV/cm} \cdot (30/15)^{-4} = 31.25 \text{ kV/cm}$. It is noted that, due to the same scaling

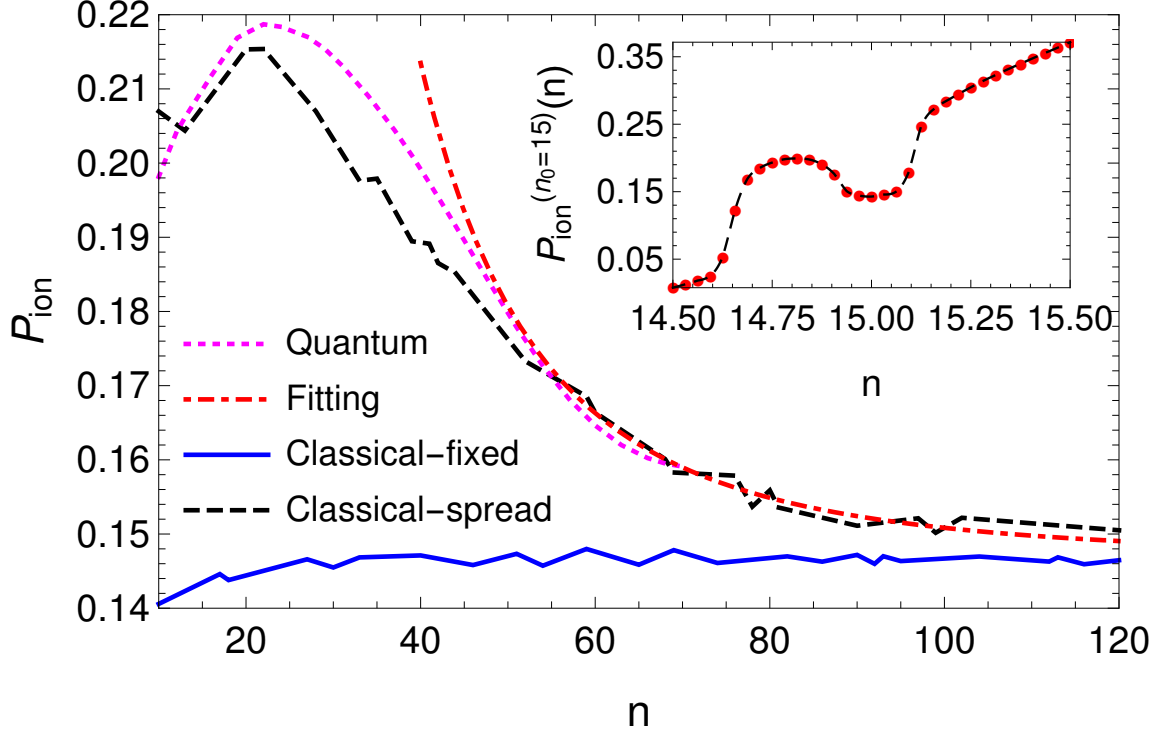


Figure 6.1. Ionization probabilities from scaled classical and quantum calculations. The black dashed line is for classical calculations with an initial energy spread of n_{cl} given in Eq. (6.12). The blue solid line is for classical calculations at a single value of n , and the ionization probability converges to 14.6%. The magenta dotted line is for quantum calculations up to $n = 70$. The red thick line is a fitting for classical results with n_{cl} spread. For $n_{\text{cl}} \geq 60$, the fitting function is $P_{\text{ion}} = 0.146 + 4573/n^{3.02}$. The inset figure gives the classical ionization probability when the pulse parameters are fixed at $n_0 = 15$ and the initial classical energy state is at a single value around $n_{\text{cl}} = 15$, see Eq. (6.15). Scaling relations are given in Eq. (6.14). Pulse parameters can be found in text. The initial angular momentum is fixed at $l = 2$.

relations for pulse duration and Rydberg period, durations of the scaled single-cycle pulses will always be the same fraction of one Rydberg period at different n .

As mentioned in Sec. 6.2.2, initial energies in classical calculations can either be a single value or be a spread using the microcanonical ensemble treatment. The initial

spread in angular momentum l only weakly affects the ionization probability, and it is not scaled versus n (see Sec. 6.3.1). With all these scaling rules, scaled results from classical calculations at different n , as a single value without spread, should be exactly the same. This is because the classical mechanics of the Coulomb interaction are fully scalable. Conversely, as given in Eq. (6.12), the microcanonical ensemble treatment requires an energy spread of $\Delta n_{\text{cl}} = 1$, which do not scale with n . This makes the classical calculations using the microcanonical ensemble non-scalable. In quantum calculations, due to the uncertainty principle $\delta x \delta p \geq 1/2$, results at different n are also different. According to the correspondence principle, the quantum and classical calculations should give the same results as n goes to infinity. For the following part of this section, scaled quantum and classical calculations with different n are performed, and the differences between them are compared.

In Sec. 6.3.1 and Sec. 6.3.2, the single-cycle pulse in Eq. (6.3) is used. In Sec. 6.3.3, the single-cycle pulse in Eq. (6.4) is used.

6.3.1 Ionization probabilities versus n

For example, scaled quantum and classical calculations at different n are performed, and the ionization probabilities versus n is shown in Fig. 6.1. In the calculations, the single-cycle pulse with the form in Eq. (6.3) is used. At $n = 15$, the pulse parameters are $F_m = 2.05 \times 10^{-6}$ a.u. = 10.5 kV/cm, $T = 1.2402 \times 10^5$ a.u., and $\beta = 1.5$. All parameters are the same as those in Ref. [148] (with a small modification¹). At other n , the pulse parameters are scaled using relations given in Eq. (6.14). The initial state always has angular momentum $l = 2$, and are not scaled with n (see next paragraph). Classical results with microcanonical ensemble treatment have much better agreement with quantum results than the classical results with a single

¹The parameters in the caption of Fig. 5 of Ref. [148] were used, except the field strength. From a private communication (J. P. Hansen), $F_m = 2.05 \times 10^{-6}$ a.u. = 10.5 kV/cm instead of 18 kV/cm was used. With that, the same ionization probability of 20% as indicated in their figure caption can be achieved.

value of n . Further details on why a spread of initial energy behaves better than a fixed energy are discussed in the next subsection.

A very important question related to perfect scaling is how the initial angular momentum l_{cl} should scale and how large the difference is with respect to scaling. The l_{cl} determines both the initial angular distribution and the angular momentum of the electron. The angular distribution is a unit-less function with respect to angle θ and ϕ , and is not scaled with n . The angular momentum is equal to $v_{\text{init}}r_{\text{outer}}$ and is scaled proportionally versus n . However, l is a discrete value and cannot be arbitrarily scaled in experiments. To check the differences in ionization probabilities with non-scaled angular momenta, several classical calculations are performed with the only difference in the angular momentum distribution. At a single value of $n = 15$ and identical remaining parameters, the initial angular distributions are kept unchanged as Y_{20} . The initial angular momenta are 0, 1, and 2. Ionization probabilities from these calculations differ by less than 0.5% in the absolute value. Note that, as presented in the blue solid curve of Fig. 6.1, $l = 2$ at $n = 15$ gives ionization probability around 14.5%. In these cases, with the perfect scaling of classical dynamics, ionization probabilities, with $(n, l) = (30, 2) \rightarrow (15, 1)$, $(n, l) = (60, 2) \rightarrow (15, 0.5)$, $(n, l) = (120, 2) \rightarrow (15, 0.25)$, etc, would only differ by less than 0.5%. This can be seen in Fig. 6.1 that the blue solid curve is mostly flat at large n , but with small variations at n near 15. It is shown that, with non-scaled l_{cl} value, the classical calculations with a single value of n are mostly scalable with small differences at small n .

