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Spectroscopy of Trapped $^{138}\text{Ba}^+$ Ions for Atomic Parity Violation and Optical Clocks

Dijck, Elwin

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**Spectroscopy of Trapped $^{138}\text{Ba}^+$ Ions
for Atomic Parity Violation
and Optical Clocks**

The cover depicts the electron shells of a Ba^+ ion on a pattern of Paul traps.

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Spectroscopy of Trapped $^{138}\text{Ba}^+$ Ions for Atomic Parity Violation and Optical Clocks

PhD Thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

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Friday 14 February 2020 at 16:15

by

Elwin Arthur Dijk

born on 23 April 1988
in Zuidhorn

Supervisor

Prof. K. H. K. J. Jungmann

Co-supervisor

Dr. L. Willmann

Assessment Committee

Prof. F. E. Maas

Prof. A. Mazumdar

Prof. M. H. M. Merk

Abstract

Trapped Ba^+ and Ra^+ ions offer the possibility to test the Standard Model by performing an independent high-precision determination of the Weinberg angle ($\sin^2 \theta_W$) at low momentum transfer. In such a measurement of atomic parity violation, table-top experiments complement studies of weak interaction effects at high energy in the search for new physics. The singly-charged heavy alkaline earth metal ions combine high intrinsic sensitivity with tractable atomic structure owing to their single valence electron. In addition, trapped Ba^+ or Ra^+ ions can serve as reference for an optical atomic clock that is sensitive to variation of the fine structure constant α . Determining $\sin^2 \theta_W$ requires localizing a single laser-cooled Ba^+ or Ra^+ ion in a standing-wave light field to a fraction of an optical wavelength. High-precision atomic theory calculations are crucial for interpreting the measurements and need experimental input.

We have performed preparatory spectroscopy measurements with trapped Ba^+ ions and investigated experimental techniques for characterizing ion traps. We have determined the optical transition frequencies between low-lying levels of $^{138}\text{Ba}^+$ with laser spectroscopy referenced to an optical frequency comb. Using a lineshape model based on eight-level optical Bloch equations, we determined the $6s\ ^2S_{1/2} - 5d\ ^2D_{3/2}$ transition frequency to be 146 114 384.0(0.1) MHz and the $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transition frequency to be 461 311 878.5(0.1) MHz, obtaining for the first time sub-MHz precision on these transitions.

Light shifts play an important role in the measurement of $\sin^2 \theta_W$ and offer a way to obtain information on (ratios of) atomic transition matrix elements. We have carried out an exploratory study of the light shift in $^{138}\text{Ba}^+$ caused by an off-resonant laser tuned close to the $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transition. The observed spectra are analyzed by combining the optical lineshapes with calculated light shifts of individual Zeeman components.

Atomic state lifetimes provide a benchmark for calculations of transition amplitudes. We have measured the lifetime of the long-lived $5d\ ^2D_{5/2}$ level in $^{138}\text{Ba}^+$ using a technique based on quantum jumps with one to four trapped ions. We have investigated known systematic effects in detail to evaluate their influence. We measured the lifetime of the $5d\ ^2D_{5/2}$ level to be 26.3(0.6) s, which is about 4σ shorter than previously published experimental results. This discrepancy needs to be clarified to ensure the reliability of atomic parity violation measurements ahead.

This work contributes toward a precise determination of $\sin^2 \theta_W$ with trapped Ba^+ or Ra^+ ions in search of physics beyond the Standard Model.

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Introduction

The unassumingly named *Standard Model of particle physics* (SM) [1] is the theory developed over the past fifty years that describes all known elementary particles and three out of four known fundamental forces (i.e. the electromagnetic, weak and strong interactions, leaving out gravity). It has been remarkably successful in predicting and explaining the dynamics of the subatomic world and, by extension, almost all of physics. The recent experimental discovery of the Higgs boson predicted by the SM further strengthened its validity.

Nevertheless, the Standard Model leaves several fundamental questions unanswered. How does gravity fit into the picture? An elegant description of gravity is provided by the theory of general relativity, which accurately describes the dynamics of planets, stars and other astronomical objects. Unifying these two theories has become something of a holy grail for physicists, but their mathematical frameworks are so different that to date all attempts at unification have been unsuccessful. Or why do particle masses and coupling constants have the particular values that are measured? What does the “dark matter” that astrophysicists observe only by its gravitational interaction consist of? What is the “dark energy” hypothesized to explain the observed accelerated expansion of the Universe which leaves just 5 % of the total energy and matter content of the Universe to the Standard Model? These and other open questions provide a strong motivation to search for new physics beyond the Standard Model.

Exploring the Limits of the Standard Model

We can follow several avenues in testing the limits of the Standard Model and looking to catch a glimpse of any physics beyond. The direct approach is to use a particle accelerator for smashing together particles at high energy and carefully studying the products of the collisions, where previously undiscovered particles may have (briefly) popped into existence. In this way the Higgs boson was discovered, along with many other subatomic particles over the years. However, this method has the downside of requiring gigantic experimental facilities like the Large Hadron Collider (LHC) near Geneva, a machine 27 kilometers in circumference, to reach the ever increasing energy needed for finding something new.

We instead follow a complementary route by using precision measurement techniques from atomic, molecular and optical (AMO) physics [2] and try to detect tiny signals

from new particles or forces at low energy. The field of AMO physics has seen major advances in recent decades, now providing fantastic control over matter and light with techniques such as laser cooling, ion trapping and precision spectroscopy. This enables us to probe the frontiers of particle physics even with experiments that still fit in a modestly-sized lab [3].

Particles or forces beyond the Standard Model can manifest themselves at low energies by slightly altering the structure of atoms from SM predictions. This occurs because the SM, a quantum field theory, describes any interaction between particles as being accompanied by a sea of virtual particles continuously appearing and annihilating. These virtual particles include both known and unknown types (if only rarely the latter). Thus undiscovered particles can have an effect on observable physical properties even without appearing directly [2,3]. Looking for tiny shifts in the energy levels of a suitable atom or molecule, we could find traces of new physics that otherwise only reveals itself at high energies.

Atomic Parity Violation

An important aspect of the Standard Model are its *symmetries*, that is, the notion that the laws of physics are unchanged under certain (mathematical) transformations. For instance, rotating the coordinate system in which a physical system is described does not affect its dynamics. In addition to such continuous transformations, three discrete transformations arise in relativistic quantum mechanics which may or may not alter the dynamics of a physical system: *charge conjugation* (C), replacing all particles with their corresponding antiparticles and vice versa, thereby changing the sign of all charges; *parity inversion* (P), inverting the three spatial coordinates, transforming a physical system into its mirror image; and *time reversal* (T), reversing the direction of the flow of time. These transformations can also be combined in any combination and each has the property that applying it twice gets us back to where we started.

Up until the late 1950s, it appeared that C, P and T were each perfectly unbroken symmetries of nature. Surprisingly, the weak interaction, which is responsible for certain radioactive decay processes, was discovered to violate all of these symmetries [4–6]. The Standard Model now describes how the weak interaction violates the individual C, P and T symmetries, whereas the other fundamental interactions do not. Only applying all three transformations simultaneously appears to be a symmetry of all physical phenomena (CPT symmetry) and so far no experimental results to the contrary are known, despite intensive searching [1]. The accuracy of a measurement is typically limited by the ability to isolate the phenomenon of interest from unwanted effects. The power of these discrete symmetries lies in their ability to tease out contributions by different fundamental interactions. In particular, finding a difference in dynamics when comparing a physical system with a mirrored configuration (P violation) is a

signature of the weak interaction.

In atomic physics the strictly parity-conserving electromagnetic interaction dominates: it is the force that binds electrons to a nucleus to form an atom. Like any bound system in quantum mechanics, the energy of an atom can only take certain discrete values. An electromagnetic field oscillating at the matching transition frequency (e.g. laser light) can induce transitions between these energy levels. However, from the way its wavefunction transforms under a P transformation, each energy level can be assigned even or odd parity and electromagnetic transitions between levels of equal parity are forbidden (to lowest order) as they would violate P symmetry. Via the short-ranged weak interaction, the electrons can also interact with the nucleons, since their wavefunctions overlap, and this slightly modifies the atomic structure. Because the weak interaction does not conserve parity symmetry, it does allow transitions between levels of equal parity. The field of physics studying weak interaction effects in atoms is known as *Atomic Parity Violation* (APV) or *Parity Non-Conservation* (PNC). Weak interaction effects at low energy are uniquely sensitive to some types of hypothetical particles beyond the SM, such as additional Z bosons that could be connected to dark matter [7, 8].

While the weak interaction effects in atoms were initially thought to be unmeasurably small [9] (the weak interaction is aptly named), it turns out that APV effects are strongly amplified in heavy elements with a large nucleus and fast-moving electrons [10]. So far, only one experiment [11] has reached sub-1 % precision in testing the Standard Model description of APV. This experiment used a beam of neutral cesium atoms (Cs, atomic number $Z = 55$). Interpreting the experimental results requires complex theoretical calculations and an intriguing 2.5σ deviation from the SM prediction found initially mostly disappeared after including previously neglected corrections in the calculations [12]. Our aim is to provide an independent, high precision verification of this result using a completely different experimental approach with trapped ions [13].

The atomic system for the APV measurement should be as heavy as possible to maximize the weak interaction effects and should have a simple electronic structure to make high precision calculations for interpreting the results possible. This suggests *heavy alkaline earth metal ions* as ideal candidates, as they have just a single valence electron making calculations tractable. Radium (Ra, $Z = 88$) is the heaviest available option where the APV effect is about a factor 50 larger than in cesium [14], but its lack of non-radioactive isotopes complicates experiments. In preparation of experiments with radium or as a candidate in its own right, the next lighter option is barium (Ba, $Z = 56$) where the APV effect is still about 2.5 times larger than in Cs [15].

Despite the enhancement, the transition amplitudes induced by the weak interaction in Ba^+ and Ra^+ ions are still many orders of magnitude too small to be measured directly. Like in the cesium experiment, this can be overcome by amplifying the effect through interference with a larger electromagnetic transition amplitude [13]. The planned experiment consists of trapping a single ion with an oscillating electric field

in vacuum, laser cooling it to remove excess motion and then measuring the shift in its transition frequencies when exposing it to a well-chosen configuration of two orthogonal laser light fields. When effectively mirroring the experimental configuration by adjusting the phase between the two light fields, the weak interaction contribution to the frequency shift changes sign, while the larger electromagnetic part does not. Many technical challenges remain and overcoming systematic effects will be daunting. The work presented in this thesis consists of several preparatory steps in developing the experimental setup and experimental procedures for an APV measurement with Ba^+ or Ra^+ ions.

Optical Atomic Clocks

The APV experiment centers around a single trapped alkaline earth metal ion. The electric trapping field barely interacts with the ion's internal degrees of freedom, the ion is essentially at rest due to laser cooling and ultra high vacuum eliminates collisions with background gas molecules, making the ion almost completely decoupled from the environment. These properties make these trapped ions also excellently suited as reference for an *atomic clock*. To describe how a trapped ion can function as a clock, we first take a few steps back.

A clock is any device that measures time by counting periods of some stable oscillator [16]. The accuracy of a clock is limited by its sensitivity to environmental perturbations. For example, the acclaimed invention of the marine chronometer by John Harrison in the 18th century was the first clock able to withstand the harsh conditions of ocean travel without losing more than one second per day and thereby enabled safe navigation through accurate determination of a ship's longitude¹ [17].

A good clock is thus one that is accurate and stable by using an oscillator with a precise, high frequency that is insensitive to disruptions. The physical object forming the oscillator can take many shapes and forms. In the early 20th century, clocks with mechanical oscillators and counting gears were superseded by those with electronic oscillators. A typical piezoelectric quartz resonator oscillates at a frequency of several thousand hertz, compared to a typical pendulum swinging only about once per second. While quartz clocks are perfectly adequate for everyday use, many technological application require accuracy beyond what quartz can provide and the quest for precise timekeeping continued.

After World War II and its surge in microwave electronics, the idea of using a transition in an atom as clock oscillator began to be explored. Unlike quartz crystals that need to be individually cut to the right shape, two atoms of the same

¹Whereas determining latitude (north-south position) at sea is fairly straightforward by observing the altitude of the North Star or the Sun, determining longitude (east-west position) is not as simple due to the rotation of the Earth. However, with an accurate clock, sailors can compare local solar time with the clock's reference time to find their longitude.

isotope are exactly alike. An atom forms an oscillator as it resonates when applying electromagnetic radiation at a frequency matching a transition between two of the atom's energy levels. The first atomic clocks started operating in the 1950s [18] and were based on a microwave transition in cesium atoms. Since then, the accuracy of this type of clock has continuously been improved and their importance was affirmed in 1967 when the second itself, the unit of time in the International System of Units (SI), was redefined as the duration of exactly 9 192 631 770 periods of the radiation corresponding to the transition between the hyperfine ground states of cesium-133 [19]. Cesium clocks have been the official timekeepers of the world ever since, but the development of more accurate clocks has not stopped.

Increasing the clock oscillator frequency further was hampered by the technical challenge of counting such fast oscillations. This was solved around the turn of the millennium by the invention of the *femtosecond frequency comb* [20], a special type of pulsed laser that maps optical frequencies (several hundred trillion hertz) into microwave frequencies (ten billion hertz) still measurable with fast electronics. In recent years, *optical atomic clocks* based on various elements have become the state of the art in time and frequency measurement [21]. Some now reach an accuracy of losing less than one second in the age of the Universe, outperforming the definition of the second itself. These optical clocks essentially consist of a laser (an optical oscillator) that is frequency-locked to a transition in a neutral atom or ion. A frequency comb is used for comparing the clock to any signal to be timed.

Atomic transitions suitable as clock reference should be narrow, that is, the natural uncertainty of their frequency, which is inversely proportional to the lifetime of the excited state, should be small. This brings us back to our trapped Ba^+ and Ra^+ ions, as these atomic system provide the appropriate type of atomic transitions with a competitive low sensitivity to perturbations by stray electric and magnetic fields [22,23]. In addition to the atomic structure, the performance of an atomic clock is influenced by the complexity of the experimental setup needed. Advantages of Ba^+ and Ra^+ ions include the availability of several isotopes with different nuclear spins to choose from and that laser light at the required wavelengths is conveniently available from cheap diode lasers.

Aside from technological applications such as global satellite navigation systems, atomic clocks have also opened up new possibilities for studying the Standard Model. The SM contains about two dozen parameters whose values are not predicted by the theory itself and are determined by measurement. These *fundamental constants of nature* set the masses of the elementary particles and the strengths of the interactions. As their name implies, the SM assumes these physical quantities to have the same value at all times at all places in the Universe [2]. Although this is known to be true at least approximately, the assumption remains subject to experimental verification. Theories beyond the SM that attempt to explain dark matter and dark energy often introduce new quantum fields permeating space that would cause the value of physical

constants to dynamically vary in time or space. The energy levels of atoms, and thus the frequencies of atomic clocks, depend on the values of the physical constants, in particular on the dimensionless *fine structure constant* α , which sets the relative strength of the electromagnetic interaction [2,21]. Investigating whether the frequencies of atomic clocks change over time is thus another way to search for physics beyond the Standard Model.

The only reliable way of detecting whether the oscillation frequency of a clock is changing is to compare it to another clock with a different dependence on the physical constants. Comparisons between optical atomic clocks over several years have so far not found any significant variation of α and set the most stringent limits on its current rate of change [2,3,21]. The sensitivity of the ticking rate of an atomic clock to a change in the value of α stems from a relativistic effect that is generally larger for heavy elements. A clock based on a single trapped Ba^+ or Ra^+ ion would have a large sensitivity to α -variation [24] and comparing them to clocks based on other elements would contribute toward answering whether the fundamental constants of physics are truly constant.

Thesis Outline

The main theme of this thesis is developing the experimental setup and techniques needed for performing the tests of Standard Model described above. All experimental parameters of the ion trapping setup need to be carefully controlled or at least sufficiently well understood to obtain the precision for either operating an optical clock or having a chance at measuring atomic parity violation with Ba^+ or Ra^+ ions.

We begin by diving a little deeper into the physics motivation of our research and presenting the relevant theory to describe the trapped ions and their interactions with laser light (Chapter 1). Then our single ion trapping setup is introduced (Chapter 2) together with techniques for characterizing and controlling various experimental parameters (Chapter 3). The following three chapters detail the results of precise laser spectroscopy of $^{138}\text{Ba}^+$ ions: an improved determination of the transition frequencies between low-lying energy levels (Chapter 4), a preliminary exploration of light shifts (Chapter 5) as a tool to advance the knowledge of this atomic system and a measurement of the lifetime of the $5d\ ^2D_{5/2}$ level (Chapter 6). Finally, a discussion and outlook on the further steps required is given. The work presented in this thesis forms several steps on the way toward using trapped heavy alkaline earth metal ions to perform a competitive measurement of atomic parity violation and to build an atomic clock.

Chapter 1

Physics Motivation and Theory

In this chapter we cover several topics connecting the physics motivation to the execution of the research. We first link electroweak theory to atomic parity violation: even though parity violation has been well-established in the Standard Model, it can still serve as a powerful tool in the search for new physics by getting rid of the usual electromagnetic background (Section 1.1). Secondly, we discuss optical atomic clocks with selected applications and an overview of factors determining clock performance (Section 1.2). Finally, we review some basic atomic theory on the interaction between atoms and light that we use throughout this thesis (Section 1.3).

1.1 Atomic Parity Violation

The central motivation for the research presented in this thesis is to measure atomic parity violation in the heavy alkaline earth metal ions Ba^+ and Ra^+ . Together with robust calculations of atomic structure to sub-% accuracy, such measurements would constitute a stringent test of the Standard Model and complement determinations of weak interaction effects at intermediate and high energy. Even though any new physics would only appear indirectly, low-energy tests are sensitive to effects that involve the violations of fundamental symmetries. In this section we briefly review how the weak interaction manifests in atoms, why heavy alkaline earth metal ions are suitable for such a measurement and what the requirements on the experimental setup are.

1.1.1 Running of the Weinberg angle

A major feat of the Standard Model [1] is the unified description of the weak and the electromagnetic interactions as two aspects of a single interaction with $\text{SU}(2) \times \text{U}(1)$ gauge symmetry. At low energy, this *electroweak interaction* splits into the two familiar interactions due to spontaneous symmetry breaking through interaction with the Higgs field. The spontaneous symmetry breaking mixes the four massless electroweak gauge bosons to produce the massive weak $W^\pm$, Z^0 bosons and the massless photon of electromagnetism. The mixing of the two neutral electroweak bosons to form the

Z boson and photon is described by an angle θ_W known as the *Weinberg angle* or *weak mixing angle*, related to the electroweak coupling constants and the W and Z boson masses (neglecting radiative corrections) as

$$\sin^2 \theta_W = \frac{g'^2}{g^2 + g'^2} = 1 - \frac{m_W^2}{m_Z^2}, \quad (1.1)$$

where g' and g are the U(1) (weak hypercharge) and SU(2) (weak isospin) gauge couplings, respectively [1, 7].

The Weinberg angle is a free parameter² of the Standard Model and its experimentally determined value at low energy is $\sin^2 \theta_W \approx 0.238$ [1] (generally $\sin^2 \theta_W$ is specified rather than the angle itself $|\theta_W| \approx 29^\circ$). Through renormalization, the values of the coupling constants of the SM depend on the energy scale of the physical process in which they are probed. As the Weinberg angle is related to the coupling constants, its value also varies with energy. This *running* of the Weinberg angle is a testable prediction of the Standard Model, even though its value at any particular point is not. Taking radiative corrections into account, the equality between the last two terms in Eq. (1.1) no longer holds and some care must be taken in defining the Weinberg angle. A handful of definitions differing by small factors are used, see Refs. 1, 7 for the various renormalization schemes.

The current best SM fit to the available experimental data for the Weinberg angle as function of momentum scale Q is shown in Fig. 1.1. Starting from low energy, $\sin^2 \theta_W(Q)$ decreases a modest 3 % primarily due to vacuum polarization effects until reaching the Z boson mass, where its value has been precisely determined by high energy accelerator experiments. At energies above the production threshold of the weak bosons, the dominant vacuum polarization changes and $\sin^2 \theta_W$ starts to increase again. All current experimental constraints are more or less consistent with the SM predicted behavior. Although the experiments at intermediate and low energy provide less stringent bounds on $\sin^2 \theta_W$, they have established its running and were crucial for the acceptance of the SU(2) $\times$ U(1) electroweak theory. We focus on the low energy domain where the Weinberg angle is determined from atomic parity violation; for details on the other experiments see Refs. 1, 7.

Low energy measurements of the Weinberg angle

Measurements of the Weinberg angle at low energy are complementary to Z pole measurements by probing different types of physics beyond the Standard Model. In general, low- Q experiments are slightly more sensitive to new tree level interactions, while collider experiments are more sensitive to new contributions to radiative corrections (expressed in terms of the Peskin–Takeuchi S, T parameters) [1, 7], also see Ref. 25.

²Note that various sets of quantities can be chosen as parameters of the Standard Model, e.g. specifying the weak boson masses or electroweak couplings would set the Weinberg angle implicitly.

Figure 1.1 Running of the (effective) Weinberg angle as function of momentum scale Q with experimental data. The SM prediction (continuous line) is fixed by the data at its minimum at the Z pole (two data points displaced for clarity). The Weinberg angle at the lowest experimentally accessible momentum transfer has been obtained from atomic parity violation in Cs atoms. An APV measurement in Ba^+ or Ra^+ ions has unique sensitivity to new physics such as an additional light weakly-coupled (dark) Z boson [8] modifying the Weinberg angle only at low energy (colored bands for two values of mass m_{Z_d}). The expected sensitivity of planned experiments is indicated at the corresponding momentum scale: this work, the MESA P2 experiment in Mainz [27], the MOLLER experiment [28] and the SoLID experiment at JLab [29]. Figure adapted from Ref. 8, updated with recent experimental results [1] and planned experiments.

Despite atomic transitions being on an energy scale of mere eV, the combination of zero electromagnetic and strong background with the high accuracy of atomic measurements and theory enables APV experiments to probe the TeV mass range for, e.g., extra Z bosons [2], competitive with direct searches. In addition, some recent models have proposed a relatively light additional Z boson that couples very weakly to SM particles and thereby has evaded detection in collider experiments [7, 8]. This ‘dark’ parity violation would modify $\sin^2 \theta_W$ only at small $Q^2 \ll m_{Z_d}^2$ (see Fig. 1.1), offering APV experiments unique discovery potential. Atomic systems have also been proposed as probe for other parity violating cosmic fields [26].

At present, the Weinberg angle at low energy is extracted solely from the measurement of atomic parity violation effects in cesium atoms. Interpreting the experimental result is far from trivial and requires precise calculation of atomic structure. While initially a 2.5σ deviation in $\sin^2 \theta_W$ from the SM was found [30], subsequent inclusion of corrections in the atomic calculations reduced the discrepancy over a period of more

than a decade to near perfect agreement with the SM [31], before the most recent calculation put the deviation again at 1.5σ [2, 12, 32]. While work on unraveling the theoretical aspects continues [33], a completely independent high precision verification of $\sin^2 \theta_W$ at low energy would clearly be valuable (see Fig. 1.1). Interpolating the estimates of Ref. 34, the typical momentum transfer for an APV measurement in barium would be nearly identical to Cs at $Q(\text{Ba}^+) \approx 2.5 \text{ MeV}/c$ and for radium slightly higher at $Q(\text{Ra}^+) \approx 10 \text{ MeV}/c$.

1.1.2 Weak neutral current in atoms

We now examine how $\sin^2 \theta_W$ can be determined from measurements in atomic systems. Atomic parity violation arises primarily from the exchange of a Z boson between an electron and a quark in the nucleus, producing nonzero parity-forbidden electric dipole ($E1$) transition amplitudes [32]. This is essentially a contact interaction due to the large Z boson mass, $\hbar/m_Z c \approx 10^{-3} \text{ fm}$.

The effective Hamiltonian describing Z boson exchange between electrons and nucleons is given by³ [2, 32] (also see Refs. 25, 35)

$$H_W = \frac{G_F}{\sqrt{2}} \sum_N (C_{1N} \bar{e} \gamma_\mu \gamma_5 e \bar{N} \gamma^\mu N + C_{2N} \bar{e} \gamma_\mu e \bar{N} \gamma^\mu \gamma_5 N), \quad (1.2)$$

where $G_F \approx (\hbar c)^3 \times 1.17 \times 10^{-5} \text{ GeV}^{-2}$ is the Fermi coupling constant, e is the electron field operator, the sum runs over all nucleon fields N and γ_μ are Dirac matrices. The constants differ between protons and neutrons due to their quark content and to lowest order in electroweak theory are given by

$$C_{1p} = \frac{1}{2}(1 - 4\sin^2 \theta_W) \quad C_{1n} = -\frac{1}{2} \quad C_{2p} = -C_{2n} = \frac{1}{2}g_A(1 - 4\sin^2 \theta_W) \quad (1.3)$$

with $g_A \approx 1.26$. The Hamiltonian (1.2) consists of two terms with different experimental signatures. The first is the interaction between the electron axial-vector current with the quark vector current: the nuclear spin independent (NSI) component; and the second term is the interaction between the electron vector current with the quark axial-vector current: the nuclear spin dependent (NSD) component. We focus on the NSI part, which dominates for heavy atoms because C_{1n} is the largest coefficient and the contributions of all nucleons add coherently here, unlike the paired-off nuclear spins for the NSD part [2, 32].

Approximating the nucleons as nonrelativistic, the nuclear spin independent part of the weak neutral current Hamiltonian simplifies to

$$H_{\text{APV}} = \frac{G_F}{2\sqrt{2}} Q_W \rho(r) \gamma_5, \quad (1.4)$$

³This is in natural units with $c = \hbar = \epsilon_0 = 1$. In the rest of this thesis, we work in SI units.

Figure 1.2 Illustration of faster than Z^3 dependence of the APV effect in alkaline earth metal ions: relativistic effects greatly enhance APV in the heaviest elements. Both curves have been normalized to Sr^+ . Figure adapted from Ref. 35.

where Q_W is the weak charge of the nucleus, defined below, $\rho(r)$ is the normalized nucleon density (assuming $\rho_p = \rho_n$) and γ_5 is the Dirac matrix associated with pseudoscalars. Analogous to electromagnetic charge, all weak interaction effects are proportional to Q_W , which is the sum of the weak charges of the Z protons and N neutrons in the nucleus, given by (at tree level)

$$Q_W(Z, N) = Z(1 - 4\sin^2 \theta_W) - N. \quad (1.5)$$

Equation (1.4) represents a pseudoscalar interaction, mixing opposite parity electronic states of equal total angular momentum ($\Delta J = 0$) [2, 32]. This means that the total atomic Hamiltonian no longer has a definite parity and the atomic energy eigenstates are no longer pure parity eigenstates (J is still a good quantum number). The mixing is largest for the penetrating s and p orbitals with significant overlap with the nucleus.

Enhancement in heavy elements

Weak interaction effects are strongly enhanced in heavy atoms [10]: the mixing between the $^2S_{1/2}$ ground state and a $^2P_{1/2}$ level of a single valence electron system scales as

$$\langle ns^2S_{1/2} | H_{APV} | np^2P_{1/2} \rangle \propto Q_W(Z, N) Z^2 K_{rel}(Z, r_n), \quad (1.6)$$

due to the electron momentum and density at the nucleus both growing with atomic number Z , and $K_{rel}(Z, r_n)$ is a relativistic factor that depends on Z and the nuclear radius r_n . Because the magnitude of the weak charge defined in Eq. (1.5) also scales linearly with the atomic number ($Z \approx N$), the scaling can be summarized as *faster than Z^3* (see Fig. 1.2).

Parity violating transition amplitudes

What observable effects are caused by the Z boson exchange? Although the APV effect is greatly enhanced in heavy elements, the matrix elements are still exceptionally small (in atomic units $G_F \approx 10^{-14}$ a.u.) and any new physics would constitute an even smaller correction on top. We can treat H_{APV} as a perturbation to the electromagnetic Hamiltonian and find that it leads to nonzero transition⁴ dipole moments between levels of equal parity.

To first order in perturbation theory [36], the ground state for a single valence electron system becomes

$$|\widetilde{ns^2S_{1/2}}\rangle = |ns^2S_{1/2}\rangle + \sum_{n'} \frac{\langle n'p^2P_{1/2} | H_{\text{APV}} | ns^2S_{1/2} \rangle}{E_{ns^2S_{1/2}} - E_{n'p^2P_{1/2}}} |n'p^2P_{1/2}\rangle \quad (1.7)$$

and similarly all other levels also acquire an admixture of opposite parity levels of the same angular momentum J . This induces a dipole transition amplitude between, for example, the perturbed $^2S_{1/2}$ ground state and lowest $^2D_{3/2}$ level in an alkaline earth metal ion (in the sum-over-states approach) [32]

$$\begin{aligned} E1_{\text{APV}} = \langle \widetilde{ns^2S_{1/2}} || D || (n-1)\widetilde{d^2D_{3/2}} \rangle = \\ \sum_{n'} \left[\frac{\langle ns^2S_{1/2} || D || n'p^2P_{1/2} \rangle \langle n'p^2P_{1/2} | H_{\text{APV}} | (n-1)d^2D_{3/2} \rangle}{E_{(n-1)d^2D_{3/2}} - E_{n'p^2P_{1/2}}} \right. \\ \left. + \frac{\langle ns^2S_{1/2} | H_{\text{APV}} | n'p^2P_{1/2} \rangle \langle n'p^2P_{1/2} || D || (n-1)d^2D_{3/2} \rangle}{E_{ns^2S_{1/2}} - E_{n'p^2P_{1/2}}} \right]. \quad (1.8) \end{aligned}$$

Using the definition of the weak Hamiltonian (1.4), this parity-violating transition amplitude can be written as

$$E1_{\text{APV}} = -\frac{Q_W}{N} k_{\text{APV}}, \quad (1.9)$$

where the weak charge Q_W provides the connection to $\sin^2 \theta_W$ as in Eq. (1.5), N is the number of neutrons and k_{APV} is an enhancement factor containing all the atomic physics. The goal of the APV experiment is encapsulated in Eq. (1.9): measure $E1_{\text{APV}}$, calculate k_{APV} and then extract the weak charge Q_W .

Recent calculations of k_{APV} for the heavy alkali metals and alkaline earth metal ions are given in Table 1.1. The results are given in the usual units of a pure imaginary dipole moment $E1_{\text{APV}}$ with a factor $-Q_W/N$ divided out ($Q_W \approx -N$). Note that

⁴The weak Hamiltonian of Eq. (1.4) is P-odd but T-even and thus cannot produce permanent electric dipole moments (EDMs), which violate both P and T symmetry. This is also why its matrix elements are pure imaginary [13].

Table 1.1 Calculations of the parity-violating transition amplitude $E1_{\text{APV}}$ in heavy alkaline metals and alkaline earth metal ions. The $S - S$ transitions are used with the Stark interference technique, while the $S - D$ transitions are suitable for the light shift technique and tend to have a larger APV effect. Per convention, quoted values are the $m = 1/2$ to $m' = 1/2$ transition amplitudes. Based on corrections and agreement with experiment, the uncertainty in values without explicit errors is a few percent.

Isotope	Z	Transition	$E1_{\text{APV}} (10^{-11} i e a_0 (-Q_W/N))$
^{85}Rb	37	$5s\ ^2S_{1/2} - 6s\ ^2S_{1/2}$	0.1333(7) [37]
^{133}Cs	55	$6s\ ^2S_{1/2} - 7s\ ^2S_{1/2}$	0.8977(40) [12]
^{223}Fr	87	$7s\ ^2S_{1/2} - 8s\ ^2S_{1/2}$	15.4 [14]
$^{87}\text{Sr}^+$	38	$5s\ ^2S_{1/2} - 4d\ ^2D_{3/2}$	0.302 [15]
$^{138}\text{Ba}^+$	56	$6s\ ^2S_{1/2} - 5d\ ^2D_{3/2}$	2.36 [14]
$^{226}\text{Ra}^+$	88	$7s\ ^2S_{1/2} - 6d\ ^2D_{3/2}$	46.6 [14]

in addition to the faster-than- Z^3 enhancement, the magnitude of k_{APV} is determined by atomic structure and choice of transition. In some elements with closely-spaced opposite-parity levels, the parity-violating effect is further enhanced (e.g. Yb, Dy), but these carry larger theoretical uncertainties.

Since even in the heaviest elements of Table 1.1 the parity-violating amplitude is smaller than a typical electromagnetic transition by about ten orders of magnitude, directly driving it is unfeasible. Nevertheless, the parity-violating amplitude can be observed in processes where the APV amplitude is made to interfere with another, larger, amplitude. In terms of Rabi frequencies, the observable quantity is then represented by the coherent sum

$$|\Omega|^2 = |\Omega_{\text{allowed}} + \Omega_{\text{APV}}|^2 \approx |\Omega_{\text{allowed}}|^2 + 2 \text{Re}(\Omega_{\text{allowed}} \Omega_{\text{APV}}^*), \quad (1.10)$$

where we neglect the doubly-suppressed term quadratic in Ω_{APV} . The last term is P-odd (pseudoscalar) and amplifies the APV effect by amplitude Ω_{allowed} , which is typically an $E2$ or $M1$ transition. The two terms can be distinguished by their differing behavior under a parity flip of the experimental setup, allowing Ω_{APV} to be obtained.

Beyond cesium

Parity-violating dipole amplitudes have been experimentally observed in multiple elements, starting forty years ago with optical rotation experiments in bismuth and thallium [2, 32]. An experimental precision of 1 % or better has since been reached for lead, thallium and cesium (0.35 %); however, the accuracy of the extracted $\sin^2 \theta_W$ value is in practice limited by the theoretical accuracy of k_{APV} from Eq. (1.9). Cesium is favored for high precision atomic calculations due to its simple electronic structure,

leading to the current most accurate low-energy test of the electroweak sector. Atomic parity violation was measured in Cs by interfering the parity-violating amplitude with a Stark-induced $E1$ amplitude in an atomic beam [11]. Two decades of theoretical efforts in interpreting the experimental measurement have changed the resulting agreement with the Standard Model significantly [2, 12, 30–32]. While the present 1.5σ deviation from the SM (Fig. 1.1) could widen or disappear with further refinement of the atomic theory, basing such an important result on just a single experiment is unsatisfactory.

Tractable atomic calculations are vital to improve on the Cs result and suggest the use of other monovalent systems (or possibly isotopic chains). Our approach is to follow the proposal by Fortson [13] to measure APV in light shifts in singly-ionized heavy alkaline earth metal ions (originally Ba^+ , but the technique can be extended to Ra^+ and other elements). Their similar electronic structure ensures that the same theoretical techniques as Cs can be applied and the relevant transitions have a significantly larger APV effect (see Table 1.1). Measuring APV in Ba^+ is also being investigated at the University of Washington in the group where the proposal originated [38–40]. Alternative approaches being pursued include neutral francium [41, 42] and isotopic ratios in dysprosium [43] and ytterbium [44].

Although the experimental technique is yet to be demonstrated, measuring APV with light shifts in trapped ions has several advantages, besides the enhanced effect magnitude: ion trapping is a mature technology offering precise control, it involves no atomic beam or vapor with a complicated thermal distribution (causing Doppler broadening), it offers long coherence times due to the absence of collisions and the small spatial extent of a laser-cooled trapped ion limits exposure to nonuniform (stray) fields. This allows systematic errors to be analyzed and controlled to high precision. The heaviest elements with the largest APV effect, Fr and Ra, are radioactive and thus require special experimental consideration, although several isotopes of Ra are sufficiently long-lived to be available from low-activity sources.

1.1.3 Atomic parity violation with light shifts in ions

Fortson’s proposal [13] consists of measuring the interference between parity-conserving and parity-violating transition amplitudes by observing the corresponding light shift (AC Stark shift) components. We only give a brief overview here, based on the considerable previous work [25, 38, 46–48]. A single alkaline earth metal ion is confined in an RF trap, laser-cooled and subjected to two standing-wave light fields resonant with the electric quadrupole transition from the $^2\text{S}_{1/2}$ ground state to the (long-lived) lowest $^2\text{D}_{3/2}$ level. The field geometry is chosen such that one light field couples to the electric quadrupole moment and the other to the parity-violating dipole moment, resulting in interference as described by Eq. (1.10) between these $E2$ and $E1_{\text{APV}}$ amplitudes in the shifts of $^2\text{S}_{1/2}$ sublevels. A magnetic field lifts the degeneracy of Zeeman sublevels. The on-resonant $E2$ light shift is equal for the two Zeeman sublevels

Figure 1.3 Sketch of the experimental method for measuring atomic parity violation using light shifts in a trapped ion [13]. Levels acquire a small admixture of opposite-parity levels through the weak interaction, leading to a parity-violating dipole transition amplitude $E1_{APV}$ between the $^2S_{1/2}$ ground state and the $^2D_{3/2}$ level. The ion is placed in two light fields resonant with this transition: light field $\mathcal{E}'$ couples to $E2$ and light field $\mathcal{E}''$ couples to $E1_{APV}$. A magnetic field splits the Zeeman sublevels of the ground state by $\Delta\nu_0$ of about 0.1 kHz to 1 kHz, light field $\mathcal{E}''$ induces a common shift of 10 kHz to 100 kHz and a cross term from both light fields produces the parity-violating vector shift $\Delta\nu_{APV}$ of about 1 Hz. Figure adapted from Ref. 45.

of the ground state, while the parity-violating interference term produces a vector light shift (shift $\propto m$), like an effective additional P-odd magnetic field (see Fig. 1.3). This shift in the ground-state Zeeman splitting (Larmor precession frequency) is determined by RF spectroscopy using electron shelving to detect successful spin flips. The P-odd reversal properties of the parity-violating observable allow it to be isolated from other effects.

Field geometry

The total electric field amplitude $\mathcal{E}$ at position $\mathbf{x} = (x, y, z)$ is given by the sum of field $\mathcal{E}'$ interacting with $E1_{APV}$ and field $\mathcal{E}''$ interacting with $E2$:

$$\mathcal{E}(\mathbf{x}) = \mathcal{E}'(\mathbf{x}) + \mathcal{E}''(\mathbf{x}) \quad (1.11)$$

Assuming the ion to be positioned at the coordinate origin, one suitable combination of spatial and temporal phases of the two light fields at identical frequencies is [13]

$$\mathcal{E}'(\mathbf{x}) = \hat{\mathbf{x}}\mathcal{E}'_0 \cos kz \quad \text{and} \quad \mathcal{E}''(\mathbf{x}) = i\hat{\mathbf{z}}\mathcal{E}''_0 \sin kx, \quad (1.12)$$

with wavenumber $k = 2\pi/\lambda$. The ion is positioned in an antinode of field $\mathcal{E}'$ (maximum amplitude, zero spatial gradient) to selectively drive the dipole interaction and in a node of field $\mathcal{E}''$ (zero amplitude, maximum gradient) to drive the quadrupole interaction (see Fig. 1.3). The ion must be localized to a fraction of optical wavelength λ to realize this geometry, this requires a single ion laser-cooled to the Lamb-Dicke regime (see Section 1.3.2). In addition, the 90° temporal phase shift between the fields is needed because the parity-violating $E1_{\text{APV}}$ amplitude is pure imaginary. Although the $E2$ light shift has both a scalar and vector component in general, the vector part vanishes in the chosen light field geometry.

The resulting light shifts for the two $^2S_{1/2}$ sublevels are [47]

$$\begin{aligned} \Delta\nu_{\text{APV}} &= \Delta\nu_{m=+1/2}^{E1} - \Delta\nu_{m=-1/2}^{E1} \approx \pm \frac{1}{2\sqrt{2}h} \mathcal{E}'_0 |\langle ^2S_{1/2} \| E1_{\text{APV}} \|^2 D_{3/2} \rangle| \\ \Delta\nu_{m=+1/2}^{E2} &= \Delta\nu_{m=-1/2}^{E2} \approx \frac{1}{4\sqrt{5}h} k\mathcal{E}''_0 |\langle ^2S_{1/2} \| E2 \|^2 D_{3/2} \rangle|. \end{aligned} \quad (1.13)$$

Even though the interference term in Eq. (1.10) depends on the strength of both fields, it is much smaller than the pure $E2$ term and thus the parity-violating component in the total shift is to first order independent of $\mathcal{E}''_0$. The sign of the vector light shift flips when changing the overall parity of the experiment, e.g. by inverting the temporal phase shift between $\mathcal{E}'$ and $\mathcal{E}''$.

Sensitivity and systematic effects

Aiming for an experimental precision of 0.1 % on the $E1_{\text{APV}}$ dipole amplitude (1.13), we now briefly discuss the sensitivity and systematics of an experiment of this type. With some generality, the figure-of-merit for an APV experiment is given by⁵ [13]

$$\frac{E1_{\text{APV}}}{\delta E1_{\text{APV}}} = \kappa \frac{E1_{\text{APV}}\mathcal{E}'_0}{\hbar} \eta \sqrt{NT_c\tau} \quad (1.14)$$

for electric field strength $\mathcal{E}'_0$, some experimental efficiency factor η , number of atoms observed N , coherence time T_c and total observation time τ . The constant of proportionality κ depends on the details of the experiment and the definition of $E1_{\text{APV}}$. From (1.13), in our case with $E1_{\text{APV}}$ representing the reduced matrix element, the constant is $\kappa = 1/2\sqrt{2}$.

⁵This formula sometimes appears (erroneously?) smaller by a factor 2π , e.g. in Refs. 38,49.

Table 1.2 Comparison of Ba^+ and Ra^+ concerning a single-ion APV experiment. The transition amplitudes are given as reduced matrix elements, see Eq. (1.40). The vector light shift is for the quoted electric field strength. The given total measurement time is for reaching 0.1 % statistical uncertainty from Eq. (1.14).

	$^{138}\text{Ba}^+$	$^{226}\text{Ra}^+$ ($t_{1/2} = 1600 \text{ yr}$)
Weak charge (SM) Q_W	-79.36 [1]	-133.8 [1]
$^2\text{S}_{1/2} - ^2\text{D}_{3/2}$ wavelength λ	2052 nm [50]	828 nm [51]
Dipole amplitude $E1_{\text{APV}}$	$5.6 \times 10^{-11} i e a_0$ [14]	$1.1 \times 10^{-9} i e a_0$ [14]
Quadrupole amplitude $E2$	$13.0 e a_0^2$ [52]	$14.6 e a_0^2$ [53]
$^2\text{D}_{3/2}$ natural lifetime $\tau_{\text{D}_{3/2}}$	80 s	0.6 s
Optimal field strength $\mathcal{E}'_0$	$15\,000 \text{ V/cm}$ [46]	7000 V/cm [46]
Vector light shift $\Delta\nu_{\text{APV}}$	0.38 Hz	3.4 Hz
Needed measurement time τ	15 h	25 h

Compared to other methods using atomic beams or vapors, the single-ion APV experiment has a considerably lower atomic density with $N = 1$ but makes up for it by the high field strength $\mathcal{E}'_0$ reached in a tightly focused laser beam and a superior coherence time $T_c \approx 2\tau_{\text{D}_{3/2}}$ due to the long $^2\text{D}_{3/2}$ lifetimes and absence of collisional relaxation. The efficiency factor depends on experimental details (shelving efficiency), we take a conservative $\eta \approx 0.2$. From (1.14) it appears that light field amplitude $\mathcal{E}'_0$ coupling to the APV dipole moment should be made as large as possible, but off-resonant dipole coupling decreases the effective lifetime of the $^2\text{D}_{3/2}$ and $^2\text{S}_{1/2}$ states (quenching) and leads to the maximum useful field strength being the point where the coherence time is reduced to $T_c = \tau_{\text{D}_{3/2}}$ [25, 46] (see Table 1.2). Beyond this field strength, further increases in signal size will be negated by a corresponding reduction in coherence time. To reach high signal-to-noise, it is also necessary to prevent broadening of the linewidth by other mechanisms. Magnetic field noise on the $\approx 100 \text{ nT}$ applied field and from external sources must be limited to $< \text{nT}$ using stable power supplies and magnetic shielding [25, 54]. Laser frequency and intensity noise should also be manageable as the spin-dependent splitting is to first order independent of the quadrupole field strength and laser frequency [25].

