

**Systematics shifts
of the 467 nm
electric octupole
transition in $^{171}\text{Yb}^+$**

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K. Hosaka, G. P. Barwood,
and P. Gill**

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Abstract

A comprehensive review of systematic frequency shifts for the $^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0$ electric octupole transition in $^{171}\text{Yb}^+$.

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Authorised for publication on behalf of the Managing Director of NPL by
Prof. Patrick Gill

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Chapter 1

Introduction

One of the main attractions of single trapped ions as optical frequency standards is that they have extremely low susceptibility to environmental perturbations. These perturbations include low-frequency electric and magnetic fields, and the light fields used in cooling and interrogating the ion. These external fields can all lead to systematic shifts of the transition frequency. They must be characterized and understood in order that the unperturbed transition frequency may be realized.

An optical frequency standard is being developed at NPL based on the electric octupole transition in a single ytterbium ion. Figure 1.1 shows the partial term scheme for $^{171}\text{Yb}^+$. The $^2\text{F}_{7/2}$ state is the lowest lying excited state and it can only decay to the ground state by electric octupole radiation. Consequently, it has an

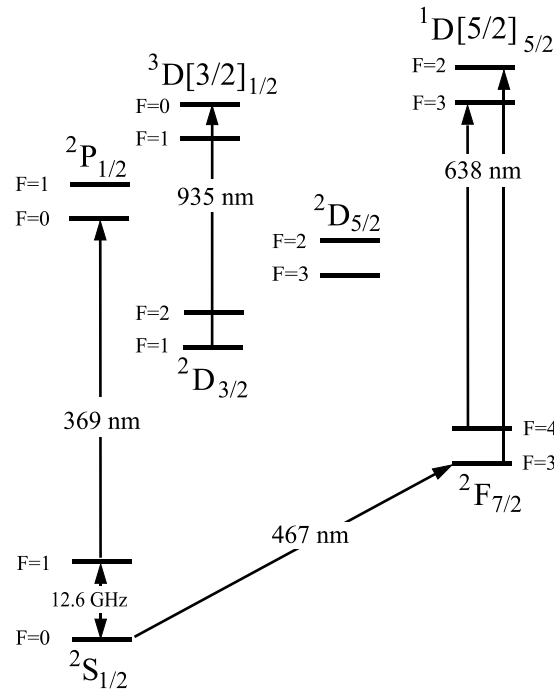


Figure 1.1: Term scheme of $^{171}\text{Yb}^+$. Light at 467 nm is used to drive the $^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0$ electric octupole transition.

extremely long lifetime, of order several years [1], and the transition from the ground state has a linewidth $\sim$ nHz. The stability of the standard will therefore not be limited by the intrinsic atomic lifetime, but rather by the linewidth of the laser used to probe the transition.

Due to the weakness of the transition, a relatively high light intensity is required to drive it. The electric field of the light induces an electric dipole moment in the ion which then interacts with the electric field as a second-order effect. The resulting *ac Stark shift* is covered in chapter 2. In the presence of a magnetic field, the hyperfine levels are split due to the interaction of the field with the magnetic dipole of the ion (Zeeman effect). There exist levels for which $m_F = 0$ which are insensitive to magnetic field to first-order. This has the advantage that there is no linear Zeeman effect for transitions between levels with $m_F = 0$ and the $^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0$ transition is used as the frequency reference. However, there is a second-order effect, and this is explained in chapter 3. The ion is trapped in an oscillating electric quadrupole field. The minimum of the potential coincides with the zero of the electric field, therefore, in principle, the ion should not experience any electric field. In practice however, small stray fields do exist, which are nulled out as far as possible with compensating electrodes, but a small field will still always be present at the ion. This gives rise to the *quadrupole* and *dc Stark* shifts which are described in chapters 4 and 5. The ion is Doppler cooled with light at 369 nm, and in the tightly confining trap, its motion is confined to less than the wavelength of the light (Lamb-Dicke regime). In this regime there is no first-order Doppler effect. The thermal motion of the ion and also micromotion at the trap drive frequency do give rise to a second-order Doppler effect and this is discussed in chapter 6. At room temperature, the electric and magnetic fields of the blackbody radiation from the ion trap surroundings cause small frequency shifts via the dc Stark and Zeeman effects as described in chapter 7. At the level of precision offered by an optical atomic reference, one has to consider general relativistic effects, and this is covered in chapter 8.

The purpose of this report is to provide a comprehensive review of all the known systematic effects for the $^{171}\text{Yb}^+$ system. Previous work [2, 3, 4, 5] has studied these effects in part, but here all the details have been drawn together for reference. Mat Roberts did much the early work on systematic shifts and most of the above shifts are calculated or at least estimated in his thesis [2]. The lead author calculated the ac Stark shift [3] and has recently refined that work to include the effect of the tensor polarisability in both the ac and dc Stark effects. The second-order Zeeman effect was first calculated by Geoff Barwood and is detailed in the same paper as the ac Stark effect [3]. A lot of the material in this report is taken from the thesis of Peter Blythe [5]. This builds on an earlier paper [4] in which the systematic shifts for a recent frequency measurement were evaluated and projections made as to the realistic limits to the ultimate performance of the system. In particular, P. Blythe has made the first calculation of the quadrupole shift of the octupole transition in ytterbium. The author would also like to thank Stephen Lea for his critical reading of the manuscript and for suggestions regarding the blackbody shift and gravitational red shift.

Chapter 2

AC Stark shift

Currently, the most significant shift for the octupole transition in $^{171}\text{Yb}^+$ is the light shift, or ac Stark shift. The electric field of the light induces an electric dipole moment, $\underline{\mu}$ in the ion which then, as a second order effect, interacts with the electric field of the light.

2.1 Theory

The Hamiltonian for the interaction of an external electric field $\mathbf{E}$ with an electric dipole moment, $\underline{\mu}$ takes the form

$$H_E = -\underline{\mu} \cdot \underline{E} \quad (2.1)$$

where $\underline{\mu} = -e \sum_i r_i$. First let us consider the case of an atom with zero nuclear spin, with states defined by the quantum numbers γ , J and M_J . In general, the electric field is not parallel to the quantisation axis defined by the magnetic field therefore, the Hamiltonian has both scalar and tensor parts and the light shift is given by [6]

$$\Delta W_E = -\frac{1}{2}\alpha_{\text{sc.}}(\gamma J)E^2 - \frac{1}{4}\alpha_{\text{ten.}}(\gamma J)\frac{(3M_J^2 - J(J+1))}{J(2J-1)}(3E_z^2 - E^2), \quad (2.2)$$

where scalar and tensor polarisabilities, $\alpha_{\text{sc.}}(\gamma J)$ and $\alpha_{\text{ten.}}(\gamma J)$ have been introduced. In the case of an AC electric field, $\underline{E}(t) = \underline{E}_0 \cos(\omega_L t)$, the RMS value of the electric field, $\langle E^2 \rangle$, is used in equation 2.2. Treating the interaction by second- order perturbation theory, summing over transitions of angular frequency ω to $|\gamma' J'\rangle$, the scalar polarisability is given in terms of reduced matrix elements by [6]

$$\begin{aligned} \alpha_{\text{sc.}}^{\text{AC}}(\gamma J) &= -\frac{2}{3\hbar(2J+1)} \sum_{\gamma' J'} \frac{1}{2} \left[\frac{|\langle \gamma J \| \underline{\mu}^1 \| \gamma' J' \rangle|^2}{\omega - \omega_L} + \frac{|\langle \gamma J \| \underline{\mu}^1 \| \gamma' J' \rangle|^2}{\omega + \omega_L} \right] \\ &= -\frac{2}{3\hbar(2J+1)} \sum_{\gamma' J'} \frac{\omega |\langle \gamma J \| \underline{\mu}^1 \| \gamma' J' \rangle|^2}{\omega^2 - \omega_L^2}, \end{aligned} \quad (2.3)$$

where both rotating and anti-rotating terms have been taken into account and $\underline{\mu}^1$ is a spherical tensor of rank 1.* The AC tensor polarisability is given by

$$\alpha_{\text{ten.}}^{\text{AC}}(\gamma J) = -(-)^{2J} \frac{4}{\hbar} \left[\frac{5J(2J-1)}{6(2J+3)(J+1)(2J+1)} \right]^{1/2} \times \sum_{\gamma' J'} (-)^{J'-J} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J' \end{matrix} \right\} \frac{\omega |\langle \gamma J \| \underline{\mu}^1 \| \gamma' J' \rangle|^2}{\omega^2 - \omega_L^2}. \quad (2.4)$$

One can see from the form of the numerator, that the tensor polarisability is zero for states with $J < 1$. The oscillator strength, f , for the transition $\gamma J \rightarrow \gamma' J'$ is defined by [7]

$$-g_J f = \frac{2m_e \omega}{3\hbar e^2} |\langle \gamma J \| \underline{\mu}^1 \| \gamma' J' \rangle|^2. \quad (2.5)$$

where m_e is the electron mass and $g_J = (2J+1)$. The reduced matrix elements in eqs. 2.3 and 2.4 may now be written in terms of oscillator strengths:

$$\alpha_{\text{sc.}}^{\text{AC}}(\gamma J) = \frac{e^2}{m_e(2J+1)} \sum_{\gamma' J'} \frac{g_J f}{\omega^2 - \omega_L^2} \quad (2.6)$$

$$\alpha_{\text{ten.}}^{\text{AC}}(\gamma J) = (-)^{2J} \frac{e^2}{m_e} \left[\frac{30J(2J-1)}{(2J+3)(2J+1)(J+1)} \right]^{1/2} \times \sum_{\gamma' J'} (-)^{J'-J} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J' \end{matrix} \right\} \frac{g_J f}{\omega^2 - \omega_L^2}. \quad (2.7)$$

For an atom with nuclear spin, I , and states defined by the quantum numbers, γ , J , F and M_F , the Stark shift is given by

$$\Delta W_E = -\frac{1}{2} \alpha_{\text{sc.}}(\gamma J F) E^2 - \frac{1}{4} \alpha_{\text{ten.}}(\gamma J F) \frac{(3M_F^2 - F(F+1))}{F(2F-1)} (3E_z^2 - E^2). \quad (2.8)$$

In the IJ-coupling approximation,

$$\alpha_{\text{sc.}}(\gamma J F) = \alpha_{\text{sc.}}(\gamma J) \quad (2.9)$$

$$\alpha_{\text{ten.}}(\gamma J F) = (-)^{I+J+F} \left[\frac{F(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}{(2F+3)(F+1)J(2J-1)} \right]^{1/2} \times \left\{ \begin{matrix} F & J & I \\ J & F & 2 \end{matrix} \right\} \alpha_{\text{ten.}}(\gamma J). \quad (2.10)$$

2.2 Calculation

For the $^2\text{S}_{1/2}, F=0 \rightarrow ^2\text{F}_{7/2}, F=3, M_F=0$ transition in $^{171}\text{Yb}^+$ one must consider the Stark shifts of the $^2\text{S}_{1/2}, F=0$ and $^2\text{F}_{7/2}, F=3, M_F=0$ states. For the $^2\text{S}_{1/2}, F=0$ state,

$$\Delta \nu^{\text{AC}}(\text{S}, 1/2) = -\frac{1}{2} \alpha_{\text{sc.}}^{\text{AC}}(\text{S}, 1/2) \langle E^2 \rangle / h \quad (2.11)$$

*In going from eq. 3.16 of [6] to eq. 2.3 the following relation has been used: $\langle J' \| \underline{\mu}^1 \| J \rangle = (-)^{J'-J} \langle J \| \underline{\mu}^1 \| J' \rangle^*$ [7].

and

$$\alpha_{\text{sc.}}^{\text{AC}}(\text{S}, 1/2) = \frac{e^2}{2m_e} \sum_{\gamma' J'} \frac{g_J f}{\omega^2 - \omega_L^2}. \quad (2.12)$$

The summation is evaluated using the oscillator strengths calculated in [9], for which $g_J f \geq 0.01$. The Matlab code for this calculation is given in appendix A.1, and contains a list of the oscillator strengths and corresponding energy levels taken into account. For light incident upon the ion at 467 nm,

$$\sum_{\gamma' J'} \frac{g_J f}{\omega^2 - \omega_L^2}(\text{S}, 1/2) = 1.2871 \times 10^{-31} \text{ s}^2 \quad (2.13)$$

and

$$\left(\frac{\Delta\nu^{\text{AC}}(\text{S}, 1/2)}{\text{mHz}} \right) = -13.68 \left(\frac{\langle E^2 \rangle}{(\text{V/cm})^2} \right) \quad (2.14)$$

For the $^2\text{F}_{7/2}$, $F = 3$, $M_F = 0$ state,

$$\Delta\nu^{\text{AC}}(F, 7/2, 3, 0) = -\frac{1}{2}\alpha_{\text{sc.}}^{\text{AC}}(F, 7/2)E^2/h + \frac{1}{5}\alpha_{\text{ten.}}^{\text{AC}}(F, 7/2, 3)(3E_z^2 - E^2)/h. \quad (2.15)$$