It is seen in Fig. 6.1 that, the differences between classical calculations using the microcanonical ensemble and a single value of n get smaller as n gets larger. To understand how the two types of calculations converge to the same value as $n \rightarrow \infty$, consider a classical calculation on single-cycle pulse ionization. Let $P_{\text{ion}}^{(n_0)}(n)$ be the ionization probability when the principal quantum number is a variable of n , and the

pulse parameters are scaled for n_0 . Then the averaged ionization probability with n being a spread of $n_0 - \delta n$ to $n_0 + \delta n$ can be calculated as

$$\begin{aligned}
\bar{P}(n_0, \delta n) &= \frac{1}{2\delta n} \int_{n_0 - \delta n}^{n_0 + \delta n} P_{\text{ion}}^{(n_0)}(n) dn \\
&\approx \frac{1}{2\delta n} \int_{n_0 - \delta n}^{n_0 + \delta n} [P_{\text{ion}}^{(n_0)}(n_0) + P_{\text{ion}}^{\prime(n_0)}(n_0)(n - n_0) \\
&\quad + \frac{1}{2} P_{\text{ion}}^{\prime\prime(n_0)}(n_0)(n - n_0)^2 + O[(n - n_0)^3]] dn \\
&= P_{\text{ion}}^{(n_0)}(n_0) + \frac{1}{6} P_{\text{ion}}^{\prime\prime(n_0)}(n_0)(\delta n)^2 + O[(\delta n)^4].
\end{aligned} \tag{6.15}$$

Since classical calculations are perfectly scaled, e.g. $P_{\text{ion}}^{(n_0)}(n) = P_{\text{ion}}^{(2n_0)}(2n)$, the derivatives can be calculated as

$$\begin{aligned}
P_{\text{ion}}^{(n_0)}(n_0 + \delta n) &= P_{\text{ion}}^{(2n_0)}(2n_0 + 2\delta n), \\
\frac{P_{\text{ion}}^{(n_0)}(n_0 + \delta n) - P_{\text{ion}}^{(n_0)}(n_0)}{\delta n} &= \frac{P_{\text{ion}}^{(2n_0)}(2n_0 + 2\delta n) - P_{\text{ion}}^{(2n_0)}(2n_0)}{2\delta n}, \\
P_{\text{ion}}^{\prime(n_0)}(n_0) &= 2 P_{\text{ion}}^{\prime(2n_0)}(2n_0).
\end{aligned} \tag{6.16}$$

Thus, the first order derivative $P_{\text{ion}}^{\prime(n_0)}$ scales as n_0^{-1} , and the second order derivative scales as n_0^{-2} . The average ionization probability from a spread of initial energy at 29.5 to 30.5 is the same as that of 14.75 to 15.25. With $\delta n = 0.5$, the series expansion gives n_0^{-2} asymptotic relations for the ionization probability as $n_0 \rightarrow \infty$. Also, as $n_0 \rightarrow \infty$, all derivatives of $P_{\text{ion}}^{n_0}$ go to zero, and the average ionization probability $\bar{P}(n_0, \delta n)$ converges to the single value of $P_{\text{ion}}^{(n_0)}(n_0)$.

However, as can be seen in Fig. 6.1, the ionization probability from classical calculations with n_{cl} being a spread converge as n^{-3} asymptotically to the classical calculations with a single value of n_{cl} . The n^{-3} relation is a coincidence, not a general rule. This is partially due to the fact that the ionization properties at these specific pulse parameters are very sensitive to the initial energy state n of the electron. Since the pulse duration $T_{\text{pulse}} = 2.067 \times 10^5$ a.u. is much longer than the Rydberg period at $n = 15$ ($T_{\text{Ryd}} = 2.12 \times 10^4$ a.u.), over-the-barrier ionization mechanisms dominate. The maximum field strength $\beta F_m = 3.075 \times 10^{-6}$ a.u. is in the same order as

the nuclear Coulomb field strength when the electron is at its outer turning point $((2 * 15^2)^{-2} = 4.94 \times 10^{-6} \text{ a.u.})$. Thus, with pulse parameters fixed at $n_0 = 15$, as n varies from 14.5 to 15.5, the ionization probabilities change rapidly and even non-monotonically.

As given in the inset of Fig. 6.1, the ionization probability $P_{\text{ion}}^{(15)}(n)$ is very sensitive to the initial classical state n . The average of $P_{\text{ion}}^{(15)}(n)$ for n varied from 14.5 to 15.5 gives an ionization probability around 20%, but the $P_{\text{ion}}^{(15)}(15)$ itself only gives about 15%. At $n_0 = 15$ and $\delta n > 1/16$, which is equivalent to $n_0 < 120$ and $\delta n = 0.5$, the $P_{\text{ion}}^{(15)}(n)$ in Eq. (6.15) can not be well expanded as a Taylor series only up to $O[(n - n_0)^3]$. That means the n_0^{-2} scaling relations derived in Eq. (6.15) does not hold, when n_0 is not large enough. A mixture of n_0^{-2} and n_0^{-4} coincidentally gives a scaling relation of n_0^{-3} , as presented in Fig. 6.1. It was found that only when n is large enough, e.g. $n_0 > 120$, did the Taylor series expansion in Eq. (6.15) correctly represent the ionization probability, and a n_0^{-2} asymptotic relation was found. Further details of ionization properties with n_{cl} from 14.5 to 15.5 are discussed in the next subsection.

6.3.2 Comparisons between quantum and classical methods

Originally found in Ref. [148], as well as shown in Fig. 6.1 in the previous subsection, ionization probabilities from a classical calculation at a fixed n of 15 are different from a quantum calculations for $n = 15$. In this section, three calculations are performed to study the ionization probability and physical quantities of this process: fully quantal, classical with n_{cl} fixed at 15, and classical with n_{cl} being a spread from 14.5 to 15.5. The initial angular momentum is set to $l = 2$. The pulse parameters are given in the previous paragraph at $n = 15$.

The radial distributions at the final time are given in Fig. 6.2. Both of the classical calculations give overall similar results as compared with the quantum calculation. For the ionized part around 3000 a.u., results from the classical calculation with n_{cl}

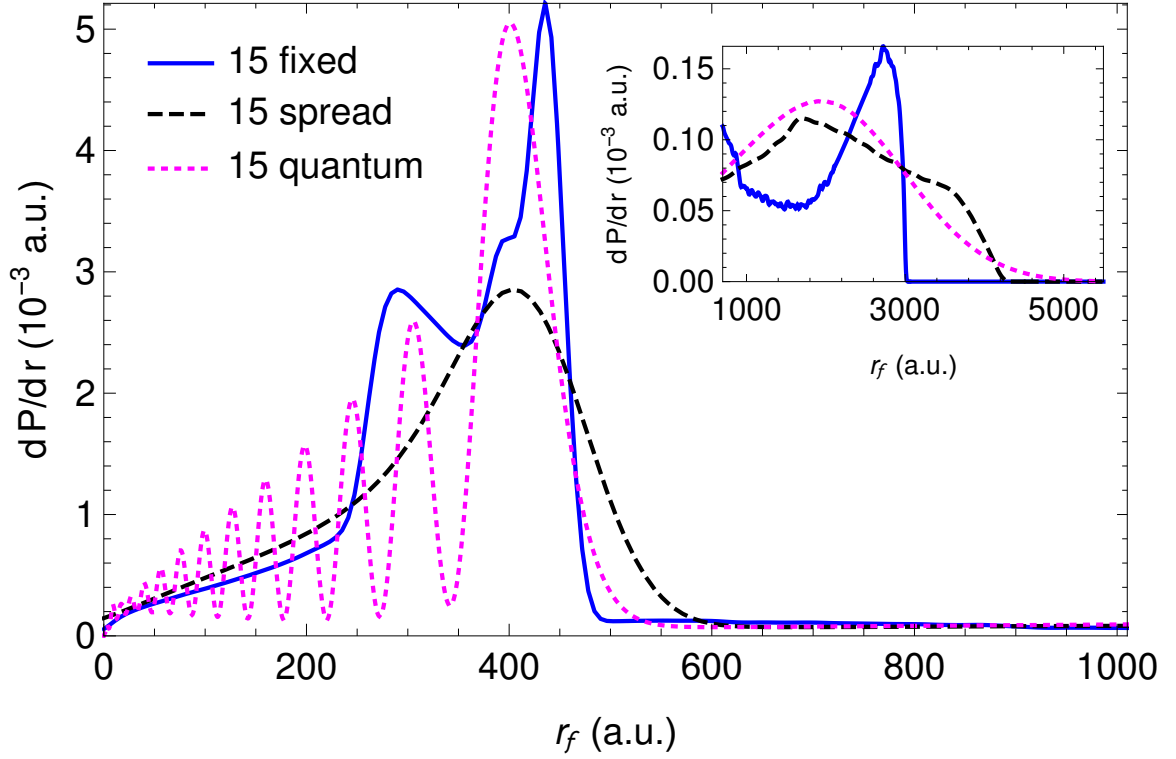


Figure 6.2. Full radial distributions at the final time of the pulse, from three different calculations. The initial angular momentum is $l = 2$. The blue solid curve is from a classical calculation with the initial n_{cl} fixed at 15. The black dashed curve is from a classical calculation with the initial n_{cl} being a spread of 14.5 to 15.5. The magenta dotted curve is from a full quantum calculation starting in a $15d$ state. The ionization probabilities from the three calculations are 14.3%, 20.7%, and 21.0%, respectively. The inset is a magnification of the distribution with r_f from 700 to 5500 a.u. Note that the probability density scale is different for the inset.

fixed at 15 do not match well with the quantum result, while the spread n_{cl} calculation gives much better agreement. As mentioned in the caption of the figure, the ionized wave function is a small portion of the whole wave function. Ionization probabilities and continuum wave functions from the fixed n_{cl} and spread n_{cl} calculations are very different.