As discussed before, the parity-violating dipole amplitude is about 20 times larger in Ra^+ than in Ba^+ . Perhaps surprisingly, the total measurement time required for reaching the target statistical precision is actually lower for Ba^+ (Table 1.2). The shorter coherence time ($^2\text{D}_{3/2}$ level lifetime) in Ra^+ and stronger quenching by off-resonant coupling at the relevant wavelength reduces the signal-to-noise ratio that can be obtained. On the other hand, the larger magnitude of the parity-violating light shift in Ra^+ eases shielding and stability requirements somewhat.

The main challenge of the experiment will be to suppress systematic effects. In the

ideal field geometry of Eq. (1.12), only the $E1_{\text{APV}}$ coupling produces a vector light shift, but any experimental realization will have imperfections in e.g. beam alignment, laser polarization or ion position. Although no systematic effect stemming from the parity-conserving electromagnetic interaction will change sign when precisely inverting the temporal phase between $\mathcal{E}'$ and $\mathcal{E}''$, combinations of such imperfections can mimic the signal by causing additional vector shifts along the $\mathbf{B}$ -direction [25, 46, 47]. Especially any displacement of the ion from the antinode of the strong field $\mathcal{E}'$ could be troublesome, since this causes a finite spatial gradient leading to $M1$ and $E2$ couplings which are, respectively, up to 10^4 and 10^7 times stronger than the $E1_{\text{APV}}$ coupling at the same field strength [55]. Combined with a small degree of circular polarization of field $\mathcal{E}'$, this leads to an additional $E2$ – $E2$ and $M1$ – $E2$ cross term in Eq. (1.10) producing a vector shift in the $^2\text{S}_{1/2}$ level that is only present with both fields [46, 47]. It appears that these systematic effects are tractable if using a modest $\mathcal{E}_0'' \approx 100 \text{ V/cm}$ and keeping polarization errors and ion displacement each at the 10^{-3} level. Maintaining long-term stability of the ion position at nm level is likely to be one of the hardest requirements of the experiment.

Some degree of circular polarization in just one of the fields will also directly produce a vector light shift, from off-resonant $E1$ coupling (field $\mathcal{E}'$) or $E2$ coupling (field $\mathcal{E}''$). Since these effects do not depend on both fields, they can be distinguished from the genuine APV effect but can cause broadening of the transition through laser power fluctuations. Purposefully introducing a known degree of circular polarization and measuring the resulting shifts could be helpful in calibrating the electric field intensity at the ion position [46], needed to extract the $E1_{\text{APV}}$ matrix element (1.13).

Using isotopes with nonzero nuclear spin for the single-ion APV measurement has been suggested [46, 47]. Their hyperfine structure provides transitions where the relatively strong $E2$ coupling is absent, so that for a suitable field geometry the interference of Eq. (1.10) could be made between the $E1_{\text{APV}}$ and $M1$ amplitude. In this case the signal would be about a factor 10^3 larger compared to the systematic effects. Also the possibility of measuring ratios of the APV effect in a chain of isotopes [2, 7, 32, 56] exists for both Ba^+ and Ra^+ . This would cancel uncertainties in the atomic structure calculations for k_{APV} (1.9), although it has the problem of neutron skin: because the weak charge of neutrons is larger than that of protons (see Section 1.1.2), ratios of the parity-violating effect are sensitive to the relatively poorly known neutron distributions in the nucleus. The new physics probed by ratio measurements will also be different from determining Q_W for a single isotope.

Current status

As described in the preceding section, measuring atomic parity violation in a single trapped Ba^+ or Ra^+ ion is a challenging experiment that has so far not been completed anywhere. It requires developing an ion trap with crossed in-vacuum optical cavities to

create intense standing waves and control the ion position in these fields to a fraction of a wavelength. Preliminary experiments with RF spectroscopy on single trapped Ba^+ ions have been performed by the Washington group [38–40, 57]. In order to extract a competitive value of $\sin^2 \theta_W$ from atomic measurements, theoretical calculations of the parity-violating amplitudes in Ba^+ [14, 15, 58–61] and Ra^+ [14, 58, 61–63] still need to be improved by one order of magnitude. This appears to be feasible but requires experimental input to serve as benchmark for the calculations, e.g. measurements of hyperfine structure and isotope shifts which scrutinize wavefunction properties in the vicinity of the nucleus and measurements of level lifetimes which test long range parts. Previous efforts in our group [45, 49, 64] have supplemented the limited spectroscopic data available on (radioactive) Ra^+ and further experiments are planned at CERN [65]. Another group has very recently demonstrated trapping and laser cooling of small numbers of Ra^+ ions [66]. Stable Ba^+ has a closely similar atomic structure and can be exploited to prepare for experiments with Ra^+ . In this thesis we present spectroscopy data on Ba^+ and develop experimental techniques working toward a measurement of atomic parity violation in a single trapped heavy alkaline earth metal ion.

1.2 Optical Atomic Clocks

Heavy alkaline earth metal ions can also be utilized for single-ion optical atomic clocks. In this section we discuss how such frequency standards are constructed, their applications and the potential performance of clocks based on Ba^+ or Ra^+ . Optical atomic clocks are based on narrow optical transitions in ions or atoms, measuring time by the oscillating electric field of a laser locked to the atomic transition. Atoms are ideal references for time and frequency, because all atoms of a certain isotope are identical. The last in a long chain of developments in timekeeping [16], optical atomic clocks now offer better time resolution and stability than microwave clocks (see Fig. 1.4), reaching a fractional frequency uncertainty at the low 10^{-18} level. These clocks consist of a narrow-linewidth laser that is locked to an optical cavity for short-term ($\lesssim 10$ s) stability and referenced to an atomic transition for long-term accuracy [21]. The atomic reference generally consist either of neutral atoms trapped in an optical lattice or a single ion in a Paul trap, as in our case. It is important to carefully control electric fields, magnetic fields, temperature and the motion of the atoms, as these can affect the transition frequency. A femtosecond frequency comb [20] can be exploited to compare optical frequencies or obtain a microwave output.

1.2.1 Applications

Optical atomic clocks have (proposed) applications in many fields, including navigation and telecommunications, geodesy, radio astronomy, metrology and fundamental physics

Figure 1.4 Illustration of recent progress in the accuracy of clock systems, comparing cesium microwave standards to optical atomic clocks (colored bands to guide the eye). In the past decade, the (estimated) systematic uncertainties of optical clocks have fallen below the uncertainty of cesium clocks (and thus the definition of the SI second itself [19]). Adapted from similar figures in e.g. Ref. 2.

research [21]. One intriguing possibility is relativistic geodesy [67]: the noticeable effect of the gravitational potential on clocks operating at 10^{-18} fractional frequency uncertainty can be used to study the shape and geology of the Earth. Optical clocks are also being considered for a potential future redefinition of the SI second [68], which has been based on microwave cesium clocks since 1967 [19].

The application that we explore in a little more depth is the search for variation of fundamental constants. Somewhat of an oxymoron, many theories beyond the Standard Model predict that the quantities considered constants in the SM are actually dynamical fields that can vary in time and space [2, 3, 21]. This would also affect the transition frequencies of atomic clocks, as these are determined by the properties and interactions of the particles constituting the atoms. Only variation of dimensionless constants is physically meaningful since variation of dimensional constants is indistinguishable from a mere change of units⁶. The three fundamental parameters relevant to clocks are the fine structure constant α , the proton-to-electron mass ratio $\mu = m_p/m_e$ and the light quark mass to QCD scale ratio $X_q = m_q/\Lambda_{\text{QCD}}$. Changes in clock frequency are detected by comparing one clock to another that is based on a different atomic reference with a different dependence on the fundamental parameters (after accounting for other shifts). We focus on variation of α here, since the other two parameters only

⁶See e.g. Ref. 69 for an interesting discussion.

Table 1.3 Sensitivity coefficient K of clock transition frequencies to temporal variation of the fine structure constant α defined in (1.15) (not isotope dependent).

Species	Z	Clock transition	ν_0 (THz)	K [24]
Al ⁺	13	$3s^2\ ^1S_0 - 3s3p\ ^3P_0$	1121.0	0.008
Sr	38	$5s^2\ ^1S_0 - 5s5p\ ^3P_0$	429.2	0.06
Cs	55	$6s^2\ S_{1/2}$ hyperfine ⁷	(microwave)	2.83
Ba ⁺	56	$6s^2\ S_{1/2} - 5d\ ^2D_{3/2}$	146.1	2.50
		$6s^2\ S_{1/2} - 5d\ ^2D_{5/2}$	170.1	2.44
Yb ⁺	70	$4f^{14}6s^2\ S_{1/2} - 4f^{14}5d\ ^2D_{3/2}$	688.4	1.00
		$4f^{14}6s^2\ S_{1/2} - 4f^{13}6s^2\ ^2F_{7/2}$	642.1	−5.95
Hg ⁺	80	$5d^{10}6s^2\ S_{1/2} - 5d^96s^2\ ^2D_{5/2}$	1064.7	−2.94
Ra ⁺	88	$7s^2\ S_{1/2} - 6d\ ^2D_{3/2}$	362.3	3.00
		$7s^2\ S_{1/2} - 6d\ ^2D_{5/2}$	412.0	2.77

affect hyperfine transition frequencies (e.g. the cesium clock frequency) [2, 70].

By looking at present-day variation with extraordinary sensitivity, clock comparisons are complementary to other searches for temporal or spatial variation of the fine structure constant α , such as quasar absorption spectra [71] or the Oklo natural nuclear reactor [72]. Electronic transition frequencies depend on α through a relativistic correction that scales with $(Z\alpha)^2$, so transitions in heavy elements are generally more sensitive. Defining the relative transition drift rate for $\dot{\alpha} = d\alpha/dt$ as [24]

$$\left. \frac{\dot{\nu}}{\nu_0} \right|_{\alpha_0} = K \frac{\dot{\alpha}}{\alpha}, \quad (1.15)$$

the calculated enhancement factor K for selected clock species is tabulated in Table 1.3. The current most accurate limit from a clock comparison was set by comparing an Al⁺ clock (largely insensitive to $\dot{\alpha}$) to a Hg⁺ clock (highly sensitive to $\dot{\alpha}$) [73], finding $\dot{\alpha}/\alpha = -1.6(2.3) \times 10^{-17} \text{ yr}^{-1}$. Combined with comparisons with cesium clocks, variations in α , μ and X_q can be disentangled [74]. Table 1.3 shows that optical clocks based on Ba⁺ and Ra⁺ would be of interest to searches for variation of α due to their similarly large sensitivity of opposite sign compared to Hg⁺.

Optical fiber networks

The various technological and scientific applications of optical atomic clocks often require disseminating their frequency signal or comparing clocks at different locations.

⁷Hyperfine transition frequencies contain a factor α^2 in addition to the relativistic correction [24]; quoted is the total sensitivity in a clock comparison with an electronic transition frequency.

Optical clocks tend to involve large and cumbersome experimental setups that are not easily transported (although compact mobile optical clocks are also being developed [75]). The solution is to optically transfer frequency signals over (existing) optical fiber connections [76]. On links with phase-coherent amplification, 10^{-20} fractional frequency uncertainty has been demonstrated, so fiber links do not limit the clock signal uncertainty. Efforts are underway to establish a network of fiber connection between European research institutes, including preliminary work on a 298 km link in the Netherlands between Amsterdam and Groningen [77].

1.2.2 Clock performance

To assess the suitability of Ba^+ and Ra^+ ions for an atomic clock, we discuss some aspects of what makes for a good clock. Ba^+ ions have been considered for atomic clocks already since the 1980s [22, 78–81]. A design for a Ba^+ clock setup appears in Ref. 47. The suitability of Ra^+ ions for a clock has been explored previously in Ref. 23. We examine and summarize the main findings here.

The performance of frequency standards is typically characterized by two quantities: statistical instability and systematic uncertainty, also termed *precision* and *accuracy*, respectively. The (in)stability describes statistical fluctuations of the output frequency, known as type A uncertainty (symbol u_A), which is improved with longer averaging times. The systematic uncertainty quantifies the uncertainty in the deviation of the output frequency from the unperturbed atomic reference frequency ν_0 , known as type B uncertainty (u_B). The latter is more difficult to determine since it is not statistical in nature and thus generally estimated by enumerating all known effects that shift the observed frequency. A good clock needs to perform well on both counts: low systematic uncertainty and high stability to reach this uncertainty in a reasonable amount of time. The most advanced optical clocks now have systematic uncertainties better than cesium microwave clocks (see Fig. 1.4), but their absolute center frequencies cannot be determined to this level until a redefinition of the SI second. The clocks with the lowest published systematic uncertainties currently are an Yb lattice clock [82] ($u_B = 1.4 \times 10^{-18}$) and an Al^+ ion quantum logic clock [83] ($u_B = 9.4 \times 10^{-19}$).

Stability

The fractional frequency instability $\delta\nu/\nu$ of an atomic clock is equivalent to the Allan deviation $\sigma_y(\tau)$ in the regime where it is limited by fundamental noise sources [21, 84]:

$$\sigma_y(\tau) = \kappa \frac{\Delta\nu_{\text{obs}}}{\nu_0} \frac{\delta S}{S} \sqrt{\frac{T_c}{\tau}}, \quad (1.16)$$

where ν_0 is the clock transition frequency, $\Delta\nu_{\text{obs}}$ is the observed linewidth, $S/\delta S$ is the signal-to-noise for a single measurement, T_c is the duration of one measurement

cycle, τ is the total averaging time and κ is a constant of order unity that depends on the lineshape. The lower limit for the signal-to-noise ratio is given by quantum projection noise; for typical measurements around the detuning corresponding to the half-maximum intensity point (where frequency sensitivity is largest) $S/\delta S \approx \sqrt{N}$ for N atoms being measured simultaneously. Equation (1.16) shows that a good clock has a high frequency ν_0 , a narrow linewidth $\Delta\nu_{\text{obs}}$ within cycle time T_c and a high signal-to-noise $S/\delta S$. The statistical uncertainty then converges as $\propto \tau^{-1/2}$, typical of white frequency noise. The observed linewidth $\Delta\nu_{\text{obs}}$ depends on the natural linewidth of the transition, the linewidth of the clock laser, the observation time and the chosen interrogation scheme (e.g. Rabi or Ramsey). Assuming a clock laser with a linewidth of the same order as the natural transition, low cycle dead time (for laser cooling, state preparation and detection) and realistic experimental parameters [84], we find the ultimately achievable stability for a particular clock species:

$$\sigma_y(\tau) \approx \frac{2}{\sqrt{2\pi\nu_0 Q N \tau}}, \quad (1.17)$$

where $Q = \nu_0/\Delta\nu$ is the (natural) quality factor of the clock transition set by the excited state lifetime.

The clock frequencies of Ba^+ are relatively low, in the near infrared (IR), but the long lifetimes of its D levels compensate for this, provided a clock laser system with sufficient short-term stability is developed. The ultimate stability of a mature Ba^+ clock system could potentially be somewhat better than Ca^+ or Sr^+ , though not beyond the ultraviolet (UV) Al^+ clock transition or the octupole transition in Yb^+ with nHz linewidth. The shorter D level lifetimes in Ra^+ offer a stability comparable to Ca^+ and Sr^+ .

From Eq. (1.17), the ultimate stability of single-ion optical clocks ($N = 1$, $\nu_0 \approx 10^{15}$ Hz, $Q \approx 10^{15}$) is of order $10^{-15} \sqrt{s}/\sqrt{\tau}$. Optical lattice clocks have an edge in stability through the large number of atoms trapped simultaneously ($N = 10^4$ to 10^5) providing higher signal-to-noise. However, ion clocks can typically operate with less dead time and offer better potential for compactness with their lower required optical powers and simpler loading schemes, which is advantageous for some applications. Alternatively, the possibility of multi-ion crystals ($N > 1$) in a specially tuned trap to prevent shifts and broadening for ions outside the field-free trap center exists for both Ba^+ and Ra^+ [85], and could be explored to improve short-term clock stability.

The ultimate accuracy of an optical frequency standard cannot be summarized in a single formula but requires evaluating various systematic effects, in particular their uncertainties: the observed transition frequency is affected by the motion of the trapped ion, electromagnetic fields, etc. Technical effects such as servo locking errors and AOM phase chirp can also cause systematic frequency shifts; these may require significant effort to reduce but are generally not the fundamental limiting factor. Since many of these frequency shifts do not scale with the transition frequency,

clock transitions with a higher frequency tend to have smaller fractional frequency uncertainties (this is also an important advantage of optical clocks over microwave clocks). Additionally, a good clock transition is intrinsically insensitive to external perturbations, e.g. by having a small differential polarizability and electric quadrupole moment. We discuss the relevant systematic effects for single-ion clocks below.

Doppler effect

Motion of the ion relative to the clock laser directly causes a frequency shift through the Doppler effect. The first-order Doppler shift is eliminated by laser cooling to the Lamb-Dicke regime and thus the second-order Doppler shift (time dilation) is the dominant effect. The frequency shift due to time dilation is given by [86]:

$$\Delta\nu_{D2} = -\frac{\langle v^2 \rangle}{2c^2} \nu_0 \approx -\frac{3k_B T}{mc^2} \nu_0, \quad (1.18)$$

where v is the velocity of the ion of mass m . The last expression assumes an ion trapped in a spherical Paul trap with equal temperature T in all three dimensions and includes the kinetic energy contribution from unavoidable micromotion associated with the thermal motion. The achieved temperature T depends on the cooling method and atomic properties (see Section 1.3.2); it is of order mK for Doppler cooling. An advantage of Ba^+ and Ra^+ is that their heavy masses suppress the fractional frequency uncertainty from typical temperature uncertainties to about 1×10^{-18} . However, if the ion is displaced from the trap center by uncompensated stray electric fields, the driven micromotion may dominate over the thermal motion discussed here. Minimization of the displacement from the trap center is therefore crucial [87, 88].

Zeeman effect

Coupling of atomic states to magnetic fields via their magnetic moment causes energy shifts. The linear Zeeman shift for a state (F, m_F) is given by [36]

$$\Delta\nu_{Z1}(F, m_F) = \frac{1}{h} \mu_B g_F m_F B, \quad (1.19)$$

where B is the magnetic field strength and g_F is the Landé g -factor. Linear Zeeman shifts are typically of order 10 kHz/ μT and would limit a clock's accuracy by magnetic field fluctuations and uncertainty in the shift factors. The relevant quantity is the differential shift $\Delta\nu_{Z1} = \Delta\nu_{Z1}(F', m_{F'}) - \Delta\nu_{Z1}(F, m_F)$ on the clock transition. It is absent for $m_F = 0$ to $m_{F'} = 0$ transitions in odd isotopes of Ba^+ and Ra^+ . For even isotopes without hyperfine structure, the technique of averaging over symmetric pairs of Zeeman components to mimic such a transition has been developed [89].

Interaction with the magnetic field couples atomic states of equal m_F and leads to a quadratic shift due to nearby states in addition to the linear Zeeman effect;

second-order perturbation theory [36] for a state with quantum numbers (I, J, F, m_F) coupling to other states within the hyperfine manifold yields

$$\Delta\nu_{Z2}(F, m_F) = \frac{1}{h} \mu_B^2 (g_J + g_I)^2 B^2 J(J+1)(2J+1) \times \sum_{F', m_{F'}} \left\{ \begin{matrix} J & F' & I \\ F & J & 1 \end{matrix} \right\}^2 \left(\begin{matrix} F & 1 & F' \\ -m_F & 0 & m_{F'} \end{matrix} \right)^2 \frac{(2F+1)(2F'+1)}{E_F - E_{F'}}, \quad (1.20)$$

where g_J, g_I are the electronic and nuclear g -factors (in multiples of μ_B) and E_F are the state energies. Averaging over Zeeman components does not cancel the second-order Zeeman shift. For clock transitions in odd isotopes of Ba^+ and Ra^+ , the differential shift magnitude is $10^{-5} \text{ Hz}/\mu\text{T}^2$ to $10^{-4} \text{ Hz}/\mu\text{T}^2$. For even isotopes without hyperfine structure, the dominant contribution comes from coupling to other levels within the J -manifold (calculated with a similar expression); due to the larger level spacing, the quadratic Zeeman shift is suppressed by about a factor 10^6 in this case. Through the second-order Zeeman shift, the clock's frequency uncertainty is affected by magnetic field fluctuations, requiring magnetic shielding and operating with a small magnetic field (order $1 \mu\text{T}$ to $10 \mu\text{T}$) during clock probing. In addition, AC magnetic fields from unbalanced RF currents in the trap contribute an RMS term (the RF frequency is negligible compared to state splittings, so the DC expression can be used).

Dipole Stark effect

Electric fields cause energy shifts by coupling to transition electric dipole (and higher order) moments. Various sources of electric fields play a role for ion clocks: trapping fields, stray fields, blackbody radiation and laser fields. The dipole Stark shift of an atomic state (F, m_F) due to DC electric fields is proportional to its static dipole polarizabilities⁸ α_{0F} (scalar) and α_{2F} (tensor) [91]:

$$\Delta\nu_{S2}(F, m_F) = -\frac{1}{2h} \alpha_{0F} \mathcal{E}^2 - \frac{1}{2h} \alpha_{2F} \frac{3m_F^2 - F(F+1)}{F(2F-1)} \frac{3\mathcal{E}_z^2 - \mathcal{E}^2}{2}, \quad (1.21)$$

where $\mathcal{E}$ is the electric field strength. The clock transition shift thus depends on the differential polarizabilities. Although a trapped ion experiences a net electric field of zero, it samples a nonzero field $\langle \mathcal{E}^2 \rangle$ in the RF trapping potential through its thermal and driven motion. Again, although some motion of the ion is unavoidable, the effective electric field can be greatly increased by uncompensated stray electric fields displacing the ion from the trap center and driving excess micromotion [87]. As mentioned, this micromotion also causes a frequency shift through time dilation.

⁸Note that Eq. (3) in Ref. 23 is incomplete: the full expressions for the hyperfine polarizabilities α_{kF} in terms of the fine structure values α_{kJ} can be derived using Ref. 90 and are given in Appendix A.

The clock transitions in Ba^+ and Ra^+ have a negative differential polarizability (see Table 1.4). Therefore, it is possible to make both shifts caused by micromotion to cancel by operating at a specific trapping frequency [86, 87] (for Ba^+ and Ra^+ these are around 3.5 MHz and 6 MHz, respectively). The tensor contribution to the dipole Stark shift (for $F \geq 1$) depends on the difficult-to-determine direction of the electric field (the magnetic field defines the quantization axis). Methods of suppressing it are the same as for the quadrupole Stark shift and are discussed there. In addition to uncertainties from the electric field, uncertainties in the relevant polarizabilities limit the clock accuracy.

In addition to static electric fields, the oscillating electric fields of lasers also cause dipole Stark shifts. This means that ideally the clock laser has low intensity and any cooling lasers are completely extinguished during the probing cycle. The AC dipole Stark shift caused by laser light of intensity I_l at frequency ν_l is given by [90, 92]

$$\Delta\nu_{S2\nu_l}(F, m_F) = -\frac{I_l}{2\varepsilon_0\hbar c} \left(\alpha_{0F}(\nu_l) + \alpha_{1F}(\nu_l) \frac{m_F}{2F} A_l + \alpha_{2F}(\nu_l) \frac{3m_F^2 - F(F+1)}{F(2F-1)} T_l \right), \quad (1.22)$$

where the factors A_l and T_l depend on laser polarization and propagation direction. Expressions for the fine-structure dynamic dipole polarizabilities $\alpha_{k,J}(\nu_l)$ are given in Section 5.1. For quadrupole clock transitions, it may be necessary to include the quadrupole polarizability contributions that also scale with laser intensity but sharply peak around the clock frequency, while all dipole contributions are far detuned [93].

Blackbody radiation

A further source of shifts are the electromagnetic fields corresponding to the thermal radiation of the trapping environment. This blackbody radiation shift is one of the limiting factors for the uncertainty of optical clocks operating at room temperature. Integrating the Planck formula for the spectral energy density of a body at temperature T gives the mean square electric field strength [94, 95]

$$\langle \mathcal{E}^2 \rangle_T = \frac{\pi^2}{15c^3\varepsilon_0\hbar^3} (k_B T)^4 = (8.319 \text{ V/cm})^2 \left(\frac{T}{300 \text{ K}} \right)^4, \quad (1.23)$$

which induces a Stark shift of

$$\Delta\nu_{\text{BBR}}(F, m_F) = -\frac{1}{2\hbar} \alpha_{0F} \langle \mathcal{E}^2 \rangle_T (1 + \eta_F), \quad (1.24)$$

where η_F is a small dynamic correction to the static polarizability as the peak of the blackbody radiation shifts with temperature (at room temperature $|\eta_F| < 10^{-2}$). There is no tensor shift because the blackbody radiation is isotropic. In addition to uncertainties in the atomic parameters, the T^4 -dependence of this shift demands the

effective temperature seen by the ion to be precisely known. This requires temperature sensors and detailed modeling of the trap environment [96], or operating at cryogenic temperatures to greatly reduce the magnitude of the shift (like the Hg^+ clock). Further steps include using low RF power to limit heating of electrodes, reducing emissivity of hot surfaces or shielding them from view.

The blackbody shift would likely limit the fractional frequency uncertainty of a Ba^+ clock at room temperature to about 1×10^{-16} due to its relatively large static dipole polarizability and low clock transition frequency (see Table 1.4). For Ra^+ , the fractional blackbody shift is moderate, comparable to Sr^+ where 2×10^{-17} has been achieved at room temperature [86]. Cooling the trap to liquid nitrogen temperature would reduce the uncertainty to negligible levels at the cost of complicating the setup.

Thermal radiation also has a magnetic part $\langle B^2 \rangle_T = \langle \mathcal{E}^2 \rangle_T / c^2 = (2.8 \mu\text{T})^2 (T/300 \text{ K})^4$ which produces a shift due to the dipole magnetizability (i.e. the quadratic Zeeman effect) [95]. However, this shift is suppressed by α^2 compared to the electric dipole part and can be neglected.

Quadrupole Stark effect

Electric quadrupole moments Θ_F of atomic states interact with static electric field gradients. First order perturbation theory yields a shift of [91]

$$\Delta\nu_{Q1}(F, m_F) = -A_{\mathcal{E}} \Theta_F (-1)^{F-m_F} \begin{pmatrix} F & 2 & F \\ -m_F & 0 & m_F \end{pmatrix} X_{\mathcal{E}}, \quad (1.25)$$

where $A_{\mathcal{E}}$ gives the magnitude of the gradient and $X_{\mathcal{E}}$ is an angular factor of order unity that depends on the orientation and shape of the gradient with respect to the z -axis. Atomic states with total angular momentum $F < 1$ have no electric quadrupole moment, so this shift generally only affects the excited state of clock transitions but tends to be one of the larger shifts at typically $10 \text{ mHz}/(\text{V}/\text{cm}^2)$. It introduces uncertainty because electric field gradients are difficult to determine to high precision and may change over time (patch potentials). Odd isotopes of Ba^+ and Ra^+ offer combinations of quantum numbers where the quadrupole shift is zero (the tensor part of the dipole Stark effect also vanishes for these clock transitions). Alternatively, two methods are used to cancel the shift using its symmetries: averaging over measurements at any three orthogonal magnetic field directions [91] or over a suitable combination of different m_F components [89].

In second order perturbation theory [36], the quadrupole shift is quadratic in the field gradients and thus the oscillating gradients from the trapping field do not average out. The second-order interaction couples states within the hyperfine manifold, including other m_F -states of the same F -level⁹. However, the latter coupling results in an odd

⁹This depends on the orientation of the gradient; Eq. (9) in Ref. 23 assumes perfect $\hat{z}$ -alignment and

function of m_F which vanishes for $m_F = 0$ states and symmetric Zeeman pairs [89]. The coupling between different F -levels still leaves a quadratic quadrupole shift for clock transitions in odd isotopes that are free from the linear effect [23].

Background gas collisions

A further effect to include in the uncertainty budget of a single-ion clock is a frequency shift due to background gas collisions. However, when operating at pressures of 10^{-10} mbar or below, the fractional collisional shift is typically below the 10^{-18} level [73,97].

Gravitational redshift

Clock frequencies are affected by the Earth's gravitational potential. The frequency shift when a clock moves a vertical distance Δh is [67]

$$\Delta\nu_{\text{GR}} \approx \frac{g\Delta h}{c^2}\nu_0, \quad (1.26)$$

where g is the local gravitational acceleration. A height difference of 1 cm corresponds to a fractional frequency shift of one part in 10^{-18} . Therefore, detailed information on the geoid is required to compare remote clocks to high precision. Furthermore, fluctuations (e.g. tidal) in the local gravitational field may cause fractional frequency shifts of up to 10^{-17} if averaging over short time periods.

Current status

In conclusion, the systematic uncertainty of an optical clock based on a single Ba^+ or Ra^+ ion would depend both on atomic properties (see Table 1.4) and technical characteristics. The limiting uncertainties of different ion clock species are likely to all lie within about one order of magnitude. The heavy mass of Ba^+ and Ra^+ gives a high sensitivity to changes in fundamental constants and limits the second-order Doppler shift. The odd barium isotopes $^{135}\text{Ba}^+$ and $^{137}\text{Ba}^+$ offer hyperfine clock transitions that are (to first order) immune to electric field gradients, tensor Stark shifts and magnetic fields without requiring averaging techniques. Their modest nuclear spin of $I = 3/2$ compares favorably to that of the stable odd isotopes of calcium ($I = 7/2$) and strontium ($I = 9/2$) for the purpose of laser cooling, but the relatively large blackbody shift of Ba^+ is a downside. The radium isotope $^{223}\text{Ra}^+$ ($I = 3/2$) has a sufficiently long nuclear lifetime of two weeks and offers the same type of hyperfine clock transitions. All laser wavelengths required for Ba^+ or Ra^+ can be obtained from semiconductor diode lasers. This offers possibilities for simple, compact clocks.

misses the possible coupling between m_F -states of the same F -level, significantly underestimating the shift for states ($F \geq 1$, $m_F \neq 0$) due to the smaller energy difference of coupled states.

Table 1.4 Relevant atomic parameters of Ba^+ and Ra^+ ion clocks, to compare with other ion species in Table I of Ref. 21. Chosen isotopes and transitions are illustrative; where available, experimental measurements are given. The differential quadratic Zeeman shift $\Delta\nu_{Z2}$ from LS -coupling is averaged over $m_{F'}$ states to mimic a $m_F = 0 \rightarrow m_{F'} = 0$ transition. The differential polarizabilities are $\Delta\alpha_i = \alpha_{iF'} - \alpha_{iF}$. The differential blackbody shift $\Delta\nu_{\text{BBR}} = -\Delta\alpha_0/(2h)\langle\mathcal{E}^2\rangle(1 + \Delta\eta)$ is given for $T = 300\text{ K}$; the dynamic correction $\Delta\eta$ is calculated with the expression from Ref. 94. The reduced electric quadrupole moment of the excited level is given by $\Theta_{J'}$ (see Appendix A).

	$^{138}\text{Ba}^+$	$^{226}\text{Ra}^+$
m (u)	137.905 [103]	226.025 [103]
I	0	0
Transition	$^2\text{S}_{1/2} \rightarrow ^2\text{D}_{5/2}$	$^2\text{S}_{1/2} \rightarrow ^2\text{D}_{5/2}$
ν_0 (THz)	170.126 [50]	412.008 [51]
g_F	2.002 491 92(3) [104]	2.0058 [53]
$g_{F'}$	1.200 372(8) [105]	1.2007 [53]
$\Delta\nu_{Z2}$ (Hz/mT ²)	1.0928	0.5277
$\Delta\alpha_0$ ($10^{-41}\text{ Jm}^2/\text{V}^2$)	-110(4) [98, 100]	-37(3) [106]
$\Delta\alpha_2$ ($10^{-41}\text{ Jm}^2/\text{V}^2$)	-53.04(5) [100]	-86.7(0.7) [106]
$\Delta\eta_{300\text{ K}}$	0.002	-0.006
$\Delta\nu_{\text{BBR}, 300\text{ K}}$ (Hz)	0.578(21)	0.190(14)
$\Theta_{J'}$ (ea_0^2)	3.42(4) [107]	4.34(4) [63]

To realize a Ba^+ or Ra^+ optical clock requires developing an ultra-stable laser system and an experimental setup with exquisite control over electromagnetic fields, temperature and ion motion. In addition, the uncertainty in atomic parameters needs to be reduced. Particularly the polarizabilities which determine the magnitude of frequency shifts due to electric fields (see Table 1.4) need to be determined to higher accuracy. Currently, there is experimental data available only on the polarizability of the Ba^+ ground state [98, 99], with some unresolved inconsistencies between different measurements and calculations [98–100], and an older measurement of the differential polarizability of the Ba^+ $^2\text{S}_{1/2} - ^2\text{D}_{5/2}$ transition [80], but also see the recent Ref. 101 on assessing the differential polarizability. A first precision measurement of a Ba^+ clock transition has very recently appeared on arXiv [102].

1.3 Atom–Light Interaction

All of the measurements in this thesis have to do with the interaction between atoms and light in one way or another. For optical transitions, the potential energy due to the electric field interacting with the charge density of an atom’s electrons is given by the dipole approximation [36]

$$H_{\text{int}}(t) = -\mathcal{E}(t) \cdot \mathbf{D}, \quad (1.27)$$

where $\mathcal{E}(t)$ is the oscillating electric field strength and $\mathbf{D} = -e\mathbf{x}$ is the electric dipole moment operator, which operates between opposite-parity electronic states of the atom. We briefly review some of the basics for a two-level system, laser cooling techniques and then discuss the optical Bloch equations for describing the spectra observed in the experiments of this thesis.

1.3.1 Two-level system

The Hamiltonian in the lab frame for a two-level atom interacting with a classically-modeled monochromatic light field in the rotating wave approximation is [36]

$$H = H_0 + H_{\text{int}}(t) = \frac{\hbar}{2} \begin{pmatrix} -\omega_0 & \Omega e^{i\omega t} \\ \Omega e^{-i\omega t} & \omega_0 \end{pmatrix}, \quad (1.28)$$

where ω_0 is the transition frequency and ω is the laser frequency. The Rabi frequency Ω depends on the electric field amplitude $\mathcal{E}$ and the interaction dipole moment¹⁰ D between ground state $|1\rangle$ and excited state $|2\rangle$,

$$\Omega = \frac{\mathcal{E}|\langle 1|\mathbf{D}|2\rangle|}{\hbar}. \quad (1.29)$$

We can remove the time-dependence of the Hamiltonian by applying the unitary transformation to the co-rotating basis $|1\rangle \rightarrow e^{-i\omega t/2}|1\rangle$, $|2\rangle \rightarrow e^{i\omega t/2}|2\rangle$ to find

$$\tilde{H} = \frac{\hbar}{2} \begin{pmatrix} \Delta\omega & \Omega \\ \Omega & -\Delta\omega \end{pmatrix}, \quad (1.30)$$

where $\Delta\omega = \omega - \omega_0$ is the detuning of the laser from resonance.

Rabi oscillations

The equations of motion for the density matrix operator $\tilde{\rho}(t)$ of the system described by the Hamiltonian in Eq. (1.30) are given by the Liouville–von Neumann equation [36]

$$\frac{d}{dt}\tilde{\rho}(t) = \frac{1}{i\hbar} [\tilde{H}, \tilde{\rho}(t)] + \tilde{\mathcal{R}}(\tilde{\rho}(t)), \quad (1.31)$$

¹⁰For real atoms, we need to take into account that $\mathcal{E}$ and D are magnitudes of vector quantities. Here we effectively assume that $\mathcal{E}$ is aligned with D and interacts with the full dipole moment.

with $\tilde{H}$ modeling stimulated absorption/emission and $\tilde{\mathcal{R}}$ modeling incoherent processes such as spontaneous emission. This forms a system of four coupled first-order differential equations. Note that the observable populations are identical for $\tilde{\rho}$ and ρ .

Setting $\tilde{\mathcal{R}} = 0$ for now, the analytical solution to the time evolution of the excited state population, starting with all population in the ground state, is

$$\tilde{\rho}_{22}(t) = \frac{\Omega^2}{\Omega'^2} \sin^2 \frac{\Omega' t}{2}, \quad (1.32)$$

using the generalized Rabi frequency Ω' which includes the laser detuning, defined as

$$\Omega' = \sqrt{\Omega^2 + \Delta\omega^2}. \quad (1.33)$$

This shows that the light field causes the population to coherently transfer back and forth between the ground and excited state at frequency Ω' : these are the so-called *Rabi oscillations*.

Adding the terms for spontaneous emission at rate Γ dampens the Rabi oscillations:

$$\tilde{\mathcal{R}} = \begin{pmatrix} \Gamma\tilde{\rho}_{22} & -\frac{1}{2}\Gamma\tilde{\rho}_{12} \\ -\frac{1}{2}\Gamma\tilde{\rho}_{21} & -\Gamma\tilde{\rho}_{22} \end{pmatrix}. \quad (1.34)$$

Calculating the steady-state excited state population by setting $\frac{d}{dt}\tilde{\rho} = 0$ then gives

$$\tilde{\rho}_{22}(t \rightarrow \infty) = \frac{\Omega^2}{2\Omega^2 + 4\Delta\omega^2 + \Gamma^2}. \quad (1.35)$$

This Lorentzian lineshape has a full-width half-maximum (FWHM) of $\Gamma\sqrt{1 + 2\Omega^2/\Gamma^2}$, showing power broadening with saturation parameter $S = 2\Omega^2/\Gamma^2$.

Light shift

The interaction with the light field causes mixing of the two levels of the atom and shifts their energies by inducing atomic polarization. Diagonalizing the co-rotating Hamiltonian in Eq. (1.30) and applying the (reverse) transformation to recover the level energies in the lab frame yields¹¹ $E = \mp \frac{\hbar}{2}(\omega \pm \Omega')$. Comparing these to the uncoupled energies $E_0 = \mp \frac{\hbar}{2}\omega_0$ and assuming far off-resonant light $|\Delta\omega| \gg \Omega$, we find that the energies of the two levels are shifted by

$$\Delta E = \pm \hbar \frac{\Omega^2}{4\Delta\omega}. \quad (1.36)$$

¹¹Here we have chosen the signs such that the coupled states are adiabatically connected to the uncoupled states when far detuned. In fact there are two more energy solutions, explained in the dressed atom picture taking into account the quantized photon states of the light field [36].

This is known as the *light shift* (AC Stark effect): if the light field is red-detuned (below resonance, $\Delta\omega < 0$), the levels shift apart and if blue-detuned ($\Delta\omega > 0$), the levels move closer together. The shifts of both levels are opposite, so that the total shift is zero as required by energy conservation.

1.3.2 Laser cooling

Ions typically start out with energies in the electronvolt range when they are produced. Precision spectroscopy for APV measurements and atomic clocks requires reducing the (thermal) movement of trapped ions to increase the brightness of the signal and minimize the Doppler effect. The APV experiment described in Section 1.1 additionally demands the localization of a trapped ion to a fraction of an optical wavelength. We can achieve this by using the family of techniques known as *laser cooling* [108–110], where some combination of the momentum imparted by absorbing photons or a difference in the average energy between absorbed and emitted photons (anti-Stokes scattering) transfers kinetic energy from the ion to the photon field. For laser cooling a trapped ion moving at velocity $\mathbf{v}$, for now assuming a two-level system illuminated by a monochromatic laser with wavevector $\mathbf{k}$, several regimes can be distinguished based on the following rates [110] (also see Ref. 47): the spontaneous emission rate Γ , the ion's secular oscillation frequency ω_{sec} in the (time-averaged) quadratic trap potential and the single photon recoil energy (expressed as rate) $\omega_R = \hbar|\mathbf{k}|^2/2m$.

Doppler cooling

We first consider Doppler cooling for $\Gamma \gg \omega_{\text{sec}}$, the weak binding regime, which is the typical case for dipole allowed optical transitions. Here the absorption of a photon and subsequent emission is instantaneous with respect to the secular motion of the ion in the trap, making this case similar to cooling free atoms. Many absorption-emission cycles are generally needed for cooling; the momentum transferred by absorbing a single photon is $\hbar\mathbf{k}$. We multiply this by the photon scattering rate $\Gamma\rho_{22}$ to find the force

$$\mathbf{F}(v) = \hbar\mathbf{k}\Gamma \frac{S/2}{1 + S + (2\Delta\omega'(v)/\Gamma)^2}, \quad (1.37)$$

where we have written Eq. (1.35) in terms of the saturation parameter S and $\Delta\omega'(v) = \Delta\omega - \mathbf{k} \cdot \mathbf{v}$ is the laser detuning taking the Doppler shift into account. If the laser is red-detuned ($\Delta\omega < 0$), Eq. (1.37) forms a velocity-dependent drag force, cooling the ion. The spontaneously emitted photons average to a zero momentum change but do cause the ion to undergo diffusion. When the cooling exactly balances this recoil heating, the minimum temperature is reached:

$$T_D \approx \frac{\hbar\Gamma}{2k_B}. \quad (1.38)$$

This assumes the optimal detuning $\Delta\omega \approx -\Gamma/2$. The precise limit depends on laser intensity, geometry and emission pattern [108, 109]. For the strong $^2S_{1/2} - ^2P_{1/2}$ transition in both Ba^+ and Ra^+ ions, the Doppler limit is $T_D \approx 0.5$ mK.

Resolved sideband cooling

Going beyond the Doppler limit is possible in the strong binding regime, $\Gamma \ll \omega_{\text{sec}}$, which can be reached by continuing cooling on a more narrow (e.g. electric quadrupole) transition. The absorbed and emitted light is then modulated by the motion of the ion in the trap, which manifests as resolved motional sidebands spaced at ω_{sec} from the central carrier frequency. These sidebands correspond to changes in the motional eigenstate n of the ion in the harmonic trap potential and when tuning the laser to a red sideband, the missing energy will be provided by vibrational quanta Δn . To describe the degree of localization of ions, we introduce the *Dicke parameter* η , the ratio of the size of the zero-point vibrational wavefunction and the laser wavelength [108–110]

$$\eta = |\mathbf{k}|x_0 = \sqrt{\omega_R/\omega_{\text{sec}}}, \quad (1.39)$$

where x_0 is the spatial extent of the vibrational ground state. When the condition $\eta^2(2n+1) \ll 1$ holds, the amplitude of the ion motion $\langle x^2 \rangle$ is small compared to the laser wavelength λ and the ion is well-localized: this is the *Lamb–Dicke regime* where coupling between motional states is sufficiently small that transitions with $|\Delta n| > 1$ (and corresponding sidebands) are strongly suppressed. With resolved sideband cooling, the motional ground state can be reached, potentially lowering the temperature to a limit $T_{n=0} = \hbar\omega_{\text{sec}}/2k_B$ of order microkelvin. The carrier signal is totally free of the first order Doppler effect, while the second order (relativistic) Doppler effect also becomes negligible for the motional ground state.

