Review

High-Precision Atomic Mass Measurements for Fundamental Constants

Edmund G. Myers

Department of Physics, Florida State University, Tallahassee, FL 32306-4350, USA; emyers@fsu.edu

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Abstract: Atomic mass measurements are essential for obtaining several of the fundamental constants. The most precise atomic mass measurements, at the 10^{-10} level of precision or better, employ measurements of cyclotron frequencies of single ions in Penning traps. We discuss the relation of atomic masses to fundamental constants in the context of the revised SI. We then review experimental methods, and the current status of measurements of the masses of the electron, proton, neutron, deuteron, tritium, helium-3, helium-4, oxygen-16, silicon-28, rubidium-87, and cesium-133. We conclude with directions for future work.

Keywords: atomic mass; fundamental constants; precision measurement; Penning trap

1. Introduction

The fundamental constants enable the quantitative unification of physical science. At the highest level of precision, values for dimensionless constants such as the fine-structure constant, obtained from different types of measurement, can be used to test the validity of fundamental theory and search for physics beyond the so-called Standard Model [1]. While the atomic masses of the electron, the isotopes of hydrogen and helium, and the neutron are themselves regarded as fundamental constants, others are necessary for various routes to obtaining other constants. Here we discuss precision atomic mass measurements that are relevant to the determination of fundamental constants as in the Committee on Data for Science and Technology (CODATA) evaluations [2,3]. Our aim is not to attempt any rigorous analysis of the relevant data as is done by the authors of the comprehensive Atomic Mass Evaluations (AME), (e.g., see references [4,5]), but to enable the reader to see those measurements that have the greatest impact. A previous review of precision atomic mass measurements can be found in reference [6]. Other related reviews, which also discuss applications to nuclear physics are references [7–10].

After some remarks about the unified atomic mass unit "u" and its relation to the "New-SI" kg, we review current techniques for precision atomic mass measurements. These generally involve measuring cyclotron frequency ratios of ions in Penning ion traps. As well as these methods, we outline the main sources of measurement uncertainty. We then discuss mass measurements of the "light ions", i.e., the isotopes of hydrogen and helium; and then of the alkali metal atoms ^{87}Rb and ^{133}Cs, which are important for the atom-recoil method for the fine-structure constant. Next, we discuss the special case of the atomic mass of the electron, which has now been most accurately obtained from the electronic *g*-factor (Zeeman effect) of hydrogen-like ions. Here, and for related *g*-factor measurements, the atomic mass of the ion is also needed. We then briefly consider atomic masses relating to Avogadro's number and the Boltzmann constant. We conclude by indicating where future atomic mass measurements are needed.

1.1. Relative Atomic Masses, the Unified Atomic Mass Unit (u) and Dalton (Da)

The most precise measurements of the masses of atoms are obtained using Penning ion traps, which yield mass ratios of ions from (inverse) cyclotron frequency ratios (CFRs). The mass ratios of ions, including molecular ions, can be corrected to give mass ratios of atoms by allowing for the mass of the missing electrons and the "energies of formation" (EOF) of the ions from their constituent atoms, (e.g., see references [2,11]). In the case of monatomic ions, the EOFs are simply ionization energies, while in the case of molecular ions they must also include the binding energy of the molecule, (e.g., see reference [12]). For low charge-states of all atoms, all charge-states of lighter atoms, and for simple molecular ions in known ro-vibrational states, this can usually be done without any significant loss of precision. If the mass of the atom (or other particle) can then be related to the mass of an atom of ^{12}C (either through a single CFR, or sometimes, through a chain, or even an intricate web of related CFRs) then the atom's mass can be expressed in so-called "unified atomic mass units", with symbol u, which is defined as $1/12$ of the mass of a free atom of ^{12}C at rest. This is what is meant by (relative) "atomic mass" (it is the mass of a particle, which may or may not be an atom, expressed in u). While physicists favor u, chemists generally use the name dalton (Da) for the identical unit. The u is also distinct from the older and deprecated amu, which was based on the mass of ^{16}O [4], although this is not always recognized in the literature. It should also be appreciated that relating masses of atoms to the u, although conventional, is not always necessary. For instance, as regards the determination of the Rydberg from spectroscopy of hydrogen, what matters is the mass ratio of the electron to the proton. As a point of notation, in this article we use upper case, e.g., $M[e]$ or $M[^3\text{He}]$ to denote (relative) masses expressed in u, and lower case, e.g., m_e, when this distinction is not needed.

