

# VARIATION OF FUNDAMENTAL CONSTANTS FROM THE BIG BANG TO ATOMIC CLOCKS: THEORY AND OBSERVATIONS

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Theories unifying gravity with other interactions suggest the possibility of temporal and spatial variation of the fundamental “constants” in an expanding Universe. In this review we discuss the effects of variation of the fine-structure constant and fundamental masses on measurements covering the lifespan of the Universe from a few minutes after Big Bang to the present time. Measurements give controversial results, including some hints for variation in Big Bang nucleosynthesis and quasar absorption spectra data. Furthermore there are very promising methods to search for the variation of fundamental constants by comparison of different atomic clocks. Huge enhancements of the relative variation effects happen in transitions between accidentally degenerate nuclear, atomic, and molecular energy levels.

## 1. Introduction

It is widely believed that the Standard Model of elementary particles is a low-energy manifestation of a more complete theory that unifies gravity with the other interactions (electromagnetic, weak nuclear, and strong nuclear forces). Many well-motivated extensions to the Standard Model include variation of fundamental constants as a possibility, or even as a necessity in an expanding Universe (see e.g. review 1). Additionally, the fundamental constants may be slightly different near massive bodies (see e.g. review 2). There are some hints for the variation of different fundamental constants in quasar absorption spectra<sup>3-8</sup> and Big Bang nucleosynthesis<sup>9,10</sup> data. However, a majority of publications report limits on the variations (see e.g. recent reviews 11,12).

We can only detect variation of dimensionless fundamental constants. Here we will discuss variation of the fine structure constant  $\alpha$ , the proton  $g$ -factor  $g_p$ , and the dimensionless ratios  $X_e = m_e/\Lambda_{QCD}$  and  $X_q = m_q/\Lambda_{QCD}$  where  $m_e$  and  $m_q$  are the electron and quark masses, and  $\Lambda_{QCD}$

is the quantum chromodynamics (QCD) scale, defined as the position of the Landau pole in the logarithm of the running strong coupling constant,  $\alpha_s(r) \sim 1/\ln(\Lambda_{QCD}r/\hbar c)$ . The proton mass  $m_p$  is proportional to  $\Lambda_{QCD}$ , therefore the relative variation of  $\mu = m_e/m_p$  is equal to the relative variation of  $X_e = m_e/\Lambda_{QCD}$  (if we neglect a small contribution of quark masses ( $m_q \sim 5$  MeV) to the proton mass,  $m_p = 938$  MeV). In the Standard Model electron and quark masses are proportional to the vacuum expectation value of the Higgs field.

The hypothetical unification of all interactions implies that variations of different fundamental constants may be related.<sup>13-17</sup> For example, grand unification theories predict

$$\frac{\delta X_q}{X_q} \sim 35 \frac{\delta \alpha}{\alpha} . \quad (1)$$

The coefficient here is model-dependent, but large values are generic for models in which variations come from high energy scales (for a simple explanation see Ref. 10). If these ideas are correct, the variation in  $X_{e,q} = m_{e,q}/\Lambda_{QCD}$  or  $\mu = m_e/M_p$  may be easier to detect than the variation in  $\alpha$ .

In Sec. 2 we discuss variation of fundamental constants in Big Bang nucleosynthesis. The factor of three disagreement between the calculations and measurements of the BBN abundance of  ${}^7\text{Li}$  may, in principle, be explained by the variation of  $m_q/\Lambda_{QCD}$  at the level of  $\sim 10^{-2}$ ; there have also been several publications studying variation of  $\alpha$  and gravitational constant in BBN which we do not consider here, see review 1. The claim of detection of variation of fundamental constants based on the Oklo data in Ref. 18 is not confirmed by recent studies<sup>19-21</sup> which give a stringent limit on the possible variation of the resonance in  ${}^{150}\text{Sm}$  during the last two billion years (Sec. 3). We discuss the variation of fundamental constants in atomic (Sec. 4) and molecular (Sec. 5) spectra, which can be used both in laboratory-based clocks as well as over cosmological timescales by comparison with astrophysical data. Additionally, we discuss possible enhancements in these systems as well as in nuclear clocks (Sec. 6) and ultracold systems near Feshbach resonances (Sec. 7).

## 2. Big Bang nucleosynthesis

The result of our work<sup>9</sup> suggested that a reduced deuteron binding energy of  $\Delta Q/Q = -0.019 \pm 0.005$  would yield a better fit to observational data (the WMAP value of barion-to-photon ratio  $\eta$  and measured primordial

${}^2\text{H}$ ,  ${}^4\text{He}$ , and  ${}^7\text{Li}$  abundances) for Big Bang Nucleosynthesis. Using our calculations<sup>22</sup> we obtained an estimate of the strange quark mass variation.

Recently Dent, Stern, and Wetterich<sup>23</sup> calculated the sensitivity of BBN abundances for  ${}^2\text{H}$ ,  ${}^4\text{He}$  and  ${}^7\text{Li}$  to the variation of binding energies of  ${}^2,{}^3\text{H}$ ,  ${}^3,{}^4\text{He}$ ,  ${}^6,{}^7\text{Li}$  and  ${}^7\text{Be}$  in a linear approximation. We calculated the dependence of these binding energies on the light quark mass variation and estimated the sensitivity of BBN yields to variation of the quark mass.<sup>10,24-26</sup> Then we used the observational data to obtain the following equations for  ${}^2\text{H}$ ,  ${}^4\text{He}$  and  ${}^7\text{Li}$ :<sup>10</sup>

$$1 + 7.7x = 1.07 \pm 0.15 , \quad (2)$$

$$1 - 0.95x = 1.005 \pm 0.036 , \quad (3)$$

$$1 - 50x = 0.33 \pm 0.11 , \quad (4)$$

where  $x = \delta X_q / X_q$ . These equations yield 3 consistent values of  $x$ :  $0.009 \pm 0.019$ ,  $-0.005 \pm 0.038$  and  $0.013 \pm 0.002$ . The statistically weighted average of  $\delta X_q / X_q = 0.013 \pm 0.002$  is dominated by the  ${}^7\text{Li}$  data. Allowing for the theoretical uncertainties, we should understand this BBN result as  $\delta X_q / X_q = K \cdot (0.013 \pm 0.002)$  where  $K \sim 1$  and the expected accuracy in  $K$  is about a factor of 2. Note that here we neglected effects of the strange quark mass variation. A rough estimate of these effects on BBN due to the deuteron binding energy variation was made in Refs. 9,22.

