Developing a field independent frequency reference

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Abstract
We show that by averaging over transitions to multiple hyperfine levels, quadrupole shifts and dominant Zeeman effects exactly cancel whenever the nuclear spin, $I$, is at least as large as the total electronic angular momentum, $J$. The average frequency thus defines a frequency reference which is inherently independent of external magnetic fields and electric field gradients. We use Lu$^+$ to illustrate the method although the approach could be readily adapted to other atomic species. This approach practically eliminates the quadrupole and Zeeman shift considerations for many potential clock transitions.

1. Introduction
The realization of accurate, stable frequency references have enabled important advances in science and technology. Well-known examples include the global positioning system, geodesy, and test of fundamental physical theories. Increasing levels of accuracy continue to be made with atomic clocks based on optical transitions in isolated atoms [1–8]. By now a number of groups have demonstrated superior performance over the current caesium frequency standard with the best clocks to date having inaccuracy at the $10^{-18}$ level [1, 2]. To date, all optical clocks are based on the frequency of a single atomic transition. For this reason transitions between $J = 0$ levels have had a prominent role in the development of optical clocks due to their inherent insensitivity to electromagnetic fields. In almost all cases averaging over near-degenerate Zeeman transitions is used to cancel or deduce residual shifts from external fields. This need not be the only approach: averaging over multiple, non-degenerate transitions can provide a frequency standard less susceptible to external perturbations.

Recently it was shown that averaging over two clock transitions could be used to suppress blackbody radiation (BBR) shifts [9]. The basic idea of the method relies upon the fact that a frequency comb, when referenced to two different frequencies $f_1$ and $f_2$, provides access to frequencies of the form $f_n = f_1 + n f_2$ for integers $n$, $m$. When $f_1$ and $f_2$ vary due to an external influence, a suitably chosen pair of integers provides a frequency $f_n$ in which the external influence can be substantially minimized. More recently a similar idea has been proposed for molecular spectroscopy in which a weighted average of multiple frequencies was shown to be much less susceptible to external influences than the composite or average frequency [10]. However, in both of these cases, the component transitions and their systematic shifts have no direct relationship. Hence, the correct weights for the averaging are subject to measurement or calculation errors in their determination, which is problematic in so far as defining a frequency standard is concerned.

Here we show that a composite frequency can be constructed in which the cancellation of systematic shifts comes directly from invariant properties of the underlying Hamiltonian. Specifically we show that averaging over transitions to multiple hyperfine levels can lead to an exact cancellation of quadrupole shifts and dominant Zeeman effects whenever $I \geq J$, where $I$ is the nuclear spin and $J$ is the total electronic angular momentum. This generalizes currently established methods of averaging to cancel important systematic shifts of a single transition frequency. Our approach practically eliminates Zeeman and quadrupole shifts in developing a frequency standard by realizing an effective $J = 0$ level. We start with a description of the general idea, treating first the Zeeman shifts from external magnetic fields and then the quadrupole shifts from electric field gradients. We
then illustrate our method using Lu⁺ and Sr⁺ as concrete examples but the method would be applicable to many other atomic species.

2. Averaging method

Let us first consider the effects of an external magnetic field. The Hamiltonian for a given fine structure level is block diagonal in \( m_F \). Each block has the general form

\[
H = H_0 + H_1 + H_2
\]

where \( H_0 \) is a diagonal matrix of the zero field energies \( E_F \), \( H_1 \) is diagonal with entries \( g_F \mu_B B \) corresponding to the first order Zeeman shifts, and \( H_2 \) has only off-diagonal entries responsible for deviations from the from the first order Zeeman effect. If we consider the average value of the diagonal elements, \( H_2 \) does not contribute and we are left with

\[
\langle H_{F,F} \rangle = \langle E_F \rangle + m_F \langle g_F \rangle \mu_B B
\]

(2)

If \( I > J \), it is easily shown that \( \langle g_F \rangle = g_f \). This average is an invariant of \( H \) and hence, for a given \( |m_F| \leq I - J \), the average shift over all \( F \) states is simply \( m_F \mu_B B \) identical to that for a \( I = 0 \) level. When \( I = J \) the result still applies although we are restricted to the consideration of \( m_F = 0 \) states. We note that this is an invariant property of \( H \) and applies even if there is significant mixing of the hyperfine states.