1.2. Relation of u to the Kilogram in the New SI

In late 2018, it was agreed by the international General Conference on Weights and Measures, that from May 2019, the base units of the International System of Units (SI) were to be redefined by adopting fixed values for the Planck constant h, the elementary electric charge e, the Boltzmann constant k_B, and the Avogadro constant N_A. The speed of light in vacuum c was already a fixed constant. Given that the second is defined in terms of the frequency of the hyperfine transition in the ground state of the ^{133}Cs atom, it follows (Special Relativity and Quantum Mechanics being assumed) that the kg is now defined by the fixed h, the ampere by the fixed e, the kelvin by the fixed k_B, and the mole by the fixed N_A. A general consequence is the conceptual shift that measurements (often chains of measurements), that formerly measured these fundamental constants, no longer do that. After the redefinition, these measurements are just as important, but now have the role of *realizing* the SI base units from the fundamental constants. An example of this is the Kibble (or Watt) balance [13], which effectively compares the mechanical and electrical watt, the latter being related to h using the Josephson effect and the quantized Hall effect. Formerly the Kibble balance measured h relative to the artifact kg; now it realizes the kg from the defined h. Because this can now be done reproducibly at the few 10^{-8} level, the re-defined kg is more stable and reproducible than the platinum-iridium alloy artifact kg standard adopted in 1889.

Another related example, and where atomic masses are involved, is the X-Ray-Crystal-Density (XRCD) technique for determining the number of atoms in a near-perfect spherical crystal of silicon, by precision x-ray measurements of the crystal's lattice spacing, combined with optical measurements of the crystal's diameter, (e.g., see reference [14]). Formerly, after measuring the crystal's mass against the artifact SI kg, and knowing the atomic mass of Si [15], this related u to the kg, and equivalently, measured the Avogadro constant N_A, at the few 10^{-8} level. Now, with N_A fixed, N_A no longer relates u to the kg (and, from the physicist's point of view, has lost significance). The "atom counting" of the XRCD technique still relates the atomic mass unit u to a macroscopic mass. However, since u can now be related to the redefined-SI kg in other and more precise ways, see below, this procedure is now an alternative way of realizing the macroscopic kg (also at the few 10^{-8} level).

In the new-SI with a defined h, the u and the kg can be accurately related using atom-recoil measurements that yield h/m_{atom} combined with atomic mass measurements of the particular atom relative to ^{12}C (e.g., see [16]). Atom recoil measurements are further discussed in relation to the fine-structure constant in Section 4. One can also use the relation between the Rydberg constant R_∞, the fine-structure constant α, and the absolute electron mass m_e,

$$2hR_\infty = \alpha^2 \, m_e \, c. \tag{1}$$

In this expression, the least well-known quantity is α, which in CODATA14 has a fractional uncertainty of 2.3×10^{-10}, while R_∞ has a fractional uncertainty of 5.9×10^{-12} [2]. Thus, m_e is determined relative to the SI-kg essentially with the same precision as α^2. In addition, $M[e]$, the mass of the electron relative to ^{12}C, has now been experimentally determined with an uncertainty of 2.9×10^{-11} [17] (see Section 5), also significantly less than the uncertainty of α^2. Hence, u can be related to the new-SI kg with a relative uncertainty equivalent to that of α^2, i.e., to better than 5×10^{-10}, an improvement of more than 20 compared to its relationship to the "old-SI" kg. (Using the new-SI value for h [3], and CODATA14 values for R_∞, α and $M[e]$, one obtains u = 1.660 539 067 95(78) $\times 10^{-27}$ kg, c.f. the CODATA14 value, u = 1.660 539 040(20) 10^{-27} kg). Since this is substantially better than what can be obtained from the XRCD technique, it follows that the XRCD technique now has the practical role of providing an alternative to the Kibble balance in realizing the new-SI kg from its definition.

2. Precision Measurement of Atomic Masses Using Penning Ion Traps

2.1. The Precision Penning Trap

A Penning trap consists of a set of cylindrically symmetric electrodes, a central ring, and two end-caps, immersed in a uniform magnetic field. In a precision trap [18], extra field-compensation electrodes are placed between the ring and endcaps to adjust the shape of the potential, and the uniform magnetic field is produced by a carefully shimmed superconducting magnet. In some Penning traps, the electrodes have hyperboloidal inner surfaces, while in others the electrodes, including those that function as the endcaps, consist of circular tubes. This "open endcap" design facilitates moving ions between adjacent traps and the introduction of microwave or laser radiation. The electrostatic field is produced by applying voltages to the electrodes, typically <100 V, using high stability voltage sources through low-pass filters.