We have performed a preliminary, more accurate calculation that takes into account the effect of the  ${}^8\text{Be}$  binding energy variation (which is not included in Ref. 23), the variation of the virtual  ${}^1\text{S}_0(np)$  level, and non-linear corrections in  $x$  which are important for  ${}^7\text{Li}$  (with  $\eta$  given by WMAP, the discrepancy between  ${}^7\text{Li}$  abundances predicted by theory and inferred from observations is now a factor of 2.4 – 4.3 at the 4 – 5 $\sigma$  level<sup>27</sup>). Taking the observed  ${}^7\text{Li}/\text{H} = 1 - 2 \times 10^{-10}$ , we obtain a variation of  $\delta X_q / X_q = 0.015 \pm 0.003$ .

### 3. Oklo natural nuclear reactor

The results from the Oklo natural nuclear reactor are based on the measurement of the position of a very low energy resonance ( $E_r = 0.1$  eV) in neutron capture by  ${}^{149}\text{Sm}$  nucleus. The shift of this resonance induced by variation of  $\alpha$  was estimated a long time ago in Refs. 28,29. Recently we performed a rough estimate of the effect of the variation of  $X_q = m_q / \Lambda_{QCD}$ .<sup>9,22,30</sup> The final result is

$$\delta E_r \approx 10^6 \text{ eV} \left( \frac{\delta \alpha}{\alpha} - 10 \frac{\delta X_q}{X_q} + 100 \frac{\delta X_s}{X_s} \right) \quad (5)$$

with  $m_q = (m_u + m_d)/2$  and  $m_s$  the strange quark mass. Refs. 19–21 found that  $|\delta E_r| < 0.1$  eV. This gives us a limit

$$\left| 0.01 \frac{\delta\alpha}{\alpha} - 0.1 \frac{\delta X_q}{X_q} + \frac{\delta X_s}{X_s} \right| < 10^{-9} \quad (6)$$

The contribution of  $\alpha$  variation to this equation is very small and should be neglected since the accuracy of the calculation of the main term is low. Thus, the Oklo data can not give any limit on the variation of  $\alpha$ . Assuming linear time dependence during last 2 billion years we obtain an estimate  $|\dot{X}_s/X_s| < 10^{-18}$  yr<sup>-1</sup>.

## 4. Atomic spectra

### 4.1. Comparison of quasar absorption spectra with laboratory spectra

Savedoff<sup>31</sup> proposed the use of a fine structure multiplet to perform measurements of  $\alpha$  variation by comparison of cosmic and laboratory optical spectra. There were numerous works successfully implementing this “alkali-doublet” method (see review 1).

Later we developed a different approach: the many-multiplet method.<sup>32,33</sup> The relative value of any relativistic corrections to atomic transition frequencies is proportional to  $\alpha^2$ . These corrections can exceed the fine structure interval between the excited levels by an order of magnitude (for example, an  $s$ -wave electron does not have the spin-orbit splitting but it has the maximal relativistic correction to energy). The relativistic corrections vary very strongly from atom to atom and can have opposite signs in different transitions (for example, in  $s$ - $p$  versus  $d$ - $p$  transitions). Thus, any variation of  $\alpha$  could be revealed by comparing different transitions in different atoms in cosmic and laboratory spectra. The number of spectral lines of different elements involved is 1-2 orders of magnitude larger. This method improves the sensitivity to any variation of  $\alpha$  by more than an order of magnitude compared to the alkali-doublet method.

Relativistic many-body calculations are used to reveal the dependence of atomic frequencies on  $\alpha$  for a range of atomic species observed in quasar absorption spectra<sup>32–38</sup> (a 2004 summary may be found in Ref. 39). It is convenient to present results for the transition frequencies as functions of  $\alpha^2$  in the form

$$\omega = \omega_0 + qx, \quad (7)$$

where  $x = (\frac{\alpha}{\alpha_0})^2 - 1 \approx \frac{2\delta\alpha}{\alpha}$  and  $\omega_0$  is a laboratory frequency of a particular transition. We stress that the second term contributes only if  $\alpha$  deviates from the laboratory value  $\alpha_0$ . We performed accurate many-body calculations of the coefficients  $q$  for all transitions of astrophysical interest (strong E1 transitions from the ground state) in Mg I, Mg II, Fe I, Fe II, Cr II, Ni II, Al II, Al III, Si II, Zn II, Mn II, and many other atoms and ions which are seen in quasar absorption spectra, but have not yet been used in the quasar measurements because of the absence of accurate UV transition laboratory wavelengths. For a “shopping list” of needed measurements, see Ref. 39. It is very important that this set of transitions contains three large classes: positive shifters (large positive coefficients  $q > 1000 \text{ cm}^{-1}$ ), negative shifters (large negative coefficients  $q < -1000 \text{ cm}^{-1}$ ) and anchor lines with small values of  $q$ . This gives us an excellent control of systematic errors since systematic effects do not “know” about sign and magnitude of  $q$ . Comparison of cosmic frequencies  $\omega$  and laboratory frequencies  $\omega_0$  allows us to measure  $\frac{\delta\alpha}{\alpha}$ .

