

Testing spatial α -variation with optical atomic clocks based on highly charged ions

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Abstract. We review recent works illustrating the potential use of highly charged ions as the basis of optical atomic clocks of exceptional accuracy and very high sensitivity to variation of the fine structure constant, α . The tendency towards large transition energies in highly charged ions can be overcome using level crossings, which allow transitions between different orbitals to be within the range of usual lasers. We present simple scaling laws that demonstrate reduced systematics that could be realised in highly charged ion clocks. Such clocks could allow us to corroborate astronomical studies that suggest a spatial gradient in values of α across the Universe.

1. INTRODUCTION

In this review we will focus on the use of optical transitions in highly charged ions (HCIs) as potential reference transitions for atomic clocks. The motivation for such clocks came from the need for tighter limits on the variation of the fine-structure constant, α , over time; HCI clocks were expected to be very sensitive probes of such variations. It was realised that atomic clocks using HCIs could have strongly reduced systematics since HCIs are smaller than neutral atoms, and more recently HCI clocks with no special sensitivity to the fine-structure constant have been proposed to exploit these properties [1, 2]. However, we begin this review with a discussion of the astrophysical result that motivated the need for clocks with higher sensitivity to α -variation.

The fine-structure constant, $\alpha = e^2/\hbar c \approx 1/137$, is a dimensionless fundamental “constant” of nature that indicates the strength of the electromagnetic interaction. The Standard Model of particle physics is unable to predict its value; instead, the value of α can only be taken from experiment, and must be applied by hand in Standard Model predictions. It is, however, widely believed that the Standard Model is a low energy manifestation of a more complete theory that unifies the forces of the Standard Model (electromagnetism and the strong and weak nuclear forces) with gravity. Several such theories predict variations in the fundamental constants in an evolving Universe [3–7].

Measurements of cosmological α -variation by comparison of astronomical and laboratory optical spectra were first performed by Savedoff as early as 1956 [8]. In order to separate the effect of α -variation from the redshift, alkali doublets were used. The separation of the two lines in an alkali-doublet is proportional to α^2 , and since two lines are used it is possible to measure the size of α -variation independently of their redshift. While the first studies used emission spectra, better limits were obtained using metal absorption lines in quasar spectra. These are often found in so-called “damped Lyman- α ” systems, when the light emitted from distant quasars passes through gas clouds that may contain trace metal elements on the way to terrestrial based observatories. As a result, metal absorption lines are observed in the final spectra. There are numerous works successfully implementing this “alkali-doublet” method (see review [9]).

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In 1999, a different approach was developed: the many-multiplet method [10, 11]. It exploits the fact that relativistic corrections to atomic transition frequencies can exceed the fine-structure interval between the excited levels by an order of magnitude. Thus, variations in α may be revealed by comparing different transitions in different atoms in cosmic and laboratory spectra. A statistical improvement is also realised because many more spectral lines in different elements can be used, as opposed to only alkali-doublet lines. This method improves the sensitivity to a potential variation of α by more than an order of magnitude compared to the alkali-doublet method.

Relativistic many-body calculations can be used to reveal the dependence of atomic frequencies on α . Accurate many-body calculations have been performed for all transitions of interest to quasar absorption spectra studies of α -variation [10–18]. These are strong E1 transitions from the ground states of Mg I, Mg II, Ti II, Fe II, Cr II, Ni II, Al II, Al III, Si II, Zn II, Mn II. Several other transitions in that are seen in quasar absorption spectra have not yet been used in quasar measurements because of the absence of accurate UV transition laboratory wavelengths. For a recent list of transitions, see [19].