Taking first the scalar polarisability,

$$\alpha_{\text{sc.}}^{\text{AC}}(F, 7/2) = \frac{e^2}{8m_e} \sum_{\gamma' J'} \frac{g_J f}{\omega^2 - \omega_L^2}. \quad (2.16)$$

The summation is evaluated using the code in appendix A.2, again using the oscillator strengths calculated in [9].

$$\sum_{\gamma' J'} \frac{g_J f}{\omega^2 - \omega_L^2}(F, 7/2) = 4.564 \times 10^{-31} \text{ s}^2 \quad (2.17)$$

and

$$\left(\frac{\Delta\nu_{\text{sc.}}^{\text{AC}}(F, 7/2)}{\text{mHz}} \right) = -12.13 \left(\frac{\langle E^2 \rangle}{(\text{V/cm})^2} \right). \quad (2.18)$$

The tensor polarisability for the $^2\text{F}_{7/2}$ state,

$$\alpha_{\text{ten.}}^{\text{AC}}(F, 7/2) = -\frac{e^2\sqrt{7}}{2m_e} \sum_{\gamma' J'} (-)^{J'-7/2} \left\{ \begin{matrix} 1 & 1 & 2 \\ 7/2 & 7/2 & J' \end{matrix} \right\} \frac{g_J f}{\omega^2 - \omega_L^2}. \quad (2.19)$$

The summation is evaluated separately for $J' = 5/2, 7/2$ and $9/2$.

$$\begin{aligned} & \sum_{\gamma' J'} (-)^{J'-7/2} \left\{ \begin{matrix} 1 & 1 & 2 \\ 7/2 & 7/2 & J' \end{matrix} \right\} \frac{g_J f}{\omega^2 - \omega_L^2} = \\ & \quad +\frac{1}{4}\sqrt{\frac{1}{7}} \times 1.1903 \times 10^{-31} \quad : J' = 5/2 \\ & \quad -\frac{1}{3}\sqrt{\frac{1}{7}} \times 1.4491 \times 10^{-31} \quad : J' = 7/2 \\ & \quad +\frac{1}{60}\sqrt{7} \times 1.9246 \times 10^{-31} \quad : J' = 9/2 \\ & = 1.477 \times 10^{-33} \text{ s}^2 \end{aligned} \quad (2.20)$$

This gives,

$$\alpha_{\text{ten.}}^{\text{AC}}(\text{F}, 7/2) = -5.505 \times 10^{-41} \text{JV}^{-2}\text{m}^2. \quad (2.21)$$

The AC tensor polarisability of the $^2\text{F}_{7/2}$, $F = 3$ state,

$$\begin{aligned} \alpha_{\text{ten.}}^{\text{AC}}(F, 7/2, 3) &= \frac{25}{28} \alpha_{\text{ten.}}^{\text{AC}}(\text{F}, 7/2) \\ &= -4.915 \times 10^{-41} \text{JV}^{-2}\text{m}^2 \end{aligned} \quad (2.22)$$

and

$$\begin{aligned} \left(\frac{\Delta\nu^{\text{AC}}(F, 7/2, 3, 0)}{\text{mHz}} \right) &= \left(\frac{-12.13\langle E^2 \rangle - 0.15(3\langle E_z^2 \rangle - \langle E^2 \rangle)}{(\text{V/cm})^2} \right) \\ &= \left(\frac{-11.98\langle E^2 \rangle - 0.45\langle E_z^2 \rangle}{(\text{V/cm})^2} \right). \end{aligned} \quad (2.23)$$

The AC Stark shift of the $^2\text{S}_{1/2}$, $F = 0 \rightarrow ^2\text{F}_{7/2}$, $F = 3$, $M_F = 0$ transition,

$$\left(\frac{\Delta\nu^{\text{AC}}(^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) = \left(\frac{1.70\langle E^2 \rangle - 0.45\langle E_z^2 \rangle}{(\text{V/cm})^2} \right). \quad (2.24)$$

In terms of optical intensity, $I = c\epsilon_0\langle E^2 \rangle$,

$$\left(\frac{\Delta\nu^{\text{AC}}(^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0)}{\text{Hz}} \right) = \left(\frac{0.64I - 0.17I_z}{\text{W/cm}^2} \right). \quad (2.25)$$

2.3 Special case: $E // B$

For the special case where the electric field is assumed to be parallel to the quantisation axis, given by the direction of the magnetic field, the ac Stark shift may be derived by a simpler method and this serves as a useful check on the validity of the theory in section 2.1. The ac Stark shift in this case is given by,

$$\Delta W_E = -\frac{1}{2} \alpha^{\text{AC}}(\gamma I J F M_F) E^2, \quad (2.26)$$

where [3, 10]

$$\alpha^{\text{AC}} = \frac{2}{\hbar} \sum_{\gamma' J' F'} \frac{\omega |\langle \gamma I J F M_F | \mu_z | \gamma' I J' F' M_F \rangle|^2}{\omega^2 - \omega_L^2}. \quad (2.27)$$

The matrix element is related to a weighted oscillator strength by [7],

$$|\langle \gamma I J F M | \mu_z | \gamma' I' J' F' M \rangle|^2 = \frac{3\hbar e^2 g_F f_F}{2m_e \omega} \begin{pmatrix} F & 1 & F' \\ -M & 0 & M \end{pmatrix}^2, \quad (2.28)$$

so that

$$\alpha^{\text{AC}} = \frac{3e^2}{m_e} \sum_{\gamma' J' F'} \frac{g_F f_F}{(\omega^2 - \omega_L^2)} \begin{pmatrix} F & 1 & F' \\ -M & 0 & M \end{pmatrix}^2. \quad (2.29)$$

The hyperfine oscillator strength, $g_F f_F$ is related to the fine-structure oscillator strength, $g_J f_J$, by [11]

$$g_F f_F = (2F + 1)(2F' + 1) \left\{ \begin{array}{ccc} J & I & F \\ F' & 1 & J' \end{array} \right\}^2 g_J f_J \quad (2.30)$$

giving,

$$\alpha^{\text{AC}} = \frac{3e^2}{m_e} \sum_{\gamma' J' F'} \frac{g_J f_J}{(\omega^2 - \omega_L^2)} (2F + 1)(2F' + 1) \left(\begin{array}{ccc} F & 1 & F' \\ -M & 0 & M \end{array} \right)^2 \left\{ \begin{array}{ccc} J & I & F \\ F' & 1 & J' \end{array} \right\}^2. \quad (2.31)$$

The summation is again evaluated using the oscillator strengths calculated in [9]. For the $^2\text{S}_{1/2}, F = 0$ state one needs to consider excited states with $J' = 1/2, F' = 1$ and $J' = 3/2, F' = 1$, all other transitions being forbidden:

$$\begin{aligned} & \sum_{\gamma' J' F'} \frac{g_J f_J}{(\omega^2 - \omega_L^2)} (2F' + 1) \left(\begin{array}{ccc} 1 & 1 & F' \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} 1/2 & 1/2 & 0 \\ F' & 1 & J' \end{array} \right\}^2 = \\ & + \frac{1}{6} \times 5.5067 \times 10^{-32} : J' = 1/2, F' = 1 \\ & + \frac{1}{6} \times 7.3647 \times 10^{-32} : J' = 3/2, F' = 1 \\ & = 2.145 \times 10^{-32} \text{ s}^2 \end{aligned} \quad (2.32)$$

The ac stark shift of the $^2\text{S}_{1/2}, F = 0$ state is,

$$\left(\frac{\Delta\nu^{\text{AC}}(\text{S}, 1/2)}{\text{mHz}} \right) = -13.68 \left(\frac{\langle E^2 \rangle}{(\text{V/cm})^2} \right). \quad (2.33)$$

For the $^2\text{F}_{7/2}, F = 3, M = 0$ state one needs to consider excited states with $J' = 5/2, F' = 2, J' = 7/2, F' = 4$ and $J' = 9/2, F' = 4$ all other transitions being forbidden:

$$\begin{aligned} & \sum_{\gamma' J' F'} \frac{g_J f_J}{(\omega^2 - \omega_L^2)} 7(2F' + 1) \left(\begin{array}{ccc} 3 & 1 & F' \\ 0 & 0 & 0 \end{array} \right)^2 \left\{ \begin{array}{ccc} 7/2 & 1/2 & 3 \\ F' & 1 & J' \end{array} \right\}^2 = \\ & + \frac{1}{14} \times 1.1903 \times 10^{-31} : J' = 5/2, F' = 2 \\ & + \frac{1}{504} \times 1.4491 \times 10^{-31} : J' = 7/2, F' = 4 \\ & + \frac{1}{18} \times 1.9246 \times 10^{-31} : J' = 9/2, F' = 4 \\ & = 1.9467 \times 10^{-32} \text{ s}^2 \end{aligned} \quad (2.34)$$

The ac Stark shift of the $^2\text{F}_{7/2}, F = 3, M_F = 0$ state is

$$\left(\frac{\Delta\nu^{\text{AC}}(\text{F}, 7/2, 3, 0)}{\text{mHz}} \right) = -12.43 \left(\frac{\langle E^2 \rangle}{(\text{V/cm})^2} \right). \quad (2.35)$$

The ac Stark shift of the $^2\text{S}_{1/2}, F = 0 \rightarrow ^2\text{F}_{7/2}, F = 3, M_F = 0$ transition is

$$\left(\frac{\Delta\nu^{\text{AC}}(^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) = 1.26 \left(\frac{\langle E^2 \rangle}{(\text{V/cm})^2} \right). \quad (2.36)$$

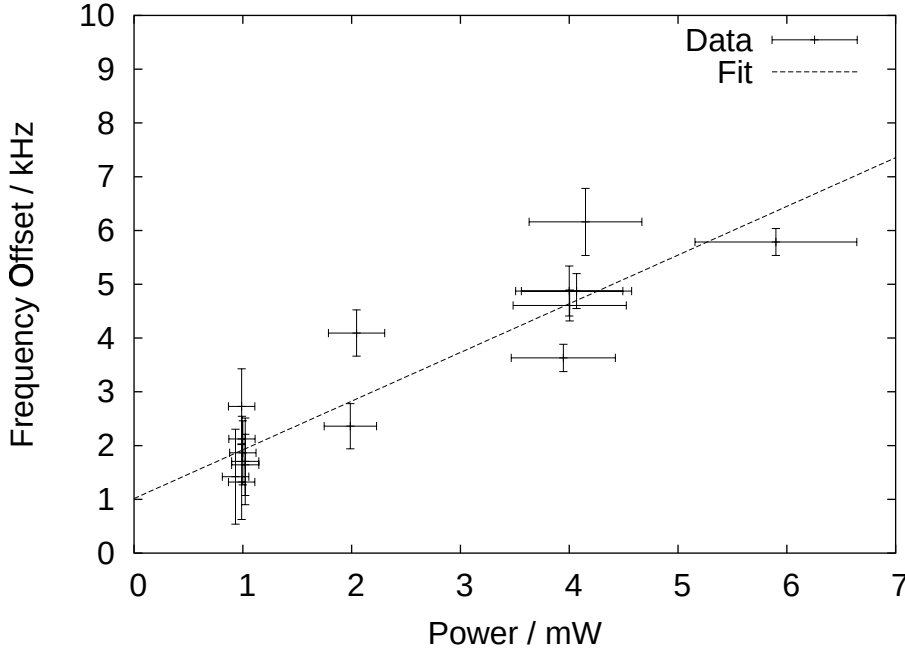


Figure 2.1: Frequency measurement data, 13–15 March 2002. The slope of the transition frequency as a function of power is 0.88 ± 0.08 kHz/mW. The error bars show the statistical frequency uncertainty and estimated power uncertainty. The straight line is a weighted least-squares fit taking both power and frequency uncertainties into account. Data are grouped by probe beam alignment and power.

In terms of optical intensity,

$$\left(\frac{\Delta\nu^{\text{AC}}(^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0)}{\text{Hz}} \right) = 0.47 \left(\frac{I}{\text{W/cm}^2} \right). \quad (2.37)$$

If one sets $I = I_z$ in equation 2.25 then $(\Delta\nu^{\text{AC}}(^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0)/\text{Hz}) = 0.47 I/(\text{W/cm}^2)$ in agreement with the value derived by the different method.

2.4 Measurement

The shift has been observed and measured in our experiments. The most accurate measurement of the coefficient of the shift was performed in 2002. The frequency of the transition, measured using a femtosecond comb, is plotted as a function of the probe laser power in figure 2.1. The power is then converted to intensity via a measurement of the probe beam diameter at its focus. The beam diameter was measured by observing the power transmitted past a micrometer-mounted knife edge as a function of micrometer position. This was done in both the vertical and horizontal directions. The measured transmission was fitted with a theoretical transmission function to obtain the beam diameters. It is this step which limits the accuracy of the determination of the coefficient of the shift. The beam is approximately $5 \mu\text{m}$ radius, and the micrometers have at best $0.5 \mu\text{m}$ accuracy. The measurements were repeated three times for each direction, but the final uncertainty on the beam size

was around 5% in each direction, leading to an 8% uncertainty in the estimated intensity, before considering other sources of error. The uncertainty of the alignment of the UV tracer beam on the ion, and of the overlap of the 467 nm and 369 nm beams, is asymmetric, as the intensity can only decrease as the alignment drifts from the original optimal setting. The uncertainty here is $^{+0}_{-17}\%$. The systematic uncertainty in intensity calibration is $^{+8}_{-15}\%$.