Analysis of three independent samples of data containing 143 absorption systems spread over redshift range  $0.2 < z < 4.2$  gives<sup>5</sup>  $\frac{\delta\alpha}{\alpha} = (-0.543 \pm 0.116) \times 10^{-5}$ . If one assumes the linear time-dependence of  $\alpha$ , the fit of the data gives  $d \ln \alpha / dt = (6.40 \pm 1.35) \times 10^{-16} \text{ yr}^{-1}$  (over time interval about 12 billion years). A very extensive search for possible systematic errors has shown that known systematic effects cannot explain the result.<sup>40</sup>

Our method and calculations<sup>32-37</sup> were used by two other groups<sup>41-43</sup> to analyse data obtained on the VLT. However, they have not detected any variation of  $\alpha$ . Recently, the results of Ref. 41 were questioned in a reanalysis of the same spectral data.<sup>6,7</sup> The re-analysis revealed flawed parameter estimation methods; a more accurate fit gives  $\frac{\delta\alpha}{\alpha} = (-0.64 \pm 0.36) \times 10^{-5}$  (instead of the  $\frac{\delta\alpha}{\alpha} = (-0.06 \pm 0.06) \times 10^{-5}$  reported in Ref. 41). However, even this revised result may require further revision.

One systematic effect that is still not completely excluded is that the effect of  $\alpha$  variation may be imitated by a large change in relative isotope abundance during last 10 billion years. Spurious observation of variation in  $\alpha$  due to a change in the relative isotope abundance of any one element has been ruled out. Nevertheless, an improbable “conspiracy” of several elements could mimic the observed effect. We have performed very complicated calculations of these isotopic shifts.<sup>44-49</sup> However, as shown in Ref. 49, calculations in atoms and ions with an open d-shell (like Fe II, Ni II, Cr II, Mn II, Ti II) are difficult, and our accuracy may be very low. Therefore measurements for at least a few lines are needed in order to benchmark

calculations. Additionally, these measurements are needed to study the evolution of isotope abundances in the Universe, and to test models of nuclear reactions in stars and supernovae.

A comparison of the hyperfine transition in atomic hydrogen with optical transitions in ions was done in Refs. 50,51. This method allows one to study time-variation of the parameter  $F = \alpha^2 \mu g_p$ . Analysis of 9 quasar spectra with redshifts  $0.23 \leq z \leq 2.35$  gave

$$\delta F/F = (6.3 \pm 9.9) \times 10^{-6}, \quad (8)$$

$$\dot{F}/F = (-6 \pm 12) \times 10^{-16} \text{ yr}^{-1}. \quad (9)$$

#### 4.2. *Optical atomic clocks*

Optical clocks also include transitions which have positive, negative or small contributions of the relativistic corrections to frequencies. We used the same methods of relativistic many-body calculations used in the quasar absorption studies to calculate the dependence on  $\alpha$  of different clocks.<sup>33,34,52-55</sup> A 2004 summary of the results for the coefficients  $q$  is presented in Ref. 56. The  $q$  coefficients for optical clock transitions may be substantially larger than in cosmic transitions since the clock transitions are often in heavy atoms (Hg II, Yb II, Yb III, etc.) while cosmic spectra contain mostly light atoms lines ( $Z < 33$ ). The relativistic effects are proportional to  $(Z\alpha)^2$ .

#### 4.3. *Enhancement of the effect of $\alpha$ -variation in atoms*

An enhancement of the relative effect of  $\alpha$ -variation can be obtained in transitions between the almost degenerate levels in Dy atom.<sup>34,55</sup> These levels move in opposite directions if  $\alpha$  varies. The relative variation may be presented as  $\delta\omega/\omega = K\delta\alpha/\alpha$  where the coefficient  $K$  exceeds  $10^8$  ( $q = 30,000 \text{ cm}^{-1}$ ,  $\omega \sim 10^{-4} \text{ cm}^{-1}$ ). Specific values of  $K = 2q/\omega$  are different for different hyperfine components and isotopes which have different  $\omega$ . An experiment is currently underway to place limits on  $\alpha$  variation using this transition.<sup>57,58</sup> The current limit is  $\dot{\alpha}/\alpha = (-2.7 \pm 2.6) \times 10^{-15} \text{ yr}^{-1}$ . Unfortunately, one of the levels has quite a large linewidth and this limits the accuracy. Several other enhanced effects of  $\alpha$  variation in atoms have been calculated.<sup>59,60</sup>

#### 4.4. *Atomic microwave clocks*

Hyperfine microwave transitions may be used to search for  $\alpha$ -variation.<sup>61</sup> Karshenboim<sup>62</sup> has pointed out that measurements of ratios of hyperfine

structure intervals in different atoms are also sensitive to variations in nuclear magnetic moments. However, the magnetic moments are not the fundamental parameters and cannot be directly compared with any theory of the variations. Atomic and nuclear calculations are needed for the interpretation of the measurements. We have performed both atomic calculations of the  $\alpha$ -dependence<sup>33,34,52–56</sup> and nuclear calculations of the  $X_q$ -dependence<sup>63</sup> (see also Ref. 26) for all microwave transitions of current experimental interest including hyperfine transitions in  $^{133}\text{Cs}$ ,  $^{87}\text{Rb}$ ,  $^{171}\text{Yb}^+$ ,  $^{199}\text{Hg}^+$ ,  $^{111}\text{Cd}$ ,  $^{129}\text{Xe}$ ,  $^{139}\text{La}$ ,  $^1\text{H}$ ,  $^2\text{H}$  and  $^3\text{He}$ . The results for the dependence of the transition frequencies on variation of  $\alpha$ ,  $X_e = m_e/\Lambda_{QCD}$  and  $X_q = m_q/\Lambda_{QCD}$  are presented in Ref. 63. Also, one can find there experimental limits on these variations which follow from the recent measurements. The accuracy is approaching  $10^{-15}$  per year. This may be compared to the sensitivity  $\sim 10^{-5} - 10^{-6}$  per  $10^{10}$  years obtained using the quasar absorption spectra.

