Measurement of the Electric Quadrupole Moment of the $4d\,^2D_{5/2}$ Level in $^{88}\mathrm{Sr}^+$

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The quadrupole moment of the $4d\,^2D_{5/2}$ level in $^{88}\mathrm{Sr}^+$ has been measured to be $2.6(3)ea_0^2$, where a_0 is the Bohr radius and e the elementary charge. A single laser-cooled strontium ion was confined in an end cap trap with a variable dc quadrupole potential, and measurements were made on the $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ transition at 674 nm using a femtosecond optical frequency comb. This work shows that measurements of the unperturbed $^{88}\mathrm{Sr}^+$ transition frequency with sub-Hz uncertainty are possible and is important in understanding the reproducibility of ion trap optical frequency standards.

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Atomic frequency standards have long played a key role in advances in science and technology, with applications ranging from the realization of the Système International (SI) base units of time and length to precision measurements of fundamental constants and investigations of their possible variation with time [1]. Optical frequency standards based on narrow-linewidth forbidden transitions in single laser-cooled trapped ions offer the possibility of improved stability and accuracy compared to microwave standards, due to the much higher Q factors of the transitions involved. A number of such optical frequency standards are currently being developed worldwide, for example, based on transitions in $^{199}\mathrm{Hg}^+$ [2], $^{171}\mathrm{Yb}^+$ [3,4], $^{115}\mathrm{In}^+$ [5], and $^{88}\mathrm{Sr}^+$ [6,7]. These standards can already be used to realize the SI meter [8], and significant improvements are expected over the next few years. Fourier-transform limited linewidths as narrow as 6.7 Hz [2] and instabilities as low as 7 parts in 10^{15} at 1 s [9] have recently been reported for the $^{199}\mathrm{Hg}^+$ ion. The development of femtosecond laser optical frequency combs has also greatly simplified the measurement of optical frequencies [10,11], and made it possible to operate these standards as optical clocks [9]. Together these results point to the potential of trapped ion optical frequency standards to outperform the cesium primary microwave standard in the longer term, and raise the possibility of a future redefinition of the second.

At present, there are a number of optical transitions in cold trapped ions and atoms that are potential candidates for a redefinition of the second, and so it is important to investigate both experimentally and theoretically the systematic frequency shifts that can be expected for each system. In many of the trapped ion systems that are being studied, it is expected that the largest source of uncertainty will arise from the electric quadrupole shift of the reference transition, which is due to the interaction between the electric quadrupole moment of the atomic states with any residual electric field gradient present at the position of the ion. The resulting frequency shift can easily be several Hz or more, although it averages to zero if measurements are carried out for three mutually perpendicular orientations of the applied magnetic field [12]. However, there has been no systematic study of this effect to date for any ion, although there has been a single-point measurement of the electric quadrupole shift in $^{199}\mathrm{Hg}^+$ [2] and a preliminary measurement has been made of the quadrupole moment of the $^2D_{3/2}$ level in $^{171}\mathrm{Yb}^+$ [13]. Here we report a detailed investigation of the electric quadrupole shift of the $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ clock transition in $^{88}\mathrm{Sr}^+$, from which we deduce a value for the quadrupole moment of the $4d\,^2D_{5/2}$ state and compare our result with theoretical predictions.

A partial term scheme showing the transitions involved in cooling and probing $^{88}\mathrm{Sr}^+$ is shown in Fig. 1. The ion is cooled on the $5s\,^2S_{1/2}$–$5p\,^2P_{1/2}$ transition at 422 nm, using a frequency doubled diode laser at 844 nm. Since the $5p\,^2P_{1/2}$ level can also decay to the $4d\,^2D_{3/2}$ metastable level, a 1092 nm laser diode is used to drive the ion back into the cooling cycle. The $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ clock transition is interrogated using a narrow-linewidth extended cavity diode laser at 674 nm. This laser is stabilized to a high-finesse ultra-low-expansion (ULE) cavity,

