PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A

Phil. Trans. R. Soc. A (2005) **363**, 2155–2163
doi:10.1098/rsta.2005.1639
Published online 1 August 2005

Precision spectroscopy of hydrogen and femtosecond laser frequency combs

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Precision spectroscopy of the simple hydrogen atom has inspired dramatic advances in optical frequency metrology: femtosecond laser optical frequency comb synthesizers have revolutionized the precise measurement of optical frequencies, and they provide a reliable clock mechanism for optical atomic clocks. Precision spectroscopy of the hydrogen 1S–2S two-photon resonance has reached an accuracy of 1.4 parts in 10^{14}, and considerable future improvements are envisioned. Such laboratory experiments are setting new limits for possible slow variations of the fine structure constant α and the magnetic moment of the caesium nucleus μ_{Cs} in units of the Bohr magneton μ_{B}.

Keywords: optical frequency metrology; fundamental constants; frequency combs; precision spectroscopy; hydrogen

1. Introduction

Precision spectroscopy of the simple hydrogen atom has played a central role in the history of atomic physics, and it has inspired many advances in high resolution laser spectroscopy and optical frequency metrology. Techniques such as laser-cooling of atomic gases, Doppler-free two-photon spectroscopy, or more recently, optical frequency metrology with femtosecond laser frequency combs, have all been conceived to advance optical spectroscopy of hydrogen. A recent new measurement of the absolute frequency of the 1S–2S two-photon transition has reached an accuracy of 1.4 parts in 10^{14} (Fischer 2004). Future experiments will permit ever more stringent tests of basic physics laws, and they may ultimately reveal 'new physics', such as possible slow changes of fundamental constants or conceivable differences between matter and antimatter.

Since 1970, the achievable relative accuracy in optical spectroscopy of hydrogen has improved by eight orders of magnitude. Major progress beyond classical spectroscopy began at Stanford University in the early 1970s with the

One contribution of 14 to a Discussion Meeting 'The fundamental constants of physics, precision measurements and the base units of the SI'.

advent of narrowband tunable dye lasers and novel techniques of Doppler-free laser spectroscopy. Over the following two decades, the accuracy advanced from a part in 10^6 to some parts in 10^{10}, approaching the limits of interferometric wavelength metrology. Since 1990, we have achieved dramatic further progress because we have learned increasingly well how to measure the frequency of light rather than the wavelength.

About 5 years ago, optical frequency metrology has been revolutionized with the advent of femtosecond laser optical frequency comb synthesizers (Udem *et al.* 2002). These instruments use the regular pulse train of a mode-locked femtosecond laser to phase coherently link optical frequencies and microwave frequencies in a single step. If successive pulses are correlated in phase, the laser spectrum consists of a regular comb of sharp spectral lines. The frequency of each comb line, $f_m = mf_r + f_{ce}$, with integer mode number m is determined by two observable radio-frequencies, the pulse repetition rate f_r and the rate f_{ce} at which the carrier phase slips relative to the pulse envelope. With a comb spanning more than an octave, it is particularly easy to determine the carrier-envelope offset frequency f_{ce} by sending comb lines from the red end of the spectrum through a frequency doubling crystal and observing a collective beat note with lines from the blue end of the comb.

We are now approaching another barrier, the limit of how well we know the unit of time, the second, which is still defined in terms of the 9 GHz ground state hyperfine splitting of atomic caesium. However, laser frequency combs are finally providing a reliable and practical 'clock mechanism' for new optical atomic clocks which can slice time into a hundred thousand times finer intervals, and which may ultimately achieve accuracies of a part in 10^{18} and beyond.

The art of laser frequency comb synthesis is beginning to mature (Ye & Cundiff 2005), with instruments based on mode-locked Ti : sapphire lasers and Er-fibre lasers now commercially available (www.menlosystems.com). Fibre laser comb synthesizers can be made particularly compact and are suitable for unattended long-term operation. Recently, agreement between two different fibre systems has been demonstrated to within a few parts in 10^{16} (Kubina *et al.* 2005). The accuracy of second harmonic generation and difference frequency generation has recently been tested with laser frequency combs to within 6×10^{-21} (Zimmermann *et al.* 2004), and neighbouring comb lines from several different frequency combs have been compared with uncertainties at the 10^{-19} level (Ma 2004). However, much remains to be learned about perturbing systematic line shifts before such accuracies can be realized in atomic spectroscopy and optical atomic clocks.

