Ion Trapping for Precision Spectroscopy

The radium atom, or ion, became recently accessible for precision experiments. Their production is essential as all radium isotopes are radioactive and Ra isotopes are mostly short-lived (see Table 10.1 in the Appendix). Ra isotopes can be produced at accelerator sites such as KVI. This opens up a number of possibilities for on-line precision spectroscopy. These isotopes can be used for experiments probing physics beyond the Standard Model of particle physics [32, 43–45]. For instance, Ra$^+$ ions are employed for experiments measuring atomic parity violation (APV) at highest precision [32]. Narrow optical transitions in these ions can be exploited for clock devices. In this thesis the focus rests on the applicability of Ra$^+$ isotopes as atomic clocks. The functioning of such clocks is discussed in this Chapter. We describe ion trapping which is a necessary prerequisite for such precision spectroscopy. Sufficient understanding of spectroscopic line shapes is indispensable to interpret obtained spectroscopic data. This topic is discussed in this Chapter. Data obtained from measurements performed on trapped Ba$^+$ ions are used to further illustrate key points. Ba$^+$ is iso-electrical to Ra$^+$ (see Fig. 2.1) and is used to perform precursor experiments, thus saving beam-time. The extraction of atomic parameters from the spectroscopic data in the form of hyperfine structure (HFS) constants and isotope shifts (IS) is discussed next.
Figure 2.1: Simplified level schemes of (a) $^{226}\text{Ra}^+$ and (b) $^{138}\text{Ba}^+$ ions. The ions have a comparable $\Lambda$-level structure. Laser light exciting the $ns^2S_{1/2} - np^2P_{1/2}$ transition is called “pump laser light”; laser light exciting the $(n-1)d^2D_{3/2} - np^2P_{1/2}$ transition is called “repump laser light”. A more detailed level scheme of Ra$^+$ can be found in Fig. 4.1.

2.1 Atomic Clock

The scientific operating principle of an optical atomic clock rests on the locking of a very stable optical laser to a very narrow resonance in a single ion which is laser-cooled to the zero-point energy of its motion. The electric-quadrupole (E2) transitions $7s^2S_{1/2} - 6d^2D_{3/2}$ and $7s^2S_{1/2} - 6d^2D_{5/2}$ in Ra$^+$ are excellent candidates for clock transitions. The level structure of the radium ion enables the detection of the weak and narrow clock transition with essentially 100% efficiency by looking for the absence of fluorescence from the strong electric-dipole (E1) S-P transitions by exploiting the technique of electron shelving [46]. As a (simplified) example we consider a Ra$^+$ ion that is fluorescing if exposed to the light of a pump laser operating at wavelength $\lambda_1 = 468$ nm and a repump laser operating at wavelength $\lambda_2 = 1080$ nm (see Fig. 2.2). These lasers are now switched off: first the pump, then the repump. Thereby the ion is prepared in the ground $7s^2S_{1/2}$ state. The ion is then irradiated with laser light from the clock laser operating at 728 nm near resonance conditions. This laser light excites the $7s^2S_{1/2} - 6d^2D_{5/2}$ transition, establishing a superposition of $7s^2S_{1/2}$ and $6d^2D_{5/2}$ levels. The time that the ions are exposed to the radiation can be tailored such that the population is transferred completely from the $7s^2S_{1/2}$ level to the metastable $6d^2D_{5/2}$ level. This is called a Rabi (half-)cycle.

The probability of finding the ion in the $6d^2D_{5/2}$ level is a function of laser light detuning from the actual resonance frequency. This probability is probed by switching on the pump and the repump lasers. If fluorescence light at wavelength $\lambda_1$ is observed, the ion has been in the $7s^2S_{1/2}$ ground level; if not, the ion has been shelved in the metastable $6d^2D_{5/2}$ level. In this step the shelving probability is obtained to sufficient accuracy. The frequency of the clock laser light is stepped subsequently over the resonance. The line center of the transition...
2.1 ATOMIC CLOCK

The frequency of the clock laser light, which is stably locked to the resonance, can then be converted to the countable regime employing a frequency comb [5]. A frequency comb consists of a large number of equally spaced frequencies, see Fig. 2.3. This way the optical spectrum between 500 and 1500 nm can be covered by a comb of frequencies spaced by $\sim 100$ MHz (the repetition rate). The optical frequency of one of the teeth of the comb is referenced to the stably locked clock laser thereby transferring the accuracy of the optical domain ($\sim 10^{15}$ Hz) to the RF domain ($\sim 10^9$ Hz) where the frequency can be counted.
A good clock is requested to be accurate, stable, and precise (see Fig. 2.4). We explicitly state here the conventions used in this thesis because these and other terms are frequently and interchangeably used in literature:

**Figure 2.4:** Bullets shot at a target: (a) precise but not accurate; (b) accurate but not precise; (c) precise and accurate.

