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STUDIES OF IONIZATION AND WAVEPACKET DYNAMICS OF VERY-HIGH-$n$ RYDBERG ATOMS USING HALF-CYCLE PULSES

by

MARK T. FREY

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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Abstract

The response of potassium Rydberg atoms with principal quantum number, $n \geq 400$, to fast, unidirectional electric field pulses, termed half-cycle pulses (HCPs), is investigated experimentally and the results compared to classical trajectory Monte Carlo calculations. The durations, $T_p$, of the HCPs span the transition from the short pulse regime, where the classical orbital period of the initial state $T_n >> T_p$, to the long pulse regime, where $T_p >> T_n$. In experiments with single HCPs, ionization probabilities measured as a function of pulse width and amplitude agree with theory on an absolute scale without any adjustable parameters, providing a benchmark test for the validity of the classical limit of ionization. HCPs are also used to create and probe very high-$n$ Rydberg wavepackets. Application of a HCP with $T_p < T_n$, delivers an impulsive momentum transfer to the excited electron leading to coherent excitation of higher-lying Rydberg states. Application of a HCP with $T_p >> T_n$ leads to population of a coherent superposition of Stark states. In each case, the time-evolution of the wavepacket is examined by applying a second short HCP after a variable time delay. This probe pulse ionizes a fraction of the atoms present and the survival probability exhibits pronounced oscillations that are well reproduced by CTMC simulations. The CTMC calculations show that the observed quantum beats reflect the time-evolution of the distribution of the $z$ component, $p_z$, of the momentum of the excited electron. The first experimental studies of excitation and ionization by a sequence of short HCPs are also reported. Application of a sequence of identical pulses results in a multi-
step excitation followed by ionization. The ionization probability of atoms with \( n_i \sim 388 \) subject to a sequence of identical, equally-spaced 2 ns HCPs were measured as a function of HCP height and pulse repetition frequency, \( \omega_p \). The experimental data show that the Rydberg atoms are considerably more stable against ionization when the frequency of the perturbation scaled to the orbital frequency of the initial state, \( \omega_0 = n_i^3 \omega_p \), is \( \omega_0 \gtrsim 1 \) than when \( \omega_0 \ll 1 \). This stability is not as pronounced in a CTMC calculation that uses \( \delta \)-function impulses.
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It is my pleasure to acknowledge the people whose contributions helped make this work possible. My advisor, Professor Barry Dunning, provided energetic leadership, encouragement and a stimulating environment in which I was exposed to many technologies. In our daily discussions, we solved many problems and discovered much new physics together. We gained great theoretical insight with our close collaboration with Carlos Reinhold and Joachim Burgdörfer who always managed to explain theory in physical terms experimentalists could understand.

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# Table of Contents

Abstract .................................................................................................................. ii
Acknowledgments .................................................................................................... iv

## Chapter 1 Introduction ......................................................................................... 1

## Chapter 2 Classical Atomic Orbits ...................................................................... 5
  2.1 Hydrogenic Orbits .......................................................................................... 5
  2.2 Non-Hydrogenic Orbits .................................................................................. 19
  2.3 The Stark Effect ............................................................................................ 21
  2.4 Field Ionization ............................................................................................. 30

## Chapter 3 Experimental Apparatus .................................................................. 33
  3.1 Vacuum System ............................................................................................. 33
  3.2 Potassium Beam ............................................................................................ 35
  3.3 Laser System .................................................................................................. 35
  3.4 Interaction Region ......................................................................................... 38
  3.5 Half-Cycle Pulses ......................................................................................... 39
  3.6 Data Acquisition System .............................................................................. 40

## Chapter 4 Experimental Techniques ............................................................... 44
  4.1 Selective Field Ionization (SFI) .................................................................. 44
  4.2 High-\(n\) Spectroscopy .................................................................................. 48
  4.3 Control of Stray Electric Fields ..................................................................... 51

## Chapter 5 Experimental Results and Discussion ............................................. 56
  5.1 Ionization by a Single Half-Cycle Pulse ....................................................... 56
  5.2 Rydberg Wavepackets Created and Probed by Short HCPs ....................... 64
  5.3 Stark Wavepackets Generated by an Electric Field Step ............................. 77
  5.4 Ionization a Sequence of Half-Cycle Pulses ................................................. 88
Chapter 1

Introduction

The physical characteristics of Rydberg atoms, i.e. atoms in which one electron is excited to a state of very large principal quantum number, $n$, are quite unlike those normally associated with atoms in ground or low-lying excited states. This is demonstrated by table 1.1 which lists a number of atomic properties, their dependence on $n$ and typical numerical values for each at several $n$. [Unless otherwise noted, all quantities will be expressed in atomic units\(^1\) (a.u.).] Atomic dimensions increase rapidly with $n$, and by $n \sim 1100$, the highest $n$ at which experiments have been undertaken so far\(^2\), the diameter of a single atom is \(\sim 0.13\) nm, large enough such that a solid object of the same size could be seen with the unaided eye. On average, the separation between the excited Rydberg electron and the nucleus and the other atomic electrons, which together comprise a compact core of unit positive charge is large, so the gross properties of any species of Rydberg atom resemble those of hydrogen. The time scale for atomic motions, given by the orbital period of an electron in a classical Kepler orbit about the core, also increases rapidly with $n$. It is of the order of tens of nanoseconds at high $n$, a time scale that is easily observed on a laboratory oscilloscope. The binding energy of the electron, decreases rapidly with increasing $n$ amounting to only tens of $\mu$eV at high $n$, so very little energy needs to be supplied to the atom in order to ionize it. The excited electron is so far from the core ion that the Coulomb field it experiences is very small. At high-$n$, even weak externally applied electric fields of only $\text{mV cm}^{-1}$ can strongly perturb electronic motion (the Stark effect). Indeed, if the field is sufficiently strong, the electron may be stripped from the atom—a process termed field ionization.
Table 1.1 Properties of Rydberg Atoms

<table>
<thead>
<tr>
<th>Property</th>
<th>scaling (a.u.)</th>
<th>n=1</th>
<th>n=30</th>
<th>n=400</th>
<th>n=1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean radius</td>
<td>( n^2 )</td>
<td>5.3 \times 10^{-9} cm</td>
<td>4.8 \times 10^{-6} cm</td>
<td>8.5 \times 10^{-4} cm</td>
<td>5.3 \times 10^{-3} cm</td>
</tr>
<tr>
<td>Orbital Period</td>
<td>( 2\pi n^3 )</td>
<td>1.5 \times 10^{-16} s</td>
<td>4.1 ps</td>
<td>9.6 ns</td>
<td>150 ns</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>( \frac{1}{2n^2} )</td>
<td>13.6 eV</td>
<td>15 meV</td>
<td>85 ( \mu )eV</td>
<td>13.6 ( \mu )eV</td>
</tr>
<tr>
<td>Energy Spacings</td>
<td>( \frac{1}{n^3} )</td>
<td>10.2 eV</td>
<td>1.0 meV</td>
<td>0.43 ( \mu )eV</td>
<td>27.2 neV</td>
</tr>
<tr>
<td>Classical Field Ionization Threshold</td>
<td>( \frac{1}{16n^4} )</td>
<td>3 \times 10^8 Vcm(^{-1})</td>
<td>400 Vcm(^{-1})</td>
<td>13 mVcm(^{-1})</td>
<td>320 ( \mu )Vcm(^{-1})</td>
</tr>
</tbody>
</table>

The response of atoms in high-lying Rydberg states to pulsed electric fields has been investigated extensively.\(^3\) Until recently however, the rise time and width of the applied pulses were much greater than the classical Kepler orbital period, \( T_n \), of the Rydberg electron. The atom can essentially respond adiabatically to such slowly varying fields and little energy is transferred from the field to the orbiting electron. In contrast, application of rapidly varying fields can transfer energy to the electron. Application of a unidirectional electric field pulse, termed a half-cycle pulse (HCP), whose duration \( T_p \) is less than \( T_n \) delivers an impulsive momentum transfer

\[
\Delta \vec{p} = - \int \vec{F}(t) dt \tag{1.1}
\]
that can impart energy to the electron resulting in coherent excitation of higher-lying Rydberg states. Application of a HCP whose risetime is $\sim T_n$, but with $T_p \gg T_n$ leads to population of a coherent superposition of Stark states. Thus rapidly varying electric fields can be used to create high-$n$ Rydberg wavepackets. Such wavepackets can display novel dynamical behavior that mimics the classical motion of the excited electron thereby providing a bridge between quantum and classical physics.4

Sufficiently strong HCPs can ionize Rydberg atoms. In the long pulse regime, $T_p \gg T_n$, ionization occurs as in DC fields from tunneling through the potential barrier generated by the atomic and applied fields or from over-barrier escape.5-7 The field required to induce such ionization decreases rapidly with increasing $n$, scaling as $1/n^4$. In contrast, application of a very short electric field pulse with duration $T_p < T_n$ lowers the Coulomb barrier only momentarily. Nonetheless if the amplitude of the pulse is sufficient, the impulse delivered to the electron by the HCP can impart energy to the electron in excess of its binding energy leading to ionization. Theory predicts that the $n$ scaling of the ionization threshold crosses over from the $1/n^4$ dependence characteristic of the adiabatic limit to a $1/n$ dependence in the limit of ultrashort pulses, $T_p \ll T_n$.8

Measurements in the short-pulse regime have been undertaken recently by applying short, fixed-duration ($\sim 0.5$ ps), freely propagating HCPs to Na Rydberg atoms with low-to intermediate $n$ ($14 \leq n \leq 35$).9-12 The HCPs were produced by illuminating photoconductive semiconductor switches with output pulses from a femtosecond laser system.13 These experimental advances have stimulated a large number of theoretical investigations of excitation and ionization by HCPs.8,14-19 However, detailed comparisons between theory and experiment are complicated by uncertainties inherent in determining the absolute amplitude and shape of these HCPs.20 Unresolved discrepancies between experiment and theory have raised questions as to the validity of the classical-quantum correspondence for high-$n$ levels and of the classical trajectory Monte Carlo.
(CTMC) method$^{8,14}$, which in the past has been successful in reproducing experimental results in systems where a large number of quantum levels are populated, such as in fast ion-atom collisions.$^{21}$

In the present work, uncertainties in the pulse height and shape have been minimized by undertaking measurements at very-high-$n$, $n \geq 400$. For such $n$, the classical electron orbital period is quite long allowing ionization and excitation to be investigated, even in the short-pulse regime, by using nanosecond pulses from conventional fast pulse generators. These pulses can be accurately characterized so that comparison can be made to theory on an absolute scale without any adjustable parameters. The results of studies of the ionization of very-high-$n$ potassium Rydberg atoms by a variety of HCPs$^{22-24}$ are reported and show that such pulses can induce and probe dynamic states in atoms.
Chapter 2

Classical Atomic Orbits

Application of rapidly varying, intense electric fields applied to a Rydberg atom in a well defined initial state with energy \( E_n \) can result in population of a broad range of final states. For example, a sufficiently strong half-cycle pulse (HCP) can, because of its broad bandwidth, induce multiphoton transitions to a range of bound final Rydberg states with energies up to the ionization limit as well as to unbound states in the continuum. Since energy differences between neighboring Rydberg states are small compared to the range of final state energies (\( \Delta E / E \sim 1/n << 1 \)) it is reasonable to expect the quantal nature of the system to be less important and for classical mechanics to provide a description of the response of the atom to the applied field. Indeed, a classical treatment of the problem is the only theory that can be performed because the large number of states involved for \( n \geq 200 \) makes quantum calculations practically impossible.\(^{23}\) A classical picture is particularly useful in understanding the time development of wave packets formed from a coherent superposition of Rydberg states produced by rapidly applied fields because the motion of the wave packet can mimic the motion of the electron in its classical orbit.

2.1 Hydrogenic Orbits

The simplest atomic system is hydrogen, one electron bound to one proton by the Coulomb potential, \( V(r) = -1/r \), where \( r \) is the distance between the charges. The mass of the proton is \(~2000\) times that of the electron, so to a good approximation, the nucleus is stationary and can be taken as the origin of coordinates. The potential possesses spherical symmetry, so the angular momentum, \( \vec{L} = \vec{r} \times \vec{p} \) is constant, which in turn implies that both the radius vector \( \vec{r} \) and the linear momentum vector \( \vec{p} \) of the electron always lie in a
plane normal to $\bar{L}$, which is fixed in space. The $z$-component of the angular momentum $L_z$ can also be taken as a constant of the motion that specifies the orientation of the orbital plane relative to a space-fixed axis. Motion in that plane is conveniently expressed in plane polar coordinates, $x = \rho \cos(\phi)$ and $y = \rho \sin(\phi)$. The total energy, $p^2 / 2 + V(\rho)$, is

$$E = \frac{1}{2} (\dot{\rho}^2 + \rho^2 \dot{\phi}^2) - \frac{1}{\rho}$$  \hspace{1cm} (2.1)$$

Since

$$L = \rho^2 \dot{\phi}$$  \hspace{1cm} (2.2)$$

equation 2.1 can be written

$$E = \frac{1}{2} \dot{\rho}^2 + \left( \frac{L^2}{2\rho^2} - \frac{1}{\rho} \right) = \frac{1}{2} \dot{\rho}^2 + V_{\text{eff}}(\rho)$$  \hspace{1cm} (2.3)$$

so the radial part of the motion can be regarded as taking place in one dimension in the field of the effective potential, $V_{\text{eff}}(\rho)$. Figure 2.1 shows the form of $V_{\text{eff}}(\rho)$ for different values of $L$. For low $L$, the electron orbits at radii extending from $\rho_{\text{max}} = -1/E$ down to $\rho \approx 0$. For increasing $L$, the centrifugal energy $L^2 / 2\rho^2$ term causes the radial motion to be increasingly localized at radii far from the nucleus. Eqs. 2.2 and 2.1 can be used to obtain the equation of the path,\textsuperscript{25}

$$\frac{2p}{\rho} = 1 + e \cos(\phi)$$  \hspace{1cm} (2.4)$$
Fig. 2.1. Plot of $V_{\text{eff}}$ as a function of the scaled radial coordinate $\rho_0 = 2|E|p$ for values of the scaled angular momentum, $L_0 = L \sqrt{2|E|}$. 
where $P = L^2$ and $e = \sqrt{1 + 2EL^2}$. For bound orbits ($E < 0$), eq. 2.4 describes an ellipse with one focus at the origin; $2P$ is called the *latus rectum* of the orbit and $e$ the *eccentricity*. The semi-major axis, $a$, and semi-minor axis, $b$, of the ellipse are

$$a = \frac{P}{1 - e^2} = \frac{1}{2|E|}, \quad b = \frac{P}{\sqrt{1 - e^2}} = \frac{L}{\sqrt{2|E|}} \quad (2.5)$$