The very first sampling of archival data from the Keck telescope in Hawaii indicated a non-zero variation of α [20], although of very low significance. Subsequent extension of the sample to 143 data samples indicated that α was smaller in the past [21, 22]. Later, this sample was combined with a new analysis of 153 quasar absorption spectra obtained using the Very Large Telescope in Chile [23, 24]. The results indicate that the value of α was larger in one direction on the sky and smaller in the other direction, an interpretation of the data preferred with 4.2σ significance. This result is known as the spatial α -dipole (or “Australian dipole”) and it has the value of

$$\frac{\delta\alpha}{\alpha_0} = (1.10 \pm 0.25) \times 10^{-6} r \cos \psi \text{ Gly}^{-1}, \quad (1)$$

where $\delta\alpha/\alpha_0 = (\alpha(\mathbf{r}) - \alpha_0)/\alpha_0$ is the fractional variation of α at a particular place \mathbf{r} in the Universe (relative to its value on Earth, α_0 , at $\mathbf{r} = 0$). The geometrical term $r \cos \psi$, where ψ is the angle between the direction of the measurement and the axis of the spatial dipole, gives the position of the quasar absorption system along the dipole axis. The axis direction corresponds to $(17.4(0.9) \text{ h}, -58(9)^\circ)$ in equatorial coordinates, while the distance function is the equivalent light-travel distance $r = ct$, measured in giga-lightyears (Gly).

Data from both telescopes independently agree on the direction and magnitude of this spatial gradient in the value of α . Furthermore, absorption spectra at redshift $z < 1.6$ and those from $z > 1.6$ (an approximately even split) independently agree on the dipole direction and magnitude. This is important since very different transitions in different atomic species are probed by optical telescopes at different redshifts. Further statistical analysis can be found in Refs. [24, 25].

Our goal now is to translate the observed spatial gradient in values of α into terrestrially observable measurements, in order to corroborate the result independently. This can be done by noticing that the Earth moves with respect to the rest frame of the cosmic microwave background (CMB), and this motion will have a component along the spatial α dipole [26]. Thus, we would expect α to vary in the terrestrial frame. The choice of the CMB as the rest frame of the α -variation is based on an assumption that the variation is caused by, for example, a co-moving scalar field. To see this, we start by neglecting the annual motion of the Earth around the Sun, which is averaged out over the course of a year. The velocity of the Sun in the CMB rest frame is known to high accuracy from the CMB itself, and is 369 kms^{-1} in the direction $(168^\circ, -7^\circ)$ [27]. This is almost perpendicular to the observed direction of the spatial dipole, and therefore is sensitive to the exact angle the motion makes with the dipole. This astronomical result thus translates into an α variation at the level of [26]

$$\frac{\dot{\alpha}}{\alpha} = 1.35 \times 10^{-18} \cos \theta \text{ yr}^{-1}, \quad (2)$$

where θ is the angle the motion of our solar system makes with the α -dipole axis. The best fit value for the spatial dipole results in a value of $\cos \psi \sim 0.07$, but this is uncertain to the level of ~ 0.1 .

Naturally, the full result must include the modulation of the Earth's annual motion around the Sun, with the angle between the ecliptic plane and the spatial dipole approximately 35° . This modulation results in an α -variation of

$$\frac{\delta\alpha}{\alpha} = 1.4 \times 10^{-20} \cos \omega t, \quad (3)$$

where ω refers to the angular frequency of the yearly orbital and $\delta\alpha/\alpha$ takes its maximal ($\cos \omega t = 1$) value on around 15 June each year. This modulation can be used to show that a drift in α such as Eq. (2) is due to a spatial, rather than temporal, variation.

Since different transitions in atoms and ions generally have a different dependence on the fine-structure constant, the comparison of two transitions over time can be used to probe α -variation [28]. Atomic clocks provide the most accurate comparisons of transition frequencies. The current best limit on time variation of α comes from comparison of Al^+ and Hg^+ ion clocks over the course of a year [29]

$$\frac{\dot{\alpha}}{\alpha} = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1}. \quad (4)$$

In this experiment the Al^+ clock is insensitive to α , while the Hg^+ has a strong dependence. This limit needs to be improved by around two orders of magnitude to be competitive with the astrophysical measurement of spatial variation. However, we note that when considering time-variation of α it is already competitive with astronomical limits if one assumes linear variations with time.