Further considerations

One aspect that we have ignored so far is that the ion has kinetic energy in three dimensions. However, for a trapped ion it turns out that one laser at an oblique angle to the principal axes of the trap is sufficient to Doppler cool all three degrees of freedom [108, 110]. Note that the secular oscillation frequency of the ion in general differs for the three axes, see Section 3.1.1. The decay to the long-lived $^2D_{3/2}$ level of Ba^+ and Ra^+ means that a repump laser is needed while performing Doppler cooling on the $^2S_{1/2} - ^2P_{1/2}$ transition. Furthermore, in this effective three-level Λ -system, additional cooling techniques are possible that surpass the Doppler limit, such as using a stimulated Raman transition for resolved sideband cooling or performing EIT cooling, where electromagnetically induced transparency (see Section 1.3.3) suppresses carrier excitation that causes heating and maximizes absorption at the red sideband [108–110].

Finally, it is possible to laser cool multiple ions trapped simultaneously, even when addressing only a subset of them and cooling the rest by sympathetic cooling [108, 110].

For the measurements in this thesis, we perform Doppler cooling of Ba^+ ions in the weak binding regime with two coaxial red-detuned lasers driving the $^2\text{S}_{1/2} - ^2\text{P}_{1/2}$ and $^2\text{D}_{3/2} - ^2\text{P}_{1/2}$ transitions. We use the same lasers also for spectroscopy, which leads to the complication that blue-detuning either laser will often cause heating and a loss of signal [49]. Although laser cooling with blue-detuned laser light is possible under certain conditions [111], we broadly limit heating by switching the repump laser at kHz rate between two frequencies: a fixed red-detuned setting for cooling and a variable detuning for spectroscopy of the transition (see Section 4.1).

1.3.3 Optical Bloch equations

To describe experimentally-observed fluorescence spectra, we move beyond a two-level system by including electron spin and electric field polarization. We use the following definition¹² for the reduced matrix elements of tensor operators in terms of Clebsch–Gordan coefficients or 3- j symbols (Wigner–Eckart theorem) [36]:

$$\langle Jm|D_q|J'm'\rangle = \frac{C_{J'1m'q}^{Jm}}{\sqrt{2J+1}} \langle J\|D\|J'\rangle = (-1)^{J-m} \begin{pmatrix} J & 1 & J' \\ -m & q & m' \end{pmatrix} \langle J\|D\|J'\rangle, \quad (1.40)$$

where q is the tensor component in spherical basis and $J, J' (m, m')$ are the (projected) total angular momentum quantum numbers of the states involved, omitting further quantum numbers for brevity. In this normalization the reduced matrix element (radial integral) of the transition dipole moment between levels J and J' is related to the (partial) spontaneous emission rate $A_{J'J}$ as [36]

$$|\langle J\|D\|J'\rangle|^2 = |\langle J'\|D\|J\rangle|^2 = \frac{3\pi\epsilon_0\hbar c^3}{\omega_0^3} (2J'+1) A_{J'J}. \quad (1.41)$$

We mostly deal with isotopes without nuclear spin in this thesis, therefore we do not treat hyperfine structure here. The $2J+1$ degeneracy of each level is lifted in an external magnetic field $\mathbf{B}$ due to the Zeeman effect. The weak-field energy shift for each state m is given by [36]

$$H_B = g_J \mu_B m |\mathbf{B}| \quad \text{with Landé factors} \quad g_J \approx \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}. \quad (1.42)$$

To model the fluorescence spectrum of a Ba^+ ion in the two light fields for laser cooling and repumping, we need to take into account the eight Zeeman sublevels of

¹²There are multiple conventions for reduced matrix elements, another common one is larger by a factor $\sqrt{2J+1}$. Unfortunately, publications don't always specify the convention used.

Figure 1.5 Low-lying energy levels of even Ba^+ isotopes without hyperfine structure, showing our numbering of the eight Zeeman sublevels. Solid lines indicate E1 transitions, dashed lines indicate magnetic or higher-order electronic transitions.

the Λ -system formed by the $6s\ ^2S_{1/2}$, $6p\ ^2P_{1/2}$ and $5d\ ^2D_{3/2}$ levels shown in Fig. 1.5. The same description can be used for the corresponding levels in Ra^+ . We again solve the Liouville–von Neumann equation (1.31), given in element notation by

$$\frac{d}{dt}\rho_{ab} = \frac{1}{i\hbar} \sum_j (H_{aj}\rho_{jb} - \rho_{aj}H_{jb}) + \mathcal{R}_{ab}(\rho), \quad (1.43)$$

where H_{ab} is the 8×8 matrix representing the Hamiltonian for the interaction with the two laser fields in the co-rotating basis (we drop the tilde notation). $\mathcal{R}$ is again the damping matrix that models relaxation and decoherence phenomena. Our calculation is based on Ref. 112, extending it to arbitrary propagation directions and polarization states of the two light fields¹³. We present a concise overview here.

Light field parametrization

The oscillating electric field $\mathcal{E}(t)$ experienced by the ion is the sum of the two laser light fields. We use subscript 1 to identify all quantities related to the light field driving the $^2S_{1/2} - ^2P_{1/2}$ transition and subscript 2 for the field driving $^2D_{3/2} - ^2P_{1/2}$:

$$\mathcal{E}(t) = \mathcal{E}_1(t) + \mathcal{E}_2(t). \quad (1.44)$$

We model both light fields $k = 1, 2$ as classical plane waves:

$$\mathcal{E}_k(t) = \mathcal{E}_k \epsilon_k \cos \omega_k t = \mathcal{E}_k \epsilon_k \frac{1}{2} (e^{i\omega_k t} + e^{-i\omega_k t}). \quad (1.45)$$

Here $\mathcal{E}_k$ are the amplitudes, ϵ_k are the polarization unit vectors and ω_k are the angular frequencies of the light fields. Although the electric field is a real physical quantity,

¹³Our MATLAB code is available with the online version of this thesis, doi:10.33612/diss.108023683.

we use complex vectors ε_k to represent phase shifts between the two polarization components of the transverse waves as is customary. We again use the rotating wave approximation, where we split each electric field into two counter-rotating complex parts of which only one interacts with each component of the dipole operator.

We parametrize the polarization state of each light field by two angles: the angle of polarization α_k and the phase shift β_k between its two orthogonal components. The normalized Jones vector ψ_k for angles (α_k, β_k) is calculated as

$$\psi_k = \frac{1}{\sqrt{1 + \sin^2 \beta_k}} \begin{pmatrix} \cos \alpha_k - i \sin \alpha_k \sin \beta_k & \sin \alpha_k + i \cos \alpha_k \sin \beta_k \end{pmatrix}. \quad (1.46)$$

In this parametrization $\beta_k = 0^\circ$ corresponds to pure linear polarization where angle α_k sets the direction, pure circular polarization has $\beta_k = \pm 90^\circ$ and the general case is some form of elliptical polarization. In our setup, the laser beams are coaxial and propagate in the same direction. Describing the direction of the co-propagating beams by polar angles (θ_l, ϕ_l) , the polarization unit vectors in the lab frame are

$$\bar{\varepsilon}_k = \psi_k \begin{pmatrix} \cos \theta_l \cos \phi_l & \cos \theta_l \sin \phi_l & -\sin \theta_l \\ -\sin \phi_l & \cos \phi_l & 0 \end{pmatrix}. \quad (1.47)$$

Finally, since the magnetic field determines the quantization axis, we rotate the lab frame vectors to a frame where the z -axis is aligned with the magnetic field vector $\mathbf{B}$ to ease the calculation of the components of the dipole operator:

$$\varepsilon_k = (\cos \theta_a) \bar{\varepsilon}_k + (\sin \theta_a) (\hat{\mathbf{a}} \times \bar{\varepsilon}_k) + (1 - \cos \theta_a) (\hat{\mathbf{a}} \cdot \bar{\varepsilon}_k) \hat{\mathbf{a}}, \quad (1.48)$$

where $\mathbf{a} = \mathbf{B} \times \hat{\mathbf{z}}$ is the rotation axis and θ_a is the angle between $\mathbf{B}$ and $\hat{\mathbf{z}}$.

Dipole operator components

The Hamiltonian H_{ab} in Eq. (1.43) that describes the coupling of the eight-level system (ordered as Fig. 1.5) to the two light fields in the rotating wave approximation is [112]

$$H = \hbar \begin{pmatrix} \Delta\omega_1 - \omega_B & 0 & \Omega_1 d_{13} & \Omega_1 d_{14} & 0 & 0 & 0 & 0 \\ 0 & \Delta\omega_1 + \omega_B & \Omega_1 d_{23} & \Omega_1 d_{24} & 0 & 0 & 0 & 0 \\ \Omega_1 d_{13}^* & \Omega_1 d_{23}^* & -\frac{1}{3}\omega_B & 0 & \Omega_2 d_{35}' & \Omega_2 d_{36}' & \Omega_2 d_{37}' & \Omega_2 d_{38}' \\ \Omega_1 d_{14}^* & \Omega_1 d_{24}^* & 0 & +\frac{1}{3}\omega_B & \Omega_2 d_{45}' & \Omega_2 d_{46}' & \Omega_2 d_{47}' & \Omega_2 d_{48}' \\ 0 & 0 & \Omega_2 d_{35}' & \Omega_2 d_{45}' & \Delta\omega_2 - \frac{6}{5}\omega_B & 0 & 0 & 0 \\ 0 & 0 & \Omega_2 d_{36}' & \Omega_2 d_{46}' & 0 & \Delta\omega_2 - \frac{2}{5}\omega_B & 0 & 0 \\ 0 & 0 & \Omega_2 d_{37}' & \Omega_2 d_{47}' & 0 & 0 & \Delta\omega_2 + \frac{2}{5}\omega_B & 0 \\ 0 & 0 & \Omega_2 d_{38}' & \Omega_2 d_{48}' & 0 & 0 & 0 & \Delta\omega_2 + \frac{6}{5}\omega_B \end{pmatrix} \quad (1.49)$$

where the Zeeman shifts (1.42) are given in terms of the Larmor frequency $\omega_B = \mu_B |\mathbf{B}|/\hbar$ and $\Delta\omega_k$ are the detunings of the two laser frequencies with respect to the corresponding transitions. The matrix elements of the interaction Hamiltonian (1.27) are given in terms of the Rabi frequencies Ω_1 and Ω_2 which depend on the electric field amplitudes $\mathcal{E}_1$ and $\mathcal{E}_2$ as¹⁴

$$\Omega_1 = \frac{\mathcal{E}_1 |\langle {}^2S_{1/2} \| D \| {}^2P_{1/2} \rangle|}{\sqrt{2}\hbar} \quad \text{and} \quad \Omega_2 = \frac{\mathcal{E}_2 |\langle {}^2P_{1/2} \| D \| {}^2D_{3/2} \rangle|}{\sqrt{2}\hbar}. \quad (1.50)$$

The polarization-dependence of the interaction Hamiltonian is expressed by the terms

$$d_{ab} = -\frac{1}{\sqrt{2}}\varepsilon_1 \cdot \frac{\langle a | \mathbf{D} | b \rangle}{\langle {}^2S_{1/2} \| D \| {}^2P_{1/2} \rangle} \quad \text{and} \quad d'_{ab} = -\frac{1}{\sqrt{2}}\varepsilon_2 \cdot \frac{\langle a | \mathbf{D} | b \rangle}{\langle {}^2P_{1/2} \| D \| {}^2D_{3/2} \rangle}. \quad (1.51)$$

Since we have calculated the electric field vectors in a frame where the z -axis corresponds to the quantization axis, we can decompose the Cartesian vector components of the dipole matrix operator into the spherical basis components D_q as [36]

$$\langle a | \mathbf{D} | b \rangle = \left(\frac{1}{\sqrt{2}}\langle a | D_{-1} | b \rangle - \frac{1}{\sqrt{2}}\langle a | D_{+1} | b \rangle \quad \frac{i}{\sqrt{2}}\langle a | D_{-1} | b \rangle + \frac{i}{\sqrt{2}}\langle a | D_{+1} | b \rangle \quad \langle a | D_0 | b \rangle \right) \quad (1.52)$$

and use Eq. (1.40) to evaluate their numerical values. The results are¹⁵

$$\begin{aligned} d_{13} &= \frac{1}{\sqrt{2}}\varepsilon_1 \cdot \begin{pmatrix} 0 & 0 & \frac{1}{\sqrt{6}} \end{pmatrix} & d_{14} &= \frac{1}{\sqrt{2}}\varepsilon_1 \cdot \begin{pmatrix} -\frac{1}{\sqrt{6}} & -\frac{i}{\sqrt{6}} & 0 \end{pmatrix} \\ d_{23} &= \frac{1}{\sqrt{2}}\varepsilon_1 \cdot \begin{pmatrix} -\frac{1}{\sqrt{6}} & \frac{i}{\sqrt{6}} & 0 \end{pmatrix} & d_{24} &= \frac{1}{\sqrt{2}}\varepsilon_1 \cdot \begin{pmatrix} 0 & 0 & -\frac{1}{\sqrt{6}} \end{pmatrix} \\ d'_{35} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} \frac{1}{2\sqrt{2}} & \frac{i}{2\sqrt{2}} & 0 \end{pmatrix} & d'_{45} &= 0 \\ d'_{36} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} 0 & 0 & \frac{1}{\sqrt{6}} \end{pmatrix} & d'_{46} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} \frac{1}{2\sqrt{6}} & \frac{i}{2\sqrt{6}} & 0 \end{pmatrix} \\ d'_{37} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} -\frac{1}{2\sqrt{6}} & \frac{i}{2\sqrt{6}} & 0 \end{pmatrix} & d'_{47} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} 0 & 0 & \frac{1}{\sqrt{6}} \end{pmatrix} \\ d'_{38} &= 0 & d'_{48} &= \frac{1}{\sqrt{2}}\varepsilon_2 \cdot \begin{pmatrix} -\frac{1}{2\sqrt{2}} & \frac{i}{2\sqrt{2}} & 0 \end{pmatrix} \end{aligned} \quad (1.53)$$

¹⁴Note that this definition of the eight-level Rabi frequencies differs from both Refs. 112 and 113. With the factor $\sqrt{2J'+1}$ in the denominator, it corresponds to the Rabi oscillation frequency for a hypothetical light field interacting with the full transition dipole moment of any of the upper states. In our Ref. 113, the elements of the Hamiltonian are actually too large by a factor 4.

¹⁵Different sign conventions can be chosen, e.g. an overall sign flip would affect the complex coherences but not any observable populations.

Incoherent processes

The relaxation matrix $\mathcal{R}_{ab}$ in Eq. (1.43) includes the spontaneous decay of the $^2P_{1/2}$ level and the decoherence effect due to finite laser linewidths (Lindblad terms). We consider the $^2D_{3/2}$ level to be stable at the timescales involved. Here Γ_1 and Γ_2 are the partial decay rates ($A_{J'J}$) of the $^2P_{1/2} - ^2S_{1/2}$ and $^2P_{1/2} - ^2D_{3/2}$ transitions, respectively, such that the total decay rate is $\Gamma = \Gamma_1 + \Gamma_2$ with the associated decoherence rate $\gamma = \Gamma/2$. The linewidths of the two lasers are both taken to be γ_l . Using $\gamma' = \gamma + \gamma_l$, the total relaxation matrix is explicitly given by [112]

$$\mathcal{R} = \begin{pmatrix} \Gamma_1(\frac{1}{3}\rho_{33} + \frac{2}{3}\rho_{44}) & -\Gamma_1\frac{1}{3}\rho_{34} & -\gamma'\rho_{13} & -\gamma'\rho_{14} & -\gamma_l\rho_{15} & -\gamma_l\rho_{16} & -\gamma_l\rho_{17} & -\gamma_l\rho_{18} \\ -\Gamma_1\frac{1}{3}\rho_{43} & \Gamma_1(\frac{2}{3}\rho_{33} + \frac{1}{3}\rho_{44}) & -\gamma'\rho_{23} & -\gamma'\rho_{24} & -\gamma_l\rho_{25} & -\gamma_l\rho_{26} & -\gamma_l\rho_{27} & -\gamma_l\rho_{28} \\ -\gamma'\rho_{31} & -\gamma'\rho_{32} & -\Gamma\rho_{33} & -\Gamma\rho_{34} & -\gamma'\rho_{35} & -\gamma'\rho_{36} & -\gamma'\rho_{37} & -\gamma'\rho_{38} \\ -\gamma'\rho_{41} & -\gamma'\rho_{42} & -\Gamma\rho_{43} & -\Gamma\rho_{44} & -\gamma'\rho_{45} & -\gamma'\rho_{46} & -\gamma'\rho_{47} & -\gamma'\rho_{48} \\ -\gamma_l\rho_{51} & -\gamma_l\rho_{52} & -\gamma'\rho_{53} & -\gamma'\rho_{54} & \Gamma_2\frac{1}{2}\rho_{33} & \Gamma_2\frac{1}{2\sqrt{3}}\rho_{34} & 0 & 0 \\ -\gamma_l\rho_{61} & -\gamma_l\rho_{62} & -\gamma'\rho_{63} & -\gamma'\rho_{64} & \Gamma_2\frac{1}{2\sqrt{3}}\rho_{43} & \Gamma_2(\frac{1}{3}\rho_{33} + \frac{1}{6}\rho_{44}) & \Gamma_2\frac{1}{3}\rho_{34} & 0 \\ -\gamma_l\rho_{71} & -\gamma_l\rho_{72} & -\gamma'\rho_{73} & -\gamma'\rho_{74} & 0 & \Gamma_2\frac{1}{3}\rho_{43} & \Gamma_2(\frac{1}{6}\rho_{33} + \frac{1}{3}\rho_{44}) & \Gamma_2\frac{1}{2\sqrt{3}}\rho_{34} \\ -\gamma_l\rho_{81} & -\gamma_l\rho_{82} & -\gamma'\rho_{83} & -\gamma'\rho_{84} & 0 & 0 & \Gamma_2\frac{1}{2\sqrt{3}}\rho_{43} & \Gamma_2\frac{1}{2}\rho_{44} \end{pmatrix} \quad (1.54)$$

Calculation parameters

As in the case of the two-level system, we can use the *optical Bloch equations* (1.43) to calculate either transient or steady-state population distributions ρ_{ab} . We have implemented the calculation in MATLAB by extending the code from Ref. 112. The effect of the oscillating Doppler shift caused by the micromotion of ions in a trap (see Section 3.1.1) is also implemented (for co-propagating lasers), parametrized¹⁶ by the trap frequency Ω_{RF} and velocity amplitude v_0 [112].

An overview of all parameters needed for a calculation is given in Table 1.5. Experimental values of the relevant atomic parameters for Ba^+ and Ra^+ are given in Table 1.6. Like in the case of the two-level system, the Rabi frequencies (1.50) can be conveniently expressed in terms of dimensionless saturation parameters S_k that we define as¹⁷

$$S_k = \frac{I_k}{I_{k,\text{sat}}} = \frac{2\Omega_k^2}{\Gamma_k^2}, \quad (1.55)$$

where $I_k = \frac{1}{2}c\epsilon_0\mathcal{E}_k^2$ is the intensity (irradiance) of light field k and the saturation

¹⁶Note that the code as given in Ref. 112 contains a bug where the actual velocity amplitude v_0 is doubled from the input value in steady-state calculations.

¹⁷This definition differs from Ref. 112, where $I_k/I_{k,\text{sat}} = 8S_{k(\text{Oberst})}^2$ is used.

Table 1.5 List of input parameters needed for the optical Bloch equations. Parameter subscripts 1, 2 refer to the $^2S_{1/2} - ^2P_{1/2}$ and $^2D_{3/2} - ^2P_{1/2}$ transitions and corresponding lasers, respectively.

Atomic parameters	
Transition wavelengths	λ_1, λ_2
Partial decay widths	Γ_1, Γ_2
Experimental parameters	
Laser intensities (Rabi frequencies)	Ω_1, Ω_2
Laser detunings	$\Delta\omega_1, \Delta\omega_2$
Laser polarization states	$(\alpha_1, \beta_1), (\alpha_2, \beta_2)$
Laser linewidth	γ_l
Laser propagation direction	(θ_l, ϕ_l)
Magnetic field vector	$\mathbf{B}$
Ion micromotion velocity amplitude	v_0
Trap frequency	Ω_{RF}

intensities are calculated from the spontaneous emission rates:

$$I_{k,\text{sat}} = \frac{\pi\hbar c}{3\lambda_k^3} A_{J'_k J_k}. \quad (1.56)$$

A Gaussian beam with waist radius w_k and total power P_k has peak intensity [36]

$$I_k = \frac{2}{\pi w_k^2} P_k. \quad (1.57)$$

Instead of the angular frequency detunings $\Delta\omega_k$, we generally use $\Delta\nu_k = \Delta\omega_k/2\pi$.

Example calculation results

An example calculation of transient behavior in Ba^+ is depicted in Fig. 1.6, showing the optical pumping from the $^2S_{1/2}$ ground state into the $^2P_{1/2}$ and $^2D_{3/2}$ levels. At first, the $^2P_{1/2}$ level is populated due to pumping by laser 1 (at 494 nm) and subsequently decays back to either the $^2S_{1/2}$ level or the $^2D_{3/2}$ level. The latter is repumped by laser 2 (at 650 nm). Initially damped Rabi oscillations are visible; after some time an equilibrium is reached with most population in the $^2D_{3/2}$ level and some population continuously pumped into the short-lived $^2P_{1/2}$ level. Steady-state values are reached after a time of order μs .

Often we want to calculate spectra to compare to experimental data, where we measure fluorescence from the decay of the $^2P_{1/2}$ level. The intensity of the observed

Figure 1.6 Example calculated transient behavior of populations in the three Ba^+ levels: $6s^2S_{1/2}$ ($\rho_{11} + \rho_{22}$), $6p^2P_{1/2}$ ($\rho_{33} + \rho_{44}$) and $5d^2D_{3/2}$ ($\rho_{55} + \rho_{66} + \rho_{77} + \rho_{88}$). Parameters are those of Fig. 1.7 at detuning $\Delta\nu_2 = 0$ MHz, starting with all population in the ground state. Calculated steady-state values are given as dashed lines.

Figure 1.7 Example calculated Ba^+ steady-state spectrum varying the 650 nm laser detuning $\Delta\nu_2$, showing (a) P level population and (b) real and imaginary parts of coherences (off-diagonal ρ elements). The 494 nm light is linearly polarized parallel to the magnetic field; the 650 nm light is circularly polarized. Dark resonances appear at detunings where the combined energy of a photon from each light field matches the energy difference between a pair of $^2S_{1/2}$ and $^2D_{3/2}$ sublevels, driving the corresponding coherence. Parameters: $S_1 = 5$, $S_2 = 25$, $\Delta\nu_1 = -5$ MHz, $(\alpha_1, \beta_1) = (0^\circ, 0^\circ)$, $(\alpha_2, \beta_2) = (0^\circ, 90^\circ)$, $\gamma_l = 100$ kHz, $(\theta_l, \phi_l) = (90^\circ, -90^\circ)$, $\mathbf{B} = (0, 0, 1 \text{ mT})$, $v_0 = 0 \text{ m/s}$.

Table 1.6 Wavelengths, partial decay rates and saturation intensities for the relevant transitions in Ba^+ and Ra^+ . The partial decay rates for Ra^+ have not been experimentally determined; the quoted values are calculation results.

Atomic transition	λ_k (nm)	Γ_k ($10^7/\text{s}$)	$I_{k,\text{sat}}$ (mW/cm^2)
Ba^+			
$6s\ ^2\text{S}_{1/2} - 6p\ ^2\text{P}_{1/2}$	493.55 [50]	9.32(1) [114]	16.1
$5d\ ^2\text{D}_{3/2} - 6p\ ^2\text{P}_{1/2}$	649.87 [50]	3.38(2) [115]	2.6
Ra^+			
$7s\ ^2\text{S}_{1/2} - 7p\ ^2\text{P}_{1/2}$	468.35 [51]	10.6(0.2) [106]	20.4
$6d\ ^2\text{D}_{3/2} - 7p\ ^2\text{P}_{1/2}$	1079.09 [51]	1.66(1) [106]	0.17

fluorescence depends linearly on the $^2\text{P}_{1/2}$ level population. Calculating this population ($\rho_{33} + \rho_{44}$) as function of laser parameters, e.g. when scanning one of the lasers across the corresponding atomic resonance, gives us spectra such as the one shown in Fig. 1.7. Here the detuning of laser 2 is varied, while the frequency of laser 1 is kept constant at a detuning of $\Delta\nu_1 = -5\text{ MHz}$. The spectrum consists of a wide one-photon resonance with a natural linewidth of $\Gamma = 2\pi \times 20.2\text{ MHz}$ with a number of narrow dark resonances centered around $\Delta\nu_2 = \Delta\nu_1$, dependent on the polarization states of the two lasers. The latter effect is known as electromagnetically induced transparency (EIT) or coherent population trapping. The dark resonances are caused by a two-photon process similar to Raman transitions that occurs when the combined energy of a photon from each light field matches the energy difference between sublevel a of $^2\text{S}_{1/2}$ and sublevel b of $^2\text{D}_{3/2}$, driving the corresponding coherence ρ_{ab} (see Fig. 1.7b) to bring the ion into a superposition of the two states. The related frequency condition is $\Delta\nu_1 + \Delta\nu_2 = (2m_a - \frac{4}{5}m_b)\omega_B/2\pi$, with $\omega_B = 2\pi \times 14\text{ MHz}$ in this example and taking the Landé factors from Eq. (1.42).

Using the optical Bloch equations, we can also study the sensitivity of the spectra to the various parameters from Table 1.5. Figure 1.8 illustrates the dependence of the spectral shape on a number of parameters. The saturation parameters (laser intensities) S_1 and S_2 affect the spectral shape in different ways, S_2 mostly changes the level of fluorescence without affecting the spectral shape much. Note that saturation effects like the broadening of various features of the spectrum as function of S_k are not directly comparable to the two-level case of Eq. (1.35) due to optical pumping. The magnetic field magnitude $|\mathbf{B}|$ determines the frequency spread of the dark resonances around the $\Delta\nu_2 = \Delta\nu_1$ point. The linewidth of the lasers γ_l especially dampens the coherences, affecting the sharpness of the dark resonances.

Figure 1.9 shows how the shape of spectra depends on the polarization states of the two light fields. The magnetic field and laser saturation parameters differ somewhat

Figure 1.8 Dependence of the Ba^+ spectrum of Fig. 1.7 (dashed) on various parameters: varying (a) 494 nm laser saturation parameter S_1 , (b) 650 nm laser saturation parameter S_2 , (c) magnetic field strength $|\mathbf{B}|$, (d) laser linewidth γ_l .

Figure 1.9 Example Ba^+ spectral shapes for different combinations of polarization states of the 494 nm (rows) and 650 nm lasers (columns). Parameters: $S_1 = S_2 = 10$, $\gamma_l = 500 \text{ kHz}$, $\mathbf{B} = (0, 0, 0.5 \text{ mT})$, other values and axes as Fig. 1.7. Laser polarization determines which of the eight coherences between $^2S_{1/2}$ and $^2D_{3/2}$ produce dark resonances. In the left-most column, all population is pumped into dark states.

from the previous figures to more closely match typical experimental values (see caption). The combination of the polarization states of both light fields determines which of the eight coherences between the sublevels of the $^2S_{1/2}$ and $^2D_{3/2}$ levels are most prominent. For a magnetic field in z -direction, the (α_k, β_k) parameters that correspond to the four polarization states in Fig. 1.9 are $(0^\circ, 0^\circ)$, $(90^\circ, 0^\circ)$, $(0^\circ, 90^\circ)$ and $(0^\circ, -90^\circ)$, respectively.

The complete lack of fluorescence if the 650 nm laser light is polarized linearly parallel to the magnetic field (Fig. 1.9 left-most column) is because the $m = \pm 3/2$ states of the $^2D_{3/2}$ level are not coupled to the $^2P_{1/2}$ level then and thus all population ends up in these *dark states*. In general, dark states exist for all transitions where the multiplicity of the lower level is higher than that of the upper level and these must be destabilized for fluorescence to occur [116, 117]. Here the external magnetic field takes care of this for most polarization states; other solutions (e.g. when low magnetic field strength is desirable) include polarization modulation or utilizing unpolarized, incoherent repumping light.

In this chapter we have outlined the requirements posed on experiments that aim for a quantitative determination of the Weinberg angle in a single trapped ion. We have provided a detailed review of the systematic effects for an atomic parity violation measurement, as well as for an optical atomic clock based on Ba^+ or Ra^+ ions. We have developed a lineshape model for fluorescence spectra based on the optical Bloch equations and discussed how the relevant experimental parameters affect the signal. After introducing the trapping hardware and its characterization in the coming chapters, this lineshape model is put to use for analyzing experimental spectroscopy data in Chapters 4 and 5, enabling us to extract transition frequencies and light shifts.

Chapter 2

Experimental Apparatus

Here we provide a description of the experimental setup, techniques and some practical issues. We cover the various systems determining the environment of the trapped ions: the Paul trap, the vacuum system, the spectroscopy lasers, as well as the signal detection system. First the apparatus for creating and trapping ions is treated (Section 2.1), then the lasers and optics (Section 2.2) and finally the data acquisition and experiment control system (Section 2.3).

2.1 Single Ion Trapping

An ion with electric charge Q in an electric field $\mathcal{E}$ experiences a Coulomb force of

$$\mathbf{F}(\mathbf{x}) = Q\mathcal{E}(\mathbf{x}). \quad (2.1)$$

There is no static electric field configuration that confines a charged particle in three spatial directions simultaneously (Earnshaw's theorem) [108]; this limitation is overcome by using an oscillating electric field. The simplest configuration that can stably trap ions is an oscillating quadrupole field, with a frequency typically in the radio-frequency (RF) domain for traps of centimeter dimensions. This type of ion trap is known as the *Paul trap*¹⁸.

Various electrode configurations can be used to generate the quadrupole field; the two main categories are linear traps where the oscillating field provides two-dimensional confinement complemented with a static electric field, and axially-symmetric traps where the oscillating field provides three-dimensional confinement. A pure quadrupole field is created by using hyperbolically-shaped electrodes, but simpler electrode shapes also work and are often used in practice. In fact, any electrode geometry that produces a saddle point in the equipotential surfaces creates an electric field that to lowest order has a quadrupole shape around this point [108]. We discuss the hardware of our axially-symmetric three-dimensional trap here; the dynamics of such a hyperbolic Paul trap are examined in the next chapter.

¹⁸Named after Wolfgang Paul who invented this type of device in the 1950s and shared the Nobel Prize in Physics in 1989 for this work [118].

Figure 2.1 Basic design of the Paul trap for trapping ions: (a) drawing and (b) photograph (March 2013). The trap consists of copper electrodes mounted on a Macor holder; an AC and DC potential is applied between the ring and two end caps.

2.1.1 Hyperbolic Paul trap

The experiments described in this thesis were performed in hyperbolic Paul traps such as the one shown in Fig. 2.1. The trap consists of three electrodes made from oxygen-free high conductivity (OFHC) copper: a ring electrode situated between two end cap electrodes, all mounted on a Macor holder. The surfaces facing the ions were polished after machining and are shaped like hyperboloids of revolution. The ring electrode has an inner diameter of 5 mm and the tips of the end caps are 3.5 mm apart. An AC voltage is applied between the ring and the two end caps to make a quadrupole electric field for trapping ions in the center of the trap. Charge buildup on the Macor holder was prevented by applying a grounded thin layer of graphite from a solvent-free pencil to surfaces in direct line of sight of the trap center. The trap assembly is fastened to a copper base plate that is suspended from the top flange of the vacuum chamber.

This trap design with large, hyperbolically shaped electrodes provides a rather large trapping volume which is advantageous for trapping small samples of (radioactive) elements. On the other hand, optical access to the trapped ions is limited to the small gap between the electrodes (see Fig. 2.1b). In a later iteration, we drilled a hole all the way through the end cap electrodes and the bolts holding them to provide additional optical access along the trap axis. We also experimented with adding four correction electrodes to the ring, formed by wire ends inserted in holes drilled through the ring in radial direction. Additional details may be found in Ref. 119.

RF system

The trap is operated by applying a high voltage oscillating at RF frequency between the ring and end cap electrodes. We generate voltage amplitudes of up to about 1000 V

Figure 2.2 Overview of the RF system for generating trapping voltages of up to 1000 V; configuration implemented September 2015 with RF applied to the ring electrode. The signal from a function generator is attenuated, amplified and filtered before driving a resonant LC circuit. See main text for further details.

by driving a resonant LC circuit with the two-stage amplified signal from a function generator (see Fig. 2.2). The operating frequency is set by the resonant frequency of the resonator coupled to the trap. Two resonators were used during the experiments in this thesis; the first operated around 5.3 MHz and the second around 6.3 MHz, the resonant frequency depending also on which trap was connected to the circuit and whether the high voltage was connected to the ring or to the end caps (Fig. 2.2 shows the former configuration, with the end caps grounded).

The RF signal from the function generator (HP 33120A) is sent to a preamplifier (Mini-Circuits ZHL-1A+) feeding into an AM radio linear amplifier (RM KL500-24). Higher harmonics are suppressed by an 11 MHz low-pass filter (Allen Avionics HPLP-11P00-C-300-N). The final boost in voltage is provided by the LC circuit mounted in a brass cylinder on top of the vacuum chamber. Its resonance frequency $\Omega_{\text{RF}} \approx 1/\sqrt{LC_{\text{tot}}}$ is set by the inductance L of the toroidal air-core coil (of order 10^{-5} H) and the total capacitance (including C_{trap}). The circuit's impedance is determined by the capacitances and the internal resistance R_{int} (of order Ω) and is matched at resonance to the characteristic impedance $Z_0 = 50 \Omega$ of the amplifiers and transmission line. The voltage amplification ratio is then approximately $V_{\text{out}}/V_{\text{in}} \approx 1/(\Omega_{\text{RF}} C_1 Z_0) \approx 30$. A photograph of the circuit can be found in Ref. 119. For a precise calibration of the produced trap voltages, we use trapped ions as sensor as described in the next chapter.

An attenuation system is implemented after the function generator, before ampli-

cation. An earlier version consisted of a manual variable attenuator; the later version shown in Fig. 2.2 consists of several splitters (Mini-Circuits ZFRSC-42-S+/ZMSC-2-1), fixed attenuators and TTL-controlled switches. Including losses in the switches, this system provides four phase-coherent attenuation levels at about -15 dB, -18 dB, -30 dB and -47 dB with computer-controlled switching.

The RF amplitude is monitored at two points. Before the resonant circuit, an RF probe is inserted in the transmission line (Rohde & Schwarz URV35 with URV5-Z7 probe, 20 dB plug-on divider) and recorded by the data acquisition system. In addition, the circuit features a capacitive voltage divider (see Fig. 2.2), providing a pickup signal which is sent through a splitter to a spectrum analyzer and an oscilloscope to monitor the amplitude and spectral purity of the RF drive. The oscilloscope signal is used to tune the function generator frequency to the resonance of the LC circuit.

DC system

In addition to the AC potential, DC potentials can be applied to the end caps to produce a DC quadrupole field and/or compensate stray electric fields in the axial direction of the trap. A custom-built multi-channel power supply is used to individually bias the two end caps with respect to ground with mV resolution (as well as the four additional correction electrodes, if present). The power supply is battery powered and includes a read out of the voltages. The end cap voltages are also recorded by the data acquisition system. More details can be found in Ref. 119.

2.1.2 Vacuum system

The ion trap is mounted in an ultra high vacuum (UHV) chamber to reduce collisions with background gas molecules to a negligible level. To prevent the loss of ions from the trap and perturbations to their quantum states, we maintain the residual gas pressure below 10^{-10} mbar. The chamber of diameter 20 cm and height 25 cm (316L/316LN ESR stainless steel, vacuum fired and glass bead blasted) is rigidly mounted on an optical table (see Ref. 119 for a photograph of the chamber).

Pumping down the chamber is done in three stages. Initially, an oil-free roughing pump (Scroll Meister) is used to evacuate to about 10^{-3} mbar. A 70 L/s turbo-molecular pump (Leybold TURBOVAC TW70H) then takes over to reach a pressure around 10^{-8} mbar. Finally, a 75 L/s ion pump (Gamma Vacuum TITAN 75S) is used to reach and maintain UHV conditions with the turbo pump switched off. The ion pump is mounted some 20 cm from the trap on a 10 cm diameter flange.

To reach residual gas pressures below 10^{-10} mbar, the whole vacuum chamber is baked for several days at temperatures >120 °C. Whenever the vacuum needs to be broken, the chamber is vented with dry nitrogen to limit (re)accumulation of water. In addition to the ion pump, a titanium sublimation pump (Vacom SUBLI-CON51) is

periodically activated for about a minute to give a boost to the pumping speed and lower the pressure. A baffle blocks the direct path from the pump to the ion trap to prevent coating the trap with Ti atoms.

To measure the pressure, a nude UHV Bayard–Alpert type ion gauge (Granville–Phillips 274023) is installed in the vacuum chamber. Additionally, the ion pump current is monitored (functioning like a Penning gauge). During experiments, the ion gauge is usually switched off, as its hot cathode increases the pressure in the chamber. Both pressure measurements are continuously recorded by the data acquisition system.

2.1.3 Magnetic field coils

To control the magnetic field environment of the trapped ions, three pairs of rectangular coils are positioned around the vacuum chamber in a cubic arrangement. This enables us to compensate any (static) background magnetic field and apply a well-defined field $\mathbf{B}$ of typically 0.1 mT to 1 mT for resolving the degeneracy of Zeeman levels and remixing dark states in the fluorescence cycle. The pairs of opposing coils are wired together and have current supplied by a multichannel power supply (Rohde & Schwarz HMP4040). The use of low magnetic-susceptibility materials for the vacuum chamber and trap prevents distortions of the applied magnetic field. Further development would require installing magnetic shielding to improve magnetic field stability.

2.1.4 Ion sources

The conservative potential of an ion trap dictates that (without background gas collisions) ions are not captured unless the trapping field is switched on only after injection, or the ions are produced inside the trapping volume [108]. For loading Ba^+ ions into the trap, we use the latter method, photoionizing Ba atoms from a beam passing through the trap.

Ba oven

The oven producing a beam of ^{138}Ba atoms consists of a 30 mm stainless steel hypodermic needle with inner diameter 0.9 mm in a holder built from stainless steel and Macor. One end of the needle is crimped to close it. The oven assembly is mounted about 2 cm from the trap center on one side of a v-shaped copper piece (visible at the top of Fig. 2.1b). The needle is partially filled with a fine-grained mixture of isotopically enriched (99.7%, Campro Scientific) barium-138 carbonate ($^{138}\text{BaCO}_3$) and zirconium powder. The needle is resistively heated with DC current from a computer-controlled power supply (Delta Elektronika ES015-10). The open end of the needle sticks out of the holder a bit and remains cold to produce a collimated beam.

A vapor of barium atoms is produced by a chemical reaction in vacuum. The details of the reaction taking place in the oven remain somewhat elusive, but the barium is

Figure 2.3 Partial energy level diagram of (a) neutral barium [50] and (b) radium [51] illustrating possible photoionization excitation pathways. We produce Ba^+ ions by ionizing ^{138}Ba atoms with two 413 nm photons via the $5d6p \text{ } ^3D_1$ level.

freed from the carbonate in a two-step process reacting with the zirconium powder (some groups use tantalum powder instead [47, 120]). After initially heating the oven to $>1000^\circ\text{C}$, we can operate the oven at lower temperatures to produce a beam of barium atoms. At a typical current of 6.5 A, the oven produces an atom flux of order 10^6 s^{-1} [49]. The outgassing rate of the oven is low after initial heating and we can reload the trap for months before the oven needs to be refilled (for a constant flux, we increase the current over the oven's lifetime, typically until the needle breaks). See Refs. 49, 119 for additional details and tests of the oven by detecting neutral barium fluorescence at wavelength 554 nm.

Photoionization

We create barium ions inside the trapping volume by resonantly photoionizing ^{138}Ba atoms from the oven. An earlier iteration of the experiment used electron impact ionization to load large numbers of ions [49], but photoionization has several key advantages. Photoionization limits charge deposition on trap components, minimizing (variation in) stray electric fields disturbing the trap potential. It is several orders of magnitude more efficient, reducing the required vapor pressure from the oven. Adjustments to the ionization laser system can be made without breaking the vacuum. Finally, photoionization via resonant transitions is isotope selective.

Various excitation pathways are possible for photoionizing neutral barium (see Fig. 2.3a). Single-photon photoionization would require UV radiation of wavelength

<238 nm, which is technically involved and causes problems with photoelectric charging, while lacking isotope specificity. Neglecting atomic resonances, the ionization potential is reached by two photons of <476 nm. We successfully implemented this two-photon method as a first attempt at photoionization using a diode laser operating at wavelength 405 nm. However, a greatly increased ionization cross section and isotope selectivity are achieved with a resonant first step (or multiple resonant steps). The subsequent excitation to the continuum does not require a narrow-band light source, although efficiency can be enhanced by tuning to an autoionizing resonance. Several such schemes have been implemented for barium [121–123], starting either with the strong 554 nm transition to the $6s6p\ ^1P_1$ level, the 791 nm transition to $6s6p\ ^3P_1$ or the 413 nm transition to $5d6p\ ^3D_1$ (see Fig. 2.3a). The last option has the distinct advantage that the $5d6p\ ^3D_1$ level lies above the halfway point to the ionization potential, so that a second 413 nm photon can then ionize the atom. Although its first step is not the most efficient since the 413 nm transition is a weak intercombination line, we chose this simple resonant photoionization scheme as it requires only a single laser.

We operate a Sanyo DL5146-101S laser diode in ECDL (external-cavity diode laser) configuration at a temperature of about 75°C to reach the resonance wavelength of 413.359 22 nm [50]. A neutral density (ND) filter wheel and a Glan–Thompson polarizer attenuate the laser power to a few mW (see Fig. 2.6). The laser beam is directed into the trap by a dichroic mirror (Thorlabs DMLP425). Ideally, the photoionization laser beam would be perpendicular to the atomic beam to minimize the Doppler effect, but in our current setup both beams are aimed between the trap electrodes, one in the horizontal plane and one in the vertical plane, giving an angle of 71° . A wavelength meter (WLM) monitors the wavelength of the free-running laser (HighFinesse/Ångstrom WS6 UV), which is sufficiently accurate to tune the laser to the Doppler-broadened resonance with a FWHM of about a GHz. With better control of the laser frequency and a perpendicular beam configuration, isotope selective loading would be possible.

Using resonant photoionization we are typically able to load a single Ba^+ ion within seconds, adjusting the laser intensity and oven temperature to control the loading rate. After loading, we manipulate the RF amplitude in an attempt to bring all loaded ions into the laser cooling beams. The trap is generally reloaded every few hours; the barium oven is turned off and the photoionization laser blocked during measurements.