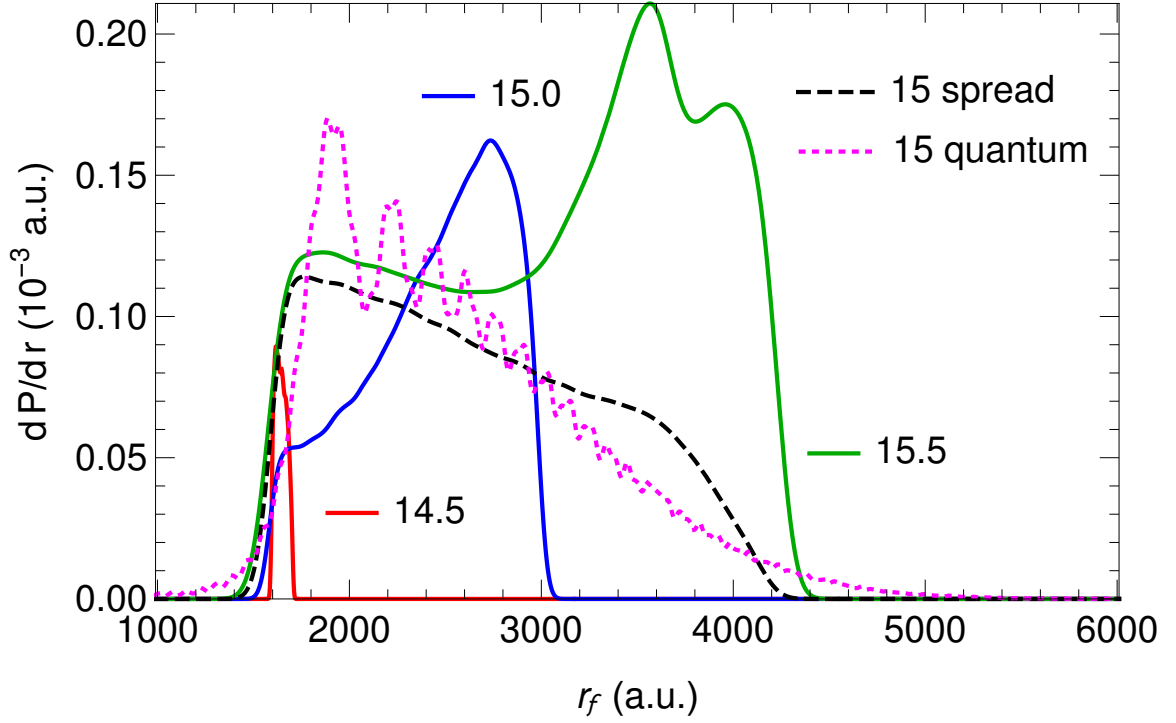


Figure 6.3. Radial distributions at the final time of the pulse from classical and quantum calculations. Only those from the ionized part of the distributions are plotted. The red solid curve with small extent around 1600 a.u. is from a classical calculation with n_{cl} fixed at 14.5, and the ionization probability for this case is 0.77%. The green solid curve with the largest extent is from a classical calculation with n_{cl} fixed at 15.5, and the ionization probability for this case is 37.2%. The other three curves are the same calculations as those introduced in the caption of Fig. 6.2.

To further study the details of the ionized part of the wave function, two more classical calculations for n_{cl} fixed at 14.5 and 15.5 are performed. The continuum radial distributions from quantum and classical calculations are given in Fig. 6.3. One notable quantity is the ionization probability. For $n_{cl} = 14.5$, the ionization probability is only 0.77%, but it is 37.2% for $n_{cl} = 15.5$. As shown in the inset of Fig. 6.1 and discussed in Sec. 6.3.1, field ionization processes with these specific field

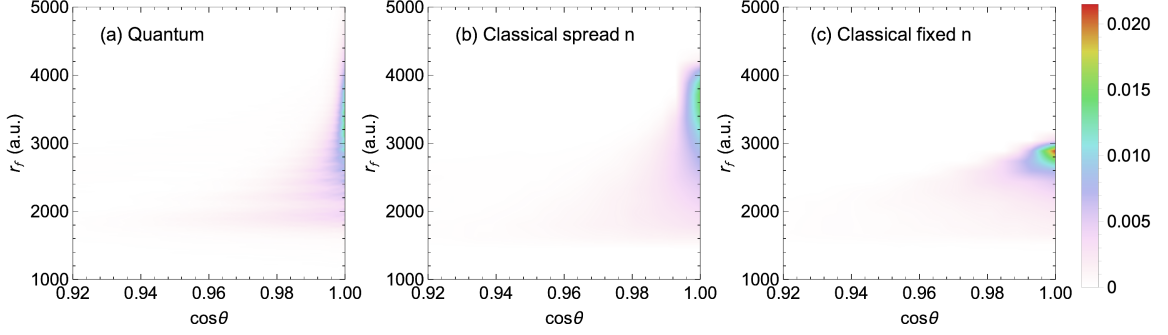


Figure 6.4. Correlated distribution of the ionized electron's radial position, and its emission angle at the final time of the pulse. Parameters of the field are given in the text of Sec. 6.3.1. Figure (a) is from a full quantum calculation, figure (b) is from a classical calculation with n_{cl} being a spread of 14.5 to 15.5, and figure (c) is from a classical calculation with n_{cl} fixed at 15. The density distributions in all three figures are normalized to their respective ionization probabilities, which can be found in the caption of Fig. 6.2.

parameters are very sensitive to the initial Rydberg state for this range of n , because the ionization probability and the ionized part of the wave function depends strongly on the initial energy of the Rydberg electron. With that, it is better to use a spread in initial energy, i.e. microcanonical ensemble treatment, in the classical calculation rather than just a fixed energy as used in Ref. [148].

To verify our applications of the initial energy spread in the classical calculations, the ionized radial and angular distributions at the final time of the pulse are shown in Fig. 6.4. It can be seen in the figure that the classical calculation with an initial energy spread has a much better agreement with the quantum calculation. Additionally, some interference patterns, with respect to the radial distribution, appear in the quantum results, but not in the classical results. Oscillations of the quantum interference amplitudes will be discussed in the next subsection.

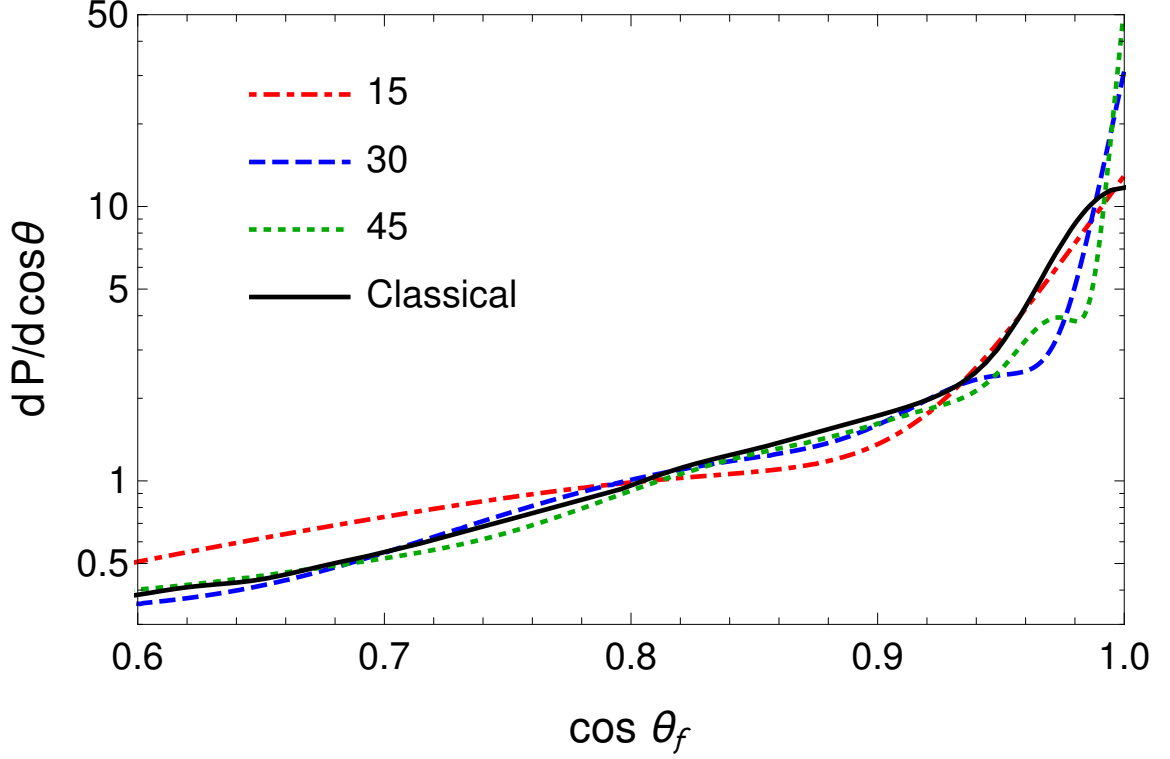


Figure 6.5. Angular distributions for ionized electrons from quantum and classical calculations. The initial angular momentum is $l = 0$. Calculations are performed with different n as indicated by the legends, and different scaled pulse parameters as indicated in Eq. (6.14). At $n = 15$, $F_m = 500$ kV/cm and $t_w = 500$ a.u. are used. Classical results at all three n are the same.