Figure 2.2 shows that for low $L$ values, $L \sim 0$ ($e \sim 1$), the orbit is essentially a line between the nucleus and the outer turning point, whereas for large $L$, $L \sim 1 / \sqrt{2|E|}$ ($e \sim 0$), the orbit becomes a circle. The position of the electron has the following parametric dependence on time, $t$

$$x = a(\cos(\xi) + e), \quad y = a\sqrt{1 - e^2} \sin(\xi) \quad (2.6)$$

where the parameter, $\xi$, the *eccentric anomaly*, varies between 0 and $2\pi$ over one orbital period. It is defined by

$$t = a^3 (\xi + e\sin(\xi)) \quad (2.7)$$

The period $T$ of revolution is

$$T = 2\pi a^{3/2} = \pi \sqrt{2|E|^3} \quad (2.8)$$

and depends only on the energy of the electron, which in turn depends only on $a$. Thus orbits of different eccentricity can have the same energy and orbital period. The scaled $x$ position $(x/a)$ of the electron as a function of scaled time $t/T$ is plotted in figure 2.3 for a) a low $L$ orbit ($e \sim 1$) and b) a high $L$ orbit ($e \sim 0$). Figures 2.2 and 2.3 taken together show that
Fig. 2.2. (a) Relation of the parameters $a$, $b$, $e$, and $P$ to the shape of the orbit. (b) Orbit shapes for various values of scaled angular momentum, $L_0 = L/\sqrt{2|E|}$. 
Fig. 2.3. Plot of $x/a$ as a function of scaled time, $t/T$, for (a) a low $L$ orbit ($e\sim 1$) and (b) a high $L$ orbit ($e\sim 0$).
the orientation of the major axis remains fixed in time, i.e. its orientation is a constant of the motion. This constant vector, \( \vec{A} = \vec{p} \times \vec{L} - \vec{r} / r \) is called the Lenz vector or the Runge-Lenz vector.\(^{26}\) It has magnitude \( e \) and is directed from O to N in fig. 2.2. As is evident from fig. 2.3, for low \( L \) orbits the electron spends nearly all of its time on one side of the atom. Thus the existence of such a constant of motion \( \vec{A} \) is related to the existence of a permanent dipole moment.\(^{27}\)

The momentum of the electron is

\[
p = \sqrt{2|E|} \left[ \frac{1 - e \cos(\xi)}{1 + e \cos(\xi)} \right]^{1/2}
\]

(2.9)

with

\[
p_x = -\sqrt{2|E|} \frac{\sin(\xi)}{1 + e \cos(\xi)}, \quad p_y = \sqrt{2|E|} \frac{\sqrt{1 - e^2} \cos(\xi)}{(1 + e \cos(\xi))}
\]

(2.10)

Figure 2.4 shows a plot of \( p \) and \( p_x \) (scaled by the root mean square momentum, \( p_{rms} = \sqrt{2|E|} \)) for orbits with low and high \( L \). In order to conserve energy and angular momentum, an electron in a low \( L \) orbit moves slowly at the outer turning point of the orbit and speeds up as it approaches the proton (at times that are integer multiples of \( 7/2 \)). For a high-\( L \) orbit, the electron undergoes approximately uniform circular motion with \( p = p_{rms} = \sqrt{2|E|} \).

Let us now consider correspondence between hydrogenic classical orbits and quantal wave functions, \( \psi_{n\ell m} \), where \( E_n = -1/2n^2 \), \( L = \sqrt{\ell(\ell + 1)} \), and \( L_z = m \). In general, one expects a system to evolve according to classical mechanics when the deBroglie wavelength, \( \lambda = 1/p \) of an object is small compared to the dimensions of the system, \( D \).

For hydrogen \( D \) is of the order of the mean radius of the atom, i.e. \( D = n^2 \). The electron
Fig. 2.4. Total electron momentum, $p$, and $x$-component of electron momentum, $p_x$, as a function of time for (a) a low $L$ orbit ($e-1$) and (b) a maximum $L$ orbit ($e-0$).
deBroglie wavelength in state \( n \), \( \lambda_n \), is of the order of \( 1/ p_{rms} \sim n \). For hydrogen then, one expects a transition from quantum to classical mechanics when \( n \gg 1 \). However, there is not a one for one correspondence between a wave function and a classical orbit. For example, consider an electron in a high-\( n \) s state. The spatial probability distribution, \( |\psi_{n00}(r)|^2 \) does not tend to classical motion in a path. Unlike the classical orbit, \( |\psi_{n00}(r)|^2 \) is spherically symmetric and independent of time. A correspondence can be made, however between \( |\psi_{n00}|^2 \) for \( n \gg 1 \) and the classical probability distributions (both momentum and spatial) of an ensemble of \( L=0 \) classical orbits with \( \langle L_z \rangle = m = 0 \) and completely random initial phases. Such an approach underlies classical trajectory Monte Carlo (CTMC) calculations. In CTMC calculations, a large ensemble of electronic initial conditions are sampled from a classical phase-space probability density which mimics the corresponding quantal position and momentum distributions. Each initial condition in phase space is then propagated according to Hamilton's equations of motion.

Figure 2.5 shows the quantal momentum probability distribution for \( 50p \) state and the corresponding classical momentum distribution. The quantal distribution is oscillatory (in general it posses \( n - \ell - 1 \) nodes) while the classical distribution is smooth. The two distributions closely resemble each other, however, if at every point, the distribution is averaged over an interval larger than the node spacings. Thus we see that the classical and quantal distributions agree only when \( n \gg 1 \) and when quantal oscillations are finer than the precision of measurement of an observable. In momentum space, the node spacings scale as \( 1/n \), so for a fixed measurement precision, quantal oscillations will not be detected for sufficiently large \( n \).

Classically, application of a HCP whose duration is much less than the classical orbital period to an orbiting electron with momentum \( \vec{p} \) imparts net momentum \( \Delta \vec{p} \) and energy \( \Delta E = (\Delta p)^2 / 2 + \vec{p} \cdot \Delta \vec{p} \) to it. Thus the final electron energy distribution depends on the electron momentum distribution. For an HCP applied in a given direction, a one
Fig. 2.5. (a) Quantal electron momentum distribution for a H(50p) state (thin line). (b) Quantal distribution in (a) for which neighboring points in the distribution are averaged (thin line). In both (a) and (b) the corresponding classical distribution is shown by the dark line.
dimensional momentum distribution is relevant. The classical momentum distribution $f(p_x)$ of the $x$ component of $p$ is determined by

$$f(p_x) dp_x = \frac{dt}{T} \quad (2.11)$$

then

$$f(p_x) = \frac{1}{T} \left| \frac{dt}{dp_x} \right| = \frac{1}{T} \left| \frac{dt}{d\xi} \right| dp_x \quad (2.12)$$

Evaluating the derivatives using eqs. 2.7 and 2.10 gives

$$f(p_x) = \frac{1}{2\pi p_{rms}} \frac{(1 + e \cos(\xi))^3}{e + \cos(\xi)} \quad (2.13)$$

This distribution is plotted vs. $p_x$ in fig. 2.6. The distribution is sharply peaked at $p_x = 0$ for low $L$ orbits while for circular orbits it is spread out between $\pm p_{rms}$.

Following application of the HCP, the position and momentum distributions of the electron will evolve in time. A quantum probability distribution has a time dependence when the wave function of the system is a coherent superposition of energy eigenstates. The term coherent is used to emphasize that not only must the relative occupation of different eigenstates of the system be specified, but also the relative phase difference between the eigenstates. Consider the simplest case of a superposition of two nearby energy eigenstates of hydrogen (for the purpose of this discussion, the $\ell$ and $m$ quantum numbers are suppressed)

$$\Psi(t) = c_n e^{-iE_n t} \psi_n + c_{n+1} e^{-iE_{n+1} t} \psi_{n+1} \quad (2.14)$$
Fig. 2.6. The distribution $f(p_x)$ of the $x$ component of electron momentum for different values of the scaled angular momentum, $L_0 = L \sqrt{2|E|}$. 
The coefficients are the weighting factors in the superposition, given in terms of the initial wave function by $c_n = \langle \psi_n | \Psi(0) \rangle$. The quantal probability distribution

$$|\Psi(t)|^2 = |c_n|^2 |\psi_n|^2 + |c_{n+1}|^2 |\psi_{n+1}|^2 + 2 \Re \left[ c_n c_{n+1}^* \psi_n \psi_{n+1}^* e^{i(E_{n+1} - E_n)t} \right]$$

(2.15)

oscillates with a frequency of

$$\omega_n = E_{n+1} - E_n = -\frac{1}{2} \left( \frac{1}{(n+1)^2} - \frac{1}{n^2} \right)$$

(2.16)

For $n \gg 1$, $\omega_n = 1/n^3 = 1/\sqrt{2|E_n|^3} = 2\pi/\tau$ where $\tau$ is the classical orbital period given by eq. 2.8. This is the Bohr correspondence principle: the energy difference between adjacent energy levels is approximately equal to the classical orbital frequency for large $n$.

As will be discussed in Chapter 5, application of a HCP to an atom can produce a localized wavepacket, that is a superposition of many eigenstates

$$\Psi(t) = \sum_n c_n \psi_n e^{-iE_n t}$$

(2.17)

with the weighting probabilities $|c_n|^2$ strongly centered around a mean value, $\bar{n}$. (In general, states of different $\ell$ and $m$ will also be involved in the superposition, but since we are only interested in the time dependence of the wave function, the quantum numbers $\ell$ and $m$ will again be suppressed.) Only those states with energies $E_n$ near the value $E_{\bar{n}}$ enter appreciably into the sum in eq. 2.17, thus for $\bar{n} \gg 1$, the energy can be expanded in a Taylor series in $n$ around the mean value $\bar{n}$:

$$E_n \equiv E_{\bar{n}} + E''_{\bar{n}} (n - \bar{n}) + \frac{1}{2} E''''_{\bar{n}} (n - \bar{n})^2 + \ldots$$

(2.18)
where each prime on $E_\pi$ denotes a derivative. The expansion coefficients of each term in eq. 2.18 are related to distinct time scales:

$$T_{cl} = \frac{2\pi}{|E_\pi'|} = 2\pi\bar{n}^3, \quad t_{rev} = \frac{2\pi}{3|E_\pi'|} = \frac{\bar{n}}{3} T_{cl}$$

(2.19)

The first term is simply the period of a classical orbit with energy $E_\pi$. The second time scale $t_{rev}$ is called the revival time and is associated with dephasing (collapse) and rephasing (revival) of the wavepacket. Substituting eq. 2.18 into eq. 2.17 and disregarding the overall time-dependent phase gives

$$\Psi(t) = \sum_n c_n \psi_n \exp \left[ -2\pi i \left( \frac{(n-\bar{n})t}{T_{cl}} + \frac{(n-\bar{n})^2 t}{2t_{rev}} \right) \right]$$

(2.20)

At early times, the first term in the phase of eq. 2.20 dominates so that $\Psi(t)$ is approximately periodic in time with period $T_{cl}$. As time advances, the second term in the phase modulates this behavior, causing a damping of the oscillations. This collapse of the wavepacket results from the fact that the energy levels are not equally spaced. Different states in the superposition evolve differently in time leading to dephasing. At times near $t_{rev}$, the second term in the phase in eq. 2.20 is approximately equal to $\pi t$ so the motion is once again governed by the first term. The motion is again periodic with period $T_{cl}$ (although one half-cycle out of phase with the original motion). This is called a full revival. Revivals are purely quantum mechanical, arising from the discreteness of the energy levels. At times that are rational fractions of $t_{rev}$, the wavepacket partially revives with a period given by a rational fraction of $T_{cl}$. For times greater than $t_{rev}$, higher order terms in the expansion modulate the revival behavior.
2.2 Non-Hydrogenic Orbits

Figure 2.7 shows the classical model of an alkali atom consisting of the valence electron bound to a compact core of unit positive charge made up of the nucleus and the inner-shell electrons. When outside the core, the electron can polarize it and be attracted by the resulting induced dipole. Inside the core, the electron experiences a nuclear charge, \( Z > 1 \), because the nucleus is not completely screened by the inner-shell electrons. Thus the electron is more strongly bound than the corresponding orbit in hydrogen and the deviation from a \( 1/r \) potential breaks the dynamical symmetry so the major axis of the orbit precesses in the orbital plane\(^{28}\) (the core is a closed shell and is therefore spherically symmetric so \( L \) is still a constant of the motion).

The energy levels of thealkalis can be written

\[
E_{nt} = -\frac{1}{2(n - \delta_t)^2}
\]  

(2.21)

where \( \delta_t \), the quantum defect, depends strongly on \( \ell \) but only weakly on \( n \). Quantum defects are large for low \( \ell \) states that penetrate the core and small for states in which the centrifugal barrier prevents penetration. Empirically, the defects are large \((\delta_t \approx 1)\) when \( \ell \) is less than \( \ell_c \), which is the maximum angular momentum of a core electron. When \( \ell \) is greater than \( \ell_c \), the defects are small, typically \( 10^{-2} \) or less.\(^{27}\)

Using the correspondence principal, the classical precession frequency, \( \omega_\ell \), is approximately

\[
\omega_\ell = \left( -\frac{1}{2n^2} \right) - \left( -\frac{1}{2(n - \delta_t)^2} \right) = \frac{\delta_t}{n^3}
\]

(2.22)

For penetrating orbits, the precession frequency can be as large as the electron orbital frequency.
Fig. 2.7. Change in electron orbits with increasing core penetration, from ref. 28.
2.3 The Stark Effect

First consider a hydrogen atom in a uniform electric field, $\vec{F} = F\vec{z}$. The electron moves in the combined Coulomb-external-field potential $V = -1/r + Fz$. The total energy can be written (in cylindrical polar coordinates)

$$E = \frac{1}{2} \left( p_\rho^2 + p_z^2 \right) + \frac{L_z^2}{2\rho^2} + V$$

(2.23)

Since $V$ is symmetric about the $z$ axis, $L_z$ is still a constant of the motion, but $\vec{A}$ and $\vec{L}$ are not. The resulting classical electron orbit is complicated because the field causes the position and eccentricity of the orbit to vary continuously.\[^{29,30}\] However, the dynamical symmetry of the Coulomb potential translates into a new constant of the motion in a field: the $z$-component of the atomic dipole moment, $d_z$. Consider an initial hydrogenic orbit with an orientation as in fig. 2.8. The angle $\vartheta$ is the angle which the major axis makes with the $z$ axis while $\rho', \phi'$ are the plane polar coordinates in the plane of the elliptic orbit. Let the field strength be small such that the electron orbit changes little over an orbital period and the field does not significantly polarize the atom then

$$E = E_0 - d_z F$$

(2.24)

where $E_0$ is the unperturbed energy. The average $z$ position of the electron in this orbit is

$$\langle z \rangle = \frac{1}{T} \int_0^T \rho' \cos(\phi') \cos(\vartheta) dt = \frac{\cos(\vartheta)}{T} \int_0^T \rho' \cos(\phi') dt$$