The slope of the transition frequency as a function of power for this measurement was 0.88 ± 0.08 kHz/mW. Combining this with the measured spot size and related uncertainties gives a measurement of the AC Stark shift coefficient as

$$\left(\frac{\Delta\nu^{\text{AC}}}{\text{Hz}}\right) = [0.48 \pm 0.04 \text{ (stat.) } ^{+0.07}_{-0.04} \text{ (syst.)}] \left(\frac{I}{\text{W/cm}^2}\right). \quad (2.38)$$

In these experiments the electric field of the probe beam is at 65° to the z-axis, therefore, $E_z = \cos 65^\circ E$ and $I_z = \cos^2 65^\circ I$. From eq. 2.25 one expects the ac Stark shift to be

$$\begin{aligned} \left(\frac{\Delta\nu^{\text{AC}}}{\text{Hz}}\right) &= [0.64 - (0.1786 \times 0.17)] \left(\frac{I}{\text{W/cm}^2}\right) \\ &= 0.61 \left(\frac{I}{\text{W/cm}^2}\right). \end{aligned} \quad (2.39)$$

This is 1.6σ above the experimental value; a reasonable agreement considering that the theoretical calculation is the difference between two large, similar numbers. For further discussion on the uncertainty in the calculated shift, see section 7.1.

2.5 Correcting for the shift

Two methods of correcting for the AC Stark shift have been used in these experiments. The first, used only for the preliminary measurement of September 2001, is to measure the beam size and power used in the experiment, and to calculate a correction using a previously measured coefficient. This leads to large uncertainties, of around 20% in the calculated intensity, largely due to the beam size measurement. This error also appears twice — first in the measurement of the coefficient and then in calculating the correction at a later date. This makes this method unsatisfactory for high-precision work.

The second method is more direct, and misses out the beam size measurement step. Here, the transition frequency is measured directly as a function of probe laser power, and it is assumed that the beam size does not change between measurements. The frequency can then be extrapolated back to zero probe laser power, and this represents the unperturbed transition frequency. The uncertainties involved in this method are otherwise common with the first method. These are the beam pointing stability, the initial alignment accuracy of the 467 nm beam with the 369 nm tracer beam, and the accuracy of the alignment of the tracer beam. These errors become fractionally smaller as the beam diameter increases, and so defocusing the probe laser beam is a good method of controlling the uncertainties, provided that there is enough power in the beam to drive the transition at the required rate.

2.6 Scaling of the AC Stark shift

While the AC Stark shift is currently the largest shift, it scales with the probe laser linewidth in an advantageous manner. This scaling is not because the AC Stark shift is dependent on the linewidth (to first order), but because the two are interlinked by the experimental method.

The AC Stark shift is proportional to the intensity I . The transition rate is proportional to the spectral intensity S , itself proportional to I/Γ for a laser of linewidth Γ . The excitation probability for a single interrogation of the ion, of length t , is proportional to $St \propto It/\Gamma$, assuming the interrogation is well below saturation. By setting this quantity to be conserved, whatever the experimental configuration, then generalisations about the scaling of the AC Stark shift with linewidth can be deduced. Currently, the excitation probability is around 25% per interrogation at line centre, for a pulse length of 300 ms, a beam waist of $10\text{ }\mu\text{m}$, and 1 mW of laser power in a 150 Hz bandwidth. Typical pulse lengths for the current state of the experiment are around 100-300 ms. There is little to be gained from reducing this further, as the experimental cycle becomes dominated by the state-detection time. In the situation where t is fixed, the AC Stark shift (proportional to I) is therefore directly proportional to the linewidth. As the linewidth shrinks, the probe time t must be extended, otherwise the linewidth of the laser will be Fourier-limited. In this regime, the pulse length is inversely proportional to linewidth ($t \propto 1/\Gamma$). Hence, for very narrow linewidths $I \propto \Gamma^2$. This is illustrated in Figure 2.2, and possible combinations of pulse length, beam power and beam size to obtain this are shown in Figure 2.3.

Because of the extreme weakness of the octupole transition, and the currently large size of the AC Stark shift it is often thought of as a major weakness of the octupole transition amongst candidate frequency standards. Currently, it must be accepted, it is a major limitation on our ability to make absolute frequency measurements. However, the probe laser linewidth must be narrowed significantly to take full advantage of the octupole transition. The quadratic scaling of the AC Stark shift with linewidth means that the shift is vanishing for small linewidths.

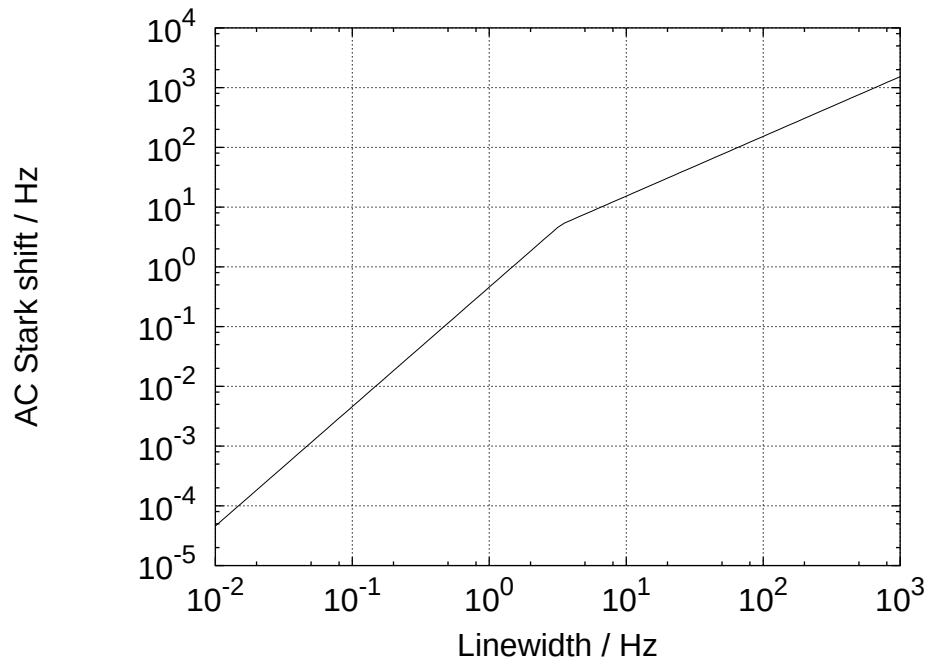


Figure 2.2: Approximate relationship between the AC Stark shift and probe laser linewidth for typical operating conditions. The data are scaled from the current conditions of $\Gamma = 200$ Hz, $I = 10^7$ Wm^{-2} and $t = 0.3$ s. A summary of the operating conditions for this curve is shown in Figure 2.3.

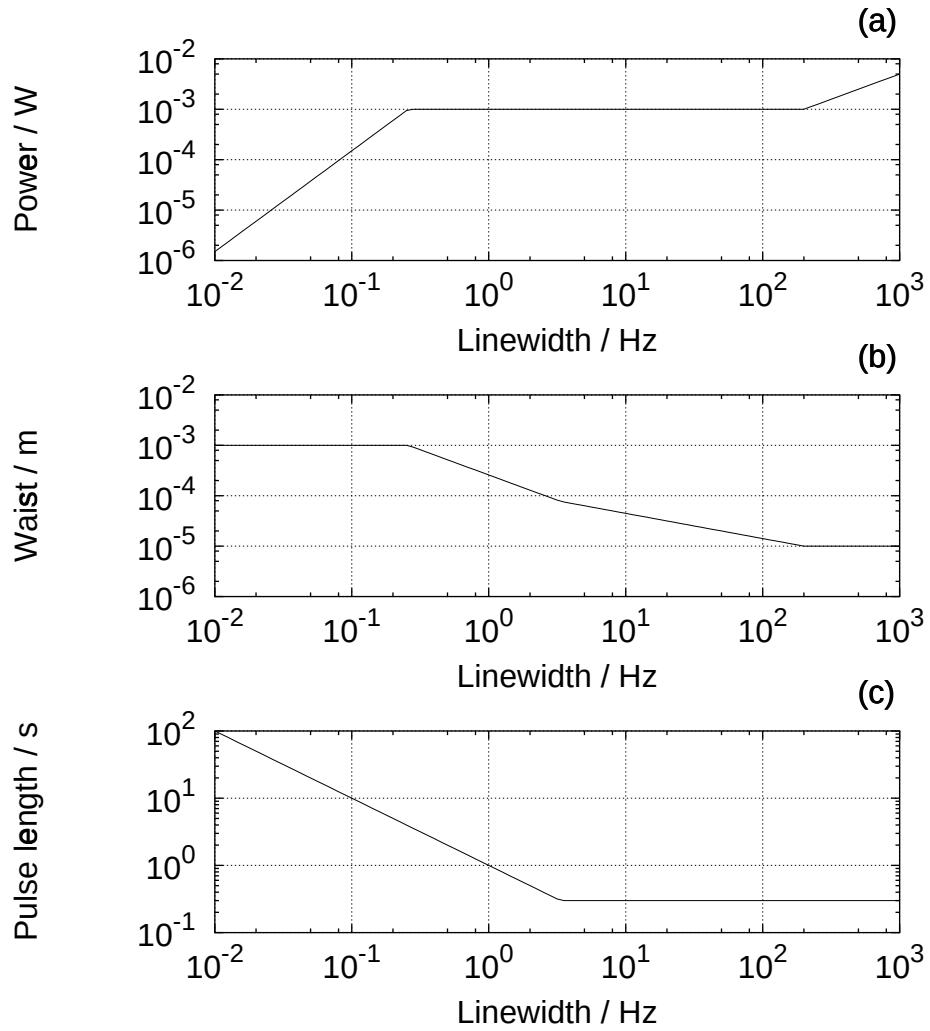


Figure 2.3: Possible operating conditions, as a function of probe laser linewidth, for the AC Stark shift shown in Figure 2.2. (a) Probe beam power. (b) Probe beam diameter at the ion. (c) Probe pulse length. All the conditions are extrapolated from the current operating conditions at $\Gamma = 200$ Hz.

Chapter 3

Second-order Zeeman effect

The second-order Zeeman effect arises from the interaction of a magnetic field with the $^2S_{1/2}$ and $^2F_{7/2}$ states. The transition frequency is not affected by the linear Zeeman shift as the $m_F = 0 \rightarrow m_F = 0$ component is used as the frequency reference. However, this component is still affected by the second-order Zeeman shift.

3.1 Theory

The energy shift induced by a magnetic field strength B is calculated using second-order perturbation theory [12] and is given by

$$\Delta W_B(F, M_F) = -(g_J \mu_B B)^2 \sum_{F'} \frac{|\langle F' M_F | J_z | F M_F \rangle|^2}{W_{F'} - W_F} \quad (3.1)$$

where it has been assumed that the quantisation axis is set by the applied field, so the matrix elements are zero for states of different M_F . The matrix elements can be written in terms of Wigner $3j$ and $6j$ symbols [7]

$$\begin{aligned} |\langle F' M_F | J_z | F M_F \rangle|^2 &= I(I+1)(2I+1)(2F+1)(2F'+1) \\ &\times \left(\begin{array}{ccc} F & 1 & F' \\ -M_F & 0 & M_F \end{array} \right)^2 \left\{ \begin{array}{ccc} I & F & J \\ F' & I & 1 \end{array} \right\}^2 \end{aligned} \quad (3.2)$$

For the $^2S_{1/2}(F=0)$ state in $^{171}\text{Yb}^+$, the only non-zero matrix element is that with the $^2S_{1/2}(F=1, M_F=0)$ state. The shift for this state in terms of frequency,

$$\Delta\nu(0,0) = - \left(\frac{g_J e B}{4\pi m_e} \right)^2 \frac{|\langle 10 | J_z | 00 \rangle|^2}{\Delta\nu_{HFS}} \quad (3.3)$$

The matrix element is equal to $1/2$, $g_J = 2$ and the hyperfine splitting $\Delta\nu_{HFS} = 12.643$ GHz. This makes the shift coefficient for the $^2S_{1/2}(F=0)$ state

$$\left(\frac{\Delta\nu(0,0)}{\text{mHz}} \right) = -15.49 \left(\frac{B}{\mu\text{T}} \right)^2. \quad (3.4)$$

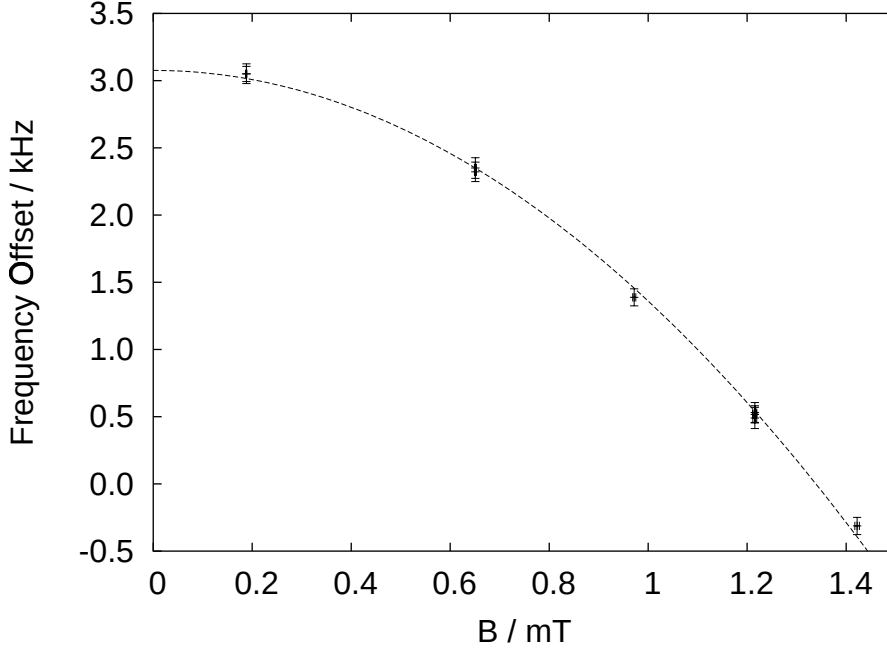


Figure 3.1: Second-order Zeeman shift of the octupole transition, and least-squares fit.