In the ideal Penning trap the electrostatic potential $V(\rho,z)$ has the purely quadratic form given (in cylindrical co-ordinates) by $V(\rho,z) = (V_0/2d^2)(z^2 - \rho^2/2)$, where the z-axis is aligned with the uniform magnetic field, V_0 is the voltage between the ring and endcaps and d is a parameter characterizing the trap size. For the hyperboloidal electrode trap, $2d^2 = z_0^2 + \rho_0^2/2$, where $2z_0$ is the shortest distance between the endcaps and $2\rho_0$ is the smallest internal diameter of the ring. The motion of a single trapped ion is the superposition of a simple harmonic motion along the z-axis (called the axial motion, at frequency f_z), and two circular motions, the modified (by the electrostatic potential) cyclotron motion at frequency $f_c{}'$, and the magnetron motion, which is a lower frequency motion of the ion about the center of the trap—and thus provides the radial confinement—at frequency f_m. The "true" cyclotron frequency, which in a magnetic field of magnitude B without any electrostatic field is given by $f_c = (1/2\pi)qB/m$, is now given by a relation involving all three measurable frequencies, $f_c^2 = f_c{}'^2 + f_z^2 + f_m^2$.

Remarkably, in the limit of small amplitudes of the motion, this relation is still true in a trap where the electrostatic potential is not perfectly cylindrically symmetric, and is not perfectly aligned with the magnetic field, where $f_c{}'$, f_z, and f_m are now the frequencies of the motions that approximate those in the ideal trap. This is known as the Invariance Theorem [18]. Hence, if all three mode frequencies are measured, $f_c^2 = f_c{}'^2 + f_z^2 + f_m^2$ provides a robust prescription for obtaining the "true" cyclotron frequency, which is inversely proportional to the mass of the ion. Further, by arranging that f_z <<

f_c', f_m can be obtained from $f_m = (f_z^2/2f_c')(1 + \delta)$, where δ, which is typically $<< 10^{-3}$, can be used to parameterize the combined effect of the ellipticity of the electrostatic field and its tilt with respect to the magnetic field. Because of the frequency hierarchy, the absolute uncertainties of f_z and f_m that can be allowed without compromising the measurement of f_c are greater than that of f_c' by factors of f_c/f_z and f_c/f_m, respectively. Hence, while in order to increase statistical precision it is necessary to repeat measurements of f_c' and f_z, measurements of f_m are only needed to obtain and check the stability of δ. In Penning traps used for the most precise measurements, the chamber housing the electrodes is maintained at close to LHe temperature, resulting in extreme ($<<10^{-15}$ mbar) high-vacuum [19]. Hence single ions can be trapped and manipulated, and measurements made on them for many days.

2.2. Measuring the Cyclotron Frequency

2.2.1. Detecting the Axial Motion

In cryogenic Penning traps the axial motion of a single ion can be detected, and also damped, by bringing it into resonance with a high-quality-factor tank circuit, whose main component is a low-loss inductor, i.e., a coil, often superconducting, connected across the trap electrodes. The oscillating ion induces oscillating image charges on the trap electrodes, and hence a current through the detection circuit. Due to the high-impedance of the detection circuit at its resonance frequency, this results in a significant oscillatory voltage that back-acts on the ion, damping its motion till it comes to thermal equilibrium with the coil, which is typically at close to 4.2 K. The coil is electrically coupled to an amplifier consisting of an FET transistor, (e.g., see references [18,20]) or else a dc-SQUID [21]. The axial frequency can hence be measured by Fourier-transforming the amplified signal due to the axial motion of the ion. This motion can be the damped "ring-down" after the ion has been axially excited by an rf-drive pulse. Alternatively, since an unexcited ion partially cancels the Johnson noise from the resonant circuit at the ion's axial frequency, the axial frequency can be determined from the resulting dip in the noise spectrum [18].

2.2.2. Swept Continuous Cyclotron Drive with Axial Frequency Shift Detection

Although the cyclotron motion can also be directly detected and damped using image current techniques, (e.g., see references [22,23]), for a single ion the $1/e$ damping times are typically several minutes and thus inconveniently long. More often, the radial modes are detected by coupling them to the axial mode. In the case of the technique used by the Penning trap group at the University of Washington (UW) [24], f_c' was measured by making use of the shift in axial frequency that occurs when the cyclotron radius changes in an imperfectly homogeneous magnetic field. Hence, as a weak rf drive is swept through f_c', either from below or from above, the excitation of the cyclotron motion is signaled by a shift in axial frequency as the drive frequency passes through f_c'. The best estimate of f_c' is obtained by interpolating between the two corner frequencies corresponding to the different directions of the scan. Disadvantages of this method are the requirements for high magnetic field and trap voltage stability, and that the responses to the up and down scans are not symmetrical and depend on various instrumental settings [25].