(2.25)
Fig. 2.8. Hydrogenic orbit whose major axis is oriented at an angle of $\theta$ with respect to the $z$ axis. The plane polar coordinates, $\rho'$ and $\phi'$ describe the position of the electron in the orbital plane.
According the fig. 2.8, \( \rho' \cos(\phi') = x' \), where \( x' = a(\cos(\xi) + e) \) as given by eq. 2.6. From eq. 2.7 \( \frac{dt}{d} = \omega^{-1}(1 + e \cos(\xi))d\xi \) where \( \omega \) is the frequency of the unperturbed motion. Evaluating the integral in eq. 2.19 gives

\[
\langle z \rangle = \frac{\cos(\vartheta)}{2\pi} \int_0^{2\pi} a(\cos(\xi) + e)(1 + e \cos(\xi))d\xi = \frac{3}{2} e \alpha \cos(\vartheta) \tag{2.26}
\]

Finally, substituting the expression 2.5 for \( a \),

\[
\langle z \rangle = \frac{3}{4|E_0|} e \cos(\vartheta) \tag{2.27}
\]

The average potential energy \( -\langle z \rangle F \) over a revolution of the electron must be the same for all revolutions, thus \( \langle z \rangle = -d_z \) is a constant. Since \( E_0 \) is constant, the orbit must change such that \( e \cos(\vartheta) \) remains constant, but \( e \) and \( \cos(\vartheta) \) will change with time. Figure 2.9 shows how the orbit changes with time in the (moving) orbital plane. Note that for each precession cycle of the major axis, the eccentricity cycles twice. Thus the "precession" frequency of \( L \) and \( A_z \) (\( A_z \propto \cos(\vartheta) \)) is twice that of the major axis, which Bohr calculated to be \( 31 \)

\[
\omega_F = \frac{3F}{2a \omega} \tag{2.28}
\]

For larger fields, the polarization of the atom by the external field becomes more important. To first order, this induced dipole is proportional to \( F \) and is usually written as \( \alpha F \) where \( \alpha \) is the atomic polarizability. The interaction energy between the electron and the induced dipole is \(-\alpha F^2 / 2\). For even higher field strengths, the external field can further stretch the orbit until the electron is removed, i.e. until the atom field ionizes.

Quantum mechanically, the eigenstates of a hydrogen atom in an weak external field are a mixture of degenerate eigenstates of the unperturbed atom with different values of \( \ell \) (the
Fig. 2.9.  Stark precession of an initial $n=400$, $\ell=1$ orbit in the (moving) orbital plane.
first order Stark effect). Higher field strengths mix nondegenerate states. The Schrödinger equation can be separated in parabolic coordinates and the quantum Stark energy levels calculated using perturbation theory. To second order in $F$, the energy levels are given by

$$E_{n_1n_2m} = \frac{-1}{2n^2} + \frac{3nF}{2}(n_1 - n_2) - \frac{F^2}{16} n^4 \left[ 17n^2 - 3(n_1 - n_2)^2 - 9m^2 + 19 \right]$$

(2.29)

where $n_1$ and $n_2$ are the parabolic quantum numbers and are related to $n$ and $|m|$ by $n = n_1 + n_2 + |m| + 1$. Figure 2.10 is a plot of the H $|m|=1$ energy levels from $n=8$ to $n=14$ in electric fields up to $10^5$ Vcm$^{-1}$, strong enough to field ionize the atom. First, notice that the levels shift approximately linearly with $F$ right up to field strengths sufficient to ionize the atom. Second, notice that the Stark levels of adjacent $n$ manifolds cross, a consequence of the extended dynamical symmetry. The extreme red and blue $m = 0$ states have Stark shifts of approximately $\pm 3n^2 F / 2$. Equating the Stark shift to the $n \rightarrow n+1$ energy spacing gives the Stark crossing field $F = 1 / 3n^5$.

Since the first order Stark effect dominates at virtually all field strengths, let us consider then the first order Stark effect only

$$E_{n_1n_2m} = \frac{-1}{2n^2} + \frac{3nF}{2}(n_1 - n_2)$$

(2.30)

While there is no explicit $m$ dependence in eq. 2.30, there is an implicit dependence due to the fact that $n = n_1 + n_2 + |m| + 1$. For $m = 0$, allowed values of $n_1 - n_2$ are $n - 1$, $n - 3 \ldots - n + 1$ while for $m = 1$ they are $n - 2$, $n - 4 \ldots - n + 2$. The even and odd levels are interleaved. For a Stark manifold characterized by the quantum numbers $n$ and $m$, there are $n - |m|$ Stark levels. Comparison with eq. 2.24 shows that $d_z = -3n(n_1 - n_2) / 2$ so that the quantity $n_1 - n_2$ is associated with the orientation of a permanent dipole moment relative to the field direction. States with $n_1 - n_2 \sim n$ (extreme blue-shifted states) are localized along
Fig. 2.10. Stark structure and field ionization properties of the $|m| = 1$ states of the H atom. The zero field manifolds are characterized by the principal quantum number $n$. Quasi-discrete states with lifetime $\tau > 10^{-6}$ s (solid line), field broadened states $5 \times 10^{-10} < \tau < 5 \times 10^{-6}$ (bold line), and field ionized states $\tau < 5 \times 10^{-10}$ (broken line). The saddle point limit $E_c = -2\sqrt{F}$ is shown by a heavy curve. Field broadened Stark states appear approximately only for $E > E_c$. (from ref. 3).
the $+z$ axis while states with $n_1 - n_2 = -n$ (extreme red-shifted states) are localized along the $-z$ axis. States with $n_1 - n_2 = 0$ are localized near the $z=0$ plane. The energy difference between nearest neighboring Stark states of the same $n$ with values of $m$ differing by $|\Delta m| = 1$ ($n_1 - n_2 = 1$) is $3nF/2$ and is equal to the classical precession frequency, $\omega_F$ of the major axis given by eq. 2.28 when the variables $a$ and $\omega$ are written in terms of $n$ ($a = n^2$, $\omega = 1/n^3$). The energy difference between neighboring Stark levels of the same manifold, i.e. states with the same $n$ and $m$, is $3nF$ and corresponds to the "precession" frequency of $L$ and $A$.

Now consider an alkali atom in a uniform electric field. The calculated energy levels of potassium Rydberg states near $n$~100 as a function of field strength are shown in fig. 2.11 ($m = 0$ states) and fig. 2.12 ($|m| = 1$ states). For penetrating orbits in weak fields, the large precession frequency of the major axis $\omega_L$ in the orbit plane due to the presence of the core means that the time average dipole moment in any direction vanishes. With no dipole moment there is no first order Stark effect. Thus states with large quantum defects will evolve according to the second order quadratic Stark effect in weak fields. For non penetrating orbits, $\omega_L$ is small and they will evolve much like hydrogenic orbits in a field. Note that, unlike hydrogen, the Stark states do not cross, i.e. the red and blue states from different manifolds couple ($n_1$ is no longer a good quantum number). This coupling can be pictured classically as blue-shifted orbit scattering off the core into a red-shifted orbit (or vice-versa). The size of the avoided crossings decrease rapidly as $|m|$ increases because the centrifugal potential, $L_z^2 / 2p^2 = m^2 / 2p^2$ acts to keep the electron away from the $z$ axis (and hence the core). For low $m$, $|m| << n$, the energy separation at avoided crossings between Stark states from neighboring $n$ manifolds scales approximately as $3/n^4$. Close comparison of figures 2.11 and 2.12 reveals that the $m = 0$ and $|m| = 1$ levels are not interleaved at they are in H.
Fig. 2.11. Potassium $|m| = 0$ Stark levels near $n=100$. 
Fig. 2.12. Potassium $|m_l| = 1$ Stark levels near $n = 100$. 
Finally, it is worthwhile to note that the classical equations of motion scale. Inspection of the field-free equations of motion for $H$ show that they remain unchanged if

$$\rho_0 = \frac{\rho}{n^2}, \quad p_0 = np, \quad t_0 = \frac{t}{n^2}, \quad E_0 = n^2 E, \quad L_0 = \frac{L}{n} \quad (2.31)$$

For motion in an electric field, the expressions in 2.31 remain valid with the addition of the scaled field strength,

$$F_0 = n^4 F \quad (2.32)$$

Consider the Hamiltonian of an electron in combined Coulomb and external fields

$$H = \frac{1}{2} \left[ \left( \frac{dp}{dt} \right)^2 \right] + \frac{L^2}{2\rho^2} + \frac{1}{r} - zF \quad (2.33)$$

substituting $t = t_0 / n^2$, $p = n^2 p_0$, $r = n^2 r_0$, $E = E_0 / n^2$, $L = nL_0$, $F = F_0 / n^4$ leaves the form of eq. 2.33, and hence the equations of motion, unchanged.

### 2.4 DC Field Ionization

From eq. 2.23, the effective potential for a hydrogen atom in a DC electric field is

$$V_{\text{eff}} = -\frac{1}{r} + Fz + \frac{m^2}{2\rho^2} \quad (2.34)$$

For $m = 0$ states, this potential has a saddle point on the $z$ axis at $z = -1 / \sqrt{F}$. The potential at the saddle point is $V_{sp} = -2\sqrt{F}$. Classically, for an electron to be bound, its
energy must lie below $V_{sp}$, therefore the highest electron energy possible is $E = -2\sqrt{F}$.

Thus for a given binding energy, the atom will ionize at the critical field

$$F_c = \frac{E^2}{4}$$  \hspace{1cm} (2.35)

For higher $m$ states, the centrifugal barrier raises the threshold field. The fractional increase in the field required for ionization compared to an $m = 0$ state of the same energy is

$$\frac{\Delta F}{F_c} = \frac{|m|\sqrt{|E|}}{\sqrt{2}}$$  \hspace{1cm} (2.36)

This simple classical model neglects quantum mechanical tunneling. However, for the red-shifted Stark states of H, the tunneling rate increases exponentially for field strengths near the classical ionization threshold, so that the ionization probability is essentially unity for fields that exceed the threshold. The energy of the extreme $m = 0$ red-shifted Stark state is approximately

$$E = -\frac{1}{2n} - \frac{3n^2F}{2}$$  \hspace{1cm} (2.37)

Substituting this energy into eq. 2.35 gives

$$F_c = \frac{1}{9n^4}$$  \hspace{1cm} (2.38)
For other Stark states of H, it is not possible to estimate simply the threshold field, but the less red-shifted, the higher the field required to ionize the atom. Blue and red $m = 0$ states of the same $n$ often have threshold fields differing by a factor of 2.

In alkali atoms red and blue states are coupled by the core interaction. Inspection of fig. 2.11 and fig. 2.12 shows that the energy levels undergo only a small net shift with increasing field. Thus substitution of $E = -1/2n^2$ in eq. 2.35 is more appropriate. In this case, the threshold field becomes

$$F_c = \frac{1}{16n^4}$$

(2.39)

For fields exceeding $F_c$, ionization proceeds by a process akin to autoionization.\textsuperscript{27}
Chapter 3

Experimental Apparatus

The apparatus used in this work is shown in figure 3.1. Potassium atoms contained in a collimated beam from an effusive source are photoexcited to selected Rydberg states by a frequency doubled tunable ring dye laser. Excitation occurs near the center of an interaction region defined by three pairs of planar copper electrodes which are independently biasable in order to minimize stray electric fields. The laser output is chopped into a train of pulses and measurements are conducted in pulsed mode. Following each laser pulse, the Rydberg atoms are exposed to one or more half-cycle pulses (HCPs), which are generated by applying voltage pulses to a small circular copper disc inset in the top electrode. The number and/or excited state distribution of the Rydberg atoms surviving the HCP(s) are determined by selective field ionization (SFI). For SFI, a voltage ramp is applied to the lower electrode. Electrons resulting from field ionization are accelerated to, and detected by, a particle multiplier. Because atoms in different Rydberg states ionize at different applied fields, measurements of the field ionization signal as function of time, provides a measure of the excited-state distribution of those atoms present at the time of application of the ramp. Measurements in which no HCPs are applied are interspersed at routine intervals during the data acquisition. The Rydberg atom survival probability is obtained by comparing the Rydberg atom signals observed with and without HCPs present.

3.1 Vacuum System

The vacuum system consists of two differentially pumped stainless steel chambers, the source chamber and the main chamber. The source chamber houses an oven in which potassium metal is heated to produce the effusive ground state beam and is pumped by a 4"
Fig. 3.1. Schematic diagram of the apparatus.
diffusion pump. It is separated from the oven chamber by a vacuum wall with a small (~1 mm) aperture that allows the potassium beam to enter the main chamber while keeping contamination to a minimum.

The main chamber houses the interaction region in which Rydberg atoms are created and then field ionized. It is pumped by one 6" diffusion pump. The laser enters and exits the chamber through quartz windows set at Brewster's angle to minimize scattering of the laser beam. The pressure in the main chamber is monitored by a Bayard-Alpert type ionization gauge and is typically ~1 x 10^{-7} torr.

3.2 Potassium Beam

To produce the ground state atomic beam, potassium metal in the form of one 5 gram ampoule is heated in a stainless steel oven which consists of an enclosed reservoir for potassium metal with a ~0.5 mm diameter beam exit hole. The oven is heated by resistance cartridge heaters controlled by microprocessor temperature controllers. The reservoir is normally heated to ~300 C, while the exit hole is maintained ~40 C hotter to prevent potassium from condensing and clogging it. The potassium beam effusing from the oven is collimated by a ~1 mm aperture before it enters the interaction region resulting in a beam divergence of ≤1 degree. The potassium beam density can be monitored by a hot wire surface ionization detector and is estimated to be ~10^9 cm^{-3} at the center of the interaction region. The beam contains the isotopes of potassium in approximately the natural abundance of 93% for ^{39}K and 7% for ^{41}K. The concentration of K_2 dimers in the beam is calculated to be ≤1% at the operating temperature of the oven.\(^{33}\)

3.3 Laser System

The wavelengths needed to excite very high-\(n\) potassium Rydberg atoms by single photon excitation are in the range ~2860 - 2856.35 Å. The light is produced by an
intracavity frequency doubled ring dye laser, a Coherent model CR-699-21 (equipped with a model 7500-06 doubling package) pumped by a Coherent Innova 400 Argon Ion laser. Briefly, ~9.7 W of 514.5 nm light is focused on a flat stream of dye positioned in a ring shaped resonator. The dye, Rhodamine 6G Chloride dissolved in ethylene glycol, has a continuous florescence spectrum that allows laser oscillation over a wide range of wavelengths (~610 - 570 nm). Three intra-cavity frequency selection elements limit the laser bandwidth and confine lasing to a selected cavity mode: a three plate birefringent filter with a passive bandwidth of 380 GHz, a thin etalon with 225 GHz free spectral range (FSR) and a thick etalon with 10 GHz FSR. The ring resonator configuration of the laser allows traveling waves to propagate in either direction. One direction is selected by an optical diode which consists of a glass element in a magnetic field and a polarization rotating element. Due to the Faraday effect, one direction of propagation suffers a net polarization rotation. The resulting losses at Brewster surfaces within the cavity are sufficient to insure unidirectional lasing. The circulating visible radiation passes through an intra-cavity non linear potassium dihydrogen phosphate (KDP) crystal that converts a small fraction of it into UV by second harmonic generation, producing ~2-5 mW output.