According to Ref. 63 the frequency ratio  $Y$  of the 282 nm  $^{199}\text{Hg}^+$  optical clock transition to the ground state hyperfine transition in  $^{133}\text{Cs}$  has the following dependence on the fundamental constants:

$$\dot{Y}/Y = -6\dot{\alpha}/\alpha - \dot{\mu}/\mu - 0.01\dot{X}_q/X_q \quad (10)$$

This ratio has been measured<sup>64</sup> as  $\dot{Y}/Y = (0.37 \pm 0.39) \times 10^{-15} \text{ yr}^{-1}$ . Assuming a linear time dependence we obtained from the quasar result<sup>65</sup> (see Sec. 5.2)  $\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1}$ . Combining this result and the atomic clock result for  $Y$  gives the best present limit on the variation of  $\alpha$ :

$$\dot{\alpha}/\alpha = (-0.8 \pm 0.8) \times 10^{-16} \text{ yr}^{-1} . \quad (11)$$

Here we neglected the small ( $\sim 1\%$ ) contribution of  $X_q$ .

## 5. Molecular spectra

Recently we wrote a review<sup>66</sup> about search for the variation of the fundamental constants in quasar and laboratory molecular spectra. One recent noteworthy result is a limit on cosmological variation of  $\mu$  in quasar spectra using molecular hydrogen transitions in the Ly- $\alpha$  forest.<sup>67</sup> By carefully controlling systematics, the authors obtained  $\Delta\mu/\mu = (2.6 \pm 3.0) \times 10^{-6}$  at redshifts  $z \approx 2.6 - 3.0$ . Below we present several examples related to our works.

### 5.1. Comparison of hydrogen hyperfine and molecular rotational quasar spectra

The frequency of the hydrogenic hyperfine line is proportional to  $\alpha^2 \mu g_p$ ; molecular rotational frequencies are proportional to  $\mu$ . Comparison places limits on the variation of the parameter  $F = \alpha^2 g_p$ .<sup>68</sup> Recently a similar analysis was repeated by Murphy *et al.*<sup>69</sup> using more accurate data for the same object at  $z = 0.247$  and for a more distant object at  $z = 0.6847$ , and the following limits for the relative variation of  $F$  were obtained:

$$\delta(\ln F) = (-2.0 \pm 4.4) \times 10^{-6} \quad (12)$$

$$\delta(\ln F) = (-1.6 \pm 5.4) \times 10^{-6} \quad (13)$$

The object at  $z = 0.6847$  is associated with the gravitational lens toward quasar B0218+357 and corresponds to lookback time  $\sim 6.5$  Gyr.

### 5.2. Enhancement of variation of $\mu$ in inversion spectrum of ammonia and limit from quasar spectra

A few years ago van Veldhoven *et al.* suggested using a decelerated molecular beam of  $\text{ND}_3$  to search for the variation of  $\mu$  in laboratory experiments.<sup>70</sup> The ammonia molecule has a pyramidal shape and the inversion frequency depends on the exponentially small tunneling of three hydrogens (or deuteriums) through the potential barrier. Because of that, it is very sensitive to any changes of the parameters of the system, particularly to the reduced mass for this vibrational mode. This fact was used in<sup>65</sup> to place the best limit on the cosmological variation of  $\mu$ .

The inversion vibrational mode of ammonia is described by a double well potential with the first two vibrational levels lying below the barrier. Because of the tunneling, these two levels are split in inversion doublets. The lower doublet corresponds to wavelength  $\lambda \approx 1.25$  cm and is used in ammonia masers. Molecular rotation leads to the centrifugal distortion of the potential curve, therefore the inversion splitting depends on the rotational angular momentum  $J$  and its projection on the molecular symmetry axis  $K$ :

$$\omega_{\text{inv}}(J, K) = \omega_{\text{inv}}^0 - c_1 [J(J+1) - K^2] + c_2 K^2 + \dots, \quad (14)$$

where we omitted terms with higher powers of  $J$  and  $K$ . Numerically,  $\omega_{\text{inv}}^0 \approx 23.787$  GHz,  $c_1 \approx 151.3$  MHz, and  $c_2 \approx 59.7$  MHz.

In addition to the rotational structure (14) the inversion spectrum has a much smaller hyperfine structure. For the main nitrogen isotope  $^{14}\text{N}$ ,

the hyperfine structure is dominated by the electric quadrupole interaction ( $\sim 1$  MHz). Because of the dipole selection rule  $\Delta K = 0$  the levels with  $J = K$  are metastable. In astrophysics the lines with  $J = K$  are also narrower and stronger than others, but the hyperfine structure for spectra with high redshifts is still not resolved. We obtained the following results for  $\text{NH}_3$ <sup>65</sup> (in atomic units):

$$\delta(\ln \omega_{\text{inv}}^0) \approx 4.46 \delta(\ln \mu) \quad (15)$$

$$\delta(\ln c_{1,2}) = 5.1 \delta(\ln \mu). \quad (16)$$

For  $\text{ND}_3$  the inversion frequency is 15 times smaller and this leads to a higher relative sensitivity of the inversion frequency to  $\mu$ :

$$\delta(\ln \omega_{\text{inv}}^0) \approx 5.7 \delta(\ln \mu) \quad (17)$$

$$\delta(\ln c_{1,2}) = 6.2 \delta(\ln \mu). \quad (18)$$

We see that the inversion frequency  $\omega_{\text{inv}}^0$  and the rotational intervals  $\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)$  have different dependencies on the constant  $\mu$ . In principle, this allows one to study time-variation of  $\mu$  by comparing different intervals in the inversion spectrum of ammonia. For example, if we compare the rotational interval to the inversion frequency, then Eqs. (15) and (16) give:

$$\delta \ln ([\omega_{\text{inv}}(J_1, K_1) - \omega_{\text{inv}}(J_2, K_2)]/\omega_{\text{inv}}^0) = 0.6 \delta(\ln \mu). \quad (19)$$

The relative effects are substantially larger if we compare the inversion transitions with the transitions between the quadrupole and magnetic hyperfine components. However, in practice this method will not work because of the smallness of the hyperfine structure compared to typical line widths in astrophysics.