**Accuracy:** Closeness of the agreement between the result of a measurement and a “true” value.

**Frequency Instability:** The frequency jitter, typically averaged for a time interval
2.2 Ion Traps

A charged particle in general cannot be trapped with only static electric fields. This is a consequence of Maxwell’s laws, in particular of $\nabla \cdot E = 0$ in vacuum. An all-electric trap can be constructed, however, using a time-varying quadrupole field. The motion of an ion in such a trap can be described by the Mathieu equations [48]. Two geometry types are described below: a linear and a hyperbolic Paul trap.
Figure 2.5: Schematic overview of a linear Paul trap. (a) Illustrates the creation of a radially confining RF potential in the x, y-plane; (b) illustrates the creation of an axially confining DC potential (along the z-axis).

Linear Paul Trap

A time-varying voltage $V_0 \cos \Omega t$ is applied between two pairs of rods, see Fig. 2.5. This gives a potential in the x, y-plane of the form

$$\Phi = \frac{x^2 - y^2}{2r^2} (U_0 + V_0 \cos \Omega t),$$

(2.1)

where a static potential $U_0$ is added and $r$ is the distance between the trap center and electrode tips. The equations of motion for a particle with mass $m$ and charge $Q$ in this electric field are given by

$$\ddot{x} = -\frac{Q}{mr^2} (U_0 + V_0 \cos \Omega t) x,$$

(2.2)

$$\ddot{y} = \frac{Q}{mr^2} (U_0 + V_0 \cos \Omega t) y.$$

(2.3)

By substituting the trap stability parameters

$$a_x = -a_y = \frac{4QU_0}{mr^4 \Omega^2}, \quad q_x = q_y = \frac{2QV_0}{mr^4 \Omega^2},$$

(2.4)
and defining $\tau = \frac{\Omega t}{2}$, one obtains the equations of motion in the form of the Mathieu equations

$$\frac{d^2x}{d\tau^2} + (a_x + 2q_x \cos \Omega t) x = 0, \quad (2.5)$$

$$\frac{d^2y}{d\tau^2} + (a_y + 2q_y \cos \Omega t) y = 0. \quad (2.6)$$

These equations have stable solutions if $|a_x|, |q_x| \ll 1$, i.e., if the adiabatic approximation is valid. Stable solutions are also found outside the domain of this approximation: The stability domain in $(a, q)$ space is depicted in Fig. 2.6. In the adiabatic approximation the solutions to the equations of motion are given by the approximate forms

$$x(t) = x_0 \cos (\omega_x t + \phi_x) \left(1 + \frac{q_x}{2} \cos \Omega t\right), \quad (2.7)$$

$$y(t) = y_0 \cos (\omega_y t + \phi_y) \left(1 + \frac{q_y}{2} \cos \Omega t\right), \quad (2.8)$$
with $x_0$, $y_0$, $\phi_x$, and $\phi_y$ given by initial conditions. The frequencies of the secular motion $\omega_{x,y}$ are given by

\[
\omega_x = \frac{\Omega}{2} \sqrt{\frac{a_x^2}{2} + \alpha_x},
\]

\[
\omega_y = \frac{\Omega}{2} \sqrt{\frac{a_y^2}{2} + \alpha_y}.
\]

This secular motion corresponds to a harmonic oscillation in the $x,y$-plane with an amplitude that is modulated at the trap frequency $\Omega$ giving rise to the so-called micromotion. A static electric field is used to confine the ions in the axial ($z$-) direction. This field is created by applying a DC field $V_{DC}$ between the outer eight electrodes and the center four (see Fig. 2.5). This yields a pseudo-potential that is harmonic to first order. This addition of a DC field requires the adjustment of the parameters $a_x, a_y$ to include an effective potential $V_{eff}$ that is proportional to $V_{DC}$ [49]. The proportionality factor depends on the specific trap geometry. The modified parameters $\tilde{a}_x, \tilde{a}_y$ are given by

\[
\tilde{a}_x = a_x - a_{DC}, \quad \tilde{a}_y = a_y - a_{DC},
\]

where

\[
a_{DC} = -\frac{4QV_{eff}}{m\Omega^2 r^2}.
\]

