REVIEWS OF TOPICAL PROBLEMS

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Laboratory search for time variation in the fine structure constant

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<u>Abstract.</u> Laboratory methods for detecting possible time variation in the fine structure constant are reviewed. Such methods provide a large amount of controllability while at the same time approaching astrophysical tests in terms of sensitivity to the linear drift. Modern high-precision spectroscopic experiments involving atomic transition frequency measurements against the primary ¹³³Cs standard are reviewed. Combining results from different laboratory spectroscopic measurements allows contributions from the electromagnetic and strong interactions to be disentangled.

1. Introduction

The idea of temporal variability of fundamental constants has its origin in Dirac's 'large numbers' hypothesis (1937) proposed to harmonize the main physical laws [1]. This hypothesis called into question the constancy of key parameters underlying a variety of physical theories and gave incentive to the development of a large area of experimental and theoretical physics concerned with the search for time variations in fundamental constants. For the lack of a universally accepted theory predicting fundamental constant values or establishing the internal relationship between them, the search for their potential variations and fluctuations is largely the domain of experimental studies. Interest in this question is encouraged by the fact that theoretical models aimed at unifying

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Received 30 March 2004, revised 8 June 2004 Uspekhi Fizicheskikh Nauk **174** (10) 1171 – 1190 (2004) Translated by Yu V Morozov; edited by A M Semikhatov quantum mechanics and the theory of gravity allow a violation of Einstein's equivalence principle; this, in turn, implies variability of nongravitational constants, one of the causes being fluctuations in the density of the universe [2, 3]. Therefore, knowledge of the magnitude and the upper limit of potential variations in fundamental constants makes it possible to estimate the validity and applicability of new theoretical models. Most hypotheses concerned with possible causes of variations are based on the relationship of the fundamental constants and the boundary conditions between the respective inflationary processes and phase transitions (e.g., within the first seconds after the Big Bang), as well as the continuing expansion of the universe and its residual density fluctuations. It is beyond the scope of the present paper to dwell on possible causes of temporal variability of the fundamental constants that are extensively discussed in the literature (see, e.g., Refs [2, 4-6]). Instead, we focus on the methods and results of the experimental search for the time variation in the electromagnetic coupling constant $\alpha = e^2/\hbar c$.

A number of astrophysical and laboratory experiments have been carried out in the last few decades with the purpose of elucidating the feasibility of time variation in fundamental constants, such as the fine structure constant α , the electron-to-proton mass ratio $\mu = m_e/m_p$, the gravitational interaction constant, etc. A variety of physical objects and phenomena, viz. absorption and emission spectra of galaxies, chemical composition of meteorites and minerals, planets' orbits, transitions in atomic systems, radioactive decay, and many others, are being investigated with an increasingly higher degree of precision. A comprehensive review of this issue was published by J-P Uzan in 2003 [7]. Astrophysical surveys are discussed at length in comprehensive articles by D A Varshalovich [8] and J Bahcall [9].

The area of research in question may be subdivided into two, one comprising experimental studies and the other focused on extralaboratory objects, such as geological specimens and astrophysical data. Pioneering works published in 1956 [10, 11] were concerned with the redshift of fine structure doublet transitions and initiated the epoch of cosmological tests for the time variation in the fine structure constant α . Despite a relatively low sensitivity to α changes (presently amounting to $\Delta \alpha / \alpha = 10^{-6}$ [12]), the method proved to be highly sensitive to the monotonic drift of α due to the enormous time intervals (up to 1.3×10^{10} years) between an emission (absorption) event and the present time. Methods based on the evaluation on nuclear reactions [13, 14] and radioactive decay [15] have similar precision. The methods of extralaboratory object investigation have until recently been recognized as the leading methods for exploring the area in question and having the highest sensitivity (up to 10^{-16} year⁻¹) to relative changes in fundamental constant values. It must be noted, however, that systematic errors intrinsic to these methods are very difficult to estimate numerically. When searching for the degree of variation in the fundamental constants, a number of verisimilar assumptions are made that are virtually unamenable to direct verification, such as the constancy of the isotopic composition of elements in the universe, weak interstellar magnetic fields, temperature values of the earth's surface in the remote past, etc.

On the other hand, laboratory studies highly sensitive to variations in α and other fundamental quantities highlight changes that have taken place over the last few years. Also, systematic errors inherent in laboratory methods are easy to control; moreover, these methods clear the way for independent experiments.

One of the main methods for elucidating temporal variations in the fine structure constant is observing the dynamics of transition frequency ratios in atomic systems over a certain time interval. Considerable progress achieved in the measurement of optical atomic transition frequencies [16, 17] over the last few years is due to the possibility of using phase-coherent comparison of the optical transition frequency and the hyperfine transition frequency in the ¹³³Cs atom currently adopted as the sole definition of the second in the SI. The relative precision of measuring absolute optical transition frequencies reached 10^{-14} by the year 2000 [18] and currently approaches 10^{-15} [19]. Measurements of optical transition frequencies are available for hydrogen [18, 20], calcium [21], ions of strontium [22], indium [23], vtterbium [24-26], mercury [27, 28], and other atomic systems. Also worth noting is the substantial improvement in the stability and absolute precision of primary frequency standards; specifically, the precision of cesium and rubidium standards has reached 8×10^{-16} and 6×10^{-16} , respectively [28, 29].

In 2003–2004, a series of absolute measurements of transition frequencies in several atomic systems were repeated in the US, France, and Germany. The results allowed some stringent constraints to be imposed on the variation in α . These studies came to be known after Ref. [7] had been published. For this reason, the role and the importance of laboratory measurements appear to have been incompletely and imperfectly highlighted in this work. The precision of current measurements amounts to 10^{-15} per year, i.e., almost as high as that of geophysical and astrophysical methods. The potential of laboratory techniques is far from exhausted; both the accuracy of frequency measurements and the time interval separating them continue to increase. It may be conjectured that in a few years, the sensitivity of laboratory spectroscopic techniques to varia-

tions in the fundamental constants will exceed the sensitivity of most extralaboratory methods.

Also, it should be emphasized that laboratory measurements are complementary to astrophysical and geological surveys because they are used to test variations in totally different epochs. For example, it seems logical to assume that variations in the fundamental constants at the time when the universe began were much greater than they are now by virtue of the rapid dynamics of the processes that followed the Big Bang.

The present review describes the main experimental methods in the search for the time variation in the fine structure constant and analyzes results of spectroscopic measurements carried out in different metrological laboratories. For comparison, results obtained by the most sensitive extralaboratory methods are outlined, including data from Oklo studies and the spectra of distant cosmic objects. We also note the new astrophysical findings in Refs [9, 30, 31] that were obtained after review [7] and the statistically significant observations of the α variation [12] had been published. However, these findings are not discussed at length in this paper and are presented only for comparison. Section 3.10 deals with a method intended to disentangle contributions of different types of interactions from the measurements of transition frequencies in atomic systems and to impose stringent constraints on the variability of the fine structure constant $\dot{\alpha}/\alpha$ without model assumptions of the evolution of various types of interactions.

2. Overview of the main results pertaining to the time variation in the fine structure constant α obtained by geological and astrophysical methods

2.1 The Oklo reactor

One of the most accurate estimates of the time variation in the fine structure constant α was obtained from the analysis of events believed to have taken place around 2×10^9 years ago in the Oklo natural nuclear reactor (Gabon, West Africa) [32]. About two billion years ago, a natural mixture of uranium isotopes contained a much higher percentage of 235 U with the half-life $T_{1/2} \simeq 7 \times 10^8$ years. Formation of rich uranium ore deposits gave rise to a slow chain reaction, with water playing the role of moderator of neutrons during the fission process. Studies of uranium fission products and the isotopic composition of other observations that did not originate from fission but underwent intense irradiation by neutrons make it possible to calculate the velocities and cross sections of reactions that occurred at that time. It has been noticed that the ratio of samarium isotopes ¹⁴⁹Sm/¹⁴⁷Sm (which are not uranium fission products) in the Oklo reactor is around 0.02 rather than the much higher ratio of 0.9 in the natural isotopic mixture. The change in the isotope composition is believed to be due to the thermal neutron flux onto ¹⁴⁹Sm resulting in the reaction $n+{}^{149}Sm \rightarrow {}^{150}Sm + \gamma.$ The cross section of this reaction is determined by an almost perfect resonance with a detuning of only 0.1 eV [13]. Thorough analysis of these data makes it possible to estimate the neutron capture cross section at the time of reactor activity and to find the resonance detuning range in the remote past. Recent analysis [14] has demonstrated that α has not changed significantly in 2×10^9 years from its present-day value,

the relative deviation being

$$\frac{\Delta \alpha}{\alpha} = (-0.8 \pm 1.0) \times 10^{-8} \,. \tag{1}$$

However, this result is ambiguous, being essentially dependent on the reaction parameters (temperature) adopted in a given model. The same authors propose the alternative value

$$\frac{\Delta \alpha}{\alpha} = (8.8 \pm 0.7) \times 10^{-8} \,,$$
 (2)

which suggests a statistically significant time variation. This analysis takes only the effect of α variation into consideration and disregards possible correlations between the fine structure constant and other coupling constants. From this standpoint, the result obtained appears to be strongly model-dependent (cf. [15]).

2.2 Astrophysical studies

In the mid-1960s, it was proposed for the first time to use the analysis of astrophysical spectra to estimate stability of the fine structure constant [10]. It can be seen from Table 1 that the ratio of the splitting of fine structure components to the optical transition frequency depends on α^2 alone; when the ratio of the respective frequencies is computed for distant sources, the cosmological redshift *z* becomes smaller. The same is true of the Rydberg constant $Ry = m_e c^2 \alpha^2 / 2h$ (expressed in Hertz units) that, in turn, contains the α -dependence. The redshift of spectral lines is defined as

$$1 + z = \frac{v_{\text{emiss}}}{v_{\text{observ}}}, \qquad (3)$$

where v_{emiss} is the frequency at the moment of emission (absorption) by a distant source in the past and v_{observ} is the observed value. Comparison of the ratios of transition line frequencies from distant sources to those measured in the laboratory allows us to deduce α values in the past. Modern techniques are suited to measuring time intervals that separate moments of light emission (absorption) and the present time as large as 1.3×10^{10} years, i.e., approximately the age of the universe. In the 1960s, measurements of the fine structure doublet splitting in ions of NII and NeIII from Cygnus A having the cosmological redshift z = 0.057 (i.e., an epoch of $\sim 10^9$ years ago) yielded the value $\Delta \alpha / \alpha = (1.8 \pm 1.6) \times 10^{-3}$ [11].

 Table 1. Scaling factors for various types of atomic transitions in the nonrelativistic approximation.

Transition	Scaling factor
Optical Fine structure Hyperfine structure	$ \begin{array}{c} \mathbf{R}\mathbf{y} \\ \alpha^2 \ \mathbf{R}\mathbf{y} \\ g_{nucl}(\mu_N/\mu_B) \ \alpha^2 \ \mathbf{R}\mathbf{y} \end{array} $

Note. Here, Ry is the Rydberg constant in frequency units (Hz), g_{nucl} is the *g*-factor of the nucleus, μ_N is the nuclear magneton, and μ_B is the Bohr magneton.