The laser frequency is actively stabilized by locking it to a temperature controlled Fabry-Perot etalon. Changes in the laser frequency away from the lock point are corrected by slightly changing the length of the cavity. Fast deviations are corrected by a piezoelectric translator (PZT) mounted mirror resulting in a frequency jitter of less than ~250 kHz. Long term drifts are corrected by rotating a vertex mounted galvo driven quartz plate about Brewster's angle. The laser can be scanned over a 30 GHz range by adjusting the lock point of the reference cavity.

Although the reference cavity is temperature stabilized, it still suffers from enough temperature drift to shift the transmission fringes (and hence the lock point) by ~40 MHz/hr in the fundamental, which is unacceptable for the present work. To minimize the long term
drift, the laser is locked to a frequency stabilized Helium-Neon laser using a second temperature controlled Fabry-Perot etalon. A fraction of the visible radiation emerging through the end mirror of the dye laser is superposed with the output of a polarization-balanced, frequency-stabilized helium-neon laser and directed through a sealed temperature-stabilized confocal Fabry-Perot etalon (FSR 750 MHz, Finesse ~125). The mirror spacing in the etalon is repetitively scanned at 50 Hz using a PZT, producing two series of sharp transmission peaks, one associated with each input wavelength. Changes in the separation between the first pair of neighboring peaks in the scan are monitored and used to generate an error signal that restores the dye laser to the desired frequency. Since this method depends only on the separation of the two peaks and not on their absolute positions, the lock point is insensitive to temperature changes. The frequency stability is limited by the HeNe to ~±1 MHz/8 hours in the fundamental (±2 MHz UV). By changing the lockpoint, the frequency can be scanned over a 500 MHz range and can be controlled externally using a DC voltage in the range -5 V to +5 V.

The laser wavelength is monitored using a scanning Michelson interferometer. The system counts the fringes of the unknown wavelength and compares this number to the fringe count of a reference laser, in this case a polarization balanced HeNe. The accuracy of the wavemeter is approximately ±1 GHz at the operating wavelength.

The continuous output of the dye laser is chopped into short pulses, typically of ~4 μs, using an acousto-optic modulator (AOM). The AOM consists of a PZT transducer mounted on high purity fused quartz. The transducer generates a high frequency RF acoustic traveling wave inside the quartz. The resulting periodic variation of the refractive index produces a diffraction grating which can deflect up to 90% of the light out of the zero order. To produce a pulse of light, the sound wave is pulsed to deflect the light into the first order, which is directed into the apparatus.
3.4 Interaction Region

The interaction region is located in the center of the main chamber and is defined by three pairs of planar copper electrodes, each $\sim 10 \text{ cm} \times 10 \text{ cm}$ (see fig. 3.1). Rydberg atoms are photoexcited near the center where the laser beam is focused ($\sim 100 \mu\text{m}$ horizontal beam waist, $\sim 200 \mu\text{m}$ vertical waist) onto the potassium beam. After photoexcitation, the Rydberg atoms are exposed to one or more HCPs created by applying voltage pulses to a circular copper disc 4 cm in diameter inset into the top plate. The HCP electrode is fed by semi-rigid 50 $\Omega$ coaxial cable (RG 402) through the vacuum wall. To minimize reflections, the HCP electrode is terminated by 50 $\Omega$ to ground. To eliminate radiofrequency (RF) pickup on the other electrodes, the HCP electrode is shielded, the top plate is hard-grounded to the apparatus, and RF-shunting 0.1 $\mu\text{F}$ capacitors are connected between the side plates and ground. Rydberg atoms surviving the HCP are field ionized in the electric field generated by a slow voltage ramp (slew rate $\sim 6 \text{ V \mu s}^{-1}$) applied to the bottom plate. The ramp is produced by a custom-built generator which can provide output pulses with amplitudes up to $\sim 40 \text{ V}$ with a DC baseline stable to $\sim 0.5 \text{ mV}$. Electrons resulting from field ionization are accelerated by the ramp and exit the interaction region through a $\sim 1 \text{ inch}$ diameter fine mesh-covered opening in the bottom plate. After exiting the interaction region, the electrons are accelerated to $\sim 100 \text{ eV}$ and detected by a Johnston Laboratory MM-1 electron multiplier.

Small patch electric fields exist on the interaction region electrode surfaces due mainly to potassium deposition (K metal has a work function of $\sim 2.3 \text{ eV}$, while Cu metal has a work function of $\sim 4.5 \text{ eV}$). These patch fields, along with the small DC offset of the SFI pulser, produce an electric field at the center of the interaction region of $\sim 2 \text{ mV cm}^{-1}$. Such fields can have a dramatic effect on photoexcitation. The use of large electrodes well separated from the central excitation volume minimizes electric field gradients due to these
patch fields so that they can be reduced to \( \leq 50 \) \( \mu \text{V cm}^{-1} \) by application of DC electrical potentials to the HCP electrode and side plates. These bias potentials are determined by a technique utilizing the Stark effect (see section 4.3). The potentials are precisely controlled using low-drift voltage references and stable operational amplifiers. Magnetic fields are reduced to \( \sim 20 \) mG by a \( \mu \)-metal shield that surrounds the interaction region (the electric field resulting from motional \( (\mathbf{v} \times \mathbf{B}) \) fields due to the residual magnetic field is \( \leq 12 \) \( \mu \text{V/cm} \)).

3.5 Half-Cycle Pulses

Two externally-triggered voltage pulsers can be used to generate HCPs. An Avtech model AVI - V pulse generator can provide output pulses with amplitudes up to \( \sim 40 \) V and widths adjustable from \( T_p \sim 2 \) to \( \sim 110 \) ns. The risetime of the pulses is fixed at \( \sim 1 \) ns and the maximum pulse repetition frequency (PRF) is 20 kHz. The other pulser, a Hewlett Packard HP8082A, can generate one or a sequence of identical pulses with amplitudes up to \( \sim 5 \) V and widths adjustable from \( T_p \sim 2 \) ns to \( \sim 5 \) ms. The pulse risetime is adjustable from \( \sim 1 \) ns to 5 ms and the maximum PRF is 250 MHz. To maintain constant pulse shapes, the amplitudes of the pulses are varied using broadband (DC - 2 GHz) attenuators connected in series with the pulse generators. The outputs of the pulse generators can be combined with a Mini-Circuits broadband (200 kHz - 2 GHz) power combiner. In order to supply a stable DC bias the HCP electrode, the pulses are passed through an Avtech AVX-TB bias tee (bandwidth: 100 kHz - 4 GHz) before being transported to the HCP electrode by rigid RG 402 coaxial cable.

The pulse shape and amplitude at the HCP electrode are directly measured using a Tektronics P6156 DC-3.5 GHz voltage probe and a Tektronics 7603 sampling oscilloscope equipped with an S-2 type sampling head (\( \leq 75 \) ps risetime). The applied pulses contain
Fourier components whose frequencies $\leq 350$ MHz are all much smaller than the characteristic frequencies associated with the cavity created by the interaction region electrodes (the lowest accessible mode in the present configuration is $\approx 2.1$ GHz). Full time-dependent electric field calculations show that under these conditions the electric field generated in the experimental volume by the pulse essentially maps the applied voltage and is very nearly equal to that expected for application of a DC potential of the same size$^{38}$. Spatial variations in the field produced by the HCP electrode, and uncertainties inherent in the measurement of the HCP amplitude, introduce a small uncertainty, $\approx \pm 10\%$, in the applied fields.

### 3.6 Data Acquisition System

Data is accumulated over many identical acquisition cycles under computer control. Figure 3.2 shows the general setup of the data acquisition system. The master pulse generator produces logic pulses to synchronize other electronics and timing devices at a repetition rate of $\approx 10$ kHz. Each pulse from the master pulse generator begins the timing sequence shown in fig. 3.3. One output pulse triggers the acousto-optic modulator to allow a laser pulse of $\approx 4$ $\mu$s duration to enter the apparatus and produce Rydberg atoms. Another pulse from the master pulser triggers a computer-controlled gate (CCG) which, when enabled by the computer, in turn triggers a SRS DG535 precision computer-controlled delay generator. The DG535 dual outputs trigger the HCP pulse generators to control the time separation between the two HCPs to better than 50 ps. A third pulse from the master pulser triggers a Evans 4145 programmable delay module. The Evans delay module triggers the SFI voltage ramp and simultaneously starts the time-to-amplitude converter (TAC) at a selected delay time, typically a few $\mu$s. Electrons resulting from field ionization are swept out of the interaction region by the voltage ramp and are detected by the MM-1 electron multiplier. Output pulses from the MM-1 are amplified and compared to
a preset threshold by a LeCroy MVL100 low level amplifier/comparator. The first output
pulse of the MVL100 is used to stop the TAC (the probability that a Rydberg atom is
produced in any one laser pulse is low, \( \leq 0.05 \)). The TAC produces an output pulse
whose height ranges between 0 and 10 V and is proportional to the time difference between
the start and stop pulses, i.e. to the time between the start of the voltage ramp and the time
the electron arrives at the detector. Because atoms in different Rydberg states ionize at
different applied fields, measurement of the field ionization signal as a function of electron
arrival time, i.e. of applied field, provides a measure of the excited-state distribution of
those atoms surviving the HCPs (see section 4.1). The TAC output amplitude is digitized
by a 12-bit analog-to-digital converter (ADC) and recorded by the computer. The computer
disables the CCG so that no HCPs are applied in alternate sets of experimental cycles to
monitor the rate of production of Rydberg atoms. The Rydberg atom survival probability
is obtained by comparing the Rydberg atom signals observed with and without HCPs
present.

The ADC and the digital lines that control the CCG and Evans delay module are located
on a National Instruments LAB-NB NuBus multifunction data acquisition board plugged
into an Apple MacIntosh Quadra 800. The LAB-NB also has two 12-bit digital-to-analog
converters (DACs) which can each produce analog voltages from -5 V to +5 V. These
analog voltages are used as control voltages to scan the laser frequency or the potential
difference across an interaction region electrode pair.

The SRS DG535 delay generator is interfaced to the computer a by a General Purpose
Instrument Bus (GPIB) \( \text{via} \) a GPIB controller, which is also NuBus board plugged into the
computer.
Fig. 3.2. Block diagram of the data acquisition system.
Fig. 3.3. Data acquisition timing sequence. The pulse amplitudes are not to scale. The pulses represented by broken lines are gated off in alternate sets of experimental cycles.
Chapter 4

Experimental Techniques

4.1 Selective Field Ionization (SFI)

As mentioned earlier in chapter 3, selective field ionization (SFI) is a technique that permits absolute detection of Rydberg atoms and can give information on the excited state distribution. In SFI, an electric field whose amplitude is steadily rising is applied to the Rydberg atom. Since atoms in different states ionize at different applied fields, the field ionization electron signal observed as a function of time, i.e., of applied field, provides a measure of the excited-state distribution of those atoms present at the time of application of the ramp.

The physics of ionization of non-hydrogenic atoms by ramped electric fields can be rather complicated and has been treated in detail elsewhere. Consider first field strengths less than the Stark crossing field. As the ramp is applied, a nondegenerate state, such as an np state, adiabatically evolves into a single Stark state (see figs. 2.11 and 2.12). A nlm state with a small quantum defect, however, is projected onto degenerate $n_{1}n_{2}m$ states, each of which then evolve adiabatically in the field. In both cases, when $F \geq 1/3n^5$, avoided crossings with Stark states of the same $m$ but adjacent $n$ are encountered. In the present work, the frequency separations between adjacent Stark states of $n \geq 400$ at the avoided crossings are much less than the rate at which the applied ramp rises. As a result, the avoided crossings are traversed diabatically. The Stark states essentially follow hydrogenic paths to ionization. As in hydrogen, ionization occurs over a range of field strengths beginning at $1/9n^4$. As the ramp rises, atoms with higher values of $n$ ionize before atoms with lower $n$ values. Electrons resulting from ionization of higher $n$ Rydberg atoms will arrive at the detector before those originating from ionization of
lower-$n$ atoms. Thus measurement of the time of arrival of the electrons resulting from field ionization can give information on the distribution of excited states present at the time of application of the ramp. It is important to note that free low-energy electrons present in the interaction region can also be accelerated by the ramp to the detector and contaminate the SFI spectrum.

Figure 4.1 shows SFI spectra obtained at $n\sim 388$ following laser excitation (a), and after application of a short $\sim 2$ ns ($T_p / T_n \sim .24$) HCP. In the absence of the HCP, the SFI spectrum consist a single narrow feature corresponding to ionization of atoms with $n\sim 388$. In fig. 4.1(b), the ramp is applied immediately after the HCP so that any free electrons produced by the HCP will be collected. The prominent peak at early arrival times corresponds to free electrons produced by the HCP that are swept to the detector at the beginning of the ramp. In fig 4.1(c), free electrons are allowed to drift out of the collection volume of the detector by delaying the onset of the ramp. The free electron peak has disappeared, however, signal still remains at earlier times. This signal is independent of the delay between the HCP and the ramp and corresponds to ionization of Rydberg atoms by lower ionizing fields, indicating that the HCP populates higher-$n$ states.