The sign of the additional factor is the same for both $\tilde{a}_x, \tilde{a}_y$ parameters. If $U_0 = 0$ and the adiabatic approximation holds, the pseudo-potential $\Psi$ for a single ion is given by

\[
\Psi = \frac{1}{2} (-a_{DC} + \frac{1}{2} q^2) (x^2 + y^2) + a_{DC} z^2,
\]

where a change in sign convention in $a_{DC}$ with respect to Ref. [49] is adopted to stress the reduction of the radial potential well depth caused by $a_{DC}$. An additional Coulomb repulsion term is added to the pseudo-potential if more than one ion is trapped.

**Hyperbolic Paul trap**

In an ideal hyperbolic Paul trap, which is comprised of a center hyperbolic doughnut and two hyperbolic end-caps (see Fig. 2.7), the applied potential is given by [48, 50]

\[
\Phi = \frac{x^2 + y^2 - 2z^2}{2r^2} (U_0 + V_0 \cos \Omega t).
\]

Here, $r^2 \equiv \frac{1}{2} r_0^2 + \frac{z^2}{2}$, where $r_0$ is the inner radius of the center hyperbolic doughnut and $2z_0$ is the minimum distance between the two endcaps. No additional DC
2.3 Spectroscopic Line Shapes

The trapped ion cloud can be interrogated with laser light. Atomic properties can be extracted from this laser spectroscopy. On the one hand, spectroscopy data yield information about the wavelengths necessary for state-addressing. On the
Figure 2.8: Stability diagram in $(a,q)$ space near the origin for the three-dimensional quadrupole ion trap. The $q_z$-axis is intersected at $q_z = 0.91$. Lines of constant values for the stability parameters $\beta_{r,z}$ are depicted. Figure modified from [51].

On the other hand, accurate determination of the Ra$^+$ atomic structure provides indispensable tests of the atomic theory needed for APV experiments as well as for an accurate atomic clock. It is important to understand the spectroscopic line shapes in order to be able to interpret the obtained spectroscopy data. The observable
in all experiments described in this thesis is the fluorescence rate at 493 nm for Ba$^+$ and at 468 nm for Ra$^+$. The steady-state fluorescence rate $F$ is given by

$$F(\epsilon, I_p, I_r, \delta_p, \delta_r, N, T, V_{RF}, \Omega, P_i),$$

(2.16)

with photo-collection efficiency $\epsilon$ (see Chapter 3), pump laser light intensity $I_p$, repump laser light intensity $I_r$, pump laser light detuning $\delta_p$, repump laser light detuning $\delta_r$, ion number $N$, cloud temperature $T$, RF amplitude $V_{RF}$ with angular frequency $\Omega$, and partial gas pressures $P_i$. Pump and repump laser light intensities used in the experiments were typically near saturation values. The fluorescence rate can be factorized to

$$F(\epsilon, I_p, I_r, \delta_p, \delta_r, N, T, V_{RF}, \Omega, P_i) = \epsilon \Gamma_2 N \times \rho_{22}(I_p, I_r, \delta_p, \delta_r, T, V_{RF}, \Omega, P_i),$$

(2.17)

where $\rho_{22}$ is the population of excited level $np^2P_{1/2}$ and $\Gamma_2$ is the decay rate of this level. The motion of the ions in the trap make that the line shape cannot easily be further factorized. The micromotion of the ions need to be taken into account explicitly as well as the influence of the buffer gas. The buffer gas admixes and quenches atomic (hyper)fine levels. This is an essential property in case of laser spectroscopy of leaky systems, e.g., Ra$^+$ isotopes with hyperfine structure. The velocity distribution of the trapped ions and the effects of buffer gases will be discussed next.