Compared to the very first measurements, the accuracy increased by a few orders of magnitude and reached $\Delta \alpha / \alpha \sim 10^{-6}$. The improvement was due to the use of large telescopes and to significantly higher resolving power and sensitivity of spectroscopic methods. Modern measuring instruments register signals corresponding to much earlier epochs and thus increase sensitivity to the linear drift of the constants. Intriguing results have been obtained by the so-



Figure 1. Result of the analysis of astrophysical data on absorption spectra of atoms and ions in interstellar clouds. The lower horizontal line shows time counted from the present epoch toward the beginning of the universe, whose age is assumed to be 13.9×10^9 years. The data are borrowed from [12]. Triangle is the result of an independent measurement [30].

called many-multiplet method in which relativistic corrections (see Section 3.4) for the transition levels in various atomic systems are taken into account [12]. The reader is referred to Refs [7-9] for the complete data on astrophysical measurements of α variation.

The authors of Refs [12, 33, 34] employed the manymultiplet method to study spectra of absorption of radiation from distant quasars (bright astrophysical sources) in gas clouds of galaxies intersecting the sight lines towards these objects. Spectra displaying very large redshifts (0.2 < z < 3.7) were recorded by the Keck/HIRES (telescope/spectrograph) complex, Hawaii [35]. The quasi-continuous spectrum of a quasar was found to contain narrow absorption lines of atoms and ions, such as MgII, CrII, FeII, ZnII, NiII, and AlIII; their wavelengths were measured and compared with the respective laboratory values. Unlike the classical method for the examination of fine structure doublet transitions from the same ground state [10], the manymultiplet method takes the large relativistic shift of the ground state levels into account and then compares the wavelengths of transitions in various atomic systems. An increase in statistics is achieved by assuming that different elements of the cloud have identical velocities (their lines have equal redshifts) relative to the observer, although this is true only upon averaging over a large ensemble of systems [33].

Results of the spectral analysis of 72 absorbing systems are presented in Fig. 1. In addition to the data obtained by the many-multiplet methods (circles), it shows the results of analysis of atomic (HI, 21 cm) and molecular (H₂) hydrogen (open squares). The authors of Refs [12, 36] arrived at the conclusion that the value of the fine structure constant in the past (0.5 < z < 3.5) differed from its current value:

$$\frac{\Delta\alpha}{\alpha} = (-0.54 \pm 0.12) \times 10^{-5} \,, \tag{4}$$

with the statistical significance of the calculation being 4.7σ (where σ is the standard deviation). We note that this is not the sole observation of probable discrepancy between fundamental constants in the past and present. Measurements of

the molecular hydrogen spectrum from quasar Q 0347-382 allow concluding that the ratio μ of the mass of the electron to that of the proton might also have been different some 10¹⁰ years ago [37],

$$\frac{\Delta\mu}{\mu} = (5\pm2) \times 10^{-5} \text{ or } \frac{\Delta\mu}{\mu} = (3.0\pm2.4) \times 10^{-5}$$
 (5)

depending on the method of analysis.

Recent astrophysical studies of multiplet emission lines of the OIII ion (500 and 496 nm) falling into the redshift range 0.16 < z < 0.80 allowed the upper bound of a probable α change in the past to be reliably determined. The studies were carried out with the participation of J Bahcall, a reputable scientist who devoted more than 40 years of his life as a researcher in this field and proposed, in 1965, to use 500 and 496 nm lines of the OIII ion to test the constancy of α . The constraint

$$\frac{\Delta\alpha}{\alpha} = (0.7 \pm 1.4) \times 10^{-4} \tag{6}$$

was derived in 2003 using 17 different variants of data sorting and processing [9]. Analysis of part of these data by the manymultiplet method yielded $\Delta \alpha / \alpha = (1.2 \pm 0.7) \times 10^{-4}$, in some disagreement with (4).

In 2003, the VLT/UVES registering complex was used to study the absorbing system in the spectrum of quasar HE 0515-4414 with the redshift z = 1.15. Analysis of FeII spectra by the many-multiplet method allowed a stringent constraints to be imposed on α changes in the past [30]:

$$\frac{\Delta \alpha}{\alpha} = (0.1 \pm 1.7) \times 10^{-6} \,. \tag{7}$$

This observation is in conflict with (4) (see Fig. 1) and practically excludes any drift at the level indicated in Ref. [36]. The authors of Ref. [31] employed the manymultiplet method to study a number of systems with 0.4 < z < 2.3 and came to a similar conclusion of the lack of statistically significant relative deviation at the 10^{-6} level:

$$\frac{\Delta \alpha}{\alpha} = (-0.6 \pm 0.6) \times 10^{-6} \,. \tag{8}$$

Astrophysical measurements are based on certain models of the evolution of the universe (Hubble's constant, luminosity scale, etc.). The accuracy of Hubble's constant measurement has been substantially improved in recent years. Also, the age and the curvature of the universe have been determined with greater precision [38, 39]. However, the enormous distances and time intervals separating the emission and detection episodes make it extremely difficult to estimate systematic effects (the Doppler shift from different parts of the gas cloud, relative occurrence of isotopes, Zeeman splitting, effects of the earth's motion). Errors inherent in instrumental methods (inadequate calibration of a spectrograph or poor accuracy of wavelength measurement) constitute another source of difficulties. All astrophysical tests are based on the assumption that the observed changes of transition frequencies are correlated with time-dependent changes of the constants, the existence of spatial gradients being ruled out. Despite convincing arguments in support of this assumption (see [5] and references therein), it should be borne in mind that objects analyzed by astrophysical methods are remote from the earth not only in time but also in space. Moreover, postulates of the Lorentz and spatial invariance

are used to compare the available data. Cosmological tests highly susceptible to the monotonic variation of the constants (up to 10^{-16} per year) cannot be used to estimate their dynamics today, especially on the assumption of their oscillatory character (see, e.g., Ref. [5]). Currently employed laboratory methods complementary to astrophysical and geological ones permit us to impose constraints on the present-day changes of the constants using a few model assumptions; their sensitivity to variations is very close to that of extralaboratory methods.

3. Laboratory experiments in the search for time variation of *a*

3.1 Atomic clock

Laboratory methods for the study of time dependence of the fine structure constant α are based on the comparison of frequencies of stable oscillators having a high quality factor, e.g., atomic transition frequencies or frequencies of solid-state resonators. The measurements have good statistics and reproducibility and ensure reliable control of systematic errors. One of the first laboratory tests of this type was the experiment performed in 1974 [40] in which the mode frequency of a superconducting microwave resonator was compared over a span of 10 days with the transition frequency

$$6S_{1/2}(F=3, m_F=0) \leftrightarrow 6S_{1/2}(F'=4, m'_F=0)$$

in the ¹³³Cs atom. Because the resonator dimensions are rescaled by the Bohr radius $r_{\rm B} \sim 1/\alpha$ and the hyperfine transition frequency in cesium by $g_{\rm Cs}(\mu_{\rm N}/\mu_{\rm B}) \alpha^2 \,\rm Ry$ (see Section 3.4), it was concluded that

$$\left|\frac{\partial}{\partial t}\ln\left(g_{\rm Cs}\,\frac{\mu_{\rm N}}{\mu_{\rm B}}\,\alpha^3\right)\right| < 4.1 \times 10^{-12}\,\,{\rm year}^{-1}\,,\tag{9}$$

where g_{Cs} is the *g*-factor of the cesium nucleus.

The majority of subsequent laboratory studies in this field were also based on the comparison of the frequencies of a certain stable oscillator and the hyperfine transition

$$6S_{1/2}(F=3, m_F=0) \leftrightarrow 6S_{1/2}(F'=4, m'_F=0)$$

in the atom of 133 Cs adopted as the definition of the second in SI. Since 1967, the second has been defined as exactly equal to 9,192,631,770 cycles of the radiation corresponding to the transitions between the hyperfine sublevels of the ground state in 133 Cs atom (Fig. 2). The word combination '*absolute* frequency measurement' regularly used in the literature implies a direct comparison of a certain frequency with the primary cesium standard. Therefore, the frequency measured in *Hertz* units is scaled in terms of the hyperfine splitting energy in 133 Cs. It appears appropriate to describe the principles of functioning of the cesium beam standard and





cesium fountain before moving to the analysis of laboratory methods in the search for variations of the fine structure constant α .

3.2 Cesium-beam time standard

The standard based on the transition between the hyperfine sublevels of the cesium ground state (see Fig. 2) is characterized by high stability and equally good reproducibility: average frequencies of two different standards coincide with a high degree of precision. A frequency signal generated by the cesium standard provides the best reference for comparative experiments over long time intervals by virtue of its availability and stability. Today, signals of primary frequency standards from laboratories in different countries are properly averaged into the Universal Coordinated Time (UTC) signal. Primary standards are also the main contributors to signal formation in the Global Positioning System (GPS) that allows any user to receive a time signal synchronized with reference to UTC to the nearest 100 ns.

We consider the principle of operation of an HP5071A cesium-beam time standard (Hewlett Packard) used, for example, on GPS satellites. A schematic diagram of the instrument is presented in Fig. 3. Cesium atoms leaving furnace 1 are collimated by a system of diaphragms and enter a nonuniform magnetic field created by a system of polarizer magnets 2. Atoms of the beam have different F, m_F values (the starting beam contains about 44% of the atoms with F = 3 and 56% with F' = 4, the population of magnetic sublevels at room temperature being regarded as identical). These atoms are deflected differently by the field; interactions between them and escape of part of the atoms from the beam result in the different populations of the sublevels F = 3, $m_F = 0$ and F' = 4, $m'_F = 0$. Ramsey spectroscopy of the reference transition is performed using a microwave resonator having two spaced zones [41].

Because the energy of the magnetic sublevels depends on the magnetic field strength, the area of interatomic interactions and the radiofrequency field is screened from external fields. The magnetic sublevels in the interaction zone are spaced in a well-controlled and uniform small magnetic field **B**; the spacing is necessary for spectroscopy of the reference transition $m_F = 0 \leftrightarrow m'_F = 0$ characterized by low sensitivity to the magnetic field (the quadratic Zeeman effect). The selected atoms enter the first area of interaction with the microwave field (the left-hand part of resonator 5), whence they exit in a coherent superposition of the states F' = 4, $m'_F = 0$ and F = 3, $m_F = 0$. As the atoms approach the second



Figure 3. Schematic diagram of an atomic clock with a cesium tube: 1 -cesium oven, 2 and 3 - magnets of the polarizer and analyzer, 4 - absorber, 5 - microwave resonator, 6 - detector of atoms, FB - feedback loop.

area, the character of their interaction with the field is determined by the relative phase of the exciting field and the dipole moment of the atomic transition. Having passed the second interaction area in the same resonator, beam atoms with different F are again spaced in the nonuniform field of analyzer 3. The net result is an interference pattern that depends on the offset of the generator frequency from the atomic resonance frequency, whose bandwidth is given by the time of flight between the interaction zones. The signal of the detector is used to control the phase of the generator feeding the microwave resonator and to stabilize its frequency with respect to the center of atomic resonance.

Short-term stability of the cesium standard depends on the characteristics of the microwave field scanning the reference resonance. The error signal produced in the course of scanning governs the frequency of the highly stable quartz generator that serves to create a field in the microwave generator; in this way, the quartz generator frequency is related to the frequency of the reference transition. For example, short-term stability of the HP5071A clock is 5×10^{-12} per second. Nonuniformity and instability of the magnetic field, along with other systematic effects, restrict both the long-term stability and absolute precision of the HP5071A clock to 10^{-12} . Calibration of the clock frequency using a GPS signal allows its absolute precision to be increased to 10^{-13} . A sharp rise in short-term stability is achieved by the combination in a single block of the cesium frequency standard maintaining high long-term stability with the hydrogen maser having extraordinarily high phase stability but subject to slow variations and jumps of frequency.