In this review, we will show how HCIs can provide the additional two orders of magnitude required to bridge this result with the astronomical limit. The improvements come from a combination of higher clock accuracy and from higher clock sensitivity to α -variation. With the refinement of electron beam ion trap (EBIT) technology and higher beam energies, the production of a wide range of HCIs for virtually any atomic species is feasible nowadays [30]. The challenge with building a practical clock based on HCIs has been trapping, cooling, and accurate spectroscopy on transitions that are generally are in the x-ray region. X-ray spectroscopy is around 10 orders of magnitude less accurate than optical spectroscopy.

In the following sections, we will examine the concept of level crossings, which introduces useful optical $E1$, $M1$ and $E2$ transitions that could be used to make optical clocks based on transitions in HCIs. We show that these optical transitions can be very sensitive probes of α -variation. Following that, we will introduce scaling laws to help estimate systematics by extrapolating from near-neutral systems to highly charged ions. Finally, we provide a brief overview of the computational methods that are used to accurately determine the theoretical properties of HCIs.

2. SENSITIVITY OF ATOMIC TRANSITIONS TO α -VARIATION

A good candidate ion for detecting α -variation must have accessible transitions that exhibit a large change in transition frequency for a given change in the fine-structure constant. In particular, it is preferable that for the two clock transitions we are interested in comparing, one is a positive shifter (frequency increases with increasing α) and the other is a negative shifter (frequency decreases). The measured ratio of frequencies of these transitions, in a region of space with an altered value of the fine-structure constant, will then be the difference between the individual shifts of these two transitions. We parametrize this frequency shift using the quantity q , defined as

$$q = \left. \frac{d\omega}{dx} \right|_{x=0}, \quad (5)$$

where $x = \alpha^2/\alpha_0^2 - 1 \approx 2(\alpha - \alpha_0)/\alpha_0$ is the fractional change of the square of the fine-structure constant, α , from its current value α_0 . q is therefore a measure of the rate of change of a transition

frequency with respect to the fractional change in the fine-structure constant, with all quantities measured in atomic units ($e = m_e = \hbar = 1$).

Let us consider the leading relativistic corrections (order v^2/c^2) to the central-field Schrödinger equation for a valence electron, which can be written as (see, e.g. [31])

$$q = -\frac{\alpha^2}{2} \int R^2(r)(E_0 + V(r))^2 r^2 dr + \frac{\alpha^2}{4} \int R(r) \left(\frac{dR}{dr} - X \frac{R}{r} \right) \frac{dV}{dr} r^2 dr, \quad (6)$$

where $R(r)$ and E_0 are the non-relativistic radial wavefunction and energy respectively, $V(r)$ is the potential and $X = j(j+1) - l(l+1) - s(s+1)$. Near the origin, the potential $V(r) \approx Z/r$ as it is unscreened by the electrons. Near the origin, the wavefunction squared for a many-electron ion with atomic number Z and ion charge Z_{ion} is [32–34]

$$\psi(0)^2 \approx \frac{Z(Z_{ion} + 1)^2}{\nu^3} = \frac{Z Z_a^2}{\nu n^2}, \quad (7)$$

where ν is the effective principal quantum number and we have introduced an effective charge Z_a , defined by the relation $Z_a/n = (Z_{ion} + 1)/\nu$. With the appropriate substitution, we are then able to write

$$q_n \approx -I_n \frac{(Z\alpha)^2}{\nu(j+1/2)}. \quad (8)$$

Here $I_n = -E_n = Z_a^2/2n^2$ is the (positive) ionization energy of an electron in that atomic orbital, Z is the atomic charge, ν is the non-integer effective principal quantum number and j the angular momentum of the orbital.