Figure 2.3b shows some of the possible two-step photoionization paths in radium. The ionization potential is very similar to barium, requiring a wavelength of <470 nm for nonresonant two-photon photoionization. Note that isotope selectivity would not be that important in the case of radium, as a source would typically only produce a single isotope of the radioactive element. The particularly simple resonant photoionization scheme we use in barium does not have an exact analogue in radium, since the corresponding level $6d7p\ ^3D_1$ lies at significantly higher energy. Recently, photoionization of radium has successfully been implemented at the TRIUMF and

Figure 2.4 Offline $^{223}\text{Ra}^+$ ion source design: (a) generation of ^{223}Ra from ^{227}Ac , (b) technical drawing. In a separate setup, radium is collected on a needle (1) mounted on a linear manipulator (2). For loading, the needle is quickly inserted into a tube (3) heated by wires (4) to release Ra^+ ions (and atoms) into an ion trap (5).

ISOLDE accelerator facilities [124, 125] to increase the yield of radioactive ions over surface ionization (using schemes with more than two excitation steps). In any case, the radioactivity of radium prevents us from simply filling an oven as with barium and we took the first steps to build a radium ion source using a different approach, detailed in the next section.

Offline Ra^+ source design

Except for the longest-lived isotope ^{226}Ra ($t_{1/2} = 1600\text{ yr}$), radium isotopes generally need to be produced before any trapping is done. Radiation safety is a major concern in working with radioactive materials and complicates experiments. An ideal radium source would be efficient (minimizing contamination), controllable (facilitating single ion loading) and simple to operate. One method is to use a particle accelerator. This technique is used at the TRIUMF [124] and ISOLDE facilities [125] and has previously been used in our group to study the neutron-poor isotopes $^{209-214}\text{Ra}$ [45, 49, 64]. However, for further experiments an offline source was desired for greater flexibility and simplicity.

Several experimental groups use radium isotopes produced at an accelerator facility, shipped after implantation on a filament [126] or as a dissolved radium salt [66, 127]. We investigated the possibility of using one of two offline Ra sources already available at the (former) KVI institute. In both cases, a radium isotope is generated from the decay of a longer-lived parent.

The first source was one developed for experiments on neutral radium and comprises

an oven containing 370 kBq of ^{229}Th ($t_{1/2} = 7300\text{ yr}$), which α -decays to ^{225}Ra ($t_{1/2} = 15\text{ d}$) [128]. Heating the oven produces an atomic beam of radium, which could in principle be coupled to an ion trap using (photo)ionization. We have established a protocol to deal with the radiation safety aspects of opening and modifying the oven setup but did not pursue this further at the time.

The second option was an ^{227}Ac ($t_{1/2} = 22\text{ yr}$) source generating ^{223}Ra ($t_{1/2} = 11\text{ d}$) through an intermediate step (see Fig. 2.4a) [129]. This source is used as follows: the α -decay of ^{227}Th releases enough energy for ^{223}Ra ions to recoil out of the open source. Placing a needle at a negative electric potential close to the source under a He atmosphere collects radium on the needle tip. The needle can then be transferred to another setup and was used as a ^{219}Rn source (α -decay product of ^{225}Ra). In our case, we would like to use the radium itself and we took initial steps in designing and building an apparatus for this.

The design of the offline $^{223}\text{Ra}^+$ source is shown in Fig. 2.4b. After collecting sufficient radium, the needle holder is (re)connected to the vacuum vessel containing the ion trap, which is then pumped down. The needle is mounted on a linear manipulator which is used to quickly insert it into a W tube heated to about 1000°C by a W filament. Through surface ionization, a fraction of the collected ^{223}Ra would be released as singly-charged ions and these can then be trapped, using buffer gas for initial cooling of the ions. A drawback of this design is that each needle can only be used once for loading and replacing it requires breaking the vacuum of (a section of) the setup. At least collecting ^{223}Ra on multiple needles at once should be possible. Parts for this setup have been manufactured but not yet tested in this PhD project. Moving forward, the first step would be to test and optimize the setup with barium. Alternatively, the ablation technique of Ref. 66 could be tried after collecting ^{223}Ra on a suitable substrate. In the rest of this thesis we focus on the experiments with trapped $^{138}\text{Ba}^+$ ions.

2.2 Laser Cooling and Spectroscopy

To laser cool Ba^+ ions, we excite the $6s\ ^2\text{S}_{1/2} - 6p\ ^2\text{P}_{1/2}$ transition at wavelength 494 nm and repump the long-lived $5d\ ^2\text{D}_{3/2}$ level via the transition at 650 nm (see Section 1.3.3). Emission of 494 nm photons from the $6p\ ^2\text{P}_{1/2}$ level decaying back to the ground state is used to detect the ions and perform spectroscopy.

2.2.1 Light sources

For high precision spectroscopy, we need narrow-linewidth CW lasers operating at 494 nm and 650 nm. Simplest to operate are semiconductor diode lasers, which are available for these wavelengths (using second harmonic generation for 494 nm [130]).

Figure 2.5 Optical diagram of the spectroscopy lasers. Light at 494 nm for cooling and detection is produced by SHG of light from a Ti:sapphire laser in a PPLN crystal; the light is then single-passed through AOM-1. Light at 650 nm for repumping is produced by a dye laser, offset-locked to an iodine-stabilized laser; the light is double-passed through AOM-2, overlapped with the other beam and sent into an optical fiber. Each beam can be blocked by a mechanical shutter. See main text for further details.

A typical diode laser in ECDL configuration has a linewidth of order MHz, which can be narrowed using a high-finesse cavity. However, we opted to use two laser systems already available to us: an ultra-stable tunable Ti:sapphire laser and a tunable dye laser. To increase stability, the laser systems are situated in a separate lab from where the ion trap setup is located. The light is transported through single-mode optical fibers of about 50 m length. For some experiments, additional Ba^+ repump transition need to be addressed without the need for precise frequency control. Our setup incorporates two fiber-coupled LEDs for this purpose. All optics are set up on optical tables with active self-leveling isolators.

Spectroscopy lasers

Light at wavelength 494 nm^{19} to drive the $\text{Ba}^+ 6s^2S_{1/2} - 6p^2P_{1/2}$ transition is produced by second harmonic generation (SHG) of light at 987 nm from a single-frequency Ti:sapphire laser (Coherent MBR-110). The Ti:sapphire laser has a linewidth of order 100 kHz and is pumped by 532 nm light from a solid-state laser (Coherent Verdi v10). The infrared light is transported to the ion trapping lab before frequency doubling to limit losses in the optical fiber. Second harmonic generation occurs in a temperature-tuned MgO-doped periodically-poled lithium niobate (PPLN) crystal

¹⁹In some labs, the 494 nm laser is referred to as the *blue* laser, while in others it's called *green*. Somehow the more accurate description as *cyan* is not very popular.

(Covesion MSHG976-0.5) inside a linear cavity (see Fig. 2.5). Quasi-phase matching is achieved by heating the crystal to 156.8 °C. Typically, around 100 mW of 987 nm light is coupled into the crystal to generate 5 mW of 494 nm light in both directions. Dichroic mirrors (DM) are used to separate the two wavelengths. The SHG process is monitored using a beamsplitter (BS) to send a fraction of the light to a photodiode (PD) and a Fabry–Pérot interferometer. A computer-controlled mechanical shutter can block the 494 nm light from reaching the trap. An acousto-optic modulator (AOM-1) shifts the frequency and can be used for power stabilization. The first-order diffracted beam goes through a half-wave plate ($\lambda/2$) and is coupled to the trapping setup via a single-mode optical fiber.

The frequency of the IR light is roughly measured by a WLM (HighFinesse/Ångström WS6 IR). The internal cavity lock of the Ti:sapphire stabilizes the frequency to the level of several MHz. To achieve frequency stability of order 5 kHz, the Ti:sapphire laser is locked to an optical frequency comb (Menlo Systems FC1500-250) with its long-term stability derived from a GPS-disciplined Rb frequency standard (SRS FS725). We discuss determining the 494 nm optical frequency in more detail in Chapter 4.

Light at wavelength 650 nm to drive the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition is produced by a single-frequency ring dye laser (Coherent CR-699), also pumped by the Verdi v10. The dye laser is stabilized to an internal reference cavity and has a linewidth of about 500 kHz. It is operated with 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) dye dissolved in a mixture of benzyl alcohol and ethylene glycol. The coarse frequency of the dye laser is monitored by the same WLM used for the photoionization laser at 413 nm (HighFinesse/Ångström WS6 UV) using a multiplexer. Typically, about 20 mW is delivered to the ion trapping lab and sent through an optical isolator (OI) (see Fig. 2.5). Using a polarizing beamsplitter (PBS) and a quarter-wave plate ($\lambda/4$), the beam is double-passed through AOM-2 (selecting the first diffraction order) to shift the frequency without changing the beam pointing. The 650 nm beam passes a computer-controlled mechanical shutter and is combined with the light at 494 nm in a polarizing beamsplitter before being transported to the trapping setup.

The dye laser is offset-locked to a diode laser also operating at 650 nm that is locked to a molecular I_2 reference. The lock signal is derived from a beatnote between both lasers on a high-bandwidth silicon photodiode. Additional details on the frequency locking scheme are given in Chapter 4. For diagnostic purposes, a fraction of the light from the dye laser is also sent to a photodiode and a Fabry–Pérot interferometer.

In addition to control over the laser frequencies and intensities, we need to overlap the beams with the trapped ion(s) position and control the polarization. This is achieved with the optics and diagnostics set up around the vacuum chamber that houses the ion trap (Fig. 2.6). The single-mode fiber transporting the combined 494 nm and 650 nm laser beams produces a clean Gaussian mode. A set of achromatic lenses (L1 and L2) produces a focus at the trap center located about 170 cm downstream with

Figure 2.6 Optical diagram of light sources and diagnostics around the vacuum chamber (not to scale). Spectroscopy laser light at 494 nm and 650 nm is transferred from the laser table (Fig. 2.5); before and after the trap, the intensity of both lasers is measured with photodiodes and power meters. Lenses $L1$ and $L2$ produce a focus at the trap center; a set of mirrors on piezo motor mounts steers the beam. Light from two fiber-coupled LEDs for (de)shelving can be added to the beam and light from the 413 nm photoionization laser is sent through the trap in counter-propagating direction. See main text for further details.

a waist radius ($1/e^2$) of order $100\text{ }\mu\text{m}$. Typically, intensities of up to 100 mW/cm^2 are reached for both wavelengths. Polarization of the light is set by a Glan–Taylor polarizer and a combination of $\lambda/2$ and $\lambda/4$ plates. Two mirrors on computer-controlled piezo motor mounts (Newport Agilis AG-M100N) steer the bichroic beam. Its position and shape is monitored by splitting off a fraction of the light with a pellicle beamsplitter to a position sensor (PS) (Thorlabs PDP90A) and beam profiler (Thorlabs BC106-VIS) located at approximately the same distance as the trap center. Before and after the trap, the power of both components of the beam are monitored by photodiodes (Thorlabs SM1PD1A) and power meters (PM) (Thorlabs S120C), separating the components using dichroic mirrors and low-pass/high-pass filters. Most of the light is dumped on a power meter (Thorlabs S140C) after the trap.

The light enters the vacuum chamber through 3 mm thick glass windows with a custom anti-reflective coating. The windows are angled about 5° by mounting them on bellows. A set of three apertures is mounted inside each window to act as a light baffle minimizing stray light. All apertures have been blackened with UHV-compatible paint. Finally, the light from the photoionization laser at 413 nm discussed in Section 2.1.4 is sent through the trap in counter-propagating direction (see Fig. 2.6). Additional

Figure 2.7 Imaging optics for the PMT and the EMCCD camera (size of trap and optics exaggerated, locations to scale). To maximize light collection to the PMT, a lens is mounted in vacuum close to the trap. Magnification of 16 $\times$ is achieved for the EMCCD camera image. All optics are housed in lens tubes.

lasers used for light shift experiments are discussed in Chapter 5.

Incoherent light sources

In addition to the spectroscopy lasers, our optical setup (see Fig. 2.6) includes two fiber-coupled LEDs to drive transitions where precise control over frequency is not needed (e.g. in measurements using electron shelving). The first LED (Thorlabs M455F1) produces light at wavelength 456 nm to drive the $\text{Ba}^+ 6s^2S_{1/2} - 6p^2P_{3/2}$ transition. A band-pass filter with 10 nm bandwidth (Thorlabs FB450-10) is installed to block any light at other wavelengths from reaching the ions. The light is combined with the spectroscopy laser beam using a dichroic mirror (Thorlabs DMLP490), reflecting only the light at 456 nm and transmitting the longer wavelengths. A second LED (Thorlabs M617L3) can be used to drive the $5d^2D_{5/2} - 6p^2P_{3/2}$ (deshelving) transition at 614 nm. A notch filter (Edmund Optics #67-111) is used to also overlap this light with the spectroscopy laser beam going into the vacuum chamber.

2.2.2 Signal detection

Laser-induced fluorescence is our primary means of gleaning information from the trapped ions. The experimental setup includes a light collection system on opposite sides of the ion trap for detecting fluorescence at wavelength 494 nm from decay of the $6p^2P_{1/2}$ level to the ground state (see Fig. 2.7). A photomultiplier tube (PMT) on one side provides time resolution and an electron multiplying (EMCCD) camera on the other side provides spatial resolution.

Photon counting

The count rate of the PMT (Hamamatsu H11123) is recorded per 100 ms interval. The imaging system includes a 1" lens (L1) mounted in vacuum on the copper base plate about 4 cm from the trap center to maximize light collection (see Fig. 2.7). The maximum solid angle of light collection set by the trap geometry and in-vacuum lens is 0.1 sr; apertures to block stray light reduce the solid angle to about 0.03 sr. The PMT has a quantum efficiency of about 15 % at 494 nm. At saturation, we typically get a signal of about 1000 cnt/s per ion. Also mounted on the base plate is a blackened 1 mm slit placed in the beam path of the spectroscopy lasers to reduce laser light scattering. Outside the vacuum chamber window, the PMT optics include several apertures to select only light originating from the trap center. A band-pass filter (Edmund Optics #65-148) with 10 nm bandwidth blocks light at wavelengths other than 494 nm. Room lights still cause a small increase in the observed count rate and are switched off during measurements. To reduce thermal noise, we cool the cathode of the PMT to 13 °C (well above the dew point) with an in-house built cooling system to arrive at a dark count rate of some 10 cnt/s. With these measures, we get a background including scattered laser light of typically 100 cnt/s.

EMCCD camera

The EMCCD camera optics form a telescope with a magnification of 16× in its latest iteration (see Fig. 2.7 and Fig. 3.3c). The 2" objective lens (L5) can be moved perpendicularly to choose the image center and the 1" ocular lens (L6) is mounted in a zoom housing to adjust the focus. Apertures suppress stray light. The spatial resolution is typically about 6 μm in object space (radius of first minimum of observed Airy pattern), corresponding to a numerical aperture of $NA = 0.05$. The EMCCD camera (Andor iXon DU-897E-CSB-#BB) has 512×512 pixels with a pitch of 16 μm. The camera features internal cooling to reduce thermal noise and amplification to obtain nice images within an exposure time of order 1 s.

2.3 Data Acquisition and Experiment Control

As part of this thesis project, a data acquisition (DAQ) system has been developed for monitoring the status of the Ba^+ experiments, storing spectroscopy data and remotely controlling various parameters. It is based on **Caddie**²⁰, a data acquisition and control program written in C++ that was developed at KVI for the TRIP program. **Caddie** can be run on multiple platforms, including Windows, Linux and ELinOS (embedded Linux). The DAQ for the Ba^+ experiments consists primarily of several **Caddie** instances in a computer network that are configured to acquire data from

²⁰Developed by F. Zwarts, KVI.

Figure 2.8 Schematic overview of the data acquisition and control system for the Ba^+ experiments. Solid lines indicate data flow handled by several instances of the *Caddie* program. Data storage and online display is implemented in *Bogey*. Dashed lines indicate computer control of equipment through the *ExpControl* user interface.

and/or control particular hardware systems, with a master node combining all data streams (see Fig. 2.8).

2.3.1 Data, display and storage

The heart of the data acquisition is formed by a VME crate with several electronics modules for converting analog signals to digital (see Fig. 2.8):

Scalers (two SIS 3820). Most signal are digitized by counting a pulse frequency, including the discriminated PMT signal, synthesizer frequencies, beatnote frequencies and various voltages after passing through a voltage-to-frequency converter (photodiodes, pressures, AC and DC trap potentials). Normalization is provided by the internal 50 MHz clock of the scaler modules (10^{-5} accuracy).

GPS clock (Symmetricom TTM637VME). The high precision time base provided by a GPS-derived 10 MHz signal is also sent to the scalers and can be used to correct the scaler count rates.

Time-to-digital converter (Caen V1290N). In addition to the PMT count rate, the correlation between the times of photon detection and the RF cycle is recorded

(see Section 3.4). The TDC module is operated in Trigger Matching Mode, using the discriminated PMT signal and discriminated RF signal as inputs.

I/O registers (two Caen V977). One input/output register is used for generating TTL-signals to control various experimental hardware (see next section) with the second module reading back these states.

The interface to the modules is provided by a CPU board (MEN A19) running **Caddie** on Linux. Analog signal processing and logic is done with modular NIM electronics. Every 100 ms the VME modules are read out, producing a data event.

Three PCs run additional **Caddie** instances collecting data from other hardware (see Fig. 2.8). The choice of operating system was dictated by the physical interfaces and availability of hardware drivers. The first computer runs **Caddie** on Windows and is connected to various laser diagnostics via USB. It continuously acquires data from the power meters, producing a data event whenever a meter has a reading ready. The second computer contains the PCI card connecting to the EMCCD camera and runs **Caddie** on Linux, producing a data event whenever the camera has acquired an image at the chosen exposure settings. The final **Caddie** instance runs on a Windows computer in the laser lab, collecting data from the frequency comb via its web server which refreshes data every 1 s.

The aforementioned **Caddie** instances are all configured as slaves of the master node on the main computer in the ion trapping lab. This **Caddie** instance combines the data streams and has a simple user interface to start/stop taking data. This computer also serves as NTP time server in the local network to keep all computer clocks synchronized. The final element in the DAQ is a program called **Bogey** that was also developed in-house and greatly expanded for this thesis project. It is built on the **ROOT** data analysis framework²¹ and is written in C++. When the master **Caddie** program starts streaming data, **Bogey** stores it in duplicate on two external disks and provides online display of crucial experimental parameters.

2.3.2 Experiment control

Several aspects of the experiment are controlled remotely from the main lab computer (see Fig. 2.8). **Caddie** can be configured to provide a network server for controlling hardware connected to the computer it is running on and this operates independently of data streaming. One of the mentioned I/O registers in the VME crate produces TTL signals to set the RF attenuation level (see Section 2.1.1), toggle laser shutters (see Section 2.2.1) and signal the AOM-2 synthesizer to start a frequency scan of the 650 nm light. The computer connected to the laser power meters also controls two rotation stages with optics used in the experiments detailed in Chapter 5. In addition, the power supply for the barium oven has a network interface for remote control.

²¹<https://root.cern.ch/>

A convenient way to control the experimental systems has been developed under the name **ExpControl**. This program is also based on **ROOT** and provides a graphical user interface for toggling and adjusting parameters. Additionally, it supports the programming of simple patterns, e.g. a sequence taking about 30 s for loading ions with a single button push: letting the oven heat up, then briefly unblocking the photoionization laser, while adjusting the RF amplitude and finally unblocking the lasers for cooling and detection. Though not currently implemented, the VME crate includes an 8-channel 12-bit analog output module (MEN M11) that could be used for continuously variable control.

Other systems were controlled from the lab computer through their dedicated user interfaces and are not integrated into **ExpControl** at present. This includes the piezo motors steering the spectroscopy laser mirrors and setting the frequency comb repetition rate frequency. Also with regards to data acquisition, some hardware, including beam profilers and wavelength meters, are not currently included in the **Caddie** data stream and could still be integrated.

In this chapter we have introduced the experimental apparatus used for the experiments in this thesis. In addition to describing a design for a Ra^+ ion source, we have discussed our setup for single $^{138}\text{Ba}^+$ ion trapping, including the lasers and data acquisition system used for the optical fluorescence measurements in the following chapters.

Chapter 3

Characterizing the Ba^+ Ion Trap

The defining characteristic of ions is their nonzero electric charge, causing them to experience a force in electric fields. This can be used to guide or trap ions by designing suitable electric field configurations. We achieve three-dimensional confinement in a Paul trap by using a quadrupole electric field oscillating at a suitable frequency.

In this chapter we first summarize the dynamics of an ion confined in a Paul trap (Section 3.1). The behavior of a trapped ion when varying the trapping parameters is then used to determine the amplitude of the oscillating electric field at the ion's position, which is difficult to measure directly (Section 3.2). We take a closer look at the requirements on the trapping parameters to provide stable confinement (Section 3.3) and the influence of an ion's movement in the trap on its fluorescence (Section 3.4). The behavior of multiple ions confined together in the same trap is studied (Section 3.5), showing what information is contained in ion configurations imaged by the EMCCD camera. Finally, we discuss how to determine ion temperature (Section 3.6).

3.1 Ion Trapping Dynamics

The experiments described in this thesis are performed in an axially-symmetric Paul trap (see Section 2.1.1). It consists of a ring electrode between two end caps (see Fig. 3.1); the surfaces of the electrodes form parts of two hyperboloids of revolution. In an ideal hyperbolic Paul trap, the potential at position $\mathbf{x} = (x, y, z)$ created by applying an oscillating voltage between the ring and the end caps is given by [108, 118]

$$\Phi(\mathbf{x}, t) = \frac{U_0 + V_0 \cos \Omega_{\text{RF}} t}{2d^2} (2z^2 - x^2 - y^2), \quad (3.1)$$

where V_0 is the amplitude of the applied AC voltage at frequency Ω_{RF} , U_0 is the applied DC voltage and $d^2 = \frac{1}{2}r_0^2 + z_0^2$ is the characteristic dimension of the trap with end caps separated by $2z_0$ and center ring radius of $r_0 = \sqrt{2}z_0$. This is an oscillating quadrupole field with its node at the coordinate origin. The chosen ratio of the dimensions creates the purest quadrupole field and therefore the largest effective trapping range.

Figure 3.1 Schematic diagram of a hyperbolic Paul trap, consisting of a ring electrode between two end caps. In the setup used for the experiments in this thesis, the inner radius of the ring is $r_0 = 2.5$ mm and the half-distance between the end cap electrodes is $z_0 = 1.77$ mm. The trap-based coordinate system is also shown.

3.1.1 Equations of motion

The motion of a charged particle moving in the potential defined by Eq. (3.1) is described by a set of decoupled Mathieu equations [108, 109, 118]:

$$\begin{aligned} \frac{d^2x}{d\tau^2} + (a_x - 2q_x \cos 2\tau) x &= 0 \\ \frac{d^2y}{d\tau^2} + (a_y - 2q_y \cos 2\tau) y &= 0 \\ \frac{d^2z}{d\tau^2} + (a_z - 2q_z \cos 2\tau) z &= 0. \end{aligned} \quad (3.2)$$

Due to the axial symmetry of the trap, the coefficients in the equations for the radial directions x and y are identical. The dimensionless radial and axial stability parameters for a particle with mass m and electric charge Q are given by

$$\begin{aligned} a_x = a_y = a_r &= -\frac{4QU_0}{md^2\Omega_{\text{RF}}^2} & a_z &= -2a_r \\ q_x = q_y = q_r &= \frac{2QV_0}{md^2\Omega_{\text{RF}}^2} & q_z &= -2q_r \end{aligned} \quad (3.3)$$

and the dimensionless time variable is given by

$$\tau = \frac{\Omega_{\text{RF}}}{2} t. \quad (3.4)$$

The equations of motion (3.2) have stable solutions for some ranges of the stability parameters a_i and q_i (where $i = x, y, z$) as shown in Fig. 3.2. The regions with stable

Figure 3.2 Lowest order stability region for an ideal hyperbolic Paul trap [109], taking into account both radial and axial stability. Stable solutions do exist in some regions at larger values of a_i and q_i , but these are not used for ion trapping. Lines of constant values of the secular frequency parameters β_r and β_z are indicated.

solutions are generally plotted in terms of a_z and q_z , taking into account also the limits on a_r and q_r . Note that the stability diagram is symmetric in $\pm q_z$ and the sign of q_z is usually taken positive.

In the case $|a_i|, |q_i| \ll 1$, an approximation to the equations of motion can be made [108]. In this so-called adiabatic approximation, the motion of ions is described as a combination of two oscillations: a fast oscillation (*micromotion*) at the trap frequency Ω_{RF} and a slow oscillation (*secular* or *macromotion*) at frequency $\omega_{\text{sec},i}$ in a harmonic pseudopotential:

$$u_i(t) = A_i \cos(\omega_{\text{sec},i}t + \phi_i) \left(1 - \frac{q_i}{2} \cos(\Omega_{\text{RF}}t)\right) \quad \text{for } i = x, y, z, \quad (3.5)$$

where u_i denotes the coordinate variable (x , y or z) and A_i , ϕ_i are constants that depend on initial conditions (A_i relates to ion temperature). The secular frequencies $\omega_{\text{sec},i}$ depend on the corresponding stability parameters:

$$\omega_{\text{sec},i} = \beta_i \frac{\Omega_{\text{RF}}}{2} \quad \text{with} \quad \beta_i^2 \approx a_i + \frac{q_i^2}{2}. \quad (3.6)$$

In the general case, the solutions of the Mathieu equations can be written as a linear combination of harmonic functions [108]. The secular frequency parameters β_i can be

expressed exactly as recurrent continued fractions:

$$\beta_i^2 = a_i + \frac{q_i^2}{(\beta_i + 2)^2 - a_i - \frac{q_i^2}{(\beta_i + 4)^2 - a_i - \dots}} + \frac{q_i^2}{(\beta_i - 2)^2 - a_i - \frac{q_i^2}{(\beta_i - 4)^2 - a_i - \dots}}. \quad (3.7)$$

For stable solutions, $0 \leq \beta_i \leq 1$, as shown in Fig. 3.2.

3.1.2 Trap depth

The potential depth of the ion trap can be calculated under the adiabatic approximation. Neglecting the fast micromotion, the ion behaves as a harmonic oscillator in the radial and axial directions with frequencies $\omega_{\text{sec},r}$ and $\omega_{\text{sec},z}$, respectively. Taking the axial direction as example, this corresponds to the equation of motion [108]

$$\frac{d^2 z}{dt^2} = -\omega_{\text{sec},z}^2 z = -\left(\frac{Q^2 V_0^2}{2m^2 z_0^4 \Omega_{\text{RF}}^2} + \frac{QU_0}{mz_0^2} \right) z, \quad \text{using } r_0^2 = 2z_0^2. \quad (3.8)$$

This can be rewritten as

$$m \frac{d^2 z}{dt^2} = -Q \frac{dD_z}{dz}, \quad \text{with } D_z(z) = \left(\frac{QV_0^2}{4mz_0^4 \Omega_{\text{RF}}^2} + \frac{U_0}{2z_0^2} \right) z^2. \quad (3.9)$$

Here D_z is the parabolic pseudopotential corresponding to the harmonic motion of the ion in axial direction. The depth of this axial potential is

$$\bar{D}_z = D_z(z_0) - D_z(0) = \frac{QV_0^2}{4mz_0^2 \Omega_{\text{RF}}^2} + \frac{U_0}{2} \quad (3.10)$$

and similarly, the potential depth in radial direction is

$$\bar{D}_r = \frac{QV_0^2}{4mr_0^2 \Omega_{\text{RF}}^2} - \frac{U_0}{2}. \quad (3.11)$$

The potential depth thus scales quadratically with the physical size of the trap: larger ion traps have a larger trapping volume and can hold more ions simultaneously. This can be an advantage if efficient capturing is desired (e.g. to trap radioactive isotopes) but also increases the likelihood of trapping unwanted ions in addition to the ions of interest. The trap depth for Ba^+ ions for our typical trapping parameters (a 2.5 mm trap with a 500 V electric field oscillating at 5 MHz) is $\bar{D}_z = 2\bar{D}_r = 14$ V.

The DC voltage U_0 changes the depth of the radial and axial potentials in opposite directions. If U_0 becomes too large, the radial potential depth goes to zero, corresponding to the $\beta_r = 0$ line at the limit of the stability region (see Fig. 3.2). Similarly, the axial potential depth becomes zero at the negative voltage U_0 that corresponds to the $\beta_z = 0$ line.

3.2 Determining RF Amplitude and Stray Electric Field

In the experimental setup used for this work, the AC trapping field is produced using a resonant circuit, as is common practice (see Section 2.1.1). This makes it difficult to measure the AC amplitude directly, since connecting any measurement device tends to change the resonant properties of the circuit and thereby the amplitude to be determined. An alternative approach is to use the most sensitive probe of the electric fields, a trapped ion directly held in place by them. In the following method, the time-averaged position of the ion is monitored by a camera while the depth of the pseudopotential is varied [87].

Ion displacement by stray electric fields

In an ideal trap, an ion will always be trapped in the geometrical center of the trap irrespective of the AC or DC amplitudes of the trapping field (disregarding the effect of gravity which is generally negligible). This situation is changed by adding an additional static electric field displacing the ion from the geometrical trap center. Now the position of the ion is determined by the balance between the trapping field and the displacing field. The simplest case is to have a uniform electric field $\mathcal{E}_{\text{stray}}$ in addition to the trapping field. In practice it was found that a stray electric field was always present in the setup, changing slowly on a timescale of hours to days. This field is likely caused by patch charges on the trap components [131] and is assumed to be uniform over the central volume of the trap sampled by the trapped ion. An approximately uniform electric field can also be generated by applying a DC voltage difference between the two end caps or using additional electrodes.

The displacement of ions from the geometrical trap center can be found by equating the magnitude of the displacing force with the restoring force of the trapping field [87]. The displacing force experienced by ions in a uniform electric field is

$$\mathbf{F}_{\text{Coulomb}} = Q\mathcal{E}_{\text{stray}}. \quad (3.12)$$

To find the displacement δ from the trap center, this force is balanced by the trapping force (using trap coordinates as before: x and y are radial directions and z is axial),

$$\mathbf{F}_{\text{trap}} = -m \begin{pmatrix} \omega_{\text{sec},r}^2 \delta_x & \omega_{\text{sec},r}^2 \delta_y & \omega_{\text{sec},z}^2 \delta_z \end{pmatrix}, \quad (3.13)$$

to give

$$\delta = \frac{Q}{m} \begin{pmatrix} \frac{\mathcal{E}_x}{\omega_{\text{sec},r}^2} & \frac{\mathcal{E}_y}{\omega_{\text{sec},r}^2} & \frac{\mathcal{E}_z}{\omega_{\text{sec},z}^2} \end{pmatrix}. \quad (3.14)$$

Defining the y -axis to be the radial direction that is vertical in the lab, the calibration of the RF fields in this direction is straightforward in our setup, since it corresponds to the vertical position of ions on the camera image. The horizontal position on the

camera image is then determined by a combination of the x and z displacements, as the viewing direction is 55° rotated from the axial direction (see Fig. 2.7). Fortunately, the contributions from δ_x and δ_z can be disentangled on the camera image, because axial and radial displacements behave differently when changing V_0 and U_0 (see Section 3.1.2). Under the adiabatic approximation (3.6), the three displacement components are given by

$$\delta_{x(y)} = \frac{2md^4\Omega_{\text{RF}}^2}{QV_0^2 - 2md^2\Omega_{\text{RF}}^2U_0}\mathcal{E}_{x(y)} \quad \text{and} \quad \delta_z = \frac{md^4\Omega_{\text{RF}}^2}{2QV_0^2 + 2md^2\Omega_{\text{RF}}^2U_0}\mathcal{E}_z. \quad (3.15)$$

Increasing the AC amplitude V_0 will pull ions closer to the trap center, while the DC voltage U_0 will either increase the axial displacement and decrease the radial displacement, or vice versa, depending on its sign.

Calibration procedure

Let us review all quantities in expression (3.15). The ion mass m and charge Q are accurately known. The size of the trap d and AC frequency Ω_{RF} are also known to sufficient accuracy. The horizontal and vertical position of the ion on the EMCCD camera image is used to determine $(\cos 55^\circ \delta_x - \sin 55^\circ \delta_z)$ and δ_y , respectively, which requires the magnification of the image to be established. This is accomplished by placing the ion at different y positions on the image by adjusting trapping parameters and then moving the focused spectroscopy laser beams to maximize the fluorescence, while monitoring the beam profiler to track the physical distance moved (see Section 2.2.1). The quantities to be determined are the AC amplitude V_0 and the three components of the stray electric field $\mathcal{E}_{\text{stray}}$. The DC voltage U_0 is calibrated separately to set the scale. The displacement of the ion when V_0 and U_0 are varied are fitted with Eqs. (3.15) to determine V_0 and $\mathcal{E}_{\text{stray}}$. The RF meter provides a relative measure of V_0 for combining measurements at different RF levels.

Experimental data

Figure 3.3 shows an example of a characterization of the AC trapping field where the stray electric field pulled the ion mostly downward (this was typical in our trap). The position of the ion on the camera image was measured at four different values of the AC amplitude V_0 while varying the DC voltage U_0 between²² -1 V and $+1$ V. The data are fitted with expression (3.15) to determine the absolute V_0 amplitude and the stray electric field strength, showing good agreement with the observed behavior. In this particular measurement, the stray electric field is determined to be $\mathcal{E}_{\text{stray}} = (+3.5 \text{ V/m}, -44.3 \text{ V/m}, -6.9 \text{ V/m})$. The largest component is $\mathcal{E}_y$, with

²²The DC voltage range was limited by the power supply and the voltage drop in the connections to the electrodes.

Figure 3.3 Example characterization of the fields in the trap (29 October 2015). Fitted (a) horizontal and (b) vertical position of a single trapped ion on the EMCCD camera image as function of DC voltage U_0 for four values of AC amplitude V_0 ($q_z = 0.07$ to 0.15 , note that the horizontal movement is far less than the vertical); dashed lines indicate the corresponding trap center. (c) Determination of camera magnification: vertical position of spectroscopy lasers on the beam profiler that optimizes the fluorescence for different ion positions on the camera image ($\approx 1 \mu\text{m}/\text{px}$).

the negative sign indicating a field pointing downward in the lab frame. A similar characterization of the AC amplitude was performed after each time the RF system of the setup had been changed.

3.3 Trap Stability and Instability

Stable trapping of ions is only possible for some combinations of the AC and DC quadrupole trapping field amplitudes. The stability region was depicted in Fig. 3.2 in terms of the corresponding trapping parameter values (a_i, q_i). As given by Eq. (3.3), the range of voltages U_0 and V_0 corresponding to the stability region depends on the charge-to-mass ratio of the ions in the trap: heavier ions require larger voltages to obtain the same trap depth. The fact that the stability condition depends on the charge-to-mass ratio can be used to selectively trap ion species. In addition, the trap stability is not the same at all positions in the stability region. Higher-order multipole components in the trapping field can lead to instabilities at certain trap parameters.

Figure 3.4 Calculated stability region of Ba^+ ions compared with that of e.g. CO^+ ions, plotted as function of the voltages V_0 and U_0 . This illustrates the possibility of cleaning the trap from light ions by (briefly) raising V_0 . The trap parameters used are $d = 2.5 \text{ mm}$ and $\Omega_{\text{RF}} = 2\pi \times 6.53 \text{ MHz}$.

3.3.1 Mass filter

As the stability region differs between ion species, quadrupole ion traps function as charge-to-mass filters: an application of quadrupole fields that in fact predates their use as ion traps [108]. This property makes it possible in principle to select just the charge-to-mass ratio of the ions of interest. Figure 3.4 shows how the stability region scales with ion mass by comparing Ba^+ ions ($m = 138 \text{ u}$) with CO^+ molecular ions ($m = 28 \text{ u}$), an example ion species that could be present from background gas. The figure illustrates how increasing the AC amplitude V_0 beyond the stability range of CO^+ would clear the trap of any ions with this charge-to-mass ratio (or lower).

In general, getting rid of lighter ions is achieved by setting V_0 to a large value still within the stability region of the desired species and getting rid of heavier ions by setting $|U_0|$ to a large value. Clearly this works best for removing ions of very different charge-to-mass ratios. Technical limitations of the electrical system also limit to what extent the stability diagram can be covered (see Section 2.1.1). Our loading procedure included operating the trap at $V_0 \approx 1 \text{ kV}$ for a few seconds to rid the trap of lighter ions ($m < 40 \text{ u}$). Another method to selectively remove ions from the trap is to modulate the AC field or add an additional AC quadrupole field with a frequency chosen to drive parametric excitation [132]. We did not attempt this method.

Figure 3.5 (Left) Lines of instability with $n_r, n_z \geq 0$ up to order $n = 10$ calculated with Eq. (3.16). Line thickness distinguishes different orders and n is indicated for the lowest orders. **(Right)** Comparison with experimental trap stability of H_2^+ ions in a Paul trap. The intensity at each point is proportional to the number of ions trapped at those trapping parameters. Figure reproduced from Ref. 108 (data from Ref. 134). We typically operate at $q_z \approx 0.1$, $a_z \approx 0$, away from the strongest resonances.

3.3.2 Parametric resonances

The potential of any real ion trap will not be a perfect quadrupole but contain higher order multipole components as well. This can be caused by misalignments, deviations from the ideal hyperbolic electrode shape or the space charge of trapped ions. A consequence is the appearance of parametric resonances: these occur when trapping parameters are such that a linear combination of the secular frequencies $\omega_{\text{sec},r}$ and $\omega_{\text{sec},z}$ forms a simple ratio with the trap frequency Ω_{RF} , driving RF heating. The resonant condition for the most prominent parametric resonances is [108, 126, 133]

$$n_r \omega_{\text{sec},r} + n_z \omega_{\text{sec},z} = \Omega_{\text{RF}} \quad \Leftrightarrow \quad n_r \beta_r + n_z \beta_z = 2 \quad \text{with} \quad n_r, n_z \in \mathbb{Z}. \quad (3.16)$$

The strength of the heating effect varies with n_r, n_z and generally decreases with the order of the resonance $n = |n_r| + |n_z|$.

Figure 3.5 shows calculated lines in the stability diagram where resonances occur

Figure 3.6 Parametric resonances observed as dips in fluorescence while scanning the AC amplitude V_0 (with $U_0 = 0$ V, $\Omega_{RF} = 2\pi \times 6.5$ MHz, 24 May 2016). The AC amplitude scale was calibrated by matching the pattern of dips to the resonance positions calculated with Eq. (3.16), indicated by the vertical lines.

according to Eq. (3.16) with $n_r, n_z \geq 0$ (resonances with negative coefficients are expected to be weak [133]). Each order of resonances corresponds to several lines crossing at one point in parameter space. The strongest, lowest order resonances occur at large values of q_z and a_z , with two edges of the stability diagram actually corresponding to the $n = 2$ (quadrupole) resonances. This pattern of lines of instability is also observed experimentally [126, 134] (see Fig. 3.5).

The RF heating effect caused by parametric resonances manifests itself as a decrease in fluorescence per ion and a lowered number of ions that can be stored in the trap. In the worst case, the ions keep gaining energy from the RF field, increasing the amplitude of their motion until they are lost from the trap.

Experimental data

We have measured the fluorescence of a cloud of Ba^+ ions while changing trapping parameters along the line $U_0 = 0$ V ($a_z = 0$). A pattern of dips in the fluorescence is observed (see Fig. 3.6). Close inspection of Fig. 3.5 reveals that when changing RF amplitude V_0 (and thereby q_z) from low to high along this line, groups of parametric resonances are encountered with increasing intervals between them. For instance,

all resonances of the form $(2k)\omega_{\text{sec},r} + (16 - k)\omega_{\text{sec},z} = \Omega_{\text{RF}}$ with $k \in \mathbb{Z}$ make up one such group; moving to higher q_z , the next group is formed by the resonances $(2k + 1)\omega_{\text{sec},r} + (16 - k)\omega_{\text{sec},z} = \Omega_{\text{RF}}$, followed by the group of resonances $(2k)\omega_{\text{sec},r} + (15 - k)\omega_{\text{sec},z} = \Omega_{\text{RF}}$, then $(2k + 1)\omega_{\text{sec},r} + (15 - k)\omega_{\text{sec},z} = \Omega_{\text{RF}}$, etc. Here we identify each group by its lowest order (and presumed strongest) resonance ($k = 0$).

In Figure 3.6 the RF amplitude was calibrated by matching the spacing of observed dips in the fluorescence to the calculated values of V_0 where the indicated resonances cross the $U_0 = 0$ V line. Note that the resonance groups $\omega_{\text{sec},r} + n\omega_{\text{sec},z} = \Omega_{\text{RF}}$, which lie between the indicated groups $n\omega_{\text{sec},z} = \Omega_{\text{RF}}$, were not observed. In addition to generally decreasing in strength with increasing order, the strength of certain parametric resonances can be related to symmetries of the trapping fields: resonances of odd orders and resonances with odd coefficients vanish for a trap with perfect mirror and axial symmetry, respectively [133, 134]. Assuming that our trap only weakly breaks these symmetries and the corresponding resonances are suppressed, just the indicated resonance groups remain. The RF amplitude calibration obtained here by mapping out the parametric resonances agrees with the displacement measurement detailed in Section 3.2. It also shows that for optimizing the fluorescence rate, it is important to ensure that the trapping field parameters do not happen to correspond with (strong) parametric resonances.

3.4 Micromotion: Photon–RF Correlation

As discussed in Section 3.1.1, the motion of an ion trapped in a Paul trap can generally be split into two components: a fast oscillation at the trap frequency and a slower motion in an effective harmonic potential. The amplitude of the former (micromotion) scales with the amplitude of the trap electric field that the ion experiences. At the geometric trap center, the electric field is zero and any displacement of the ion away from the trap center causes excess micromotion.

Ion motion Doppler shifts

Including the displacement due to stray electric fields, the equations of motion (3.5) in the adiabatic approximation become as follows:

$$u_i(t) = (\delta_i + A_i \cos(\omega_{\text{sec},i}t + \phi_i)) \left(1 - \frac{q_i}{2} \cos(\Omega_{\text{RF}}t)\right) \quad \text{for } i = x, y, z. \quad (3.17)$$

From this expression it is clear that the amplitude of the micromotion scales with the displacement from the geometric trap center δ_i and stray fields thus cause increased micromotion [87, 88]. A large micromotion amplitude (in combination with photon scattering) can lead to RF heating, when energy from the trapping field is transferred to the ion, heating it up (i.e. increasing the macromotion amplitudes A_i).

Setting $A_i \approx 0$ for a cold ion and taking the derivative with respect to time yields the time-varying velocity

$$\dot{u}_i(t) \approx \frac{q_i}{2} \delta_i \Omega_{\text{RF}} \sin(\Omega_{\text{RF}} t), \quad (3.18)$$

which leads to a first-order Doppler shift for a laser with angular wavevector $\mathbf{k}$ of

$$\Delta\nu(t) = \dot{\mathbf{u}}(t) \cdot \mathbf{k} / 2\pi. \quad (3.19)$$

Micromotion causes the ion to experience a time-varying Doppler shift for any laser illuminating it, in sync with the trapping field at frequency Ω_{RF} . The detuning from resonance of the effective laser frequency now varies within the RF cycle, leading to an oscillating rate of photon absorption and subsequent fluorescence (the lifetime of the $6p\ ^2P_{1/2}$ level is short compared to the RF cycle). This smears out the frequency-sensitivity of the experiment or produces additional sidebands and is another reason why large micromotion is undesirable. If unwanted static potentials in the trap are not compensated, the excess micromotion can lead to heating of ions even if the cooling lasers are red-detuned from the resonance center at rest [109, 135].