6.3.3 Scaled physical quantities and quantum interferences

Scaled physical quantities from single-cycle pulse ionization with scaled pulse parameters at different n are studied in this subsection. The single-cycle pulse in Eq. (6.4) is used in this subsection, and the pulse parameters are changed to $F_m = 500$ kV/cm, $t_w = 500$ a.u. for $n = 15$ from the previous subsection. The Rydberg period for the $n = 15$ state is $T_{\text{ryd}} = 2\pi n^3 = 21206$ a.u. Electrons are initiated in stationary Rydberg eigenstates with angular momentum being zero. Although a single-cycle pulse process with these parameters only gives about 3.8% ionization

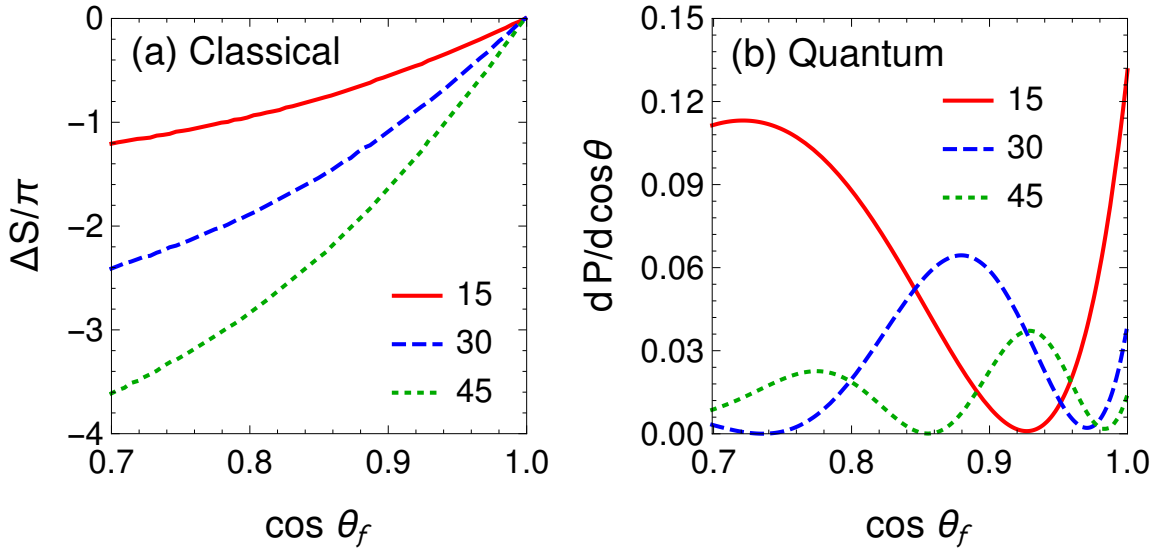


Figure 6.6. Figure (a) gives the classical action differences between two paths versus the final angle, at a scaled final energy. The final energy is scaled for different n , which are $E_f = (15/n)^2 \cdot 0.002$ a.u. The action differences are aligned as $\Delta S = 0$ at $\cos \theta_f = 1$. Figure (b) gives angular distributions at scaled final energies from quantum calculations.

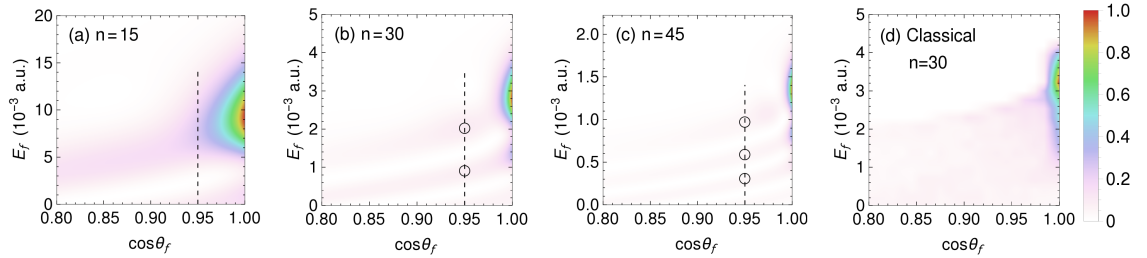


Figure 6.7. The correlated energy and angular distributions with scaled pulse parameters at $n = 15, 30, 45$ for quantum calculations, and at $n = 30$ for classical calculation. The maximum densities are normalized to 1.0 for all figures. The dashed lines are at $\cos \theta_f = 0.95$, while the circles are interference maxima calculated by the semiclassical method introduced in the text.

probability, the small portion of the ionized wave function gives a clear picture for the properties of the ionized electron. The ionization probability is the same for $n = 15$, 30, and 45. As discussed in Sec. 6.3.1 and in Eq. (6.15), with the same ionization probability for 15, 30, 45 in quantum calculations, the classical ionization curvature P''_{ion} is negligible in this case. Thus, to mimic the quantum calculation, classical calculations with a single value of n and a single value of l can be performed instead of spreads, and the results would be the same.

The angular distributions for ionized electrons are given in Fig. 6.5. In the figure, the classical results at different n are scaled and overlapped. However, the results for scaled quantum calculations are different near $\cos \theta_f = 1$. Although not shown in the figure, the rest of the angular distributions for $\cos \theta_f$ from -1 to 0.6 are nearly the same for both quantum and classical, at different n , and they are much smaller than those near $\cos \theta_f = 1$. As can be seen in the figure, as n increases, the quantum angular distributions near $\cos \theta_f = 1$ gets sharper. This is very different from the classical results, and the reason for the sharp peak is quantum interference. Quantum interference can strengthen distribution at some angles, and weaken distribution at other angles.

Using the scaling relations for physical quantities in Eq. (6.14), the classical action is also scaled, and the scaling is

$$S = \int L dt \propto n, \quad (6.17)$$

where L is the classical Lagrangian. In the present problem, with a small ionization probability, only two classical trajectories can be found that go into the same final angle and same final energy. Actions from the two trajectories scale as n , as well as the difference ΔS between the two trajectories. Since interference maxima can be found at every 2π phase difference, oscillations of interference amplitudes, with respect to scaled physical quantities, would be n times faster at a higher n .

To study the angular distributions in detail, results at scaled final energy slices, $E_f = (15/n)^2 \cdot 0.002$ a.u., are presented in Fig. 6.6. In Fig. 6.6(a), the classical action versus final angle is given. It can be seen that the action differences, ΔS , from the

two paths changes faster as n gets larger, scaled as the factor of n . In Fig. 6.6(b), the quantum angular distributions are given. With a larger n , the action varies more rapidly. The amplitudes of angular distributions also oscillate faster. Since the total angular distributions are incoherent summations of angular distributions at all positive energy slices, faster oscillations of the angular distributions away from $\cos\theta_f = 1$ lead to rapid cancellation and flattening of the full angular distribution. With the same ionization probability, constructive summations and sharper peaks around $\cos\theta_f = 1$ can be expected at higher n .

Finally, the correlated distributions of final emission angle and final energy are given in Fig. 6.7. As mentioned in Sec. 6.3.2 and Fig. 6.4, quantum interferences may appear in the correlated distributions at the final time. In Fig. 6.7, quantum interference with respect to the scaled final energy is found. The differences for classical actions between the two paths are used to determine the quantum interference maxima at E_f . The action differences are aligned at the first interference maximum, and all further maxima are found at multiples of 2π phase differences. The classical results are the same for $n = 15, 30$, and 45 . No interference is found in classical results. In the figure of $n = 15$, only one interference maximum can be found in the given range along $\cos\theta_f = 0.95$, while two maxima can be found for $n = 30$ and three for $n = 45$. This interference behavior is due to the fact that semiclassical action is scaled proportional to n while all physical parameters are scaled as those in Eq. (6.14). Thus, the oscillations of interference amplitudes are also scaled as n versus other scaled parameters. As discussed in Fig. 6.5, Fig. 6.6 and earlier in this section, sharper peaks in angular distributions near $\cos\theta_f = 1$ can be found when n is larger. Since the maximum angular momentum scales as n , there are not enough angular channels that can localize the angular distribution near $\cos\theta_f = 1$ at a smaller n .