2.2.3. Double Dip (Avoided Crossing) Technique

The radial and axial modes of motion can be resonantly coupled by applying a "tilted" quadrupolar rf electric field at the frequency $f_c' - f_z$ for the cyclotron mode (and $f_z + f_m$ for the magnetron mode) [26]. If the rf drive is applied continuously at $f_c' - f_z$, the "action" oscillates between the cyclotron and axial modes at a frequency proportional to the coupling strength, usually called the Rabi frequency. The Fourier transform of the axial signal is then split into two components, separated by the Rabi frequency and symmetric about the original axial frequency. This enables f_c' to be determined from either the double peaks after pulsed excitation of the axial motion [26], or,

by detecting a "double dip" in the noise spectrum, (e.g., see reference [27]). Similar methods can be used to measure f_m.

2.2.4. Pulse-and-Phase and Pulse-and-Amplify Techniques

The so-called "Pulse-and-Phase" (PnP) technique was first developed by the atomic mass measurement group at the Massachusetts Institute of Technology (MIT) [26,28], and has since been used extensively at Florida State University (FSU), where the MIT Penning trap was relocated in 2003, (e.g., see references [15,29–32]). Here, after centering the ion by applying the coupling drives at f_c' $- f_z$ and $f_z + f_m$, and allowing the axial motion to damp, a pulse is applied at a frequency close to f_c'. This produces a cyclotron motion with a well-defined radius and phase. This is followed by a delay, T_{evol} (the phase evolution time), during which the cyclotron motion continues, unperturbed, evolving phase. The final phase of the modified cyclotron motion is then "read out" by applying a "pi-pulse" (producing half a Rabi oscillation) at close to $f_c' - f_z$, which converts the cyclotron motion phase-coherently into axial motion. Thus, the final cyclotron phase $\varphi_{c'}$ is mapped onto the axial motion, which is then detected. By repeating the process with different values of T_{evol}, f_c' is obtained from $f_c' = (1/2\pi) \, d\varphi_{c'}/dT_{evol}$. In the MIT/FSU trap, with a cyclotron frequency of ~4 MHz (~40 MHz), $\varphi_{c'}$ can be typically measured with an uncertainty <1/10 of a cycle after a maximum $T_{evol} = 100$ s (10 s), corresponding to a fractional frequency resolution of ~2.5×10^{-10}. However, because the phase must be "unwrapped", as many as 12 PnPs with a range of T_{evol} are often used to give a single measurement of f_c' [26].

In the Pulse-and-Amplify (PnA) method [33], instead of the pi-pulse, the coupling drive is applied at the end of T_{evol} as the sum frequency $f_c' + f_z$. As in the PnP, this maps the cyclotron phase onto the axial phase. However, it also produces parametric amplification of both modes and thus results in a larger axial signal, enabling measurements with smaller initial cyclotron radii (see Section 2.3.7).

2.2.5. Cyclotron Frequency Measurement Using Time-of-Flight Detection

An exception to the use of a cryogenic Penning trap with image charge detection is the work of the SMILETRAP group at the University of Stockholm, who used a room temperature trap connected to an external ion source to make cyclotron frequency measurements using the "time-of-flight" (TOF) detection technique [34], as is often used for nuclear physics [10]. In this method, an ion is injected into the trap and excited to a significant magnetron radius, after which a rf pulse is applied at close to the magnetron-to-cyclotron coupling frequency $f_c' + f_m$, which is approximately equal to the free-space cyclotron frequency f_c [35]. Depending on the detuning of the drive from $f_c' + f_m$, this converts some of the magnetron motion to cyclotron motion. The ion is then ejected from the trap and detected in a micro-channel plate. Because the fringing field of the magnet exerts an axial force on the ion proportional to the cyclotron radius, the TOF measures the cyclotron radius and hence signals that the drive was on resonance. By repeating the process with many ions and different coupling frequencies, a resonance curve can be mapped out. The resolution of this procedure has been improved by using two pulses to produce Ramsey fringes [36–38], and, more recently, by using the so-called "phase imaging technique" [39], which is an ingenious adaptation of the PnP technique. However, disadvantages of these methods, compared to image-charge techniques, are that the motions of the ions in the Penning trap are relatively large and uncontrolled and that impurity ions perturb the measurements.