If we label the lower state in the clock transition i and the upper state f , then we say that the measured sensitivity to α variation is $q = q_f - q_i$. To measure a variation in α requires comparing the frequencies of two atomic clocks. As an example we consider the ions used to obtain the current best limit on α -variation [29] mentioned in the introduction. The transition used as the optical frequency standard in the Al^+ clock is from the $3s^2 1S_0$ state to the $3s3p^3 P_0$ state, this transition is relatively insensitive to α variation (small q). On the other hand, the Hg^+ clock uses a transition which is strongly dependent on α variation (large q). In fact, the Hg^+ transition is a strong negative shifter, $q \approx -52\,000 \text{ cm}^{-1}$. The ratio of these transition frequencies would therefore change if α were changing. By comparing how the ratio of these frequencies changes over a year, a terrestrial limit was placed on α -variation of $\dot{\alpha}/\alpha = (-1.6 \pm 2.3) \times 10^{-17} \text{ yr}^{-1}$. This limit could in principle be improved by using a strongly positive shifting clock transition, rather than the Al^+ clock transition.

3. LEVEL CROSSINGS IN HIGHLY CHARGED IONS

Using Eq. (8), we see that the sensitivity to α -variation can be maximized by considering highly charged ions because of their large ionization energy I_n . This can be further enhanced by using heavier elements to provide for a large Z . Finally, significant differences in the configuration of the states involved allows for larger ranges of q . To maximize $|q| = |q_f - q_i|$, Eq. (8) should be used to look for maximal q values of both levels with opposite signs. However at the same time we also wish to constrain the transition energy to be within the range of optical lasers so that accurate optical spectroscopy techniques can be used. This is problematic for highly charged ions, since just like I_n the transition frequencies also grow with ion charge as $\sim Z_a^2$. Fortunately we can solve this problem using the phenomenon of level crossings [35].

In short, a level crossing in an ion occurs when the energy ordering of two or more orbitals changes. In hydrogen-like ions in the non relativistic limit, the energy levels are sorted only by principal quantum number n . That is, the energy of levels with the same principal quantum number n are degenerate and thus we will refer to this as the Coulomb degenerate limit. An atom or ion with many electrons fills

its electron orbitals significantly differently from the above scheme. The presence of the first electron modifies the electric potential experienced by the second electron, which modifies the energy of the second electron. Electrons near the nucleus of the ion tend to reduce the “visible” charge experienced by the external electrons – an effect known as screening. Consider then, a singly ionized ion (K^+) with completely filled $1s$, $2s$, $2p$, $3s$, and $3p$ orbitals. The Bohr model would reason that the $3d$ orbital be filled next, but we see in neutral potassium that the $4s$ level is filled first. An electron in the $3d$ orbital would spend a large amount of time further away from the nucleus, and hence experiences a smaller screened charge. As a result, the electron is more tightly bound to the nucleus in the $4s$ orbital than the $3d$ orbital, and correspondingly the $4s$ orbital is more energetically favorable than the $3d$ orbital. Thus we see that in the periodic table the energy levels fill in a different order; for most atoms the ordering follows the Madelung rule (also known as the Klechkowski rule).

Consider an isoelectronic sequence, where we add additional protons to the nucleus while keeping the number of electrons constant. We start again with neutral potassium. Successively adding protons brings the ion closer to the Coulomb degenerate limit, where screening effects no longer dominate the energy ordering. This implies that there is some point along this isoelectronic sequence where having the valence electron in the $3d$ orbital becomes more energetically favorable than the $4s$ orbital. We call the point which this occurs a level crossing. For the isoelectronic sequence of neutral potassium, the ground state of Sc^{2+} is $3d$. Here the level crossing occurs at a relatively low ion charge.

Near such level crossings, the ionisation energies of the two levels can be equal to better than 99% accuracy, and the energy of transitions between the crossing orbitals may be within the range of optical lasers even in highly charged ions. This is of significant importance, because as mentioned previously, the energy intervals in highly charged ions are usually in the x-ray regime. On the other hand, fine-structure transitions may also be within optical range, but such transitions would most likely have relatively small q -values, as predicted by Eq. (8). The most promising level crossings in HCIs have been identified as the $4f - 5s$, $4f - 5p$ and $5f - 6p$ crossings [36], which take place at ion charges of between $8+$ and $20+$. See [36] for an exhaustive listing of all available level crossings in the periodic table.