The quadrupole shift due to electric field gradients can be treated as a perturbation on the previous result, as the shift is typically much less than the Zeeman splitting between \( m_I \) levels. The shift for each \( |F, m_F\rangle \) state is simply the diagonal elements of the interaction given, in the low field limit, by [11]

\[
\langle F, m_F| H_Q |F, m_F \rangle = (-1)^{2F-m_F + I+J} (2F+1) \left( \begin{array}{cc} F & m_F \\ -m_F & 0 \end{array} \right) \left( \begin{array}{cc} F & 2 \\ 2 & F \end{array} \right) \left( \begin{array}{cc} F & 2 \\ 0 & F \end{array} \right)
\]

(3)

\[
x^{(j)} \left( \begin{array}{cc} 1 & 2 \\ -2 & 1 \end{array} \right) \Theta(j) \left[ A \left( 3 \cos^2 \beta - 1 + \epsilon \sin^2 \beta \right) \left( \cos^2 \alpha - \sin^2 \alpha \right) \right].
\]

(4)

In this expression, the first line determines the relative size of the shift for each of the \( |F, m_F\rangle \) states. The terms in square parentheses on the second line concern only the trap geometry with respect to the quantization axis.

Specifically, the electric potential, \( \Phi \), in a neighbourhood of the atom, is given in the principal-axis coordinates by

\[
\Phi(x, y, z) = A \left[ x^2 + y^2 - 2z^2 + \epsilon \left( x^2 - y^2 \right) \right].
\]

(5)

The Euler angles, \( \alpha \) and \( \beta \), determine the rotation of the principal-axis coordinate system with respect to the laboratory frame defined by the quantization axis. The rest of the terms on the second line characterize the magnitude of the quadrupole coupling, with \( \Theta(j) \) giving the quadrupole moment for the fine structure level of interest as defined in [11].

It is known that averaging the quadrupole shift over all \( m_F \) states for a fixed \( F \) yields zero [12]. This follows immediately from the expression above and \( 3j \)-symbol identities. It has also been pointed out that averaging over three orthogonal spatial orientations of the quantization axis also gives zero [11]. However this approach is limited by the accuracy at which the field orientations can be set [3]. What is perhaps less well known is that averaging over all hyperfine states for a fixed \( m_F \) also gives zero provided \( I \geq J \) and \( |m_F| \leq I - J \). Under these conditions, the expansion of \( |F, m_F\rangle \) in the ladder basis includes all possible values of \( m_J \) and may be written

\[
|F, m_F\rangle = \sum_{m_J} C_{F,m_J} \left( \begin{array}{cc} J & m_F - m_J \end{array} \right). 
\]

(6)

From this expansion we have

\[
\sum_F \langle F, m_F| H_Q |F, m_F \rangle = \sum_{m_J} C_{F,m_J} C_{F',m_J'} \langle J, m_J | H_Q |J, m_J \rangle \delta_{m_J', m_J} 
\]

(7)

\[
= \sum_{F,m_J} C^2_{F,m_J} \langle J, m_J | H_Q |J, m_J \rangle 
\]

(8)

\[
= \sum_{m_J} \langle J, m_J | H_Q |J, m_J \rangle .
\]

(9)

where we have used that fact that \( H_Q \) is independent of nuclear spin and \( \sum_{F} C^2_{F,m_J} = 1 \). Since the average of the quadrupole shift over all \( m_J \) is zero [4, 11], it therefore follows that the shift vanishes when averaged over all \( F \).
The \( \Delta m T \) and \( \Delta m F \) in equation (7) is then simply a label for the \( 2F + 1 \) eigenstates associated with the particular \( m_F \). We also note that the average over all \( m_F \) for any tensor operator is zero, which follows directly from the Wigner–Eckart theorem. Hence the derivation above is quite generally applicable.