2. Hydrogen 1S–2S two-photon spectroscopy

In our laboratory at Garching, we have long concentrated on precision spectroscopy of the particularly sharp 1S–2S two-photon resonance of hydrogen and deuterium. In the first measurement of an absolute optical frequency with a femtosecond laser frequency comb in 1999, we have compared the ultraviolet 1S–2S frequency with the microwave frequency of a transportable caesium atomic fountain clock, developed at BNM-SYRTE in Paris, to within 1.8×10^{-14} (Niering 2000).

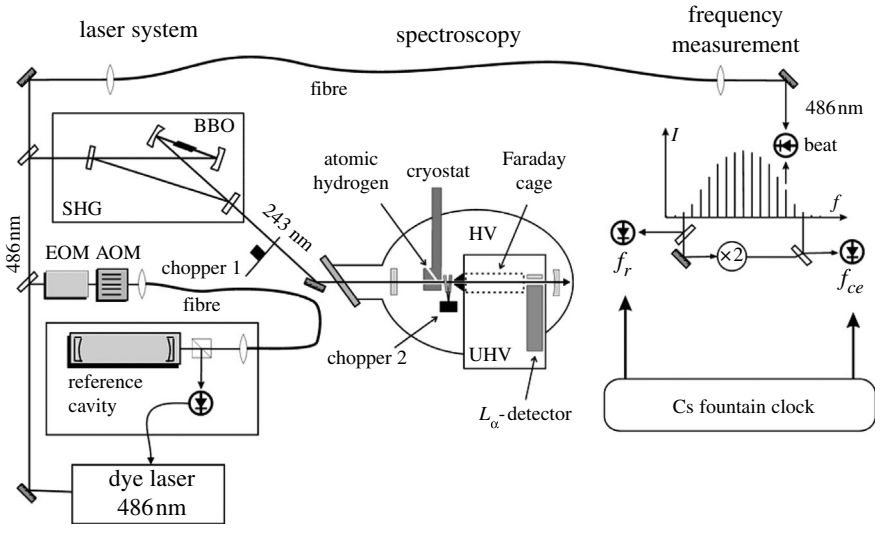

Figure 1. Layout of the experiment for the comparison of the hydrogen 1S–2S frequency with a primary frequency standard (Fischer 2004).

Since then, the hydrogen spectrometer (figure 1) has been improved in several ways. As before, ultraviolet radiation at 243 nm is produced by frequency doubling of a blue dye laser. The dye laser frequency is locked to an improved passive reference cavity by the Pound–Drewer–Hall method, reducing the laser line width to about 60 Hz at 486 nm. A spacer of zero expansion glass (Corning ULE) reduces the cavity drift rate to about $0.5\,\mathrm{Hz\,s^{-1}}$ compared to $25\,\mathrm{Hz\,s^{-1}}$ obtained with the Zerodur spacer in 1999. Up to 20 mW of UV light at 243 nm is coupled into a linear build-up cavity inside the vacuum chamber of the hydrogen atomic beam apparatus. Hydrogen atoms are produced in a microwave discharge and cooled to 5–6 K by a nozzle mounted to a helium cryostat. Afterwards, they travel collinearly in the standing wave field of the cavity, restricted by two narrow apertures. After a distance of about 10 cm they reach the 2S detection region where a quenching electric field forces the emission of Lyman-α photons, which are observed with a photomultiplier. The exciting UV light is periodically blocked with a chopper at 160 Hz, and Lyman-α photons are detected only during the dark period, in order to avoid background counts due to stray light. The signal counts are sorted into 12 bins corresponding to different delay times. This time-of-flight method makes it possible to separate the contributions of different velocity classes. A correct line shape model has to account for all the observed signals. The atomic beam is periodically blocked with a fork chopper synchronized to the optical chopper to reduce the loss of slow atoms by collisions with faster atoms that escape continuously from the nozzle. The vacuum system has been upgraded to allow differential pumping of the interaction region to a pressure of 10^{-8} to 10^{-7} mbar to reduce line shifts and the loss of slow atoms due to collisions with background gas atoms.

In one series of measurements, the interaction region was shielded from magnetic fields in order to measure the hyperfine splitting between the $F=1$ and $F=0$ line components in hydrogen or deuterium (Kolachevsky *et al.* 2004*a*,*b*).