For the $^2\text{F}_{7/2}(F=3, M_F=0)$ state, the only non-zero matrix element is that with the $^2\text{F}_{7/2}(F=4, M_F=0)$ state and the shift,

$$\Delta\nu(3,0) = - \left(\frac{g_J e B}{4\pi m_e} \right)^2 \frac{|\langle 40 | J_z | 30 \rangle|^2}{\Delta\nu_{HFS}} \quad (3.5)$$

The matrix element is $1/2$, $g_J = 8/7$ and $\Delta\nu_{HFS} = 3.620$ GHz, giving

$$\left(\frac{\Delta\nu(3,0)}{\text{mHz}} \right) = -17.67 \left(\frac{B}{\mu\text{T}} \right)^2. \quad (3.6)$$

The shift of the transition frequency is the difference between these two coefficients and hence the predicted second-order Zeeman shift for the octupole transition in $^{171}\text{Yb}^+$ is

$$\left(\frac{\Delta\nu(^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) = -2.176 \left(\frac{B}{\mu\text{T}} \right)^2. \quad (3.7)$$

3.2 Measurement

Figure 3.1 shows a measurement of the shift where the transition frequency, measured using the femtosecond comb is plotted against magnetic field. The least-squares fit to the measurement data gives a coefficient of the second-order Zeeman shift $\Delta\nu_{\text{Zeeman}} = -1.72 \pm 0.03 \text{ mHz } (B/\mu\text{T})^2$. This is in good agreement with a previously measured value of $-1.9 \pm 0.3 \text{ mHz } (B/\mu\text{T})^2$ [3], however, the theoretical calculation does not precisely match the measured coefficient. Despite the discrepancy of about 20% in the shift coefficient, the difference is equivalent to a less than

3% error in the calculations of the individual level shifts and could be due to a departure from LS-coupling for the $^2\text{F}_{7/2}$ state. The agreement observed between theory and experiment is therefore reasonable.

3.3 AC Second-order Zeeman shifts

Because the shift is second-order, an oscillating perturbation will not average to zero. For low frequencies $\omega \ll \omega_{HFS}$, the coefficient of the shift is the same as for a DC field. For a field composed of static and oscillating components,

$$\langle B^2 \rangle = \langle B_{DC}^2 \rangle + \langle B_{AC}^2 \rangle \quad (3.8)$$

The shifts can therefore be calculated separately and independently for the different frequency components of a field. The shift caused by a low-frequency oscillating field will be equal to that produced by a static field of the same strength as the rms (root-mean-square) oscillating field strength. The most obvious source of such a low-frequency magnetic field is the mains electricity supply.

For higher frequency fields, the shift is calculated in a similar manner to the AC Stark shift. The energy shift for a field of angular frequency ω_L interacting with a state $|\gamma I J F M_F\rangle$, summing over transitions of angular frequency ω to $|\gamma I J' F' M_F\rangle$, is

$$\Delta W_B^{AC}(\gamma, I, J, F, M_F) = -\frac{(g_J \mu_B B)^2}{\hbar} \sum_{J' F'} \frac{\omega |\langle \gamma I J' F' M_F | J_z | \gamma I J F M_F \rangle|^2}{\omega^2 - \omega_L^2} \quad (3.9)$$

It is expected that this shift is much smaller than the DC shift due to the scarcity of magnetic dipole transitions at optical frequencies, and the interaction with microwave magnetic dipole transitions is smaller than for DC by a factor $[\omega/\omega_L]^2$. While the coefficient of the optical second-order Zeeman shift has not been fully calculated, this is not an issue for the experiment. The shift scales with B^2 , and is therefore a linear function of the intensity of an optical field, as with the AC Stark shift. It is therefore automatically compensated for by the experimental method.

3.4 Reducing the shift

It is, at present, necessary to apply an external DC magnetic field to the trapped $^{171}\text{Yb}^+$ ion. This is because there is a fluorescence null on the $F = 1 \rightarrow 0$ component of the 369 nm transition in zero field [13], and this is the component used for Doppler cooling. This field is typically 200 μT , giving a shift on the order of 80 Hz. Due to the accuracy of the calibration, the uncertainty on this is small (~ 3 Hz). This can still be improved by working in a lower, or zero, magnetic field. To do this it is necessary to spin the polarization of the Doppler cooling beam to prevent loss of fluorescence [13]. The technique involves projecting two beams into the trap at an angle to each other, and modulating the phase of the polarisation components of the light such that all three polarisations have a different time-dependence. This has been tested in $^{171}\text{Yb}^+$ and the technique does maintain fluorescence in magnetic

fields down to a few tens of nanotesla. Below this, a narrower fluorescence null on the 935 nm repumper transition begins to affect the fluorescence rate. This can also be overcome by polarisation spinning, enabling work in zero (or very close to zero) DC magnetic field. The field itself can be nulled very accurately by observation of the Zeeman components of the octupole transition. The lower limit to the shift is expected to be set by the 50 Hz field from the mains electricity supply. This has been measured at around 500 nT in the current laboratory, and it is expected that a mu-metal shield around the ion trap could reduce this to around 50 nT. This shifts the transition by just a few microhertz.

Chapter 4

Quadrupole shift

The electric quadrupole shift is one of the more significant systematic shifts for trapped-ion frequency standards. We follow the treatment of the shift by W. Itano for the $^{199}\text{Hg}^+$ ion [8]. The shift itself is caused by the interaction of the quadrupolar spatial component of a DC electric field, with the quadrupole moment of an atomic state. The $^2\text{S}_{1/2}$ state has no quadrupole moment, so the shift of the 467 nm transition is entirely due to the shift of the $^2\text{F}_{7/2}$ state.

The shift occurs only for states with $J \geq 2$, and does not affect the $^2\text{S}_{1/2}$ state. The physical cause is the interaction of the electric quadrupole moment of an electronic state with a quadrupolar electric field, such as might be produced by the electrodes of an ion trap. The shift for the 467 nm transition is caused by any DC electric quadrupole field which may be present in the trap interacting with the quadrupole moment of the $^2\text{F}_{7/2}(F = 3, M_F = 0)$ state in $^{171}\text{Yb}^+$.

4.1 Reference frames

Two co-ordinate systems are used in the following calculation. The first, ‘laboratory’ frame has co-ordinates (x, y, z) , and has its z -axis aligned with the direction of the magnetic field B . The ‘trap’ frame, denoted by primed co-ordinates (x', y', z') , has its z -axis aligned with the trap z -axis, along the endcaps. The assumption is made that any DC quadrupole field is being produced by DC offset potentials on the trap electrodes.

4.2 The Hamiltonian

The Hamiltonian for the quadrupole shift is

$$H_Q = \nabla E^{(2)} \cdot \Theta^{(2)} = \sum_{q=-2}^2 (-1)^q \nabla E_q^{(2)} \Theta_{-q}^{(2)} \quad (4.1)$$

where the $E_q^{(2)}$ are the quadrupole components of the electric field, and $\Theta_{-q}^{(2)}$ are the components of the electric quadrupole moment of the atom.

4.3 The electric field

The quadrupolar field has the form, in the trap frame,

$$\phi(x', y', z') = A \left[(x'^2 + y'^2 - 2z'^2) + \epsilon (x'^2 - y'^2) \right], \quad (4.2)$$

where A represents the quadrupole field strength. Henceforth it will be assumed that the trap is radially symmetric and that $\epsilon = 0$. This simplifies the derivation from that in [8] without losing the essential physics. In particular, both the electric field gradient tensors and quadrupole moment operator have several components. Setting $\epsilon = 0$ allows us to ignore all but the $q = 0$ components. The relevant component of the electric field gradient tensor is

$$\nabla E_0^{(2)} = -\frac{1}{2} \frac{dE_z}{dz}. \quad (4.3)$$

The electric field gradient for this field, in the trap frame, is

$$\nabla E_0^{(2)'} = -2A. \quad (4.4)$$

The Hamiltonian in the trap frame is simply

$$H_Q = -2A\Theta_0^{(2)'}. \quad (4.5)$$

Note that the quadrupole moment is expressed in the trap frame here, and not in the ‘lab’ frame defined by the magnetic field.

4.4 Matrix elements

The shift of a state $|\gamma J F M_F\rangle$ is given by the expectation value of the Hamiltonian interacting with that state:

$$\Delta E(\gamma J F M_F) = \langle \gamma J F M_F | H_Q | \gamma J F M_F \rangle. \quad (4.6)$$

This is the expression in the laboratory frame. The states $|\gamma J F M_F\rangle$ in the lab frame are related to the states $|\gamma J F M'\rangle$ in the trap frame by rotation matrix elements $D_{M' M_F}^{(F)}(\beta)$, where (β) is the angle of rotation relating the two frames. Only one angle is required for calculating the $q = 0$ components due to the symmetry of the situation.

$$|\gamma J F M'\rangle = \sum_{M_F} D_{M' M_F}^{(F)}(\beta) |\gamma J F M_F\rangle. \quad (4.7)$$

The matrix element which must be calculated to evaluate the shift is

$$\langle \gamma J F M_F | \Theta_0^{(2)'} | \gamma J F M_F \rangle. \quad (4.8)$$

It can be shown [8] that this can be written

$$\begin{aligned} \langle \gamma J F M_F | \Theta_0^{(2)'} | \gamma J F M_F \rangle = \\ (-1)^{F-M_F} \langle \gamma J F || \Theta^{(2)} || \gamma J F \rangle \begin{pmatrix} F & 2 & F \\ -M_F & 0 & M_F \end{pmatrix} D_0^{(2)*}(\beta). \end{aligned} \quad (4.9)$$

The rotation matrix element is $D_0^{(2)*}(\beta) = \frac{1}{2}(3\cos^2\beta - 1)$. The shift can therefore be written

$$\Delta E(\gamma J F M_F) = -A(3\cos^2\beta - 1)K_1(\gamma J F || \Theta^{(2)} || \gamma J F), \quad (4.10)$$

with the constant K_1 defined by

$$K_1 = (-1)^{F-M_F} \begin{pmatrix} F & 2 & F \\ -M_F & 0 & M_F \end{pmatrix}. \quad (4.11)$$

For the $^2\text{F}_{7/2}(F=3, M_F=0)$ state, $K_1 = -\frac{2}{3}\sqrt{\frac{3}{35}}$.

The remaining undefined quantity is the reduced matrix element $(\gamma J F || \Theta^{(2)} || \gamma J F)$. This can be related to the quadrupole moment of the state $\Theta(\gamma, J)$ which is defined as the matrix element of the quadrupole operator for the state of maximum M_J . That is

$$\Theta(\gamma, J) = \langle \gamma J J | \Theta_0^{(2)} | \gamma J J \rangle. \quad (4.12)$$

In the IJ -coupling approximation,

$$\begin{aligned} &(\gamma(IJ)F || \Theta || \gamma(IJ)F) = \\ &(-1)^{I+J+F}(2F+1) \begin{Bmatrix} J & 2 & J \\ F & I & F \end{Bmatrix} \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}^{-1} \Theta(\gamma, J). \end{aligned} \quad (4.13)$$

Hence the shift (Equation (4.10)) can be written

$$\langle H_Q \rangle = -A(3\cos^2\beta - 1)K_1K_2\Theta(\gamma, J), \quad (4.14)$$

with the constant K_2 being defined by

$$K_2 = (-1)^{I+J+F}(2F+1) \begin{Bmatrix} J & 2 & J \\ F & I & F \end{Bmatrix} \begin{pmatrix} J & 2 & J \\ -J & 0 & J \end{pmatrix}^{-1}. \quad (4.15)$$

For the $^2\text{F}_{7/2}(F=3, M_F=0)$ state, $K_2 = +\frac{5}{2}\sqrt{\frac{15}{7}}$.