Figure 4.2 shows the ratio of the number of electrons detected with an HCP applied to atoms with $n\sim 388$ to the number detected without an HCP applied as a function of delay time between the HCP and the start of the SFI ramp. At early delay times all electrons are collected, hence the signal ratio is unity. After $\sim 5$ $\mu$s, the free electrons that were produced by the HCP have drifted out of the collection volume of the detector so the signal ratio falls to $\sim 0.5$ and remains constant. The constant value of this ratio is the probability that a Rydberg atom survives this HCP. The residence times for free electrons produced by a variety of HCPs were measured in this way and were found to always be $\leq 5$ $\mu$s. For all the data presented in this thesis, delay times of at least 6 $\mu$s were used.
Fig. 4.1. SFI profiles observed for (a) parent np atoms with n~388, and following application of a 2 ns, ~140 mV cm⁻¹ HCP for different delay times between the HCP and the start of the SFI ramp: (b) 0 μs delay; (c) (— — —) 6 μs delay, (— — —) 9 μs delay.
Fig. 4.2. Ratio of the detected electron signal observed with a \(-2\) ns, \(-140\) mVcm\(^{-1}\) HCP applied to atoms with \(n\sim388\) to that detected with no HCP applied as a function of the delay between the HCP and the beginning of the SFI ramp. The error bars are statistical.
4.2 High-\(n\) Spectroscopy

The Rydberg atom signal observed as the laser is scanned over a frequency interval corresponding to excitation of states with \(n\sim 450\) is shown in fig. 4.3. Note that there are actually two Rydberg series in the spectrum shifted by 461.70 MHz relative to each other. These two series result from transitions originating from the \(^{39}\text{K} 4s(F=1)\) and \(4s(F=2)\) ground-state hyperfine levels. The relative intensity of the two series is approximately proportional to \((2F+1)\), i.e. to the relative degeneracy of the two hyperfine ground states. The width of the lines, ~18 MHz, is due mostly to Doppler broadening resulting from the divergence (~1 degree) of the potassium beam. (Transit time broadening amounts to only ~6 MHz.) For higher \(n\), the lines overlap and Stark mixing induced by the residual field becomes important, resulting in the excitation of a narrow distribution of Stark states.

Because many atomic properties depend strongly on \(n\), it is important to know accurately which \(n\) the laser is tuned to. The energy levels of high-\(n\) potassium Rydberg atoms can be expressed as

\[
E(n, \ell) = -\frac{R}{[n - \delta(n, \ell)]^2}
\]

(4.1)

where \(R\) is the Rydberg constant and \(\delta(n, \ell)\) is the quantum defect, which in turn can be evaluated using a modified Rydberg-Ritz formula\(^3\)

\[
\delta(n, \ell) = a_0 + \frac{a_1}{(n - a_0)^2} + \frac{a_2}{(n - a_0)^4} + \frac{a_3}{(n - a_0)^6} + \ldots
\]

(4.2)

where \(a_0, a_1, a_2, a_3\ldots\) etc are the modified Rydberg-Ritz coefficients that have been determined empirically. Using the above formulae with the constants appropriate for potassium, the energy levels can be calculated to an accuracy of ~\(\pm 30\) MHz. The excitation wavelength is given by
Fig. 4.3. Rydberg atom excitation spectrum observed near \( n \sim 455 \).
Fig. 4.4. Rydberg atom excitation spectrum observed near \( n \sim 388 \).
\[ \frac{hc}{\lambda} = E(n, p) - E(4, s, F) \quad (4.3) \]

For low values of \( n \), the resolution of our wavemeter (±2 GHz) is finer than the \( n \rightarrow n+1 \) frequency separation so a direct comparison of the wavemeter reading to the calculated wavelength is sufficient to determine which Rydberg state is being excited by the laser. At high-\( n \), the wavemeter is not sufficiently accurate, instead the adjacent \( n \) separation along with relative placement of the \( 4s(F=1) \rightarrow np \) and \( 4s(F=2) \rightarrow np \) spectral features is used.

Figure 4.4 shows the Rydberg atom excitation spectrum near \( n \approx 388 \), a region where the two Rydberg series overlay each other. The highest peak, where the overlap is the best, corresponds to \( n=384 \) and \( n=390 \) (weighted average \( = 388 \)). Once calibrated, the laser frequency can then be moved by a known frequency offset to excite the selected higher lying Rydberg state(s). The signal between the peaks in fig. 4.4 results from excitation of Rydberg states of \(^{41}\text{K} \) along with \(^{39}\text{K} \) states made optically accessible by the presence of the small residual electric field. The typical Rydberg atom production rate at \( n \approx 388 \) is \( \sim 200 \) Hz with a laser output power of \( \sim 3 \) mW, a laser pulse width of \( \sim 4 \) µs, and a repetition rate of 10 kHz.

### 3.3 Control of Stray Electric Fields

The presence of an external electric field can have a dramatic effect on Rydberg atom excitation. Figure 4.5 shows the effect of a field of only a few hundred µV/cm on the production of Rydberg atoms with \( n \approx 270 \). The electric field causes Stark mixing of the \( np \) states with the neighboring \( n\ell \) manifold, allowing states in the Stark manifold to be excited optically. This Stark mixing means that the initial state excited by the laser is no longer a well defined p state and results a diffusion of the \( 4s \rightarrow np \) oscillator strength, causing a lower excitation probability per laser linewidth. A field strength of only \( \sim 100 \) µV/cm is enough to reduce the excitation probability at \( n \approx 400 \) by a half.\(^{40} \)
Fig. 4.5. Effect of an applied electric field on the excitation of potassium Rydberg states in the vicinity of $n-270$ with (a) $m = 0$ and (b) $|m| = 1$. 
In order to measure and reduce stray electric fields in the excitation volume, the following technique has been developed utilizing the quadratic Stark effect. The laser is detuned a few MHz to the red of a particular $4s \rightarrow np$ transition and the Rydberg atom production is recorded as a function of the bias applied between each opposing pair of electrodes in turn. The bias superposes a variable component of the electric field in the experimental region perpendicular to the plane of the biased electrodes. The dependence of Rydberg atom production on the applied field that results from biasing a particular pair of electrodes is shown in fig. 4.6 for excitation to states $n=150$ and $n=250$. Two separate peaks are evident that correspond to the applied fields at which the absolute magnitude of the total field in the experimental region Stark shifts the $np$ state into resonance with the (fixed) laser frequency. (The separation of the peaks is governed by the laser detuning and the size of the Stark effect, which depends strongly on $n$.) Thus, were no stray field component parallel to the axis of the applied field present, the observed peaks would be symmetrically positioned about zero applied field. This, however, is not the case, revealing a stray field component parallel to the applied field axis. The applied field required to cancel this stray field component corresponds to the midpoint between the peaks which is located by determining the value $E_0$ that minimizes the quantity

$$
\varepsilon(E_0) = \sum_n |S_{E_0+n\Delta E} - S_{E_0-n\Delta E}|,
$$

(4.4)

where $S_{E_0 \pm n\Delta E}$ are the Rydberg atom signals observed with the applied fields $E_0 \pm n\Delta E$, and the selected offsets $n\Delta E$ encompass the observed peaks. A well defined minimum is observed, allowing the midpoint between the peaks, $E_{om}$, to be accurately determined. From fig 4.6, it is apparent that $E_{om}$ can be determined, and thus each stray field component zeroed, to better than $\pm 30 \mu V/cm$ resulting in a total residual field of $\leq 50 \mu V/cm$. 
Fig. 4.6. Rydberg atom signal observed as a function of applied electric field for excitation of Stark states with $n=150$ and $n=250$. (b) Dependence of $\varepsilon(E_0)$ (see eq. 4.4) on the assumed value of $E_0$. The midpoint between the peaks is denoted by $E_{0m}$. 
The above procedure is actually slightly different for the "y" electrode pair (see apparatus diagram in fig. 3.1). The electric field produced by biasing this pair is parallel to the laser polarization therefore Rydberg states in the $m=0$ Stark manifold will be photoexcited. Figure 4.5 shows that in this case oscillator strength is rapidly transferred to the "s-like" Stark state at small applied field strengths. This state is instead used to zero the field as its energy also has a quadratic dependence on the applied electric field.
Chapter 5

Results and Discussion

5.1 Ionization by a single Half Cycle Pulse

The initial motivation for this work was the experiment of Jones et. al. in which ionization in the short pulse regime was investigated using freely propagating, fixed-duration ($T_p \sim 0.5$ ps) HCPs produced by illuminating photoconductive semiconductor switches with output pulses from a femtosecond laser system. Their measurements on sodium Rydberg atoms with $14 \leq n \leq 35$ suggest that in the range $0.1 \leq T_p / T_n \leq 1$ the threshold field for ionization varies approximately as $\sim 1/n^2$. Theoretical analyses reproduce this scaling, but detailed comparisons between experiment and theory are difficult because of uncertainties inherent in determining the absolute amplitude and shape of their HCPs. Unresolved discrepancies between the absolute threshold fields measured in their experiment and those predicted by theory have raised questions as to the validity of classical trajectory Monte Carlo (CTMC) method and of the classical-quantum correspondence for high-$n$ levels. Moreover, since most quantum calculations for ionization to date are performed for hydrogen rather than for alkali atoms, possible deviations due to core effects have to be considered.

In the present work, we have minimized uncertainties in the pulse height and shape by undertaking measurements at very-high-$n$, $n \geq 400$. For such $n$, the classical electron orbital period is quite long allowing ionization to be investigated, even in the short-pulse regime, by using nanosecond pulses that can be accurately characterized so that comparison can be made to CTMC theory on an absolute scale without any adjustable parameters. Fig. 5.1 shows the measured and calculated survival probabilities for potassium atoms with $n \sim 388$ and $n \sim 520$ as a function of pulse height for several different durations of the HCP.22
Fig. 5.1. Measured and calculated survival probabilities for atoms with (a) \( n \approx 388 \) and (b) \( n \approx 520 \) as a function of pulsed field amplitude for HCPs of \( \sim 2 \) ns (\( \bullet \)), \( \sim 5 \) ns (\( \circ \)), \( \sim 10 \) ns (\( \triangle \)), \( \sim 20 \) ns (\( \blacktriangle \)) and \( \sim 110 \) ns (\( \square \)) duration.
Fig. 5.2. HCP pulse shapes of (a) the shortest and (b) the longest pulses used.
Figure 5.2 shows the shapes of the shortest and longest pulses used. The calculation uses the actual measured HCP profile and incorporates the estimated initial state distribution after the laser excitation. Because of the presence of small stray fields, at \( n \approx 388 \) it is assumed that \( p \) states with a statistical distribution of \( m \) are formed. This corresponds in the CTMC method to a subset of a microcanonical ensemble with the classical angular momentum restricted to \( [\ell, \ell+1] \) with \( \ell = 1 \). For \( n \approx 520 \) the presence of the residual field causes states in adjacent Stark manifolds to overlap and a mixture of Stark states is assumed. Tests revealed, however, that the theoretical predictions are not particularly sensitive to the exact choice of parent state or \( m \) distribution. Each initial condition in phase space is propagated according to Hamilton's equation of motion taking into account the experimentally-determined time-dependence of the HCP field, and the final energy, \( E \), of the evolved electron is determined. True ionization corresponds to \( E > 0 \) while \( E_n < E < 0 \) corresponds to excitation to higher Rydberg states. The interaction between the electron and the \( K^+ \) core is represented by a model potential that yields accurate quantum defects and satisfies the correct boundary conditions at small and large distances. However, core effects are found to be negligible for the present high-\( n \) values.

The calculations indicate that as \( T_p/T_n \) changes from the adiabatic to the sudden limit impulsive energy transfer to the electron increases. To verify this experimentally, SFI spectra were recorded after application of a number of different HCPs to Rydberg atoms with \( n \approx 388 \) and the resulting data are presented in fig. 5.3. In each case, the amplitude of the HCP pulse was adjusted to achieve \( \approx 10\% \) ionization, thereby providing the best opportunity to observe possible energy transfer (i.e. excitation). In the absence of an applied pulse, a single relatively narrow SFI feature is observed that corresponds to ionization of parent atoms with a well-defined initial energy. The SFI profile is little changed following application of a HCP \( \approx 110 \) ns long demonstrating that in the long-pulse
Fig. 5.3. SFI profiles observed for (a) parent \( np \) atoms with \( n \sim 388 \), and following application of HCPs of (b) \( \sim 110 \) ns, (c) \( \sim 10 \) ns, and (d) \( \sim 2 \) ns duration.
regime \((T_p/T_n \sim 12)\) very little energy is transferred to the excited electron. In fact, highly excited states cannot exist in the presence of the HCP because the electron has enough time to escape the atom over the potential barrier. The situation changes dramatically, however, when \(T_p/T_n \leq 1\). The SFI profile measured following application of a HCP pulse \(~10\) ns long \((T_p/T_n \sim 1)\) is significantly broader than that for the parent atoms and extends towards lower ionizing fields pointing to significant population of higher-\(n\) states. The production of high-\(n\) states becomes even more pronounced as \(T_p\) is decreased further. Indeed, after application of a HCP \(~2\) ns duration \((T_p/T_n \sim 0.2)\) the peak SFI signal is observed at field strengths well below those characteristic of parent state ionization.

One consequence of impulsive excitation to \(n\) levels much higher than those initially prepared by the laser is that the measured ionization probability may be larger than the true ionization probability because small residual fields present after the HCP can ionize very-high-\(n\) Rydberg states. The importance of excitation to higher \(n\) states is illustrated in fig. 5.4 which shows the apparent survival probability for different scaled fields \(F_0\) and durations \(T_0 = T_p/T_n\) assuming cut-off quantum numbers \(n_c\) for field ionization of \(n_c = 800, 1200,\) and \(\infty\). Clearly, in the short pulse regime, the presence of residual fields sufficient to ionize very-high-\(n\) atoms can introduce a systematic error in measured threshold ionization fields, especially when \(T_p/T_n \ll 1\). This effect is included in the calculated survival probabilities shown in fig. 5.1.

The excellent agreement between theory and experiment demonstrates the validity of a classical description of ionization, i.e. the classical limit is reached for large \(n\). As already shown fig. 5.4, an immediate consequence is that the experimental data satisfy the classical scaling invariance. These invariances imply that the ionization probabilities for different quantum levels of hydrogenic atoms, field strengths and duration of the pulses are interrelated to each other. Deviation from classical scaling invariances is a signature of
Fig. 5.4. Calculated survival probabilities as a function of the scaled pulse field amplitude $F_0 = n^4 F$ (a.u.) for different $T_0 = T_p / T_n$ and varying cut-off: $n_c = 800$ (---); $n_c = 1200$ (-----); $n_c = \infty$ (----). Experimental data (□) included for comparison.
Fig. 5.5. Scaled field for 10% ionization as a function of the scaled pulse duration: CTMC results for inverse parabolic (——) and rectangular (---) pulses; quantum calculations for ionization of H(10d) (Δ) and H(5d) (▽) states with rectangular pulses; experimental data of Jones et al. (ref. 9) for Na(nd) atoms, multiplied by a factor of 2.5 (☐); present results for ionization of K atoms with \(n\approx388\) (●) and \(n\approx520\) (■).
non-classical dynamics.42 Plotted as a function of the scaled field strength \( F_0 = n^4 F \), the survival probabilities display a universal behavior governed only by the scaled duration \( T_0 = T_p / T_n \) of the pulse, even though the scaled angular momentum \( \ell_0 = \ell / n \) is not conserved. The monotonic dependence by the survival probability on \( F_0 \) indicates that semiclassical path interference effects are negligible. The latter become visible for lower \( n \) and polarized initial states.14,17,43 Since the "frequency" of oscillations associated with such interferences scale as \( -n \), they are averaged out as \( n \to \infty \).