We compared the inversion spectrum of  $\text{NH}_3$  with rotational spectra of other molecules, where

$$\frac{\delta \omega_{\text{rot}}}{\omega_{\text{rot}}} = \frac{\delta \mu}{\mu}. \quad (20)$$

High precision data on the redshifts of  $\text{NH}_3$  inversion lines exist for the previously mentioned object B0218+357 at  $z \approx 0.6847$ .<sup>71</sup> Comparing them with the redshifts of rotational lines of CO,  $\text{HCO}^+$ , and HCN molecules from Ref. 72 one can get the following limit:

$$\frac{\delta \mu}{\mu} = \frac{\delta X_e}{X_e} = (-0.6 \pm 1.9) \times 10^{-6}. \quad (21)$$

Assuming a linear time dependence over the 6.5 Gyr (corresponding to  $z \approx 0.68$ ), we obtain the most stringent present limit for the variation of  $\mu$  and  $X_e$ .<sup>65</sup>

$$\dot{\mu}/\mu = \dot{X}_e/X_e = (1 \pm 3) \times 10^{-16} \text{ yr}^{-1}. \quad (22)$$

This result is combined with atomic clock results (Sec. 4.4) to give the best current limits on variation of  $\alpha$  (Equation 11).

### 5.3. Proposals for enhanced effects in diatomic molecules

In transitions between very close narrow levels of different natures in diatomic molecules the relative effects of the variation may be enhanced by several orders of magnitude. Such levels may occur due to cancellation between the hyperfine and rotational structures,<sup>73</sup> or between the fine and vibrational structures of the electronic ground state.<sup>74</sup> The intervals between the levels are conveniently located in microwave frequency range and the level widths are very small, typically  $\sim 10^{-2}$  Hz.

#### 5.3.1. Molecules with cancellation between hyperfine structure and rotational intervals

Consider diatomic molecules with unpaired electron and ground state  $^2\Sigma$ , for example, LaS, LaO, LuS, LuO, YbF.<sup>75</sup> The hyperfine interval  $\Delta_{\text{hfs}}$  is proportional to  $\alpha^2 Z F_{\text{rel}}(\alpha Z) \mu g_{\text{nuc}}$ , where  $F_{\text{rel}}$  is additional relativistic (Casimir) factor. The rotational interval  $\Delta_{\text{rot}} \sim \mu$  is roughly independent of  $\alpha$ . If we find a molecule with  $\Delta_{\text{hfs}} \approx \Delta_{\text{rot}}$  the splitting  $\omega$  between hyperfine and rotational levels will depend on the following combination

$$\omega \sim [\alpha^2 F_{\text{rel}}(\alpha Z) g_{\text{nuc}} - \text{const}]. \quad (23)$$

Relative variation is then given by

$$\frac{\delta\omega}{\omega} \approx \frac{\Delta_{\text{hfs}}}{\omega} \left[ (2 + K) \frac{\delta\alpha}{\alpha} + \frac{\delta g_{\text{nuc}}}{g_{\text{nuc}}} \right], \quad (24)$$

where the factor  $K$  comes from variation of  $F_{\text{rel}}(\alpha Z)$ , and for  $Z \sim 50$ ,  $K \approx 1$ . Using data from Ref. 75 one can find<sup>73</sup> that  $\omega = (0.002 \pm 0.010) \text{ cm}^{-1}$  for  $^{139}\text{La}^{32}\text{S}$ . Note that for  $\omega = 0.002 \text{ cm}^{-1}$  the relative frequency shift is:

$$\frac{\delta\omega}{\omega} \approx 600 \frac{\delta\alpha}{\alpha}. \quad (25)$$

### 5.3.2. Molecules with cancelation between fine structure and vibrational intervals

The fine structure interval  $\omega_f$  rapidly grows with nuclear charge  $Z$

$$\omega_f \sim Z^2 \alpha^2, \quad (26)$$

while the vibration energy quantum decreases with the atomic mass:

$$\omega_{\text{vib}} \sim M_r^{-1/2} \mu^{1/2}, \quad (27)$$

where the reduced mass for the molecular vibration is  $M_r m_p$ . Therefore, we obtain an equation  $Z = Z(M_r, v)$  for the lines on the  $Z$ - $M_r$  plane where we can expect approximate cancelation between the fine structure and vibrational intervals:

$$\omega = \omega_f - v \omega_{\text{vib}} \approx 0, \quad v = 1, 2, \dots \quad (28)$$

Using Eqs. (26–28) it is easy to extract the dependence of the transition frequency on the fundamental constants:

$$\frac{\delta\omega}{\omega} = \frac{1}{\omega} \left( 2\omega_f \frac{\delta\alpha}{\alpha} + \frac{v}{2} \omega_{\text{vib}} \frac{\delta\mu}{\mu} \right) \approx K \left( 2 \frac{\delta\alpha}{\alpha} + \frac{1}{2} \frac{\delta\mu}{\mu} \right), \quad (29)$$

where the enhancement factor  $K = \frac{\omega_f}{\omega}$  determines the relative frequency shift for the given change of fundamental constants. Large values of  $K$  suggest potentially favorable cases for making experiment, because it is usually preferable to have larger relative shifts. However, there is no strict rule that larger  $K$  is always better. In some cases, such as very close levels, this factor may become irrelevant. Thus, it is also important to consider the absolute values of the shifts and compare them to the linewidths of the corresponding transitions.

Because there are a finite number of molecules we cannot have  $\omega = 0$  exactly. However, a large number of molecules have  $\omega/\omega_f \ll 1$  and  $|K| \gg 1$ . Moreover, an additional “fine tuning” may be achieved by selection of isotopes and rotational,  $\Omega$ -doublet, and hyperfine components. Therefore, we have two large manifolds, the first one built on the electron fine-structure excited state and the second one built on the vibrational excited state. If these manifolds overlap one may select two or more transitions with different signs of  $\omega$ . In this case the expected sign of the  $|\omega|$ -variation must be different (since the variation  $\delta\omega$  has the same sign) and one can eliminate some systematic effects. Such control of systematic effects was used for transitions between close levels in two dysprosium isotopes.<sup>57,58</sup> The sign of the energy difference between two levels belonging to different electron configurations is different in <sup>163</sup>Dy and <sup>162</sup>Dy.