Using the constants calculated above, $K_1 = -\frac{2}{3}\sqrt{\frac{3}{35}}$ and $K_2 = +\frac{5}{2}\sqrt{\frac{15}{7}}$, the quadrupole shift for the $^2\text{F}_{7/2}(F=3, M_F=0)$ state in $^{171}\text{Yb}^+$ is

$$\langle H_Q \rangle = +\frac{5}{7}A(3\cos^2\beta - 1)\Theta(\gamma, J). \quad (4.16)$$

4.5 The quadrupole moment

To evaluate the quadrupole moment given in eq. 4.12, one needs to calculate the quadrupole operator,

$$\Theta_0^{(2)} = -\frac{e}{2} \sum_j (3z_j^2 - r_j^2). \quad (4.17)$$

The summation is over all the atomic electrons, and z_j and r_j are the electronic position operators. A closed atomic shell has no quadrupole moment, and so only unfilled shells need be considered. Writing in terms of spherical harmonics, this is

$$\Theta(\gamma, J) = -e\sqrt{\frac{4\pi}{5}}\langle\gamma JJ|Y_{20}|\gamma JJ\rangle, \quad (4.18)$$

but

$$\langle 4f\ ^2F_{7/2}, m_j = 7/2 | Y_{20} | 4f\ ^2F_{7/2}, m_j = 7/2 \rangle = \langle 4f, m_l = 2 | Y_{20} | 4f, m_l = 2 \rangle. \quad (4.19)$$

Therefore, the quadrupole moment can be written

$$\Theta(\gamma, J) = -e\sqrt{\frac{4\pi}{5}}\langle\gamma|r^2|\gamma\rangle \int_0^{2\pi} \int_0^\pi Y_{LL}^* Y_{20} Y_{LL} \sin\theta d\theta d\phi. \quad (4.20)$$

The integrals over spherical harmonics can be written in terms of 3j symbols and normalisation factors. In the general case [7],

$$\begin{aligned} \int_0^{2\pi} \int_0^\pi Y_{l_1 m_1}^* Y_{l_2 m_2} Y_{l_3 m_3} \sin\theta d\theta d\phi = \\ (-1)^{m_1} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \end{aligned} \quad (4.21)$$

Therefore,

$$\Theta(\gamma, J) = -(-1)^L e \langle\gamma|r^2|\gamma\rangle (2L+1) \begin{pmatrix} L & 2 & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} L & 2 & L \\ -L & 0 & L \end{pmatrix}. \quad (4.22)$$

For the $^2F_{7/2}$ state in $^{171}\text{Yb}^+$ the quadrupole moment is due to the *absence* of an electron, or hole in, an otherwise full f-shell. This changes the sign of the quadrupole moment, from that calculated above, which was treated as a single electron in the 4f state, rather than a single hole. The orbital angular momentum is $L = 3$ for the $^2F_{7/2}$ state. The quadrupole moment is therefore

$$\Theta(4f, 7/2) = -e\frac{1}{3}\langle 4f|r^2|4f\rangle. \quad (4.23)$$

4.6 Matrix elements of $\langle r^2 \rangle$

The matrix elements of $\langle r^2 \rangle$ can be estimated from atomic structure calculations. The Cowan atomic structure code [11] calculates atomic orbitals, and related properties, for many-electron atoms. From these calculations, the expectation values in Table 4.1 have been found.

The value for $^{199}\text{Hg}^+$ agrees with that calculated in [8], using the same code. The value for $^{88}\text{Sr}^+$ does not agree with the published value in [14]. However, if the calculation is performed for the 4d orbital of neutral strontium, there seems to be agreement [15]. This perhaps points to an error in the initialisation of the Cowan code, though this has not been confirmed with the authors of [14].

Species	Orbital	$\langle r^2 \rangle / a_0^2$
$^{171}\text{Yb}^+$	4f	0.657
$^{171}\text{Yb}^+$	5d	10.8
$^{199}\text{Hg}^+$	5d	2.32
$^{88}\text{Sr}^+$	4d	10.6
$^{40}\text{Ca}^+$	3d	6.64

Table 4.1: Expectation values of the squared electronic co-ordinate for various atomic orbitals, in units of the Bohr radius a_0 .

The size of the 4f-orbital in $^{171}\text{Yb}^+$ is particularly small. In common with the 5d orbital in mercury, it is not the ‘outermost’ occupied orbital. In both cases the $6s^2$ orbital is full, and the source of the quadrupole moment is a hole in an inner shell. The d-orbitals in ytterbium, strontium and calcium ions are occupied by a single electron, ‘outside’ completely full inner shells, which gives some indication as to why those orbitals are relatively larger.

Using the calculated $\langle r^2 \rangle$, the quadrupole moment of the $^2\text{F}_{7/2}(F=3, M_F=0)$ state in $^{171}\text{Yb}^+$ is

$$\begin{aligned}\Theta(4f, 7/2) &= -0.22ea_0^2 \\ &= -9.83 \times 10^{-41} \text{ Cm}^2.\end{aligned}\tag{4.24}$$

For the ion trap used in these experiments, the angle between the B -field and the trap axis is $\beta = 90^\circ$. The shift is then

$$\begin{aligned}\langle H_Q \rangle &= 7.02 \times 10^{-41} A \text{ J} \\ \frac{\langle H_Q \rangle}{h} &= 1.06 \times 10^{-7} A \text{ Hz}.\end{aligned}\tag{4.25}$$

4.7 Trap parameters

A rf trap of the end-cap design [16] is used in these experiments. A voltage, $V_{\text{AC}} = 291 \text{ V}$, oscillating at $\omega_{\text{RF}} = 2\pi \times 12.8 \text{ MHz}$, is applied to the inner endcaps whilst the outer endcaps are nominally grounded ($V_{\text{DC}} = 0$). The characteristic dimension of the trap is the separation between the inner endcaps, $2z_0 = 0.56 \text{ mm}$. The radius of the endcaps, $r_0 = 0.25 \text{ mm}$. The quadrupole field strength is given by

$$A = \frac{\mathcal{E}(V_{\text{DC}} + V_{\text{AC}} \cos(\omega_{\text{RF}} t))}{2z_0^2},\tag{4.26}$$

where the parameter $\mathcal{E}$, known as the efficiency of the trap, is characteristic to the particular trap geometry and in this case is equal to 0.63(3). The time-averaged force experienced by the ion in the trap gives rise to an effective harmonic potential. The axial and radial *secular* frequencies of motion in the harmonic potential of an ion, mass m , charge e are given by

$$\omega_{\text{sec}} = \frac{\beta \omega_{\text{RF}}}{2},\tag{4.27}$$

where

$$\beta = \sqrt{a + \frac{q^2}{2}} \quad (4.28)$$

and

$$+a_z = -2a_r = +\frac{4e\mathcal{E}V_{\text{DC}}}{mz_0^2\omega_{\text{RF}}^2} \quad (4.29)$$

$$-q_z = +2q_r = +\frac{2e\mathcal{E}V_{\text{AC}}}{mz_0^2\omega_{\text{RF}}^2}. \quad (4.30)$$

For the trap parameters given above, $\omega_z = 2\omega_r = 2\pi \times 1.846$ MHz. Equation 4.28 is a first order approximation, which is sufficient for most purposes. However, if a precise knowledge of the trap frequencies is required, as in section 4.8, the secular frequencies may be calculated to a higher order in q in which case the expression for β is

$$\beta = \left(a - \frac{a-1}{2(a-1)^2 - q^2} q^2 - \frac{5a+7}{32(a-1)^3(a-4)} q^4 \right)^{\frac{1}{2}}, \quad (4.31)$$

and $\omega_z = 2.050\omega_r = 2\pi \times 1.912$ MHz

4.8 Estimating the shift

By assuming that the quadrupole field is caused by a common dc offset potential V_{Offset} on the upper and lower inner endcaps, relative to the outer endcap electrodes, a typical values for A is estimated using

$$A = -\frac{\mathcal{E}V_{\text{Offset}}}{2z_0^2}. \quad (4.32)$$

When no potential is deliberately applied, V_{Offset} is expected to be in the range ± 1 V, due to offset potentials on the electrodes. Possible sources of these potentials include contact potentials between atomic ytterbium ejected from the trap ovens and the tantalum of the electrode structure [17]. The 1 V estimate is backed up by the fact that micromotion compensation voltages required in the z direction are typically $\pm 0 \rightarrow 0.2$ V. Using 1 V as a conservative estimate gives typical values of A in the range $\pm 4.0 \times 10^6$ Vm $^{-2}$. The uncorrected quadrupole shift is therefore expected to be approximately ± 0.4 Hz. By assuming that the field is produced by the trap electrodes, it is possible to express the quadrupole shift in “hertz per volt on the inner endcap”. This is an artificial, but practically useful, way to express the shift and is unique to each individual trap. When this is done, the shift is 0.4 HzV $^{-1}$.

4.9 Nulling the shift

It may be possible to control and reduce both the shift and its uncertainty by various means. The first of these is that if frequency measurements are made for any three orthogonal directions of the magnetic field, the quadrupole shift sums to zero over the three measurements [8].

A second method is to use the information provided by the secular frequencies of the trapped ion to either infer the size of the quadrupole field, or to null it. For our trap parameters, the predicted ratio of the trap frequencies for zero DC quadrupole potential is $r = \omega_z/\omega_r = 2.050$. By adjusting the potentials applied to the trap electrodes such that this ratio is realised, with good micromotion control, then it is known that there is no DC quadrupole field in the trap, and the shift has been nulled* [4]. The accuracy with which this ratio may be set is limited by the knowledge of the trap efficiency $\mathcal{E}$ which, from experimental characterization of the trap is 5%. This corresponds to an uncertainty in r of 0.005 for $r = 2.054$. The gradient dr/dV_{DC} for our operating conditions is calculated to be 0.10 V^{-1} . Combining these gives an uncertainty in locating $V_{DC} = 0$ of 0.02 V, corresponding to a quadrupole shift of 7 mHz.

The trap frequencies can also be used to infer the quadrupole potential and therefore can be used to measure the quadrupole moment. This will give a more reliable measure of the quadrupole moment than the atomic structure calculations. This method has recently been used at NPL to measure the quadrupole moment of the upper state of the 674 nm electric quadrupole transition in $^{88}\text{Sr}^+$ [18].

4.10 Related shifts

In a similar vein to the quadrupole shift, the $^2\text{F}_{7/2}$ state may also have an electric octupole shift, caused by any DC electric octupolar field in the trap interacting with the electric octupole moment of the state. It is expected that this is much smaller than the quadrupole shift both because the shift itself is weaker and because any octupole field in the trap will be comparatively weaker than the quadrupole field.

There is also the possibility of a second-order quadrupole shift affecting the $^2\text{F}_{7/2}$ state. Even in zero DC quadrupole field, there is still a strong ($A \sim 3 \times 10^8$) AC quadrupole field, confining the ion. While the lowest-order quadrupole shift calculated here averages to zero for this AC field, any second-order shift would not. It is expected that this will again be smaller than the shift due DC quadrupole field, or that due to the DC and low frequency Stark effect, as the coupling with other atomic states occurs via the electric quadrupole interaction and the interaction is a much weaker one than the electric dipole interaction.

Another shift which could occur, but has not been investigated in detail, is a magnetic quadrupole (M2) shift. This would only affect the $^2\text{F}_{7/2}$ state, and is expected to be very small, for several reasons. The applied magnetic field is small, and will have a correspondingly small magnetic quadrupole component. The magnetic quadrupole interaction is also a weak one.

*Assuming the potentials on the outer endcaps are being adjusted, it is the common potential of these which gives rise to the quadrupole shift, while the difference potential causes micromotion.

Chapter 5

DC and low-frequency Stark shift

The dc Stark shift is simply the static-field equivalent of the ac Stark shift, discussed in chapter 2. In a low frequency field, where the frequency is much lower than any electric dipole transitions, the shift has the same coefficient, the relevant physical quantity being the mean-square electric field.