6.4 Ionization of wave packets

When dealing with strong field ionization of Rydberg atoms, the initial state can be either a stationary eigenstate, or a coherent superposition of those eigenstates, which is known as a wave packet. For field ionization with single-cycle pulses, several studies of stationary states have been conducted [51,55,56,147,148]. Since the spatial distribution for stationary states and wave packets can be totally different, the field ionization results are also different for these two scenarios. In this section, the effects of strong, short and medium duration single-cycle pulses on different initial Rydberg states are studied. The single-cycle pulses with the form of Eq. (6.4) are used.

Short duration single-cycle pulses have been studied before [56]. A single-cycle pulse with duration much shorter than one Rydberg period only shifts the position of the Rydberg electron by a small amount without changing its kinetic energy. The small shift in space may introduce large Coulomb potential energy change if the electron is close to the nucleus. If the electron is far from the nucleus, then the small spacial shift barely changes the Coulomb potential energy. Thus, a short duration single-cycle pulse provides a tool to probe the spatial distribution of an atomic system. Due to the coherent superposition of the Rydberg wave functions from different energies, the spatial distribution of a Rydberg wave packet changes with time. A short duration single-cycle pulse applied at different times yields different ionization probabilities.

Similarly, a medium duration single-cycle pulse can also be used to probe the spatial distributions of a Rydberg wave packet. In this chapter, a medium duration single-cycle pulse is defined as a single-cycle pulse with its duration approximately the same as one Rydberg period of the Rydberg electron. With a medium duration single-cycle pulse, the highest ionization probability is achieved when most of the electron distribution is near the nucleus when the single-cycle pulse goes through zero. This can be understood that an electron reverses velocity at the inner turning point at the same time as the electric field of a single-cycle pulse reverses [47].

Thus, a medium duration single-cycle pulse provides similar ionization properties as a short duration single-cycle pulse, with respect to the probe of the electron spatial distribution. It is similar to those many-cycle long pulse ionizations on Rydberg wave packet experiments [139–141], where the Rydberg wave packets absorb energy and get ionized when they are near the nucleus.

The type of Rydberg wave packet used in this chapter is the superposition of two adjacent Rydberg eigenstates with a variable relative phase:

$$|\psi(t_i)\rangle = \frac{n^{3/2}|nl\rangle + e^{i\varphi}(n+1)^{3/2}|(n+1)l\rangle}{\sqrt{n^3 + (n+1)^3}}, \quad (6.18)$$

where $\varphi = -(E_{n+1} - E_n)t_i + \varphi_0$. t_i is the starting time of the pulse. The φ_0 is a controllable parameter between 0 and 2π , which gives the superposition phase of wave packets at $t = 0$.

The two stationary states in Eq. (6.18) are not superposed with equal weight. The $n^{3/2}$ factor before the $|nl\rangle$ state is due to the properties of radial wave functions of hydrogenic eigenstates [9]

$$R_n(r) \sim n^{-3/2}f(r) \quad \text{at small radius } r, \quad (6.19)$$

where $f(r)$ is an energy normalized radial function. This asymptotic behavior at small radius can be used to add up the radial wave functions from $|nl\rangle$ and $|(n+1)l\rangle$ constructively or destructively at small radius. The wave packet in Eq. (6.18) can thus have most of its radial distributions near the nucleus or far from the nucleus. As an example, radial wave functions of the coherent superpositions of 15s and 16s states are shown in Fig. 6.8. Experimentally, the $n^{3/2}$ factor can be achieved by fine tuning the frequency and width of a laser pulse used to generate the Rydberg wave packet.

Several quantum calculations were performed to study the ionization probabilities versus φ_0 , and the results can be found in Fig. 6.9. In the figure, the ionization probabilities have huge differences at different superposition phase. At $\varphi_0 \approx 0$, the wave packets add constructively at small radius, and the ionization probabilities are

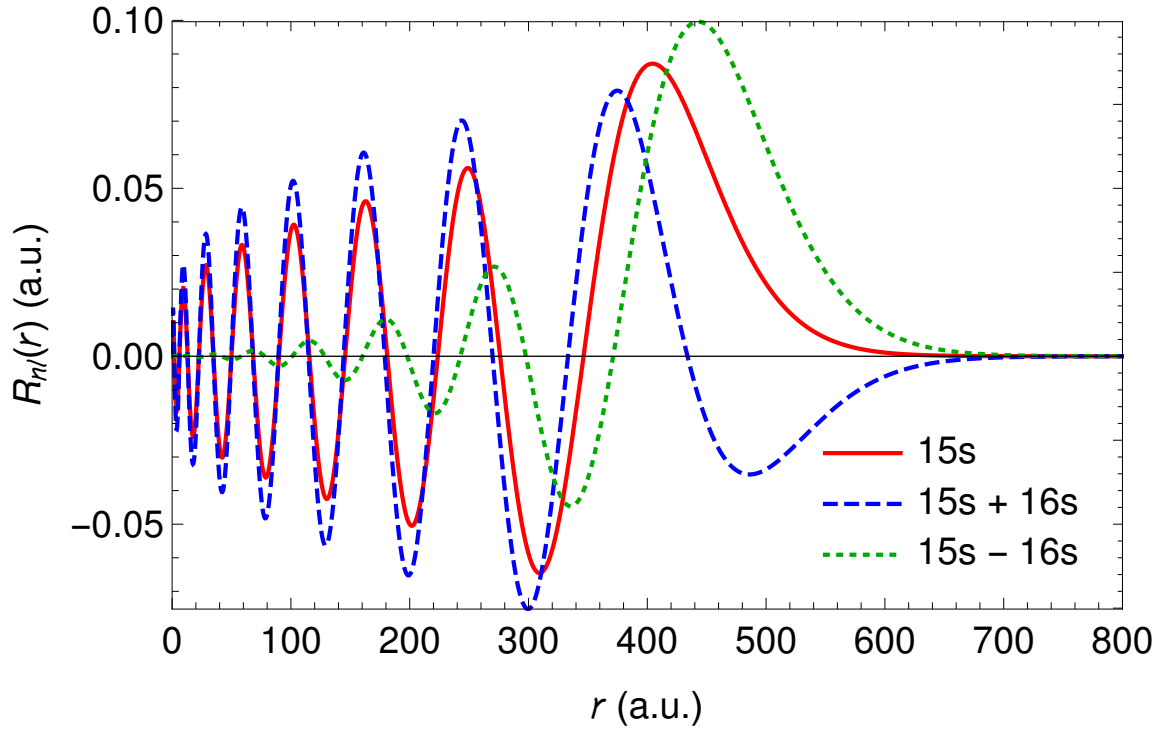


Figure 6.8. Radial wave functions of the hydrogen $15s$, “ $15s + 16s$ ”, and “ $15s - 16s$ ” states. Note that the $15s$ and $16s$ states do not have the equal weight ($1/\sqrt{2}$) in the superpositions, see Eq. (6.18). The “ $15s + 16s$ ” represents a wave packet of $\varphi_0 = 0$, while “ $15s - 16s$ ” represents $\varphi_0 = \pi$.

at a maximum. At $\varphi_0 \approx \pi$, the wave packets add destructively at small radius. Most of the electron probability is away from the nucleus, and the ionization probabilities are at a minimum. The ionization probabilities satisfy simple cosine relations versus the initial phase, and the fitting functions are given in the figure caption. Also, the φ_0 -averaged ionization probabilities are the same as the weighted average ionization probabilities for $15s$ and $16s$. These properties can be derived from the coherent superposition of the wave packets. Details for the ionization probability versus φ_0 can be found in the Appendix Sec. 6.6.