3. Discussion

The averaging we have described leads to an effective \( J = 0 \) level in so far as magnetic fields and electric field gradients are concerned. This provides a greater degree of flexibility in considering potential clock transitions. It allows one to capitalize on other favourable properties of a transition and still retain the benefits provided by a \( J = 0 \) level. To illustrate these considerations we first consider Lu\(^{176}\) as a concrete example.

We have recently begun to explore singly ionized lutetium as a possible clock candidate. The ion has a similar level structure to neutral barium with a spin singlet \( ^1S_0 \) ground state and a low lying triplet of \( D \) levels as illustrated in figure 1(a). Our focus is on the highly forbidden \( M_1 \) transition, \( ^1S_0 \rightarrow ^3D_1 \), at approximately 848 nm. Recent calculations indicate a lifetime of one day giving a Q-value of \( 2.4 \times 10^{20} \) [13]. The differential static polarizability, \( \Delta \alpha \), gives a fractional BBR shift of \( 5.4 \times 10^{-17} \) at room temperature and the sign of \( \Delta \alpha \) allows for the possibility of eliminating micro-motion effects with the appropriate choice of trap drive frequency [4, 14]. The \( ^3D_2 \rightarrow ^3P_0 \) transition has a linewidth of \( 2\pi \times 2.45 \) MHz which allows for both clock state detection and a low Doppler cooling limit relative to most ion transitions.

The clock transition, with the \( J = 1 \) excited state, would be limited by its interaction with magnetic fields and electric field gradients\(^3\). However, from the previous arguments, the average value of the frequencies, \( \nu_F \), corresponding to the transitions \( ^1S_0 \rightarrow ^3D_1 \), \( ^3P_0 \rightarrow ^3D_0 \) would be free of these effects. This, of course, neglects coupling to other fine structure levels which results in a residual quadratic shift. This is due almost entirely to the \( ^3D_2 \) level and is given by

\[
\hbar \nu_F = -\left[ \mu_B B (g_L - g_S) / 2 \hbar \omega_{FS} \right]^2,
\]

where \( \omega_{FS} = 2\pi \times 19.16 \) THz is the fine-structure splitting between the \( ^3D_1 \) and \( ^3D_2 \) levels. Taking \( g_L \approx 1 \) and \( g_S \approx 2 \) we find a residual quadratic shift of just 5 Hz mT\(^{-2}\). What remains to consider is the field dependence of the individual component transitions which affects the short term stability of the average frequency.

Lutetium has two naturally occurring isotopes, \(^{175}\)Lu and \(^{176}\)Lu, with nuclear spins \( I = 7/2 \) and \( I = 7 \) respectively. The latter provides the possibility of using \( m_F = 0 \) transitions, as shown in figure 1(b) which are inherently field insensitive at low field. With its large hyperfine splittings of approximately 10 GHz [15], the quadratic Zeeman shifts of the \( |F', 0\rangle \) states are approximately \( 2.32, -0.15, \) and \( -2.17 \) kHz mT\(^{-2}\) for \( F' = 6, 7 \) and 8 respectively. At an operating field of 10 mT the component transitions \( |F, 0\rangle \rightarrow |F', 0\rangle \) have field sensitivities below \( 50 \) Hz mT\(^{-1}\). The \( |F = 7, 0\rangle \rightarrow |F = 7, 0\rangle \) transition is \( M_1 \) forbidden. Nevertheless it can be realized as an effective transition by averaging \( |F = 7, m_F = \pm 1\rangle \rightarrow |F = 7, 0\rangle \). This gives a faithful representation of the forbidden transition since the ground states do not contribute to either the quadratic

\(^3\)Calculations reported in [13] give a value of zero for the quadrupole moment. However we believe this is most likely in error as there appears no fundamental reason for it to vanish exactly.
Zeeman shift or the quadrupole shift. However the linear Zeeman shifts in the $^1S_0$ states increase the field sensitivities to $g_J\mu_B/h \approx 3500 \text{ kHz mT}^{-1}$, where we have used the value of $g_J = -2.46 \times 10^4$ [16, 17] with the sign convention given in [18].