5.1 Theory

To re-iterate eq. 2.8, the light shift,

$$\Delta W_E = -\frac{1}{2}\alpha_{\text{sc.}}(\gamma J F) E^2 - \frac{1}{4}\alpha_{\text{ten.}}(\gamma J F) \frac{(3M_F^2 - F(F+1))}{F(2F-1)} (3E_z^2 - E^2). \quad (5.1)$$

and

$$\alpha_{\text{sc.}}(\gamma J F) = \alpha_{\text{sc.}}(\gamma J) \quad (5.2)$$

$$\begin{aligned} \alpha_{\text{ten.}}(\gamma J F) &= (-)^{I+J+F} \left[\frac{F(2F-1)(2F+1)(2J+3)(2J+1)(J+1)}{(2F+3)(F+1)J(2J-1)} \right]^{1/2} \\ &\quad \times \left\{ \begin{matrix} F & J & I \\ J & F & 2 \end{matrix} \right\} \alpha_{\text{ten.}}(\gamma J). \end{aligned} \quad (5.3)$$

The polarisabilities, $\alpha_{\text{sc.}}(\gamma J)$ and $\alpha_{\text{ten.}}(\gamma J)$ are given in terms of reduced matrix elements by [6]

$$\alpha_{\text{sc.}}^{\text{DC}}(\gamma J) = -\frac{2}{3\hbar(2J+1)} \sum_{\gamma' J'} \frac{|\langle \gamma J \| \mu^1 \| \gamma' J' \rangle|^2}{\omega} \quad (5.4)$$

$$\begin{aligned} \alpha_{\text{ten.}}^{\text{DC}}(J) &= -(-)^{2J} \frac{4}{\hbar} \left[\frac{5J(2J-1)}{6(2J+3)(J+1)(2J+1)} \right]^{1/2} \\ &\quad \times \sum_{\gamma' J'} (-)^{J'-J} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J' \end{matrix} \right\} \frac{|\langle \gamma J \| \mu^1 \| \gamma' J' \rangle|^2}{\omega}, \end{aligned} \quad (5.5)$$

which is also what one derives from the AC polarisabilities (equations 2.3 and 2.4) in the limit $\omega_L \rightarrow 0$. In terms of oscillator strengths,

$$\alpha_{\text{sc.}}^{\text{DC}}(\gamma J) = \frac{e^2}{m_e(2J+1)} \sum_{\gamma' J'} \frac{g_{Jf}}{\omega^2} \quad (5.6)$$

$$\alpha_{\text{ten.}}^{\text{DC}}(J) = (-)^{2J} \frac{e^2}{m_e} \left[\frac{30J(2J-1)}{(2J+3)(2J+1)(J+1)} \right]^{1/2} \times \sum_{\gamma'J'} (-)^{J'-J} \left\{ \begin{matrix} 1 & 1 & 2 \\ J & J & J' \end{matrix} \right\} \frac{g_J f}{\omega^2}. \quad (5.7)$$

5.2 Calculation

The calculation of the dc Stark shift is identical to that for the ac shift except that in the summations, evaluated using the code in appendix A, the laser frequency is set to zero.

$$\sum_{\gamma'J'} \frac{g_J f}{\omega^2} (\text{S}, 1/2) = 6.2477 \times 10^{-32} \text{ s}^2 \quad (5.8)$$

and

$$\left(\frac{\Delta\nu^{\text{DC}}(\text{S}, 1/2)}{\text{mHz}} \right) = -6.643 \left(\frac{E^2}{(\text{V/cm})^2} \right). \quad (5.9)$$

$$\sum_{\gamma'J'} \frac{g_J f}{\omega^2} (\text{F}, 7/2) = 3.0448 \times 10^{-31} \text{ s}^2 \quad (5.10)$$

and

$$\left(\frac{\Delta\nu_{\text{sc.}}^{\text{DC}}(\text{F}, 7/2)}{\text{mHz}} \right) = -8.093 \left(\frac{E^2}{(\text{V/cm})^2} \right). \quad (5.11)$$

$$\begin{aligned} \sum_{\gamma'J'} (-)^{J'-7/2} \left\{ \begin{matrix} 1 & 1 & 2 \\ 7/2 & 7/2 & J' \end{matrix} \right\} \frac{g_J f}{\omega^2} = \\ +\frac{1}{4}\sqrt{\frac{1}{7}} \times 7.828 \times 10^{-32} \text{ s}^2 & : J' = 5/2 \\ -\frac{1}{3}\sqrt{\frac{1}{7}} \times 9.866 \times 10^{-32} \text{ s}^2 & : J' = 7/2 \\ +\frac{1}{60}\sqrt{7} \times 1.2754 \times 10^{-31} \text{ s}^2 & : J' = 9/2. \end{aligned} \quad (5.12)$$

This gives,

$$\alpha_{\text{ten.}}^{\text{DC}}(\text{F}, 7/2) = -2.203 \times 10^{-41} \text{ JV}^{-2}\text{m}^2. \quad (5.13)$$

The dc tensor polarisability of the $^2\text{F}_{7/2}$, $F = 3$ state,

$$\begin{aligned} \alpha_{\text{ten.}}^{\text{DC}}(\text{F}, 7/2, 3) &= \frac{25}{28} \alpha_{\text{ten.}}^{\text{DC}}(\text{F}, 7/2) \\ &= -1.967 \times 10^{-41} \text{ JV}^{-2}\text{m}^2 \end{aligned} \quad (5.14)$$

and

$$\begin{aligned} \left(\frac{\Delta\nu^{\text{DC}}(\text{F}, 7/2, 3, 0)}{\text{mHz}} \right) &= \left(\frac{-8.093E^2 - 0.059(3E_z^2 - E^2)}{(\text{V/cm})^2} \right) \\ &= \left(\frac{-8.033E^2 - 0.177E_z^2}{(\text{V/cm})^2} \right). \end{aligned} \quad (5.15)$$

The DC Stark shift of the $^2\text{S}_{1/2}, F=0 \rightarrow ^2\text{F}_{7/2}, F=3, M_F=0$ transition,

$$\begin{aligned} \left(\frac{\Delta\nu^{\text{DC}}(^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) &= \Delta\nu^{\text{DC}}(\text{F}, 7/2, 3, 0) - \Delta\nu^{\text{DC}}(\text{S}, 1/2) \\ &= \left(\frac{-1.391 E^2 - 0.178 E_z^2}{(\text{V/cm})^2} \right). \end{aligned} \quad (5.16)$$

5.3 Estimate of the shift

5.3.1 Micromotion

In the presence of stray DC electric fields, the ion is displaced from the trap centre and experiences a non-zero electric field oscillating at the trap drive frequency. This frequency is much lower than any transition frequency, therefore, the shift will be equal to that produced by a static field of the same strength as the rms (root-mean-square) oscillating field strength. The displacement may be reduced by applying an electric field to cancel out the stray field, and the extent to which one can do this determines the size of the shift. Displaced from the trap centre, the ion also experiences excess micromotion at the trap drive frequency. The amplitude of the ion's motion is measured using a rf-photon correlation technique [19] and this is used as a diagnostic for measuring and reducing the ion's displacement and motion. In order to estimate the size of the shift, the micromotion was first minimized, and the experiment left to run for one hour, and then the micromotion was measured again. This represents the typical maximum level of micromotion during frequency measurements, as it was done at a time of relatively high micromotion drift. The measured mean offset of the ion from the centre of the trapping potential was $\bar{x} = 70$ nm, $\bar{y} = 150$ nm, $\bar{z} = 310$ nm where z is the displacement along the trap axis. The electric field experienced by the ion is

$$\langle E^2 \rangle = \left(\frac{m\omega_{\text{RF}}}{e} \right)^2 \left((\omega_x \bar{x})^2 + (\omega_y \bar{y})^2 + (\omega_z \bar{z})^2 \right). \quad (5.17)$$

For the trap parameters given in section 4.7, using $\omega_z = 2\omega_x = 2\omega_y = 2\pi \times 1.846$ MHz, the total field strength squared is $28.1 (\text{V/cm})^2$. The magnetic field is applied along x , therefore one substitutes E_x for E_z in eq. 5.16 and the field strength squared along the quantisation axis is $0.33 (\text{V/cm})^2$. The DC Stark shift of the $^2\text{S}_{1/2}, F=0 \rightarrow ^2\text{F}_{7/2}, F=3, M_F=0$ transition is then estimated to be -39 mHz.

The stray electric field at the trap originates from the static charge built up on the trap surrounds after loading the trap using electron bombardment and also from the contact potential between ytterbium deposited on the trap electrodes and the tantalum from which they are made. The electron charge leaks away after a period of hours whilst the contact potential is relatively stable, and subsequently the drift in the stray field reduces over time. More recently, photoionisation has been used to load ions into the trap, precluding the use of electron bombardment, and further reducing the drift in the stray field over time. With micromotion minimisation performed in three dimensions, and under conditions where either photoionisation has been used to load the trap, or when a period of hours has passed since loading

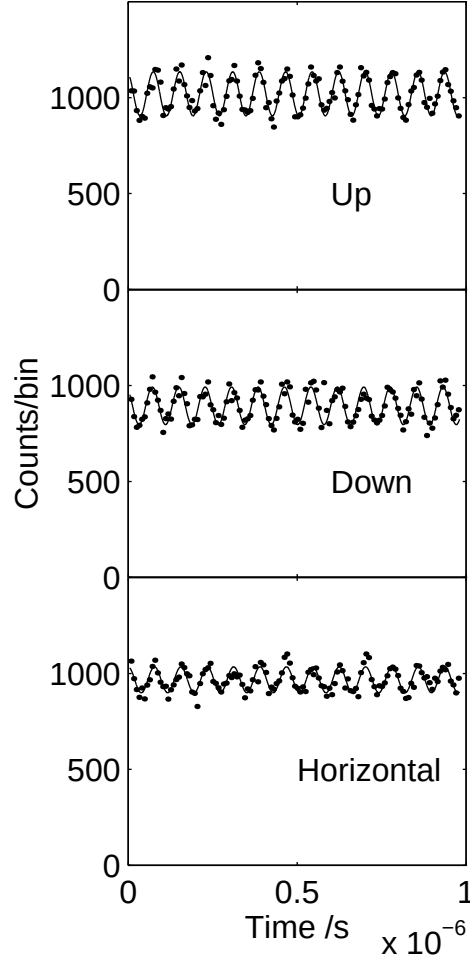


Figure 5.1: Micromotion for three beam directions after minimisation to less than 5%.

by electron bombardment, the displacement of the ion is reduced to a much smaller level. Figure 5.1 shows the micromotion after minimisation to less than 5% in three directions. From the modulation amplitude of the rf-photon correlation signals, the following displacements are derived: $\bar{x} = +80$ nm, $\bar{y} = +46$ nm, $\bar{z} = +2.6$ nm. For this data, a DC field has been applied to the inner electrode, to equalize the axial and radial secular frequencies and $\omega_x = \omega_y = \omega_z = 2\pi \times 1.33$ MHz. The total electric field squared experienced by the ion is then 1.21 (V/cm)². Again the magnetic field is applied along x so one uses E_x in place of E_z and the electric field squared along the quantisation axis is 0.908 (V/cm)². This gives rise to an estimated shift of -1.84 mHz or 3 parts in 10^{18} .

5.3.2 Secular motion

A more fundamental limit to the field experienced by the ion, is the secular (thermal) motion of the ion in the trap. On average, the ion experiences the same electric field for each degree of freedom, therefore the frequency shift of the $^2F_{7/2}$ state is simply that due to the scalar polarisability, given in equation 5.11. Therefore, the DC Stark

shift of the $^2\text{S}_{1/2}, F=0 \rightarrow ^2\text{F}_{7/2}, F=3, M_F=0$ transition due to secular motion,

$$\begin{aligned} \left(\frac{\Delta\nu_{\text{sc.}}^{\text{DC}}(^2\text{S}_{1/2}, 0 - ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) &= \Delta\nu_{\text{sc.}}^{\text{DC}}(F, 7/2) - \Delta\nu^{\text{DC}}(S, 1/2) \\ &= -1.45 \left(\frac{E^2}{(\text{V/cm})^2} \right). \end{aligned} \quad (5.18)$$

An ion at temperature, T , experiences an electric field [20],

$$\langle E^2 \rangle = \frac{m\omega_{\text{RF}}^2 k_{\text{B}} T}{e^2}. \quad (5.19)$$

which at the Doppler limit, kinetic energy $= 1/2 k_{\text{B}} T = \hbar\gamma/4$, where γ is the natural linewidth if the Doppler cooling transition, becomes,

$$\langle E^2 \rangle = \frac{\hbar\gamma m\omega_{\text{RF}}^2}{2e^2}. \quad (5.20)$$

The transition used to cool $^{171}\text{Yb}^+$, at 369 nm has a natural linewidth of $2\pi \times 19.6$ MHz, and the average total electric field squared experienced by the ion, $\langle E \rangle = 0.465(\text{V/cm})^2$. This leads to a DC Stark shift of -0.07 mHz or 1 part in 10^{19} , which is negligible compared to the shift arising from micromotion.

5.3.3 Total shift and uncertainty

The total fractional dc Stark shift with the minimum level of micromotion and with the ion cooled to the Doppler limit, is estimated to be 3×10^{-18} . The uncertainty on the calculation of the dc polarisability is unknown, as there has been no opportunity to calibrate this shift experimentally, but it is expected to be of the correct order of magnitude, as the same calculation for the ac Stark shift gives a coefficient which agrees reasonably well with the measured value, as discussed in section 2.4.