Practically all the world's metrological centers possess cesium beam standards. The accuracy and stability of beam standards depend on their linear dimension (time of flight between zones) and intrinsic systematic shifts due to the Doppler effect, nonuniformity of the magnetic field, and other factors. Stationary beam standards, such as NIST-7 at the National Institute of Standards and Technology (NIST), Boulder, USA, have the uncertainty less than 5×10^{-15} [42]. Further improvement of precision is feasible by lowering the cesium beam temperature.

3.3 Cesium fountain

The advent of laser cooling techniques for atomic systems made it possible to reduce atomic cloud temperature to several microkelvins [43]. The fact that the ¹³³Cs atom has a strong and readily available cyclic cooling transition $6^{2}S_{1/2}(F = 4) \leftrightarrow 6^{2}P_{3/2}(F' = 5)$ at the wavelength 852 nm gave impetus to the development of cesium fountains, i.e., time standards using cold atoms. Atoms of ⁸⁷Rb are used to produce time signals in the fountains as they are in beam standards. Today, several cesium fountains function worldwide as primary frequency standards, viz. the F1 cesium fountain at NIST [42], the CSF1 fountain at Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany [44], the cesium and cesium-rubidium fountains FO1 and FO2 at the Bureau National de Mètrologie (BNM), Paris, France [45], and the mobile fountain FOM developed at BNM. A few more fountains are projected including one at NIIFTRI, Russia [46].

The layout of a cesium fountain (exemplified by FOM) is shown in Fig. 4. In this device, unlike in the beam standard, atoms interacting with microwave radiation pass *the same resonator area* twice during the time of flight along a ballistic



trajectory. Atoms of ¹³³Cs are subject to laser cooling by three orthogonal pairs of broad laser beams, the frequency of which is tuned to be redshifted with respect to the frequency of the transition $6S_{1/2}(F=4) \leftrightarrow 6P_{3/2}(F'=5)$. As many as $10^7 - 10^8$ atoms are cooled in the trap to a temperature of several microkelvins, the equivalent to their relative velocity of a few millimeters per second (roughly four orders of magnitude lower than the speed of atoms in a thermal beam). Thereafter, the atoms receive a vertical impulse produced by a change in the laser beam intensity. The atomic cloud is accelerated upward to 4 m s^{-1} and propagates freely along a ballistic trajectory about 1 m in height. Prior to entering the resonator, the atomic cloud is subjected to the effect of microwave and light impulses that select atoms in the state $6S_{1/2}(F = 3, m_F = 0)$. The principle of Ramsey spectroscopy is used in both the beam standard and the cesium fountain; that is, atoms that have already interacted with the resonator field return to the interaction zone, pulled down by the gravitational force. The time of flight T_0 in the fountain is slightly smaller than 1 s, which allows the resolving power of Ramsey spectroscopy to be substantially increased. Specifically, the width of the central interference band in the FOM fountain is about 1 Hz (Fig. 5b).

The ballistic region and the area of interaction with the microwave field are reliably shielded from external magnetic fields and superimposed (as in the beam standard) by a weak constant magnetic field necessary for the magnetic sublevels to be split. After the second interaction with the field, the atoms enter the detection region lying beneath the source. In the detection region, populations of either level $6S_{1/2}(F = 3,$ $m_F = 0$) and $6S_{1/2}(F' = 4, m'_F = 0)$ are controlled. The number of atoms in the state with F' = 4 is estimated from the luminescence of a probing beam that is actually a standing light wave with a frequency slightly shifted into the red region with respect to the frequency of the cyclic transition $6S_{1/2}(F=4) \leftrightarrow 6P_{3/2}(F'=5)$. Thereafter, the atoms are pushed out from the detection region by a traveling wave of the same frequency. The number of atoms in the state with F = 3 is then determined. For this, they are optically pumped into the vacant state with F' = 4, after which the detection is carried out as above. Control of the population of both sublevels makes it possible to introduce correction for the number of atoms cooled during one cycle and thus improve the referencing precision. The working cycle of the atomic fountain is roughly 1 s long and periodically repeated.

Figure 5a shows experimental interference bands of the FOM1 fountain. The frequency of the ultrastable quartz oscillator is referred to the midst of the central band of the interference pattern (Fig. 5b). The microwave radiation frequency in the resonator slightly varies between cycles so as to switch from one slope of the interference band to the other. The difference between these signals is a source of an error used by the feedback (FB) loop to stabilize the frequency of the quartz resonator.

Most of the systematic effects inherent in primary standards are fairly well known and amenable to quantitative assessment. The main contribution to the frequency shift relative to the real position of the resonance frequency is made by the magnetic field and estimated at 10^{-14} . Highprecision measurement of the magnetic field from the results of spectroscopy of the transition $m_F = 1 \leftrightarrow m'_F = 1$ makes it possible to compensate for the shift. Parallel estimation of a shift caused by blackbody radiation, Doppler quadratic shift, collisional shift, and other systematic effects allows increasing the absolute accuracy of the frequency signal produced by stationary fountains to 5×10^{-16} . The FOM fountain, in its turn, is as accurate as 2×10^{-15} or better.



Figure 5. (a) FOM interference pattern obtained by spectroscopy of the reference transition $6S_{1/2}(F = 3, m_F = 0) \leftrightarrow 6S_{1/2}(F' = 4, m'_F = 0)$ in the ¹³³Cs atom. Its width is determined by the duration of interaction with the resonator field. (b) Central fringe. Its full mid-height width (FMHW) of 1.3 Hz depends on the time T_0 needed for the atoms to travel along the ballistic trajectory (see Fig. 4). Improvement in sensitivity is achieved by adjustment along the fringe slope.

3.4 Fine and hyperfine structure

In a hydrogen-like system, the energy of hyperfine splitting between the levels $nS_{1/2}(I-1/2)$ and $nS_{1/2}(I+1/2)$ in the nonrelativistic approximation is given by [47]

$$E_{\rm HFS}(nS) = \frac{8}{3n^3} Z^3 \alpha^2 \operatorname{Ry} \frac{g_{\rm nucl} \,\mu_{\rm N}}{\mu_{\rm B}} \left(I + \frac{1}{2}\right) \left(\frac{m_{\rm r}}{m_{\rm e}}\right)^3, \quad (10)$$

where m_r is the reduced electron mass and *I* is the nuclear spin. The leading relativistic corrections (Breit's corrections [48]) of the order of $(Z\alpha)^2$ are small for light systems. Therefore, relation (10) perfectly expresses the dependence of the hyperfine splitting energy on the fundamental constants for light hydrogen-like atoms.

For multielectron relativistic systems, the expression for $E_{\text{HFS}}(nS)$ becomes more complicated. For example, for alkali atoms, the energy can be represented in the form

$$E_{\rm HFS}^{\rm alkali} = \frac{8}{3n_*^3} Z z^2 \operatorname{Ry} \frac{g_{\rm nucl}\mu_{\rm N}}{\mu_{\rm B}} \left(I + \frac{1}{2}\right) \left(1 - \frac{\mathrm{d}\Delta_n}{\mathrm{d}n}\right) \\ \times F_{\rm rel}(Z\alpha)(1-\delta)(1-\varepsilon) \,. \tag{11}$$

The value of the electron wave function on the nucleus is calculated from the solution of the nonrelativistic Schrödinger equation and is given by the semiempiric Fermi–Segre formula $|\psi(0)|^2 = (Zz^2/\pi a_0^3 n_*^3)(1 - d\Delta_n/dn)$ [49], where Z is the nucleus charge, z is the charge of the system after the removal of the external electron, and n_* is the effective principal quantum number chosen such that the Bohr energy level $(E_{n_*} = -z^2 \text{ Ry}/n_*^2)$ corresponds to the experimental energy level. The quantity $\Delta_n = n - n_*$ is a quantum defect for the state n. The correction $1 - \delta$ arises from the distortion of the Coulomb potential for atoms with large Z (e.g., $\delta \approx 0.04$ for Cs), whereas the correction ε shows up when a finite size of the nucleus ($\varepsilon = 5 \times 10^{-3}$ for Cs) is taken into account.

The appearance of the relativistic correction $F_{\rm rel}(Z\alpha)$ can be explained as follows. If an electron is located far from the nucleus, the Coulomb interaction potential is determined by the effective charge z because the nucleus is screened by other electrons. Because the wave function of the given electron penetrates the electron cloud formed by other electrons, the electron interacts for some time with the poorly shielded nucleus and the initial Coulomb potential is distorted. The largest relativistic shift occurs at the s and p levels of the ground state; this shift is often greater than the fine splitting between the levels. Such a single-particle relativistic correction of the form $(1 - F_{\rm rel}) \sim (Z\alpha)^2/n_*$ is similar to the correction for hydrogen-like systems, however the principal quantum number n is here substituted by the effective principal quantum number n_* . For large Z, the correction is also large, but the many-particle structure of the electron cloud must be taken into consideration to correctly calculate the position of the level.

Unlike the single-particle relativistic correction for the energy resulting in the enhanced interaction between the nucleus and the electrons and the decreased energy levels, the many-particle correction has the opposite sign. Indeed, the single-particle relativistic interaction enhances the attraction between the electron cloud and the atomic nucleus, leading to a decrease in the electron cloud size. This, in turn, modifies the potential of the screened nucleus (the Hartree – Fock potential), making it smaller at small distances and increases the energy of the external electron levels. Relativistic corrections are calculated in the framework of the computation of many-particle systems with electron – electron correlations taken into account. By way of example, V Dzuba and V Flambaum have calculated corrections for a series of transitions in various atomic systems using the relativistic Hartree–Fock Hamiltonian (see, e.g., [33] and references therein).

The relativistic correction depends on α alone and is independent of other fundamental constants. The functional dependence of the transition frequency on α for complex atomic systems undergoes modification, compared with the dependence in the nonrelativistic case (see Table 1). This opens new possibilities for astrophysical and laboratory studies of the relative $\dot{\alpha}/\alpha$ variation.

We consider the drift structure of the quantity Θ being measured, in which $\Theta = f_1/f_2$ is the ratio between frequencies of two hyperfine transitions in an atomic system. It is the frequency ratio that is normally measured in experiments with a very high accuracy. Neglecting inessential small corrections δ and ε , Θ variation may be represented as

$$\frac{\partial \ln \Theta}{\partial t} \left(= \frac{1}{\Theta} \frac{\partial \Theta}{\partial t} \right) \approx \frac{\partial}{\partial t} \ln \frac{g_{\text{nucl}1}}{g_{\text{nucl}2}} + \frac{\partial}{\partial t} \ln \frac{F_{\text{rel}1}}{F_{\text{rel}2}} \,. \tag{12}$$

The second term on the right-hand side of (12) can be rewritten as

$$\frac{\partial}{\partial t} \ln \frac{F_{\text{rel1}}}{F_{\text{rel2}}} = \left(\frac{\partial}{\partial \ln \alpha} \ln \frac{F_{\text{rel1}}}{F_{\text{rel2}}}\right) \frac{\partial \ln \alpha}{\partial t} \,. \tag{13}$$

As a result, the variation of the fine structure constant α turns out to be related to the drift of Θ by

$$\frac{\partial \ln \Theta}{\partial t} \approx \frac{\partial}{\partial t} \ln \frac{g_{\text{nucl1}}}{g_{\text{nucl2}}} + \left(\frac{\partial \ln F_{\text{rel1}}}{\partial \ln \alpha} - \frac{\partial \ln F_{\text{rel2}}}{\partial \ln \alpha} \right) \frac{\partial \ln \alpha}{\partial t} . \quad (14)$$

Thus, the comparison of transition frequencies of the *same type* in atomic systems with essentially different relativistic corrections and with

$$\frac{\partial \ln F_{\text{rel1}}}{\partial \alpha} \neq \frac{\partial \ln F_{\text{rel2}}}{\partial \alpha}$$

permits us to estimate the magnitude of the variation of the fine structure constant. This method was first proposed in Ref. [50], where hyperfine transition frequencies in different systems were compared.