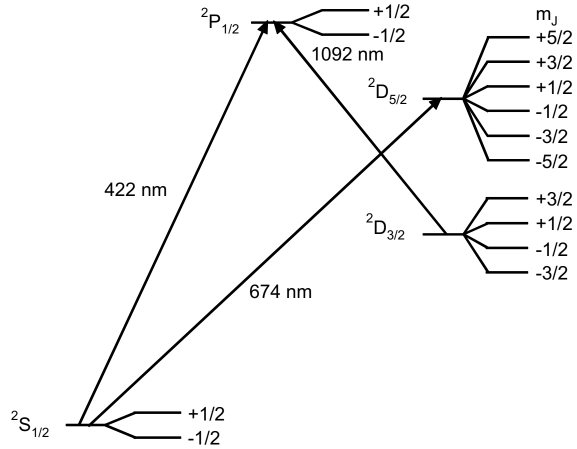

FIG. 1. Partial term scheme for $^{88}\mathrm{Sr}^+$, showing the energy levels relevant to the operation of the optical frequency standard.

which is housed in a temperature-controlled evacuated chamber, within a two-stage temperature-controlled enclosure. This reduces the cavity drift rate to typically 0.1–0.2 Hz/s. The probe laser is locked to the ULE cavity using a Pound-Drever-Hall lock [14] with a modulation frequency of ≈15 MHz and has a linewidth of less than 100 Hz.

Previous National Physical Laboratory (NPL) frequency measurements of the $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ transition in $^{88}\mathrm{Sr}^+$ were made on single ions confined in a ring (Paul) trap [7]. The limited optical access in this trap meant that we were unable to monitor the motion of the ion transverse to the cooling and probe beam direction, and so it is possible that the frequency of the 674 nm transition was perturbed by transverse Doppler shifts. In the new NPL system, an end cap trap [15] is used, similar in design to that described by Roberts *et al.* [16]. The rf trap voltage (260 V amplitude at a frequency $\Omega/2\pi = 17.8$ MHz) is applied to the inner end cap electrodes, which have a spacing of 0.56 mm.

With the end cap trap, it is possible to monitor and minimize the ion micromotion along three orthogonal axes using rf-photon correlation techniques [17,18]. Minimization of the micromotion is achieved by adjusting the bias voltages on the outer end cap electrodes and on two compensation electrodes positioned in the plane perpendicular to the trap axis which move the ion in the radial direction. The rf-photon correlation signals observed indicate that the residual second-order Doppler shifts (longitudinal and transverse to the probe beam) due to excess micromotion have been reduced to less than 10 mHz.

The trap is mounted inside a mu-metal shield to reduce the effect of the Earth's magnetic field. Three pairs of coils are mounted in orthogonal directions around the trap to further reduce the dc magnetic field. In order to determine the direction of the applied magnetic field, the coils were initially used to null the field to a level of 70 nT, which was measured from the Zeeman splitting of the $^2S_{1/2}$–$^2D_{5/2}$ transition at 674 nm. The nulling was achieved by iteratively minimizing the field using the three coils in turn. The magnetic field applied by each coil for a given current was also determined. A magnetic field of typically 1.2 μT was then applied in a known direction using one of the three coils.

The clock transition is interrogated with a computer-controlled sequence during which the ion is cooled at 422 nm and then probed at 674 nm [19]. During the probe laser pulses, the cooling and repumping lasers are blocked by a combination of shutters and acousto-optic modulators. This prevents broadening and frequency shifts of the 674 nm transition resulting from Stark shifts caused by the 422 and 1092 nm beams. The probe laser pulses are typically 5 ms in duration, giving a Fourier-transform-limited linewidth of approximately 200 Hz. The probe laser frequency is locked to the center of the Zeeman structure using a four-point servo scheme which employs the two $\Delta m_J = 0$ components which are symmetrically placed around line center. In contrast to earlier NPL work which used a servo scheme with fixed-size frequency corrections [20], we use a proportional correction scheme similar to that described by Bernard *et al.* [21]. However, the proportional servo can lead to offsets from the true line center, depending on the ULE cavity drift rate, the servo gain, and the observed transition linewidth. To reduce the effect of this problem, we have introduced a "feed-forward" drift compensation scheme. Since the ULE cavity drift is fairly linear over time scales of a few minutes, a frequency correction is applied at each servo step based on the ULE cavity drift measured over the previous few minutes. This correction is applied before the servo correction and reduces the servo errors caused by the ULE cavity drift. With these improvements, the standard error of the mean of a set of one hundred 10 s measurements is typically 8–10 Hz.