As an example, we consider the $5s - 4f$ level crossing in the Ag isoelectronic sequence. In neutral Ag ($Z = N = 47$) the valence electron is in the $5s$ orbital, with the $4f$ empty. As the nuclear charge is increased along the isoelectronic sequence, the $4f$ orbital eventually goes below the $5s$ orbital; this occurs at $Z \approx 61$. In Ref. [35] the energy levels of the single-valence-electron HCIs Nd^{13+} , Pm^{14+} , and Sm^{15+} were calculated. The $4f - 5s$ transitions were indeed found to be within laser range, even though the ionisation energies are ~ 250 eV. The spectrum of the two-valence-electron ion Sm^{14+} was also calculated in [35]. This ion has $E1$ transitions that could potentially be used for trapping and cooling, as well as weak clock transitions with very high sensitivity to α -variation. Indeed, comparison of two different transitions in Sm^{14+} would have sensitivity to α of $\Delta q \approx 260\,000\text{ cm}^{-1}$, around five times larger than the sensitivity of the Hg^+ ion clock.

The potential of high-precision HCI clocks using Nd^{13+} and Sm^{15+} was explored in [37]; there a potential fractional clock accuracy of $\sim 10^{-19}$ was estimated. This level of accuracy would allow for determination of α -variation to within parts in 10^{-20} per year, competitive with astronomical bounds on spatial variation.

4. HOLE CROSSINGS

To find further enhancement to the sensitivity coefficient q , consider a system with one or two holes in otherwise closed shells. Since the ionisation potential of closed shells is much larger due to the hole state spending a larger amount of time closer to the nucleus, the relativistic corrections will be much larger. In Ref. [38] it was shown that $q \sim I_n^{3/2}$ for holes. This makes it possible to achieve higher sensitivity to α variation by using holes.

One complication that using holes presents is that it greatly increases the complexity of the configuration interaction calculations performed that are normally used to calculate the theoretical energy levels. In the case of two electrons above closed shells, virtual excitations from the closed shells can be neglected for a reasonably accurate physical representation of the system. With two holes, however, one needs to treat all the electrons in the two orbitals that are near the level crossing as valence electrons. This is because the energy difference between these two orbitals are similar, by construction of taking ions near level crossings. The result of this is that in the $p - f$ crossing, it essentially becomes an 18-valence-electron problem.

Nevertheless, the benefits of increased q coefficients conferred by hole crossings make them worth studying. From an experimental perspective, a two hole ion is not particularly more complex than the two-valence-electron ion. With this in mind, the most promising candidates for building an atomic clock for the detection of α variation studied so far are W^{7+} , W^{8+} , Ir^{16+} and Ir^{17+} , and they are representative of one and two hole systems with $4f - 5p$ and $4f - 5s$ crossings, respectively [38]. Comparison of two transitions in Ir^{17+} could yield a total sensitivity to α -variation up to $\Delta q \approx 730\,000\text{ cm}^{-1}$.

5. SCALING LAWS FOR ATOMIC CLOCKS BASED ON HIGHLY CHARGED IONS

Atomic clocks are the most accurate instruments ever built, with existing optical lattice clocks and trapped ion clocks measuring frequencies down beyond the seventeenth significant figure. Of interest to this work are ion clocks such as the Al^+ and Hg^+ clocks built at the National Institute of Standards and Technology (NIST). These clocks have achieved remarkable accuracy, able to measure differences of one part in 10^{17} [29]. Of course, such an accuracy requires a high level of understanding and control of systematic effects. It is the aim of this section to generalise the size of systematic effects from existing ion clock systems towards highly charged ions, in an endeavour to understand the systematic effects that can be expected in future HCI clocks. Therefore, in this section we will present approximate scaling laws which can be used in conjunction with known properties of near-neutral ions to compute properties of highly charged ions. A previous topical review on highly charged ions [39] provides estimates for the scaling of some of these effects in hydrogen-like ions. In this review, we will consider how to generalise these scaling laws to multi-electron ions.