Experimental data

The Doppler shift induced by micromotion can be observed by recording the correlation between the time of photon emission and the RF phase [87, 88]. We have implemented this in our data acquisition system (see Section 2.3). Using correction electrodes, the stray electric fields present in the trap can be compensated, which corresponds to minimizing the amplitude of the photon-RF correlation. This technique is sensitive to the micromotion component along the direction of laser propagation $\mathbf{k}$. Note that the micromotion components in radial and axial direction are 180° out of phase because q_r and q_z have opposite signs (3.3). This means that the direction of displacement that is compensated when minimizing the photon-RF correlation does not in all cases coincide with the propagation direction of the laser.

The effect of the Doppler shift induced by excess micromotion is demonstrated in Fig. 3.7. The time within the RF cycle of photon detection by the PMT is recorded while a voltage difference is applied between the end caps to vary the displacement δ_z of the trapped ions from the geometric center of the trap. At each voltage setting, the photon-RF correlation data are fitted with a sine function to determine the modulation depth. The modulation depth is here plotted against the Doppler shift amplitude of the laser at wavelength 494 nm that corresponds to each voltage setting, calculated with Eqs. (3.15) and (3.19) (assuming the displacement δ_z is the sole source of micromotion). The signs of the fitted modulation depth and the Doppler shift have been chosen arbitrarily here; a sign change corresponds to a 180° phase difference.

Figure 3.7 shows that the modulation depth increases with the Doppler shift up to about 50 MHz, beyond which the modulation depth decreases again. The frequency

Figure 3.7 Measured correlation of photon emission with the RF cycle for a two-ion crystal ($2\pi/\Omega_{\text{RF}} = 153 \text{ ns}$, 18 September 2015). A differential voltage U_{bias} was applied between the end caps of -0.1 V to $+0.5 \text{ V}$ to induce a displacement δ_z . This causes excess micromotion and a corresponding first-order Doppler shift on the cooling and detection lasers, modulating the photon emission.

dependence of the fluorescence that causes the observed modulation is related to the shape of the excitation spectrum around the Doppler-free frequency of the laser. The Doppler shift at the peak of the modulation depth matches the -48.5 MHz detuning from resonance of the laser at wavelength 494 nm during this measurement. Naturally, the light of the laser at wavelength 650 nm is also Doppler shifted; its shift is smaller by a factor 1.3 due to the lower laser frequency. This laser was detuned by -1.1 MHz from resonance here and its effect on the modulation depth is less apparent in Fig. 3.7. The optical Bloch equations model discussed in Section 1.3.3 includes the effect of micromotion and can be used to calculate the expected modulation depth as shown in Fig. 3.7 to find good agreement.

This type of measurement using the photon-RF correlation can be used to minimize the displacement of ions from the geometrical trap center. The measurement shown in Fig. 3.7 was actually performed with a crystal of two ions and the fits of the photon-RF correlation also include the second harmonic that arises at larger micromotion amplitudes [88] or from summing the fluorescence of two ions in motion [135]. In this way the photon-RF correlation can in principle also be used to infer the presence of additional ions. Finally, it should be pointed out that besides the Doppler shift due

to the micromotion at the trap frequency Ω_{RF} , any macromotion also causes Doppler shifts that oscillate at frequencies $\omega_{\text{sec},i}$. Because the macromotion velocity is generally smaller than the micromotion velocity, this modulation effect is also smaller and we did not attempt to measure it.

3.5 Ion Crystals and Dark Ions

When multiple ions are stored in the same ion trap, they can form *Coulomb crystals*, i.e. the ions sit at positions equally distant from each other like in a crystal lattice. Such spatial configurations arise from the interplay of the trapping field pulling the ions to the trap center and the Coulomb repulsion between the ions when they are sufficiently cold [108, 135, 136].

3.5.1 Calculating ion crystal structure

A complete description of the behavior of ions in a trap would require taking into account the motion of the ions, their interaction with the various lasers and the dynamical electric fields. However, using a much simplified model can already provide a wealth of information and form a useful tool for understanding the crystal structures observed with the EMCCD camera. The model considered here consists of numerically finding the ion positions corresponding to the lowest potential solution in a time-averaged trap potential. Since ion dynamics are not taken into account at all, this model only applies to ions that are sufficiently laser-cooled to form a stable ion crystal and for instance cannot describe ion crystal configurations that occur when the radial and axial secular frequencies are nearly degenerate [137].

The modeled potential Φ depends only on the positions $\mathbf{x}_i$ of the n ions in the trap. It consists of three components, the approximate harmonic effective trapping field, the Coulomb repulsion between the ions and an additional stray electric field term:

$$\Phi(\mathbf{x}_1, \dots, \mathbf{x}_n) = \sum_i \Phi_{\text{trap},i} + \sum_{i < j} \Phi_{\text{Coulomb},ij} + \sum_i \Phi_{\mathcal{E}\text{-field},i}, \quad (3.20)$$

where the harmonic pseudopotential is defined as in Eq. (3.6) by the secular frequencies $\omega_{\text{sec},r}$ and $\omega_{\text{sec},z}$,

$$\Phi_{\text{trap},i} = \frac{1}{2} m_i (\omega_{\text{sec},r,i}^2 (x_i^2 + y_i^2) + \omega_{\text{sec},z,i}^2 z_i^2). \quad (3.21)$$

The model can be used to simulate ions of different masses m_i trapped together. As the secular frequencies $\omega_{\text{sec},r}$ and $\omega_{\text{sec},z}$ depend on ion mass, these frequencies also carry a subscript i to indicate that they might differ between ions. The Coulomb

potential contribution for each pair of ions is given by

$$\Phi_{\text{Coulomb},ij} = \frac{1}{4\pi\epsilon_0} \frac{Q_i Q_j}{|\mathbf{x}_i - \mathbf{x}_j|} \quad (3.22)$$

and the potential due to the (position-independent) stray electric field is

$$\Phi_{\mathcal{E}\text{-field},i} = -Q_i \mathbf{x}_i \cdot \boldsymbol{\mathcal{E}}_{\text{stray}}. \quad (3.23)$$

Starting from random initial positions, the potential is numerically minimized by varying the positions $\mathbf{x}_i$. Generally, the calculation was repeated dozens of times to guard against finding a local minimum. In many cases, multiple configurations exist with (almost) the same minimum value of the potential Φ , e.g. due to the symmetry of the system. More detailed descriptions that include micromotion and heating effects can be obtained from molecular dynamics calculations, such as those described in Ref. 138, but our simple model suffices here.

Results and general observations

Without stray electric fields, the axial symmetry of the trap is reflected in the ion crystals. As can be seen from Eq. (3.6), the relative strengths of the harmonic pseudopotentials in radial and axial directions depend on the magnitudes of the AC and DC voltages applied to the trap electrodes. When the DC component is small ($U_0 \approx 0$), then $a_i \approx 0$ and $|q_z| = 2|q_r|$, so that the pseudopotential in axial direction is about twice as strong as the potential in radial direction (see Section 3.1.2). For small numbers of trapped ions, this produces circular ion crystal configurations lying in the plane of the ring electrode. From about a dozen trapped ions or more, the lowest energy configuration is no longer planar, with instead the ions arranging themselves in multiple coaxial rings roughly forming a flattened sphere.

Figure 3.8 shows example calculation results for six Ba^+ ions trapped simultaneously for typical trapping conditions with $U_0 = 0$ V. The results show that the lowest-energy configuration consist of one central ion surrounded by a ring of five equally spaced ions lying in the plane of the ring electrode ($z = 0$). There is an infinite set of such configurations, since the potential Φ is unchanged by any rotation around the z -axis. In the actual setup, we often found that the ion crystals collectively rotated around the trap axis, likely due to the (near) axial symmetry and a small torque caused by nonuniform laser illumination. On camera images, this gives the appearance of a ring of light. As Fig. 3.8b shows, for some numbers of ions the potential can have a local minimum for a configuration different from the lowest-energy one. Whether these are experimentally observed likely depends on ion temperature and possible small imperfections of the trap. A negative DC voltage U_0 can make the pseudopotential in radial direction stronger than in axial direction, producing linear ion crystals along the z -axis instead.

Figure 3.8 Calculated crystal configurations for six $^{138}Ba^+$ ions under typical trapping conditions ($d = 2.5$ mm, $\Omega_{RF} = 2\pi \times 6.5$ MHz, $V_0 = 450$ V, $U_0 = 0$ V, $\mathcal{E}_{stray} = \mathbf{0}$). (a) Distribution of radial ion positions when repeatedly minimizing the potential Φ from random initial positions, showing the axial symmetry of the trap fields (all results lie in the ring electrode plane). (b) Same data, where in every case the configuration has been rotated around its center-of-mass to place one ion on the positive x -axis. The lowest-energy configuration is a five-ion ring with one in the center (circles, $\Phi = 1.75$ meV), but in some cases, the minimization finds a solution at a slightly higher potential where all six ions form a ring (dashed circles, $\Phi = 1.76$ meV).

The model can also be used to investigate the behavior of multiple ion species trapped together in the same ion trap. Ions of different mass (or charge) will sit at different points in the stability region (see Fig. 3.2) and experience differing strengths of the trapping potential. An example of this is shown in Section 3.5.3.

Ion crystal size

The size of a crystal consisting of two identical ions is straightforward to calculate analytically under the same assumptions as before. For both ions, the restoring force of the harmonic pseudopotential is exactly balanced by the Coulomb force. In the case of an ion crystal lying in the radial plane ($\beta_z > \beta_r$) with a separation of δ between the two ions, the magnitudes of the two forces are given by [135]:

$$F_{\text{trap}} = m\omega_{\text{sec},r}^2 \frac{\delta}{2} \quad \text{and} \quad F_{\text{Coulomb}} = \frac{Q^2}{4\pi\epsilon_0} \frac{1}{\delta^2}. \quad (3.24)$$

Equating the forces and solving for δ gives

$$\delta^3 = \frac{Q^2}{2\pi\epsilon_0 m \omega_{\text{sec},r}^2}. \quad (3.25)$$

Under the adiabatic approximation and no DC component in the trapping field ($U_0 = 0$), the radial ion separation is

$$\delta^3 = \frac{m d^4 \Omega_{\text{RF}}^2}{\pi \epsilon_0 V_0^2}. \quad (3.26)$$

This expression shows how the size of an ion crystal scales with the AC trapping field amplitude, $\delta \propto V_0^{-2/3}$, and ion mass, $\delta \propto m^{1/3}$, etc. The radial separation between two trapped $^{138}\text{Ba}^+$ ions for typical trapping parameters (a 2.5 mm trap with a 500 V electric field oscillating at 5 MHz) is 11 μm .

3.5.2 Calibrating AC amplitude using ion crystals

The described method of simulating ion crystals can be used to analyze EMCCD camera images. One application is the determination of the magnitude of trapping and stray electric fields. Compared with the single ion method detailed in Section 3.2, using ion crystals has the advantage that the Coulomb force between ions is precisely known and thus the separation between ions can be used as yardstick. This obviates the need to measure the absolute voltage of the DC trapping field of the trap electrodes (U_0) since a relative measurement suffices. Essentially, an ion crystal is sensitive not only to the minimum of the potential but also to its steepness, yielding additional information.

Experimental data

An example measurement of the AC trapping field amplitude was performed before a shelving measurement (see Chapter 6). Four $^{138}\text{Ba}^+$ ions were loaded into the trap and formed a rotating ion crystal. The AC amplitude of the trapping field V_0 was varied between three settings, while the DC connection was grounded ($U_0 = 0$). Figure 3.9 shows the images of the ion crystals captured by the EMCCD camera (with integration times of order 10 s). The four²³ ions rotate in the ring electrode plane and the shift of the crystal center indicates the presence of a stray electric field. The known magnification of the camera (see Section 2.2.2) yields the absolute displacement of the ions, noting that the horizontal direction has to be compressed to account for the 55° angle of the viewing axis from head-on to the trap ring plane²⁴. Relative V_0 amplitudes were provided by the RF meter.

²³The ion number can't be devised directly from the images as the crystals are rotating (a single ring is consistent with between two and five ions). However, it was determined retroactively by observing the number of steps in the fluorescence rate during a subsequent shelving measurement.

²⁴This also means that very large crystals could come out of the focal plane of the camera.

Figure 3.9 EMCCD images of a sequence of four-ion crystals (18 March 2015) with increasing AC amplitude V_0 from (a) to (c). Overlays indicate the simulated ion crystal ring position and size (dashed ellipses), the geometric trap center where the RF amplitude vanishes (crosses) and the projected stray field direction (dashed lines).

The ion crystal simulation was made to match the images by adjusting the AC voltage multiplier to change the crystal size, and the stray field vector to change the shift of the crystal center. The results of the simulation are shown overlaid on the camera images in Fig. 3.9. A good fit of the experimental data is obtained for absolute AC amplitudes of $V_0 = 182 \text{ V}$ to 391 V corresponding to $q_z = 0.07$ to 0.15 at $\Omega_{\text{RF}} = 2\pi \times 5.29 \text{ MHz}$. The stray electric field strength was determined to be $|\mathcal{E}_{\text{stray}}| \gtrsim 11.5 \text{ V/m}$ at this time. This is a lower bound since only two components of the shift are accounted for; a shift along the viewing axis could also be present.

3.5.3 Dark ions: chemical reactions

The lasers and fluorescence detection system used in our experiment are tailored specifically to the $^{138}\text{Ba}^+$ ion. However, the ion trap is not element-selective; any ion with a suitable charge-to-mass ratio can be trapped, depending on the trapping parameters chosen (see Section 3.3). This leads to the possibility of dark ions: trapped ions of species other than $^{138}\text{Ba}^+$ that do not fluoresce. Such dark ions still interact through the Coulomb interaction, enabling sympathetic cooling so that crystallization remains possible [108, 138, 139]. The presence of dark ions could be determined by making them fluoresce with an additional laser system, or exciting mass-dependent eigenmodes in the crystal by modulating the RF field [140]. However, we can also infer their presence by studying the crystal configuration of the bright $^{138}\text{Ba}^+$ ions.

Figure 3.10 Sequence of ion crystals observed during a three hour shelving measurement (18 September 2015). At time (a), the ion crystal rotated; the axial symmetry and seven fluorescence levels observed during shelving indicate the presence of six $^{138}\text{Ba}^+$ ions with no dark ions. From (b) to (f), one by one the ions stopped fluorescing while presumably remaining trapped at the corners of the crystal where no ion is visible, away from the geometric trap center (cross).

Experimental data

We have often observed the formation of dark ions in our trap. Figure 3.10 shows the fluorescence of six trapped Ba^+ ions disappearing over a period of several hours. If ions were lost from the trap, we would expect to see the rotating ion crystal shrink in size while remaining centered on the same location. Instead, we observe the crystal stopping rotating and the center of the visible ions shifting. This behavior can be explained by all six ions remaining trapped but in turn undergoing a chemical reaction forming a molecular ion that does not fluoresce at the employed laser wavelengths. Due to the change in charge-to-mass ratio, the trapping potential is weaker for the molecular ions and they sit further away from the trap center but close enough to remain strongly coupled in a single ion crystal, sympathetically cooled by the Ba^+ ions still interacting with the lasers.

Figure 3.11 Simulation of ion crystals similar to Figs. 3.10a and 3.10b with stray field in $-y$ direction. The symmetry (a) of a crystal of six $^{138}\text{Ba}^+$ ions is broken when one Ba^+ reacts with background gas to form a molecular ion such as (b) BaH^+ or (c) BaO^+ . The heavier molecular ion sits further away from the trap center and the resulting lowest-energy crystal configuration depends on its mass.

We can use our ion crystal simulations to study the effect of the molecular ion mass on the crystal shape. Chemical reactions of trapped Ba^+ ions with background gases are known from literature [139,141]. The resulting molecular ions include BaH^+ and BaO^+ (although formation of the former was not observed in Ref. 139). Calculated lowest-energy configurations for ion crystals consisting of six Ba^+ ions, and five Ba^+ plus one molecular ion are shown in Fig. 3.11. Although itself not visible on the camera image, the molecular ion affects the configuration of the remaining Ba^+ ions, allowing its mass to be inferred. Comparing the configuration in Fig. 3.10b with the calculations, e.g. looking at the angle of the bend in the middle row of three Ba^+ ions, we conclude that the dark ions in our trap are most likely BaH^+ ions.

It appears no study of the formation of barium hydride in ion traps has been published; analogously to the known formation of MgH^+ [142] and CaH^+ [143], it is probably formed in a photochemical reaction with hydrogen gas:

We expect hydrogen to be present as residual gas in our setup as is typical for UHV systems. Most of the disappearances of fluorescence we observed over a long period were, like those in Fig. 3.10, consistent with the formation of a BaH^+ molecular ion where the small mass difference hardly changes the overall crystal configuration. This process seems to be the main factor limiting our effective Ba^+ trapping time to about 2 h (see Fig. 3.12) at a residual gas pressure of order 10^{-10} mbar.

Figure 3.12 (a) Mean time before the fluorescence of any $^{138}\text{Ba}^+$ ion disappeared versus the number of fluorescing ions before, where we believe that the ion was not lost from the trap (data span several years). (b) Same data interpreted as dark ion formation rate. Assuming Poisson statistics with a constant probability per remaining $^{138}\text{Ba}^+$ ion, we find a reaction rate of about $1.3 \times 10^{-4} \text{ s}^{-1}$. Note that we cannot always tell from the crystal configurations whether an ion remained trapped (e.g. when the last bright ion disappears). However, the data appear consistent with a single process.

3.6 Ion Temperature

Finally, we briefly discuss ways to determine the temperature of trapped ions. Assigning a temperature to a single ion strictly only makes sense if its kinetic energy follows a thermal distribution when probed repeatedly. This is not necessarily the case in a Paul trap [108]. As discussed before, the motion of a trapped ion consists of macromotion and driven micromotion (see Eq. (3.17)). Laser cooling (Section 1.3.2) brings the macromotion amplitude into a thermal distribution allowing a temperature to be assigned, while the micromotion amplitude is fully determined by the macromotion combined with any displacement from the trap center by stray electric fields. The macromotion can then be described as a quantum harmonic oscillator with mean vibrational number $\langle n \rangle = 1/(\exp[\hbar\omega_{\text{sec}}/k_B T] - 1)$ for each trap axis [108, 109]. For a single ion, the added (average) kinetic energy of the intrinsic micromotion is equal to that of the macromotion, while the kinetic energy of excess micromotion caused by uncompensated stray electric fields could be significantly larger [87].

Temperature from ion crystal formation

For multiple trapped ions, observing the formation of ion crystals (Section 3.5) puts a rough upper bound on their temperature. Trapped ions can be described as a non-neutral plasma [108] and crystallization occurs when the Coulomb coupling constant $\Gamma_C = Q^2/(4\pi\epsilon_0\langle\delta\rangle k_B T)$ becomes larger than about 170, where $\langle\delta\rangle$ is the typical

distance between ions. With $\langle \delta \rangle \approx 10 \mu\text{m}$, this gives an ion temperature of $T < 10 \text{ mK}$, still far above the Doppler limit. The precise dynamics of crystal formation are more involved [135, 136].

Temperature from camera images

Camera images of trapped ions show the size of their orbit in the trap and enable extracting their temperature (spatial thermometry). The fluorescence from a cold ion presents a point source with a size on the camera image determined by the diffraction limit of the imaging optics, whereas hot ions have a larger spatial distribution. The time-averaged spatial distribution of a quantum harmonic oscillator in thermal equilibrium is Gaussian with variance $\langle x^2 \rangle = \hbar(\langle n \rangle + 1/2)/m\omega_{\text{sec}}$ [144]. The intrinsic micromotion causes some additional broadening, but for typical trapping parameters $|a|, |q| \ll 1$, this effect is limited to a few percent and the distribution remains approximately Gaussian [145]. Note that if a single coherent oscillation dominates an ion's motion, as with excess micromotion, the ion will have a bimodal spatial distribution along this direction instead. A camera image is formed by the convolution of a two-dimensional projection of an ion's spatial distribution with the imaging system's point spread function, allowing the ion temperature to be extracted [144]. Molecular dynamics calculations can aid the extraction of temperatures from images of ion crystals [138].

Temperature from spectroscopy

Because the motion of an ion causes a Doppler shift, ion temperature can also be determined from its effect on spectroscopy. These methods probe an ion's velocity distribution rather than its spatial distribution and offer greater accuracy than camera images. Since only the velocity component along the laser propagation direction is probed, fully characterizing an ion's motional state requires measurements along three axes.

In the weak binding regime (see Section 1.3.2) where motional sidebands are unresolved, a thermal velocity distribution causes Doppler broadening of spectral features [108]. In the fluorescence spectrum of a Ba^+ ion, the narrow dark resonances are most sensitive to this. An ion's temperature can be extracted from the contrast of dark resonances [146] or their width [147]. We discuss this further with the spectra presented in Chapters 4 and 5. Calibrating the temperature in absolute terms from spectra is difficult since it requires precise knowledge of many experimental parameters; a method working around this achieving sub-mK accuracy has been demonstrated recently [148].

The most sensitive methods of determining ion temperature rely on resolved motional sidebands in the strong binding regime. This requires that the transition linewidth is less than the ion's vibrational frequencies ω_{sec} , so generally the sidebands of a Raman or $E2$ transition are used [108]. The ion's motional state can then be determined from

the intensity ratio of the first blue and red sidebands [81,109] or the sideband-to-carrier ratio [86].

We have discussed the dynamics of ions in a Paul trap and the crystal configurations formed by multiple ions trapped simultaneously. Based on this, we have presented several diagnostic tools for characterizing the electric fields experienced by the ions, including stray electric fields, as well as experimental techniques for detecting and ejecting unwanted ions from the trap. This understanding of the properties of the trap is used in the experiments in the following chapters.

Chapter 4

Determination of Transition Frequencies in a Single $^{138}\text{Ba}^+$ Ion

Trapped single ions are exploited to investigate the interaction between light and matter, and to construct optical clocks [21]. For these applications based on high precision spectroscopy, a good understanding of the optical lineshapes involved is indispensable. We have employed a model based on optical Bloch equations to extract atomic parameters from fluorescence spectra, and an optical frequency comb [149] to measure transition frequencies in Ba^+ . These are essential ingredients for high precision experiments, in particular for atomic parity violation measurements in single Ba^+ [13, 38] and Ra^+ ions [62, 150] in the search for new physics [7].

Figure 4.1 Low-lying energy levels of the Ba^+ ion. The wavelengths of the investigated optical transitions are given.

In this chapter the transition frequencies between three of the lowest fine-structure levels in the $^{138}\text{Ba}^+$ ion are addressed. These levels form a Λ -configuration as shown in Fig. 4.1. The $6p\ ^2P_{1/2}$ level decays to the $6s\ ^2S_{1/2}$ and $5d\ ^2D_{3/2}$ levels with a branching ratio of about 3:1 [151]. We have measured the transition frequencies in a single Ba^+ ion by driving the $6s\ ^2S_{1/2} - 6p\ ^2P_{1/2}$ and $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transitions,

This chapter is based on Ref. 113: E. A. Dijck et al., Phys. Rev. A **91**, 060501(R) (2015).

Figure 4.2 Schematic diagram of the hyperbolic Paul trap used for trapping Ba^+ ions, consisting of a ring electrode and two end caps. The inner diameter of the ring is 5 mm. Light scattered by ions is detected with a photomultiplier tube and an electron-multiplying CCD camera. The lab coordinate system is also shown, given by the orientation of the magnetic field coils.

employing an optical frequency comb as frequency reference (see Section 4.1). We describe the dynamics of the population of the $^2\text{P}_{1/2}$ level using optical Bloch equations and demonstrate that this model adequately describes our experimental data (see Section 4.2). Coherent coupling between the $^2\text{S}_{1/2}$ and $^2\text{D}_{3/2}$ levels is observed when the two laser fields are detuned by the same amount from the respective atomic resonances. In this condition a two-photon process causes coherent population trapping, reducing the population of the $^2\text{P}_{1/2}$ level. By extracting the frequencies of one-photon and two-photon components of the lineshape using an eight-level optical Bloch equations model, we achieved 100 kHz accuracy for the $5\text{d } ^2\text{D}_{3/2} - 6\text{p } ^2\text{P}_{1/2}$ and $6\text{s } ^2\text{S}_{1/2} - 5\text{d } ^2\text{D}_{3/2}$ transition frequencies, and 200 kHz for the $6\text{s } ^2\text{S}_{1/2} - 6\text{p } ^2\text{P}_{1/2}$ transition frequency (see Section 4.3).

4.1 Experimental Setup

For the measurements reported here, a single $^{138}\text{Ba}^+$ ion is confined in a hyperbolic Paul trap (see Chapter 2). The trap is operated at a frequency $\Omega_{\text{RF}} = 2\pi \times 5.44 \text{ MHz}$ with a peak-to-peak RF voltage of typically $V_0 = 600 \text{ V}$. A bias DC potential is applied along the trap axis to compensate the effect of mechanical imperfections and stray fields, minimizing the micromotion of the ion in the trap (see Fig. 4.2). The trap is loaded by photoionization of ^{138}Ba atoms with laser light at wavelength 413.6 nm. The trap is mounted in a UHV chamber with a residual gas pressure below 10^{-10} mbar .

Doppler cooling and detection of the Ba^+ ions is achieved with laser light at wavelengths λ_1 and λ_2 (see Fig. 4.1). Laser light to drive the $6\text{s } ^2\text{S}_{1/2} - 6\text{p } ^2\text{P}_{1/2}$ transition

(at wavelength λ_1) is generated by frequency-doubling light at wavelength 987 nm from a single-frequency Ti:sapphire laser (Coherent MBR-110) in a temperature-tuned MgO:PPLN crystal (Covesion MSHG976-0.5) operated at 156.8 °C in a linear enhancement cavity. Light to drive the $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transition (at wavelength λ_2) is generated by a ring dye laser (Coherent CR-699) operated with DCM dye, pumped by a solid-state laser at 532 nm (Coherent Verdi v10).

The laser beams at wavelengths λ_1 and λ_2 are delivered to the trap via one single-mode optical fiber (Thorlabs PM460). The polarization is controlled with linear polarizers and half-wave plates. The bichromatic light is focused to a waist radius²⁵ of order $w_0 = 100\ \mu\text{m}$ at the trap center with a set of achromatic lenses. Typical laser light intensities at the position of the ion are a few times saturation intensity for λ_1 and ten times saturation intensity for λ_2 . A static magnetic field breaks the degeneracy of the magnetic sublevels; the direction and magnitude of the magnetic field are controlled with three pairs of coils surrounding the vacuum chamber.

Ba^+ ions are detected by fluorescence of the $6p\ ^2P_{1/2} - 6s\ ^2S_{1/2}$ transition. The light is imaged onto a photomultiplier tube (Hamamatsu H11123) and onto an electron-multiplying CCD camera (Andor iXon DU-897E-CSB-#BB), see Fig. 4.2. Background light is suppressed by a band-pass filter with 10 nm bandwidth and >85 % transmission at wavelength λ_1 (Edmund Optics #65-148). Light for the PMT is collected within a solid angle of about 0.03 sr; the count rate is of order $2 \times 10^3\ \text{cnt/s}$ for a single ion with both laser fields on resonance. Light is imaged onto the EMCCD camera with a $16\times$ magnifying telescope. The camera provides for the observation of localized single ions and crystals formed by several ions. The size of the image of an ion is proportional to the amplitude of its motion and gives an upper limit for its temperature (see Section 3.6). For a single laser-cooled ion, this limit is of order $\leq 10\ \text{mK}$ ($\approx 1\ \text{m/s}$); the Doppler limit for the Ba^+ cooling transition is 0.5 mK.

Determination of optical frequencies

A fiber-based femtosecond frequency comb (Menlo Systems FC1500-250) is used to measure the frequency of the light at wavelengths λ_1 and λ_2 (see Fig. 4.3). Its long term stability is provided by a GPS-disciplined rubidium clock (SRS FS725) with an intrinsic frequency stability of 10^{-11} in 1 s integration time and 10^{-12} in 10 000 s. This clock also serves as long term reference for all RF frequencies in the experiment and its stability has been verified to $\Delta\nu/\nu \approx 10^{-11}$ via an optical fiber network [77].

The frequency of the light at wavelength λ_1 is determined by counting beatnote frequency ν_{B_1} between light from one mode of the frequency comb and light from the Ti:sapphire laser (see Fig. 4.3), which is actively stabilized to better than 10 kHz. Varying the frequency of the light at wavelength λ_1 is achieved by changing the

²⁵This (effective) value differs from the published article, it was deduced using Eq. (1.57), comparing intensities determined with the Bloch equations model with total beam power measurements.

Figure 4.3 Scheme to transfer the $\Delta\nu/\nu = 10^{-11}$ frequency stability via the frequency comb to light at wavelengths λ_1 and λ_2 . The light at wavelength λ_1 is produced by second harmonic generation of light from a Ti:sapphire laser, locked to the frequency comb with beatnote B_1 . The light at wavelength λ_2 is referenced to the frequency comb via a diode laser stabilized to I_2 line R25 (6–5) a_3 . The frequency of this laser is measured with beatnote B_2 . The light at wavelength λ_2 itself is produced with a dye laser offset-locked to the reference diode laser with beatnote B'_2 . AOM-2 is switched between two frequencies for laser cooling and for probing the signal.

Figure 4.4 Visual representation of intermediate steps linking laser frequencies (a) ν_1 and (b) ν_2 in the trap to two modes of the frequency comb (see Table 4.1).

repetition rate of the comb. After frequency doubling, the light passes through an acousto-optic modulator operated at a fixed frequency $\nu_{\text{AOM-1}}$ (see Section 2.2.1).

The frequency of the second light field at wavelength λ_2 is determined via an intermediate diode laser (see Fig. 4.3), the long-term frequency stability of which is provided by saturated absorption spectroscopy [152] of hyperfine component a_3 of line²⁶ R25 (6–5) in molecular $^{127}\text{I}_2$. The frequency of the diode laser is determined by counting beatnote frequency ν_{B_2} with light from the frequency comb. This setup has also provided the frequency of the iodine line as

$$\nu_{\text{R25 (6-5)} a_3} = 461\,312\,288.10(2) \text{ MHz} \quad (4.1)$$

²⁶In the published article, we mislabeled the line as P25. The concerning hyperfine component is the third counting from low frequency, this is component s in the notation of Ref. 153. Another recent (though not unique) implementation of stabilizing a 650 nm laser to I_2 can be found in Ref. 154.

Table 4.1 Intermediate frequencies to determine the laser frequencies in the trap (see Fig. 4.4). Between measurements, the repetition rate of the frequency comb $\nu_{\text{comb,rep}}$ is varied to change frequency ν_1 . Offset $\nu_{B'_2}$ is varied to change frequency ν_2 for recording excitation spectra.

Frequency	Value
$\nu_{\text{comb,rep}}$ (typical)	250 000 233.5 Hz
$\nu_{\text{comb,offset}}$	−40 000 000.0 Hz
For the light at wavelength $\lambda_1 = 494$ nm:	
$\nu_1 = 2 \times (\nu_{\text{comb,offset}} + m_1 \times \nu_{\text{comb,rep}} + \nu_{B_1}) + \nu_{\text{AOM-1}}$	
Mode number m_1	1214851
ν_{B_1}	+29.01(1) MHz
$\nu_{\text{AOM-1}}$	+198.90 MHz
For the light at wavelength $\lambda_2 = 650$ nm:	
$\nu_2 = \nu_{\text{comb,offset}} + m_2 \times \nu_{\text{comb,rep}} + \nu_{B_2} + \nu_{B'_2} + 2 \times \nu_{\text{AOM-2}}$	
Mode number m_2	1845248
ν_{B_2} (at $\nu_{\text{comb,rep}}$ given)	−27.33(1) MHz
$\nu_{B'_2}$	−1116.8(0.1) MHz to −1274.2(0.1) MHz
$\nu_{\text{AOM-2}}$ (double pass)	+348.00 MHz

at an I₂ cell (cold finger) temperature of 25 °C, corresponding to a vapor pressure of 0.4 mbar. This particular line had not previously been calibrated to this accuracy in a compilation [153,155]. See Refs. 49,119,156 for more details on our iodine spectroscopy setup.

The dye laser producing the light at wavelength λ_2 is locked to the reference diode laser at a variable offset using an additional beatnote at frequency $\nu_{B'_2}$. The light is then frequency-shifted by double passing through AOM-2 (see Section 2.2.1). Since the lasers are used simultaneously for laser cooling and performing spectroscopy, blue-detuning either laser can lead to heating of the ions and loss of signal. To prevent this, a fast switch (Mini-Circuits ZASW-2-50) is used to switch the RF drive of AOM-2 between two settings at a rate of 53.6 kHz with a 20 % duty cycle:

Spectroscopy setting. A constant frequency $\nu_{\text{AOM-2}}$, which combined with the variable offset $\nu_{B'_2}$ serves for probing the transition of interest during 3.7 μ s.

Laser cooling setting. A varying AOM frequency that compensates offset $\nu_{B'_2}$, which provides a fixed resulting red-detuned frequency for laser cooling the ion during the remaining 14.9 μ s of each cycle.

The RF switching time is <25 ns; the time constant for optical pumping is typically a fraction of a microsecond (see Fig. 1.6), while rethermalization takes on the order

of $\geq 100 \mu\text{s}$ [147]. The block pulse controlling the switch is also used for gating the PMT signal in the DAQ, allowing cooling and spectroscopy signals to be analyzed separately. An overview of the settings relevant for determining both laser frequencies is given in Table 4.1.

4.2 Lineshape Fitting

We use the optical Bloch equations introduced in Section 1.3.3 to calculate the Doppler-free spectrum of a single Ba^+ ion [112, 157–159]. This description includes the interaction of the ion with the two laser fields as well as relaxation and decoherence effects. We record the spectrum of a Ba^+ ion by measuring the fluorescence signal with the PMT while scanning frequency ν_2 across the $5d^2D_{3/2} - 6p^2P_{1/2}$ resonance. To fit this data, the population of the $^2P_{1/2}$ level ($\rho_{33} + \rho_{44}$) is obtained from the steady-state solution of the optical Bloch equations while varying $\Delta\nu_2$. The detuning parameters $\Delta\nu_1$ and $\Delta\nu_2$,

$$\begin{aligned}\Delta\nu_1 &= \Delta\omega_1/2\pi = \nu_1 - \nu_{(6s^2S_{1/2} - 5d^2D_{3/2})} - \nu_{(5d^2D_{3/2} - 6p^2P_{1/2})} \\ \Delta\nu_2 &= \Delta\omega_2/2\pi = \nu_2 - \nu_{(5d^2D_{3/2} - 6p^2P_{1/2})},\end{aligned}\tag{4.2}$$

relate the known laser frequencies ν_1 and ν_2 to the Ba^+ transition frequencies; the chosen parametrization (4.2) minimizes the correlation between fit parameters. The full set of parameters needed for a calculation is given in Table 1.5. The effects of the various parameters on the spectra are not fully orthogonal and a single spectrum typically contains insufficient information for their unambiguous determination. For the partial decay rates Γ_k , we use the values in Table 1.6. The Rabi frequencies are related to the measured laser powers, through the saturation intensities and the (effective) beam size. The laser polarization states and magnetic field are also externally measured, although the recorded spectra remain the most sensitive probe of the conditions at the position of the ion.

We perform a numerical χ^2 minimization, generally fitting the atomic transition frequencies $\nu_{(5d^2D_{3/2} - 6p^2P_{1/2})}$, $\nu_{(6s^2S_{1/2} - 5d^2D_{3/2})}$, the Rabi frequencies Ω_1 and Ω_2 , and the laser linewidth γ_l to background-subtracted data, fixing the other parameters and setting the micromotion velocity v_0 to zero for the single ion data presented here. We take the optimal value for the vertical scaling factor, effectively fitting only the shape of the spectra. Before extracting the atomic transition frequencies, we present a few examples showing that our lineshape model describes the data well.

4.2.1 Laser power and detuning

Figure 4.5a shows a set of four spectra recorded at different intensities of the light at wavelength λ_2 , corresponding to different Rabi frequencies Ω_2 as per Eq. (1.55). The

Figure 4.5 Example fluorescence spectra of the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition in a single $^{138}\text{Ba}^+$ ion (5 November 2014). The magnetic field is $170\mu\text{T}$ in z -direction, the 494nm laser light is linearly polarized parallel to $\mathbf{B}$ and the 650nm laser light is circularly polarized. Solid lines are the results of fitting the optical Bloch equations to the data. (a) Spectra recorded at different 650nm light intensities; frequency ν_1 is kept constant with $\Delta\nu_1 \approx 0\text{MHz}$. (b) Spectra recorded at different detunings $\Delta\nu_1$ at constant light intensities. Note that baselines have been shifted to display the spectra (dashed lines).

spectra are fitted with the lineshape model, assuming perfect linear polarization for the laser at 494nm $(\alpha_1, \beta_1) = (0^\circ, 0^\circ)$, perfect circular polarization for the laser at 650nm $(\alpha_2, \beta_2) = (0^\circ, 90^\circ)$ with the lasers propagating against the y -direction $(\theta_l, \phi_l) = (90^\circ, -90^\circ)$. The saturation parameter S_2 ranged from 2.4 to 32, demonstrating power broadening. Frequency ν_1 was kept constant during these measurements. The most prominent features in the spectra are the wide one-photon peak of the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition centered at $\Delta\nu_2 = 0\text{MHz}$ and a dip in fluorescence (electromagnetically induced transparency) caused by the two-photon process at $\Delta\nu_1 = \Delta\nu_2$, which is centered at the same frequency in this case, since $\Delta\nu_1 \approx 0\text{MHz}$. The polarizations of the two laser fields determine which coherences cause a fluorescence dip. For the measurements presented here, the dominant contributions are from coherences $|1\rangle\langle 5|$ and $|2\rangle\langle 8|$ (refer to Fig. 4.1); the magnitude of the magnetic field is too small to resolve the two individual components. Figure 4.5b shows spectra recorded at constant laser intensities with different detunings $\Delta\nu_1$. We find good

Figure 4.6 Example fluorescence spectra of the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition for different laser polarization and magnetic field settings (2 September 2014). The solid line corresponds to the adjusted optical Bloch equations model, including the laser polarizations in the fit. Both light fields are partially circularly polarized with $\beta_1 = -13^\circ$ and $\beta_2 = +35^\circ$. (a) The angles between the linearly-polarized components of the light fields and the magnetic field are 88° and 67° , respectively, with $|\mathbf{B}| = 570 \mu\text{T}$; (b) the angles are changed to 62° and 87° with $|\mathbf{B}| = 460 \mu\text{T}$. The chosen detuning of $\Delta\nu_1 \approx 0 \text{ MHz}$ results in symmetric lineshapes; even for a positive detuning the ions remain cooled and localized by rapidly switching $\Delta\nu_2$ between the spectroscopy setting and a red-detuned laser cooling setting.

agreement between the data and fitted lineshapes in all cases.

4.2.2 Magnetic field and laser polarization

We have recorded additional spectra for different magnetic field settings, laser intensities and laser polarizations to study systematic effects. An example of such spectra is shown in Fig. 4.6 where the angles between the direction of polarization of the light at wavelength λ_1 and λ_2 and the magnetic field are changed. In these polarization states, multiple dips appear in the fluorescence. The relative strengths of the coherences producing the pattern of dips are sensitive to changes in the polarization. For example, in Fig. 4.6a, the outermost features are due to coherences $|1\rangle\langle 8|$ and $|2\rangle\langle 5|$; the frequency difference between these dips can be used as a calibration of the magnetic field strength $|\mathbf{B}|$ at the position of the ions.

4.2.3 Ion micromotion

Even when not leading to complete signal loss, ion motion can affect the observed optical spectra (see Section 3.6), requiring ion temperature and displacement to be minimized to prevent distortions. As discussed before, ion motion consist of driven micromotion at the trap frequency Ω_{RF} and thermal macromotion. The optical Bloch

Figure 4.7 Extracted transition frequency $\nu_{(5d^2D_{3/2} - 6p^2P_{1/2})}$ as function of saturation parameter S_2 (corresponding to Ω_2) for (a) $\Delta\nu_1 = 0.0$ MHz, including the spectra of Fig. 4.5a, and (b) $\Delta\nu_1 = -1.2$ MHz (5 November 2014). An intensity-dependent shift can be seen, which we attribute to a small mismatch between fit model and experiment in polarization or magnetic field direction. The solid line is a linear extrapolation to zero laser light intensity, with 1σ confidence bounds indicated.

equations model includes the effect of micromotion on the spectra, modeled using the matrix continued fraction formalism [112]. The micromotion is parametrized by the (projected) velocity amplitude v_0 which can be included when fitting the data. This encompasses both intrinsic micromotion and excess micromotion due to displacement from the RF minimum. In principle, the macromotion at secular frequencies $\omega_{\text{sec},i}$ could be treated in the same way, adding additional motion components and velocity amplitude parameters. However, when investigating this effect on generated spectra by summing over oscillation states to model a thermal distribution, it becomes clear that the resulting Doppler broadening is hard to distinguish from a combination of increased laser linewidth, frequency shifts, changed laser intensities, magnetic field strength and overall scaling (also see Refs. 146, 147). Therefore, for extracting frequencies, we only use data obtained from a single well-cooled ion (Fig. 4.5), where the axial bias voltages $U_{\text{bias},i}$ were set to minimize excess micromotion.

4.3 Results and Discussion

We extract the transition frequencies $\nu_{(5d^2D_{3/2} - 6p^2P_{1/2})}$ and $\nu_{(6s^2S_{1/2} - 5d^2D_{3/2})}$ by individually fitting a lineshape calculated by numerically solving the eight-level optical Bloch equations to a selection of single-ion fluorescence spectra. The scaling of the Rabi frequencies Ω_1 and Ω_2 with recorded laser powers, and the laser linewidth γ_l are taken

from a global fit to the full data set, the rest of the parameters are set as described before. Each of the spectra yields a value for the two Ba^+ transition frequencies. The fit results are found to be consistent, except for transition frequency $\nu_{(5d^2D_{3/2} - 6p^2P_{1/2})}$. Here a small dependence on the laser intensity corresponding to Ω_2 , with other experimental parameters unchanged, is found (see Fig. 4.7).

Intensity-dependent light shift effects are included in the optical Bloch equations [157–159] and should drop out in the fitting procedure. However, a mismatch in polarization or magnetic field orientation between the fit model and experiment could modify a transition amplitude component that results in a mismatched light shift. This would be explained by the misalignment of laser polarization angles with respect to the magnetic field of a few degrees. We determine the atomic transition frequency by extrapolating the fitted $\nu_{(5d^2D_{3/2} - 6p^2P_{1/2})}$ to zero laser intensity $S_2 = 0$ (see Fig. 4.7). A second set of spectra recorded at detuning $\Delta\nu_1 = -1.2\text{ MHz}$ yields the same result within errors. Note that the extrapolation is an approximate method, an alternate approach would be not to fix the laser polarization to pure linear/circular polarization under perfect right angles to the magnetic field but to fit also these parameters to the data in a global fit. The apparent intensity-dependent shift then vanishes and this yields the same atomic frequencies at the present uncertainty level. The weighted average of the $5d^2D_{3/2} - 6p^2P_{1/2}$ and $6s^2S_{1/2} - 5d^2D_{3/2}$ transition frequencies as well as their sum, the $6s^2S_{1/2} - 6p^2P_{1/2}$ transition frequency, are given in Table 4.2.