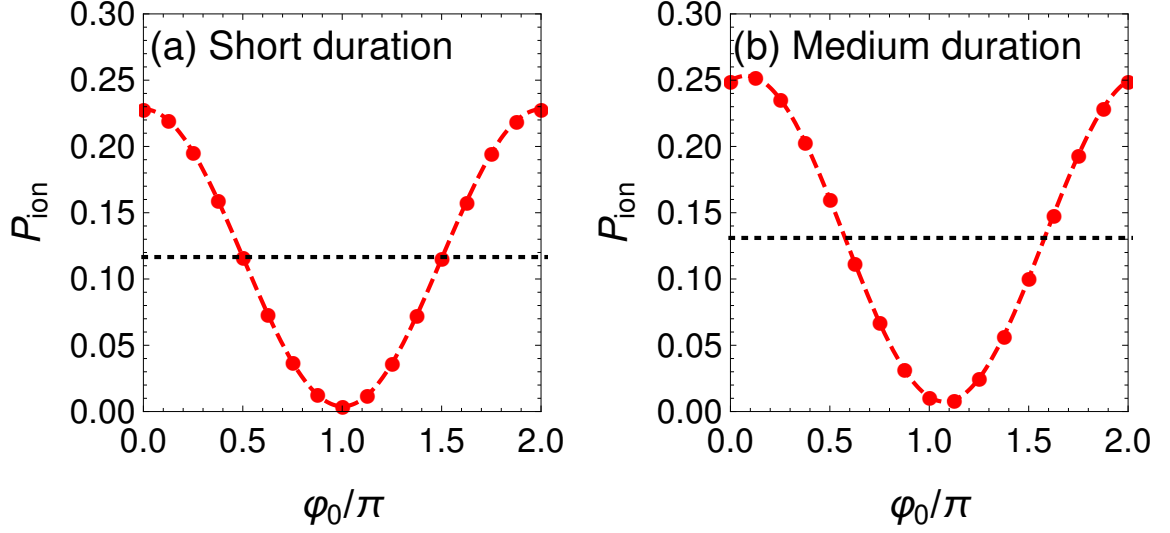


Figure 6.9. Ionization probabilities for $15s + \exp(i\varphi_0)16s$ wave packets versus the superposition phase φ_0 as given in Eq. (6.18). Figure (a) describes a short duration pulse process with $F_m = 2000$ kV/cm and $t_w = 606$ a.u. Figure (b) describes a medium duration pulse process with $F_m = 60$ kV/cm and $t_w = 3029$ a.u., where the pulse duration is approximately one Rydberg period for $15s$ state: $7.0t_w = T_{\text{Ryd}} \approx 21206$ a.u. The black dotted lines are weighted averages of ionization probabilities for stationary $15s$ and $16s$ states, separately. The averages are 11.7% and 13.1% for the two processes, respectively. The red points are from quantum calculations, while the red dashed lines are their fittings. The fitting functions are $0.116 + 0.112 \cos(\varphi_0 - 0.057)$ and $0.130 + 0.123 \cos(\varphi_0 - 0.245)$ for the two processes, respectively. Details for the fitting functions can be found in the Appendix Sec. 6.6.

As derived in the Appendix Sec. 6.6, the ionization probability versus superposition phase φ_0 satisfies (assuming initial weights of the two stationary states are approximately the same)

$$P_{\text{ion}} \simeq \bar{P}_{\text{st}} + A \cos(\varphi_0 + \varphi_s), \text{ where } Ae^{i\varphi_s} = \sum_l \int_0^\infty d\epsilon \langle \psi_{f1} | \epsilon l \rangle \langle \epsilon l | \psi_{f2} \rangle. \quad (6.20)$$

The $\bar{P}_{\text{st}}$ is the φ_0 -averaged ionization probability. The $|\psi_{f1}\rangle$ and $|\psi_{f2}\rangle$ are continuum wave functions ionized from the two stationary states in Eq. (6.18). The maximum

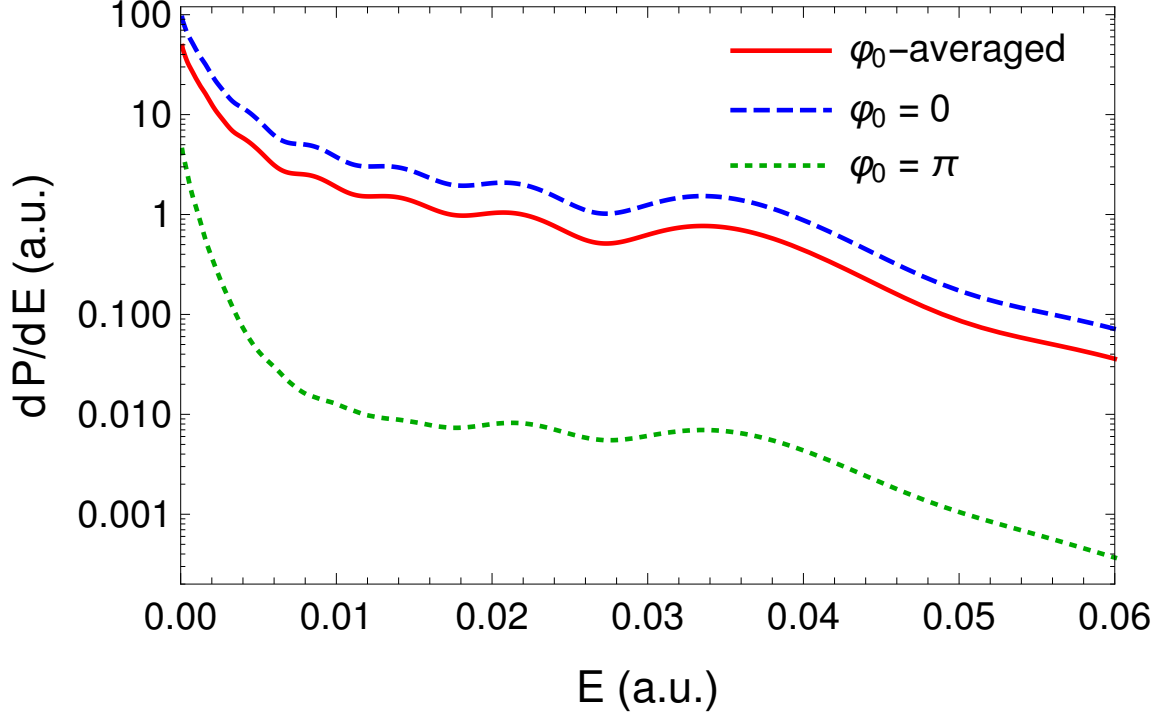


Figure 6.10. Energy distributions for ionizations from $15s + \exp(i\varphi_0)16s$ wave packets as introduced in Eq. (6.18). A short duration single-cycle pulse with parameters in the caption of Fig. 6.9(a) is used. The results are plotted for $\varphi_0 = 0$, π , and averages of φ_0 ranging from 0 to 2π .

ionization probabilities are slightly shifted from zero phase, where the shift φ_s of 0.057 and 0.245 radians are found. The small phase shift is the argument of the overlap integral of continuum wave functions ionized from the two stationary states. The depth of the ionization curve is determined by the amplitude of the overlap integral. For both short and medium duration single-cycle pulse ionizations, the minimum allowed ionization probability is very close to zero. This indicates that $A \simeq \bar{P}_{st}$, and the overlap integral nearly reaches the maximum. As a comparison, the ionization curve due to a medium duration single-cycle pulse is slightly deeper than that of a short duration single-cycle pulse. In this case, the continuum wave functions ionized

from two adjacent states due to a medium duration single-cycle pulse have a slightly larger overlap than those due to a short duration single-cycle pulse.

Energy distributions of the ionized wave functions from wave packets with different superposition phase φ_0 are given in Fig. 6.10. In the calculations, short duration single-cycle pulses are used. Pulse parameters and ionization probabilities can be found in Fig. 6.9(a). Most of the ionized wave functions are at low energies and the energy distribution is decreasing versus E . Since the majority of the electron radial distributions from wave packet of $\varphi_0 = \pi$ are at the outer turning point, the displacement-caused potential energy change by a short single-cycle pulse is much smaller than that of the $\varphi_0 = 0$ case. Thus, the energy distribution from $\varphi_0 = \pi$ decreases much faster and earlier than that of $\varphi_0 = 0$ and the φ_0 -averaged results. Ionization probability from $\varphi_0 = 0$ is at maximum, while $\varphi_0 = \pi$ is at minimum. It can be proved that $P_{\text{ion}}(\varphi_0) + P_{\text{ion}}(\varphi_0 + \pi) = 2\bar{P}_{\text{st}}$. This can be seen in the figure that the φ_0 -averaged ionization probability is always the average of those from $\varphi_0 = 0$ and π , at all energies.

Additionally, scaling relations for ionizations from Rydberg wave packets are also studied. Instead of $|15s\rangle + e^{i\varphi_0}|16s\rangle$ state, the initial wave packet is changed to $|30s\rangle + e^{i\varphi_0}|31s\rangle$ and $|45s\rangle + e^{i\varphi_0}|46s\rangle$ states. Using the scaling relations given in Eq. (6.14), the pulse parameters are scaled versus the principal quantum number n . For all three wave packets given here, although $\Delta n = 1$ is not scaled as n , curves of ionization probabilities versus φ_0 due to both short and medium duration pulses are nearly the same as those in Fig. 6.9. For short or medium duration pulse, at $t = 0$, only those electrons within a small radius near the nucleus can be ionized [55]. The critical radius is proportional to the free electron shift in a field pulse, $r_c \propto F_m t_w^2$, and is also scaled as n^2 . In all three wave packets $|15s\rangle + e^{i\varphi_0}|16s\rangle$, $|30s\rangle + e^{i\varphi_0}|31s\rangle$, and $|45s\rangle + e^{i\varphi_0}|46s\rangle$, the probabilities to find electron within a small radius ($r_c < 2n^2$) are nearly the same, since they all have $\Delta n = 1$. Thus, the curves of ionization probability are also the same for all the three wave packets, and for both short and medium duration pulses.