Among the interesting molecules where the ground state is split in two fine-structure levels and (28) is approximately fulfilled, there are  $\text{Cl}_2^+$  (enhancement  $K = 1600$ ),  $\text{SiBr}$  ( $K = 360$ ),  $\text{CuS}$  ( $K = 24$ ) and  $\text{IrC}$  ( $K = 160$ ). The list of molecules is not complete because of the lack of data in Ref. 75. The molecules  $\text{Cl}_2^+$  and  $\text{SiBr}$  are particularly interesting. For both of them the frequency  $\omega$  defined by (28) is of the order of  $1 \text{ cm}^{-1}$  and comparable to the rotational constant  $B$ . Reducing  $\omega$  further by the proper choice of isotopes, rotational quantum number  $J$  and hyperfine components, we may expect  $K \sim 10^3 - 10^5$ . New dedicated measurements are needed to determine exact values of the transition frequencies and find the best transitions. However, it is easy to find necessary accuracy of the frequency shift measurements. According to (29) the expected frequency shift is

$$\delta\omega = 2\omega_f \left( \frac{\delta\alpha}{\alpha} + \frac{1}{4} \frac{\delta\mu}{\mu} \right) \quad (30)$$

Assuming  $\delta\alpha/\alpha \sim 10^{-15}$  and  $\omega_f \sim 500 \text{ cm}^{-1}$ , we obtain  $\delta\omega \sim 10^{-12} \text{ cm}^{-1} \sim 3 \times 10^{-2} \text{ Hz}$ , which is larger than the natural width  $\sim 10^{-2} \text{ Hz}$ . (In order to obtain similar sensitivity comparing hyperfine transition frequencies for Cs and Rb one has to measure the shift at the  $\sim 10^{-5} \text{ Hz}$  level.)

### 5.3.3. *Molecular ion HfF<sup>+</sup>*

The ion  $\text{HfF}^+$  and other similar ions are considered by Cornell's group in JILA for experiments to search for the electric dipole moment (EDM) of the electron. Recent calculations<sup>76</sup> suggest that the ground state of this ion is  $^1\Sigma^+$  and the first excited state  $^3\Delta_1$  lies only  $1633 \text{ cm}^{-1}$  higher. Calculated vibrational frequencies for these two states are  $790$  and  $746 \text{ cm}^{-1}$  respectively. For these parameters the vibrational level  $v = 3$  of the ground state is only  $10 \text{ cm}^{-1}$  from the  $v = 1$  level of the state  $^3\Delta_1$ . Thus, instead of (28) we now have:

$$\omega = \omega_{\text{el}} + \frac{3}{2}\omega_{\text{vib}}^{(1)} - \frac{7}{2}\omega_{\text{vib}}^{(0)} \approx 0, \quad (31)$$

where superscripts 0 and 1 correspond to the ground and excited electronic states. The electronic transition  $\omega_{\text{el}}$  is not a fine structure transition and (26) is not applicable. Instead, we can write:

$$\omega_{\text{el}} = \omega_{\text{el},0} + qx, \quad x = \alpha^2/\alpha_0^2 - 1. \quad (32)$$

Our estimate is<sup>74</sup>

$$\frac{\delta\omega}{\omega} \approx \left( \frac{2q}{\omega} \frac{\delta\alpha}{\alpha} + \frac{\omega_{\text{el}}}{2\omega} \frac{\delta\mu}{\mu} \right) \approx \left( 2000 \frac{\delta\alpha}{\alpha} + 80 \frac{\delta\mu}{\mu} \right), \quad (33)$$

$$\delta\omega \approx 20000 \text{ cm}^{-1} (\delta\alpha/\alpha + 0.04\delta\mu/\mu). \quad (34)$$

Assuming  $\delta\alpha/\alpha \sim 10^{-15}$  we obtain  $\delta\omega \sim 0.6$  Hz. The natural width is about 2 Hz.

We also present the result for transition between close levels in  $\text{Cs}_2$  molecule suggested in.<sup>77,78</sup> Our estimate is:<sup>66</sup>

$$\delta\omega \approx \left( -240 \frac{\delta\alpha}{\alpha} - 1600 \frac{\delta\mu}{\mu} \right) \text{cm}^{-1}, \quad (35)$$

## 6. Enhanced effect of variation of $\alpha$ and strong interaction in UV transition of $^{229}\text{Th}$ nucleus (nuclear clock)

A very narrow level ( $7.6 \pm 0.5$ ) eV above the ground state exists in  $^{229}\text{Th}$  nucleus.<sup>79</sup> The position of this level was determined from the energy differences of many high-energy  $\gamma$ -transitions to the ground and excited states. The subtraction produces the large uncertainty in the position of the 7.6 eV excited state. The width of this level is estimated to be about  $10^{-4}$  Hz.<sup>80</sup> This would explain why it is so hard to find the direct radiation in this very weak transition. However, the search for the direct radiation continues.<sup>81</sup>

The  $^{229}\text{Th}$  transition is very narrow and can be investigated with laser spectroscopy. This makes  $^{229}\text{Th}$  a possible reference for an optical clock of very high accuracy, and opens a new possibility for a laboratory search for the variation of the fundamental constants.<sup>82</sup> As is shown in Ref. 83 there is an additional very important advantage: the relative effects of variation of  $\alpha$  and  $m_q/\Lambda_{QCD}$  are enhanced by 5 orders of magnitude. This estimate has been confirmed recently by more accurate calculations.<sup>84,85</sup>

A rough estimate for the relative variation of the  $^{229}\text{Th}$  transition frequency is

$$\frac{\delta\omega}{\omega} \approx 10^5 \left( 0.1 \frac{\delta\alpha}{\alpha} + \frac{\delta X_q}{X_q} \right) \quad (36)$$

Therefore, the experiment would have the potential of improving the sensitivity to temporal variation of the fundamental constants by many orders of magnitude. Indeed, we obtain the following energy shift in the 7.6 eV  $^{229}\text{Th}$  transition:

$$\delta\omega \approx \frac{\delta X_q}{X_q} \text{MeV} \quad (37)$$

This corresponds to the frequency shift  $\delta\nu \approx 3 \cdot 10^{20} \delta X_q / X_q$  Hz. The width of this transition is  $10^{-4}$  Hz so one may hope to get the sensitivity to the variation of  $X_q$  about  $10^{-24}$  per year. This is  $10^{10}$  times better than the current atomic clock limit on the variation of  $X_q$ .