In a quadrupole trap, the potential in the vicinity of the ion can be written as

$$\phi = (Q_{\mathrm{dc}} + Q_{\mathrm{ac}}\cos\Omega t)(x^2 + y^2 - 2z^2), \qquad (1)$$

where Q_{dc} and Q_{ac} are the dc and ac components of the quadrupole field gradient, respectively. Here Q_{dc} includes not only the quadrupole field gradient arising from the voltages applied to the outer end cap electrodes, but also additional field gradients due to contact potentials arising from strontium metal deposited on the trap electrodes or dc voltages applied to the compensation electrodes. Equation (1) assumes that the trap is symmetric about the quadrupole axis. Evidence that this is the case for our trap comes from the observation that the radial secular frequencies ω_x and ω_y are degenerate within the experimental uncertainty. For the $5s\,^2S_{1/2}$–$4d\,^2D_{5/2}$ clock transition in $^{88}\mathrm{Sr}^+$, the electric quadrupole shift of the transition frequency is entirely due to the shift of the $4d\,^2D_{5/2}$ level, since the $5s\,^2S_{1/2}$ state has no quadrupole moment. If the angle between the quadrupole axis and the magnetic field is given by β, the frequency shift for the $4d\,^2D_{5/2}$ ($m_J = \pm\frac{1}{2}$) levels in $^{88}\mathrm{Sr}^+$ is

$$\Delta\nu = k(3\cos^2\beta - 1), \qquad (2)$$

where

$$k = \frac{2}{5\pi\hbar} Q_{\mathrm{dc}}\Theta(D, 5/2) \qquad (3)$$

and $\Theta(D, 5/2)$ is the quadrupole moment of the $4d\,^2D_{5/2}$ state.

A quadrupole trap is normally characterized by dimensionless parameters a and q which relate to the dc and ac components of the quadrupole field gradient, respectively. For an ion of mass m and charge e, the parameter a is defined by

$$a = \frac{8eQ_{\mathrm{dc}}}{m\Omega^2}. \tag{4}$$

The radial and axial secular frequencies ω_r ($\equiv \omega_x$ or ω_y) and ω_z are related to the parameters a and q by the approximate relationship [22,23]

$$\left(\frac{2\omega_i}{\Omega}\right)^2 = a_i - \left(\frac{a_i - 1}{2(a_i - 1)^2 - q_i^2}\right)q_i^2 - \left(\frac{5a_i + 7}{32(a_i - 1)^3(a_i - 4)}\right)q_i^4, \tag{5}$$

which is correct to order q_i^4. Here $i \in \{r, z\}$, $a \equiv a_r = -a_z/2$, and $q \equiv q_r = -q_z/2$. This pair of equations can be solved to determine a and q from the measured secular frequencies ω_r and ω_z, and Eq. (4) is then used to determine the dc quadrupole field gradient Q_{dc}. In order to arrive at a standard uncertainty in the determination of Q_{dc}, we allow 1% for a possible calculation error due to the terms neglected in the expansion series [22], and also a 20 kHz measurement uncertainty in ω_r and ω_z. The latter arises both from ULE cavity drift and from day-to-day changes observed in the secular frequencies due to changes in contact potentials arising from strontium metal deposits and the radial compensation electrode voltages required to minimize the micromotion. This uncertainty was evaluated by measuring the secular frequencies on different days, having reloaded the trap and reminimized the micromotion in each case. When making the quadrupole shift measurements, the secular frequencies were measured on the day prior to frequency measurements, in order to minimize the uncertainty caused by variations of Q_{dc} over longer periods.