In the case of hyperfine transitions, the relativistic correction $F_{\rm rel}(Z\alpha)$ is referred to as the Casimir correction [51, 52]. It can be found for electrons in the state $S_{1/2}$ from the equation

$$F_{\rm rel}(Z\alpha) = \frac{3}{\lambda(4\lambda^2 - 1)},$$
(15)

where $\lambda = \sqrt{1 - (Z\alpha)^2}$. For heavy systems, the function $F_{\rm rel}(Z\alpha)$ is significantly different from unity [e.g., $F_{\rm rel}(Cs) = 1.39$, $F_{\rm rel}(Hg) = 2.26$] and is highly sensitive to changes in α . The relative sensitivity to α changes is defined as the partial derivative of function (15) with respect to α :

$$L_{\alpha} = \alpha \frac{\partial}{\partial \alpha} \ln \left[F_{\text{rel}}(Z\alpha) \right] = (Z\alpha)^2 \frac{12\lambda^2 - 1}{\lambda^2 (4\lambda^2 - 1)} \,. \tag{16}$$

Ζ	Atom	Transition	L_{lpha}	Frequency, Hz	References
1	^{1}H	$(F=0) \leftrightarrow (F'=1)$	$2 imes 10^{-4}$	1 420 405 751.766 7(9)	[53]
37	⁸⁷ Rb	$(F=1) \leftrightarrow (F'=2)$	0.3	6834682610.90429(9)	[29]
55	¹³³ Cs	$(F=3) \leftrightarrow (F'=4)$	0.74	9 192 639 770 (exactly)	
80	$^{199}{ m Hg^{+}}$	$(F=0) \leftrightarrow (F'=1)$	2.2	40 507 347 996.841 59(14)	[54]

Table 2. Frequencies of transitions between hyperfine sublevels of the ground state in certain atomic systems. The numbers in parentheses are measurement errors (one standard deviation). Also presented is the sensitivity of the relativistic correction to α changes for the given transitions (L_{α}).

The sensitivities L_{α} for certain atomic systems with reference to hydrogen (the nonrelativistic case) are listed in Table 2. A more accurate evaluation of relativistic corrections for the hyperfine splitting energy undertaken in Ref. [33] leads to a slight modification of the Casimir corrections. For example, calculations for the cesium atom yield $L_{\alpha}(Cs) = 0.83$ rather than 0.74. Errors in such calculations have an insignificant effect on the accuracy of drift assessment, which is largely defined by experimental errors. Also, it is worth noting that the expression for the frequency ratio contains the ratio between nuclear magnetic moments, in addition to a power of α .

The frequency of transition between hyperfine components of the ground state can be measured with very high accuracy (see Table 2). Atomic resonances of this type are characterized by a high quality factor; they are quite insensitive to perturbations and lie in a microwave range that is convenient in terms of frequency transformation. A series of high-precision experiments to compare atomic clock rates were undertaken in the early 1990s. Frequencies of a hydrogen maser ($f_{\rm H}^{\rm (HFS)} \approx 1.42$ GHz) and primary beam standards CS1 and CS2 ($f_{\rm Cs}^{\rm (HFS)}$) at PTB were compared over a one-year period [55]. Similar measurements have been made at the US Naval Observatory [56]. The results are indicative of a less than 5 × 10⁻¹⁴ per year relative frequency drift. Using (11) and Table 2, it is easy to show that

$$\frac{\partial}{\partial t} \ln \frac{f_{\rm H}^{\rm (HFS)}}{f_{\rm Cs}^{\rm (HFS)}} \approx \frac{\partial}{\partial t} \ln \frac{g_{\rm H}}{g_{\rm Cs}} + \left(\frac{\partial}{\partial \ln \alpha} \ln \frac{F_{\rm rel}({\rm H})}{F_{\rm rel}({\rm Cs})}\right) \frac{\partial \ln \alpha}{\partial t}$$
$$\approx \frac{\partial}{\partial t} \ln \left(\frac{g_{\rm H}}{g_{\rm Cs}} \alpha^{-0.74}\right), \qquad (17)$$

ignoring minor corrections arising from the dependence of n_* and δ on fundamental constants. The main contribution to the relative frequency variation is made by the drift of magnetic moments and the relativistic correction depending on α alone [50]. We note that at first sight, the form $\alpha^{-0.74}$ looks somewhat incorrect in the sense that it inadequately reflects the form of the complex functional dependence of the frequency ratio on α in Eqns (15) and (16). However, such a representation is traditional for the determination of frequency ratio variations and is equivalent to a more complicated expression after the proper substitutions.

The absolute frequency of the transition between fine components of the metastable triplet state ${}^{3}P_{1} \leftrightarrow {}^{3}P_{0}(\Delta m_{j} = 0)$ in ${}^{24}Mg$ [60 227.16(5) MHz] was measured over the one-year period of 1991–1992 [57]. The study showed that the time variation of the quantity $g_{p}(\mu_{N}/\mu_{B})$ (where g_{p} is the g-factor of the proton) was less than 5.4×10^{-13} per year. The authors disregarded the contribution of relativistic corrections; moreover, they substituted the g-factor of the cesium nucleus by the g-factor of the proton. In the case of a magnesium atom, the disregard of the relativistic correction is permissible because this atom belongs to light systems ($Z\alpha \simeq 0.08$). However, it follows from Table 2 that such an assumption is virtually unacceptable as far as the cesium atom is concerned.

Thus, it is more correct to write the constraint in the form

$$\left| g_{\rm Cs} \, \frac{\mu_{\rm N}}{\mu_{\rm B}} \, \alpha^{0.74} \right| < 5.4 \times 10^{-13} \, {\rm year}^{-1} \,.$$
 (18)

We note that the results of measuring the time variation of absolute frequencies of any *fine* structure transitions contain the nuclear magnetic moment of the cesium atom.

In 1995, frequencies of a hydrogen maser and an intermediate atomic standard were compared over a span of 140 days on the hyperfine transition

$${}^{2}\mathbf{S}_{1/2}(F=0,m_{F}=0) \leftrightarrow {}^{2}\mathbf{S}_{1/2}(F=1,m_{F}=0)$$

in the mercury ion ¹⁹⁹Hg⁺ ($f_{Hg}^{(HFS)} \approx 40.5$ GHz) [50]. The relativistic correction $F_{rel}(Hg)$ was twice that for ¹³³Cs, resulting in an enhanced sensitivity of measurement to the α variation. It was found that

$$\left|\frac{\partial}{\partial t}\ln\left(\frac{g_{\rm H}}{g_{\rm Hg}}\,\alpha^{-2.2}\right)\right| < 3.7 \times 10^{-14} \,\,{\rm year}^{-1}\,. \tag{19}$$

Further improvement in sensitivity was achieved in atomic fountain experiments carried out in Paris in 1998 - 2003. The authors compared frequencies of three atomic fountains, viz. the mobile fountain FOM, cesium fountain FO1, and cesium fountain FO2 (the last device was operated alternately with cesium and rubidium) [19]. The hydrogen maser signal was used as a basic stable nonabsolute reference. As a result of four measuring runs spaced by approximately one-year intervals, the following constraint was imposed on the relative frequency variation of ground state hyperfine transitions in 87 Rb and 133 Cs:

$$\frac{\partial}{\partial t} \ln \frac{f_{\rm Rb}^{\rm (HFS)}}{f_{\rm Cs}^{\rm (HFS)}} = (0.2 \pm 7.0) \times 10^{-16} \text{ year}^{-1} \,.$$
(20)

Based on the data listed in Table 2, it may be concluded that the drift of the following combination of fundamental constants is tested in this way:

$$\frac{\partial}{\partial t} \ln \left(\frac{g_{\rm Rb}}{g_{\rm Cs}} \, \alpha^{-0.44} \right) = (0.2 \pm 7.0) \times 10^{-16} \, \text{year}^{-1} \,. \tag{21}$$

Today, this is the most stringent constraint on the relative frequency variation of hyperfine transitions in various atomic systems. It can be seen from (19) and (21) that the results of measurements characterize variability of a simple combination of constants given by the nuclear magnetic moment ratio times a certain power of α . The nature of these contributions is essentially different: if α is the coupling constant of electromagnetic interactions, then the nuclear moments (g-factors)

Table 3. Magnetic moments of certain nuclei $\mu_{\rm S}$ calculated from the Schmidt model [5]. The table also includes experimental-to-theoretical nuclear moment ratios.

Atom	Schmidt model $\mu_{\rm S}/\mu_{\rm N}$	Experiment/model $\mu_{\rm exp}/\mu_{\rm S}$
Н	$g_{\rm p}/2$	1.00
⁸⁵ Rb	$5/14(8-g_{\rm p})$	1.57
⁸⁷ Rb	$g_{\rm p}/2 + 1$	0.74
¹³³ Cs	$7/18(10 - g_p)$	1.5
$^{171}Yb^{+}$	$-g_{\rm n}/6$	0.77
$^{199}{ m Hg^{+}}$	$-g_{\rm n}/6$	0.8

are first and foremost determined by the strong intranuclear interactions.

Nuclear magnetic moments in the framework of the simplified Shmidt model based on the calculations of quantum chromodynamics [5] may be approximately expressed via the *g*-factors of proton $g_p \simeq 5.58$ and neutron $g_n \simeq -3.83$. The model roughly describes the interplay between neutron and proton magnetic moments in the nucleus, which is acceptable for low-precision experimental estimates of variations. Table 3 shows selected Shmidt's values of the nuclear magnetic moments $\mu_{\rm S}$. It is easy to show that the sensitivity of the $g_{\rm Rb}/g_{\rm Cs}$ ratio to changes in g_p for ⁸⁷Rb and ¹³³Cs atoms is

$$\frac{\partial}{\partial \ln g_{\rm p}} \ln \frac{g_{\rm Rb}}{g_{\rm Cs}} \approx \frac{\partial}{\partial \ln g_{\rm p}} \ln \frac{\mu_{\rm Rb}^{\rm (S)}}{\mu_{\rm Cs}^{\rm (S)}} = \frac{12g_{\rm p}}{(g_{\rm p}+2)(10-g_{\rm p})} \approx 2 \quad (22)$$

and constraint (21) can be rewritten in a somewhat simplified form as

$$\frac{\partial}{\partial t} \ln \left(g_p^2 \alpha^{-0.44} \right) = (0.2 \pm 7.0) \times 10^{-16} \text{ year}^{-1} \,. \tag{23}$$

The authors of Ref. [19] suggest that the contributions from strong and weak interactions should be neglected in order to disentangle different types of contributions in the above expression; in doing so, they allude to the arguments in Ref. [50] concerning 'saturation' of the nuclear coupling constant. This allows a tight constraint to be placed on α variations:

$$\frac{\partial \ln \alpha}{\partial t} = (-0.4 \pm 16) \times 10^{-16} \text{ year}^{-1}$$
. (24)

Table 4 presents the results of high-precision experiments in the microwave range described in the present section. The discrimination between contributions from variations of different constants without resorting to additional models is possible by the combination of measurements in [40] and [57] alone even though they have relatively low sensitivity. The method for the discrimination between contributions is discussed at greater length in Section 3.10 using optical frequency measurements by way of illustration.