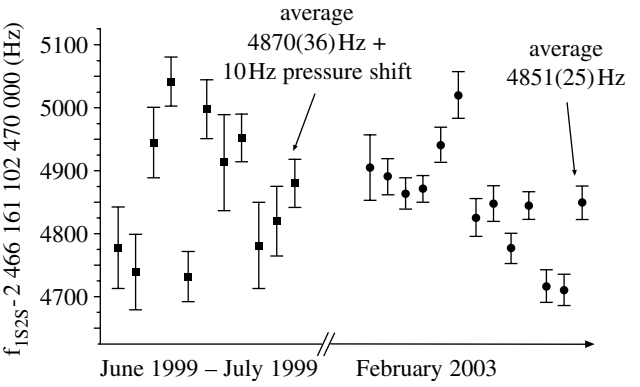

Figure 2. Experimental results and averages for the 1999 and 2003 measurements of the absolute 1S–2S ($F=1$, $M=\pm 1$) transition frequency in atomic hydrogen (Fischer 2004). Each point represents the data accumulated during 1 day with their statistical error.

Since the ground state hyperfine interval of hydrogen $f_{\mathrm{HFS}}(1\mathrm{S})$ is known very well, this optical measurement yields a value of the 2S hyperfine splitting $f_{\mathrm{HFS}}(2\mathrm{S})$. Our result is now more accurate than earlier values obtained by radiofrequency spectroscopy. Disturbing nuclear structure corrections cancel in the combination

$$D = 8f_{\mathrm{HFS}}(2\mathrm{S}) - f_{\mathrm{HFS}}(1\mathrm{S}).$$

A comparison of experiment and theory provides a test for QED corrections of the order α^4 and $\alpha^3\, m_{\mathrm{e}}/m_{\mathrm{p}}$.

In February 2003, we have performed a new absolute frequency measurement of the 1S–2S resonance. About 10 mW of the 486 nm light from the dye laser is sent through an optical fibre into the frequency metrology laboratory, where it is compared with the microwave frequency of a caesium atomic clock, using the octave-spanning frequency comb synthesizer (Holzwarth *et al.* 2000). As in 1999, the FOM atomic fountain clock built in Paris has been transported to Garching for this measurement. The relative accuracy of this clock has been verified to 8×10^{-16} at BNM–SYRTE (Abgrall 2003) but for the Garching experiments, we attribute a conservative accuracy of 2×10^{-15} for both measurements.

Figure 2 shows a comparison of measurement results from the two experiments during 10 days in 1999 and 12 days in 2003. Each data point represent the measurements of 1 day with statistical errors, after correcting for the AC Stark effect by extrapolating to zero intensity. Both sets of data have been analysed with the same theoretical line shape model and are therefore comparable. The quality of the data obtained during a given day is obviously much improved in 2003. However, the fluctuations from day-to-day are similar to those of 1999, pointing at some uncontrolled systematic frequency shifts on the order of 40–80 Hz at 121 nm.

After the completion of these measurements, we have performed a series of careful experimental tests to rule out many conceivable sources of such systematic line shifts, such as intra-beam pressure shifts, background gas pressure shifts, or line shifts due to stray microwaves from the hydrogen discharge. In hindsight we have now identified two likely causes for the observed

fluctuations. The most plausible candidate is the inadvertend excitation of (lossy) higher order transverse modes of the build-up cavity, or the distortion of wavefronts by a not ideally mode-matched travelling wave entering through the coupling mirror with its transmission of 2%. These conditions can change, e.g. after realignment of the dye laser system or the build-up cavity. If the wavefronts of forward and backward running waves inside the cavity do not match perfectly, first-order Doppler shifts do not cancel completely in two-photon excitation. Another contributing cause may be the insufficient stabilization of the laser frequency. In nonlinear spectroscopy, any correlations between frequency fluctuations and amplitude fluctuations can lead to significant line shifts. Such correlations can, e.g. be introduced by an imperfect servo lock of the build-up cavity. Both kinds of systematic line shifts can have either signs, so that these effects should cancel when averaging over many measurements.

For future experiments, we are planning to increase the finesse of the build-up cavity at least 10-fold to reduce the spurious excitation of unwanted modes. We have also made very encouraging progress with an acoustically quieter semiconductor laser system with two stages of frequency doubling that produces up to 20 mW at 243 nm so that it can replace the frequency doubled dye laser. In order to reduce the laser line width to a few Hz, we plan to employ a vibration-compensating suspension of the reference cavity, as recently pioneered by John L. Hall and Jun Ye at JILA (Hall & Ye 2004, private communication).