We have determined the optical transition frequencies of the $6s^2S_{1/2} - 6p^2P_{1/2}$, $5d^2D_{3/2} - 6p^2P_{1/2}$, and $6s^2S_{1/2} - 5d^2D_{3/2}$ transitions in $^{138}\text{Ba}^+$ to sub-MHz accuracy using a single trapped ion (see Table 4.2). The eight-level optical Bloch equations satisfactorily describes the lineshapes under the conditions in our experiment. Previous measurements had obtained these transition frequencies between low-lying levels to order 100 MHz accuracy using Fourier transform spectroscopy in large ion samples [50, 160]. This work improved upon the earlier measurements by more than two orders of magnitude. Since publishing, a new measurement of the $6s^2S_{1/2} - 6p^2P_{1/2}$ transition has appeared [161] that is consistent with our result. Very recently an improved measurement of the $6s^2S_{1/2} - 5d^2D_{5/2}$ clock transition has been put on arXiv [102].

Table 4.2 Determined transition frequencies of the $5d^2D_{3/2} - 6p^2P_{1/2}$ and $6s^2S_{1/2} - 5d^2D_{3/2}$ transitions in $^{138}\text{Ba}^+$. Their sum yields the frequency of the $6s^2S_{1/2} - 6p^2P_{1/2}$ transition, and combining our result with Ref. 79 yields the frequency of the $6s^2S_{1/2} - 5d^2D_{5/2}$ transition.

Transition	Frequency (MHz)	Relative uncertainty
$\nu(5d^2D_{3/2} - 6p^2P_{1/2})$	461 311 878.5(0.1)	2×10^{-10}
$\nu(6s^2S_{1/2} - 5d^2D_{3/2})$	146 114 384.0(0.1)	6×10^{-10}
$\nu(6s^2S_{1/2} - 6p^2P_{1/2})$	607 426 262.5(0.2)	3×10^{-10}
$\nu(6s^2S_{1/2} - 5d^2D_{5/2})$	170 126 432.3(0.1)	6×10^{-10}

Chapter 5

Light Shifts and Lineshapes in $^{138}\text{Ba}^+$

The term *light shift* refers to the phenomenon that the energy levels of an atom change when placed in a light field. This is the dynamic (AC) Stark effect, where the energy eigenstates of the combined system of the atom and the time-varying electric field differ from those of the atom in vacuum due to their interaction. An atom reacts most strongly to a light field at resonance with one of its transitions, causing population transfer between atomic states. However, light shifts are still present for off-resonant light fields that weakly couple atomic states and this provides a method for experimentally investigating the structure of an atom (e.g. transition amplitudes). The planned atomic parity violation measurement relies on determining the small additional light shift due the dipole transition amplitude induced by the weak interaction, and clock transitions in atomic clocks are also affected by light shifts (see Chapter 1).

We start this chapter by establishing equations to calculate light shifts for barium ions in a light field of arbitrary frequency (Section 5.1). We have performed proof-of-principle spectroscopy measurements of trapped Ba^+ ions by adding an off-resonant laser producing light shifts to the setup (Section 5.2). The experimental data are analyzed by combining the light shift calculations with the optical Bloch equations lineshape model (Section 5.3). Finally, we present the experimental results and reflect on the lessons learned for a measurement of the Weinberg angle (Section 5.4).

5.1 Calculating Light Shifts

Light shifts have been introduced in Chapter 1; here we expand the discussion to calculating light shifts for a general (many level) atomic system.

Two-level system

We have shown in Section 1.3.1 that the far off-resonant energy shifts ΔE for a two-level system placed in a (classical) light field with amplitude $\mathcal{E}$ and angular frequency ω is

given by

$$\Delta E(\omega) = \pm \frac{1}{4} \frac{|\langle J'|D|J\rangle|^2}{\hbar\omega - \hbar\omega_0} \mathcal{E}^2, \quad (5.1)$$

where ω_0 is the transition frequency and $\langle J'|D|J\rangle$ is the transition dipole moment. The positive and negative sign should be taken for the ground and excited state, respectively. This expression is valid as long as $|\omega - \omega_0| \gg \Gamma$, where Γ is the linewidth of the excited state. Light shifts are often given in terms of the dynamic dipole polarizability $\alpha(\omega)$, which is independent of the light field. It is defined for the two levels as

$$\alpha(\omega) = \mp \frac{|\langle J'|D|J\rangle|^2}{E_J - E_{J'} + \hbar\omega}, \quad (5.2)$$

where E_J and $E_{J'}$ are the level energies of the ground and excited state with total angular momentum quantum numbers J and J' , respectively. The light shift is now written as

$$\Delta E(\omega) = -\frac{1}{4} \alpha(\omega) \mathcal{E}^2. \quad (5.3)$$

The above expressions all use the rotating wave approximation, where only the co-rotating term was kept. For the more general case, the counter-rotating term (Bloch–Siegert shift) must also be taken into account.

5.1.1 Multi-level system

We use the sum-over-states approach to generalize Eqs. (5.2) and (5.3) to an atomic system with many levels and transitions. The dipole polarizability for a sublevel with quantum numbers (J, m) in a light field with (complex) normalized polarization vector $\boldsymbol{\varepsilon}$ is given by [46, 90, 92]

$$\alpha_{Jm}(\omega) = - \sum_{J'm'} \left(\frac{|\langle J'm'|\boldsymbol{\varepsilon} \cdot \mathbf{D}|Jm\rangle|^2}{E_J - E_{J'} + \hbar\omega} + \frac{|\langle Jm|\boldsymbol{\varepsilon} \cdot \mathbf{D}|J'm'\rangle|^2}{E_J - E_{J'} - \hbar\omega} \right), \quad (5.4)$$

where the summation runs over all sublevels $(J'm')$.

We must be careful in dealing with the tensor nature of the dipole operator $\mathbf{D}$ [90, 92] when evaluating Eq. (5.4). The light shift can be split into a scalar term with spherical symmetry (independent of the polarization of the light field), a vector term with the symmetry of a magnetic dipole interacting with a fictitious magnetic field (only present for circularly polarized light) and a tensor term corresponding to an electric quadrupole interacting with a fictitious electric field gradient [162]. Taking the z -axis as the quantization axis²⁷ and following the notation of Ref. 106, the light shift can

²⁷In our experiment, the quantization axis is set by the magnetic field, so Eq. (5.5) should be evaluated in a coordinate system where the z -axis has been rotated to point along the magnetic field vector. Alternatively, the $\mathcal{E}$ -dependence of the light shift components for an arbitrary quantization axis can be found in Ref. 100.

be written as

$$\Delta E_{Jm}(\omega) = -\frac{\alpha_0(\omega)}{4} |\mathcal{E}|^2 - \frac{\alpha_1(\omega)}{4} \frac{m}{2J} (i\mathcal{E} \times \mathcal{E}^*)_z - \frac{\alpha_2(\omega)}{4} \frac{3m^2 - J(J+1)}{J(2J-1)} \frac{3|\mathcal{E}_z|^2 - |\mathcal{E}|^2}{2} \quad (5.5)$$

where the three components of the dynamic polarizability for level J (but independent of m) are given by

$$\begin{aligned} \alpha_0(\omega) &= -\frac{2}{3(2J+1)} \sum_{J' \neq J} \frac{E_J - E_{J'}}{(E_J - E_{J'})^2 - (\hbar\omega)^2} |\langle J \| D \| J' \rangle|^2 \phi_0(J, J') \\ \alpha_1(\omega) &= -\frac{2}{(2J+1)} \sum_{J' \neq J} \frac{\hbar\omega}{(E_J - E_{J'})^2 - (\hbar\omega)^2} |\langle J \| D \| J' \rangle|^2 \phi_1(J, J') \\ \alpha_2(\omega) &= -\frac{2}{3(2J+1)} \sum_{J' \neq J} \frac{E_J - E_{J'}}{(E_J - E_{J'})^2 - (\hbar\omega)^2} |\langle J \| D \| J' \rangle|^2 \phi_2(J, J') \end{aligned} \quad (5.6)$$

with angular factors ϕ_k defined as²⁸

$$\begin{aligned} \phi_0(J, J') &= \delta_{J-1, J'} + \delta_{J, J'} + \delta_{J+1, J'} \\ \phi_1(J, J') &= \delta_{J-1, J'} + \frac{J}{J(J+1)} \delta_{J, J'} - \frac{J}{J+1} \delta_{J+1, J'} \\ \phi_2(J, J') &= -\delta_{J-1, J'} + \frac{2J-1}{J+1} \delta_{J, J'} - \frac{J(2J-1)}{(J+1)(2J+3)} \delta_{J+1, J'}. \end{aligned}$$

The vector light shift is only present for levels with total angular momentum $J \geq 1/2$ and the tensor light shift only for levels with $J \geq 1$.

In the limit $\omega \rightarrow 0$, the dynamic polarizabilities $\alpha_0(\omega)$ and $\alpha_2(\omega)$ reduce²⁹ to the static scalar and tensor polarizabilities of the DC Stark effect (taking $\mathcal{E} = \mathcal{E}_z \hat{z}$) [91]:

$$\Delta E_{Jm}(0) = -\frac{\alpha_0(0)}{2} \mathcal{E}_z^2 - \frac{\alpha_2(0)}{2} \frac{3m^2 - J(J+1)}{J(2J-1)} \mathcal{E}_z^2. \quad (5.7)$$

Note that the vector polarizability α_1 vanishes for static electric fields because its frequency dependence differs from that of the scalar and tensor components, as can be seen from Eq. (5.6). The calculated static polarizabilities can be compared to measured values [98].

²⁸Note that our definition of ϕ_1 differs by a factor $-2J$ from the definition given in Ref. 106 to bring Eq. (5.5) into a form where each term has the same structure.

²⁹The overall difference by a factor 2 is probably explained by time-averaging the amplitude of an oscillating electric field.

Alternate expression

The following compact expression for the light shift in a many-level system also shows up in the literature (e.g. in Refs. 163, 164):

$$\alpha_{Jm}(\omega) = - \sum_{J'm'} \frac{E_J - E_{J'}}{(E_J - E_{J'})^2 - (\hbar\omega)^2} \begin{pmatrix} J & 1 & J' \\ -m & q & m' \end{pmatrix}^2 |\langle J \| D \| J' \rangle|^2, \quad (5.8)$$

where q indicates the polarization of the light field in the spherical basis ($q = 0$ is linearly polarized light, $q = \pm 1$ is circularly polarized light). However, the differing frequency dependence of the vector component is not captured in the compact expression above, making it in fact valid only³⁰ for linearly polarized light fields ($q = 0$).

5.1.2 Determining transition matrix elements

To calculate light shifts using Eqs. (5.5) and (5.6), we need level energies and transition strengths for the atomic system under consideration. For our calculations on Ba^+ , we include the 21 levels with $l \leq 3$ and $E_J \leq 65\,000\text{ cm}^{-1}$, taking level energies from Refs. 50, 113 and matrix elements from Ref. 106. We neglect contributions from core excitations and coupling to continuum states. Calculated dynamic dipole polarizabilities for the three levels in the Ba^+ Λ -system are shown in Fig. 5.1. The figure shows the divergent behavior of the polarizability of each level around the wavelengths of transitions linking it to other levels. The finite natural linewidth of transitions has to be taken into account when the detuning becomes comparable, but this plays no role at the scale of this figure. The scalar polarizability α_0 is independent of $\mathcal{E}$ -polarization and identical for all m sublevels. The contributions by the vector (α_1) and tensor components (α_2) depend on polarization and m , leading to a range of possible values, indicated by shaded areas. Note that since the polarizabilities of the $6s\ ^2\text{S}_{1/2}$ and $6p\ ^2\text{P}_{1/2}$ levels do not have a tensor component, the light shift of their two $m = \pm 1/2$ sublevels only differs in a circularly (or elliptically) polarized light field.

Experimentally measuring light shifts can thus be used to probe the transition matrix elements (the level energies are known to much higher accuracy). Light shifts scale with the intensity of the light field, but measuring this to sufficient accuracy at the location of a trapped ion is difficult in general. Determining the ratio of light shift components makes this systematic effect drop out [38, 39]. From Eq. (5.6), it is clear that the sensitivity of the light shift to a particular matrix element is greatest when the frequency of the light field is close to that of a corresponding atomic transition. Picking the right frequency for a light shift measurement allows to maximize the new information gained [106].

³⁰This expression was, however, used to calculate light shifts for circularly polarized light fields in Refs. 163, 164; these results are thus invalid. Discrepancies in the results for circularly polarized light were also pointed out in Ref. 165.

Figure 5.1 Calculated polarizabilities of the $6s^2S_{1/2}$, $6p^2P_{1/2}$ and $5d^2D_{3/2}$ levels of Ba^+ (atomic units). Thick lines indicate the scalar component α_0 , light shaded areas indicate the extent of possible values for individual m sublevels for any polarization of the light field and dark shaded areas indicate possible values for linear polarization only (i.e. scalar plus tensor component α_2 , only applicable for $^2D_{3/2}$ sublevels). Atomic transitions where polarizabilities diverge are indicated by vertical lines.

5.2 Experimental Setup

The experimental setup used for the measurements in this chapter is the same as has been used up to this point, with one additional light field besides the two used for laser cooling and spectroscopy. The additional electromagnetic field induces light shifts in the trapped Ba^+ ions and we refer to it as the *light shift laser*. As Eq. (5.5) shows, the effect depends on the intensity, wavelength and polarization of this light field. The experiments were performed with a Paul trap adapted by drilling 1 mm holes all the way through both end cap electrodes to provide optical access along its axial direction (see Fig. 5.2).

In a first attempt to observe light shifts, an available high-power CW fiber laser (Toptica DL-RFA-SHG PRO) was used [119]. It operated around the sodium D line wavelength of 589 nm, which is close to the $5d^2D_{3/2} - 6p^2P_{3/2}$ transition in Ba^+ at 585.5 nm. However, using a light field at this wavelength to induce light shifts presented two issues. First off, at this wavelength, light shift contributions from various transitions happen to cancel almost (see Fig. 5.1), producing only a small effect for a

Figure 5.2 Schematic diagram of the Paul trap used for trapping Ba^+ ions with an additional electromagnetic field for inducing light shifts produced by a laser beam passing axially through both end cap electrodes.

Figure 5.3 Optical diagram of the 650 nm diode laser for inducing light shifts (addition to Fig. 2.6). The polarization direction is set by a $\lambda/2$ plate in a computer-controlled rotation stage; beam steering is by a computer-controlled mirror.

given intensity. Secondly, light at this wavelength also induces transitions from the $^2\text{D}_{3/2}$ to the $^2\text{P}_{3/2}$ level, shelving ions into the $^2\text{D}_{5/2}$ dark state. The latter effect was found to be dominant and (without installing an additional laser to repump the $^2\text{D}_{5/2}$ level) precluded the observation of the light shift effect [119].

The fiber laser was replaced by a diode laser (Opnext HL6366DG) in ECDL configuration operating at 650 nm close to the $5d\ ^2\text{D}_{3/2} - 6p\ ^2\text{P}_{1/2}$ transition but at greater detuning than the spectroscopy laser driving the same transition (see Fig. 5.3). The magnitude and sign of the light shift effect are controlled by varying the detuning of the laser frequency from resonance within a range of ± 20 GHz and its power up to about 3 mW. Off-resonant transitions driven by this laser are not as troublesome since the same transitions already take place as part of the laser cooling cycle. The frequency of the additional laser is monitored by a wavelength meter and its intensity

by photodiodes. The diode laser produces linearly polarized light, the orientation of which is controlled by a $\lambda/2$ plate mounted in a motorized rotation stage (Thorlabs PRM128) placed before the vacuum chamber housing the trap. A linear polarizer in a second motorized rotation stage is placed after the vacuum chamber to analyze the polarization state of the light.

Since the light shift effect scales with the light intensity, it is sensitive to changes in beam size and overlap with the trapped ions. The overlap of the light shift laser beam with the trapped ions was checked by blocking the other 650 nm laser, using the light shift laser for repumping and maximizing the fluorescence [119]. We have used the setup as described here for a set of exploratory experiments demonstrating the observation of light shift effects. To obtain quantitative results of transition matrix elements in future experiments, more care has to be taken in controlling the wavelength, polarization and intensity at the position of the ions.

5.3 Data Analysis

The experimental results reported in this chapter consist of frequency spectra obtained through recording the fluorescence at 494 nm while varying the frequency ν_2 of the 650 nm spectroscopy laser, as in Chapter 4.

5.3.1 Combining Optical Bloch equations with light shifts

As long as the detuning of the additional light field at 650 nm is much larger than the detuning of the 650 nm spectroscopy laser, $\Delta\nu_{\text{LS}} \gg \Delta\nu_2$, we can treat the effect of the former as a small perturbation to the spectra described by the Bloch equations. We use Eq. (5.5) (implemented in Mathematica) to calculate the shifts of all eight sublevels in the $6s^2S_{1/2}$, $6p^2P_{1/2}$, $5d^2D_{3/2}$ Λ -system for a given intensity, detuning and polarization state of the light shift laser. A diagonal matrix H_{LS} with these shifts is added to the Hamiltonian H defined in Eq. (1.49), similar to the energy shifts due to the Zeeman effect:

$$H_{\text{LS}} = \begin{pmatrix} \Delta E_{|1\rangle}(\omega) & 0 & \dots & 0 \\ 0 & \Delta E_{|2\rangle}(\omega) & & \\ \vdots & & \ddots & \\ 0 & & & \Delta E_{|8\rangle}(\omega) \end{pmatrix}. \quad (5.9)$$

Playing around with Eq. (5.5), various relations between the light shifts of the eight sublevels can be derived. Because the light shift laser frequency is close to that of the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition, the corresponding term dominates in the sums of Eq. (5.6). This means that only the $^2D_{3/2}$ and $^2P_{1/2}$ sublevels shift appreciably (the total shift is zero). Furthermore, Eq. (5.4) shows that the sign of the shift is

Figure 5.4 Example lineshape combining Bloch equations with light shift calculation: (a) unshifted (dashed) and shifted (solid) fluorescence lineshape as function of 650 nm laser frequency ν_2 for a light shift laser linearly polarized parallel to the magnetic field and detuned below resonance; (b) magnitude of coherences for unshifted and shifted spectra. Parameters: $\Delta\nu_1 = -10$ MHz, $S_1 = 4$, $S_2 = 8$, light shift laser linearly polarized in z -direction and magnetic field 800 μT in z -direction.

determined by the detuning in the denominator, meaning that the shifts of both $^2\text{P}_{1/2}$ sublevels have the same sign, opposite to that of the shifts of all $^2\text{D}_{3/2}$ sublevels. Finally, from Eq. (5.5) it can be seen that the shift depends only on the absolute value $|m|$ in case the light shift laser has no circularly polarized component.

An example incorporating the effect of light shifts into a spectrum calculated with the Bloch equations is shown in Fig. 5.4. Here the frequency of the light shift laser is assumed to be negatively detuned from the $^2\text{D}_{3/2} - ^2\text{P}_{1/2}$ transition and the light to be linearly polarized parallel to the magnetic field. The center of the wide one-photon peak is shifted toward higher frequencies for a light shift field detuned below the resonance (i.e. at longer wavelength, see Fig. 5.1). As the dips in the spectrum are caused by coherences between sublevels of $^2\text{S}_{1/2}$ and $^2\text{D}_{3/2}$, here the frequency shifts of the dips are determined by the light shift of the $^2\text{D}_{3/2}$ sublevels (since the $^2\text{S}_{1/2}$ sublevels are not shifted). The relative shift magnitude of the four $^2\text{D}_{3/2}$ sublevels depends on the polarization of the light shift field.

5.3.2 Parametrizing the light shift effect

Extracting light shift magnitudes in a fit to experimental data adds additional parameters to the lineshape model. We find that the parametrization of light shift effects needs be carefully chosen to ensure reliable convergence and avoid unphysical results. The discussed constraints indicate that for a linearly polarized light field, we effectively have only three independent light shift components: the shift of each pair of sublevels $^2P_{1/2,m=\pm 1/2}$, $^2D_{3/2,m=\pm 1/2}$ and $^2D_{3/2,m=\pm 3/2}$. Furthermore, around the chosen wavelength all shift magnitudes $|\Delta E_{|a\rangle}|$ depend linearly on squared matrix element $|\langle 5d\ ^2D_{3/2} \| D \| 6p\ ^2P_{1/2} \rangle|^2$, with coefficients determined by the detuning, intensity and polarization of the light shift laser. Similar to the fit constraints discussed in Section 4.2, we can calculate the light shift ratios of the three pairs of sublevels for a given polarization state and apply these as constraints, fitting only the overall shift magnitude.

In practice, we did not independently measure the intensity of the light shift laser at the position of the ions to sufficient accuracy in these experiments to extract information on the matrix element. Instead, we study how well our lineshape model describes the fluorescence spectra and use the observed frequency shifts to deduce the intensity of the light shift laser. As an example, for a light shift field polarized orthogonally to the magnetic field and detuned by $\Delta\nu_{LS} = -1$ GHz, the diagonal elements of H_{LS} in Eq. (5.9) are calculated using Eq. (5.5) to be

$$\Delta E_{|a\rangle} = h \{-0.01, -0.01, +453, +453, -340, -113, -113, -340\} \text{ kHz}/(\text{W}/\text{cm}^2) \times I_{LS}, \quad (5.10)$$

where I_{LS} is the intensity of the light shift field at the position of the ions.

5.4 Results and Discussion

Typically, data were collected by alternating between spectra with and without blocking the light shift laser in order to isolate its effect. Experimental conditions were monitored as before; the number of trapped ions during the measurements varied from a single ion up to crystals of about a dozen ions. Here we present several series of spectra with/without light shift where a single parameter (e.g. light shift laser wavelength) was varied. For each spectrum, a double scan was performed, scanning detuning $\Delta\nu_2$ once up and once down. Stretches of data where the signal dropped for any reason are excluded and then the two scans are averaged.

While fitting the lineshape model, the atomic transition frequencies are fixed to the values determined in Chapter 4. The saturation intensities in terms of 494 nm and 650 nm laser power are fitted individually for each spectrum, since these vary somewhat over time depending on the overlap between the laser beam and the trapped ions. The laser linewidth γ_l is set to 500 kHz for all spectra, determined to be a reasonable value

based on selected spectra with narrow features. The polarization of the 494 nm and 650 nm lasers was experimentally determined by measuring the intensity transmitted through a linear polarizer as function of angle. The polarization states are linear vertical for the laser at 494 nm $(\alpha_1, \beta_1) = (0^\circ, 0^\circ)$ and elliptical diagonal for the laser at 650 nm $(\alpha_2, \beta_2) = (-54^\circ, -55^\circ)$. The z and x magnetic field coils are calibrated using selected spectra (the y coils were not used here). The propagation direction of the lasers defined by the geometry of our setup (in the coordinate system of the field coils) is $(\theta_l, \phi_l) = (90^\circ, -98^\circ)$. For the data collected with multiple ions, it is found to be important to include the velocity parameter v_0 when fitting spectra to account for the effect of micromotion. The fitted velocity parameter increases with the number of ions, from <1 m/s for spectra taken with a single ion to around 8 m/s for crystals of six or more ions. With multi-ion crystals, micromotion is unavoidable since not all ions can sit in the RF minimum.

The effect of the light shift laser on the spectra qualitatively matches the calculations. The magnitude of the light shift effect at a given wavelength and intensity is found to vary somewhat over time, depending on the overlap between the light shift laser beam and the trapped ions. Another observed effect is some off-resonant scattering, visible as a vertical offset in the spectra where the light shift laser was on. To deal with this effect, only the shapes of spectra are fitted by setting the scale and offset always to their optimal values. We also take some care in picking reasonable initial parameter values to ensure fit convergence.

5.4.1 Varying intensity of light shift field

Experimental results of varying the power of the light shift laser are displayed in Figure 5.5. The intensity of the light shift laser was varied at two detunings $\Delta\nu_{\text{LS}}$, one above and one below resonance, to show shifts with both signs. The spectra are fitted with the lineshape model and fits to spectra where the light shift laser was blocked are shown for comparison (dashed). The light shift laser was polarized parallel to the magnetic field (in z -direction) and in this configuration only the $m = \pm 1/2$ sublevels of the $^2\text{P}_{1/2}$ and $^2\text{D}_{3/2}$ levels are shifted. We can describe the magnitude of the fitted light shift by taking, e.g., the scalar shift of the $^2\text{P}_{1/2}$ levels, defining

$$\Delta E_{\text{LS}} = \frac{\Delta E_{|3\rangle} + \Delta E_{|4\rangle}}{2} \approx -2 \times \frac{\Delta E_{|5\rangle} + \Delta E_{|6\rangle} + \Delta E_{|7\rangle} + \Delta E_{|8\rangle}}{4}. \quad (5.11)$$

This shift magnitude is independent of the polarization of the light shift laser polarization. It can be seen how the wide one-photon peak is shifted and some of the dark resonances are too, while dark resonances involving the $^2\text{D}_{3/2, m=\pm 3/2}$ sublevels remain at the same frequency. The fitted shifts correspond to intensities of the light shift field of up to 150 W/cm^2 . Although the lineshapes do not fit the data perfectly, combining the optical Bloch equations with calculated light shifts clearly captures the

Figure 5.5 Example data showing light shift effect varying the intensity of the light shift laser polarized parallel to the magnetic field (27 May 2016); fitted frequency shift of the $^2P_{1/2}$ sublevels (scalar light shift) is indicated. Top row: light shift laser detuned $\Delta\nu_{LS} = +13.7$ GHz, bottom row $\Delta\nu_{LS} = -5.8$ GHz. Smooth lines are the fitted lineshape model, dashed lines indicate fits to unshifted spectra for comparison (data not shown). Experimental parameters: $\Delta\nu_1 = -8.9$ MHz, single ion, light shift laser linearly polarized in z -direction, magnetic field 410 μ T in z -direction.

salient features. Some distortion of the spectra is likely caused by fluctuations in the wavelength and intensity of the light shift laser.

Figure 5.6 shows data similar to the bottom row of Fig. 5.5 at a higher magnetic field strength. This makes it easy to identify the various two-photon dips, based on their frequency relative to $\Delta\nu_2 = \Delta\nu_1$ governed by the Landé g -factors from Eq. (1.42) and their behavior when the light shift laser is on. The central two dips that do not shift are due to coherences $|1\rangle\langle 5|$ and $|2\rangle\langle 8|$ (refer to Fig. 4.1), the dips on either side that shift (by a frequency difference $\Delta E_{LS}/h$) are due to coherences $|2\rangle\langle 7|$ and $|1\rangle\langle 6|$, and the weaker dips further out that shift by the same amount are due to coherences $|2\rangle\langle 6|$ and $|1\rangle\langle 7|$. The overall shift of the lineshape envelope (one-photon peak) is given by the frequency shift of the $^2D_{3/2} - ^2P_{1/2}$ transition, which is $\frac{3}{2}\Delta E_{LS}/h$.

Changing the magnetic field to the x -direction changes the angles between the polarization directions of the lasers and the quantization axis. This results in the

Figure 5.6 Example data showing light shift effect at higher magnetic field amplitude (31 May 2016); frequency shift of the $^2P_{1/2}$ sublevels (scalar light shift) is indicated, light shift laser detuning $\Delta\nu_{\text{LS}} = -6.9$ GHz. Smooth lines are the fitted lineshape model, dashed lines are fits to unshifted spectra for comparison (data not shown). Experimental parameters: $\Delta\nu_1 = -8.9$ MHz, single ion, light shift laser linearly polarized in z -direction, magnetic field 850 μT in z -direction.

different lineshapes shown in Fig. 5.7 where now all dark resonances shift, by distinctive amounts. Similar agreement between the data and the lineshape model is found.

5.4.2 Varying wavelength of light shift field

Experimental results of varying the wavelength of the light shift laser while keeping its intensity constant are shown in Fig. 5.8. This series of spectra was recorded with light shift laser detunings $\Delta\nu_{\text{LS}}$ between -4 GHz and $+5$ GHz. The light shift laser was polarized parallel to the magnetic field direction. The intensity of the spectroscopy lasers was fairly high and the laser at 494 nm was only slightly detuned from resonance, resulting in nearly symmetrical lineshapes (see insets). The fit for spectra where the light shift laser is closest to resonance is not perfect, probably because these are most sensitive to fluctuations in the frequency of the light shift laser. The spectrum at $\Delta\nu_{\text{LS}} = +0.3$ GHz also has some missing data due to mode hopping of the light shift laser. The additional scattering due to the light shift laser is visible in the spectra as a constant vertical offset varying with the detuning of the light shift laser.

The light shift as a function of detuning $\Delta\nu_{\text{LS}}$ in Fig. 5.8 shows the characteristic dispersion-like behavior. From Eq. (5.5), we calculate the scalar light shift ΔE_{LS} close to the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition to be

$$\Delta E_{\text{LS}} \approx h \frac{-4.53 \times 10^{14} \text{ Hz}^2 / (\text{W}/\text{cm}^2)}{\Delta\nu_{\text{LS}}} I_{\text{LS}}. \quad (5.12)$$

Comparing this to our experimental result enables us to determine the (effective) Gaussian beam size of the light shift laser at this time using Eq. (1.57), finding

Figure 5.7 Example data showing light shift effect by varying the intensity of the light shift laser polarized orthogonal to the magnetic field (26 May 2016); frequency shift of the $^2P_{1/2}$ sublevels (scalar light shift) is indicated. Top row: light shift laser detuned $\Delta\nu_{LS} = +16.8$ GHz, bottom row $\Delta\nu_{LS} = -1.0$ GHz. Smooth lines are the fitted lineshape model, dashed lines indicate fits to unshifted spectra for comparison (data not shown). Experimental parameters: $\Delta\nu_1 = -8.9$ MHz, 6 to 10 ions, light shift laser linearly polarized in z -direction and magnetic field 230 μ T in x -direction.

$w_0 = 76 \mu\text{m}$. During some measurements higher intensities were achieved, corresponding to waist radii down to about $w_0 = 30 \mu\text{m}$. This variation can be explained by sub-optimal alignment of the light shift laser beam with the trapped ions in the former case, owing to movement of the mirrors or changing positions of the ions within the trap.

In conclusion, we have observed the light shift induced in $^{138}\text{Ba}^+$ by an off-resonant laser operating at a wavelength close to the $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transition at 650 nm in recorded fluorescence spectra. Light shifts play an important part in the planned atomic parity violation experiments. Combining the optical Bloch equations with calculated light shifts of the various sublevels, we have been able to reproduce the resulting lineshapes and extract the light shift magnitude with a precision of some 100 kHz. In this method the light shifts of eight sublevels are measured simultaneously. Determining ratios of light shift components in principle allows extracting information

Figure 5.8 Light shift as function of detuning $\Delta\nu_{LS}$ with light shift laser polarized parallel to the magnetic field (6 April 2016). Plotted is the shift of the $^2P_{1/2}$ sublevels (scalar light shift), normalized by laser power. Insets show selected fitted data with fit of unshifted data (dashed). Experimental parameters: $\Delta\nu_1 = -1.4$ MHz, $S_1 \approx 12$, $S_2 \approx 35$, 1 to 3 ions, light shift laser linearly polarized in z -direction, magnetic field $510 \mu\text{T}$ in z -direction.

on matrix elements without needing to precisely determine the intensity of the light shift laser at the position of the ions [38, 39]. However, this only works when the light shift components have different dependencies on the matrix elements, which was not the case at the operating wavelength of the off-resonant laser, where a single matrix element dominates. Calculations of the contributions by individual couplings can be exploited to identify the wavelength for gaining the maximum amount of information on any matrix element of interest [106]. Still, using the present method for a competitive measurement of transition matrix elements would require far better stabilization of the intensity and frequency of the light shift laser. A full investigation of systematic effects would also be necessary to compare it to methods based on RF spectroscopy.

Chapter 6

Lifetime of the $5d\ ^2D_{5/2}$ Level in $^{138}\text{Ba}^+$ from Quantum Jumps

An atomic state's lifetime is set by the strength of its coupling to lower energy states: a strongly-coupled excited state will typically spontaneously decay within nanoseconds by emitting a photon, while a weakly-coupled state may live far longer. The lowest D levels of the singly charged heavy alkaline earth metal ions are particularly long lived (seconds, up to a minute for the D levels in Ba^+) and are often referred to as metastable. The reason for this difference in lifetime of more than nine orders of magnitude is that the lowest D levels have a lower energy than the lowest P levels in these ions (see Fig. 6.1) and so the D levels ($l = 2$) decay directly to the S ground state ($l = 0$). Since both levels have the same parity, the usually dominant electric dipole transition ($E1$) is forbidden and the decay proceeds via weaker transitions, e.g. magnetic dipole ($M1$), electric quadrupole ($E2$), two photon ($2E1$), etc.

Figure 6.1 Energy level structure of singly ionized alkali earth metal ions, including Ba^+ ($n = 6$) and Ra^+ ($n = 7$). Strong $E1$ transitions are indicated with solid lines; weaker $E2$ and $M1$ transitions are shown as dashed lines for the long-lived D levels that lack decays via $E1$ transitions (two-photon transitions can be neglected [167]).

Atomic state lifetimes provide experimental access to transition amplitudes and thereby probe the long range parts of an atom's wavefunction. The transition amplitude

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between the $(n-1)d^2D_{3/2}$ level and the $ns^2S_{1/2}$ ground state is important for APV measurements where the perturbation of these levels by the weak interaction is studied [13]. Sub-percent level accuracy in experiment and theory is required for a competitive measurement of $\sin^2\theta_W$ (see Chapter 1). More generally, experimentally determined lifetimes provide a benchmark for atomic theory calculations; see e.g. Ref. 168 for a review of lifetime measurements with ion traps for many atomic system using various experimental techniques.

In this chapter we discuss a series of experiments that we performed with the aim of determining the lifetime of the $5d^2D_{5/2}$ level in $^{138}\text{Ba}^+$ to higher accuracy than before. This level's long lifetime $\tau_{D_{5/2}} \approx 30\text{ s}$ requires good control over experimental parameters on long timescales and thus these measurements also constitute a test of our experimental setup and techniques. Besides Ba^+ , lifetime measurements have been performed by other groups in various laser-cooled ionic systems stored in RF traps with similar long-lived levels³¹, including Sr^+ [169], Yb^+ [170], Hg^+ [171] and Ca^+ [172]. An early lifetime measurement in Ba^+ reported some indication of cooperative effects in an experiment with multiple ions [173], although later calculations show this explanation to be unlikely [174]. Correlation effects and a dependence of the lifetime on the number of stored ions have also been investigated in trapped Ca^+ ions [175–177], where within experimental uncertainty no dependence was found. The long-lived levels in Ba^+ are particularly sensitive to perturbations as their lifetimes are more than an order of magnitude longer than those of the other species. We have performed measurements both with single trapped Ba^+ ions and small ion crystals. Experimental parameters that could cause systematic effects have been scrutinized.

We have performed the lifetime measurements by trapping a single or a small number of Ba^+ ions in a hyperbolic Paul trap (Section 6.1) using the technique of *quantum jump spectroscopy* (Section 6.2). The experimental data are analyzed, taking into account the effect of the averaging window (Section 6.3) and several systematic effects (Section 6.4). Our final value for the $5d^2D_{5/2}$ level lifetime is compared to previous measurements and found to be significantly lower (Section 6.5). We find no dependence of the observed lifetime on the number of trapped ions.

6.1 Experimental Setup

We recap some aspects of the setup used for the experiments described here³², see Chapter 2 for further details. We trap $^{138}\text{Ba}^+$ ions in a hyperbolic Paul trap consisting of a hyperbolically shaped ring electrode with an inner diameter of 5 mm and two hyperbolically shaped end cap electrodes with their tips separated by 3.5 mm. The

³¹See e.g. Ref. 126 for an interesting overview of possible measurement schemes.

³²Several improvements to the setup were implemented during the period of lifetime measurements; this description pertains to the final iteration, used for the bulk of the data at the lowest pressure.

Figure 6.2 Energy level scheme of Ba^+ [50]. The ions are laser cooled by driving the $6s^2S_{1/2} - 6p^2P_{1/2}$ and $5d^2D_{3/2} - 6p^2P_{1/2}$ transitions. Light from an LED at wavelength 456 nm is used to populate the $5d^2D_{5/2}$ level via decay from the $6p^2P_{3/2}$ level (light at 586 nm forms an alternative). The $5d^2D_{5/2}$ level decays to either the $5d^2D_{3/2}$ level or the $6s^2S_{1/2}$ ground state with branching ratios of 15 % and 85 %, respectively [178].

trap is typically operated at frequency $\Omega_{\text{RF}} = 2\pi \times 6.5$ MHz with a voltage amplitude V_0 ranging from 100 V to 1000 V applied to the ring. The end caps can be individually biased with DC voltages $U_{\text{bias},i}$ of order ± 50 mV with respect to ground to decrease (axial) micromotion.

The trap is mounted in a stainless steel UHV chamber pumped by a 75 L/s ion pump (Gamma Vacuum TITAN 75S) and periodic use of a Ti sublimation pump (Vacom SUBLICON51) maintaining the residual gas pressure $p < 10^{-10}$ mbar. The trap is loaded with Ba^+ ions by resonantly photoionizing a beam of isotopically enriched ($>99\%$) ^{138}Ba atoms with laser light at wavelength 413 nm. The trap is reloaded every couple of hours; the oven and photoionization laser are off during the measurements.

Laser light at wavelengths 494 nm and 650 nm is employed for Doppler cooling by simultaneously driving the strong $6s^2S_{1/2} - 6p^2P_{1/2}$ and $5d^2D_{3/2} - 6p^2P_{1/2}$ transitions, respectively (see Fig. 6.2). The laser frequency stabilization is described in more detail in Chapter 4. Typical detunings from resonance are -50 MHz for the light at wavelength 494 nm and -2 MHz for the light at 650 nm. The intensity of the light at 494 nm is 0.1 W/cm^2 to 0.6 W/cm^2 and the intensity of the light at 650 nm is 0.01 W/cm^2 to 0.09 W/cm^2 . We apply a static magnetic field of typically $200 \mu\text{T}$ to remix dark states. Fluorescence from the $6p^2P_{1/2} - 6s^2S_{1/2}$ transition is detected with a PMT (Hamamatsu H11123) and an EMCCD camera (Andor iXon DU-897E-CSB-#BB). The photon-counting PMT signal is read out with a time resolution of 100 ms. The EMCCD camera views the ions through a $16\times$ magnifying telescope, enabling the trapped ions' positions to be monitored with sub-micrometer precision.

For our measurement scheme, discussed in the next section, we need to excite ions to the $5d^2D_{5/2}$ level. Three pathways are feasible (see Fig. 6.2): direct excitation from the $6s^2S_{1/2}$ ground state, which requires precise frequency stabilization ($\Delta\nu \approx 5$ mHz), excitation from the $5d^2D_{3/2}$ level [179], or via decay after intermediate excitation to the $6p^2P_{3/2}$ level. We employ the latter option and have used two light sources for this: an LED producing light at wavelength 456 nm driving the $6s^2S_{1/2} - 6p^2P_{3/2}$ transition and laser light at wavelength 586 nm driving the $5d^2D_{3/2} - 6p^2P_{3/2}$ transition. The efficiency obtained with the laser is far higher but also sensitive to frequency fluctuations. The fiber-coupled high-power LED (Thorlabs M455F1) is simple and reliable to operate and was used for the measurements reported here. A band-pass filter with 10 nm bandwidth centered at 450 nm and about 10^{-6} suppression (Thorlabs FB450-10) prevents light from the LED at other wavelengths³³ from reaching the ions.

6.2 Quantum Jump Spectroscopy

We determined the lifetime of the $5d^2D_{5/2}$ level in Ba^+ using continuous quantum jump spectroscopy (also known as *electron shelving*, first experimentally demonstrated³⁴ by several groups in 1986 [171, 182, 183]). This experimental method yields access to the time evolution of the decay of the $5d^2D_{5/2}$ level. In contrast, the most recent experimental determination of Ref. 178 relies on probing the ions only at set intervals, requiring accurate knowledge and reproducibility of the state change probabilities.

While the ions continuously scatter photons in the closed laser cooling cycle (see Fig. 6.2), light from the LED at wavelength 456 nm populates the $5d^2D_{5/2}$ level via intermediate excitation to the $6p^2P_{3/2}$ level. Successfully shelving an ion into the $5d^2D_{5/2}$ level breaks the laser cooling cycle and stops its fluorescence. The fluorescence subsequently reappears when the ion spontaneously decays, either to the $2S_{1/2}$ or to the $2D_{3/2}$ level, and the laser cooling cycle recommences. Note that the continuous quantum jump technique cannot easily be adapted to determine the lifetime of the lower-lying $5d^2D_{3/2}$ level, since all closed laser cooling cycles include this level; one solution can be found in Ref. 184 which demonstrates measurement techniques in Ca^+ that could also be applied to the $5d^2D_{3/2}$ level in Ba^+ .

We analyze the resulting dark and bright periods to determine the $5d^2D_{5/2}$ level lifetime and the shelving rate which is experimentally controlled by the LED intensity. An example of the photon count rate versus time for a single Ba^+ ion is shown in Fig. 6.3, which displays two distinct levels in the count rate. The PMT typically has a

³³The 456 nm light driving the $6s^2S_{1/2} - 6p^2P_{3/2}$ transition is itself also attenuated by a factor 10, since it lies close to the edge of the filter transmission band.

³⁴Before their experimental observation, the existence of quantum jumps was for some time controversial. Itano et al. [180] provide an interesting overview of the history of theoretical doubts and subsequent discovery. Unifying the conventional formulation of quantum mechanics with the discontinuous transitions observed in quantum jump measurements is still a subject of interest [181].

Figure 6.3 Example quantum jump data of a single trapped Ba^+ ion (14 September 2015). (a) 12 min recorded trace of fluorescence at wavelength 494 nm. Arrows indicate crossing the threshold set in the analysis. (b) Projection of the count rate at 100 ms time resolution showing clear discrimination between the dark and bright state. The peaks are fitted with a model based on Poisson statistics to determine the threshold level. (c) Example EMCCD images of the ion.

dark count rate of about 200 cnt/s and the fluorescence signal is about 1000 cnt/s per ion for 0.25 W/cm^2 of 494 nm light (the signal count rate depends on the intensities and detunings of the cooling lasers, see Chapter 4). For a statistical precision of 5% on the lifetime $\tau_{D_{5/2}}$, 800 state changes (quantum jumps) are required, corresponding to some 6 h of data taking with a single ion.

We have performed measurements with ion crystals consisting of up to four ions to assess potential effects caused by simultaneously trapped additional ions of the same or different species (the number of fluorescence levels observed with quantum jumps provides an easy way to count the trapped ions). Since the statistical precision depends on the number of observed state changes limited by the long lifetime of the $5d^2D_{5/2}$ level, multiple simultaneously trapped ions can provide higher precision within the same measurement time. However, since we generally lowered the shelving rate for multi ion data sets, the precision we achieved for a given measurement time differed little between single and multi ion data sets in practice. Figure 6.4 shows example data for three ions: the photon count rate shows four distinct levels in this case, corresponding to between zero and three ions in the dark state. The EMCCD

Figure 6.4 Example quantum jump data of a three Ba^+ ion crystal (17 September 2015). (a) 3 min recorded trace of fluorescence at wavelength 494 nm. Arrows indicate crossing the thresholds set in the analysis. (b) Projection of the count rate at 100 ms time resolution fitted with a model based on Poisson statistics to determine the threshold levels. (c) Example EMCCD images of the ion crystal.

camera provides a spatially resolved image of the bright ions. When any of the ions is shelved into the $5d^2D_{5/2}$ level, no change in the position of the remaining bright ions is observed, proving that the dark ions keep their position in the crystal. Disappearance of an ion or joining of an ion of any species would have expressed itself as displacement by several μm of the remaining bright ion positions (see also Section 3.5.3).