### 2.3.1 Characterization of the Trapped Ion Cloud

A hot trapped ion cloud has a Maxwell-Boltzmann velocity distribution to good approximation [48]. Typical temperatures $T$ are given by the rule of thumb $1/2 k_B T \approx 0.1 \Psi$, where $k_B$ is the Boltzmann constant and $\Psi$ the pseudo-potential well depth. It should be noted that the term temperature is slightly misleading as it includes the energy of the micromotion which cannot be described by a “temperature”. The ion density $n(r)$ as function of radius $r$ of the cloud follows a Gaussian distribution [53]. Experimental results on the width of the ion density distribution are found [54] to be best reproduced by so-called Brownian motion models or by a modified pseudo-potential approach which explicitly takes into account the micromotion of the individual ions. This micromotion is of importance for the interpretation of spectroscopic line shapes [55]. It is found that the trapped ion velocity distribution should be described in terms of classes of velocity amplitudes, and not just in velocities [55]. This effect plays a role when the laser light interrogating the ions is irradiated along an axis that has a non-zero projection of the RF fields. The influence of such a non-zero projection of the micromotion on the laser light propagation axis on the observed spectroscopic line

2.3 SPECTROSCOPIC LINE SHAPES 21
An ion oscillating at angular frequency $\omega$ with amplitude $A$ has a position $x(t)$ at time $t$ given by

$$x(t) = A \sin(\omega t + \theta),$$

(2.18)

where $\theta$ is an arbitrary phase. The normalized position distribution function $p_x(x)$ is given by

$$p_x(x) = \frac{1}{\pi \sqrt{A^2 - x^2}},$$

(2.19)

which is independent of phase $\theta$. Similarly, the velocity $v(t)$ is given by

$$v(t) = A \omega \cos(\omega t + \theta).$$

(2.20)

The normalized velocity distribution function $p_v(v)$ is given by

$$p_v(v) = \frac{1}{\pi \sqrt{(A \omega)^2 - v^2}}.$$  

(2.21)

The divergences found in Eqs. 2.19 and 2.21 are non-consequential. The velocity amplitudes $A \omega$ are drawn from a Maxwell-Boltzmann distribution. Ion position and velocity are correlated [56]. The periodic oscillation of the trapped ions also plays a role in laser excitation of three level systems [55] which are of particular interest for this thesis. The micromotion splits up expected (thermal) Gaussian

![Figure 2.9: Illustration of the velocity distribution functions of thermal (red) and harmonically oscillating (blue) particles. In the inset a typical result of the resulting convolution of the two PDF's is depicted (green).](image)
resonance line shape into a broad bull-horned shape via the Doppler effect. An illustration of this effect is shown in Fig. 2.9. In the on-line Ra\(^{+}\) experiments all laser light beams propagated co-linearly along the axial (\(z\)-) direction of a linear Paul trap (see Chapter 3) so that the effects of micromotion are minimized. In an ideal linear Paul trap no RF field component exists in the \(z\)-direction. However, even small %-level asymmetries in RF field amplitude between electrodes can create an electric dipole field in any direction. This leads to line splitting. Measurements were performed on trapped Ba\(^{+}\) ions to study the effects of the micromotion in our traps.

![Figure 2.10: Typical line shape. Both pump and repump laser light frequencies are scanned over the resonance at different scan speeds (Repump at 157 mHz period; pump at 20 mHz). The black solid line is a simple spline connecting the points. The doubly peaked structures (each representing a full scan of the repump laser light frequency) are caused by micro-motion along the laser light beam propagation direction (see Fig. 2.9). The Gaussian envelope (black dotted line) illustrates the dependence of the signal size on the pump laser light frequency.]()
frequency of the repump laser light is scanned over the $5d^2D_{3/2} - 6p^2P_{1/2}$ transition more quickly at 157 mHz. The fluorescence of the trapped ions is monitored using a PMT (see Chapter 3 for more details concerning the experimental setup). The observed line shape is qualitatively well described by a convolution of a bullhorn-shaped velocity distribution with a Gaussian envelope with a splitting of order 500 MHz. This indicates that there is a non-zero projection of the micromotion of order 200 m/s on the axis defined by the laser light beam propagation direction. This projection can be caused by misalignment of the laser light beam with respect to the trap axis and/or by asymmetries in the RF fields applied to the electrodes. The laser light misalignment is geometrically constrained. Therefore these data indicate that there are RF field asymmetries creating an axial dipole field of order 10 V/cm. These asymmetries are to be expected with the current trap construction using capacitive coupling (see Chapter 3).