Chapter 6

Second-order Doppler shift

6.1 Theory

The second order Doppler shift, like the DC Stark shift, is directly related to the motion of the ion. If the ion is observed at an angle θ to its direction of motion, and is moving with a velocity v , the observed transition frequency ν_{Obs} is related to the emission frequency ν_{Em} by the relationship

$$\frac{\nu_{Obs}}{\nu_{Em}} = \frac{\sqrt{1 - v^2/c^2}}{1 - (v/c) \cos \theta} \quad (6.1)$$

This can be expanded in powers of (v/c)

$$\begin{aligned} \frac{\nu_{Obs}}{\nu_{Em}} &= \left(1 - \frac{v^2}{2c^2} + \dots\right) \left(1 + \frac{v}{c} \cos \theta + \frac{v^2}{c^2} \cos^2 \theta + \dots\right) \\ &= 1 + \frac{v}{c} \cos \theta + \left(\cos^2 \theta - \frac{1}{2}\right) \frac{v^2}{c^2} + \dots \\ &= 1 + \frac{v}{c} \cos \theta + \frac{v^2}{2c^2} \cos 2\theta + \dots \end{aligned} \quad (6.2)$$

The fractional shift in the transition frequency due to the second-order Doppler shift is $\frac{1}{2}(v^2/c^2) \cos 2\theta$.

6.2 Estimate of the shift

6.2.1 Micromotion

If the ion is displaced from the trap centre by stray fields, it undergoes excess micromotion at the trap drive frequency. The timescale over which the ion is probed is much longer than the period of this motion, therefore, one considers the mean-square velocity of the ion in calculating the shift. This is given by

$$\langle v^2 \rangle = \left(\frac{q_z \omega_{RF}}{2\sqrt{2}} \right)^2 \left[\left(\frac{\bar{x}}{2} \right)^2 + \left(\frac{\bar{y}}{2} \right)^2 + \bar{z}^2 \right] \quad (6.3)$$

where, q_z is the AC stability parameter of the trap introduced in section 4.7. For our particular trap parameters this is equal to 0.408.

At present, micromotion minimisation is performed for 2 dimensions only, and as such, the dominant motion of the ion is perpendicular to the direction of observation and $\theta = \pi/2$. For the level of micromotion observed, the second-order Doppler shift is calculated to be -0.05 Hz. With good micromotion minimisation in 3-D, as shown in section 5.3.1 with $\bar{x} = +80$ nm, $\bar{y} = +46$ nm, and $\bar{z} = +2.6$ nm, one calculates a mean-square velocity, $\langle v^2 \rangle = 0.287 \text{ ms}^{-2}$ and the motion of the ion is at an angle of 55° to the probe beam. This gives a fractional shift of -5.5×10^{-19} or in absolute terms, a shift of 0.4 mHz. The maximum fractional shift, for a similar magnitude of motion, but either along or perpendicular to the beam, is $\pm 1.6 \times 10^{-18}$

6.2.2 Secular motion

The secular or thermal motion of the ion has a mean square velocity,

$$\langle v^2 \rangle = z_a^2 \omega_z^2 \quad (6.4)$$

where, z_a is the amplitude of motion. In the case of a Doppler cooled ion, $z_a = 20$ nm and the trap frequency, $\omega_z = 2\pi \times 1.846$ MHz thus $\langle v^2 \rangle = 0.05 \text{ m}^2\text{s}^{-2}$. The motion of the ion is random, with no well-defined angle to the direction of observation, therefore, the shift has an expectation value of 0. The uncertainty on the fractional shift is 3×10^{-19} or 0.2 mHz in absolute terms. The total fractional second-order Doppler shift, taking into account both secular and micromotion, is estimated to be at most 2×10^{-18} .

Chapter 7

Blackbody shifts

The stainless steel vacuum chamber, its viewports, and the trap electrodes all contribute to the blackbody radiation field experienced by the ion. The electric and magnetic components of this field respectively lead to Stark and second-order Zeeman shifts. The larger of these is the Stark shift.

7.1 Blackbody Stark shift

The blackbody radiation field is isotropic, therefore, the tensor polarisability does not contribute to the shift. The peak of the blackbody spectrum at room temperature lies well below the frequencies of electric dipole resonance transitions from the S and F states. At 297 K, half of the intensity is at wavelengths longer than 14 μm , and 99% is longer than 5 μm therefore, the blackbody radiation field can be approximated by a DC field of the same mean-square field strength and the dc scalar polarisability is used to calculate the shift. The blackbody Stark shift of the $^2\text{S}_{1/2}, F=0 \rightarrow ^2\text{F}_{7/2}, F=3, M_F=0$ transition,

$$\left(\frac{\Delta\nu^{\text{BB}}(^2\text{S}_{1/2}, 0 \rightarrow ^2\text{F}_{7/2}, 3, 0)}{\text{mHz}} \right) = -1.45 \left(\frac{\langle E^2 \rangle}{(\text{V/cm}^2)} \right). \quad (7.1)$$

The electric field is calculated using Plank's law for electromagnetic density (see for example [21]):

$$\begin{aligned} \frac{\epsilon_0}{2} \langle E^2 \rangle + \frac{1}{2\mu_0} \langle B^2 \rangle &= \int_0^\infty \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1} d\omega \\ &= \frac{\pi^2 k^4 T^4}{15 \hbar^3 c^3}. \end{aligned} \quad (7.2)$$

The energy in the magnetic field is equal to the energy in the electric field, thus

$$\langle E^2 \rangle = (7.94 \text{ V/cm})^2 \left(\frac{T_{\text{BB}}}{293 \text{ K}} \right)^4, \quad (7.3)$$

where T_{BB} is the temperature of the radiation field. This gives a blackbody Stark shift of -96 mHz at 297 K. The coefficient of the shift is $-1.24 \times 10^{-11} \text{ HzK}^{-4}$.

The largest uncertainty in the shift arises from the uncertainty in the coefficient, especially as it is the difference between the shifts of the $^2\text{S}_{1/2}$ and $^2\text{F}_{7/2}$ states which are similar in value and have the same sign. The g -factors used in the calculation [9] do not have associated uncertainties, however, they are used to calculate the lifetimes of selected states for which experimental lifetimes are available. If one scales each g -factor with the ratio of the experimental lifetime to the calculated lifetime, and recalculates the coefficient, one arrives at value for the blackbody shift of 57(10) mHz at 297K, where the uncertainty is due to the uncertainty in the experimental lifetime.

Calculating the ac Stark shift using the same procedure, one arrives at a value of 1.12 Hz $I/(\text{W}/\text{cm}^2)$. This is different from the experimental value of $0.48^{+0.07}_{-0.06}$ Hz $I/(\text{W}/\text{cm}^2)$ by more than a factor of two. In fact, making adjustments in the theory using experimental lifetimes takes the calculated value further from the experimental value than if no adjustment is made at all, in which case it is 0.61 Hz $I/(\text{W}/\text{cm}^2)$. There are some transitions with significant contribution to the polarisability for which no lifetime data is available, and perhaps it is the g -factor for these that is cause of the discrepancy. Whatever the cause of the discrepancy, the calculation of the blackbody shift must be treated with caution, and an uncertainty of 100 % does not seem unreasonable. Either further refinement of the calculation so that it agrees better with the measured ac Stark shift, or a direct measurement of the blackbody Stark shift will be required before this uncertainty can be reduced.

One also has to consider the uncertainty in the measured temperature. The shift has a dependence of -0.77 mHz K^{-1} at 297 K which is negligible compared to the uncertainty in the coefficient. An interesting possibility would be if a future definition of the second were to be defined at room temperature. In this case, the uncertainty in the blackbody shift would be reduced to the part in 10^{18} level for a one degree uncertainty in the operating temperature.

7.2 Blackbody second-order Zeeman shift

The magnetic field strength is given by $\langle B^2 \rangle = 6.97 \times 10^{-12} (T_{\text{BB}}/293)^4 \text{ T}^2$. This gives a blackbody second-order Zeeman shift of -13 mHz, using the DC shift coefficient. However, this is not appropriate, as around 99% of the radiation is at frequencies higher than 1.8 THz ($175 \mu\text{m}$), and this is a much higher frequency than the 12.6 GHz and 3.6 GHz transitions taken into account in calculating the DC shift coefficient. Hence their contribution to the blackbody second-order Zeeman shift is very small. There are magnetic dipole transitions in $^{171}\text{Yb}^+$ with wavelengths in the 1–3 μm range, and it is likely that these will make a larger contribution to the coefficient, but this has not been calculated.

Chapter 8

Gravitational redshift

The gravitational redshift is a general relativistic effect, whereby clocks run comparatively slower in stronger gravitational fields. It is necessary to take into account the height of a clock above some defined surface of constant gravitational field strength when coordinating clocks in different locations to produce a global timescale. The fractional shift in frequency, between two clocks at heights h_1 and h_2 ,

$$\begin{aligned}\frac{\Delta\nu}{\nu} &= \frac{1}{c^2} \int_{h_1}^{h_2} \underline{g} \cdot d\underline{h} \simeq \frac{g\Delta h}{c^2} \\ &\simeq 1 \times 10^{-16} \text{m}^{-1}\end{aligned}\tag{8.1}$$

where height is defined as the distance above the mean geoid (a ‘mean earth’). The uncertainty in the local value of g will be $\ll 10^{-4}$, therefore the largest contribution to the uncertainty will be in determining the height above the geoid. The best accuracy to which this has been measured to date, is 0.3 m for the location of the frequency standards at NIST, Boulder [22]. An absolute determination of this height is only necessary if comparing clocks remotely and time transfer techniques, which are currently only good to the part in 10^{15} level, must first be improved before this limits the accuracy. For local comparison of clocks it is sufficient just to know their relative heights, which it should be possible to do at the 0.1 m level.

Chapter 9

Conclusion

9.1 Summary of coefficients

A summary of the well-known and characterised coefficients of the atomic systematic shifts for the octupole transition is shown in Table 9.1. Shifts such as the second-order Doppler shift and gravitational redshift are well-characterised shifts which are independent of the atomic physics of ytterbium ions. Coefficients not included, because they are not well known, include the blackbody and optical second-order Zeeman shifts, the octupole shift and the second-order quadrupole shift.

9.2 Projected limits

Using the measured and calculated coefficients of the systematic shifts, it is possible to estimate the typical sizes of all the shifts for current operating conditions. It is also possible to project the levels to which the shifts may be reduced by improvements in the experiment. The shifts and their uncertainties obtained by this process are tabulated in Table 9.2, and plotted in Figures 9.1 and 9.2. The assumptions for the projected shifts are:

AC Stark shift Moving from 1 mW of light, in a 200 Hz bandwidth, with a spot size of 10 μm and a pulse length of 0.3 s, to 20 mW of light in a 0.1 Hz

Shift	Coefficient	Units
AC Stark*	$(48^{+8}_{-6}) \times 10^{-6}$	Hz W ⁻¹ m ²
DC Stark	$\left(\frac{-1.39 E^2 - 0.18 E_z^2}{(\text{V/cm})^2} \right)$	mHz
Second-order Zeeman	$(-1.72 \pm 0.03) \times 10^9$	Hz T ⁻²
Quadrupole	1.06×10^{-7}	Hz V ⁻¹ m ²
Blackbody AC Stark	-1.24×10^{-11}	Hz K ⁻⁴

Table 9.1: The well-characterised atomic systematic shifts of the octupole transition in $^{171}\text{Yb}^+$. The uncertainties shown are from experimental calibrations. * Note: the measured coefficient is with the electric field of the light at an angle of 25° to the quantisation axis.

bandwidth, with a 1 mm spot size and a 10 s interrogation time.

DC Stark shift The current estimate is based on ‘worst case’ measurements of the motion of the ion, obtained by rf-photon correlation. These give mean displacements of the ion from the centre of the rf field as +70 nm, +150 nm and -310 nm along the x, y, z trap axes, respectively. The projection assumes that micromotion is minimized in 3-D to the levels demonstrated in fig. 5.1.

DC second-order Zeeman shift The current applied DC field is 188 μT , and it is anticipated that this can be reduced to near zero by using polarisation spinning on the 369 nm and 935 nm transitions. A small field will be required to set a quantisation axis for the ion, and separate the Zeeman components of the 467 nm transition. The projected uncertainty assumes that the field can be nulled only with the currently available accuracy of about 1 μT . In fact, the field could be set much more accurately by observation of the Zeeman components of the octupole transition.

50 Hz second-order Zeeman shift Based on measurements made on the NPL strontium-ion frequency standard, the 50 Hz (mains electricity) field is expected to be 500 nT at the present time, and this can be reduced by a factor of 10 with the addition of mu-metal shields around the trap.

Blackbody stark shift The shift is expected to remain the same size, as the operating temperature of the experiment will not change in the near future. The uncertainty is a rough estimate of our confidence in the theoretical calculation of the DC Stark shift coefficient.

Quadrupole shift The effective quadrupole potential on the trap electrodes is assumed to be rectangularly distributed between +1 V and -1 V at the present time. It is expected that the uncertainty can be reduced to 0.02 V by monitoring the trap frequencies.