In order to accomplish this, it is first necessary to parametrize the evolution from neutral atom to a highly-charged ion. There are two natural ways of doing this: starting with a neutral atom and then removing electrons one at a time (isonuclear sequence); or considering starting with a neutral atom and then adding protons one at a time (isoelectronic sequence). While the former way is how one would actually produce highly charged ions (such as the production of U^{92+} in an electron beam ion trap by removing electrons from neutral uranium one at a time), it turns out that the use of isoelectronic sequences is more convenient for calculations because the electronic structure of the ion is kept roughly constant. For example, it is meaningful to ask how a particular $6s - 6p$ transition changes along the isoelectronic sequence, but the same transition may not be present along the corresponding isonuclear sequence once the electronic structure changes.

It is tempting to use the ion charge, Z_{ion} , as a parameter for traversing along an isoelectronic sequence. However, the ion charge does not take into consideration the changes to the screening that the valence electron experiences. A far more useful parameter is the effective charge experienced by the valence electron, Z_a . In deriving this parameter, we assume that the electron is moving in a screened Coulomb potential

$$V(r) \sim -\frac{Z_a}{r}. \quad (9)$$

If we recall the formula for the nonrelativistic energy of an electron in such a potential,

$$E_n = -\frac{Z_a^2}{2n^2} = -\frac{(Z_{ion} + 1)^2}{2\nu^2}, \quad (10)$$

where n is the integer principal quantum number. The second equality relates this equation to the formalism where an effective (non-integer) principal quantum number ν is used to parametrize the screening. We see that multi-electron ions require two parameters to characterise the effective interaction: the bare nuclear charge Z (important for short-range effects), and the effective charge Z_a that the electron sees at larger distances. For example, the fine-structure scaling cannot be described by Z_a alone since it is a relativistic effect and depends on the wavefunction at the nucleus and hence depends on Z as well.

The value of Z_a for a particular orbital in an ion can be extracted from the Dirac-Fock energy of the level via (10). This approximation yields reasonable results whenever the dominant contribution of the potential experienced by the electron is well described by the mean field. Alternatively, one may turn to tabulated tables for Z_a , such as those presented in [36]. The evolution of Z_a from the neutral atom to highly charged ions can be fit to a linear function of the ion charge Z_{ion} over restricted intervals ($Z_a = AZ_{ion} + B$). We find that near-neutral ions ($0 < Z_{ion} < 5$) of the isoelectronic sequence can be described by a different set of coefficients A and B than ions in the same sequence with $5 < Z_{ion} < 30$.

5.1 Scaling of EJ and MJ transition matrix elements

In this section we present the approximate analytical scaling of the EJ and MJ transition matrix elements. As a starting point, we first examine the scaling of the non-relativistic $E1$ matrix element,

$$\langle nl|r|n'l' \rangle = \int P_{nl}rP_{n'l'}dr. \quad (11)$$

We can approximate the radial wavefunction P_{nl} by the non-relativistic single-electron wavefunction in a central Coulomb potential with effective charge Z_a by

$$P_{nl} = N_{nl} \left(\frac{2Z_a r}{n} \right)^{2l+1} e^{-\frac{Z_a r}{n}} F\left(-n+l+1, 2l+2, \frac{2Z_a r}{n}\right) \quad (12)$$

where

$$N_{nl} = \frac{1}{n(2l+1)!} \sqrt{\frac{Z_a(n+l)!}{(n-l-1)!}} \quad (13)$$

is a normalization coefficient and $F(a, b, x) = \sum_{m=0}^{\infty} \frac{a^{(m)} x^m}{b^{(m)} m!}$ are confluent hypergeometric functions. This radial wavefunction which is a reasonable approximation at distances far from the nucleus where the electron wavefunction has its peak.