2.3. Limitations to Precision Measurement of Cyclotron Frequency Ratios

Here we discuss sources of uncertainty that limit the precision with which a cyclotron frequency ratio can be measured in a Penning trap, and some of the methods used to mitigate them. For definiteness, we focus on measurements using the pulse-and-phase technique, but similar considerations apply to other techniques. More details can be found in reference [6].

2.3.1. Magnetic Field Variation

Any variation of the magnetic field between measurements of f_c of the two ions in a pair adds uncertainty to the measurement of the CFR. This can be addressed by careful engineering of the superconducting magnet to have high stability. For example, with a magnet with a fractional field drift $< 2 \times 10^{-11}$/h [40], the UW group was able to take data with runs that consisted of repeated cyclotron frequency measurements on one ion for several days, followed by repeated measurements on the second ion, also for many days. With a less stable magnet, it is desirable to alternate between measurements on the two ions as frequently as possible. At MIT, a semi-automated procedure for making and remaking ions within the trap ("make and remake technique") was developed, sometimes allowing up to 8 pairs of measurements in a single 4 h run [41]. This procedure was initially adopted at FSU [29,30]. However, subsequently at FSU the "ion swapping" was greatly facilitated by trapping the two ions simultaneously, and alternating them between the center of the trap, where f_c is measured using the PnP technique, and a large radius cyclotron "parking" orbit [22,42]. Alternatively, as developed at MIT in 2002, if the two ions have the same charge, and have masses with a fractional difference less than about 10^{-3}, it can be arranged that the two ions orbit the center of the trap, 180 degrees apart, in a coupled magnetron orbit [43]. In the FSU technique, the measurements of f_c are still alternate, with a delay of about 5 minutes between them due to the time taken to re-center the outer ion. In the MIT method, the measurements are truly simultaneous, thus the variation in the magnetic field can be almost completely cancelled. Another method, which has been developed by a collaboration of MPIK-Heidelberg, University of Mainz, GSI, and RIKEN (MPIK* for short), is to use multiple adjacent traps aligned along the axis of the same superconducting magnet [27,44–46]. Each ion is alternately shuttled from its own storage trap into the measurement trap where f_c is measured. This scheme can be extended by having a third ion in an additional trap, which simultaneously monitors the magnetic field, or, by having two nearly identical measurement traps and swapping the ions to be compared between them, also with simultaneous measurement of their cyclotron frequencies [21,47].

2.3.2. Amplitude-Dependent Shifts Due to Field Imperfections and Special Relativity

Other limiting sources of error in measurements of a CFR are the shifts in f_c' and f_z due to magnetic and electrostatic field imperfections, and special relativity, combined with the finite amplitude of the axial motion, a_z, and the radii of the cyclotron and magnetron motions, ρ_c and ρ_m. As discussed in detail in reference [18,48–50], the trap field imperfections can be quantified using the coefficients C_n of the expansion of the electrostatic potential in Legendre polynomials, and the coefficients B_n of the expansion of the magnetic field in associated Legendre polynomials. Of these, the most important are the lowest order even terms, C_4, C_6, and B_2, which lead to shifts that depend on even powers of the mode amplitudes. (The odd-order terms can produce frequency shifts proportional to $B_1{}^2$, $B_1 C_3$, etc., but none that are first order in the coefficients.) For example, due to C_4, B_2, and special relativity, f_c' is shifted according to

$$\Delta f_c'/f_c' \approx -(3/2)(f_m/f_c')(C_4/C_2)(2a_z{}^2 - \rho_c{}^2 - 2\rho_m{}^2)/d^2 + (1/2)(B_2/B_0)(a_z{}^2 - \rho_c{}^2 - \rho_m{}^2) - (1/2)(2\pi f_c'/c)^2 \rho_c{}^2, \quad (2)$$

where the three groups of terms correspond to the shifts due to electrostatic and magnetic imperfections, and special relativity, respectively. Fortunately, because the axial and cyclotron frequencies have different dependencies on the mode amplitudes, measurements of the variation of f_z versus ρ_m and ρ_c can be used to independently measure the electrostatic and magnetic imperfections [48]. Further, the relativistic shift can be used for calibrating the cyclotron radius. Clearly, the strategy for reducing errors due to anharmonic shifts is to minimize the field imperfections by careful trap design and to use the smallest mode amplitudes possible during the measurement of f_c' and f_z. Equation (2) also shows that for a large m/q ratio and thus low f_c', electrostatic imperfections become more important. Conversely, for small m/q, that is for light ions and highly-charged ions, electrostatic imperfections are less important and special relativity becomes dominant.