Anticipated improvement in the accuracy and stability of atomic fountains (up to 10^{-16}) in conjunction with lengthening the time interval between high-precision measurements gives hope that an order-of-magnitude gain in the accuracy of (20) will be achieved in the near future [19]. In addition to laboratory experiments, it is planned to launch an earth satellite carrying aboard atomic clocks simultaneously operating on hyperfine transitions in ¹⁹⁹Hg⁺ (40.5 GHz), ¹¹¹Cd⁺ (14.7 GHz), and ¹⁷¹Yb⁺ (12.6 GHz) ions (Space Time Mission project, NASA). The apparatus will be put into a very eccentric solar orbit to enhance the effects of gravity field gradients. The expected sensitivity to α variation is 10^{-20} per year [58]. Despite rigid constraints on the frequency ratio variation, the discrimination between contributions from electromagnetic, strong, and weak interactions requires the use of additional measuring techniques and experimental data.

3.5 High-precision measurement of optical frequencies

The advent of Ramsey spectroscopy and optical cooling techniques has greatly promoted high-precision measurements in the microwave range described in Section 3.4. Further considerable improvement in accuracy is expected to result from increasing the time of free evolution of atoms on a ballistic trajectory in orbital space missions (the PHARAO project [58, 59]). But such projects, for all their attractiveness, encounter serious technical and financial difficulties.

Physics of the late 20th century was marked by a major breakthrough in optical transition frequency measurements, besides the development of methods for microwave range studies. Optical transitions between metastable levels are characterized by a high quality factor (10^{18} and higher) due to both the long lifetime of these levels and the high resonance frequency (of the order 10^{15} Hz). The progress in optics promoted by the advent of stable laser devices and optical cooling techniques for atomic systems has brought about a significant improvement in the reproducibility and relative precision of optical measurements. Figure 6 illustrates the dynamics of relative measurement accuracy in the optical range that nowadays exceeds 10^{-14} . It is expected that secondary optical frequency standards will very soon create serious competition to ¹³³Cs-based microwave standards.

Methods previously employed to measure optical frequencies were based on the standard of length and did not allow the full realization of the advantages of laser spectroscopy of atoms and molecules. The problem of absolute frequency measurements in the optical range proved to be far from trivial because it required a comparison of the frequency standard and a more than four orders of magnitude higher optical frequency (corresponding to 15 consecutive doubling cascades!). In the 1980s – 1990s, cumbersome frequency converters that allowed the primary cesium standard to be linked to the frequency of the optical

Table 4. Constraints on the relative variations of fundamental constants coming from the comparison of hyperfine (HFS) and fine (FS) microwave transition frequencies. The table also includes measurements of frequency variation in a superconducting microwave resonator [40].

System	Quantity tested	Constraint, year ⁻¹	Years, references
$\begin{split} HFS(Cs)-resonator\\ HFS(Cs)-HFS(H)\\ HFS(Cs)-FS(^{24}Mg)\\ HFS(Cs)-HFS(^{199}Hg^+)\\ HFS(Cs)-HFS(^{87}Rb) \end{split}$	$\begin{array}{l} g_{\rm Cs}(\mu_{\rm N}/\mu_{\rm B})\alpha^{3}\\ (g_{\rm H}/g_{\rm Cs})\alpha^{-0.74}\\ g_{\rm Cs}(\mu_{\rm N}/\mu_{\rm B})\alpha^{0.74}\\ (g_{\rm H}/g_{\rm Hg})\alpha^{-2.2}\\ (g_{\rm Rb}/g_{\rm Cs})\alpha^{-0.44} \end{array}$	$ < 4.1 \times 10^{-12} < 5 \times 10^{-14} < 5.4 \times 10^{-13} < 3.7 \times 10^{-14} (0.2 \pm 7.0) \times 10^{-16} $	1976, [40] 1992, [55, 56] 1993, [57] 1995, [50] 2003, [19]



Figure 6. Improvement in relative accuracy of optical frequency measurements during the 20th century (from the results of spectroscopy of the 1S-2S transition in the hydrogen atom)

transition being studied via nonlinear processes and intermediate frequency standards were created. Optical frequency measurements were revolutionized in 1999 when spectral characteristics of femtosecond lasers were used to relate, in the phase-coherent way, the primary standard frequency to the laser longitudinal mode frequencies that overlapped the entire optical frequency range [16].

3.6 Optical 'comb'

The most common methods for the transformation of optical frequencies are based on phenomena that occur in nonlinear media under the effect of intense electromagnetic radiation. Metrologically most important are phase-coherent processes rigidly (mathematically) connecting a transformed frequency with incoming frequencies. Frequency doubling $(2f \rightarrow f')$ provides a characteristic example of a phase-coherent process: an experiment has demonstrated the frequency ratio f'/f = 2 to an accuracy of at least 6×10^{-21} [60].

Phase-coherent methods of frequency transformation also comprise modulation techniques. Phase and frequency modulation of the carrier wave with a frequency ω_0 by a signal at Ω produces the frequency spectrum ('comb') that may be represented as $\omega_0 \pm n\Omega$, where *n* is an integer. Such a 'comb' can overlap a wide range in which it is possible to measure frequencies. The modulation is either introduced by an external modulator or may be an intrinsic property of the emitter, as is the case with current-modulated diode lasers or pulse-periodic lasers.

The use of spectral characteristics of the emission of pulseperiodic lasers was proposed over 20 years ago when a picosecond dye laser was first employed to measure frequency intervals on Na [61]. Let a pulse-periodic laser emit a field varying over time as

$$E(t) = A(t) \exp\left(-\mathrm{i}\omega_0 t\right) + \mathrm{c.c.}, \qquad (25)$$

where A(t) is a periodic function of time, ω_0 is the carrier optical frequency, and c.c. is the complex conjugate. To simplify further transformations, we assume that A(t) can be represented as

$$A(t) = \sum_{m=0}^{N} \exp\left[-\frac{(t-mT)^2}{4\tau^2}\right],$$
(26)

where T is the pulse period, τ is the pulse duration, and the integer N defines the length of the pulse train.

In this case, the Fourier transform E(t) is easy to compute,

$$S(\omega) = A' \exp\left(-\omega'^2 \tau^2\right) \frac{1 - \exp\left(iN\omega'T\right)}{1 - \exp\left(-i\omega'T\right)} + \text{c.c.}, \quad (27)$$

where $\omega' = \omega - \omega_0$. The signal spectrum is an array of narrow lines $2\pi/NT$ in width spaced by $2\pi/T$ intervals. The lines lie beneath the smooth Gaussian envelope of the width $1/2\tau$ defined by the pulse length [62].

With decreasing the pulse duration τ , the spectrum of laser radiation overlaps an increasingly broader interval (up to dozens of tetrahertz for femtosecond lasers producing pulses some 20 fs in length). The intermode distance is determined by the repetition frequency $f_{rep} = 1/T$ or by the length of the laser resonator. The laser radiation spectrum at $N \rightarrow \infty$ is composed of infinitely narrow (of course, only in the ideal case) equidistant modes with a constant phase difference between them. The repetition frequency $f_{\rm rep}$ normally lies within an interval of 50-1000 MHz; this ensures the availability of all optical frequencies contained in the laser spectrum. The 'frequency comb' technique was developed in the 1980s-1990s and frequently used as a complementary tool to span small optical intervals in frequency measurement. In 1999-2000, a number of measurements were made at the Max-Planck Institute of Quantum Optics (MPQ) (Garching, Germany) that demonstrated the leading role of femtosecond lasers in the measurement of optical frequencies [16, 63].

We now turn to the structure of laser spectrum (27). The frequency f_n of the radiation monochromatic mode can be written as

$$f_n = \frac{\omega_0}{2\pi} + \frac{n}{T} \quad \text{or}$$

$$f_{n'} = f_0 + n' f_{\text{rep}} , \quad f_0 < f_{\text{rep}} ,$$
(28)

where *n* and *n'* are integers. Generally, $f_0 \neq 0$ because the frequency ω_0 is not necessarily proportional to $2\pi/T$. This relation links two radiofrequencies f_0 and f_{rep} with the optical frequency f_n (*n* is a large number of the order $10^5 - 10^6$). The offset f_0 is due to the difference between group and phase velocities in the laser resonator and the corresponding phase increment $\Delta \varphi$ between the envelope and the carrier in consecutive laser pulses.

The high peak intensity in femtosecond laser pulses opens the possibility for the further extension of the spectral range spanned by the 'comb'. The main physical process used to extend the spectrum of the femtosecond laser is phase selfmodulation in nonlinear media. If the refractive index n_{max} of a medium depends on the passing radiation intensity *I*,

$$n_{\max} = n_0 + n_2 I, \tag{29}$$

a laser pulse with the envelope A(t) of intensity $I(t) = |A(t)|^2$ acquires an additional phase increment over length *l* given by

$$\Phi(t) = -\frac{n_2 I(t)\omega_0 l}{c} \,. \tag{30}$$

This time-dependent phase shift is responsible for the frequency modulation of the signal, which is proportional to the time derivative of the phase shift $\partial \Phi(t)/\partial t$. When fused silica with a positive Kerr coefficient $n_2 = 3.2 \times 10^{-16} \text{ cm}^2 \text{ W}^{-1}$ is used, the incoming pulse front brings in additional redshifted frequencies (because $\partial \Phi(t)/\partial t < 0$), while the outgoing front gives rise to frequencies shifted to the blue region of the spectrum.



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Figure 7. (a) Cross section of the core of a PCF fiber. The waveguide 1.5 μ m in diameter is 'suspended' inside the surrounding structure of air cells. (b) Extension of the femtosecond laser spectrum in a PCF fiber. The figure shows the power spectrum of the 'original comb' generated by a femtosecond Ti: Sa laser and the spectrum of the 'comb' at the outlet of the fiber. Logarithmic energy units are used: 1 dBm = 1 mW.

The phase self-modulation process modifies the envelope function A(t):

$$A(t) \to A(t) \exp\left(i\Phi(t)\right).$$
 (31)

Because the field-induced phase shift $\Phi(t)$ has the same periodicity as the field itself, the mode structure of the extended 'comb' remains equivalent to the incident radiation structure.

Despite the low value of the coefficient n_2 of melted quartz, the process of phase self-modulation in an optical fiber is much more efficient than in crystals by virtue of larger interaction time and smaller beam diameter. Other processes proceed in the fiber, along with self-modulation, such as Raman scattering, which makes the pulse propagation picture much more complicated. However, it has been demonstrated in experiments that the structure of the extended 'comb' leaving the fiber is identical with the structure of the incoming radiation to an accuracy of at least 5×10^{-16} [63]. This approach allowed the optical 'comb' spectrum to be extended to 100 THz and directly relate large optical intervals to the radiofrequency range.

Further extension of the 'comb' spectrum proved possible due to the availability of fibers produced by the photonic crystal technology. Positive quartz dispersion in a conventional fiber is responsible for the lengthening of the pulse in the course of propagation along the fiber, the drop in peak intensity, and the decrease of the nonlinear transformation efficiency. Fibers of a new type [64] consist of a thin quartz core (1.5 μ m in diameter) sheathed by a structure of air cells in which it is suspended (PCF fibers). A section through the core and the surrounding structure is shown in Fig. 7a. Due to the large jump in the refractive index at the core border, dispersion characteristics of such a waveguide are advantageous in that the group velocity dispersion in a PCF fiber at 800 nm is close to zero. As the pulse propagates along the fiber core, its length changes, but only insignificantly; as a result, there is an additional gain in the efficiency of nonlinear effects. The optical 'comb' at the outlet of a 10 cm PCF fiber segment may overlap the optical octave and occupy a range from 450 to 1200 nm (see, e.g., Fig. 7b). Such unique spectral characteristics of outgoing radiation clear the way for simultaneous control of the 'comb' degrees of freedom (f_{rep} and f_0) and the construction of a universal phase-coherent

bridge connecting the radiofrequency range with optical frequencies.