The Z_a dependence of the integral in Eq. (11) can be calculated as

$$\int r P_i P_j dr \sim \frac{1}{Z_a}. \quad (14)$$

This is simply a formal way of stating that the ion gets smaller in size as its charge increases. As a result, the strength of $E1$ matrix elements is reduced in highly charged ions. On the other hand, $M1$ matrix elements are proportional to the magnetic moment (and hence angular momentum) of the external electron, which does not reduce as the ion gets smaller. Therefore the $M1$ matrix element does not scale with the charge. In neutral atoms, $E1$ transitions are usually the strongest transitions available. Our scaling law, however, tells us that in highly charged ions, $E1$ transitions grow weaker with increasing ion charge, yet $M1$ transitions remain relatively constant in strength.

For higher multipoles, one obtains higher powers of the atomic radius,

$$\langle r^n \rangle \sim \left(\frac{a_B}{Z_a} \right)^n, \quad (15)$$

where a_B is the Bohr radius, a characteristic length in atomic systems. The general scaling law for EJ matrix elements is

$$\langle \kappa_i || q_J^{(E)} || \kappa_j \rangle \sim (Z_a)^{-J} \quad (16)$$

and for MJ matrix elements is

$$\langle \kappa_i || q_J^{(M)} || \kappa_j \rangle \sim (Z_a)^{1-J}. \quad (17)$$

5.2 Scaling of polarizability and blackbody radiation shift

The blackbody radiation shift, in the lowest order, is proportional to the difference in the dipole polarizabilities of the two energy levels involved in the atomic clock transition. For an adiabatic system, this can be evaluated using the formula (see, e.g., [40])

$$\delta E = -\frac{1}{2}(831.9 \text{ V/m})^2 \left[\frac{T(K)}{300} \right] \alpha_0 (1 + \eta) \quad (18)$$

where $T(K)$ is the temperature in Kelvins, α_0 is the static dipole polarizability and η is a small dynamic correction due to the frequency distribution, which will be disregarded for our purposes. The valence scalar polarizability of an atom in a state v can be expressed as a sum over all excited intermediate states n allowed by $E1$ selection rules,

$$\alpha_0 = \frac{2}{3(2j_v + 1)} \sum_n \frac{\langle v || r || n \rangle \langle n || r || v \rangle}{E_n - E_v}. \quad (19)$$

We are interested in the approximate scaling of the blackbody radiation shift in highly charged ions. The reduced matrix elements in Eq. (19) have been shown to scale as $1/Z_a$ in Eq. (14). The nonrelativistic energy scales as Z_a^2 using Eq. (10). This means that all terms in the summation have the same $1/Z_a^4$ scaling, so that the total polarizability must also scale as

$$\delta E \sim \alpha_0 \sim \left(\frac{1}{Z_a} \right)^4. \quad (20)$$

Equation (20) implies that the blackbody shifts in highly charged ions (large Z_a) would be largely suppressed compared to near-neutral ions.

5.3 Scaling of the Hyperfine structure

Operators with large negative powers of radius will not follow the Coulomb radius scaling, Eq. (15), since the wavefunction at small distances cannot be described by P_{nl} that we introduced in Section 5.1. The hyperfine interaction is an example of such an interaction, with operators proportional to large negative powers of the radius r . Instead we must use the approach of Fermi-Segré [33, 34] where the normalised squared wavefunction at the origin is proportional to $Z(Z_{ion} + 1)^2/\nu^3$. Note that since $\nu = n(Z_{ion} + 1)/Z_a$, we can substitute these results into the formulae for the non-relativistic magnetic dipole hyperfine constant [41] A of a one-valence-electron system:

$$A = \begin{cases} \frac{2}{3} g_I \lim_{r \rightarrow 0} \left(\frac{P_{nl}(r)}{r} \right), & \text{for } l = 0 \\ \frac{l(l+1)}{j(j+1)} g_I \int_0^\infty P_{nl}(r) \frac{1}{r^3} P_{nl}(r), & \text{for } l \neq 0 \end{cases} \quad (21)$$

to obtain the following scaling law

$$\frac{A}{g_I} \sim \frac{Z Z_a^3}{(Z_{ion} + 1)}. \quad (22)$$

Table 1. Magnetic dipole hyperfine coefficients A (calculated in [42]) and their scaling with increasing Z along the lithium isoelectronic sequence. Values of Z_a were obtained from Dirac-Fock calculations using the relation $Z_a = \sqrt{|2n^2 E|}$ where n is the principal quantum number and E is the orbital energy in atomic units. The notation $|_p$ means to use the values in the previous row of the table.

Isotope	I	g_I	A (MHz)	Z_a	$\frac{(A/g_I)}{(A/g_I) _p}$	$\frac{\frac{ZZ_a^3}{Z_{ion}+1}}{\frac{ZZ_a^3}{Z_{ion}+1} _p}$
${}^7_3\text{Li}$	3/2	2.1709	399.34	1.25		
${}^9_4\text{Be}^+$	3/2	-0.7850	-625.55	2.31	4.35	4.20
${}^{11}_5\text{B}^{2+}$	3/2	1.7924	3603.77	3.33	2.53	2.49
${}^{13}_6\text{C}^{3+}$	1/2	1.4048	5642.40	4.35	2.00	2.00
${}^{15}_7\text{N}^{4+}$	1/2	-0.5664	-3973.68	5.36	1.74	1.74
${}^{17}_8\text{O}^{5+}$	5/2	-0.7575	-8474.13	6.36	1.59	1.59
${}^{19}_9\text{F}^{6+}$	1/2	5.2578	88106.93	7.37	1.50	1.50

Table 2. Scaling dependences for HCIs for various sources of systematic shifts in optical clocks.

2 nd order Stark shift	$\sim 1/Z_a^4$
Blackbody shift	$\sim 1/Z_a^4$
2 nd order Zeeman shift	suppressed
Electric quadrupole shift	$\sim 1/Z_a^2$
Fine-structure	$\sim Z^2 Z_a^3 / (Z_{ion} + 1)$
Hyperfine A coefficient	$\sim Z Z_a^3 / (Z_{ion} + 1)$

Here we have factored out the nuclear g -factor g_I which varies greatly between nuclei to facilitate comparison with experimental results. We compare this scaling law with experimental data in Table 1. The table shows that the scaling law in this case very accurately predicts the experimental result. A similar result may be derived for the electric quadrupole hyperfine constant B . We should also point out that the widths of hyperfine transitions will scale as $\omega^3 \sim A^3$, therefore relaxation of excited hyperfine levels will occur much faster in HCIs.

6. SUMMARY

As we have illustrated, HCI clocks could provide a significant increase in the sensitivity of laboratory measurements to variation of α over the best current day limits. The most sensitive HCI system identified thus far is the two-valence-electron Cf^{16+} [43], which is near the $5f - 6p$ level crossing. Transitions between the crossing levels may be up to 23 times more sensitive to α -variation than the Hg^+ clock transition from which current day limits are derived. Coupled with improved clock accuracy, this may allow us to achieve the two orders-of-magnitude improvement required to test the astrophysical α -gradient result.

We present a summary of the scaling laws in Table 2. One may extrapolate from known values of systematic shifts in near-neutral ions to estimate their values in HCIs; one only needs to know the relevant Z_a values which are tabulated in [36]. The second-order Zeeman effect is slightly more complicated, since it may depend on the particular fine or hyperfine structure of the ion. Nevertheless it will generally be suppressed in HCIs due to a larger energy denominator [44]. As a result of the reduced

systematic effects, atomic clocks using HCs could reach 10^{-19} relative accuracy using fine-structure transitions when α -sensitivity is not required [1].

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