2.3.3. Equilibrium Position Shifts

In order to bring the two ions' axial motions into resonance with the narrow-band detection circuit, the trap voltage must be changed according to the change in *m/q*. In an ideal trap, this would not change the ion's average (or "equilibrium") position. However, due to construction imperfections, contact potentials and charge patches on the electrodes, symmetry is broken and small shifts in position do occur, both axially and radially, as the trap voltage is changed. Combined with gradients in the magnetic field, this leads to a shift in the CFR [21]. This effect can be quantified by measurements using different charge-states of the same atom.

2.3.4. Image Charge Shifts

The oscillating image charge the ion induces on the electrodes back-acts on the ion, hence perturbing all three mode frequencies. The fractional shift in cyclotron frequency it produces is proportional to the ion's mass and thus is independent of the charge state. Hence, this systematic shift cannot be measured by using different charge states. Instead, it must be calculated [51] or obtained by measurement of the magnetron frequency, or by using molecular ions. The contributions from the end-caps and ring vary as $1/z_0^3$ and as $1/\rho_0^3$, thus this systematic is reduced by using a larger trap.

2.3.5. Shifts Due to Interaction with the Detector

The back-action on the axial motion from the resonant detection circuit produces a shift to the axial frequency, which has a dispersion-like dependence on the detuning between the axial frequency and the detector resonance [21]. Consequently, the shift can be nulled by minimizing this detuning. Alternatively, given sufficient detector sensitivity, as is the case at the FSU trap using a dc-SQUID, the shift and its derivative with respect to detuning can be reduced by detecting the axial motion several detector resonance linewidths away from the detector resonance.

2.3.6. Ion–Ion Interaction Shifts

If two ions are simultaneously trapped in the same trap it is necessary to allow for ion–ion interaction. These shifts have been treated in detail in references [42,52]. In general, for the case of ions separated in the radial plane by a fixed distance ρ_s, the shifts can be separated into "ring-of-charge" effects, due to the modification to the time-averaged potential experienced by the ion whose cyclotron frequency is being measured; and "dynamical" effects, due to the coupling of the motions of the two ions. In the limit of small motional amplitudes of the ion being measured, the modification to the potential produced by the other ion satisfies the conditions of the Invariance Theorem. Thus, provided f_c' and f_z are measured together, the derived f_c is unaffected. However, the ring-of-charge does modify the effective C_4 and higher-order coefficients of the potential, leading to shifts that vary as a_z^2/ρ_s^5, etc. The dynamical effects can be considered as due to the measured ion inducing a small, non-resonant motion on the other ion, which then resonantly back-acts on the measured ion, shifting its mode frequencies. These shifts vary as $1/\rho_s^6$ and are inversely proportional to the detuning between the respective mode frequencies of the ions. Hence, they are a particular problem for an ion pair whose *m/q* values are very close. In principle, ion–ion interaction effects can be made negligible by using a sufficiently large ρ_s. However, in the MIT two-ion technique, increased ρ_s leads to a decoupling of the magnetron motion and to rapidly increasing anharmonic shifts to the CFR [48]. Therefore, the useful range of ρ_s is limited.

2.3.7. Detector Noise and Ion Temperature

In the PnP technique, detector noise leads to uncertainty in the measurement of the phase of the axial motion after the pi-pulse, and hence in the determination of the final cyclotron phase. In addition, because of the initial (thermal) motion of the ion, which combines vectorially with the cyclotron motion impressed by the cyclotron drive pulse, there is variation in the ion's cyclotron phase at the start of

T_{evol}, which also contributes jitter to the measured phase. Both of these "phase noise" effects limit the minimum cyclotron radius that can be used for the PnP measurement. The impressed cyclotron radius, combined with the trap imperfections and special relativity, then results in a systematic shift to the cyclotron frequency.

Further, the thermal cyclotron motion before the cyclotron drive pulse is applied also leads to variation, from PnP to PnP, in the cyclotron radius, and hence in the anharmonic frequency shift during T_{evol}. This creates noise on f_c' itself, and thus limits the maximum useful T_{evol}. Since the lowest-order anharmonic frequency shifts vary as ρ_c^2, it follows that fluctuations in the thermal radius lead to frequency fluctuations approximately proportional to ρ_c [48]. This then limits the maximum useful ρ_c. If cyclotron-to-axial coupling is used to cool the cyclotron motion, the resulting effective temperature is $(f_c'/f_z)T_z$, where T_z is the axial temperature [18]. Combined with the fact that relativistic shifts to the cyclotron frequency scale as $f_c'^2$, the initial cyclotron temperature is a particularly significant source of frequency noise for ions with small m/q.