### 2.3.2 Gas Collisions

Buffer gases are employed to cool and compress trapped ion clouds [48]. The experiments that led to this thesis were performed using He, Ne, and N$_2$ buffer gases. Elastic collisions between buffer gas atoms and the trapped ions effectively take away kinetic energy and thus cool the ion cloud. However, this is only the case if the buffer gas has atomic mass lower than that of the trapped ions; at higher mass, collisions result in an increase in the ion kinetic energy [48]. Thermal equilibrium is reached typically at temperatures above room temperature as RF heating takes place, in part caused by asymmetric trapping fields. A temperature higher than room temperature would occur even without these effects; in a finite size ion cloud the outer ions always experience micromotion. Next to the elastic processes there are inelastic effects. Two contributions are distinguished: “quenching”, which is the de-excitation of an excited (e.g. D-) state to the ground state, and “mixing”, which describes the population transfer between excited states such as the $5d^2D_{3/2}$ and $5d^2D_{5/2}$ [57, 58] level. This mixing effect scales exponentially with the energy splitting between coupled states, see Fig. 2.11. The fine structure mixing rates in Ba$^+$ ($\Delta E \simeq 801$ cm$^{-1}$) and Ra$^+$ ions ($\Delta E \simeq 1659$ cm$^{-1}$) are therefore expected to be well below the Ca$^+$ level of $1-6 \times 10^{-10}$ s$^{-1}$ cm$^3$ [58]. Hyperfine structure mixing occurs between various hyperfine $F$-substates within a $J$-multiplet. The combined effects of quenching and mixing is that the lifetimes of certain dark states are strongly reduced. This effect was employed to perform laser spectroscopy on the isotopes $^{209,211,213}$Ra$^+$ which have dark hyperfine levels (see Chapters 4 and 5). Lifetime studies of atomic states are influenced by these mixing effects (see Chapter 4). As such, (hyper)fine structure mixing effects play an important role in the precision spectroscopy of Ra$^+$. These effects can also be studied using stable Ba$^+$ [59]. An experimental study of these quenching and
mixing effects of neon buffer gas interacting with trapped $\text{Ba}^+$ ions is presented next. In this study non-steady state conditions exist, and transient effects can be studied. Eq. 2.16 needs to be modified to include an explicit time dependence.

Figure 2.11: The $J$-mixing constants for different alkaline atoms and alkaline-earth ions in presence of He buffer gas as a function of the energy difference between the mixing levels (i.e. the fine structure splitting in case of $\text{Ba}^+$ and $\text{Ra}^+$). Figure from taken from [57].

The effects of fine-structure mixing can be quantified by the following method. A $\text{Ba}^+$ ion cloud is trapped in the RFQ ion trap (see Chapter 3) employing Ne buffer gas. The ions are continuously replenished from an ion source. The fluorescence of the trapped ions, obtained by irradiating the ions with light from pump and repump lasers, is monitored using a PMT (see Chapter 3 for more details concerning the experimental setup). The laser light of the repump laser is blocked for $\sim 10\text{ s}$ while the pump laser light still irradiates the trapped ion cloud, thus shelving the ions in the metastable $5d^2D_{5/2}$ level. This happens on very short $\sim \mu\text{s}$ time scales. The buffer gas subsequently mixes the fine-structure levels, thus populating the $5d^2D_{3/2}$ level. The $5d^2D_{5/2}$ level is almost immediately depopulated when the repump laser light is unblocked, while the $5d^2D_{5/2}$ level is more slowly pumped out via the $5d^2D_{3/2}$ level by means of the mixing effect. The lifetime
of the build-up of the fluorescence signal on unblocking the repump laser light gives a measure of the mix (and quench) rates. The dependence of this build-up lifetime on the buffer gas pressure was studied, see Fig. 2.12. The model fit with

\[
\text{Fitted life time [s]} = 0.1(3) \text{ s; } [1] = 6(2) \times 10^{-4} \text{ mbar; } [2] = -9(5) \times 10^{-6} \text{ mbar with reduced } \chi^2 = 0.3 \text{ at 5 d.o.f.}
\]

No change in rate was observed when the repump laser light power was varied between 50 and 270 μW. The measured rate is lower than that found for trapped Ca\(^+\) as described in Ref. [58] but is higher than the trend given in Ref. [57] would indicate. However, this trend (see Fig. 2.11) is based on experiments employing He buffer gas. As such, the discrepancy could be attributed to difference between the buffer gases used. Generally, He and Ne have comparable quench rates while Ne has a higher mix rate (this is a factor 2 in case of Ca\(^+\)). Nitrogen, also present as an impurity, has quench and mix rates that are two and one orders of magnitude higher still, respectively.