Note that there are other narrow low-energy levels in nuclei, e.g. 76 eV level in  $^{235}\text{U}$  with lifetime 26.6 minutes (see, e.g. Ref. 82). One may expect a similar enhancement there. Unfortunately, this level cannot be reached with usual lasers. In principle, it may be investigated using a free-electron laser or synchrotron radiation. However, the accuracy of the frequency measurements is much lower in this case.

## 7. Enhancement of variation of fundamental constants in ultracold atom and molecule systems near Feshbach resonances

Scattering length  $A$ , which can be measured in Bose-Einstein condensate and Feshbach molecule experiments, is extremely sensitive to the variation of the electron-to-proton mass ratio  $\mu = m_e/m_p$  or  $X_e = m_e/\Lambda_{QCD}$ :<sup>86</sup>

$$\frac{\delta A}{A} = K \frac{\delta \mu}{\mu} = K \frac{\delta X_e}{X_e}, \quad (38)$$

where  $K$  is the enhancement factor. For example, for Cs-Cs collisions we obtained  $K \sim 400$ . With the Feshbach resonance, however, one is given the flexibility to adjust position of the resonance using external fields. Near a narrow magnetic or an optical Feshbach resonance the enhancement factor  $K$  may be increased by many orders of magnitude.

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## References

1. J.-P. Uzan, *Rev. Mod. Phys.* **75**, 403 (2003).
2. V. V. Flambaum and E. Shuryak arXiv:physics/0701220.
3. J. K. Webb *et al.*, *Phys. Rev. Lett.* **82**, 884 (1999).
4. J. K. Webb *et al.*, *Phys. Rev. Lett.* **87**, 091301 (2001).
5. M. T. Murphy, J. K. Webb and V. V. Flambaum, *Mon. Not. R. Astron. Soc.* **345**, 609 (2003).

6. M. T. Murphy, J. K. Webb and V. V. Flambaum, *Phys. Rev. Lett.* **99**, 239001 (2007).
7. M. T. Murphy, J. K. Webb and V. V. Flambaum, *Mon. Not. R. Astron. Soc.* **384**, 1053 (2008).
8. E. Reynold *et al.*, *Phys. Rev. Lett.* **96**, 151101 (2006).
9. V. F. Dmitriev, V. V. Flambaum and J. K. Webb, *Phys. Rev. D* **69**, 063506 (2004).
10. V. V. Flambaum and R. B. Wiringa, *Phys. Rev. C* **76**, 054002 (2007).
11. V. V. Flambaum, *Int. J. Mod. Phys. A* **22**, 4937 (2007).
12. S. N. Lea, *Rep. Prog. Phys.* **70**, 1473 (2007).
13. W. J. Marciano, *Phys. Rev. Lett.* **52**, 489 (1984).
14. X. Calmet and H. Fritzsche, *Eur. Phys. J. C* **24**, 639 (2002).
15. P. Langacker, G. Segre and M. J. Strassler, *Phys. Lett. B* **528**, 121 (2002).
16. C. Wetterich, *JCAP* **0310**, 02 (2003).
17. T. Dent and M. Fairbairn, *Nucl. Phys. B* **653**, 256 (2003).
18. S. K. Lamoreaux and J. R. Torgerson, *Phys. Rev. D* **69**, 121701 (2004).
19. C. R. Gould, E. I. Sharapov and S. K. Lamoreaux, *Phys. Rev. C* **74**, 024607 (2006).
20. Yu. V. Petrov *et al.*, *Phys. Rev. C* **74**, 064610 (2006).
21. Y. Fujii *et al.*, *Nucl. Phys. B* **573**, 377 (2000).
22. V. V. Flambaum and E. V. Shuryak, *Phys. Rev. D* **67**, 083507 (2003).
23. T. Dent, S. Stern and C. Wetterich, *Phys. Rev. D* **76**, 063513 (2007).
24. V. V. Flambaum, A. Höll, P. Jaikumar, C. D. Roberts and S. V. Wright, *Few-Body Syst.* **38**, 31 (2006).
25. A. Höll, P. Maris, C. D. Roberts and S. V. Wright arXiv:nucl-th/0512048.
26. V. V. Flambaum, D. B. Leinweber, A. W. Thomas and R. D. Young, *Phys. Rev. D* **69**, 115006 (2004).
27. R. H. Cyburt, B. D. Fields and K. A. Olive arXiv:0808.2818.
28. A. I. Shlyakhter, *Nature* **264**, 340 (1976).
29. T. Damour and F. J. Dyson, *Nucl. Phys. B* **480**, 37 (1996).
30. V. V. Flambaum and E. V. Shuryak, *Phys. Rev. D* **65**, 103503 (2002).
31. M. P. Savedoff, *Nature* **178**, 689 (1956).
32. V. A. Dzuba, V. V. Flambaum and J. K. Webb, *Phys. Rev. Lett.* **82**, 888 (1999).
33. V. A. Dzuba, V. V. Flambaum and J. K. Webb, *Phys. Rev. A* **59**, 230 (1999).
34. V. A. Dzuba, V. V. Flambaum and M. V. Marchenko, *Phys. Rev. A* **68**, 022506 (2003).
35. V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **71**, 052509 (2005).
36. V. A. Dzuba, V. V. Flambaum, M. G. Kozlov and M. Marchenko, *Phys. Rev. A* **66**, 022501 (2002).
37. J. C. Berengut, V. A. Dzuba, V. V. Flambaum and M. V. Marchenko, *Phys. Rev. A* **70**, 064101 (2004).
38. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **77**, 012514 (2008).
39. J. C. Berengut, V. A. Dzuba, V. V. Flambaum, M. G. Kozlov, M. V. Marchenko, M. T. Murphy and J. K. Webb arXiv:physics/0408017.
40. M. T. Murphy, J. K. Webb, V. V. Flambaum, C. W. Churchill and J. X.