After quadratically adding a systematic error of 23 Hz, the frequency of the $F=1$ to $F'=1$ hyperfine component of the 1S–2S transition obtained in 2003 is

$$f_{1S-2S} = (2\,466\,061\,102\,474\,851 \pm 34)\ \text{Hz}.$$

The uncertainty of 1.4 parts in 10^{14} is only slightly improved over that of the 1999 result

$$f_{1S-2S} = (2\,466\,061\,102\,474\,880 \pm 46)\ \text{Hz}.$$

Here, we have added a pressure shift of 10 Hz that had not been included in the 1999 analysis and a systematic error of 28 Hz. However, we now have two independent measurements of this important transition which agree within their error limits. The difference of (-29 ± 57) Hz in 44 months corresponds to a drift of the 1S–2S frequency relative to the caesium frequency standard of $(-3.2 \pm 6.3) \times 10^{-15}$ per year, consistent with a zero drift.

3. Are the fundamental constants constant?

A non-zero drift would arise if fundamental constants changed slowly with time. Any changes of non-gravitational constants are ruled out by Einstein's equivalence principle, but may be permitted within string theories aiming for the unification of all interactions. The dramatic advances in the art of precision spectroscopy and optical frequency metrology have kindled much interest in laboratory searches for time variations of fundamental constants (Bize 2003; Peik *et al.* 2004).

Recent studies of absorption lines in the light of distant quasars at the Keck observatory have been interpreted as an indication that the electromagnetic fine

structure constant α has been somewhat smaller in the early universe (Murphy *et al.* 2003). With the simplest assumption of a linear drift, the relative rate of change of alpha would be $(6.4 \pm 1.4) \times 10^{-16}$ per year, too small to be directly observed in the present hydrogen experiment. However, Harald Fritzsch, a theorist at the University of Munich (Calmet & Fritzsch 2002) and others have argued that α cannot simply change by itself, if one believes in grand unification. If all known forces are to remain unified at very high energies, other coupling constants have to change as well. Using the framework of quantum chromodynamics, Fritzsch points at an interesting amplification effect. He argues that the masses and magnetic moments of hadrons should change much faster than α: "We would expect that light emitted in hyperfine transitions should vary in time about 17 times more strongly than light emitted in normal atomic transitions, but in the opposite direction, i.e. the atomic wavelength becomes smaller with time, but the hypefine wavelength increases." This amplification should have produced an observable effect in the comparison of the two hydrogen measurements separated by almost 4 years, if the interpretation of the Keck observations were correct. However, new observations of quasar spectra at the Very Large Telescope in Chile do not support that evidence, but are consistent with a zero change of α (Srianand *et al.* 2004).

Regardless of such speculations, our experiments together with other recent precise measurements of the frequencies of optical clock transitions (Bize 2003; Peik *et al.* 2004) are already establishing new laboratory limits for possible time variations of fundamental constants. Our hydrogen results are consistent with zero changes. However, nature could conspire against us and change both the electromagnetic fine structure constant α and the magnetic moment of the caesium nucleus μ_{Cs}, in units of the Bohr magneton μ_{B}, in such a way that we do not see any relative drift when comparing the hydrogen 1S–2S frequency with the hyperfine frequency of a caesium clock. In that case, however, a drift should become observable when measuring an optical frequency in heavier atoms which respond in a different way to changes of α. The mercury ion with its strong relativistic effects is such a candidate. Spectroscopy of the ultraviolet S–D electric quadrupole clock transition in $^{199}\mathrm{Hg}^{+}$ has been perfected over decades by Jim Bergquist at NIST in Boulder, and two absolute frequency measurements have been made in 2000 and 2002, using the laser frequency comb approach (Bize 2003). In addition, a S–D quadrupole clock transition in the $^{171}\mathrm{Yb}^{+}$ ion has been measured at the PTB in Braunschweig in 2000 and in 2003 (Peik *et al.* 2004). The shaded stripes in figure 3 indicate how these three measurements establish limits for possible changes of α and the caesium magnetic moment μ_{Cs} (measured in units of the Bohr magneton μ_0). Measurements of a clock transition in Sr^{+} (Margolis *et al.* 2004) will add limits with a slope indicated by the solid line. The intersection of the three stripes defines to a 1-sigma area which gives separate laboratory limits for possible drifts of the fine structure constant α and the magnetic moment of the caesium nucleus μ_{Cs}:

$$\dot{\alpha}/\alpha = (-0.3 \pm 2.0) \times 10^{-15}\ \mathrm{yr}^{-1}.$$

$$\dot{\mu}_{\mathrm{Cs}}/\mu_{\mathrm{Cs}} = (2.4 \pm 6.8) \times 10^{-15}\ \mathrm{yr}^{-1}.$$