One strategy for reducing the ion's initial cyclotron temperature (following cyclotron-to-axial coupling) is to first reduce the axial temperature by applying electronic feedback to the axial detector [52,53]. Feedback can also be applied to the ion's axial motion with minimal effect on the detector [54]. A greater reduction in the temperature of the cyclotron mode, that is to a few K, can be achieved with a resonant circuit across the halves of a split ring electrode [22,23].

With a reduced thermal cyclotron radius, a reduced impressed cyclotron radius can then be used without excessive phase noise at the start of T_{evol}. The reduced impressed cyclotron radius then results in reduced anharmonic frequency shifts and fluctuations. However, with the PnP method, any reduction in total cyclotron radius is limited because, after the read-out cyclotron-to-axial coupling pulse, the resulting axial motion must be above the detector noise. Therefore, in this situation, the PnA method is especially advantageous. Starting with a small cyclotron radius, it can produce a large axial motion that produces a signal above the detector noise.

2.3.8. Statistical and Systematic Errors

Detector noise, fluctuations in the initial mode amplitudes combined with trap imperfections and special relativity, and variation in the magnetic field lead to statistical uncertainties in the average CFR that decrease as $N^{-1/2}$, where N is the number of measurements. However, essentially all other effects discussed above, to the extent that they are not common to the two-ions, lead to systematic shifts in the CFR. For example, a systematic difference between the cyclotron radii of the two ions will result in a systematic shift to the CFR. Likewise, any differential equilibrium position shift and any imbalance in the image-charge, ion-detector interaction and ion–ion interaction shifts produce systematic shifts in the CFR. Some of these shifts can be characterized and corrected for, but usually the uncertainties in these corrections are not random and thus lead to systematic error. The range over which parameters such as the cyclotron radius can be varied and still allow good statistical precision is usually limited. This makes it difficult to accurately characterize some systematics.

2.3.9. Mass Doublets and the Use of Molecular Ions: Stored Energy and Polarizability Shifts

When measuring a cyclotron frequency ratio, with the exception of the dynamical part of the ion–ion interaction, all the above systematic errors tend to zero for two ions of the same charge as the difference in m/q between the ions tends to zero. This motivates measurements between ions of the same total atomic number, which we call "mass-doublets". In most cases, to achieve this requires that one or both of the ions in the pair is a molecular ion. This leads to the complication that the molecular binding energy of the ions must be known [12], either by measurement or calculation.

If the ion is a homonuclear diatomic molecule, it can be in an excited vibrational state with a radiative lifetime of many days. For H_2^+ the corresponding mass shifts are at the ~5×10^{-10} level [38,55], while for ions such as N_2^+ and O_2^+ they are ~10^{-11}. For higher precision, the metastable

ro-vibrational levels must be identified. This has been done for the vibrational levels of H_2^+ [55] and, partially, for highly excited rotational levels of H_3^+ [56].

In the case of a non-homonuclear molecular ion, there can be a large body-frame electric dipole moment. This produces large rotational-state and sub-state dependent electric polarizability, particularly in the ground and the first-excited rotational states [52,57]. This polarizability leads to a shift in f_c given approximately by [58]

$$\Delta f_c/f_c = -9.93 \times 10^{-15} \, \alpha B^2/M, \tag{3}$$

where, here, α is the polarizability in atomic units, M is the mass of the ion in u, and B is the magnetic field in tesla. If the dipole moments are known from molecular structure calculations, the state-dependent polarizabilities can be calculated in the Born-Oppenheimer approximation [58]. Hence, if the rotational state of the ion can be identified, for example, if it is known that the ion is in the ground rotational level, or if a spectrum of "polarizability shifts" can be observed in the CFR data, corrections can be applied [15,57–61]. Allowance must also be made for black-body radiation induced transitions between rotational levels.