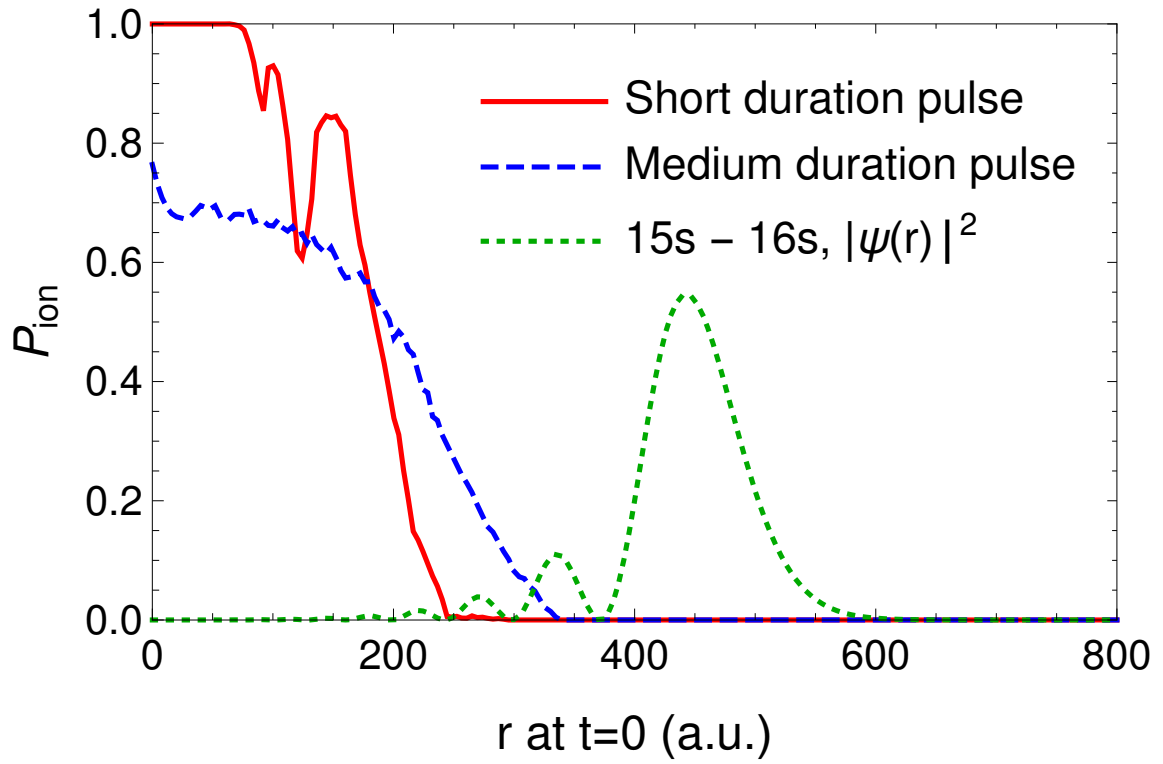


Figure 6.11. Ionization probability from classical calculations versus the radial position r of electron at $t = 0$. The electron is initiated at energy of $n = 15$ and angular momentum of zero, where the distance of the classical outer turning point is approximately $2n^2 = 450$ a.u. See text for details of r . Short and medium duration pulses are defined in the caption of Fig. 6.9. The radial distribution from a wave packet of $15s - 16s$ with $\varphi_0 = \pi$, as shown in Fig. 6.8 and Eq. (6.18), is plotted as a reference. The radial distribution is plotted in arbitrary unit.

Classical calculations are performed to investigate the ionization probability versus the radial distributions of wave packets. Electrons are initiated at the energy and angular momentum of a $15s$ state. The pulse parameters for short and medium durations pulses are defined in Fig. 6.9. For every r_{init} at $t = -3.5 t_w$, two separate classical trajectories are calculated. The first trajectory includes the field pulse and the $1/r$ core Coulomb potential, while the second trajectory only considers the $1/r$ core Coulomb potential. Then the ionization probability from the first trajectory averaged over θ is plotted versus radial position at $t = 0$ from the second trajectory, which is independent of θ . The ionization probability versus r at $t = 0$ can be found in Fig. 6.11. This figure can be compared with Fig. 6.8, since φ_0 in Eq. (6.18) gives the radial distribution of wave packets at $t = 0$ when there is no single-cycle pulse. For example, for the short pulse in Fig. 6.11, electrons only get ionized when they have $r \lesssim 250$ at $t = 0$. For the medium duration pulse, electrons can be ionized when they are slightly farther away from the nucleus at $t = 0$, and the ionization probability curve is smoother than that of a short pulse. Additionally, for a wave packet of $15s - 16s$ with $\varphi_0 = \pi$, illustrated as the green dotted line in Fig. 6.11, the probability to find the electron within $r_c \lesssim 250$ a.u. is very small. The ionization probabilities can be estimated from an integral

$$\tilde{P}_{\text{ion,est}} = \int dr |\psi(r)|^2 P_{\text{ion}}(r). \quad (6.21)$$

For $\varphi_0 = \pi$, the integral gives ionization probabilities of 0.3% for the short duration pulse and 0.9% for the medium duration pulse. These values are very close to values at the minima in the quantum calculations in Fig. 6.9.

The ionization probabilities from Rydberg wave packets at different superposition phases can differ by a factor of 5 or more. A short or medium duration single-cycle pulse can be used as highly efficient time-resolved probe to study the spatial distributions of Rydberg wave packets.

6.5 Conclusions

In this chapter, the scaling behavior for terahertz single-cycle pulse ionization from a Rydberg atom was studied. Two different forms of single-cycle pulses were used in this chapter, an asymmetric pulse [148] and a symmetric pulse [56]. A previous study [148] found discrepancies between the quantum and classical calculations for single-cycle pulse ionizations of a Rydberg atom. Results from quantum calculations, classical calculations with a single value of n , and classical calculations using a microcanonical ensemble treatment are compared in detail. In some critical cases of over-the-barrier ionizations where the field strength is near the ionization threshold, classical calculations with a spread of n give much better agreement with the quantum calculations. The scalings for pulse parameters and other physical quantities versus principal quantum number n were studied. With the scaled physical quantities, classical results with a single value of n are nearly perfectly scaled, but the quantum results are not. Interferences in the correlated distributions of electron's final energy and emission angle were studied by quantum and semiclassical methods. It was found that the oscillations of interference amplitudes scale as n .

Single-cycle pulse ionization from Rydberg wave packets were also studied. The Rydberg wave packets were introduced as a superposition of $|nl\rangle$ and $|(n+1)l\rangle$ states with different relative superposition phase. The ionization probabilities versus superposition phase were studied for both short and medium duration single-cycle pulses, and sinusoidal relations were found. The amplitude and argument of the overlap integral of ionized wave functions were discussed. The overlap integral determines the depth and shift of the ionization curve. Additionally, ionization with scaled pulses from Rydberg wave packets was also studied. Scaled pulses at higher n wave packets yield nearly the same ionization curves as for lower n , for both short and medium duration single-cycle pulse.

I would like to thank Professor C. H. Greene for helpful discussions in this project. This chapter is based upon work supported by the U.S. Department of Energy, Of-

fice of Science, Basic Energy Sciences, under Award No. DE-SC0012193. This research was supported in part through computational resources provided by Information Technology at Purdue University, West Lafayette, Indiana.