Since the canceling of both Zeeman and quadrupole shifts does not depend on the level of hyperfine mixing, one could consider defining the frequency reference at a well-defined, measurable, field independent point. Of course careful consideration to the magnetic field sensitivity of the component transitions should be given. Since the hyperfine splitting for Lu$^{175}$ is large, it is unlikely one could do better than with the $m_F = 0$ states of $^{176}\text{Lu}^+$ at low field. However for the purposes of illustration we summarize considerations applicable to $^{175}\text{Lu}^+$.

The isotope, $^{175}\text{Lu}^+$, with nuclear spin $I = 7/2$, has no $m_F = 0$ states. Hence any single transition has a significant linear Zeeman shift which may compromise the ability to accurately achieve the desired average. For the $|^{1}D_2, F, m_F = 3/2\rangle$ states the linear Zeeman shifts are approximately $-3000, 667, and 2333 \text{ kHz mT}^{-1}$ for $F = 5/2, 7/2$, and $9/2$ respectively. However, if one were to use $\Delta m_F \neq 0$ transitions as shown in figure 1(c), the average frequency has a field dependence of

$$\hbar\omega = g_J\Delta m_F \mu_B B - \frac{\mu_B B (g_L - g_S)}{2\hbar\omega_{FS}}$$

which is field independent at $B \approx 0.475 \text{ T}$ using $g_J = -3.47 \times 10^4$ from [16, 17]. In figure 2(c) we plot the frequency shifts of the three components transitions with the vertical line indicating the field independent point for the average frequency. At this point, the linear shifts of the component transitions are reduced to $255, -203, and -52 \text{ kHz mT}^{-1}$. These sensitivities place stringent requirements on the magnetic field stability needed to determine the average. However, the most sensitive level is within a factor of 6 of the component transitions used in the Al$^+$ clock. As noted in [19] this impacts on short term stability but not the long term inaccuracy.

The approach we have suggested here applies when $I \geq J$ and this is true for the ground state manifold as well provided the appropriate averaging can be done. Consider for example $^{86}\text{Sr}^+$ which has a $5_{1/2} - D_{5/2}$ clock transition. This ion requires averaging over six different Zeeman transitions in order to cancel magnetic field and quadrupole shifts, which places stringent requirements on magnetic field stability [4, 20]. Alternatively $^{87}\text{Sr}^+$ has $m = 0$ states that would be inherently more magnetically stable. This isotope has two ground states with $F = 4, 5$ and six excited states with $F = 2, \ldots, 7$. The average of the six transitions $|4, 0\rangle \leftrightarrow |F = 2k, 0\rangle$ and $|5, 0\rangle \leftrightarrow |F = 2k + 1, 0\rangle$ for $k = 1, 2, 3$ provides exactly the average needed to eliminate the magnetic field effects in both ground and excited states, and the quadrupole shifts of the $D$ state. This approach uses the same amount of averaging as for $^{86}\text{Sr}^+$, but would presumably be more stable as it utilizes only $m = 0$ states.