Frequency measurements of the 674 nm transition were carried out using a femtosecond comb [7] referenced to the 10 MHz output of a hydrogen maser, which was transmitted to the femtosecond comb laboratory via 250 m of RG213 coaxial cable. Temperature-induced shifts of the reference frequency were measured and corrected for by monitoring the round trip delay time, but typically shifted the measured frequencies by no more than 1 Hz.

The strontium ion trap was operated with different dc end cap voltages, to give different dc quadrupole field gradients Q_{dc}, with the micromotion of the ion being minimized in three dimensions and the secular frequencies being measured in each case. At each value of Q_{dc}, the frequency of the 674 nm transition was measured for each of three magnetic field directions. One of these magnetic field orientations was horizontal ($\beta = 90°$); the others, nominally orthogonal to the first, corresponded to angles β of $\approx 11°$ and $\approx 101°$. The probe beam entered the trap at an angle of about 22.5° to the horizontal, allowing the $\Delta m_J = 0$ Zeeman components to be observed in all cases [24]. For each data point, corresponding to data taken on a particular day, two to four sets of approximately one hundred 10 s readings were taken for each of the three magnetic field directions.

The measured frequencies over the three orthogonal directions were used to determine both the unperturbed transition frequency ν_0 [12] and the quadrupole shift parameter $k = 2Q_{\mathrm{dc}}\Theta(D, 5/2)/5\pi\hbar$ in Eq. (2). These parameters were estimated via a least-squares fit of the three frequency values $\{\nu_i\}$ to the equation $\nu_i = \nu_0 + kg_i$, where $\{g_i\}$ is the set of three geometrical factors. Since the second-order Zeeman shift of the transition frequency is only 5.6 μHz$/\mu$T^2, the change in this shift between the different magnetic field directions can be neglected at the typical field values used. Measurements were carried out at several different values of the mean end cap voltage between approximately -5 and $+16$ V, corresponding to values of the dc quadrupole field gradient Q_{dc} from -16 to $+36$ V/mm^2. To minimize any systematic effect on the slope due to varying contact potentials, Q_{dc} was not always changed in the same direction. Also, for some values of Q_{dc}, measurements were repeated several days apart in order to verify the reproducibility. The measured value of k deduced from each set of frequency measurements was then plotted against Q_{dc} as calculated from the measured secular frequencies, and the result is shown in Fig. 2. The vertical error bars on this plot represent a combination of the measurement statistics and a contribution from the reproducibility with which the magnetic field direction can be set. The horizontal error bars arise from the uncertainty in the determination and reproducibility of the secular frequencies. The value of k at zero dc quadrupole field gradient is 1.5(1.6) Hz, consistent with zero within experimental uncertainty, as expected. The fitted slope is 1.31(0.10) Hz mm^2/V, where the standard uncertainty is shown in parenthesis. However, uncertainties in the geometry give rise to a systematic uncertainty in the slope.

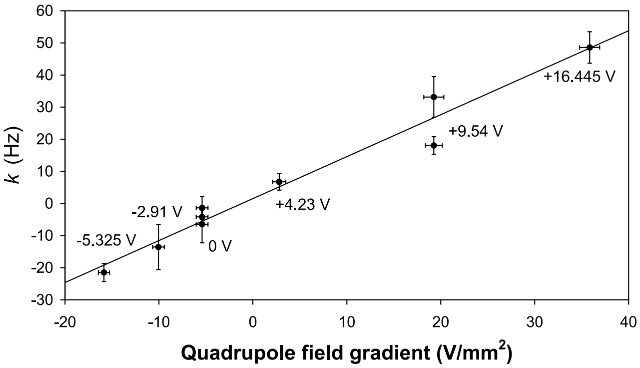

FIG. 2. Quadrupole shift parameter k of the $4d\,^2D_{5/2}$ level of ^{88}Sr$^+$ measured as a function of the dc quadrupole field gradient. Each data point represents the value of k [as defined by Eqs. (2) and (3)] determined from frequency measurements carried out at three orthogonal magnetic field directions on the same day. The voltages shown by each data point are the mean of the dc voltages applied to the two end cap electrodes.