Second-order Doppler shift The current shift is estimated from measured micromotion amplitudes, as described for the DC Stark shift. The projected shift assumes a Doppler cooled ion and micromotion minimized in 3-D at the level shown in fig. 5.1.

The biggest single shift is currently the AC Stark shift, but as the linewidth of the probe laser narrows, and interrogation times are extended, this shrinks to below the blackbody Stark shift, and has a much smaller uncertainty.

Polarisation spinning of the cooling light at 369 nm has already been demonstrated, and this should allow a large reduction of the second-order Zeeman shift.

After the second-order Zeeman shift, the largest systematic shift (in terms of its uncertainty) is currently the quadrupole shift. This can be reduced to the projected levels by monitoring the trap frequencies and adjusting the dc potentials applied to the trap.

By minimizing micromotion in three dimensions the DC Stark and second-order Doppler shifts can be reduced to very low levels, assuming that the ion is cooled close to the Doppler limit.

Systematic Shift	Current/ Hz	Projected/ Hz
AC Stark	$+(3.1 \pm 1.2) \times 10^2$	$+(4.6 \pm 0.5) \times 10^{-3}$
DC Stark	$-(3.9 \pm 3.9) \times 10^{-2}$	$-(1.8 \pm 1.8) \times 10^{-3}$
DC Zeeman	-61 ± 3	$(0 \pm 1.7) \times 10^{-3}$
50 Hz Zeeman	$-(4.3 \pm 0.4) \times 10^{-4}$	$-(4.3 \pm 0.4) \times 10^{-4}$
BB Stark	$-(6 \pm 6) \times 10^{-2}$	$-(6 \pm 6) \times 10^{-2}$
Quadrupole	0 ± 0.4	$(0 \pm 8.6) \times 10^{-3}$
Doppler	$(0 \pm 5.0) \times 10^{-2}$	$(0 \pm 1.0) \times 10^{-3}$

Table 9.2: Current and projected systematic shifts and associated uncertainties for the octupole transition. The assumptions behind these are outlined in the text.

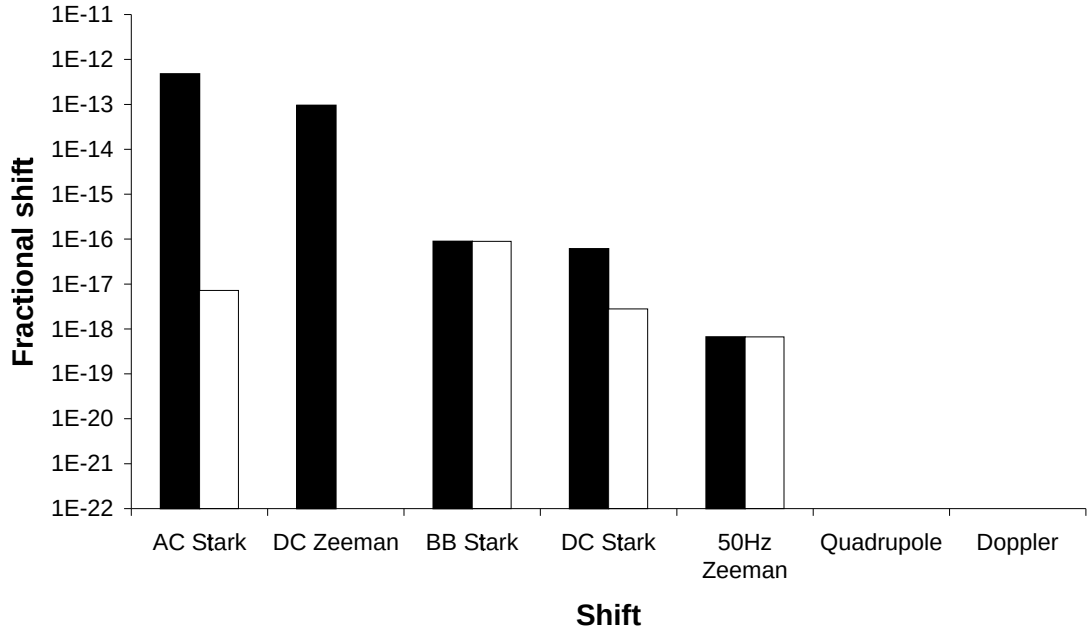


Figure 9.1: Current (black) and projected (white) systematic shifts of the octupole transition, as a fraction of the transition frequency.

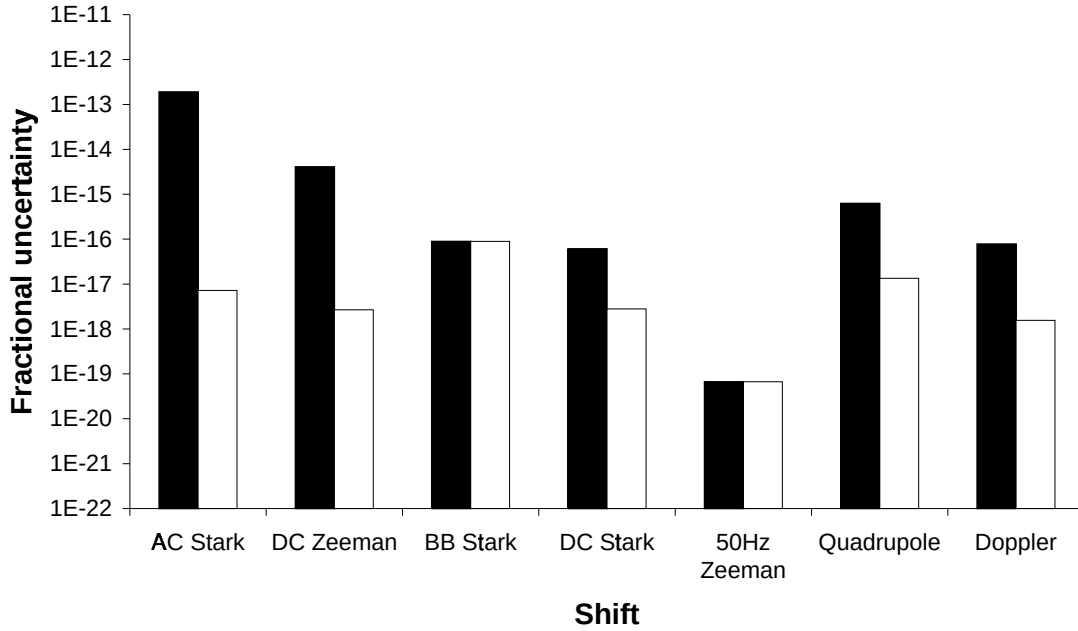


Figure 9.2: The uncertainties of current (black) and projected (white) systematic shifts, as a fraction of the octupole transition frequency.

The blackbody Stark shift has the largest projected uncertainty and this will limit operation of the standard to the part in 10^{16} level. There is potential for this to be improved by direct measurement of the coefficient, or indirectly, by measuring the DC Stark shift coefficient. If the theory were to be refined, such that there was better agreement between the experimental and calculated values of the ac Stark shift, this would give more confidence in the calculation for the blackbody Stark shift and could also lead to a reduction in its uncertainty. Alternatively, if an ‘operating temperature’, near room temperature were defined, the shift, and its uncertainty, would be reduced to the part in 10^{18} level.

If the uncertainty on the blackbody Stark shift could be reduced by calibration or measurement, the limiting factor in the projected systematic shifts would then be the quadrupole shift. This is projected to be at the 1×10^{-17} level, though careful measurement and calibration could reduce this uncertainty further. With a 0.1 Hz laser linewidth, the line profile must be subdivided by a factor of 20 to achieve a 1×10^{-17} frequency measurement uncertainty. To reduce it further below the projected levels, the scheme of averaging frequencies measured for three perpendicular directions of magnetic field can be applied [8]. The resolution of this technique is limited by the laser linewidth and variations of other systematic shifts, and will require a laser much narrower than 0.1 Hz. For the near-to medium-term, it therefore appears that the achievable performance will be around this level. This is based on the assumption that shifts not dealt with here, such as the blackbody second-order Zeeman shift, octupole shift, etc, are not significant on these scales.

For absolute frequency measurements, this analysis ignores issues involved in relating the transition frequency to the SI second via caesium. Caesium standards

have not reached, and may not reach, this level of accuracy. Once the projected performance levels are achieved, as they are expected to be over the next few years by a number of trapped-ion frequency standards, the case for re-definition of the second in terms of an optical standard will grow. The low systematic shifts and clear potential for further development offered by the octupole transition place it as one of the strong candidates to be the next primary standard.

Appendix A

Matlab code for calculation of Stark shift

A.1 $^2S_{1/2}$ state

```
% calculation of summation over excited states in Stark shift calculation
% using data from - Biemont et al J Phys B31,3321(1998).
% shift for 2S1/2 level
```

```
clear all
```

```
%   energy   gf   1/2 3/2
S=[ 27062   0.474   1   0;
    28758   0.048   0   1;
    30392   0.887   0   1;
    32982   0.034   0   1;
    33654   0.082   1   0;
    34575   0.166   0   1;
    39379   0.012   1   0;
    43075   0.024   0   1;
    44941   0.200   0   1;
    45737   0.102   0   1;
    46903   0.109   1   0;
    47005   0.139   0   1;
    47229   0.046   1   0;
    55221   0.014   0   1;
    65594   0.011   0   1];
```

```
% calculates gf/(w^2-wlaser^2)
```

```
% w=2.pi.100.c.lamdabar
```

```
% energy in cm^-1
```

```
% S level has energy 0 cm^-1
```

```
c=299792458; %ms^-1
```

```
wlaser=0; %s ^-1
```

```
% For calculation of DC shift
```

```
%wlaser=2*pi*100*c*21419; %s ^-1      % For calculation of AC shift
gfw2=S(:,1); gfw2=2*pi*100*c*gfw2;
gfw2=S(:,2)./(gfw2.^2-wlaser.^2);
S(:,3)=S(:,3).*gfw2;
S(:,4)=S(:,4).*gfw2;
sum(S(:,3))
sum(S(:,4))
```

A.2 $^2\text{F}_{7/2}$ state

```
% calculation of DC stark shift constant
% using data from - Biemont et al J Phys B31,3321(1998)
```

```
% shift for  $2\text{F}_{7/2}$  level
```

```
%   energy   gf   5/2  7/2  9/2
F=[ 47912   0.011    0    1    0;
    48900   0.121    0    1    0;
    49301   0.242    0    0    1;
    49498   0.177    1    0    0;
    53721   0.011    0    0    1;
    56376   1.065    1    0    0;
    57765   3.651    0    0    1;
    58284   0.020    1    0    0;
    58824   0.864    1    0    0;
    59090   3.286    0    1    0;
    59259   0.151    1    0    0;
    59619   0.132    0    1    0;
    61051   0.124    0    1    0;
    61215   0.465    0    0    1;
    61374   0.087    1    0    0;
    63234   0.589    1    0    0;
    63702   0.010    1    0    0;
    63727   0.329    0    0    1;
    64056   0.063    1    0    0;
    64598   0.267    0    1    0;
    65093   0.092    0    1    0;
    65200   0.299    0    0    1;
    65577   0.047    0    1    0;
    66351   0.029    1    0    0;
    66558   0.072    0    1    0;
    67416   0.035    0    0    1;
    67939   0.068    0    1    0;
    68450   0.108    0    1    0;
    68549   0.013    0    0    1;
    69080   0.017    1    0    0;
```

69395	0.047	0	1	0;
70858	0.129	0	0	1;
70954	0.15	1	0	0;
71222	0.015	0	1	0;
71469	0.10	1	0	0;
73283	0.112	0	0	1;
73751	0.192	0	0	1;
73967	0.012	0	1	0;
74270	0.019	1	0	0;
74973	0.019	0	1	0;
75551	0.083	1	0	0;
76170	0.083	1	0	0;
76323	0.013	0	1	0;
76676	0.263	1	0	0;
76839	0.103	1	0	0;
77449	0.016	0	1	0;
77607	0.457	1	0	0;
77747	0.376	0	0	1;
77882	0.048	0	1	0;
78070	1.592	0	0	1;
78815	0.012	1	0	0;
79127	0.016	0	0	1;
79629	1.408	0	1	0;
80458	0.028	0	1	0;
81313	0.083	1	0	0;
81657	0.084	1	0	0;
81693	0.084	0	1	0;
82892	0.046	1	0	0];

```
% calculate gf/(w^2)
% w=2.pi.100.c.lamdabar
% f level has energy 21419 cm^-1
c=299792458; %ms^-1
wlas=0; %s ^-1 % For calculation of DC shift
%wlas=2*pi*100*c*21419; %s ^-1 % For calculation of AC shift

gfw2=F(:,1) - 21419; gfw2=2*pi*100*c*gfw2;
gfw2=F(:,2)./(gfw2.^2-wlas.^2);
F(:,3)=F(:,3).*gfw2;
F(:,4)=F(:,4).*gfw2;
F(:,5)=F(:,5).*gfw2;
sum(F(:,3))
sum(F(:,4))
sum(F(:,5))
```


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