It is of interest to note that the requirement $I \geq J$ can be seen as a generalization of the requirement $I \neq 0$ for the $F = 0$ cases such as Al$^+$ and neutral strontium. The requirement $I \geq J$ results in an average over $2F + 1$ states to obtain an effective $J = 0$ level. In so far as the the average frequency is concerned, any $J$ level can be treated on an equal footing to that of a $J = 0$ level. In general, a field independent point can be found for the average frequency, with the $J = 0$ case requiring just one transition. The field independent point is governed by an equation of the form given in equation (11), with only a slight modification needed for the $J = 0$ case to account for hyperfine induced changes in the $g$-factor. Notably, the curvature at the field independent point is governed solely by the fine-structure splitting and is independent of the nuclear spin. Hence there is no significant advantage to using integer spin for the $J = 0$ case. For $J \neq 0$, one needs to consider the field dependence of the component transitions used to obtain the average which impacts on the short term stability. Earlier proposals [21, 22] aiming for the integer spin candidates were based on the notion of using $m = 0$ to $m' = 0$ transitions at

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**Figure 2.** Field dependence of the three transitions $|S_0, 7/2, 5/2\rangle \rightarrow |D_2, F, 3/2\rangle$ relative to the zero field values. The energies are labeled by the zero-field hyperfine quantum number, $F$. The vertical line indicates where the average of the three transitions becomes field independent.
low fields. These transitions are fundamentally forbidden and require a magnetic field to induce a non-zero coupling [23]. At a fundamental level one could simply go to a field independent point and obtain the same result. The only exceptional case would be $I = J = 0$ for which the argument does not hold [7, 23].

4. Conclusion

In conclusion, we have shown that averaging over transitions to multiple hyperfine levels can lead to an exact cancellation of quadrupole shifts and dominant Zeeman effects when $I \gg J$. Such averaging provides an effective $J = 0$ level and a more practical approach to the cancellation of important shifts of clock frequencies. For the case of Lu$^+$ averaging over $m_J$ states to cancel the quadrupole shift would be complicated by magnetic field considerations and involve no less than 11 transitions. Averaging over just three transitions, we cancel both quadrupole and magnetic field shifts. In that the averaging provides an effective $J = 0$, it provides a great deal more flexibility in considering transitions as potential clock transitions. In particular there is no need to focus on only those transitions with exceptionally small, or even zero quadrupole moment. This is important as such restrictions can lead to compromises in important properties such as the lifetime of the excited state [24]. As with any other clock which uses averaging over multiple Zeeman states, we would not expect clock stability to be adversely affected by the averaging. For completeness, we also note that our approach could be extended across multiple fine structure levels further reducing the residual magnetic field dependence. Although such averaging would typically require a frequency comb and require a significant amount of averaging to be carried out.

For ions, the most significant systematic shifts are those due to BBR, micro-motion, external magnetic and electric fields, residual thermal motion, and ac Stark shifts due to the probe light. Operating in a cryogenic environment practically eliminates the BBR shift. Hyper-Ramsey spectroscopy [25, 26] has demonstrated very high suppression of probe light ac Stark shifts. For Lu$^+$, micro-motion effects can be exactly canceled with an appropriate choice of trap drive frequency [4, 14], which we estimate to be approximately 23 MHz. Our averaging technique then leaves only Doppler shifts due to residual thermal motion of the ion, and residual magnetic field effects due to neighbouring fine-structure levels. These effects are fundamental to any frequency standard based on optical atomic transitions. Compared to other ions, Lu$^+$ has one of the narrowest cooling transitions available and we estimate a fractional second order Doppler shift of just $5 \times 10^{-20}$ at the Doppler cooling limit of this transition. It also has a large fine-structure splitting giving a fractional magnetic field shift of $1.4 \times 10^{-18}$ at 10 μT for the average frequency we have proposed. This makes Lu$^+$ a very strong clock candidate.

The cancellation of micro-motion made possible by the sign of the differential static polarizability should not be overlooked. It has both a technical component due to trap imperfections and a fundamental component related to the thermal spread of the ion position. The ability to cancel these effects by choice of trap drive frequency raises the intriguing possibility of moving towards frequency spectroscopy with multiple ions. Within the framework of the averaging proposed here, the limitation would be on inhomogeneous broadening of the component transitions which could potentially diminish the effectiveness of the averaging. The potential of multiple ion spectroscopy will be the subject of future research.

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