Taking advantage of the difference between frequency transformation mechanisms in various nonlinear processes, it is possible to detect f_0 in the 'combs' spanning a spectral range broader than the optical octave. The comb's mode frequency is described by the expression

$$f_n = f_0 + n f_{\text{rep}} \,. \tag{32}$$

If such a 'comb' is sent into a nonlinear crystal where the frequency is doubled, the radiation mode frequencies of the second harmonic are described by the expression

$$2f_n = 2(f_0 + nf_{\rm rep}).$$
(33)

On the other hand, a 'comb' overlapping the octave contains modes with numbers *n* and *n*' such that n' = 2n, and the beat signal of the frequencies $2f_n$ and $f_{n'}$ contains the frequency difference

$$2f_n - f_{n'} = 2(f_0 + nf_{\text{rep}}) - (f_0 + 2nf_{\text{rep}}) = f_0.$$
(34)

The beat-frequency waveform is rather strong because it is formed by a large number of modes n' having a counterpart in the blue region of the fundamental 'comb'. Control of f_0 is exercised by varying dispersion of the laser resonator, e.g., by modifying parameters of the Kerr lens in a titanium-activated sapphire crystal (Ti:Sa) used as an active medium in many modern femtosecond laser systems. The frequency f_{rep} is detected directly from the measured beat-frequency waveform produced by the combination of 'comb' modes, while f_{rep} is controlled by varying the resonator length.

Figure 8 shows a typical diagram of an optical frequency detector based on a ring femtosecond Ti : Sa laser pumped by the second harmonic of a continuously operating Nd : YAG laser. The Kerr lens created in a Ti : Sa crystal placed in the ring resonator with chirp mirrors synchronizes resonator modes and maintains the pulse-periodic performance. The parameters of the Kerr lens that determines the group velocity of wave propagation in the resonator are controlled by varying the pumping power. The relation between phase and group velocities, in its turn, determines the phase shift $\Delta \varphi$ and frequency f_0 . Optical modulators, such as electro- and



Figure 8. (a) Schematic of a frequency measuring device based on a femtosecond Ti : Sa laser. (b) Part of the radiation of the stabilized 'comb' is led out of the scheme to measure the laser radiation frequency used in spectroscopy. AOM — acoustico-optical modulator, MP1 — mirror on a piezoelement, MD — dichroic mirror, D1, D2, D3 — high-frequency detectors, P — polarizers, KTP — nonlinear crystal for second harmonic generation, G — diffraction grating, S — slot, PCF-fiber — optical fiber produced by photonic crystal technology, FBL — feedback loops.

acoustic-optical ones, are used to rapidly change the power to make up for f_0 fluctuations within a range of around 1 MHz. Fluctuations in f_{rep} are much slower (of the order of 1 kHz); therefore, it is sufficient to control the resonator length by means of a piezoelectric element to compensate for them.

A small part of laser radiation is isolated by the divider and fed to the high-frequency diode D1 to record f_{rep} . This signal is heterodyned with a signal of the local generator on the phase detector. The phase difference is an error signal governing the resonator length as well as f_{rep} . Hence, phaserelated referencing of f_{rep} to the signal of the radiofrequency generator is realized.

The main part of laser radiation enters a 15 cm long section of the PCF fiber. The transformed light leaves the fiber and is divided by the dichroic mirror MD. The red part of the spectrum is focused onto a nonlinear crystal that converts radiation into the second harmonic in the blue– green region of the spectrum. Following the compensation of crystal dispersion and coordination of optical wavelength, the blue– green portion of the original 'comb' is overlapped with the doubled 'comb'. The radiation is detected by diode D2 at the outlet of spectral slot S. The photodiode D2 registers a beat-frequency waveform at the frequency f_0 , which is phase-correlated with another local oscillator. The feedback loop serves to control the pumping radiation power and, therefore, the resonator dispersion.

Part of the radiation of the stabilized 'comb' combines with the laser radiation whose frequency is to be measured. Diode D3 detects the beat-frequency waveform between the laser and the nearest 'comb' mode, the frequency f_{beat} of which is measured by a counter synchronized with an external stable radiofrequency source. Thus, the optical laser frequency f_{laser} is the sum

$$f_{\text{laser}} = \pm f_{\text{beat}} \pm f_0 + n f_{\text{rep}} \,. \tag{35}$$

The value of *n* can be found with the help of a wavemeter resolving the intermode distance, while the signs of f_{beat} and f_0 are unambiguously determined by detuning frequences of the local oscillators that give f_0 and f_{rep} .

In conclusion, the optical frequency f_{laser} is expressed through readily measurable radiofrequencies; in this way, it is directly related to the primary standard frequency. Because of the large factor $n \sim 10^5 - 10^6$ entering the expression for f_{laser} , both stability and absolute precision requirements of a radiofrequency source are very high. Modern measurements of optical frequencies are made with the help of quartz or lowtemperature solid-state oscillators with frequencies stabilized according to the primary cesium standard. Also, stability is improved using a hydrogen maser signal as an intermediate source.

3.7 Measurement of specific atomic transition frequencies

A tunable laser source with a narrow emission spectrum and high stability is needed to excite a narrow transition in an atomic system. Such a system (or etalon laser) is a key constituent component of high-precision spectroscopic experiments. Solid-state and diode lasers [21, 23, 25] or dye lasers [18, 28] are used as references. The narrowest linewidth of a tunable dye laser obtained at NIST is 0.2 Hz [28]. Lasers are stabilized with reference to external stable resonators with small drift and residual vibration values. For example, a typical length *l* variation of a resonator made from ultra-low expansion glass (ULE) (producer: Corning) is below $l/l < 10^{-15}$ s⁻¹ at room temperature; residual vibrations are of the same order of magnitude provided adequate acoustic and seismic isolation is ensured.

In the course of optical transition spectroscopy, the laser slowly scans a line profile while its frequency is measured by the 'optical comb' stabilized according to the primary standard. The narrowest transition line of the width 10 Hz at the frequency 10¹⁵ Hz was obtained for the mercury ion [27]. Linewidths between 100 and 1000 Hz were recorded in other metrological experiments in the optical range. If the laser frequency and the transition line profile are known, the line center can be located with a high degree of accuracy.

By way of illustration, Fig. 9a shows the result of measuring the absolute frequency of a 486 nm laser used for spectroscopy of the 1S-2S transition in the hydrogen atom. The mobile cesium fountain FOM, temporarily moved from BNM (Paris) to MPQ (Garching), was used as the frequency standard in this experiment [18]. A smooth change in the laser frequency was attributable to the temperature variation of the ultrastable resonator with reference to which the laser system was stabilized [65, 66]. Data scattering was due to frequency noises of the cesium fountain averaged over time t as $\sim 1/\sqrt{t}$. For accurate location of the frequency axis, the data obtained were approximated by a smooth low-degree polynomial representing the drift of the reference resonator. Figure 9b depicts a typical line of the transition

$$1S(F = 1, m_F = \pm 1) \rightarrow 2S(F' = 1, m'_F = m_F)$$

in the hydrogen atom relative to the absolute frequency axis. A long period of data collection and studies of systematic effects has ended in a considerable improvement in the



Figure 9. (a) Measurement of the absolute frequency of a 486 nm laser used for spectroscopy of the 1S-2S transition in the hydrogen atom [18, 69]. (b) Narrow line of the 1S-2S transition in the hydrogen atom.

Table 5. High-precision measurements of absolute frequencies of certain optical transitions. The numbers in parentheses are uncertainties (one standard deviation).

Ζ	Atom	Transition	Frequency, Hz	Relative accuracy	References
1	Н	$1S_{1/2} \rightarrow 2S_{1/2}$	2 466 061 413 187 116(46)	$1.9 imes 10^{-14}$	[18]
20	Ca	${}^{1}S_{0} \rightarrow {}^{3}P_{1}$	455 986 240 494 158(26)	$6 imes 10^{-14}$	[21]
38	Sr^+	$^2S_{1/2} \rightarrow {}^2D_{5/2}$	444 779 044 095 520(100)	$22 imes 10^{-14}$	[22]
49	In^+	$^1\mathrm{S}_0 \rightarrow {}^3\mathrm{P}_0$	1 267 402 452 899 920(230)	18×10^{-14}	[23]
70	Yb^+	$^2\mathrm{S}_{1/2} ightarrow ^2\mathrm{D}_{3/2}$	688 358 979 309 312(6)	$0.9 imes10^{-14}$	[24]
70	Yb^+	${}^{2}S_{1/2} \rightarrow {}^{2}F_{7/2}$	642 121 496 771 260(230)	$36 imes 10^{-14}$	[26]
80	Hg^+	$^2\mathrm{S}_{1/2} \rightarrow {}^2\mathrm{D}_{5/2}$	1 064 721 609 899 144(11)	$0.9 imes10^{-14}$	[28]

accuracy of experiments that presently amounts to dozens of Hertz. Similar methods are used to measure absolute transition frequencies in other atomic systems.

In the last few years, several laboratories have completed serial measurements of absolute frequencies of optical transitions for different atoms and ions; many similar experiments are underway. The results of currently available high-precision measurements and related references are listed in Table 5. Some of these measurements, e.g., in Hg⁺, H, and Yb⁺, have been repeated over the last 5 years and have permitted the imposition of stringent constraints on the variation of fundamental constants in the modern epoch.

3.8 Variability of constants and optical transitions

The optical transition frequency $f^{(\text{opt})}$ can be represented as the product of the nonrelativistic part $f_{\text{NR}}^{(\text{opt})} \sim \text{Ry}$ and the relativistic correction $F_{\text{rel}}(Z\alpha)$,

$$f^{(\text{opt})} = f_{\text{NR}}^{(\text{opt})} F_{\text{rel}}(Z\alpha) .$$
(36)

The correction grows with Z; accordingly, in general, the sensitivity $f^{(opt)}$ to α variations also increases. Relativistic corrections for metrological transitions included in Table 5 were computed in Refs [33, 67]. Unlike in calculations for the hyperfine structure, there is no general analytic expression for optical transitions fit for roughly estimating F_{rel} for a given electron configuration [cf. (15)]. The dependence $F_{rel}(Z\alpha)$ is found by the computation of $f^{(opt)}$ at different values of the fine structure constant. For this purpose, the transition frequency is written in the form

$$f^{(\text{opt})} = f_{\text{exp}} + q_1 \left[\left(\frac{\alpha_c}{\alpha} \right)^2 - 1 \right] + q_2 \left[\left(\frac{\alpha_c}{\alpha} \right)^4 - 1 \right], \quad (37)$$

where f_{exp} is the experimental frequency value and α is the laboratory value of the fine structure constant. The necessity of taking only even powers of α into account ensues from the general structure of the relativistic correction containing only even powers of the expansion of the relativistic root $\sqrt{m_e^2 + p^2}$ in the electron momentum $p \sim (Z\alpha)$. The transition frequency is computed at a number of values of the parameter α_c slightly different from α . The dependence $f(\alpha_c)$ thus obtained is approximated by expression (37); this yields the parameters q_1 and q_2 . It is easy to show that the sensitivity of the relativistic correction for α variations is given by

$$L_{\alpha} = \alpha \frac{\partial}{\partial \alpha} \ln F_{\rm rel}(Z\alpha) = \frac{2q_1 + 4q_2}{f_{\rm exp}} \,. \tag{38}$$

We note that the authors of Refs [33, 67] assumed Ry = const to find the coefficients q_1 and q_2 . However, the results of their calculations would remain unchanged even if the value of the Rydberg constant were fixed (i.e., constraints were placed on the combination of constants $m_e c^2 \alpha^2 / h$). Table 6 illustrates the relative sensitivity of relativistic corrections for the transitions listed in Table 5. The aim of

Table 6. Sensitivity of the relativistic corrections $F_{rel}(Z\alpha)$ for α variations for certain narrow optical transitions (according to Refs [5, 33, 67]).