**Figure 2.12:** Fit results of the signal build-up time of the Ba\(^+\) fluorescence signal as a function of the Ne buffer gas pressure. The laser light intensities were approximately 400 μW/mm\(^2\) for the pump and 300 μW/mm\(^2\) for the repump light. The estimated uncertainties are based on studies of systematic effects. The black curve indicates a fit of the model \([0]+[1]/(x−[2])\) to the data, yielding \([0] = 1.0(3) \text{ s; } [1] = 6(2) \times 10^{-4} \text{ mbar; } [2] = -9(5) \times 10^{-6} \text{ mbar with reduced } \chi^2 = 0.3 \text{ at 5 d.o.f.} \]
2.4 ISOTOPE SHIFT

The frequencies corresponding to atomic transitions differ between isotopes; this is called the isotope shift. These shifts are due to differences in the volume (or “field”) and in the mass of the nuclei. The field shift is a Coulomb effect: The

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Figure 2.13: Trap lifetime of trapped Ba$^+$ ions as a function of the Ne buffer gas pressure. The estimated uncertainties are based on studies of systematic effects. The black curve indicates fit of the model $[0]+[1]/(x-\{2\})$ to the data, yielding $[0] = 4(2) \text{s}; [1] = 5(3) \times 10^{-3} \text{ mbar}; [2] = 1(1) \times 10^{-4} \text{ mbar}$ with $\chi^2 = 1$ at 1 d.o.f.

The buffer gas pressure also influences the average time that ions stay trapped. This trap lifetime of the ion cloud is an important parameter, in particular for on-line experiments: It limits the time during which particles can be accumulated in the trap, and as such it can be a limiting factor for the total signal size. The trap lifetime is defined here as the time interval between the shut-down of the ion source and the moment that the fluorescence signal reaches the “1/e” level. This trap lifetime is dependent on many parameters such as gas pressure, RF trap potentials, background gas pressure, and buffer gas cleanliness. A study of the dependence of the trap lifetime on neon buffer gas pressure is presented in Fig. 2.13. The model fit with $\chi^2 = 1$ at 1 d.o.f. to the data indicates that the ion loss rate is proportional to the buffer gas pressure, and the impurities therein.

2.4 Isotope Shift

The frequencies corresponding to atomic transitions differ between isotopes; this is called the isotope shift. These shifts are due to differences in the volume (or “field”) and in the mass of the nuclei. The field shift is a Coulomb effect:
presence of the extra neutron changes the charge distribution of the nucleus. The energy shift $\delta E$ of an atomic orbit due to the change in the charge distribution is given by

$$\delta E \equiv F \delta \langle r^2 \rangle,$$

(2.22)

where $F$ is the field shift constant and $\delta \langle r^2 \rangle$ is the change in the root mean square radius $\langle r^2 \rangle$. The second contribution to the isotope shift is due to the finite mass of the nucleus. This contribution is comprised of a normal mass shift (NMS) and a specific mass shift (SMS). For the isotope shift of transition $i$ of an isotope with atomic number $A$ with respect to a reference isotope with atomic number $A_{\text{ref}}$ holds

$$\delta \nu_i^{A,A_{\text{ref}}} \equiv \nu_i^A - \nu_i^{A_{\text{ref}}} = F_i \delta \langle r^2 \rangle^{A,A_{\text{ref}}} + (k_i^{\text{NMS}} + k_i^{\text{SMS}}) \frac{A - A_{\text{ref}}}{A_{\text{ref}}},$$

(2.23)

Here $F_i$ is the field shift constant of transition $i$ and $\delta \langle r^2 \rangle^{A,A_{\text{ref}}}$ is the difference $\langle r^2 \rangle^A - \langle r^2 \rangle^{A_{\text{ref}}}$. The mass-effect contribution is suppressed by the factor $\frac{1}{A_{\text{ref}}}$ which is small for heavy atoms. For instance, in radium the contribution from the mass shifts is less than 1% [60]. However, the mass effect can be anomalously large in some rare earth elements [61, 62]. For two transitions, 1 and 2, in a certain element, Eq. 2.23 gives