Figure 5.5 compares data for 10% ionization thresholds obtained from the present data to the data of Jones et. al.9 and classical and quantum calculations8 in terms of \( T_0 \) and \( F_0 \). All calculations were performed for hydrogen. The two classical calculations presented are for different pulse shapes, a rectangular pulse and an inverse parabolic pulse, and show that the results are relatively insensitive to the shape of the pulse. The quantum calculations are for \( n=5 \) and \( n=10 \). All classical and quantum calculations as well as the present experimental data lie on a universal curve verifying the classical-quantal correspondence for ionization. As noted in fig. 5.5, the \( N(nd) \) data only lie on the universal curve if the field strength is scaled by a factor of 2.5. The \( 1 / n^2 \) scaling of the threshold field reported by Jones et. al. can be regarded as a tangent to the universal curve. Two limiting cases of this curve are of particular interest. In the limit of ultrashort pulses (\( T_0 \ll 1 \)) the threshold field varies as \( 1 / n \). In the limit of long pulses, the universal curve approaches the asymptote \( F_0 \approx 0.1 \), which is equivalent to a threshold ionization field of \( F \approx 0.1 n^{-4} \). The coefficient 0.1 depends on the substate populated and is close to the coefficient 1/9 for the classical threshold field for the extreme red-shifted Stark state.

5.2 Rydberg wavepackets created and probed by short HCPs

In recent years there has been increasing effort devoted to the study of non-stationary states formed from a coherent superposition of nearby high-\( n \) Rydberg states. Such
wavepackets are interesting because they frequently display novel dynamical behavior. Until recently, Rydberg wavepackets have been created by photoexcitation of ground-state atoms to Rydberg states (with \( n \leq 100 \)) using ultra-short laser pulses whose bandwidth exceeds the level spacing in the final Rydberg manifold.\(^{44-46}\) Since photon absorption occurs when the electron is close to the core ion, the wavepacket is initially strongly localized in the vicinity of the core. As time advances, the wavepacket expands and contracts radially very much like a classical particle in a Kepler orbit (only low-\( \ell \) states can be photoexcited). This behavior is monitored by photoionization using a second ultrafast probe pulse, thus the wavepacket can only be observed when it is near the core.

Here we discuss an alternate approach to the generation of Rydberg wavepackets: excitation from a single (stationary) initial Rydberg state, with principal quantum number \( n_f \), using a short HCP. A wavepacket produced by a HCP differs significantly from that generated by an ultrashort laser pulse because the integral of the applied electric field is finite. In the limit of very short HCPs, \((T_0 = T_p / T_n << 1)\), the HCP simply delivers an impulsive momentum transfer

\[
\Delta \tilde{p} = - \int \tilde{E}(t) dt \tag{5.1}
\]

to the excited electron, irregardless of its proximity to the core. As we have seen, such momentum transfer not only leads directly to excitation, but, for sufficiently strong pulses, can even induce ionization. In this experiment, very high-\( n \) Rydberg wavepackets with \( n \sim 417 \) are created by applying a HCP. The properties of the wavepacket are probed following a variable time delay using a second HCP which ionizes a fraction of the atoms.

Figure 5.6 shows the measured survival probability of parent \( K(n_f p) \) atoms with \( n_f \sim 417 \) as a function of the time delay between two HCPs of \( \sim 2 \) ns duration.\(^{23}\) (The error bars indicate only the statistical uncertainties and do not include possible systematic
Fig. 5.6. Rydberg atom survival probability (left scale) following application of two HCPs in (a) the same and (b) opposite senses to $K(n, p)$ atoms with $n_i = 417$ as a function of time delay. (●), experimental data; (——), results of CTMC calculations. Multiples of $T_{n_i}$ are marked by arrows. The insets show the pulse profiles. (right scale), time development of the scaled expectation value $\langle p_z \rangle / p_n = n_i \langle p_z \rangle$ following application of the first HCP.
errors associated with uncertainties in the applied field, which are \( \leq 10\% \).) The pulse sequences used are shown in the insets and results are included for the cases where the two pulses are in both the same and opposite senses. For the data obtained in fig 5.6 as well as in fig. 5.9 only one pulse generator, the AVI-V, was available. To produce the pulse sequences, the output of the generator was split into two pulses of approximately equal amplitude by a matched resistive power divider. One of the pulses was delayed using a length of RG 402 cable. The pulses were then recombined using a matched power combiner. This setup is shown in fig. 5.7a. The relative delay between the two pulses was limited to less than 25 ns in this setup. The pulse amplitudes were selected to achieve survival probabilities of order 0.6 and correspond to a scaled momentum transfer \( \Delta p_0 = \Delta p / p_{n_i} = n_i \Delta p = 0.53 \). A pronounced quasi-periodic dependence of the survival probability on delay time is observed that can be explained by considering the time evolution of the wavepacket created by the first HCP.

If the atom is initially in some stationary Rydberg state \( |\phi_i\rangle \), the electronic wave function immediately after application of the HCP may be written

\[
|\psi(t = 0)\rangle = |\phi_i^B\rangle = e^{i\Delta \tilde{p} \cdot \vec{r}} |\phi_i\rangle \tag{5.2}
\]

and corresponds to the initial state shifted in momentum space by \( \Delta \tilde{p} \). The corresponding expectation values of the energy and momentum are

\[
\langle E \rangle_{t=0} = \langle \phi_i^B | H_{at} | \phi_i^B \rangle = \langle \phi_i | H_{at} | \phi_i \rangle + \frac{(\Delta p)^2}{2} + \langle \phi_i | \tilde{p} \cdot \Delta \tilde{p} | \phi_i \rangle \tag{5.3}
\]

\[
\langle \tilde{p} \rangle_{t=0} = \langle \phi_i^B | \tilde{p} | \phi_i^B \rangle = \Delta \tilde{p} + \langle \phi_i | \tilde{p} | \phi_i \rangle \tag{5.4}
\]
Fig. 5.7. Setups used to produce a controlled relative delay between two HCPs.
where $H_{at}$ is the atomic Hamiltonian and $\vec{r}$ and $\vec{p}$ are the electron position and momentum operators, respectively. Note that $\langle \phi_i | \vec{p} | \phi_i \rangle = 0$ and, therefore, $\langle E \rangle_{t=0} = E_{n_i} + \frac{(\Delta p)^2}{2}$ where $E_{n_i}$ is the energy of the initial Rydberg state. Classically, the application of a HCP to an electron with momentum $\vec{p}$ and energy $E_{n_i}$ changes its energy to $E_{n_i} + \frac{(\Delta p)^2}{2} + \vec{p} \cdot \Delta \vec{p}$. Thus the classical average of $E$ over an ensemble of phase-space points representing the initial quantum state $|\phi_i\rangle$ agrees with the quantum mechanical result.

The final electronic wave function can be expanded as

$$|\psi(t)\rangle = \sum_n e^{iE_{n}t} \sum_{\ell} \langle n\ell m | \psi(0) | n\ell m \rangle$$  \hspace{1cm} (5.5)

and encompasses a broad distribution of angular momentum states, including high-$\ell$ states.

We choose a quantization $z$-axis in the direction of the HCP and, therefore, $m$ is a constant of motion. As will be shown, the HCP leads to population of a range of higher $n$ states centered around $n_f = \frac{1}{\sqrt{2\langle E \rangle_{t=0}}}$. In this case, as will be discussed, it is reasonable to expect that the quantum evolution of the final wavepacket (eq. 5.5) might approach the classical limit.

Figure 5.8 shows the excitation function (or energy distribution), calculated using CTMC techniques, associated with application of a HCP to hydrogen atoms in the $n_i = 417$, $\ell_i = 1$ state. The scaled momentum transfer is equal to that for the data in fig. 5.1, i.e., $\Delta p / p_{n_i} = 0.53$ and calculations are included for both an ultrashort pulse ($T_p / T_{n_i} = 0$) and a pulse of $\sim 2$ ns duration ($T_p / T_{n_i} = 0.18$) as used in the experiments. The energy axis is scaled to the energy $E_{n_i}$ of the initial state, $E_0 \equiv E / E_{n_i}$. The final state distribution is peaked about the expectation value given by eq. 5.3, which corresponds to $n_f \sim 493$, and has a "width" that encompasses a range of $n$ values $\Delta n$ of $\Delta n \sim 20$. For HCPs of finite duration, a small secondary peak is also evident in the final state distribution.
Fig. 5.8. Calculated final state energy distribution following application of a HCP to hydrogen atoms in the 417p state: ( - - - ), ultrashort HCP; ( — — — ), a pulse of 2 ns duration ($T_p / T_n = 0.18$). The scaled momentum transfer $\Delta p_0 = 0.53$. The energy axis is scaled to the energy of the initial state, i.e., $E_0 = E / |E_n|$. 
at energies corresponding to $n_f < n_i$, and the likelihood of direct ionization is somewhat decreased.

The time evolution of the wavepacket can be understood classically by considering the time development of the expectation value of the $z$ component, $p_z$, of momentum of the excited electron following HCP application. Initially the HCP imparts net momentum to the electron in the $-z$ direction, i.e., $\langle p_z \rangle < 0$. CTMC calculations show that after approximately one half the mean orbital period $T_{n_f}$ associated with the final state distribution, quasi-classical "orbital" motion of the electron leads to a peak in the $p_z$ distribution at positive $p_z$, i.e. $\langle p_z \rangle > 0$. As orbital motion continues, the distribution once more becomes strongly peaked at negative $p_z$. This cycle then repeats and, as illustrated in fig. 5.6, continued orbital motion causes $\langle p_z \rangle$ to oscillate between negative and positive values with period $T_{n_f}$. The amplitude of the oscillation decreases steadily with time, however, because a distribution of final states is excited that evolve differently in time leading to dephasing.

Consider now the effect of applying a second half-cycle probe pulse (again along the $z$ axis) to the wavepacket. If the impulse delivered by the probe pulse is in the same direction as the initial electron momentum, i.e., $\langle p_z \rangle$, the electron momentum (and energy) will be increased. This can lead to ionization and a low survival probability. If, however, the impulse and initial electron momentum are in opposite directions the final momentum (and energy) of the electron will be lower and the likelihood of survival higher. Thus, if the two pulses are both in the same sense (and impart a negative impulse), the survival probability will be smallest [largest] at delay times such that $\langle p_z \rangle < 0 [> 0]$. The reverse is true if the probe pulse is in the opposite sense to the initial HCP (see fig. 5.6b). The structure evident in fig. 5.6 therefore reflects directly the time development of the wavepacket, i.e., $\langle p_z \rangle$.

Survival probabilities determined using the CTMC method are included in fig. 5.6.
These calculations employ the experimentally measured pulse profiles and take into account the presence of small residual fields in the interaction region that ionize states with $n \geq 1200$.

Interestingly, survival probability calculations for hydrogen and potassium were found to be indistinguishable. This results because the electron in its initial state spends the bulk of its time well removed from the core ion and because the first HCP populates predominantly high-$\ell$ states. The CTMC calculations are in very good agreement with the experimental data without use of any adjustable parameters. Figure 5.9 illustrates, for parent $K(n,p)$ atoms with $n \approx 417$, the effect of applying sequential HCPs of different amplitudes. The pulse amplitudes, indicated in the insets, were again selected to obtain survival probabilities of $\sim 0.6$. The results of CTMC calculations are also included and are in very good agreement with the experimental data. As the amplitude of the first HCP increases the time period of the oscillation in the survival probability also increases. This results because larger initial HCP amplitudes populate higher lying states whose time evolution is slower.

The very good agreement between theory and experiment demonstrates that classical dynamics can reproduce the "quantum beats" observed in the data. On general grounds, one expects the quantum and the classical evolution to depart from each other at a characteristic "break" time $t_c \equiv 2\pi / \Delta E$, where $\Delta E$ is the smallest level spacing.\textsuperscript{47} For Rydberg states, $\Delta E = n^{-3}$ and $t_c$ corresponds to the classical Kepler orbital period $T_n = 2\pi n^3$. The results presented here show that the break time exceeds $T_n$: i.e., the classical evolution can mimic the quantum evolution beyond $T_n$. This remarkable extended classical-quantum correspondence can be traced to the particular properties of the Coulomb Kepler problem and of the HCP-generated wavepackets. The energy differences in the Rydberg series determining quantum beats are given to second order in $\delta n / \delta n_f$ by

$$E_{n_f+\delta n} - E_{n_f} \equiv \delta n \omega_{n_f} \left[ 1 - \frac{3}{2} \frac{\delta n}{n_f} + 2 \left( \frac{\delta n}{n_f} \right)^2 \right]$$

(5.6)
Fig. 5.9. Rydberg atom survival probability following application of two HCPs of different amplitudes to K(n_ip) atoms with n_i=417. (*) experimental data; (——), results of CTMC calculations. The pulse profiles are shown in the insets and the arrows mark T_{n_i}.
Fig. 5.10. Calculated short (a) and long (b) time development (expressed in units of $T_{n_f}$) of the scaled expectation value $\langle p_z \rangle / p_n = n_1 \langle p_z \rangle$ following application of a HCP to hydrogen atoms in the 100s state. The scaled momentum transfer $\Delta p / p_n = 0.53$. 
where \(|\delta_n| \leq \Delta n / 2\). To leading order, the spectrum compares locally to that of a harmonic quantum oscillator, with \(\omega_{nf} = 2\pi / T_{nf}\) being the \textit{classical} orbital frequency. For a harmonic oscillator, quantum and classical expectation values agree\(^{48}\) which explains the presence in the classical simulation of beats with the mean orbital period. The damping of the beats is caused by the "anharmonic" correction. Dephasing (by \(\pi\)) or damping occurs on a time

\[
t_D \equiv \frac{4n_f}{3(\Delta n)^2} T_{nf} \sim 2 T_{nf}
\]

in agreement with the observations. The fact that classical dynamics can accurately reproduce even the dephasing is a consequence of the fact that, because \(\Delta n\) is large, the approximation of a large but discrete set by a continuous distribution is valid. Classical dynamics will fail, however, at times approaching the revival time \(t_R\) of the wavepacket. Complete revival requires \(t_R \equiv n_f T_{nf} / 3\) which, for the values of \(n_f\) of interest here, is greater than one \(\mu s\).