There is an uncertainty in the direction of the quadrupole axis defined by Eq. (1) due to imperfections in the electrode geometry, contact potentials, and voltages applied to the compensation electrodes. There is also uncertainty in the measurement and nulling of the magnetic field; for example, the 70 nT residual field, in the worst case, contributes a 3° error in an applied field of 1.2 μT. The three field directions used in the measurement therefore are not in general exactly orthogonal nor aligned with the trap axis, and our estimated total uncertainty in the value of β arising from all these effects is 10°. The effect of this uncertainty was calculated in order to determine the resulting systematic uncertainty. Since the angles chosen are nearly orthogonal, and one axis is only 11° from the trap axis, calculations show that angular errors always increase the slope estimated from the data. For errors of $\pm 10°$, the slope can increase by up to 0.24 $\mathrm{Hz\,mm^2/V}$. We therefore added a correction of 0.12(0.12) $\mathrm{Hz\,mm^2/V}$. A final uncertainty arises from the Stark shift, since this depends on the magnetic field direction and could therefore look like a quadrupole shift. The change in the measured unperturbed optical frequency at different values of Q_{dc} was zero to within 0.15 $\mathrm{Hz\,mm^2/V}$, giving a limit on the change in electric field as Q_{dc} was varied. From the calculated ratio between the tensor and scalar Stark shifts, the resulting uncertainty in the slope of Fig. 2 is estimated to be 0.07 $\mathrm{Hz\,mm^2/V}$. Adding the uncertainties in quadrature gives a final value and uncertainty of the slope as 1.43(0.17) $\mathrm{Hz\,mm^2/V}$. When multiplied by $5\pi\hbar/2$, the slope gives the quadrupole moment as $\Theta(D, 5/2) = 2.6(3)ea_0^2$, where a_0 is the Bohr radius and e the elementary charge.

This value can be compared with that obtained from calculations using the COWAN code [24]. The quadrupole moment for $^{88}\mathrm{Sr}^+$ can be related to a radial matrix element in a similar way to the formula derived for mercury [12], giving

$$\Theta(D, 5/2) = \tfrac{2}{7}e\langle 4d|r^2|4d\rangle. \tag{6}$$

The COWAN code gives a value of $10.59a_0^2$ for the radial matrix element, so that $\Theta(D, 5/2) = 3.0ea_0^2$. This is about 1.3σ higher than our experimental determination.

The relationship between mean end cap voltage and dc quadrupole field gradient can be expected to change slowly over time scales of several months. To determine the unperturbed clock transition frequency as accurately as possible therefore requires the relationship between the mean end cap voltage and the quadrupole field gradient to be remeasured close in time to the frequency measurements. Assuming similar uncertainties to the present work, we estimate that we can reduce the quadrupole shift to less than 4 Hz in the worst case when the magnetic field is aligned with the trap axis. Allowing for uncertainties in the magnetic field direction, it should therefore be possible to reduce the uncertainty due to the quadrupole shift in an absolute frequency measurement to the sub-Hz level by making repeated measurements in three orthogonal magnetic field directions. Stark shifts due to the ac trapping potential are estimated to be no larger than about 0.3 Hz for our trap. A similar size Stark shift will arise from blackbody radiation, if the transition frequency is corrected to absolute zero. This work therefore demonstrates the possibility of reducing all systematic shifts for the strontium ion standard to the sub-Hz level.

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