However, we are at a rather early stage of such studies. In many industrialized countries, there are now strong teams working towards the development of more

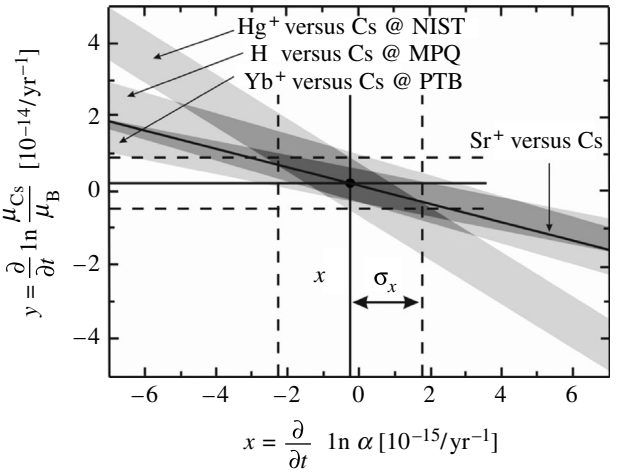

Figure 3. Limits for possible time variations of the fine structure constant and the caesium nuclear magnetic moment established by comparing optical frequencies in Hg^+ (Bize 2003), H (Fischer 2004), and Yb^+ (Peik *et al.* 2004) with the microwave frequency of a Cs clock over a period of several years.

precise atomic clocks, based on sharp optical transitions in different trapped ions (Hg^+, In^+, Yb^+, Sr^+, Ca^+,...), cold neutral atoms (H, Ca, Sr, Yb, Ag, Hg,...), or molecules (I_2, CH_4, C_2H_2,...). As such clocks are perfected, with envisioned ultimate accuracies of 10^{-18} or beyond, a comparison of different types of clocks over extended periods might eventually reveal changes of fundamental constants down to levels of 10^{-20} per year. Such changes would matter little for everyday life, but much for our understanding of the universe.

4. How can we improve the Rydberg constant?

Even though the accuracy of the hydrogen 1S–2S frequency will soon approach a few parts in 10^{15}, the accuracy of the Rydberg constant remains limited to 6.6 parts in 10^{12} by uncertain nuclear structure effects. A sixfold improvement of the Rydberg constant could be obtained immediately by an independent accurate determination of the rms charge radius of the proton (Mohr, private communication). A measurement of the 2S Lamb shift of muonic hydrogen at the Paul-Scherrer Institute (Kottmann *et al.* 2001) promises to find this proton radius to within 1 part in 10^3. Another avenue towards an improved Rydberg constant is the precise measurement of transition frequencies from the metastable 2S state to higher S and D levels in hydrogen with their correspondingly smaller nuclear size effects, as pursued in Paris (Schwob 1999) and at MIT (Kleppner 2004, private communication). Two-photon spectroscopy of the 1S–3S transition in hydrogen can serve the same purpose. At Garching, we are presently working towards Doppler-free two-photon spectroscopy of the 1S–3S resonance in a cold hydrogen beam directly with a frequency comb from a mode-locked picosecond laser with two stages of frequency doubling. In a future experiment, we will attempt two-photon spectroscopy of the 1S–2S resonance in hydrogen-like helium ions, using coherent radiation at 60 nm. To generate a frequency comb in the extreme ultraviolet, we

rely on high harmonic generation in a xenon gas jet, using femtosecond pulses from a mode-locked Ti : sapphire laser circulating inside a passive build-up cavity. We hope that these prospects will stimulate further theoretical work to extend the computation of higher order QED corrections in hydrogenic energy levels.

5. Outlook

Even beyond more precise measurements of fundamental constants and searches for their possible time variations, there are many good practical reasons for pushing the art of measuring time and frequency to the feasible limits. Advances in time and frequency metrology will enable the synchronization of clocks over large distances. Such synchronization is, e.g. needed in astronomy for very long baseline intererometry. Better clocks will improve the performanc of satellite navigation systems. They are also crucial for the precise tracking of remote space probes. In telecommunications, better atomic clocks will be needed for network synchronization, as the need for bandwidth increases. Geologists can apply better clocks to study the variability of earth's rotation or to follow the drifts of continents with millimeter precision. Astronomers can study irregularities in the periods of pulsars. For physicists interested in fundamental science, better clocks will permit new stringent tests of special and general relativity. Very likely, there will be new unexpected discoveries, as the art of precision spectroscopy and optical frequency metrology continues to advance.

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