$$\delta \nu_2 A^* - k_2^{\text{NMS}} = \frac{F_2}{F_1} (\delta \nu_1 A^* - k_1^{\text{NMS}}) + \left( \frac{F_2}{F_1} k_1^{\text{SMS}} - F_2 k_2^{\text{SMS}} / F_1 \right),$$

where

$$A^* \equiv \frac{A_{A_{\text{ref}}}}{A - A_{\text{ref}}}.$$

A King plot [63] analysis, with on the $x$-axis $\delta \nu_1 A^* - k_1^{\text{NMS}}$ and on the $y$-axis $\delta \nu_2 A^* - k_2^{\text{NMS}}$, yields a straight line with tangent $F_2 / F_1$ and offset $k_1^{\text{SMS}} - F_2 k_2^{\text{SMS}} / F_1$. Experimental IS data can thus be used to test the precise theoretical predictions of such tangents and offsets [60]. Wansbeek et al. in Ref. [60] proposed to put the equations for all transitions under consideration into one system of equations and solve this system for all unknowns. This approach is taken to extract the radial differences $\delta \langle r^2 \rangle^{A,A_{\text{ref}}}$ from the ISOLDE data [64] with minimal theoretical input. This yields information about the size and shape of the atomic nucleus which is of interest for upcoming APV experiments. The radial differences $\delta \langle r^2 \rangle^{A,A_{\text{ref}}}$ are of particular importance for APV measurements performed on isotopic chains [37, 65].
2.5 Hyperfine Structure

The Hamiltonian $H_{HFS} = -\mu_I \cdot \vec{B}_e$ describes the interaction of the nuclear magnetic moment $\mu_I$ with the magnetic field $\vec{B}_e$ caused by the electron cloud. It gives rise to the hyperfine splitting of the fine structure levels, parametrized by the dipole hyperfine structure constant $A$. The interaction is proportional to $|\psi(0)|^2$ for s-electrons: only the contact interaction plays a role, i.e. the overlap of the electron wave function $\psi(x)$ with the nucleus (at $x = 0$). So, the hyperfine structure is a sensitive probe of the electron density at the nucleus, which is of interest for the upcoming APV experiments at KVI [32]. The hyperfine interaction is also of importance for ion clocks. The additional angular momentum provided by the spin of the nucleus has an impact on the allowed interactions with external fields. Furthermore, the additional close-lying states created by the hyperfine interaction enable strong configuration mixing with possible detrimental effects on frequency stability. For nuclear spins $I = 3/2$ (e.g. $^{223,227}$Ra$^+$) the hyperfine interaction is extended to include the constant $B$ which parametrizes the interaction between the nuclear quadrupole moment $Q$ and the electric field gradient of the electronic wave function. The expression for the frequency shift $\nu_{\text{HFS}}$ of a state $|\gamma I J F \rangle$ is given by

$$h\nu_{\text{HFS}} = \frac{1}{2} AK + B \frac{3K(K + 1) - 4I(I + 1)J(J + 1)}{8I(2I - 1)J(2J - 1)},$$

(2.24)

where $K = F(F + 1) - I(I + 1) - J(J + 1)$ [66]. Here, contributions to the HFS from interactions between states of non-equal $J$ are neglected as well as the higher-order magnetic octupole interaction. The situation is more complex for nuclear spins $I = 5/2$ (e.g. $^{209,211,223}$Ra$^+$). A nucleus with spin $I$ will support multipole moments of rank $2^\kappa$ with $\kappa \leq 2I$ [66]. Parity and time reversal symmetry constrain the nuclear moments to even-rank electric and odd-rank magnetic moments. So, the next higher order terms are the magnetic octupole ($\kappa = 3$) and electric hexadecapole ($\kappa = 4$) hyperfine interaction constants which usually are negligible [67]. Higher order hyperfine terms (i.e. beyond first order perturbation theory) may play a larger role.

The hyperfine structure of the levels with electron angular momentum $l > 0$ have zero contribution from the contact interaction in the non-relativistic limit. Instead it is the orbital and dipolar interaction that contribute to $A$ [68]. The first term describes the magnetic fields produced at the nucleus by the motion of the bound electron. The second term is related to the magnetic field created by the spin of the electron. Relativistic corrections play a significant role in heavy atomic systems like Ra$^+$. Polarization effects due to the interaction of the valence electron with the closed-shell core electrons must be considered too [68, 69]. These correlation effects play a role in the heavy Ba$^+$ and Ra$^+$ systems [70].