Experimental parameters were continuously monitored to ensure that only data collected under stable conditions were included in the analysis. We have collected 68 data sets of typically 2 h length that passed the selection, during each of which experimental parameters were kept constant. Between data sets, parameters including number of ions trapped, background gas pressure and laser light intensities were varied to study their influence on the $5d^2D_{5/2}$ level lifetime. The data sets were collected between October 2013 and September 2015 in a process of constant refinement of the experiment, including improving the vacuum, signal-to-noise and implementing additional diagnostics. Analyzing each data set separately instead of combining all the data enables the search for systematic effects, discussed in detail in Section 6.4.

6.3 Data Analysis

The goal in the analysis is to determine the $^2D_{5/2}$ level lifetime from the fluorescence data. We developed an automated procedure that extracts the average time spent shelved in the $^2D_{5/2}$ level, taking into account the effect of limited time resolution due to using an averaging window (i.e. possibly missing short intervals). The analysis procedure was tested using simulated data.

6.3.1 Data quality criteria

The first step is identifying stretches of time that contain good data and discarding periods where some aspect of the experiment was not operating properly. We achieve this in an automated way by setting a range of accepted values around the median value for various experimental parameters. Each data set is typically a few hours worth of data where experimental parameters were kept constant, interrupted occasionally by efforts to fix a problem with the setup (e.g. a laser unlocked). This means that excursions from the median values of experimental parameters indicate parts of the data set to exclude from further analysis:

Laser power. The power of the laser light at wavelength 494 nm and 650 nm measured in front of the trap is used to discard data where either of the lasers dropped out for any reason (accepted intensity $> 0.1 \mu\text{W}$ for both beams).

Ti:sapph – frequency comb beatnote frequency. The Ti:sapphire laser used to produce light at 494 nm occasionally loses its lock to the frequency comb. The beatnote frequency is monitored to discard data where the laser was not at the intended frequency (accepted range $\pm 0.02 \text{ MHz}$ from the median frequency).

I₂ laser – frequency comb beatnote frequency. The frequency of the 650 nm laser is offset-locked to a second laser locked to an iodine line. The beatnote between the latter laser and the frequency comb is measured (not locked). As long as this beatnote is within the bandwidth of its electronic counter (depends on frequency comb settings), it is monitored to discard data where the 650 nm laser was not at the intended frequency (accepted range $\pm 5 \text{ MHz}$ from the median frequency).

650 nm laser offset lock frequency. The offset lock frequency is used to discard data where the 650 nm laser was not at the intended frequency (accepted range $\pm 1 \text{ MHz}$ from the median frequency).

Frequency comb settings. The repetition rate and offset synthesizer frequencies of the frequency comb are monitored to discard data where the frequency comb was not operating properly (accepted repetition rate $\text{synth} \leq 1 \text{ Hz}$ from the median frequency, offset $\text{synth} \leq 20 \text{ Hz}$ from the median frequency).

RF amplitude. The RF amplitude is monitored to discard data where the trapping field changed, e.g. (rare) problems with the amplifier or cases where the trap was reloaded during a data set (accepted range ± 15 V from the median amplitude).

If any of the above parameters is found to be outside the accepted range at any time, data are excluded from the analysis until the next moment that all ions are visible in the bright state to ensure that only changes in fluorescence due to ions being (un)shelved are counted. The recorded EMCCD images of the ions were visually checked for peculiarities and data sets with instabilities were wholly discarded. Each quantum jump data set was manually inspected and data sets with ‘unsharp’ quantum jump edges indicating heating of ions were also discarded.

6.3.2 Quantum jump extraction

The quantum jump data is analyzed by an automated procedure that determines the number of ions fluorescing at each moment in time by setting thresholds on the PMT count rate (see Figs. 6.3a and 6.4a). To determine the optimal thresholds for each data set, a set of Poisson distributions is fitted to the projection of the count rate (see Figs. 6.3b and 6.4b). The only free parameters are the dark count rate, the increase in count rate per ion and the peak heights. Averaging the PMT count rate over 100 ms is sufficient to cleanly discriminate between the dark and bright states for a single ion, while data sets with multiple ions benefit from averaging over a longer time period to better separate states. For the final analysis, we average the count rate over intervals of 500 ms to reliably discriminate fluorescence states in all data sets.

The PMT count rate with lowest probability between each of the peaks is used as threshold to discriminate between states (since the noise in the count rate is larger with more fluorescing ions, thresholds lie slightly below the midway point between adjacent peaks). Additionally, data from the power meter for the light at 494 nm is used to automatically adjust the thresholds to compensate for changes in fluorescence rate due to drifts in laser intensity during a data set. A similar compensation for the intensity of the light at 650 nm was deemed unnecessary since this sensitivity was smaller at our operating conditions and the corresponding laser more stable. The high signal-to-noise when averaging for 500 ms makes the analysis results rather insensitive to threshold choice in practice (a more in-depth investigation into optimal threshold choice and detection efficiency can be found in Ref. 185). Each time the PMT count rate crosses a threshold marks the boundary of an interval (see Figs. 6.3a and 6.4a).

Single ion data sets consist of two types of intervals: dark (shelved) and bright (unshelved) periods. The duration distributions of both are determined (see Fig. 6.5). Here the dark and bright states correspond directly to the $5d^2D_{5/2}$ level lifetime $\tau_{D_{5/2}}$ and the shelving time τ_{shelve} , respectively. The latter is determined by the (long term

Figure 6.5 Analysis results of the 2 h single ion data set of Fig. 6.3: distribution of dwell times in (a) the bright/unshelved and (b) the dark/shelved state. Exponential lifetimes are determined by taking the mean of interval durations. After corrections, for this data set the lifetime of the dark state ($5d^2D_{5/2}$ level lifetime) is $\tau_{D_{5/2}} = 26.6(1.8)$ s and the lifetime of the bright state (shelving time) is $\tau_{\text{shelve}} = 28.8(2.0)$ s.

stable³⁵) intensity of the LED at wavelength 456 nm. In the general case of a data set with n ions, there are intervals with zero up to n dark ions (see Fig. 6.6).

Distribution of quantum states

A system of n ions transitioning between shelved and unshelved states can be described as a continuous-time Markov chain³⁶ with $n+1$ experimental states, ranging from state S_0 with no ions shelved, to S_n with all n ions shelved. The transition rates between the states depend on the shelving rate $R_{\uparrow} = \tau_{\text{shelve}}^{-1}$ and deshelling rate $R_{\downarrow} = \tau_{D_{5/2}}^{-1}$ of a single ion. For state S_k where k out of n ions are shelved, additional ions are shelved at rate $(n-k)R_{\uparrow}$ and ions deshelve at rate $kR_{\downarrow}$ (see Fig. 6.7). The transition probabilities are time-independent, so the system is memoryless: the behavior only depends on the current state and not on any previous transitions. The effective exponential lifetime of experimental state S_k is given by

$$\tau_k^{-1} = kR_{\downarrow} + (n-k)R_{\uparrow} = k\tau_{D_{5/2}}^{-1} + (n-k)\tau_{\text{shelve}}^{-1}. \quad (6.1)$$

³⁵The light output power of the LED is stable within 5% over a timescale of hours [119].

³⁶Historical note: this description corresponds to the *random telegraph* signal of Cook and Kimble [186] and can also be found in the work of Javanainen [187]. The latter remarks: “The conclusion is the same as obtained by replacing the atom by a classical Markov process that executes jumps between its three states. The concept of ‘quantum jumps’ represents a questionable extrapolation of classical reasoning into quantum mechanics. Nevertheless, in the present example it leads to a prediction which agrees with the full-fledged theory of photodetection.” Also see Ref. 188.

Figure 6.6 Analysis results of the 3h data set with three ions of Fig. 6.4: (a) through (d) show the distribution of dwell times in the four experimental states with an increasing number of ions shelved. The $5d^2D_{5/2}$ level lifetime and the shelving time are determined from the four effective time constants $\tilde{\tau}_k$ and for this data set $\tau_{D_{5/2}} = 25.6(2.1) \text{ s}$ and $\tau_{\text{shelve}} = 50.6(3.9) \text{ s}$.

The transition rates together form the transition matrix Q . Elements $Q_{kk'}$ for $k \neq k'$ indicate the transition rate from state $S_k \rightarrow S_{k'}$. The diagonal elements Q_{kk} make each row of the transition rate matrix sum to zero. For example, in the case of 3 ions, the transition matrix Q is given by

$$Q = \begin{pmatrix} -3R_{\uparrow} & 3R_{\uparrow} & 0 & 0 \\ R_{\downarrow} & -R_{\downarrow} - 2R_{\uparrow} & 2R_{\uparrow} & 0 \\ 0 & 2R_{\downarrow} & -2R_{\downarrow} - R_{\uparrow} & R_{\uparrow} \\ 0 & 0 & 3R_{\downarrow} & -3R_{\downarrow} \end{pmatrix}. \quad (6.2)$$

The equilibrium probability distribution $\mathbf{p}_{\infty}$ of being in each of the 4 states is given by the solution to the equation $\mathbf{p}_{\infty}Q = \mathbf{0}$ (i.e. $\mathbf{p}_{\infty}$ is the normalized basis of the nullspace

Figure 6.7 Idealized representation of a continuous shelving experiment with n ions: for the state S_k where k out of n ions are shelved, the rates of transitioning to the state with one additional ion shelved (S_{k+1}) or one ion fewer (S_{k-1}) depend on the shelving rate $R_{\uparrow} = \tau_{\text{shelve}}^{-1}$ and deshelving rate $R_{\downarrow} = \tau_{\text{D}_{5/2}}^{-1}$ of a single ion.

of Q). The equilibrium distribution depends only on the ratio $r = R_{\uparrow}/R_{\downarrow}$:

$$\mathbf{p}_{\infty} = \frac{1}{(1+r)^3} \begin{pmatrix} 1 & 3r & 3r^2 & r^3 \end{pmatrix}. \quad (6.3)$$

Generalizing the above result, the steady-state probability of k out of n ions being shelved is given by

$$p_{\infty,k} = \frac{1}{(1+r)^n} \binom{n}{k} r^k. \quad (6.4)$$

This expression can be compared to the distribution of quantum states determined from the data to obtain the ratio $R_{\uparrow}/R_{\downarrow}$ and check for deviations in the behavior of the ion(s). This corresponds to the relative peak heights in the threshold fit of data sets (see Figs. 6.3b and 6.4b), although this constraint was not applied in the fit. We determine $R_{\uparrow}$ and $R_{\downarrow}$ as described in the next section.

Parameter estimation: lifetime from exponential data

One way to estimate the lifetime from a finite set of exponentially distributed interval durations is to collect them in a histogram and perform a χ^2 minimization (least squares fit) with an exponential function (one free parameter $\hat{\tau}$):

$$P_{\text{fit}}(t; \hat{\tau}) = \frac{N}{\Delta T} \frac{1}{\hat{\tau}} \exp \left[-\frac{t}{\hat{\tau}} \right], \quad (6.5)$$

where $N = \sum_b n_b$ is the total number of samples and ΔT is the bin width. However, a χ^2 fitting procedure is not ideal for this application as the number of samples n_b in histogram bin b typically gets small in the tail of the exponential function and the assumption of normally distributed data underlying the χ^2 statistic is not valid for very low ($n_b \lesssim 5$) numbers of samples.

A log-likelihood fitting procedure fully taking into account the probability distribution of bin counts [177] is a better³⁷ approach. For a histogram with sufficiently many bins to include (nearly) all data, the maximum likelihood estimate of the lifetime is

$$\hat{\tau} = \frac{\Delta T}{\log[\Delta T/\hat{t} + 1]} \quad \text{with} \quad \sigma_{\hat{\tau}} = \sqrt{\frac{\hat{\tau}^2}{N} + \frac{\Delta T^2}{12N} + \mathcal{O}(\Delta T^4)}, \quad (6.6)$$

where $\hat{t} = \frac{1}{N} \sum_b b \Delta T n_b$ is the mean of the binned interval durations.

Since the likelihood function is valid for any number of samples per bin n_b , there is no advantage in choosing the bin width ΔT larger than the time resolution of the data itself. In our case, the time resolution is fine compared to the lifetime and we treat the data as unbinned ($\Delta T \approx 0$). The maximum likelihood estimate now reduces to simply the mean of the interval durations t_i ,

$$\hat{\tau} = \frac{1}{N} \sum_i t_i \quad \text{with} \quad \sigma_{\hat{\tau}} = \frac{\hat{\tau}}{\sqrt{N}}. \quad (6.7)$$

Note that this is an unbiased estimator of the lifetime, but taking the mean of the inverse of the lifetime samples does not give an unbiased estimate of the decay rate.

6.3.3 Effect of averaging window

By setting thresholds on the fluorescence rate as described above, the state S_k of the ion(s) is determined at each moment in time. In principle, the lifetime of the $^2D_{5/2}$ level is extracted by tallying up the durations of time spent in each state (6.7) and comparing these to Eq. (6.1). The exponential nature of lifetimes dictates that ions have a significant probability of spending only a short time in an excited state before decaying, even if the lifetime is rather long. Since the time resolution of the DAQ is limited, intervals shorter than the time resolution cannot be detected and this affects the distribution of observed interval durations in our continuous measurement method. Moreover, to achieve a sufficiently large signal-to-noise ratio, it is beneficial to apply a longer averaging window, especially in the case of multi ion data sets (see Section 6.3.2). We calculate the effect of this analytically and verify it with simulated data, before applying it to correct the analysis of our experimental data.

We model the experiment as the Markov process from Section 6.3.2: each of the n ions can either be shelved or unshelved at any moment in time and has a constant probability of being shelved, $R_{\uparrow} = \tau_{\text{shelve}}^{-1}$ (if currently unshelved) or deshelling, $R_{\downarrow} = \tau_{D_{5/2}}^{-1}$ (if currently shelved). The data therefore consist of successive time intervals in experimental states S_k with exponentially distributed durations according

³⁷Also see Ref. 176 for a comparison of analyzing lifetime data with least squares fitting and maximum likelihood estimate: both methods give identical results for large numbers of events, but in case of lower statistics, the maximum likelihood estimate has less scatter.

Figure 6.8 A short interval missed due to applying averaging window Δt is absorbed into the surrounding intervals of the other state, which are then joined together.

to Eq. (6.1). Each interval ends when an ion is shelved or deshelves and the next interval in state S_{k+1} or S_{k-1} starts, respectively. We ignore further details of the experiment here, so the following calculation applies to any physical process producing such a sequence of intervals with exponentially distributed durations.

Analytical calculation of averaging window effect

The mean of interval durations t is given by the exponential lifetime τ if the shelved/unshelved state of all ions is perfectly detected at all moments in time, i.e. no intervals are missed and their durations exactly follow an exponential distribution:

$$\int P(t; \tau) t \, dt = \int_0^\infty \frac{1}{\tau} \exp\left[-\frac{t}{\tau}\right] t \, dt = \tau. \quad (6.8)$$

However, if the experiment uses a finite averaging window, short intervals are missed. Their duration is ‘absorbed’ into the surrounding intervals, which are then joined together (see Fig. 6.8). This modifies the distribution of interval durations by decreasing the number of short intervals and increasing the number of long intervals. The resulting distribution is no longer exponential, but its mean can still be calculated. This ‘effective’ lifetime will be longer than the lifetime of the underlying exponential distribution. For a finite averaging window $\Delta t > 0$, there is a finite probability that one or more intervals are joined together. We denote the mean interval duration of experimental state S_k with k out of n ions shelved as the effective lifetime $\tilde{\tau}_k$ and calculate it by summing over all possible interval duration sequences, weighted by their probability³⁸.

Assume we start with an initial interval of duration $t_1 > \Delta t$ in state S_k . The exponential probability distribution of t_1 is given by $P(t_1; \tau_k)$ from Eq. (6.8), where τ_k is defined by Eq. (6.1). In the simplest case, this interval is followed by another interval that is also longer than the averaging window Δt in state $S_{k'}$, so that the end

³⁸A similar calculation can be found in Ref. 189, where the correction linear in Δt for the case of two ions ($n = 2$) is derived; the calculation presented here agrees with that result and is more general.

of the first interval is correctly detected and no intervals are missed or joined together. The second interval could be either in state S_{k-1} or S_{k+1} , with probabilities $p_{k\downarrow}$ and $p_{k\uparrow}$, respectively, with $p_{k\downarrow} + p_{k\uparrow} = 1$. Let us denote the probability that this second interval has a duration longer than Δt as $P_{>\Delta t}(\tau_{k'}) = \int_{\Delta t}^{\infty} P(t; \tau_{k'}) dt = \exp[-\Delta t/\tau_{k'}]$. The contribution to the mean lifetime of this case of a single interval is then given by integrating over t_1

$$\tilde{\tau}_k(\Delta t) \Big|_{\text{one interval}} = p_0 \int_{\Delta t}^{\infty} t_1 P(t_1; \tau_k) (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})) dt_1, \quad (6.9)$$

where p_0 is the probability that accounts for our initial assumption of starting in an interval of duration $t_1 > \Delta t$ and ensures that all probabilities sum to one in the end.

Two intervals in state S_k of durations t_1 and t_2 may become joined together as illustrated in Fig. 6.8 when the intervening interval instead has a duration t'_{12} shorter than Δt . The absorbed interval can be either in state S_{k-1} or S_{k+1} . Since the short interval is missed, the sequence would be counted as a single interval of duration $t_1 + t'_{12} + t_2$. The contribution of this possibility is once again its duration weighted by the multiplication of probabilities describing this sequence of events³⁹

$$\begin{aligned} \tilde{\tau}_k(\Delta t) \Big|_{\text{two intervals}} &= p_0 \int_{\Delta t}^{\infty} dt_1 \int_0^{\Delta t} dt'_{12} \int_0^{\infty} dt_2 \times (t_1 + t'_{12} + t_2) \\ &\times P(t_1; \tau_k) \times (p_{k\downarrow} P(t'_{12}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{12}; \tau_{k+1}) p_{(k+1)\downarrow}) \\ &\times P(t_2; \tau_k) \times (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})). \end{aligned} \quad (6.10)$$

In a similar fashion, the contribution of three intervals being counted together due to two intervening short intervals being absorbed can be calculated as

$$\begin{aligned} \tilde{\tau}_k(\Delta t) \Big|_{\text{three intervals}} &= p_0 \int_{\Delta t}^{\infty} dt_1 \int_0^{\Delta t} dt'_{12} \int_0^{\infty} dt_2 \int_0^{\Delta t} dt'_{23} \int_0^{\infty} dt_3 \\ &\times (t_1 + t'_{12} + t_2 + t'_{23} + t_3) \\ &\times P(t_1; \tau_k) \times (p_{k\downarrow} P(t'_{12}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{12}; \tau_{k+1}) p_{(k+1)\downarrow}) \\ &\times P(t_2; \tau_k) \times (p_{k\downarrow} P(t'_{23}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{23}; \tau_{k+1}) p_{(k+1)\downarrow}) \\ &\times P(t_3; \tau_k) \times (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})). \end{aligned} \quad (6.11)$$

The results of the above integrals are somewhat unwieldy and can be found in Appendix B. To calculate $\tilde{\tau}_k(\Delta t)$, the contributions of any number of intervals joined together should be summed,

$$\tilde{\tau}_k(\Delta t) = \tilde{\tau}_k(\Delta t) \Big|_{\text{one interval}} + \tilde{\tau}_k(\Delta t) \Big|_{\text{two intervals}} + \tilde{\tau}_k(\Delta t) \Big|_{\text{three intervals}} + \dots, \quad (6.12)$$

³⁹Here integrals and variables of integration have been placed together for readability.

giving the final result

$$\begin{aligned} \tilde{\tau}_k(\Delta t) = & \left(-\exp\left[\frac{\Delta t}{\tau_{k-1}}\right] p_{k\uparrow\downarrow}\tau_{k+1} - \exp\left[\frac{\Delta t}{\tau_{k+1}}\right] p_{k\downarrow\uparrow}\tau_{k-1} \right. \\ & \left. + \exp\left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}}\right] (\tau_k + p_{k\uparrow\downarrow}\tau_{k+1} + p_{k\downarrow\uparrow}\tau_{k-1} - \Delta t(p_{k\uparrow\downarrow} + p_{k\downarrow\uparrow} - 1)) \right) / \\ & \left(\exp\left[\frac{\Delta t}{\tau_{k-1}}\right] p_{k\uparrow\downarrow} + \exp\left[\frac{\Delta t}{\tau_{k+1}}\right] p_{k\downarrow\uparrow} - \exp\left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}}\right] (p_{k\uparrow\downarrow} + p_{k\downarrow\uparrow} - 1) \right). \end{aligned} \quad (6.13)$$

Here we have used the notation $p_{k\uparrow\downarrow} = p_{k\uparrow}p_{(k+1)\downarrow}$ to denote the probability of the sequence of states $S_k \rightarrow S_{k+1} \rightarrow S_k$ and similarly, $p_{k\downarrow\uparrow} = p_{k\downarrow}p_{(k-1)\uparrow}$. Note that in the limit of perfect time resolution, the unaltered lifetime is recovered, as expected: $\tilde{\tau}_k(\Delta t \rightarrow 0) = \tau_k$.

For a given experimental state S_k where k out of n ions are shelved, the above expression can be filled in to find the effective lifetime observed if intervals shorter than the averaging window Δt are missed, using

$$\tau_k = \frac{1}{kR_{\downarrow} + (n-k)R_{\uparrow}}, \quad p_{k\downarrow} = \frac{kR_{\downarrow}}{kR_{\downarrow} + (n-k)R_{\uparrow}} \quad \text{and} \quad p_{k\uparrow} = \frac{(n-k)R_{\uparrow}}{kR_{\downarrow} + (n-k)R_{\uparrow}}, \quad (6.14)$$

where $R_{\uparrow} = \tau_{\text{shelve}}^{-1}$ is the shelving rate and $R_{\downarrow} = \tau_{\text{D}_{5/2}}^{-1}$ the deshelling rate of a single ion, as before.

Extracting lifetimes

For a single ion quantum jump measurement ($n = 1$), the effective lifetimes of the shelved and unshelved states of Eq. (6.13) simplify to

$$\begin{aligned} \tilde{\tau}_0(\Delta t) &= \exp\left[\frac{\Delta t}{\tau_{\text{D}_{5/2}}}\right] (\tau_{\text{shelve}} + \tau_{\text{D}_{5/2}}) - \tau_{\text{D}_{5/2}} \\ \tilde{\tau}_1(\Delta t) &= \exp\left[\frac{\Delta t}{\tau_{\text{shelve}}}\right] (\tau_{\text{shelve}} + \tau_{\text{D}_{5/2}}) - \tau_{\text{shelve}}, \end{aligned} \quad (6.15)$$

showing how the effective lifetimes of both experimental states depend on both $\tau_{\text{D}_{5/2}}$ and τ_{shelve} when $\Delta t > 0$. The effective lifetimes $\tilde{\tau}_0$ and $\tilde{\tau}_1$ are the measurable values in the experiment (and Δt is known or can be controlled), so the final step is to solve for $\tau_{\text{D}_{5/2}}$ and τ_{shelve} . No analytical solution exists, but an approximation linear in Δt can be used when $\Delta t \ll \tau_{\text{D}_{5/2}}, \tau_{\text{shelve}}$ to give

$$\tau_{\text{D}_{5/2}} \approx \tilde{\tau}_1 - \Delta t \left(1 + \frac{\tilde{\tau}_1}{\tilde{\tau}_0}\right) \quad \text{and} \quad \tau_{\text{shelve}} \approx \tilde{\tau}_0 - \Delta t \left(1 + \frac{\tilde{\tau}_0}{\tilde{\tau}_1}\right). \quad (6.16)$$

Note that if $\tau_{\text{shelve}} \approx \tau_{D_{5/2}}$, then $\tilde{\tau}_k \approx \tau_k + 2\Delta t$. In our experiment, the minimal averaging window is the time resolution of the DAQ system of $\Delta t = 100$ ms, so extracted lifetimes are increased by at least 200 ms. For data sets with multiple ions ($n > 1$), the expressions following from Eq. (6.13) are somewhat more complicated, but as a rule of thumb extracted lifetimes are still increased by around $2\Delta t$.

In an experimental data set with n ions, the mean of the observed lifetimes in each of the $n + 1$ experimental states is determined to find the values $\tilde{\tau}_k$. Following Eq. (6.7), the errors $\sigma_{\tilde{\tau}_k}$ are taken to be $\tilde{\tau}_k/\sqrt{N_k}$, where N_k is the number of observed lifetimes in state k (this is strictly only correct for exponentially distributed data and slightly overestimates the true error when $\Delta t > 0$). The $\tilde{\tau}_k$ are functions of Δt , τ_{shelve} and $\tau_{D_{5/2}}$; the value of Δt is set in the analysis and this leaves a system of Eqs. (6.13) that we numerically solve for $\tau_{D_{5/2}}$ and τ_{shelve} , using a χ^2 fit when $n > 1$ and the system is overdetermined (errors are propagated in the usual manner). The finite length of a data set and any interruptions (e.g. to re-lock a laser) cut off the tail of the distributions $\tilde{\tau}_k$. We correct for this (small) effect by subtracting the inverse of the mean uninterrupted duration from each $\tilde{\tau}_k^{-1}$ before solving for $\tau_{D_{5/2}}$ and τ_{shelve} .

Check with Monte Carlo data

We checked the procedure to correct the effect of the averaging window described above by applying it to pseudo-randomly generated data sets with known true values of $\tau_{D_{5/2}}$ and τ_{shelve} . Single ion data sets consist of interleaved intervals with exponentially distributed durations and multi ion data sets are produced by combining several of these. All intervals shorter than Δt are then absorbed into the surrounding intervals to simulate the effect of the averaging window. The mean lifetimes $\tilde{\tau}_k$ are calculated and the corrected values of $\tau_{D_{5/2}}$ and τ_{shelve} extracted.

Figure 6.9 shows example results of applying the correction to generated data sets with typical properties. It is clear how the observed values $\tilde{\tau}_k$ increase with the length of the averaging window Δt . For single ion data, Eqs. (6.15) are exact and the correct values of $\tau_{D_{5/2}}$ and τ_{shelve} can be recovered for any Δt . For multi ion data, the extracted values of $\tau_{D_{5/2}}$ and τ_{shelve} begin to deviate from the true values at larger averaging window lengths Δt . This is likely because we have neglected the possibility of more than one ion shelving and subsequently deshelling (or vice versa, i.e. changing state by more than one step) within the time window Δt in the derivation of Eq. (6.13). However, this effect only begins to play a role at far larger averaging window lengths Δt than we use. It is clear from Fig. 6.9 that the correction procedure works well for single and multi ion data sets for averaging windows of up to several seconds, which is plenty for essentially perfect state determination.

For the experimental data in Figs. 6.5 and 6.6, the exponential curves corresponding to the corrected lifetimes τ_k are plotted (red solid lines). Since the effect of the averaging window $\Delta t = 500$ ms is relatively small compared to the lifetimes, the (not

Figure 6.9 Verifying the correction for the averaging window length Δt with Monte Carlo data. Each stack of points corresponds to generated data sets of (a) a single ion, 1000 intervals, $\tau_{D_{5/2}} = 30$ s, $\tau_{\text{shelve}} = 40$ s; and (b) three ions, 1000 intervals, $\tau_{D_{5/2}} = 30$ s, $\tau_{\text{shelve}} = 80$ s. The observed means $\tilde{\tau}_k$ from the data sets are used to recover $\tau_{D_{5/2}}$ and τ_{shelve} as described in the main text (repeated 10 000 times at each value of Δt). The data follow the solid lines calculated with Eq. (6.13) from the true values of $\tau_{D_{5/2}}$ and τ_{shelve} , shown as dashed lines.

truly exponential) raw data show good agreement with the exponential curves. The corrected lifetime values of these two data sets of around 26 s is typical for our data and significantly lower than previously reported values of the $5d^2D_{5/2}$ level in Ba^+ .

6.4 Search for Systematic Effects

We have varied experimental parameters between data sets in order to understand and control systematic effects. Each data set is analyzed separately to investigate how the observed lifetime depends on experimental conditions. The lifetime can be affected by many processes, including collisions with background gas, radiation coupling the $5d^2D_{5/2}$ level to other levels and ion-ion interactions. The long lifetime of the $5d^2D_{5/2}$ level in Ba^+ makes it sensitive even to slow processes. The large discrepancy between our result and previous work calls for a detailed discussion.

Some effects perturb the ions and change the duration of excitations, while others rather affect the measurement of the ions' state. To account for the first category of

Figure 6.10 (a) Extrapolating the $5d^2D_{5/2}$ level decay rate to zero pressure, including all data sets (most data have been collected at the lowest pressure 2×10^{-11} mbar). The fitted quenching rate is $5.1(1.4) \times 10^7 \text{ s}^{-1}/\text{mbar}$, shown with 1σ (standard deviation) and 2σ bounds ($\chi^2/n = 57.6/66$). The resulting lifetime at zero pressure is $26.2(0.6) \text{ s}$. (b) Decay rate of the $5d^2D_{5/2}$ level after subtracting the collisional quenching contribution versus the shelving rate. All data are consistent with the weighted mean, showing no dependence of the lifetime on the 456 nm LED light intensity.

systematic effects, we can write the observed lifetime in the form

$$\frac{1}{\tau_{D_{5/2}}} = \frac{1}{\tau_{D_{5/2},\text{nat}}} + \sum_i \gamma_i, \quad (6.17)$$

where $\tau_{D_{5/2}}$ is the experimentally observed lifetime, $\tau_{D_{5/2},\text{nat}}$ is the natural lifetime we wish to determine and γ_i are contributions to the decay rate by other processes.

6.4.1 Background gas collisions

Of particular importance are collisions with background gas molecules that quench the $5d^2D_{5/2}$ level; this additional decay rate decreases the apparent lifetime [190, 191].

Quenching

The quenching rate depends on the density (i.e. pressure at constant temperature) and composition of the background gas, as well as on the temperature of the ions. We measure the pressure primarily by monitoring the ion pump current (see Section 2.1.2). Over the two year period of data collection, the residual (N_2 -equivalent) gas pressure p we reached in the setup decreased from about 10^{-10} mbar to a few times 10^{-11} mbar. For a few measurements, the pressure was increased by turning on the ion gauge,

sometimes additionally closing the valve to the ion pump to decrease the pumping speed. In the latter case, the ion gauge pressure reading was taken and scaled to match the corresponding ion pump pressure with the valve open⁴⁰. We expect a linear pressure-dependence of the decay rate (Stern–Volmer),

$$\gamma_{\text{collision}}(p) = \alpha p, \quad (6.18)$$

where α is the quenching rate and p is the residual gas pressure. Fitting our experimental data, we find a quenching rate of $\alpha = 5.1(1.4) \times 10^7 \text{ s}^{-1}/\text{mbar}$ in a χ^2 fit (see Fig. 6.10a). Quantitatively comparing quenching rates is hampered by the fact that we do not know the exact composition of the background gas in our setup, but our value is comparable to quenching rates reported for this level by other authors [190, 191]. The resulting lifetime at zero pressure is 26.2(0.6) s. Following Eq. (6.17), we subtract the decay rate $\gamma_{\text{collision}}$ for each data set while investigating further systematic effects (denoted as *pressure-corrected* decay rate).

Fine structure mixing

Besides quenching excited states, collisions with background gas molecules also mix fine structure levels [191, 192]. This J -mixing leads to population transfer from the $^2\text{D}_{5/2}$ to the $^2\text{D}_{3/2}$ level (and vice versa). The effect can be described by two mixing rates γ_{35} and γ_{53} that scale with density (pressure) [192], leading to an equilibrium between the two D levels after some time. This time-dependence means that, in general, fine structure mixing is not eliminated by a linear extrapolation to zero pressure.

We calculate the effect of the mixing following the derivation⁴¹ in Ref. 192. In Ba^+ lifetime measurements where the ions evolve in the dark, J -mixing would decrease the observed lifetime of the $5d\ ^2\text{D}_{3/2}$ level [191], and either increase or decrease the observed lifetime of the $5d\ ^2\text{D}_{5/2}$ level, depending on the mixing rate values. Few experimental data are available on γ_{35} and γ_{53} for Ba^+ in combination with various gasses. In principle, the Ca^+ data can be extrapolated to Ba^+ [193]. However, in our continuous measurement scheme, the lasers are never extinguished and the $5d\ ^2\text{D}_{3/2}$ level is repumped within nanoseconds. If we assume that any transfer to the $^2\text{D}_{3/2}$ level is a loss (or equivalently, that there is no remixing from the $^2\text{D}_{3/2}$ level, $\gamma_{35} \approx 0$), fine structure mixing becomes just another decay rate term that scales with pressure. This means that fine structure mixing is indistinguishable from quenching in our case and already included in $\gamma_{\text{collision}}$ in the extrapolation to zero pressure.

⁴⁰This differs from the published article where we scaled all pressures to match the ion gauge values; additionally we corrected a mistake in the calibration, resulting in a $< 1\sigma$ shift in the lifetime.

⁴¹Note that in Eqs. (7) and (8) of Ref. 192, both D levels (of Ca^+) are apparently assumed to have the same lifetime $1/\frac{1}{2}\Gamma_{\text{nat}}$. To properly model Ba^+ , this assumption shouldn't be made.

Figure 6.11 Pressure-corrected decay rate of the $5d^2D_{5/2}$ level as function of (a) the intensity of the laser light at 494 nm and (b) the intensity of the laser light at 650 nm, shown with the weighted mean. No significant dependence of the decay rate is found.

6.4.2 Off-resonant scattering

The observed lifetime could also be affected by excitation out of the $5d^2D_{5/2}$ level by continuous radiation from the lasers or the shelving LED. The former effect has been observed by various authors [194–196]. In our continuous quantum jump measurement scheme, this source of error cannot be entirely eliminated, possibly requiring varying the intensities of the various light sources and extrapolating to zero intensity. The primary excitation pathway to worry about is the $5d^2D_{5/2}$ to $6p^2P_{3/2}$ transition at 614 nm (refer to Fig. 6.2), since this is the only strong transition from the $5d^2D_{5/2}$ level with a frequency close to that of any of the employed light sources.

Off-resonant excitation by the lasers

The excitation rate R_{12} from a lower level with spin J_1 to a higher level with spin J_2 by radiation at frequency ν of intensity (irradiance) I_ν is given by [196]

$$R_{12} = \frac{2J_2 + 1}{2J_1 + 1} \frac{c^2}{8\pi h \nu_0^3} A_{21} g(\nu) I_\nu, \quad (6.19)$$

where ν_0 is the atomic resonance frequency, A_{21} is the (partial) spontaneous emission rate from the upper to the lower level and $g(\nu)$ is the normalized Lorentzian lineshape:

$$g(\nu) = \frac{\Gamma/(4\pi^2)}{(\nu - \nu_0)^2 + \Gamma^2/(4\pi)^2}, \quad (6.20)$$

where Γ is the total decay rate of the upper level. Filling in Eq. (6.19) for the two laser fields⁴² and the $5d^2D_{5/2} - 6p^2P_{3/2}$ transition with $\nu_0 = 487.99$ THz [50], $A_{21} = 3.4(0.1) \times 10^7 \text{ s}^{-1}$ [197] and $\Gamma^{-1} = 6.32(0.10) \text{ ns}$ [198] gives deshelling rate

$$\gamma_{\text{lasers}}(I_{494}, I_{650}) = 3.0 \times 10^{-6} \text{ s}^{-1} / (\text{W}/\text{cm}^2) \times I_{494} + 5.9 \times 10^{-5} \text{ s}^{-1} / (\text{W}/\text{cm}^2) \times I_{650}. \quad (6.21)$$

The intensity⁴³ of the laser light at wavelength 494 nm at the position of the ions was varied from $0.1 \text{ W}/\text{cm}^2$ to $0.6 \text{ W}/\text{cm}^2$ and the laser light at 650 nm from $0.01 \text{ W}/\text{cm}^2$ to $0.09 \text{ W}/\text{cm}^2$. This yields a negligible expected contribution to the deshelling rate of $< 10^{-5} \text{ s}^{-1}$ (contributions by transitions at $\leq 235 \text{ nm}$ to higher-lying P and F levels are smaller by at least an order of magnitude).

A further possibility would be on-resonant excitation by light at 614 nm from (amplified) spontaneous emission by one of the lasers in addition to its coherent output, an issue observed in Ca^+ measurements with diode lasers [194, 196]. In our case, the gain profile of the DCM dye of the laser producing the 650 nm light does include wavelength 614 nm [199]. We have measured the total power of the dye laser's spontaneous emission to be about 10^{-6} times its coherent laser output power. To calculate the induced deshelling rate using Eq. (6.19) for a light source with a much wider spectrum than the atomic transition, we replace the lineshape $g(\nu)$ of Eq. (6.20) by the spectral function of the spontaneous emission

$$g = \frac{\Gamma_{\text{DCM}} / (4\pi^2)}{(\nu_0 - \nu_{\text{DCM}})^2 + \Gamma_{\text{DCM}}^2 / (4\pi)^2}, \quad (6.22)$$

where ν_0 is the transition frequency as before and the emission spectrum of the DCM dye is characterized by $\nu_{\text{DCM}} \approx 460 \text{ THz}$ and $\Gamma_{\text{DCM}} \approx 2\pi \times 70 \text{ THz}$ [199]. From the maximum intensity of the coherent laser light at the position of the ions, $I_{650} < 0.1 \text{ W}/\text{cm}^2$, we find the deshelling rate by (amplified) spontaneous emission to be $< 10^{-5} \text{ s}^{-1}$. The effect is further reduced by at least one order of magnitude by a notch filter (Edmund Optics #67-111) angled to reflect light at 614 nm placed in the laser beam before reaching the trap (see Section 2.2.1).

We additionally check our experimental data for a decay rate contribution $\gamma \propto I_\omega$ and find no significant ($< 1\sigma$) increase of the pressure-corrected decay rate proportional to either laser intensity (see Fig. 6.11).

Off-resonant excitation by the shelving LED

The shelving LED at wavelength 456 nm emits a broader spectrum than the lasers. According to its specifications, light emission at 614 nm is 10^{-5} times less intense

⁴²Note that in Ref. 190, the off-resonant excitation rate by the two lasers is calculated as a Raman (anti-Stokes) process with the decay from the intermediate level being spontaneous rather than stimulated, but this appears to boil down to the same calculation.

⁴³These values differ from the published article owing to an improved laser intensity calibration.

than at 456 nm and this is further attenuated by the band-pass filter by a factor 10^{-6} , making on-resonant deshelling negligible.

The intensity of the LED was not measured directly but corresponds to the shelving rate $\tau_{\text{shelve}}^{-1}$ which we determined from the quantum jump data in addition to the lifetime, as described before. From this, we can also estimate the off-resonant excitation rate caused by light from the LED that does get transmitted through the filter. Comparing the 25 MHz [198] transition linewidth with the specifications of the LED and the 10 nm bandwidth of the filter indicates that the total transmitted light intensity is about a factor 10^6 greater than just the component that drives the $6s^2S_{1/2} - 6p^2P_{3/2}$ transition. Transition rates scale as $\Gamma^2/(4\pi\Delta\nu)^2$ for large detunings $2\pi\Delta\nu \gg \Gamma$, where Γ is the width of the upper level, see Eq. (6.19), giving a factor 10^{-14} . Multiplying the two factors (branching ratios and transition strengths are comparable) gives a deshelling rate of order $\gamma_{\text{LED}} \approx 10^{-8} \times \tau_{\text{shelve}}^{-1}$. Indeed, integrating the induced excitation rate at a given intensity for both transitions over the spectrum of the filtered LED yields

$$\gamma_{\text{LED}}(\tau_{\text{shelve}}^{-1}) = 1.6 \times 10^{-8} \times \tau_{\text{shelve}}^{-1}, \quad (6.23)$$

which is negligible since the shelving rate is of the same order as the lifetime $\tau_{D_{5/2}}^{-1}$.

We additionally check our experimental data for a decay rate contribution $\gamma \propto \tau_{\text{shelve}}^{-1}$ in any case. Varying the LED intensity yielded a shelving rate τ_{shelve} between 0.005 s^{-1} to 0.05 s^{-1} . No significant increase of the pressure-corrected $5d^2D_{5/2}$ decay rate with the shelving rate is found (see Fig. 6.10b).

6.4.3 Stray electromagnetic fields

Aside from laser and LED light, other electromagnetic fields present in the trap could also affect the observed lifetime.

Thermal radiation

Trapped ions are immersed in the blackbody radiation corresponding to the temperature of the surrounding (trap) surfaces. This electric field can induce electronic transitions like any other. The observed $^2D_{5/2}$ level lifetime is modified by stimulated emission due to this thermal radiation. The spectral intensity of the radiation of a blackbody at temperature T is given by Planck's law [200]:

$$dI(\nu, T) = \frac{8\pi h}{c^2} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}. \quad (6.24)$$

The stimulated emission rate for an excited state is given by integrating Einstein coefficient B_{21} times the electric field intensity over the normalized lineshape $g(\nu)$:

$$R_{\text{bb}}(T) = B_{21} \int g(\nu) dI(\nu, T). \quad (6.25)$$

The rates of spontaneous emission, stimulated emission and absorption for an electronic transition are linked, as expressed by the familiar relations between the corresponding Einstein coefficients. These relations are based on thermodynamics and hold irrespective of the details of a transition such as multipole component, lineshape or linewidth [200], as long as selection rules are obeyed. With the spectral intensity defined by (6.24), coefficient B_{21} is related to the spontaneous emission rate A_{21} as⁴⁴

$$B_{21} = \frac{c^2}{8\pi h\nu_0^3} A_{21}. \quad (6.26)$$

Substituting in (6.25) yields

$$R_{\text{bb}}(T) = \frac{1}{\nu_0^3} A_{21} \int_0^\infty \frac{\nu^3}{e^{h\nu/k_B T} - 1} \frac{\Gamma/(4\pi^2)}{(\nu - \nu_0)^2 + \Gamma^2/(4\pi)^2} d\nu. \quad (6.27)$$

This integral cannot be solved analytically but can be simplified by taking into account that the linewidth Γ of any atomic transition is very small compared to the width of the Planck distribution. This means that the intensity of the Planck distribution is approximately constant over the linewidth of the transition and can be taken out of the integral, leaving only the normalized lineshape $g(\nu)$ which integrates to unity.

It follows that the blackbody stimulated emission rate for an electromagnetic transition is related to its spontaneous decay rate in a simple fashion [200]:

$$R_{\text{bb}}(T) = \frac{A_{21}}{e^{h\nu_0/k_B T} - 1}. \quad (6.28)$$

The dependence on the transition frequency ν_0 makes the effect negligible at room temperature for optical transitions. However, the $5d^2D_{5/2}$ and $5d^2D_{3/2}$ levels in Ba^+ are coupled by $E2$ and $M1$ transitions (see Fig. 6.1) and lie only 800 cm^{-1} apart. Filling in the relevant atomic parameters, $\nu_0 = 24.012\text{ THz}$ [79], $A_{21} = 0.0049(8)\text{ s}^{-1}$ and $\Gamma = 0.0321(9)\text{ s}^{-1}$ [178], the blackbody deshelving rate at room temperature is

$$\gamma_{\text{bb}} = R_{\text{bb}}(300\text{ K}) = 1.1(0.3) \times 10^{-4}\text{ s}^{-1}, \quad (6.29)$$

which shortens the observed $5d^2D_{5/2}$ level lifetime by about 0.1 s. Following Eq. (6.17), we correct for this effect by subtracting the decay rate γ_{bb} for each data set. The rate $R_{\text{bb}}(T)$ increases approximately linearly with T for higher temperatures, so even if the trap electrodes would heat up significantly, γ_{bb} remains of order 10^{-4} s^{-1} . Potential ‘hotter’ sources of thermal radiation include room lights and glowing filaments, but these would cover only a fraction of the full solid angle; room lights were switched off during measurements.