Observation of revivals in this case thus requires the delay between the two HCPs to be of \(\mu s\) duration but with sub-nanosecond accuracy. A search for revivals was subsequently undertaken using the improved experimental setup shown in Fig. 5.7b). HCPs were applied to atoms with \(n_i \sim 388\). The first HCP amplitude was small so that only a relatively narrow range of \(n \sim 400\) were populated in order to observe many oscillations of the wavepacket and improve the prospects for observation of revival. Figure 5.11 shows the pulses used and the observed oscillations for delay times less than 100 ns. Measurements for delay times past 100 ns out to several \(\mu s\) however showed no indication of revival structure, although the overall survival probability rose significantly. The rise in the survival probability is related to the presence of the stray DC field in the interaction region.
Fig. 5.11. Measured Rydberg atom survival probability following application of two HCPs of different amplitudes to K(n_p) atoms with n_i~388. The pulse profiles are shown in the inset.
The HCP creates not only Rydberg wavepackets, but also Stark wavepackets which evolve on a much longer time scale. The evolution of Stark wavepackets will be discussed in more detail in the next section. The absence of revivals of the Rydberg wavepacket could be related to a loss of coherence induced by the stray field\(^{46}\) or by dephasing collisions with background gas. Revivals have been observed however, in HCP studies at \(n\approx25\).\(^{12}\)

### 5.3 Stark wavepackets generated by an electric field step

Quantum beats from a coherent superposition of Stark states with \(n\approx23\) have been observed previously using picosecond laser pulses\(^{49}\) and with \(n=2\) in beam-foil spectroscopy\(^{50}\). The present study using very-high-\(n\) atoms is unique both from an experimental and from a conceptual point of view. Classically, a simple quasiperiodic evolution is expected corresponding to the precession of the angular momentum and the Runge-Lenz vector of the electron in the electric field. However, it is not obvious \textit{a priori} that quantum mechanics will predict such simple behavior for a non-hydrogenic atom in DC fields that are sufficiently strong that many \(n\)-manifolds overlap resulting in a broad range of energy separations.

In this experiment, Stark wavepackets, i.e. coherent superpositions of Rydberg Stark states are produced by rapid application of a "DC" field to K(388p) Rydberg atoms whose amplitude is much greater than the Stark crossing field, \(1/3n^5=0.2\) mVcm\(^{-1}\). The time development of the wavepackets are examined using a half-cycle probe pulse of duration \(T_p\approx2.4\) ns. The "DC" field is a "rectangular" pulse of several microseconds duration with an adjustable risetime. Figure 5.12 shows the "DC" pulse shape for a risetime of 10 ns and an amplitude of \(\sim5\) mVcm\(^{-1}\). The field amplitude decreases by \(\sim10\%\) over a typical measurement period of 500 ns because the voltage pulse that produces the "DC" field is AC
Fig. 5.12. The ~5 mV/cm\(^{-1}\) "DC" pulse shape.
coupled to the HCP electrode through a bias T to ensure a stable DC baseline over the course of the measurement.

Data obtained at \( n \approx 388 \) with the "DC" pulse shown in fig. 5.12 are presented in fig. 5.13, which shows the survival probability as a function of the time delay between application of the "DC" and HCP pulses for different HCP amplitudes and polarities. (Classically, the DC field required to ionize Rydberg atoms with \( n \approx 388 \) is \( \approx 14 \) mVcm\(^{-1} \).) The error bars indicate the statistical uncertainties and do not include possible systematic errors associated with uncertainties in the applied field amplitudes, estimated to be \( \pm 10\% \).

Sizable periodic oscillations (quantum beats) in the survival probability are evident. The positions of the maxima and minima depend on the size of the HCP as does the overall survival probability. Figure 5.13 includes results obtained with a "DC" field of \( \approx 10 \) mVcm\(^{-1} \) (and 10 ns risetime) which demonstrate that the quantum beat frequency is proportional to the magnitude of the "DC" field.

Figure 5.13 also shows the results of classical trajectory Monte Carlo (CTMC) calculations that use the actual measured "DC" and half-cycle pulse profiles and that incorporate the estimated initial excited state distribution present immediately after laser excitation (\( p \) states with a statistical distribution of \( m \)). The interaction between the electron and \( K^+ \) core ion is represented by a model potential that yields accurate quantum defects and satisfies the correct boundary conditions at small and large distances. Even without recourse to any adjustable parameters, the general agreement between theory and experiment is good. The calculations reproduce well the observed beats and the small differences in magnitude and period can be attributed to the uncertainty inherent in determining the value of the "DC" and HCP fields. Classically, the time development of the survival probability is governed by two quite dissimilar frequencies: one corresponding to the classical electron orbital period in the atom (\( \omega_{orb} \approx n_i^{-3} \)), the other the classical precession of the electron orbit in the applied electric field \( F \). The frequency of precession
Fig. 5.13. Rydberg atom survival probability as a function of time delay between application of the "DC" and HCPs for "DC" fields with a 10 ns risetime and amplitude of a), b) 5 mVcm$^{-1}$ and c) 10 mVcm$^{-1}$. In a) the "DC" and HCP fields are in the same direction, in b), c) opposite direction. ●, ○, Δ—experimental data obtained with HCP amplitudes of ~80, ~170, and ~290 mVcm$^{-1}$, respectively; (-----), results of the CTMC calculations.
of the angular momentum and the Runge-Lenz vector is given in first-order hydrogenic Stark theory by $\omega_z = 3nF$. For $n \sim 388$ and $F = 5 (10) \text{ mV cm}^{-1}$, this corresponds to quantum beat periods $T_z \sim 134 (67) \text{ ns}$, which are close to the values measured experimentally. The experimental data contain only a hint of the high-frequency fluctuations present in the calculations, possibly as a result of small field inhomogeneities in the experimental region.

The periodic oscillations in the survival probability can be explained classically in terms of the time evolution of the $z$ component, $p_z$, of the momentum of the excited electron (the $z$ axis is taken to be parallel to the DC field). As shown in fig 2.6, the distribution of $p_z$ widens as the angular momentum increases. Thus as $\ell$ precesses, the $p_z$ distribution will widen and narrow. Figure 5.14 shows the calculated distribution of the scaled electron momentum, $np_z$, as a function of time for times before (indicated by negative times) and following the application of the "DC" pulse. Before application of the pulse, the distribution is that of a $p$ state and is sharply peaked at $p_z \sim 0$. When the pulse turns on, the peak moves to small negative values of $p_z$. As time advances, the distribution broadens. The peak moves toward more negative values and decreases in size before finally disappearing. A small peak then appears in the distribution at positive values of $p_z$ which grows and moves toward $p_z = 0$ as the distribution narrows. Ultimately the peak crosses to negative values of $p_z$, and the whole cycle repeats.

Consider now the effect of applying the half-cycle probe pulse to the evolving system. Since the HCP is short, it delivers an impulsive momentum transfer $\Delta p_z = -\int_{-\infty}^{\infty} F_z(t) dt$ to the excited electron where $F_z(t)$ is the electric field generated by the HCP. The resulting energy transfer is given by $\Delta E = \left( \Delta p_z \right)^2/2 + p_z \Delta p_z$. If $p_z \Delta p_z$, i.e. if the impulse delivered by the HCP is in the same direction as the initial $z$-component of electron momentum, $\Delta E > 0$ and this increase in electron energy can lead to ionization. The situation is more complex when $p_z \Delta p_z < 0$. If $|\Delta p_z|$ is small, the final energy of the
Fig. 5.14. Calculated time evolution of the distribution of the $z$ component, $p_z$, of electron momentum plotted as $np_z$. The contours denote 0.04, 0.08, 0.16 and 0.32 of the peak value. Regions above 0.64 of the peak value are shown in black. The vertical bars are discussed in the text.
electron will typically be lower. However, for sufficiently large $|\Delta p_z|$, $\Delta E$ becomes positive, i.e., the $(\Delta p_z)^2 / 2$ term is dominant; thus large HCPs can induce ionization even if $p_z \Delta p_z < 0$. Consider then application of a HCP for which, as in fig. 5.13a, $\Delta p_z < 0$. If the impulse is small, only atoms initially having large negative $p_z$ can be ionized. The survival probability should therefore be greatest at those times indicated by the unshaded bars in fig. 5.14 where the $p_z$ distribution has its smallest negative excursions. These times correspond well with the maxima in the upper data set in fig. 5.13a. In contrast, for large HCPs all but atoms with large initial positive $p_z$ will be ionized. The overall survival probability is therefore low, but should be greatest at those times indicated by the solid bars in fig. 5.14 where the $p_z$ distribution has its largest positive values. These times match well the maxima in the lower data set in fig. 5.13a. For intermediate HCP amplitudes, the cut off for ionization will be near $p_z \sim 0$. Atoms with $p_z \leq 0$ will be ionized and the survival probability should be greatest at those times indicated by the shaded bars in fig. 5.14 where the $p_z$ distribution peaks at positive $p_z$; these times correspond well with the maxima in the middle data set in fig. 5.13a. Similar arguments can be used to explain the data in fig. 5.13b, for which $\Delta p_z > 0$. For example, if a HCP of intermediate amplitude is employed, the survival probability should be smallest at times near those shown by the shaded bars in fig. 5.14, as is observed.

The effect of varying the risetime of the "DC" pulse is illustrated in fig. 5.15. Quantum beats are observed even when the risetime becomes greater than the final quantum beat period, i.e., when the bandwidth associated with the turn on of the "DC" pulse becomes less than the final spacing between adjacent Stark levels (of the same $n$). This is not unexpected, however, because the level separation depends on applied field and is much smaller at early times during the turn on of the "DC" field.

Quantum mechanically, if the risetime of the "DC" pulse is very short, the coherent superposition of Stark states can be written in the sudden approximation as
Fig. 5.15. Measured Rydberg atom survival probability as a function of time delay between the onset of the "DC" pulse and application of the HCP for a "DC" pulse amplitude of 10 mVcm\(^{-1}\) and risetimes of a) 10 and b) 200 ns.
\[ |\Psi(t)\rangle \equiv \sum_{\alpha} e^{-i\varepsilon_\alpha t} \langle \alpha|i\rangle |\alpha\rangle \]  \hspace{1cm} (5.8)

where \(\varepsilon_\alpha\) and \(|\alpha\rangle\) are the eigenenergies and eigenvectors in the DC field and \(|i\rangle = |n_i, \ell, m\rangle\) is the initial Rydberg state. However, only states with a narrow distribution of \(n\) values \((\Delta n \leq 4)\) centered at \(n \equiv n_i = 388\) contribute significantly to the summation in eq 5.8. Expressed in parabolic quantum numbers, the eigenenergies for hydrogen are given to first order by

\[ \varepsilon_\alpha = -\frac{1}{2n} + \frac{3}{2} F n (n_1 - n_2) \]  \hspace{1cm} (5.9)

The relevant energy differences governing the time development of the wavepacket are given therefore in terms of the classical frequencies \(\omega_{orb}\) and \(\omega_S\) approximately by

\[ \Delta \varepsilon \equiv \omega_{orb} \delta n + \omega_S k \quad ; \quad k = 1, 2, ..., (n_i - |m| - 1) \]  \hspace{1cm} (5.10)

The constant energy differences are reminiscent of a harmonic oscillator for which quantum and classical expectation values agree.

For potassium with the present \(n\) and the DC field strengths, eq. 5.9 breaks down because many Stark manifolds overlap and mixing occurs. (The Stark crossing field is \(~200 \mu \text{Vcm}^{-1}\).) To determine the quantum mechanical origin of a single dominant Stark frequency in the fully mixed regime, the weighted statistical spectrum of frequencies \((\varepsilon_\alpha - \varepsilon_\beta)\) near \(n \equiv 100\) was analyzed for a few thousand Stark levels and an applied field of 2 Vcm\(^{-1}\), sufficient to cause overlap of several adjacent \(n\)-manifolds. Motivated by eq. 5.7 the overlap factor with the initial state \(\langle \alpha|i\rangle \langle i|\beta\rangle\) was used as weight (only those
Fig. 5.16. Calculated weighted statistical spectrum of frequencies near $n \sim 100$ for (a) hydrogen and (b) potassium in an applied DC field of 2 Vcm$^{-1}$. 
Fig. 5.17. Measured Rydberg atom survival probability as a function of time delay between application of a $\sim 5 \text{ mVcm}^{-1}$ "DC" pulse and a $\sim 2 \text{ ns HCP}$. 

Stark states that have a significant overlap with the initial state should carry a sizable occupation amplitude). The resulting frequency spectrum for potassium is strongly peaked and, as shown in fig. 5.16, closely resembles that of hydrogen, i.e., the peaks are as given by eq 5.9. (These peaks would not be present had an unbiased distribution of nearest spacings been used.)

The dephasing of the Stark wavepacket is directly related to the width of the peak at $\Delta \epsilon = \omega_5 = 3nF$ in the frequency spectrum, which is somewhat larger for potassium than for hydrogen. Thus, quantum mechanics predicts that dephasing, i.e. damping, of the quantum beats will be more rapid for potassium. Classically, core effects are to be expected because, during each Stark period $T_5$, the electron angular momentum changes from $\ell = 1$ to $\ell = n - 1$ and back. The electron penetrates the core during every Stark period thereby introducing small deviations from hydrogenic behavior. However, even for potassium, the time scale for damping is long, extending over many Stark periods.

Figure 5.17 shows measured Stark beats for times extending to 1.5 $\mu$s. A voltage pulser with a stable baseline was used to generate a "DC" field of $\sim 5$ mVcm$^{-1}$, allowing the pulse to be DC coupled to the HCP electrode so the "DC" field did not droop. As evident from the figure, the oscillations damp little over the measurement period. The rise in the average survival probability is an experimental artifact. For times greater than 500 ns, the impressed DC voltage on the HCP pulser output causes the amplitude of the HCP probe pulse to decrease.

4.4 Ionization by a sequence of short HCPs

The impulsively driven hydrogenic Rydberg atom, i.e. a Rydberg atom in which the valence electron is subject to a series of instantaneous momentum transfers ("kicks"), has been the subject of a number of theoretical investigations. The model of the "kicked" Rydberg atom has been successful in describing many experimental results from ion-solid
collisions.\textsuperscript{51} If the orbital period of an excited state is much larger than a typical binary collision time inside the solid, the result of an elastic or an inelastic collision can be reduced to an impulsive momentum transfer. The impulsively driven Rydberg atom has been used as a model system for the study of quantum manifestations of classically chaotic dynamics.\textsuperscript{52,53} As the strength of the kicks is increased, chaotic orbits appear in the corresponding classical problem. An electron in a chaotic orbit can be thought of as undergoing a "random walk" in bound Coulomb state space. Studies of hydrogen Rydberg atoms in a monochromatic microwave field show that the measured threshold fields for ionization coincide with the onset of chaos in the corresponding classical problem. Ionization is a result of a random walk in bound Coulomb states space which finally reaches the continuum. Burgdörfer\textsuperscript{53} found that even though the classical system driven by δ-function impulses exhibits chaos, theory predicts that ionization by a few hundred impulses results not from a random walk in the space of bound states but rather as the result of a short, directed few-step excitation process, i.e. direct excitation occurs faster than chaotic diffusion, at least for the number of impulses studied. It is not clear, however, if this conclusion is altered for pulses of finite duration.