- Prochaska, *Mon. Not. R. Astron. Soc.* **327**, 1223 (2001).
41. R. Srikanand, H. Chand, P. Petitjean and B. Aracil, *Phys. Rev. Lett.* **92**, 121302 (2004).
  42. S. A. Levshakov *et al.*, *Astron. Astrophys.* **434**, 827 (2005).
  43. S. A. Levshakov *et al.*, *Astron. Astrophys.* **449**, 879 (2006).
  44. M. G. Kozlov, V. A. Korol, J. C. Berengut, V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **70**, 062108 (2004).
  45. J. C. Berengut, V. A. Dzuba, V. V. Flambaum and M. G. Kozlov, *Phys. Rev. A* **69**, 044102 (2004).
  46. J. C. Berengut, V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **68**, 022502 (2003).
  47. J. C. Berengut, V. V. Flambaum and M. G. Kozlov, *Phys. Rev. A* **72**, 044501 (2005).
  48. J. C. Berengut, V. V. Flambaum and M. G. Kozlov, *Phys. Rev. A* **73**, 012504 (2006).
  49. J. C. Berengut, V. V. Flambaum and M. G. Kozlov, *J. Phys. B* **41**, 235702 (2008).
  50. P. Tzanavaris, J. K. Webb, M. T. Murphy, V. V. Flambaum and S. J. Curran, *Phys. Rev. Lett.* **95**, 041301 (2005).
  51. P. Tzanavaris, J. K. Webb, M. T. Murphy, V. V. Flambaum and S. J. Curran, *Mon. Not. R. Astron. Soc.* **374**, 634 (2007).
  52. V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **61**, 034502 (2000).
  53. E. J. Angstmann, V. V. Flambaum and S. G. Karshenboim, *Phys. Rev. A* **70**, 044104 (2004).
  54. E. J. Angstmann, V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **70**, 014102 (2004).
  55. V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **77**, 012515 (2008).
  56. E. J. Angstmann, V. A. Dzuba and V. V. Flambaum arXiv:physics/0407141.
  57. A. T. Nguyen, D. Budker, S. K. Lamoreaux and J. R. Torgerson, *Phys. Rev. A* **69**, 022105 (2004).
  58. A. Cingöz *et al.*, *Phys. Rev. Lett.* **98**, 040801 (2007).
  59. V. A. Dzuba and V. V. Flambaum, *Phys. Rev. A* **72**, 052514 (2005).
  60. E. J. Angstmann, V. A. Dzuba, V. V. Flambaum, S. G. Karshenboim and A. Yu. Nevsky, *J. Phys. B* **39**, 1937 (2006), physics/0511180.
  61. J. D. Prestage, R. L. Tjoelker and L. Maleki, *Phys. Rev. Lett.* **74**, 3511 (1995).
  62. S. G. Karshenboim, *Can. J. Phys.* **78**, 639 (2000).
  63. V. V. Flambaum and A. F. Tedesco, *Phys. Rev. C* **73**, 055501 (2006).
  64. T. M. Fortier *et al.*, *Phys. Rev. Lett.* **98**, 070801 (2007).
  65. V. V. Flambaum and M. G. Kozlov, *Phys. Rev. Lett.* **98**, 240801 (2007).
  66. V. V. Flambaum and M. G. Kozlov arXiv:0711.4536.
  67. J. A. King, J. K. Webb, M. T. Murphy and R. F. Carswell, *accepted to Phys. Rev. Lett.* arXiv:0807.4366.
  68. M. J. Drinkwater, J. K. Webb, J. D. Barrow and V. V. Flambaum, *Mon. Not. R. Astron. Soc.* **295**, 457 (1998).
  69. M. T. Murphy *et al.*, *Mon. Not. R. Astron. Soc.* **327**, 1244 (2001).
  70. J. van Veldhoven *et al.*, *Eur. Phys. J. D* **31**, 337 (2004).

71. C. Henkel *et al.*, *Astron. Astrophys.* **440**, 893 (2005).
72. F. Combes and T. Wiklind, *Astrophys. J.* **486**, L79 (1997).
73. V. V. Flambaum, *Phys. Rev. A* **73**, 034101 (2006).
74. V. V. Flambaum and M. G. Kozlov, *Phys. Rev. Lett.* **99**, 150801 (2007).
75. K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
76. A. N. Petrov, N. S. Mosyagin, T. A. Isaev and A. V. Titov, *Phys. Rev. A* **76**, 030501(R) (2007).
77. D. DeMille, invited talk at 35th Meeting of the Division of Atomic, Molecular and Optical Physics, Tucson, Arizona (2004).
78. D. DeMille *et al.*, *Phys. Rev. Lett.* **100**, 043202 (2008).
79. B. R. Beck *et al.*, *Phys. Rev. Lett.* **98**, 142501 (2007).
80. E. V. Tkalya, A. N. Zherikhin and V. I. Zhudov, *Phys. Rev. C* **61**, 064308 (2000).
81. Z.-T. Lu, E. Peik and D. Habs, private communications.
82. E. Peik and Chr. Tamm, *Europhys. Lett.* **61**, 181 (2003).
83. V. V. Flambaum, *Phys. Rev. Lett.* **97**, 092502 (2006).
84. X.-T. He and Z.-Z. Ren, *J. Phys. G* **34**, 1611 (2006).
85. V. V. Flambaum and R. B. Wiringa arXiv:0807.4943.
86. C. Chin and V. V. Flambaum, *Phys. Rev. Lett.* **96**, 230801 (2006).