Ζ	Atom	Transition	λ , nm	L_{lpha}
1	Н	$1 \text{s} \text{S}_{1/2}(F = 1, m_F = \pm 1)$	121	0
		$\rightarrow 2 \mathrm{s} \mathrm{S}_{1/2}(F'=1, m'_F=\pm 1)$		
20	Ca	${}^{1}S_{0}(m_{J}=0) \rightarrow {}^{3}P_{1}(m_{J}=0)$	657	0.03
49	In^+	$5s^2 {}^1S_0 \rightarrow 5s5p {}^3P_0$	237	0.21
70	Yb^+	$6s^{2}S_{1/2}(F=0) \rightarrow 5d^{2}D_{3/2}(F=2)$	435	1.03
80	Hg^+	$5d^{10}6s^2S_{1/2}(F=0)$	282	-3.2
		$\rightarrow 5d^96s^2 {}^2D_{5/2}(F'=2, m'_F=0)$		

experimental tests being the achievement of high *sensitivity* to α variations at a relatively low *accuracy* of the calculations, the requirements for the accuracy of the q_1 and q_2 estimates are relaxed.

It follows from Table 6 that the sensitivity of corrections to α variations may be either positive or negative. For possible α changes, transitions in atoms of H, Ca, and In⁺ serve as an 'anchor' with reference to which variations in transition frequencies in Hg⁺ and Yb⁺ take place. A promising candidate for the comparison with the 'anchor' is the reference transition frequency in the Hg⁺ ion with the highest possible sensitivity $F_{rel}(Hg)$ to variations in α .

3.9 Comparison of transition frequency variations in H, Hg $^+$, and Yb $^+$

The metastable level 2S in the hydrogen atom has a long lifetime (ca 1/7 s) in agreement with the potential quality factor $\Delta f/f \simeq 5 \times 10^{-16}$ of the two-photon transition 1S-2S. Experiments on two-photon spectroscopy of the hydrogen atom initiated by T Hansch in the 1970s [68] continue at MPQ (Garching, Germany). Precisely these studies provided the incentive for the development of methods for frequency measurement and gave rise to the 'optical comb' concept in 1999. This concept promoted the achievement of the then record-beating accuracy of measurement of the absolute frequency of the 1S-2S transition (1.8×10^{-14}) [18]. The mobile cesium fountain FOM was temporarily moved from BNM to MPQ and placed on line with the hydrogen spectrometer to be used as the frequency standard in these experiments.

The hydrogen beam spectrometer registers the spectra of the transitions

$$1S(F = 1, m_F = \pm 1) \rightarrow 2S(F' = 1, m'_F = m_F),$$

whose frequencies are practically independent of the magnetic field. A characteristic line recorded by the hydrogen spectrometer for atoms with velocities $v < 80 \text{ m s}^{-1}$ is shown in Fig. 9b. The transition frequency of a resting atom is determined using a correction that takes the dynamic Stark shift and the second-order Doppler effect into account [18]. The measured frequency 2466061102474880(36) Hz (with the contributions from statistical and systematic errors taken into account) is consistent with the splitting between the hyperfine components (1S, F = 1) and (2S, F' = 1) in the hydrogen atom. In order to determine the absolute frequency between the levels 1S and 2S (see Table 5), the measured frequency is added to a value corresponding to 3/4 of the difference between frequencies of hyperfine splitting of the levels 1S and 2S (the hyperfine structure centroid frequency).

In 2003, the experiment was repeated to find the absolute frequency of the transition

$$1S(F = 1, m_F = \pm 1) \rightarrow 2S(F' = 1, m'_F = m_F)$$

in hydrogen [20, 69]. The results of the 1999 and 2003 measurements are presented in Fig. 10. Taking the contributions of statistical and systematic uncertainties into account, a change in the transition frequency over a span of 3.64 years was found to be $f_{\rm H,2003}^{\rm (opt)} - f_{\rm H,1999}^{\rm (opt)} = (-29 \pm 57)$ Hz. On the assumption of a linear frequency variation, this corresponds to the drift

$$\frac{\partial}{\partial t} \ln \frac{f_{C_8}^{(\text{HFS})}}{f_{\text{H}}^{(\text{opt})}} = (3.2 \pm 6.4) \times 10^{-15} \text{ year}^{-1}$$



Figure 10. Results of the experimental measurement of the absolute frequency of the transition

 $1S(F = 1, m_F = \pm 1) \rightarrow 2S(F' = 1, m'_F = m_F)$ in the hydrogen atom in 1999 and 2003.

Because hydrogen is a nonrelativistic atomic system (see Table 6) and the sensitivity of the relativistic correction to the hyperfine transition frequency in ¹³³Cs is $L_{\alpha}(Cs) \simeq 0.8$ (see Table 2), the constraint on frequency variations can be rewritten as

$$\frac{\partial}{\partial t} \ln \frac{f_{\rm Cs}^{\rm (HFS)}}{f_{\rm H}^{\rm (opt)}} = \frac{\partial}{\partial t} \left[\ln \left(g_{\rm Cs} \frac{\mu_{\rm N}}{\mu_{\rm B}} \right) + (2+0.8) \ln \alpha \right]$$
$$= (3.2 \pm 6.4) \times 10^{-15} \, \text{year}^{-1} \,. \tag{39}$$

Despite the paramount importance of the 1S-2S transition frequency in the hydrogen atom for the determination of the Rydberg constant and Lamb's shift [70], its measurement is not free from drawbacks (e.g., the short time of spectrometer operation, large number of systematic effects) that prevent the hydrogen spectrometer from being regarded as a real candidate for the optical frequency standard. The leading role in this area is played by ionic standards, which have some advantages over beam experiments. Taken together, the long duration of ion storage in the Pauli trap (up to several months), the absence of collisions with other particles, reliable control of systematic errors, and high reproducibility allow to use the potential of high-Q transitions in isolated ions to high extent. To date, a few ionic standards are available based on the ions of strontium [22], indium [23], itterbium [24, 26], and mercury [27]; moreover, the construction of several new devices is underway.

The NIST standard using the quadrupole transition

$$5d^{10}6s {}^{2}S_{1/2}(F=0) \rightarrow 5d^{9}6s^{2} {}^{2}D_{5/2}(F'=2, m'_{F}=0)$$

 $(\lambda = 282 \text{ nm})$ in a single mercury ion is among the most accurate optical frequency standards ever made [28]. The transition is excited by the second harmonic of a dye laser with the linewidth around 0.3 Hz. The typical transition linewidth measured in experiment is about 15 Hz. During the period from 2000 till 2003, almost 20 measurements of the absolute frequency of this transition were made using the 'frequency comb' technique. One of the hydrogen masers continuously functioning at NIST served as the primary standard; it was periodically calibrated against the NIST-F1 cesium fountain frequency and a UTC signal. It was found in a series of experiments that the transition frequency was $f_{\rm Hg}^{(\rm opt)} = 1\,064\,721\,609\,899\,143.7(1.1)$ Hz taking only the statistical error into account (the error being 1σ). It is the most accurate of all measures of the absolute optical transition frequency available thus far. The reproducibility of the results is around 10 Hz, in agreement with the calibration accuracy of the hydrogen maser. Adjusting a linear function to the results of measurements leads to the conclusion that the relative drift of the cesium standard frequencies and the optical transition in mercury is

$$\frac{\partial}{\partial t} \ln \frac{f_{\rm Cs}^{\rm (HFS)}}{f_{\rm Hg}^{\rm (opt)}} = (0.2 \pm 7.0) \times 10^{-15} \text{ year}^{-1}.$$

With the relativistic correction for the transition in a strongly relativistic mercury atom taken into account $[L_{\alpha}(Hg) = -3.2 \text{ cm}, \text{ Table 6}]$, the relative temporal variation of fundamental constants can be constrained by

$$\frac{\partial}{\partial t} \ln \frac{f_{\rm Cs}^{\rm (HFS)}}{f_{\rm Hg}^{\rm (opt)}} = \frac{\partial}{\partial t} \left[\ln \left(g_{\rm Cs} \frac{\mu_{\rm N}}{\mu_{\rm B}} \right) + (2 + 0.8 + 3.2) \ln \alpha \right]$$
$$= (0.2 \pm 7.0) \times 10^{-15} \text{ year}^{-1}. \tag{40}$$

The frequency of the transition

$$6s {}^{2}S_{1/2}(F=0) \rightarrow 6s {}^{2}D_{3/2}(F=3)$$

(436 nm) in a single ¹⁷¹Yb⁺ ion placed in a Pauli trap was determined again at PTB in the beginning of 2004. The frequency was measured versus the PTB primary standard [71] and yielded the following constraint on the variation of the optical transition frequency:

$$\frac{\partial}{\partial t} \ln \frac{f_{C_s}^{(\text{HFS})}}{f_{Yb}^{(\text{opt})}} = \frac{\partial}{\partial t} \left[\ln \left(g_{C_s} \frac{\mu_{\text{N}}}{\mu_{\text{B}}} \right) + (2 + 0.8 - 1.03) \ln \alpha \right]$$
$$= (1.2 \pm 4.4) \times 10^{-15} \text{ year}^{-1}.$$
(41)

The results of high-precision measurements of optical frequency variations are presented in Fig. 11. Absolute frequency drifts in the hydrogen atom (39) and ions of



Figure 11. Variations of optical transition frequencies in different atomic systems relative to the primary cesium standard. The horizontal axis is the sensitivity of the relativistic correction F_{rel} corresponding to each of the transitions toward α changes. The solid line shows the linear approximation of the data.

itterbium (41) and mercury (40) correspond to zero values to within one standard deviation. Although no individual measurement alone contains information about the constraint on the variation of α and cesium nuclear magnetic moment, a combination of these measurements makes it possible to disentangle the said contributions.

3.10 Disentangling contributions

from different types of interactions

The most trivial approach to distinguishing contributions from different constants is based on the assumption that time derivatives of all constants except one are equal to zero and any variation in a measured quantity is due to a change in a single selected constant. By way of example, the upper limit on the variation of α in Ref. [50] is established on the assumption of the constancy of nuclear magnetic moments determined largely by strong interactions. However, if the fundamental constants are not constant, variations in the electromagnetic α , strong α_S , and weak α_W coupling constants must be of the same order of magnitude. This, in turn, would result in both amplification and mutual compensation of the drifts (see, e.g., Ref. [5]).

A different approach proposed in Refs [72, 73] consists of analyzing a potential relation between α_S and α . Based on a number of strong model assumptions, the authors conclude that for the Grand Unification Theory (GUT), the following expression must hold:

$$\frac{\Delta m_{\rm p}}{m_{\rm p}} \approx \frac{\Delta g_{\rm nucl}}{g_{\rm nucl}} \approx 35 \, \frac{\Delta \alpha}{\alpha} \,.$$
(42)

In the absence of a universally accepted theory of supersymmetry violation or a theory explaining the value of the elementary fermion mass, any speculating about correlations between coupling constants remains strongly model-dependent.