⁴⁴Note that the definition of the Einstein B coefficients depends on what is taken as the electric field intensity in Eq. (6.25) and can differ by factors of 2π or c between authors [201].

Stray static electric fields

Ions in the trap experience stray electric fields due to patch potentials from material deposited on the electrode surfaces, which are not fully compensated (see Section 3.2). The associated DC Stark effect causes a small amount of mixing of opposite-parity levels connected by dipole transitions [196]. Here the most important is the mixing of the $5d^2D_{5/2}$ level with the $6p^2P_{3/2}$ level which has a strong electric dipole transition to the ground state. The interaction Hamiltonian is given by

$$H_{\text{Stark}} = -\boldsymbol{\mathcal{E}} \cdot \boldsymbol{D}, \quad (6.30)$$

where $\boldsymbol{\mathcal{E}}$ is the static external electric field and $\boldsymbol{D}$ is the electric dipole moment operator. This interaction results in a finite electric dipole transition amplitude from the $5d^2D_{5/2}$ level to lower levels. Using first-order perturbation theory [36], the induced decay rate to the $6s^2S_{1/2}$ level is given by

$$\gamma_{\text{Stark}} = \frac{8\pi^2}{3\epsilon_0\hbar\lambda^3} \sum_{m'q} |\langle 6s^2\widetilde{S}_{1/2,m'} | D_q | 5d^2\widetilde{D}_{5/2,m} \rangle|^2, \quad (6.31)$$

summing over $6s^2S_{1/2}$ sublevels m' and all polarization states q . The perturbative state corrections are

$$|\widetilde{Jm}\rangle = |Jm\rangle + \sum_{J'm' \neq Jm} \frac{\langle J'm' | H_{\text{Stark}} | Jm \rangle}{E_{Jm} - E_{J'm'}} |J'm'\rangle. \quad (6.32)$$

Inserting into (6.31), observing the selection rules of the dipole operator, yields

$$\begin{aligned} \gamma_{\text{Stark}} = & \frac{8\pi^2}{3\epsilon_0\hbar\lambda^3} \sum_{m'q} \left| \sum_{nm''} \frac{\langle 6s^2S_{1/2,m'} | \boldsymbol{\mathcal{E}} \cdot \boldsymbol{D} | np^2P_{3/2,m''} \rangle \langle np^2P_{3/2,m''} | D_q | 5d^2D_{5/2,m} \rangle}{E_{6s^2S_{1/2}} - E_{np^2P_{3/2}}} \right. \\ & \left. + \sum_{nm''} \frac{\langle 6s^2S_{1/2,m'} | D_q | np^2P_{3/2,m''} \rangle \langle np^2P_{3/2,m''} | \boldsymbol{\mathcal{E}} \cdot \boldsymbol{D} | 5d^2D_{5/2,m} \rangle}{E_{5d^2D_{5/2}} - E_{np^2P_{3/2}}} \right|^2. \end{aligned} \quad (6.33)$$

Taking the scalar part of the inner product for an electric field of strength $\mathcal{E}$, and filling in the level energies [50] and the dipole transition amplitudes [100] for Ba^+ gives

$$\gamma_{\text{Stark}} = 3.8 \times 10^{-15} \text{ s}^{-1} / (\text{V/m})^2 \times |\mathcal{E}|^2, \quad (6.34)$$

comparable to the value for Ca^+ in Ref. 196. The induced decay rate from $5d^2D_{5/2}$ to $5d^2D_{3/2}$ can be calculated in the same way, including both P and F levels in the sum; this contribution is several orders of magnitude smaller.

With observed stray electric field strengths in our trap of no more than 100 V/m, the shortening of the $5d^2D_{5/2}$ level lifetime is negligible, even when taking into account a possible enhancement by up to three orders of magnitude due to micromotion [87].

Figure 6.12 Pressure-corrected decay rate of the $5d^2D_{5/2}$ level as function of (a) the detuning of the laser light at 494 nm from the $6s^2S_{1/2} - 6p^2P_{1/2}$ resonance and (b) the detuning of the laser light at 650 nm from the $5d^2D_{3/2} - 6p^2P_{1/2}$ resonance, shown with the weighted mean (data has been clustered for clarity, number of averaged data sets in parentheses). No significant dependence of the decay rate is found.

Magnetic fields

We apply a static magnetic field of about 200 μT . The corresponding DC Zeeman effect also mixes states. However, the magnetic moment operator is parity-even, so the dipole transition rate in Eq. (6.31) is unaffected and the $5d^2D_{5/2}$ lifetime unchanged.

6.4.4 Ion dynamics and interactions

Finally, ion temperature or ion–ion interactions could affect our measurement.

Ion temperature

Ions are not laser cooled while shelved in the $5d^2D_{5/2}$ level, although they can experience sympathetic cooling when multiple ions are trapped and some remain unshelved. If an ion heats up so much that it leaves the central fiducial volume, fluorescence at the full level is only achieved again after significant laser cooling. While the actual excitation lifetime is unchanged, this increases the apparent lifetime and manifests itself as unsharp edges of the steps in the fluorescence rate. When trapping multiple ions, a shelved ion heating up would also disturb the ion crystal including any unshelved ions and thus show up on the EMCCD camera images. We have taken care to entirely exclude data sets exhibiting such events by visual inspection of the fluorescence and image data. The temperature of the ions is furthermore influenced by the detuning from resonance of the cooling lasers and the trapping potential. Data

Figure 6.13 Pressure-corrected decay rate of the $5d^2D_{5/2}$ level as function of (a) the RF voltage V_0 and (b) the number of Ba^+ ions in the data set (most data have been collected with a single ion), shown with the weighted mean. No significant variation in the decay rate is found.

were collected at RF voltage amplitudes V_0 ranging from 200 V to 800 V. No significant dependence of the pressure-corrected decay rate on laser detunings (see Fig. 6.12) or RF voltage (see Fig. 6.13a) is observed.

Ion-ion interactions

The temperature of an ion can change through Coulomb interaction with other ions present in the trap, Ba^+ or other. Any trapped ions of species other than Ba^+ are not laser cooled and thus contribute to the heating of Ba^+ ions. Monitoring the positions of the ions with the EMCCD camera ensures that any change in the number of trapped ions is detected. Our evolving insights into the observed crystal shapes indicate that dark ions may have been present in many data sets (see Section 3.5.3). However, any resulting heating effect should show up as described in the previous section. Within statistical precision we find no indication that the pressure-corrected decay rate differs between data sets where we can exclude additional ions and those where we cannot.

A further effect we consider are correlations in the decay of the $^2D_{5/2}$ level of multiple Ba^+ ions. The physical mechanism of superradiance and subradiance [202], where the dipole radiation from the spontaneous decay of two or more ions interferes, can produce such correlations. An enhanced rate of multiple jumps (two or more ions shelving or deshelling within the averaging window) was reported in an early experiment with three Ba^+ ions as an indication of cooperative interactions [173]. However, later calculations [174] show that the reported enhancement by several orders of magnitude cannot be explained in this way, as the effect is limited to deviations

Table 6.1 Overview of systematic effects (see Section 6.4). Corrections to the decay rate are applied using Eq. (6.17) for all identified effects $\geq 10^4 \text{ s}^{-1}$. The correction for background gas collisions is done by extrapolating the decay rate to zero pressure, since this correction differs per data set. Uncertainties are added in quadrature.

Corrections	Decay rate contribution (s^{-1})
Background gas collisions $\gamma_{\text{collision}}$	$+5.1(1.4) \times 10^7 \times p/\text{mbar}$
Off-resonant excitation by lasers γ_{lasers}	$< 10^{-5}$
Off-resonant excitation by LED γ_{LED}	$< 10^{-5}$
Thermal radiation γ_{bb}	$+1.1(0.3) \times 10^{-4}$
Stray electric fields γ_{Stark}	$< 10^{-5}$
Ion-ion interactions	$< 10^{-5}$
Analysis procedure bias	$< 10^{-4}$
Final $^2\text{D}_{5/2}$ decay rate	$0.0380(8)$
Corresponding lifetime $\tau_{\text{D}_{5/2}, \text{nat}} = 26.3(0.6) \text{ s}$	

of about $\pm 5\%$ from the rates for independent atoms at distances comparable to the wavelength $\lambda \approx 0.5 \mu\text{m}$ and quickly becomes negligible when the distance between the ions is increased. Superradiance and subradiance at the level of $\pm 1\%$ has been experimentally observed in the $6p\ ^2\text{P}_{1/2}$ to $6s\ ^2\text{S}_{1/2}$ decay rate in a pair of Ba^+ ions separated by about $1.5 \mu\text{m}$ [203]. Also in an ensemble of 10 Ca^+ ions, some unexpected double jumps were reported [194], but subsequent experiments with greater statistics found no correlations or enhanced double or triple jump rates [175–177]. In our experiment, the distance between ions is typically around $10 \mu\text{m}$ (see Section 3.5) and thus we expect cooperative effects between ions to be negligible.

We find no significant difference between the pressure-corrected decay rate for single ions and ion crystals with up to four Ba^+ ions (see Fig. 6.13b). We combine all data for our final result.

6.5 Results and Discussion

Our final result for the lifetime of the $5d\ ^2\text{D}_{5/2}$ level in Ba^+ includes the correction for the additional decay rate due to collisions with background gas molecules and the small correction for stimulated emission due to blackbody radiation (see Table 6.1). Other systematic effects are found to be negligible and the lifetimes from individual data sets with 1 to 4 ions are consistent within errors. We check for any systematic bias by running the complete analysis on pseudo-randomly generated data sets with properties (data set lengths, numbers of ions, lifetime, shelving times, PMT signal-to-noise and pressure dependence) matching those of our experimental data and find that the

Table 6.2 Compilation of published theoretical and experimental values of the lifetime of the $5d^2D_{5/2}$ level in Ba^+ .

Theory			Experiment		
$\tau_{D_{5/2}}$ (s)	Year	Ref.	$\tau_{D_{5/2}}$ (s)	Year	Ref.
30.3(0.5)	2017	[55]	26.3(0.6)	2018	This work ⁴⁵
29.8(0.3)	2012	[204]	31.2(0.9)	2014	[178]
30.3(0.4)	2010	[205]	32.0(2.9)	2007	[206]
30.3(0.4)	2008	[207]	32.3(2.6)	1997	[191] ⁴⁶
30.8	2007	[208] ⁴⁷	38(13)	1992	[179]
31.6	2007	[209]	34.5(3.5)	1990	[190]
29.9(0.3)	2006	[107]	32(5)	1986	[182]
36.5	2002	[210] ⁴⁸	47(16)	1980	[211]
30.3	2001	[58]			

analysis reproduces the simulated decay rate within $< 10^{-4}$.

An overview of previously measured and calculated values of $\tau_{D_{5/2}}$ is compiled in Table 6.2 and Fig. 6.14. Most previous measurements and calculations favor a lifetime around 30 s. Our result is some 4.5σ below the latest independent determination from Ref. 178, which used a different experimental approach. Our result also disagrees with recent theoretical results which claim uncertainties below 2 %. Most systematic effects would tend to make a lifetime appear too short, but despite our extensive search, we could not identify any systematic effect that explains the observed discrepancy. The Ba^+ ion has significantly longer D level lifetimes than any other earth alkali metal ion. The decay of the $^2D_{5/2}$ level in Ba^+ has a 15 % branching ratio to the $^2D_{3/2}$ level via the $M1$ transition amplitude [178]. This contribution is negligible in the lighter earth alkali metal ions and was missed in early theoretical calculations in Ba^+ . Nevertheless, the atomic structure of Ba^+ is very similar to that of Ca^+ and Sr^+ and no such discrepancy in lifetimes between theory and experiment appears to exist in these atomic systems [55].

The uncertainty in our result is dominated by the statistical error. We have investigated known systematic effects through calculation and inspecting our data for a dependence on a range of experimental parameters. Our sensitivity of identifying

⁴⁵This should be considered to replace the lifetime value of Ref. 166. An incomplete analysis of a subset of the same data was published previously as Ref. 212.

⁴⁶The quoted uncertainty is before extrapolation to zero pressure, no separate uncertainty is given for the final value.

⁴⁷This is a correction of the value originally published in 1991 of 37.2 s which erroneously omitted to take the $M1$ contribution to the $^2D_{5/2} - ^2D_{3/2}$ transition into account [208].

⁴⁸This value also appears to neglect the $M1$ contribution (see erratum Ref. 208).

Figure 6.14 History of experimental measurements and theoretical calculations of the lifetime of the Ba^+ $5d^2D_{5/2}$ level, as listed in Table 6.2.

systematic effects from the data sets could be improved by enlarging the probed parameter space and collecting more statistics. In practice, the latter is limited by the running time needed due to the long lifetime and a significant improvement would require weeks of data taking. Possible improvements to the experimental setup include installing additional electrodes to enable better compensation of stray electric fields. Analyzing the composition of the residual gas in the setup would enable a quantitative comparison of quenching rates. During the experiments more care could be taken to ensure the absence of any dark ions. Ion heating while shelved could be studied in more detail at various experimental settings by blocking the cooling lasers to simulate shelving and then checking whether the fluorescence signal always comes back promptly when unblocking the lasers. Nevertheless, in our extensive set of systematic checks, we have found no indication that any of these aspects affected our measured lifetime.

We have performed measurements of the $5d^2D_{5/2}$ level lifetime in Ba^+ both in single trapped ions and in crystals of up to four ions. We find a consistent lifetime significantly shorter than previously measured (see Table 6.2). For the reliability of the weak mixing angle measurements ahead, a clarification of the discrepancy in the obtained $5d^2D_{5/2}$ lifetime values is required. Including all data sets, we find

$$\tau_{D_{5/2}} = 26.3(0.6) \text{ s}. \quad (6.35)$$

Conclusions and Outlook

The motivation for this research is to perform stringent tests of the Standard Model [1] using single laser-cooled Ba^+ or Ra^+ ions in a Paul trap [2, 3]. These are good candidates for carrying out a new, independent high-precision determination of the Weinberg angle ($\sin^2 \theta_W$) at low energy [13]: the heavy alkaline earth metal ions combine tractable atomic structure with high intrinsic sensitivity [14, 15]. Such atomic parity violation measurements complement studies of the weak interaction at higher energy and, even though effects only appear indirectly, have a unique sensitivity to some beyond-the-Standard-Model physics, such as the existence of a light additional Z boson [7, 8]. Additionally, trapped Ba^+ or Ra^+ ions could serve as the reference for optical atomic clocks [21–23]. The clock frequencies of these heavy ions are particularly sensitive to variation of the fine structure constant α [24], opening another avenue of testing the Standard Model. They also offer possibilities for simple, compact clocks.

In this thesis we present several important steps working toward these goals. We have compiled an overview of relevant theory, describing systematic effects and setting experimental requirements (Chapter 1). We have further developed a single ion trapping setup for performing preparatory fluorescence measurements with Ba^+ (Chapter 2). In particular, the data acquisition and experiment control system was greatly expanded. Initial steps have been taken to design and build an offline Ra^+ ion source. We have investigated experimental techniques for characterizing ion traps, minimizing stray electric fields and detecting the presence of dark ions (Chapter 3).

We have done optical spectroscopy of $^{138}\text{Ba}^+$ for an improved determination of the $6s\ ^2S_{1/2} - 6p\ ^2P_{1/2}$ and $5d\ ^2D_{3/2} - 6p\ ^2P_{1/2}$ transition frequencies (Chapter 4). This yielded the most accurate values for the Ba^+ clock frequencies (at time of publishing) and laid the groundwork for measurements of $^{134}\text{Ba}^+$ and $^{136}\text{Ba}^+$ isotope shifts in our group [156]. For analyzing the optical spectra, we employed a lineshape model based on the optical Bloch equations, extending an existing code [112] to support arbitrary propagation directions and polarization states of the laser light fields. The obtained lineshape model was found to describe the experimentally observed spectra well.

Another method of obtaining information on atomic structure is to utilize light shifts induced by off-resonant laser light. In choosing the wavelength, different combinations of transition matrix elements can be probed. Light shifts also play an important role in the proposed method of measuring atomic parity violation in trapped Ba^+ or Ra^+ ions [13]. We have performed an exploratory study combining optical lineshapes with light shifts (Chapter 5). In principle, similar measurements could be used to obtain

ratios of light shifts to provide further input to theory, although an investigation of systematic effects would be needed to compare the merits to RF spectroscopy methods.

An accurate measurement of the Weinberg angle calls for robust calculations of atomic structure in addition to precise control over the experiment and mitigation of systematic effects. The parity violating transition amplitude needs to be calculated to sub-% accuracy and experimental input is needed to benchmark these calculations, such as level lifetimes that relate to transition matrix elements. To this end, we have measured the lifetime of the $5d^2D_{5/2}$ level in $^{138}\text{Ba}^+$ using a technique based on quantum jumps with one to four laser-cooled trapped ions (Chapter 6). This level is particularly long-lived (≈ 30 s) and therefore this measurement is highly sensitive to perturbations. We have investigated known systematic effects to evaluate their influence. It appears that our result for the $5d^2D_{5/2}$ level lifetime is significantly shorter than previous experimental results and calculations. This discrepancy needs to be clarified to ensure the reliability of atomic parity violation measurements ahead.

Looking ahead, experiments with radioactive Ra^+ require the development of a convenient and safe offline source that can be coupled to a Paul trap. The discrepancy in the Ba^+ $5d^2D_{5/2}$ level lifetime measurement shows that there is a need for improving the understanding of the systematic effects in the experiments or possibly the atomic structure calculations. A competitive measurement of the Weinberg angle at low energy using trapped Ba^+ or Ra^+ necessitates developing vacuum-compatible crossed optical cavities around an ion trap where a single ion can be localized to a fraction of a wavelength, as well as implementing RF spectroscopy techniques. We have started work on designing a suitable experimental setup. Especially the position of the ion and the polarization of the standing-wave light fields need sufficient control to prevent effects mimicking the atomic parity violation signal from causing problems for interpreting the measurements. In addition, magnetic shielding is necessary for future experiments to limit magnetic field fluctuations. Working toward an optical clock based on Ba^+ or Ra^+ requires the development of an ultra-stable laser system at the corresponding clock frequency. Precise measurements of polarizabilities are necessary to evaluate frequency shifts caused by electric fields. Excellent control over the motional state of trapped ions and stability of their thermal and electromagnetic environments is needed to limit the uncertainty in shifts of the clock frequency.

We have performed optical spectroscopy of Ba^+ ions in preparation of extracting the Weinberg angle at low energy from atomic parity violation measurements with Ba^+ or Ra^+ ions. We have provided a discussion of systematic effects, a detailed description of the influence of experimental parameters on observed spectra and investigated diagnostic tools for ion trapping. Application of this led to improved precision on $^{138}\text{Ba}^+$ transition frequencies and a measurement of the metastable $5d^2D_{5/2}$ level lifetime, challenging previous values. These are essential steps toward an experimental apparatus capable of discerning weak interaction effects in Ba^+ or Ra^+ ions from the dominant electromagnetic background for testing the Standard Model.

Nederlandse Samenvatting

Het gedrag van alle bekende elementaire deeltjes wordt beschreven in de theorie die bekendstaat als het *standaardmodel van de deeltjesfysica* (SM) [1]. Deze theorie is gedurende de laatste vijftig jaar ontwikkeld en verenigt drie van de vier fundamentele krachten (namelijk de elektromagnetische, de zwakke en de sterke wisselwerking, maar niet de zwaartekracht). Hoewel het standaardmodel met opvallend succes de subatomaire wereld beschrijft, blijven verscheidene fundamentele vragen onbeantwoord, bijvoorbeeld hoe zwaartekracht te verenigen valt met het SM. Dit motiveert het zoeken naar de grenzen van deze theorie in de hoop een glimp op te vangen van nieuwe fysica voorbij het standaardmodel.

Het onderzoek in dit proefschrift heeft als doel het standaardmodel te testen met behulp van spectroscopische metingen aan een enkel lasergekoeld barium- (Ba^+) of radium-ion (Ra^+) gevangen in een Paul-val [2]. Hierbij gebruiken we precisie-meettechnieken uit de atoomfysica om bij lage energie te speuren naar nog onbekende deeltjes of wisselwerkingen [3]. Deze zouden zich manifesteren als kleine verschuivingen van de energieniveaus van de ionen ten opzichte van de SM-voorspelling.

Atomaire pariteitsschending

Bij lage energie zijn effecten van de zwakke wisselwerking bijzonder gevoelig voor bepaalde typen speculatieve deeltjes, zoals additionele lichte Z-bosonen die verband zouden kunnen houden met donkere materie [7, 8]. Deze effecten zijn te onderscheiden van de dominante elektromagnetische effecten door te observeren hoe ze zich gedragen onder een pariteitstransformatie (spiegelen) van de experimentele configuratie van de meetopstelling: de elektromagnetische wisselwerking is hierbij invariant, terwijl de zwakke wisselwerking deze symmetrie schendt. Het bestuderen van de zwakke wisselwerking in atomaire systemen staat daarom bekend als *atomaire pariteitsschending* (Atomic Parity Violation, APV). De grootte van de zwakke effecten schaaft sterk met het atoomnummer Z en deze zijn daarom het best te meten in zware elementen [10].

Onze intentie is om een nieuwe, onafhankelijke precisiemeting van de zogenaamde *Weinberg-hoek* ($\sin^2 \theta_W$) bij lage impulsoverdracht uit te voeren. Deze hoek hangt samen met de sterkte van de interactie tussen de elektronen en de nucleonen in de atoomkern via de zwakke wisselwerking. De Weinberg-hoek vormt een vrije parameter van het standaardmodel, maar het SM voorspelt wel hoe de waarde wegens

renormalisatie afhankelijk is van de typische impulsoverdracht in het proces dat wordt bestudeerd [1]. Relatief kleinschalige precisiemetingen bij lage impulsoverdracht zijn daarom complementair aan metingen uit de hoge-energiefysica.

Op dit moment wordt de waarde van de Weinberg-hoek bij lage energie ontleend aan een enkel experiment waarbij de pariteitsschending in cesium-atomen werd gemeten [11]. De interpretatie van deze meting berust op complexe berekeningen van de atomaire structuur, waarin nog steeds verbeteringen worden gevonden [12, 30–33]. Ba^+ en Ra^+ zijn bijzonder geschikt voor een nieuwe onafhankelijke meting [13], gezien deze enkel-geladen zware aardalkalimetaalionen een eenvoudige atomaire structuur combineren met een hoge intrinsieke gevoeligheid [14, 15]. De zwakke wisselwerking zorgt voor een eindige pariteit-schennende dipool-overgangswaarschijnlijkheid tussen de $^2\text{S}_{1/2}$ grondtoestand en laagste $^2\text{D}_{3/2}$ aangeslagen toestand van de ionen. Het voorgestelde experiment bestaat uit het plaatsen van een enkel gevangen, lasergekoeld ion in twee orthogonale staande golven van laserlicht dat resonant is met deze overgang, waardoor de Zeeman-toestanden van de grondtoestand een energieverschuiving (*light shift*) ondervinden [13]. Het ion moet hierbij worden gelokaliseerd tot op een fractie van de optische golflengte. De polarisatie en geometrie worden zo gekozen dat het effect van de zwakke wisselwerking wordt versterkt door interferentie met de dominantie elektromagnetische wisselwerking. Wanneer de experimentele configuratie vervolgens wordt gespiegeld, wisselt de component van de frequentieverschuiving die wordt veroorzaakt door de zwakke wisselwerking van teken, terwijl de elektromagnetische component dat niet doet.

Optische atoomklokken

Naast het meten van atomaire pariteitsschending, is een enkel gevangen, lasergekoeld Ba^+ - of Ra^+ -ion ook geschikt om te dienen als het hart van een *optische atoomklok* [21]. Hierbij dient een geschikte elektronische overgang van het ion als referentie om de frequentie van een laser te stabiliseren om extreem nauwkeurig de tijd te meten. In Ba^+ en Ra^+ zijn de klok-overgangen de overgangen van de $^2\text{S}_{1/2}$ grondtoestand naar de laagste $^2\text{D}_{3/2}$ of $^2\text{D}_{5/2}$ aangeslagen toestanden; deze hebben een scherp-gedefinieerde frequentie en zijn zeer ongevoelig voor verstoring door elektromagnetische velden [22, 23]. Voordelen van Ba^+ en Ra^+ zijn onder andere dat er isotopen met verschillende kernspin beschikbaar zijn en dat de benodigde laserfrequenties relatief eenvoudig te produceren zijn met goedkope diodelasers, wat interessant is voor het bouwen van eenvoudige en compacte atoomklokken.

Vergeleken met bestaande kloksystemen zijn optische atoomklokken gebaseerd op de zware elementen Ba^+ en Ra^+ ook met name interessant omdat zij gevoelig zijn voor variatie in de *fijnstructuurconstante* α [24]. Hiertoe worden atoomklokken die gebaseerd zijn op verschillende elementen met elkaar vergeleken om waar te nemen

of hun frequentieverschil in de loop van de tijd verandert. Tijdsvariatie in een fundamentele natuurkundeconstante zou duiden op nieuwe fysica en zo vormt dit een tweede manier om het standaardmodel te testen.

Spectroscopische metingen aan $^{138}\text{Ba}^+$ -ionen

In dit proefschrift presenteren we een aantal belangrijke stappen op weg naar het realiseren van de geschetste doelen. Voor zowel een meting van de Weinberg-hoek als een optische atoomklok gebaseerd op Ba^+ - of Ra^+ -ionen hebben we een overzicht van de relevante theoretische onderwerpen samengesteld, de systematische effecten beschreven en de eisen aan de meetopstelling opgetekend (hoofdstuk 1). We hebben een experimentele opstelling bestaande uit een Paul-val voor het vangen van een enkel ion verder ontwikkeld voor het uitvoeren van voorbereidende fluorescentie-metingen met Ba^+ (hoofdstuk 2). Met name het data-acquisitiesysteem en het controlesysteem van het experiment werden enorm uitgebreid. Ook zijn de eerste stappen gezet voor het ontwerpen en bouwen van een offline (zonder gebruik van een versneller) Ra^+ -ionenbron. We hebben de dynamica van een of meerdere ionen die gevangen zijn in een ionenval beschreven en experimentele technieken voor het karakteriseren van ionenvallen, het minimaliseren van elektrische strooivelden en het detecteren van donkere (niet-fluorescerende) ionen uitgezocht (hoofdstuk 3). Deze technieken zijn cruciaal voor het uitvoeren van precisie-metingen.

Met optische laserspectroscopie hebben we de overgangsfrequenties tussen de laagliggende energieniveaus van $^{138}\text{Ba}^+$ -ionen gemeten (hoofdstuk 4). Door gebruik van een optische frequentiekamlaser hebben we de nauwkeurigheid van eerdere metingen verbeterd met meer dan een factor 100. We hebben de $6s\ ^2\text{S}_{1/2} - 5d\ ^2\text{D}_{3/2}$ en $5d\ ^2\text{D}_{3/2} - 6p\ ^2\text{P}_{1/2}$ overgangsfrequenties bepaald op 146 114 384.0(0.1) MHz en 461 311 878.5(0.1) MHz, respectievelijk [113]. Dit leverde ook de meest nauwkeurigste waarden voor de klok-frequenties van Ba^+ op (op het moment van publiceren) en legde de basis voor latere metingen van isotoopverschuivingen in $^{134}\text{Ba}^+$ en $^{136}\text{Ba}^+$ in onze groep [156]. Voor het analyseren van de optische spectra gebruikten we een lijnprofielmodel gebaseerd op de optische Bloch-vergelijkingen met acht toestanden, waarbij we een bestaande computercode [112] hebben uitgebreid met ondersteuning voor willekeurige propagatierichtingen en polarisatietoestanden van de laserlichtvelden. Dit lijnprofielmodel bleek de experimenteel waargenomen spectra goed te beschrijven.

Informatie over de atoomstructuur kan ook worden verkregen door de frequentieverschuivingen waar te nemen wegens het dynamische Stark-effect (light shifts) wanneer een ion wordt blootgesteld aan niet-resonant laserlicht. Met de keuze van de golflengte van het licht kunnen verschillende combinaties van overgangswaarschijnlijkheden worden onderzocht. Daarnaast is dit effect ook relevant omdat het een belangrijke rol speelt in de voorgestelde methode om atomaire pariteitsschending te meten in

gevangen Ba^+ - of Ra^+ -ionen [13]. In een verkennende meting met $^{138}\text{Ba}^+$ -ionen hebben we optische lijnprofielen gecombineerd met frequentieverschuivingen van de individuele Zeeman-toestanden wegens het dynamisch Stark-effect ten gevolge van een niet-resonante laser met een frequentie in de buurt van de $5d^2D_{3/2} - 6p^2P_{1/2}$ overgang (hoofdstuk 5). Hierbij hebben we aangetoond dat de aangepaste lijnprofielen de waargenomen effecten beschrijven. Hetzelfde meetprincipe zou toegepast kunnen worden om verhoudingen van frequentieverschuivingen te bepalen die waardevol zijn als input voor atoomtheorie; een volledige analyse van de systematische effecten zou moeten uitwijzen hoe deze methode zich verhoudt ten opzichte van radiofrequente (RF) spectroscopie.

Behalve precieze besturing van het experiment en beheersing van de systematische effecten, vereist een nauwkeurige meting van de Weinberg-hoek ook robuuste berekeningen van de atoomstructuur. De pariteit-schendende overgangswaarschijnlijk moet worden berekend met een nauwkeurigheid van minder dan een procent. Experimentele input is nodig om deze berekeningen te ijken, waaronder de levensduren van aangeglagen toestanden, die samenhangen met atomaire overgangswaarschijnlijkheden. Hiertoe hebben wij de levensduur van het $5d^2D_{5/2}$ niveau in $^{138}\text{Ba}^+$ bepaald met behulp van een meettechniek die gebaseerd is op kwantumsprongen van een tot vier gevangen, lasergekoelde ionen (hoofdstuk 6). Dit energieniveau heeft een bijzonder lange levensduur en deze meting is daarom zeer gevoelig voor verstoringen. We hebben alle ons bekende systematische effecten uitgebreid onderzocht om hun invloed te bepalen. De door ons bepaalde levensduur van het $5d^2D_{5/2}$ niveau is $26.3(0.6)$ s en is daarmee ongeveer 4σ korter dan eerdere metingen en berekeningen [166]. De oorzaak van dit verschil moet worden uitgezocht om de betrouwbaarheid van metingen van atomaire pariteitsschending te verzekeren.

Vooruitzicht

Met de blik op de toekomst is het ontwikkelen van een geschikte, veilige offline ionenbron die aan een Paul-val gekoppeld kan worden vereist voor metingen met radioactief Ra^+ . De discrepantie in de levensduur van het $\text{Ba}^+ 5d^2D_{5/2}$ niveau toont een behoefte aan een beter begrip van de systematische effecten in het experiment of mogelijk de atoomstructuurberekeningen. Voor een concurrerende meting van de Weinberg-hoek bij lage energie met gevangen Ba^+ - of Ra^+ -ionen moeten gekruiste vacuüm-compatibele optische trilhaoltes worden ontwikkeld waarin een enkel ion kan worden gelokaliseerd tot op een afstand korter dan een golflengte. Daarnaast moet RF-spectroscopie worden geïmplementeerd in de meetopstelling. We hebben een begin gemaakt met het ontwerpen van een dergelijke meetopstelling. Met name de positie van het ion en de polarisatietoestand van de staande lichtgolven moeten afdoende worden beheerst om te voorkomen dat effecten die lijken op het signaal van atomaire

pariteitsschending de interpretatie van de metingen belemmeren. Daarnaast is magnetische afscherming noodzakelijk om fluctuaties in het magnetisch veld te voorkomen bij toekomstige metingen. Voor een optische atoomklok die gebaseerd is op Ba^+ of Ra^+ is het nodig om een ultrastabiel lasersysteem te ontwikkelen voor de overeenkomstige klokfrequentie. Nauwkeurige metingen van de polariseerbaarheid zijn benodigd om frequentieverschuivingen door elektrische strooivelden te kunnen evalueren. Uitstekende controle over de beweging van gevangen ionen en een stabiele thermische en elektromagnetische omgeving is nodig om de onzekerheid in verschuivingen van de klokfrequentie te beperken.

We hebben optische spectroscopie van Ba^+ -ionen uitgevoerd in voorbereiding op het bepalen van de Weinberg-hoek bij lage energie met behulp van atomaire pariteitsschending in Ba^+ - of Ra^+ -ionen. We hebben een uiteenzetting gegeven van de systematische effecten en de invloed van experimentele parameters op de waargenomen optische spectra. Verder hebben we diagnostische gereedschappen voor ionenvallen onderzocht. De toepassing van het bovenstaande heeft geleid tot een verbeterde bepaling van de $^{138}\text{Ba}^+$ -overgangsfrequenties en een meting van de levensduur van het $5d\ ^2D_{5/2}$ niveau. Dit zijn essentiële stappen om een meetopstellingen te ontwikkelen die effecten van de zwakke wisselwerking in Ba^+ - of Ra^+ -ionen kan onderscheiden van de dominante elektromagnetische achtergrond om zo het standaardmodel nauwgezet te testen.

Appendix A

Hyperfine Atomic Properties

This appendix lists the expressions to calculate the electric dipole polarizabilities and electric quadrupole moment for a hyperfine level in the IJ -coupling approximation.

Hyperfine electric dipole polarizabilities

The dipole polarizabilities α_{iF} (static or dynamic) for hyperfine level F are calculated from the values α_{iJ} for fine structure level J with the help of $6j$ -symbols:

$$\begin{aligned}\alpha_{0F} &= \alpha_{0J} \\ \alpha_{1F} &= (-1)^{I+J+F+1} \sqrt{\frac{F(2F+1)}{F+1} \frac{(J+1)(2J+1)}{J}} \left\{ \begin{matrix} J & 1 & J \\ F & I & F \end{matrix} \right\} \alpha_{1J} \\ \alpha_{2F} &= (-1)^{I+J+F} \sqrt{\frac{F(2F-1)(2F+1)}{(2F+3)(F+1)} \frac{(2J+1)(J+1)(2J+3)}{J(2J-1)}} \left\{ \begin{matrix} J & 2 & J \\ F & I & F \end{matrix} \right\} \alpha_{2J}\end{aligned}\quad (\text{A.1})$$

Hyperfine electric quadrupole moment

The electric quadrupole moment Θ_F for hyperfine level F is given in terms of Θ_J by

$$\Theta_F = (-1)^{I+J+F} (2F+1) \left\{ \begin{matrix} J & 2 & J \\ F & I & F \end{matrix} \right\} \left(\begin{matrix} J & 2 & J \\ -J & 0 & J \end{matrix} \right)^{-1} \Theta_J. \quad (\text{A.2})$$

The explanation for the $3j$ -symbol is that the (reduced) electric quadrupole moment Θ_J of level J is conventionally defined as the diagonal matrix element for maximum m_J .

Appendix B

Lifetime Finite Averaging Window Analysis

These are the explicit expressions for the analytical analysis of the effect of a finite averaging window on the lifetime extracted from quantum jump data, see Section 6.3.3.

$$\begin{aligned}\tilde{\tau}_k(\Delta t)\Big|_{\text{one interval}} &= p_0 \int_{\Delta t}^{\infty} t_1 P(t_1; \tau_k) (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})) dt_1 \\ &= (\tau_k + \Delta t) \left(1 + p_{k\downarrow\uparrow} (P_{>\Delta t}(\tau_{k-1}) - 1) + p_{k\uparrow\downarrow} (P_{>\Delta t}(\tau_{k+1}) - 1) \right), \quad (\text{B.1})\end{aligned}$$

$$\begin{aligned}\tilde{\tau}_k(\Delta t)\Big|_{\text{two intervals}} &= p_0 \int_{\Delta t}^{\infty} dt_1 \int_0^{\Delta t} dt'_{12} \int_0^{\infty} dt_2 \times (t_1 + t'_{12} + t_2) \\ &\quad \times P(t_1; \tau_k) \times (p_{k\downarrow} P(t'_{12}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{12}; \tau_{k+1}) p_{(k+1)\downarrow}) \\ &\quad \times P(t_2; \tau_k) \times (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})) \\ &= -\exp\left[-\frac{\Delta t}{\tau_{k+1}} - \frac{\Delta t}{\tau_{k-1}}\right] \\ &\quad \times \left(\exp\left[\frac{\Delta t}{\tau_{k-1}}\right] p_{k\uparrow\downarrow}(2\Delta t + 2\tau_k + \tau_{k+1}) + \exp\left[\frac{\Delta t}{\tau_{k+1}}\right] p_{k\downarrow\uparrow}(2\Delta t + 2\tau_k + \tau_{k-1}) \right. \\ &\quad \left. - \exp\left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}}\right] (p_{k\uparrow\downarrow}(\Delta t + 2\tau_k + \tau_{k+1}) + p_{k\downarrow\uparrow}(\Delta t + 2\tau_k + \tau_{k-1})) \right) \\ &\quad \times \left(1 + p_{k\uparrow\downarrow}(P_{>\Delta t}(\tau_{k+1}) - 1) + p_{k\downarrow\uparrow}(P_{>\Delta t}(\tau_{k-1}) - 1) \right), \quad (\text{B.2})\end{aligned}$$

$$\begin{aligned}\tilde{\tau}_k(\Delta t)\Big|_{\text{three intervals}} &= p_0 \int_{\Delta t}^{\infty} dt_1 \int_0^{\Delta t} dt'_{12} \int_0^{\infty} dt_2 \int_0^{\Delta t} dt'_{23} \int_0^{\infty} dt_3 \\ &\quad \times (t_1 + t'_{12} + t_2 + t'_{23} + t_3) \\ &\quad \times P(t_1; \tau_k) \times (p_{k\downarrow} P(t'_{12}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{12}; \tau_{k+1}) p_{(k+1)\downarrow})\end{aligned}$$

$$\begin{aligned}
 & \times P(t_2; \tau_k) \times (p_{k\downarrow} P(t'_{23}; \tau_{k-1}) p_{(k-1)\uparrow} + p_{k\uparrow} P(t'_{23}; \tau_{k+1}) p_{(k+1)\downarrow}) \\
 & \times P(t_3; \tau_k) \times (p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})) \\
 & = \exp \left[-\frac{2\Delta t}{\tau_{k+1}} - \frac{2\Delta t}{\tau_{k-1}} \right] \\
 & \times \left(\exp \left[\frac{\Delta t}{\tau_{k-1}} \right] p_{k\uparrow\downarrow} + \exp \left[\frac{\Delta t}{\tau_{k+1}} \right] p_{k\downarrow\uparrow} - \exp \left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}} \right] (p_{k\uparrow\downarrow} + p_{k\downarrow\uparrow}) \right) \\
 & \times \left(\exp \left[\frac{\Delta t}{\tau_{k-1}} \right] p_{k\uparrow\downarrow} (3\Delta t + 3\tau_k + 2\tau_{k+1}) + \exp \left[\frac{\Delta t}{\tau_{k+1}} \right] p_{k\downarrow\uparrow} (3\Delta t + 3\tau_k + 2\tau_{k-1}) \right. \\
 & \quad \left. - \exp \left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}} \right] (p_{k\uparrow\downarrow} (\Delta t + 3\tau_k + 2\tau_{k+1}) + p_{k\downarrow\uparrow} (\Delta t + 3\tau_k + 2\tau_{k-1})) \right) \\
 & \quad \times \left(1 + p_{k\uparrow\downarrow} (P_{>\Delta t}(\tau_{k+1}) - 1) + p_{k\downarrow\uparrow} (P_{>\Delta t}(\tau_{k-1}) - 1) \right), \text{ etc.} \quad (\text{B.3})
 \end{aligned}$$

Here we have filled in the factor p_0 which can be found by checking that the total probability in the final infinite sum adds up to one:

$$p_0 = \exp \left[\frac{\Delta t}{\tau_k} \right] \frac{1 + p_{k\downarrow\uparrow} (P_{>\Delta t}(\tau_{k-1}) - 1) + p_{k\uparrow\downarrow} (P_{>\Delta t}(\tau_{k+1}) - 1)}{p_{k\downarrow} P_{>\Delta t}(\tau_{k-1}) + p_{k\uparrow} P_{>\Delta t}(\tau_{k+1})}. \quad (\text{B.4})$$

The final modified lifetime $\tilde{\tau}_k(\Delta t)$ is the sum over all possible numbers of intervals joined together. The result of the preceding integrals (B.1)–(B.3) can be seen to all follow the same structure, so that the final infinite sum is

$$\begin{aligned}
 \tilde{\tau}_k(\Delta t) &= \sum_{j=1}^{\infty} (-1)^{j+1} \exp \left[-\frac{(j-1)\Delta t}{\tau_{k+1}} - \frac{(j-1)\Delta t}{\tau_{k-1}} \right] \\
 & \times \left(\exp \left[\frac{\Delta t}{\tau_{k-1}} \right] p_{k\uparrow\downarrow} + \exp \left[\frac{\Delta t}{\tau_{k+1}} \right] p_{k\downarrow\uparrow} - \exp \left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}} \right] (p_{k\uparrow\downarrow} + p_{k\downarrow\uparrow}) \right)^{j-2} \\
 & \times \left(\exp \left[\frac{\Delta t}{\tau_{k-1}} \right] p_{k\uparrow\downarrow} (j(\Delta t + \tau_k) + (j-1)\tau_{k+1}) + \exp \left[\frac{\Delta t}{\tau_{k+1}} \right] p_{k\downarrow\uparrow} (j(\Delta t + \tau_k) + (j-1)\tau_{k-1}) \right. \\
 & \quad \left. - \exp \left[\frac{\Delta t}{\tau_{k+1}} + \frac{\Delta t}{\tau_{k-1}} \right] (p_{k\uparrow\downarrow} (\Delta t + j\tau_k + (j-1)\tau_{k+1}) + p_{k\downarrow\uparrow} (\Delta t + j\tau_k + (j-1)\tau_{k-1})) \right) \\
 & \quad \times \left(1 + p_{k\uparrow\downarrow} (P_{>\Delta t}(\tau_{k+1}) - 1) + p_{k\downarrow\uparrow} (P_{>\Delta t}(\tau_{k-1}) - 1) \right), \quad (\text{B.5})
 \end{aligned}$$

which evaluates to Eq. (6.13).

For small Δt a linear approximation can be used:

$$\tilde{\tau}_k(\Delta t) \approx \frac{\tau_{\text{shelve}} \tau_{\text{D}_{5/2}}}{k\tau_{\text{shelve}} + (n-k)\tau_{\text{D}_{5/2}}} + \frac{k^2 \tau_{\text{shelve}}^2 + (n+4k(n-k))\tau_{\text{shelve}} \tau_{\text{D}_{5/2}} + (n-k)^2 \tau_{\text{D}_{5/2}}^2}{(k\tau_{\text{shelve}} + (n-k)\tau_{\text{D}_{5/2}})^2} \Delta t. \quad (\text{B.6})$$

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