6.6 Appendix: Wave packets ionization probabilities versus superposition phase φ_0

The initial wave packet before the single-cycle pulse is given in Eq. (6.18):

$$|\Psi_i\rangle = c_1|n_1l\rangle + c_2e^{i\varphi_0}|n_2l\rangle, \quad (6.22)$$

where c_1 and c_2 are real amplitudes for the two states as given in Eq. (6.18) and φ_0 is the superposition phase of the wave packet. Since the Schrödinger equation is linear, the final wave function after the single-cycle pulse can be written as

$$|\Psi_f\rangle = c_1|\psi_{f1}\rangle + c_2e^{i\varphi_0}|\psi_{f2}\rangle, \quad (6.23)$$

where c_1 , c_2 , and φ_0 are exactly the same numbers as those in Eq. (6.22). Here, the $|\psi_{f1}\rangle$ and $|\psi_{f2}\rangle$ are the respective wave functions after single-cycle pulse ionization for initial stationary states $|n_1l\rangle$ and $|n_2l\rangle$. The ionization probability for the wave packet can be calculated as ($|\epsilon l\rangle$ is the energy-normalized continuum eigenstate)

$$\begin{aligned} P_{\text{ion}} &= \sum_l \int_0^\infty d\epsilon |\langle \epsilon l | \Psi_f \rangle|^2 \\ &= \sum_l \int_0^\infty d\epsilon |\langle \epsilon l | c_1\psi_{f1} + c_2e^{i\varphi_0}\psi_{f2} \rangle|^2 \\ &= \sum_l \int_0^\infty d\epsilon \left[c_1^2 |\langle \epsilon l | \psi_{f1} \rangle|^2 + c_2^2 |\langle \epsilon l | \psi_{f2} \rangle|^2 + c_1c_2e^{i\varphi_0} \langle \psi_{f1} | \epsilon l \rangle \langle \epsilon l | \psi_{f2} \rangle + \text{c.c.} \right] \end{aligned} \quad (6.24)$$

Note that integration over the first two terms is the weighted average of ionization probabilities from the two stationary states, defined to be $\bar{P}_{\text{st}}$. Let the continuum wave function projection be

$$\sum_l \int_0^\infty d\epsilon \langle \psi_{f1} | \epsilon l \rangle \langle \epsilon l | \psi_{f2} \rangle = Ae^{i\varphi_s}, \quad (6.25)$$

where A is the real amplitude, and φ_s is the argument for the projection. The ionization probability in Eq. (6.24) can be simplified as

$$P_{\text{ion}} = \bar{P}_{\text{st}} + 2c_1c_2A\cos(\varphi_0 + \varphi_s). \quad (6.26)$$

This explains that the φ_0 -averaged probabilities of P_{ion} are always the same as the weighted averages of the stationary state ionization probabilities. By comparing Eq. (6.26) with wave packet ionization curves in Fig. 6.9, the projection phase φ_s of the two continuum wave functions can be determined.

For c_1, c_2 from Eq. (6.18) at a large n , it can be shown that $2c_1c_2 \simeq 1$. Thus, Eq. (6.26) can be simplified as

$$P_{\text{ion}} \simeq \bar{P}_{\text{st}} + A\cos(\varphi_0 + \varphi_s). \quad (6.27)$$

The overlap amplitude A of the continuum wave functions, as given in Eq. (6.25), significantly affects the depth of ionization probabilities versus φ_0 . When $c_1 = c_2 = 1/\sqrt{2}$, $A \leq \bar{P}_{\text{st}}$, which gives the upper bound of the overlap integral of the two continuum wave functions.

7. SUMMARY AND OUTLOOK

In this dissertation, we have discussed five published manuscripts in the field of AMO physics.

In Chap. 2, the trapping energy and state mixing properties of Rydberg atom in optical traps were discussed. Further directions on this project can be focused on the special form of trapping lasers. For example, in Secs. 2.3.2 and 2.3.3, we presented an optical trap with four parallel beams with their centers forming a square. This model can be extended to n parallel beams forming an n -sided regular or irregular polygon. The symmetries can effectively eliminate some crossing terms in the Wigner- $3j$ symbol, and make the trapping energy shift and state mixing demonstrate novel properties.

In Chaps. 3, 4, and 5, we studied the two-electron correlations in an atom. We mainly focused on the repulsive interactions between them during the post-collision interaction (PCI). The PCI between them can cause rapid or negligible energy and angular momentum exchanges, and leads to different final distributions. For example, in Chaps. 4 and 5, we studied the PCI in two models: below-threshold photoexcitation followed by Auger decay, and sequential ionization. The PCI model can be further extended to study the effects of other parameters, e.g. non-zero initial angular momentum, different initial energies, etc. Another interesting two-electron result is known as a frozen planetary configuration [151]. The frozen planetary configuration can be achieved as follows: (1) excite the first electron to a highly excited state, with small angular momentum, (2) excite the second electron to an excited state at a lower energy when the first electron is near its outer turning point. The frozen planetary configuration is classically stable, while a general three-body $1/r^2$ problem is usually chaotic. However, there are two mechanisms that reduce the stability [151]. One is the radiative transition, the transition rate for this model is proportional to $\log n/n^5$,

where n is the principal quantum number. The other is the tunneling autoionization, where the semi-classical tunnelling rate is proportional to $\exp(-S)$, where S is the action. According to the classical scaling relation in Eq. (6.17), classical action scales as $S \propto n$. Thus, the autoionization rate drops exponentially as $\exp(-n)$. Estimates [151] showed that, when the principal quantum number n is greater than 20, resonant transition dominates, and the lifetime of frozen planetary configuration can be up to a few microsecond (10^{-6} s). This very interesting and novel nearly-stable frozen planetary configuration can be studied using the two-electron correlation method and numerical codes presented in this dissertation.

In Chap. 6, the ionization behavior from a Rydberg atom by a single-cycle pulse is studied. Our research focused on the ionization probabilities from both Rydberg stationary states and Rydberg wave packets. The ionization probability from a Rydberg wave packet changes dramatically versus the superposition phase of the Rydberg wave packet. This provides a highly efficient experimental tool to probe the radial distribution of a Rydberg wave packet. Also, we studied the scaling behavior of single-cycle pulse ionizations. All pulse parameters and the physical quantities of the electron are scaled versus the principal quantum number n . One unexpected finding in this project is that, when the pulse parameters are fixed and the field strength of over-the-barrier ionization is near the ionization threshold, the ionization probability is very sensitive to the initial energy of the electron. This is shown in Fig. 6.1. Further studies of this ionization versus energy behavior can be extended to special shapes of the laser pulse, three-, five-cycle pulses, or two-, multi-color pulses. The initial angular momentum can also be changed to non-zero values, although there are barely any differences from our single-cycle pulse calculations. As I am not certain if over-the-barrier ionization is the dominant mechanism, a model potential instead of the pure Coulomb potential can be used to study the ionization behavior at small radius. Furthermore, since a short duration single-cycle pulse picks out electron distribution near the nucleus, a model potential in this case could provide more insights on the field pulse ionization and different ionization results.

Other than the above three projects. I also participated in two other projects during my Ph.D. that are either unpublished or non-first-authored.

The first project is about cooling a hot electron plasma inside a microwave cavity [152]. In this project, a hot electron plasma ($\sim 10^4$ K) is put into a microwave cavity and trapped using a Penning-Malmberg trap. The cyclotron motion is tuned to oscillate resonantly with the microwave cavity mode. In this process, electrons transfer energy to the cavity, and are cooled to lower temperature (~ 10 K) until a balance between the external heating rate and the cooling rate is achieved. Experiments and our numerical calculations have found that, using different transverse electro-magnetic (TEM) cavity modes and different number of electrons, electron plasmas are cooled at different cooling rates and achieved different final temperatures. The model can be explained using the superradiance and subradiance theory [153], but they are well beyond the scope of this dissertation. Further details about this project can be found in [152].

The second project is to compare the speed of different time-dependent Schrödinger equation solvers for a standardized laser field ionization problem. The results were presented in the DAMOP 2018 meeting [154], and the manuscript is in preparation. In this project, we are given a laser field ionization problem, and are asked to give output on momentum distributions in the continuum at two different energies. Prof. Brett Esry proposed a method to estimate the relative numerical error without knowing the exact answer. The estimation is based on “how fast” (the exponential order) the numerical error decays versus explicitly chosen numerical parameters (grid size, step size, etc). This provides a universal definition of accuracy among all participants, and provides a very helpful tool for our future numerical projects that need convergence error estimations. Our Schrödinger equation solver used a higher order implicit time propagator, the fourth order Padé approximation instead of the more usual second order Crank-Nicolson propagator. The fourth-order Padé approximation time propagator can be converted into the multiplication of two Crank-Nicolson-like propagators. This made the programming much easier without the need to modify ex-

isting codes using Crank-Nicolson propagators. Fourteen different numerical methods were tested on the same unix workstation. The fastest 3 methods took 13 seconds, 16 seconds (our program), and 45 seconds to complete the task at the required accuracy. The slowest 3 methods took 1/2 hour, 1/2 hour, and 1 hour.

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A. ATOMIC UNITS

In atomic, molecular, and optical physics, atomic units (a.u.) are more frequently used than SI units. In atomic units, the following fundamental physical constants are defined to be unity:

- Mass of electron m_e ;
- Charge of electron e ;
- Reduced Planck constant $\hbar$;
- Coulomb constant $1/(4\pi\epsilon_0)$.

With the definitions above, there is a unique conversion between the atomic units and SI units. The values of 1 a.u. of different physical variables in SI units can be found as follows

Table A.1.
1 a.u. of physical variables in SI

dimension	value in SI	value in other units
mass	9.109×10^{-31} kg	
charge	1.602×10^{-19} C	
angular momentum	1.055×10^{-34} J·s	
Coulomb constant	8.988×10^9 N·m ² /C ²	
length	5.292×10^{-11} m	0.5292 Å
energy	4.360×10^{-18} J	27.21 eV
time	2.419×10^{-17} s	
electric field	5.142×10^{11} V/m	