We show that it is possible to distinguish between contributions from the drifts of various constants without making assumptions about their possible correlation. To make the discussion clear, we first confine it to the results of measurements in hydrogen and mercury by introducing the notation

$$x \equiv \frac{\partial}{\partial t} \ln \alpha, \qquad y \equiv \frac{\partial}{\partial t} \ln \left(g_{\rm Cs} \, \frac{\mu_{\rm N}}{\mu_{\rm B}} \right).$$
 (43)

With this notation, expressions (39) and (40) can be rewritten as

$$y + 2.8x = (3.2 \pm 6.4) \times 10^{-15} \text{ year}^{-1}$$
 (H), (44)

$$y + 6x = (0.2 \pm 7) \times 10^{-15} \text{ year}^{-1}$$
 (Hg⁺). (45)

The graphical solution of the system is presented in Fig. 12a. Solid straight lines are described by Eqns (44) and (45); pairs of dashed lines indicate confidence limits equivalent to one standard deviation from each measure. It can be seen that each individual measurement allows a variation of constants in an infinite area on the surface $\{x, y\}$. Mean values $\langle x \rangle$ and $\langle y \rangle$ are readily found from the system without the assumption of interrelations between them, which makes it possible to find average drifts of α and the magnetic moment of the cesium nucleus.



Figure 12. (a) Frequency variation of the transitions ${}^{2}S_{1/2}(F = 0) \rightarrow {}^{2}D_{5/2}(F' = 2, m'_{F} = 0)$ in ${}^{199}Hg^{+}$ and $1S(F = 1, m_{F} = \pm 1) \rightarrow 2S(F' = 1, m'_{F} = m_{F})$ in H with respect to the frequency of the ground state hyperfine splitting in ${}^{133}Cs$. Dashed lines show intervals corresponding to one standard deviation from the mean values. The ellipse is defined by the relation $R(\Delta x, \Delta y) = 1$. (b) Distribution function of the expected $\{x, y\}$ values assuming Gaussian statistics of the starting data (the function is normalized to have a maximum value of 1).

However, the computation of the confidence limit for average values is a less trivial task. Direct calculation of the second-order moments $(\langle y^2 \rangle - \langle y \rangle^2)$ and $(\langle x^2 \rangle - \langle x \rangle^2)$ from Eqns (44) and (45) appears impossible because the value of the correlator $\langle xy \rangle$ is unknown. This quantity vanishes in the absence of an interrelation between constant drifts and acquires a maximum value when there is a linear relation between them, e.g., if expression (42) is valid.

The problem of discrimination between contributions can be solved by making two generally accepted assumptions: (1) absolute frequency measurements are statistically independent and (2) the initial data distribution obeys the Gaussian statistics. Based on these assumptions and the results of experiments (44), (45), it is easy to calculate the distribution function P(x, y) (Fig. 12b), which is in fact the two-dimensional Gaussian function

$$P(\Delta x, \Delta y) \propto \exp\left[-\frac{R(\Delta x, \Delta y)}{2}\right],$$
 (46)

where the function $R(\Delta x, \Delta y)$ is defined as

$$R(\Delta x, \Delta y) = \frac{(\Delta y + 2.8\Delta x)^2}{2\sigma_{\rm H}^2} + \frac{(\Delta y + 6\Delta x)^2}{2\sigma_{\rm Hg}^2} \,. \tag{47}$$

Here, $\Delta x = x - \langle x \rangle$ and $\Delta y = y - \langle y \rangle$, while $\sigma_{\rm H} = 6.4 \times 10^{-15} \text{ year}^{-1}$ and $\sigma_{\rm Hg} = 7 \times 10^{-15} \text{ year}^{-1}$ are 1σ -errors of experimental values (44) and (45).

To determine an uncertainty equalling one standard deviation for either coordinate x or y (we are interested in the one-dimensional case), it is necessary to define a region in which the probability of finding the true value is 68% for P(x, y) integrated with respect to the other coordinate from $-\infty$ to $+\infty$. It can be shown that this range corresponds to the projection of an ellipse defined by condition $R(\Delta x, \Delta y) = 1$ on the respective axis (Fig. 12a). The method for finding uncertainties in a situation where the number of experimental relations of form (44), (45) is larger than two is described in Ref. [25].

Thus, it is possible to place *independent* constraints on the variability of the fine structure constant and cesium magnetic moment in the modern epoch [20]:

$$x = \frac{\partial \ln \alpha}{\partial t} = (-0.9 \pm 2.9) \times 10^{-15} \text{ year}^{-1}, \qquad (48)$$

$$y = \frac{\partial}{\partial t} \ln \left(g_{\rm Cs} \, \frac{\mu_{\rm N}}{\mu_{\rm B}} \right) = (0.6 \pm 1.3) \times 10^{-14} \, \rm year^{-1} \,. \tag{49}$$

The estimates in (48) and (49) remain true even in the case of some correlative relations between the constants. In this sense, the above constraints are model-independent. A correlation of type (42) can be presented by the straight line y = 35x in Fig. 12a. Naturally, constraint (48) may be much more stringent in this case.

The authors of Ref. [25] summarized the results of all three measurements (39)-(41) represented in Fig. 11. Their analysis — similar to that described in the preceding paragraph — yielded the following constraint on the variation of the fine structure constant:

$$\frac{\partial \ln \alpha}{\partial t} = (-0.3 \pm 2.0) \times 10^{-15} \text{ year}^{-1}, \qquad (50)$$

which combines the results of all three measurements. To date, it is the most accurate estimate obtained by laboratory methods without resorting to strong model assumptions.

Using the above constraint on α variability, it is possible to evaluate the variation in the g-factor of proton g_p . A combination of (50) and the results of the comparison of atomic fountain frequencies (21) gives a constraint on the variation of the rubidium-to-cesium g-factor ratio

$$\frac{\partial}{\partial t} \ln \frac{g_{\rm Rb}}{g_{\rm Cs}} = (-0.11 \pm 1.1) \times 10^{-15} \,\,{\rm year}^{-1} \,. \tag{51}$$

Within the Shmidt model, Eqn (22), the following constraint follows from this relation:

$$\frac{\partial \ln g_{\rm p}}{\partial t} = (-0.05 \pm 0.56) \times 10^{-15} \,\,{\rm year^{-1}}\,. \tag{52}$$

Method	$t_2 - t_1$, year	$\frac{\Delta \alpha}{\alpha} = \frac{\alpha_1 - \alpha_2}{\alpha}$	$\frac{\dot{\alpha}}{\alpha} = \frac{\alpha_2 - \alpha_1}{\alpha(t_2 - t_1)}$, year ⁻¹	Model assumptions
Geological (Oklo) [14]	2×10^9	$(-0.36 \pm 1.44) \times 10^{-8}$	$(0.2 \pm 0.7) \times 10^{-17}$	+
Astrophysical [12, 36] Astrophysical [30]	$\frac{5-11\times10^{9}}{8\times10^{9}}$	$(-0.34 \pm 0.12) \times 10^{-6}$ $(0.1 \pm 1.7) \times 10^{-6}$	$(0.4 \pm 1.4) \times 10^{-16}$ $(-0.1 \pm 2.0) \times 10^{-16}$	+ +
Astrophysical [31]	9.7×10^{9}	$(-0.6\pm0.6) imes10^{-6}$	$(0.9\pm0.9) imes 10^{-16}$	+
Laboratory (Rb-Cs) [19]	4	$(0.2 \pm 6.4) \times 10^{-15}$	$(-0.5 \pm 16) imes 10^{-16}$	+
Laboratory (Hg-Cs) [28]	3	$(0.1 \pm 3.5) \times 10^{-15}$	$(-0.3 \pm 12) imes 10^{-16}$	+
Laboratory (H-Cs) [20, 69]	3,6	$(4.1 \pm 8.2) \times 10^{-15}$	$(-11 \pm 23) \times 10^{-16}$	+
Laboratory (Yb-Cs) [25]	2,8	$(1.8 \pm 6.6) \times 10^{-15}$	$(-6 \pm 24) \times 10^{-16}$	+
Combined laboratory [20, 25, 28]	≈ 3	$(1\pm 6.6) imes 10^{-15}$	$(-3\pm 20) imes 10^{-16}$	

Table 7. High-precision limitations on the measurements of the fine structure constant α over a period of $t_2 - t_1$ on the assumption of linear α changes.

Note. The listed errors correspond to one standard deviation $(\pm \sigma)$. Traditionally, $\Delta \alpha$ is the difference between the values of the fine structure constant in the past α_1 and its present-day values α_2 . A '+' sign in the far right column indicates the use of model assumptions to establish limitations. These are reaction conditions and neglect of the variability of other constants [14], astrophysical models [30, 31, 36], and condition $\dot{\alpha}_S = \dot{\alpha}_W = 0$ in [19, 20, 25, 28]. A combination of measured absolute frequencies in Hg⁺, H, and Yb⁺ allows model-independent constraints to be imposed on $\Delta \alpha / \alpha$ without resorting to an assumption of correlated changes in the constants.

Thus, a combination of laboratory findings of the absolute frequencies in H [20], ¹⁷¹Yb⁺ [25], and ¹⁹⁹Hg⁺ [28] (optical range) and ⁸⁷Rb [19] (microwave range) allows us to discriminate between contributions from different types of interactions and impose practically model-independent constraints on the variation in the fine structure constant α , the proton g-factor, and the nuclear magnetic moment of the ¹³³Cs atom. In considering these issues, a few weak assumptions were used, one being the assumption of the statistical independence of the measurements. Moreover, the measurements having been made at different times (and at different segments of the earth's orbit), it is also necessary to assume the validity of Lorentz and spatial invariance.

The assumption of Lorentz and spatial invariance is no longer needed if metrological experiments are carried out simultaneously in one laboratory. The 'optical comb' technique opens the possibility of directly comparing optical frequencies using no primary cesium standard. In principle, it allows us to directly impose constraints on the variation of the fine structure constant with a markedly improved sensitivity. Realization of such a project is planned at the Los Alamos National Laboratory, USA, where the frequencies of three narrow optical transitions will be directly compared in laboratory experiments.

4. Conclusion

Table 7 summarizes results of the modern high-precision laboratory search for the time variation in the fine structure constant. For comparison, some of the latest exact constraints obtained from astrophysical and geophysical surveys are included.

It can be seen that the sensitivity of laboratory methods to α variations is almost as high as that of extralaboratory estimation. Laboratory measurements span a relatively short period of time, which can be easily increased by an order of magnitude. This would greatly enhance the sensitivity to linear drifts of fundamental constants even if the relative precision of frequency measurements remained unaltered. The use of laboratory methods clears the way for disentangling contributions from electromagnetic, strong, and weak interactions and for direct examination of the magnetic moments of nuclei and the fine structure constant. Exploration of molecular spectra, in turn, allows us to evaluate the drift of the electron-to-proton mass ratio m_e/m_p .

One more advantage of laboratory methods based on absolute frequency measurements or the comparison of frequencies of different stable oscillators is the weak model dependence of the estimates thus obtained and reliable control of systematic errors. If the degree of precision necessary to observe a nonzero drift is achieved in the future, the findings will be easy to confirm by reproducing measurements in an analogous system.

Laboratory measurements performed recently indicate that the time variation of the fine structure constant in the modern epoch is below 2×10^{-15} year⁻¹. For the majority of physical measurements, this means that the currently employed fundamental parameters of theoretical models may be regarded as true constants. However, this inference does not eliminate the problem of searching further for variations concerning many physical theories. It can be argued that the achievement of a certain degree of experimental accuracy would be instrumental in the discovery of temporal variations in the constants and hence in shedding light on their nature and relationships.

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