This work is the first experimental study of the impulsively driven Rydberg atom. A series of identical equally spaced HCPs of duration Δt=2 ns are applied to potassium Rydberg atoms with \( n=388 \) (\( T_p / T_n \approx 0.22 \)). Survival probabilities are measured as a function of pulse height \( F \) for different scaled frequencies, \( \omega_0 \), i.e. the ratio of the (angular) repetition frequency to the orbital frequency of the initial state \( \omega_n = 1 / n_i^3 \), in the range \( 0.1 \leq \omega_0 \leq 2.2 \) for the cases of 10 and 50 applied pulses.

Figure 5.18 shows an example of an experimental pulse train corresponding to a PRF of 100 MHz (\( \omega_0 \approx 1 \)). Careful measurements were made of the time dependence of the pulse trains that were used in the experiment. For PRFs greater than \( \approx 200 \) MHz, there is not enough time for one pulse to return to zero before the next pulse turns on. This results
Fig. 5.18. Measured waveform corresponding to 10 ~2 ns duration HCPs at a pulse repetition frequency of 100 MHz.
in a DC field of \( \sim 1 \) mVcm\(^{-1}\) over the duration of the pulse train. The AC coupling of the pulses to the HCP electrode caused a droop in the baseline of \( \sim 250 \) \( \mu \)Vcm\(^{-1}\) after 50 pulses. For low PRFs (PRF≤50 MHz) and 10 pulses, the field returned to the background value of \( \leq 50 \) \( \mu \)Vcm\(^{-1}\) between all the pulses. The presence of these DC fields must be taken into account in the analysis of the experimental results. As discussed in section 5.1, if there is significant excitation to higher lying states, the measured ionization probability may be larger than the true ionization probability. For example, a DC field of \( \sim 1 \) mVcm\(^{-1}\) ionizes atoms excited to values of \( n \geq 800 \).

Figures 5.19 and 5.20 show the measured survival probabilities following application of 10 and 50 pulses respectively as a function of pulse height for different PRFs. As one would expect, it takes less field to ionize in the case of 50 pulses as it does in 10. Although the absolute fields may be different, the dependence of the ionizing fields on the PRF is similar. For low frequencies, the curves are essentially independent of frequency. As the frequency increases, higher fields are required for ionization. In both cases the average energy imparted by the first kick is small. For example, an HCP of \( F \approx 46 \) mVcm\(^{-1}\) (the pulse height corresponding to 50% ionization for 10 HCPs at 10 MHz PRF) imparts momentum \( \Delta p \sim F / \Delta t \) (\( \Delta p_0 = n \Delta p = 0.28 \)) to the electron resulting in an average energy transfer of \( \Delta E = (\Delta p)^2 / 2 \) that populates a range of \( n \) centered on \( \bar{n} = 405 \). It is apparent then that ionization can only result from successive multi-step excitation that, on average, excites the electron to higher-lying levels until the continuum is reached.

Since excitation to higher-lying states must play an important role in the ionization process, SFI spectra were recorded to obtain information on the distribution of Rydberg states at the end of the pulse train. The SFI spectra corresponding to 10% ionization probability for different PRF are shown in figures 5.21 and 5.22 for 10 and 50 pulses respectively. The SFI spectra show similar behavior. In the absence of applied pulses, a single relatively narrow SFI feature is observed that corresponds to ionization of parent
Fig. 5.19. Measured survival probabilities for atoms with \( n \sim 388 \) as a function of pulsed field amplitude for 10 HCPs of 227 MHz (●), 200 MHz (○), 125 MHz (▲), 100 MHz (□), 83 MHz (■), 50 MHz (△), and 10 MHz (▽) pulse repetition frequency.
Fig. 5.20. Measured survival probabilities for atoms with $n\sim388$ as a function of pulsed field amplitude for 50 HCPs of 250 MHz (●), 166 MHz (○), 100 MHz (■), 50 MHz (□), and 20 MHz (▲) pulse repetition frequency.
Fig. 5.21. SFI profiles observed for (a) parent np atoms with $n \sim 388$, and following application of 10 HCPs of (b) 227 MHz, (c) 100 MHz, and (d) 10 MHz pulse repetition frequency.
Fig. 5.22. SFI profiles observed for (a) parent $np$ atoms with $n \sim 388$, and following application of 50 HCPs of (b) 250 MHz, (c) 100 MHz, and (d) 20 MHz pulse repetition frequency.
atoms with a well-defined initial energy. For low frequencies, the SFI profiles are broader than that of the parent atoms, extending to higher and lower field strengths, but are peaked at lower ionizing fields, indicating population of a few states with energies approximately equal to and lower than that of the parent state, but that most of the final population resides in states of much higher \( n \). As the frequency is increased, the peak in the SFI spectra shifts to higher ionizing fields. For \( \omega_0 \geq 2 \), the SFI profiles, though broad, are peaked at fields only slightly lower than those at which the parent level ionizes, corresponding to states only slightly higher in \( n \). It is important to note that the differences between the high and low frequency SFI spectra cannot be attributed to the higher DC field present at high PRF. Atoms affected by the DC field, i.e. atoms with \( n \geq 800 \), ionize over very narrow range only at the very beginning of the SFI ramp. Thus the SFI spectra suggest that the pulses are less efficient at high frequencies than at low frequencies in populating higher-\( n \) levels.

In order to obtain a partial understanding of the dynamics that lead to the observed SFI spectra and the frequency dependence of the critical fields for ionization, let us consider the creation and subsequent evolution of a Rydberg wavepacket during the first few pulses. Consider the case of 10 HCPs directed in the +z direction with \( F = 46 \text{ mV/cm}^{-1} \). The first pulse will transfer a range of energies (some energies even lower than the parent level, as shown in fig 5.8) whose mean is \( \Delta E = (\Delta p)^2 / 2 \) and create a wavepacket consisting of a range of \( n \) values centered on \( \bar{n}_1 \sim 405 \). As discussed in section 5.2, the \( z \) component, \( p_z \), of the momentum of the wavepacket will evolve in time such that average momentum \( \langle p_z \rangle \) oscillates between positive and negative values with period \( T_{\bar{n}_1} \).

For low PRF, the oscillation of \( \langle p_z \rangle \) damps before the next HCP is applied. Thus the second HCP also transfers mean energy \( \Delta E = (\Delta p)^2 / 2 \) to create a wavepacket with \( \bar{n}_2 \sim 424 \). Although the frequency \( \omega_{\bar{n}_2} \) of the oscillation of \( \langle p_z \rangle \) after the second HCP is slower, the oscillations damp faster so that again \( \langle p_z \rangle \sim 0 \) when the succeeding HCP is applied. In this way \( \langle p_z \rangle \) always returns to zero before the following HCP is applied.
Therefore after each HCP, the electron energy is on average $\Delta E = (\Delta p)^2 / 2$ higher than before. Note that the width of the bound-state energy distribution will also increase after subsequent kicks. After 10 such energy transfers, $\bar{n}_{10} \sim 1200$. An atom with $n \sim 1200$ will then subsequently be ionized by the stray DC field of $\sim 50 \mu$Vcm$^{-1}$.

For high PRFs, the oscillation of $\langle p_x \rangle$ will not have time to damp before the next HCP is applied. For example for $\omega_0 \sim 2$, the second HCP is applied at $\sim T_{\bar{n}} / 2$, i.e. at approximately one-half the oscillation period of the wavepacket created by the first HCP, for which at this time $\langle p_x \rangle > 0$ (see fig. 5.6). The resulting mean energy transfer is $\Delta E = (\Delta p)^2 / 2 - \langle p_x \rangle \Delta p$, thus $\bar{n}_2$ is closer to 388 (but still higher than 388 because of the $(\Delta p)^2 / 2$ term) than in the low PRF case. In this way, excitation to higher $\bar{n}$ is less efficient (at least during the first few pulses) than at low frequencies. Higher initial HCP field strengths are needed to excite the electron to significantly higher energies for which the HCPs are not "phase locked" to the evolution of the wavepacket. For a PRF of 100 MHz, $\omega_0 \sim 1$ and the second HCP will be applied approximately in phase with the time evolution of the wavepacket, i.e. at $\sim T_{\bar{n}}$, for which $\langle p_x \rangle < 0$. The resulting mean energy transfer is $\Delta E = (\Delta p)^2 / 2 + \langle p_x \rangle \Delta p$ and the electron is more likely to be excited to higher energies. Once significantly higher energies are reached, however, the pulse train is no longer in phase with the evolving wavepacket and further excitation may be frustrated.

Figure 5.23 displays the results of a CTMC calculation by Melles et. al.\textsuperscript{34} of the critical momentum transfer for 10% ionization probability of hydrogen Rydberg atoms subject to 100 identical equally spaced kicks as a function of $\omega_0$. The critical momentum transfer approaches a constant asymptotic limit at low frequencies and rises slightly for $\omega_0 \geq 1$. In the very high frequency limit, $\omega_0 >> 1$, much less momentum transfer is required for ionization because the momentum transfers "pileup". The time in between kicks is so small that the electron moves little during the entire pulse train. In this limit 100 kicks of magnitude $\Delta p$ become equivalent to a single kick of magnitude $100 \Delta p$. 
Fig. 5.23. Calculated scaled momentum transfer $\Delta p_0 = n_i \Delta p$ for which 10% ionization probability is obtained after 100 kicks for an electron in a Rydberg s state as a function of the scaled frequency $\omega_0 = n_i^2 \omega$ of the pulses.
Both theory and experiment show that stronger HCPs are need to ionize the atom when \( \omega_0 \geq 1 \), however the increase in HCP strength needed over that of the low frequency limit is much more pronounced in the experimental data. The theory predicts an increase of \( \sim 20\% \), while the data display and increase of \( \geq 50\% \). Based on previous observations, namely the good agreement between experiment CTMC calculations and the absence of revivals in the 2 HCP studies, it is unlikely that this discrepancy is due to quantal effects. It is likely that the presence of the stray DC field contributes to the discrepancy. The SFI obtained for low frequencies exhibited pronounced population of higher-\( n \) states that can be ionized by the stray field. For a given HCP field strength, this would increase the ionization probability over the true ionization probability (see figure 5.4). The finite width of the HCPs also may have an affect. As shown by fig. 5.8, application of a \( \sim 2 \) ns duration HCP tends to populate states with energies less that the initial level more than does an ultrashort HCP. For high PRFs, this could contribute to a population "trapped" near the parent level. Deexcitation to a level near the parent would be more efficient so the wavepacket would tend to stay phased with the pulse train longer. Clearly much more experimental and theoretical work must be done before a complete understanding of this system is reached.
Chapter 6

Conclusions

The present work demonstrates that very-high-\(n\) atoms provide an excellent vehicle with which to probe the response of atoms to rapidly varying, pulsed electric fields. For \(n \geq 400\), the classical electron orbital period is quite large allowing ionization and excitation to be investigated, even in the short pulse regime, using conventional nanosecond fast pulse generators whose output can be accurately characterized.

Studies of ionization of potassium Rydberg atoms with \(n\approx 388\) and \(n\approx 520\) by HCPs with durations that span the transition from the short-pulse to the long pulse regime show that at very-high-\(n\) the classical limit of ionization is reached and quantum corrections are negligible. CTMC theory is able to accurately predict absolute ionization and survival probabilities. The ionization probabilities satisfy the classical scaling invariance and display the predicted cross-over from a \(1/n^4\) to a \(1/n\) scaling in threshold fields as the pulse duration changes from the long-pulse to the sudden limit.

The evolution of wavepackets formed by application of HCP "pump" pulses to atoms with \(n\approx 400\) was investigated and the data compared with the results of CTMC calculations. The time-evolution of the wavepacket was examined by applying a second short probe HCP to ionize a fraction of the Rydberg atoms present after a variable time delay. The measured survival probabilities exhibit pronounced oscillations (quantum beats) that display an extended classical-quantum correspondence. The beats are well reproduced by the CTMC simulations without resort to any adjustable parameters. The CTMC calculations show that the observed quantum beats reflect the time-evolution of the distribution of the \(z\) component, \(p_z\), of the momentum of the excited electron. Application of a pump HCP whose duration, \(T_p\), is less than the classical orbital period of the initial
state, $T_n$, delivers an impulsive momentum transfer to the excited electron leading to coherent excitation of higher-lying Rydberg states. The resulting quantum beats reflect oscillations in the average $z$-component $\langle p_z \rangle$ of the electron and damp after only a few cycles because of the anharmonicity of the Coulomb potential. Application of a DC field step, i.e., a HCP with $T_p >> T_n$, leads to population of a coherent superposition of Stark states even for risetimes $T_r >> T_n$. The Stark beats reflect precession of angular momentum from $\ell-1$ to $\ell-n-1$ and the timescale for damping is long, extending over many Stark periods.

For the first time, excitation and ionization of Rydberg atoms by a sequence of short HCPs were studied experimentally. Application of a sequence of identical pulses results in a multi-step excitation followed by ionization. The ionization probability of atoms with $n_r \sim 388$ subject to a sequence of identical, equally-spaced 2 ns HCPs were measured as a function of HCP height and pulse repetition frequency, $\omega_p$. The experimental data show that the Rydberg atoms are considerably more stable against ionization when the frequency of the perturbation scaled to the orbital frequency of the initial state, $\omega_0 = n_r^3 \omega_p$, is $\omega_0 \geq 1$ than when $\omega_0 \ll 1$. This stability is not as pronounced in a CTMC calculation that uses $\delta$-function impulses. The discrepancy is possibly a result of stray electric fields in the apparatus that ionize high-lying Rydberg levels or a result of the finite width of the experimental pulses.

The present work has not exhausted all the experimental studies of interest that can be performed with HCPs and very-high-$n$ Rydberg atoms. The long timescale for damping of Stark quantum beats suggests that it might be possible to observe external damping induced by dephasing in collisions with a target gas. If so, such studies would provide a new tool for investigating elastic electron-molecule scattering at electron energies down to a few microelectronvolts. The dynamics of wavepackets created by HCPs in static electric and magnetic fields can be studied. For these systems, the underlying classical dynamics can
be chaotic. Thus such studies may provide an opportunity to study quantum manifestations of classically chaotic dynamics. Studies of ionization of a sequence of HCPs whose directions alternate may be used to test theories of intense field stabilization, which is observed when an intense laser pulse is applied to a ground state atom.
References


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