3. Atomic Masses of Hydrogen and Helium Isotopes

The atomic masses of the proton, deuteron, triton, helion, and alpha particle (the nuclei of the atoms H, D, T, ^{3}He, and ^{4}He) are considered to be fundamental constants and are included in the recent CODATA tabulations, (e.g., references [2,3]). The ratio of the electron mass to the masses of the proton and deuteron are needed for the analysis of precision laser spectroscopy of hydrogen and deuterium used to obtain the Rydberg constant. The fractional uncertainty of *1s-2s* two-photon spectroscopy in hydrogen is currently 4×10^{-15} [62]. In principle, to extract the Rydberg constant to this precision requires that m_e/m_p be known to $<8 \times 10^{-12}$. However, at present, uncertainty in the proton charge radius dominates and the CODATA14 value for R_∞ has an uncertainty of 5.9×10^{-12} [2], relaxing the precision required for m_e/m_p by three orders-of-magnitude. However, this situation could change if the so-called "proton radius puzzle" is resolved in such a way that confidence can be placed in the determination of the proton charge radius from the precise measurements of the Lamb-shift of muonic hydrogen [63].

An interesting development is the proposal to obtain m_e/m_p and m_e/m_d from precision spectroscopy of ro-vibrational transitions in H_2^+ and HD^+, in combination with precise theoretical calculations including relativistic and QED corrections, (e.g., references [64–66]). With further developments in the theory, this may lead to sub-10^{-11} values for the mass ratios, but also, by using combinations of transitions, to competitive values for R_∞ and the charge radii of the proton and deuteron [67]. Additionally, with a sufficiently developed theory, measurements of the Zeeman-hyperfine structure and cyclotron frequency of H_2^+ can be used to obtain the electron-to-proton mass ratio, and the magnetic moment of the proton [68]. All these projects motivate further measurements of $M[p]$ and $M[d]$ by Penning trap techniques.

The mass difference between tritium and helium-3 is closely related to the Q-value (available energy) of the beta-decay of tritium. This is an important parameter for testing systematics in precision measurements of the beta-electron energy spectrum of tritium near its endpoint, which set upper limits on the mass of the electron neutrino [69,70]. For this reason, the masses of T^+ and ^{3}He$^+$ are often measured together so that some systematics cancel in their difference. A precision atomic mass of ^{3}He will also be needed to convert measurements of the ratio of the nuclear spin-flip frequency of ^{3}He^{2+} to its cyclotron frequency into a value for the nuclear g-factor of the helion [71]. The same will be true for the deuteron. A precise mass for ^{4}He is needed for measurements of the electronic g-factor of ^{4}He$^+$, which can be used to obtain the electron mass and, possibly in the future, the fine-structure constant [72] (but also see Section 5).

In what follows we show those mass measurements that have sufficient precision to influence the results of least-squares adjustments such as the AME or CODATA, sometimes with additional, less precise values for context. In general, we show the atomic masses as published in the original papers. In some cases, the results are based on CFRs relative ^{12}C, while others use atoms other than ^{12}C as references. In the latter case, we attempt to show the effects of significant updates in the masses of the references. However, this is essentially illustrative and is not a substitute for a least-squares adjustment based on the relevant CFRs (or their equivalent mass difference equations) as is done by the AME.

3.1. Proton

Atomic mass results for the proton and the least-squares value from the AME2016 are shown in Table 1. The first of these, and the first with an uncertainty of $<10^{-9}$ was by the MIT group. Here the CFR of ^{12}CH$_4^+$ versus ^{12}C$^+$ was measured using a two-cyclotron-pulse (Ramsey) variant of the PnP technique [73]. By mapping the final cyclotron phase onto cyclotron amplitude, both ions' cyclotron frequencies could be measured at the same trap voltage, thereby eliminating the equilibrium position shift error discussed in Section 2.3.3. The second is a result from the UW group [74], who compared a proton against C^{4+}, using an exceptionally stable 6 T solenoid magnet and the swept cyclotron drive, axial-frequency-shift technique. Here, auxiliary measurements of C^{4+} against C^{5+} provided some check against the equilibrium-position and other systematic errors, and the error budget had contributions from anharmonicity (95 ppt), residual magnetic field drifts (70 ppt), statistics (50 ppt), and image charge shifts (40 ppt). Also notable was the use of the high axial frequency of 3.5 MHz, which reduces some anharmonic shifts and leads to a lower cyclotron temperature after cyclotron-to-axial coupling.

Table 1. Atomic mass values for the proton.

Source	Atomic Mass (u)
MIT 1993 [73]	1.007 276 466 4(7)
UW 1999 [74]	1.007 276 466 89(14)
SMILETRAP 2002 [75]	1.007 276 466 86(35)
SMILETRAP 2008 [38]	1.007 276 466 95(18)
MPIK* 2017 [46]	1.007 276 466 583(33)
AME2016 [5]	1.007 276 466 929(90)

The third is a measurement by the SMILETRAP group [75] using their time-of-flight detection technique to measure the CFRs of H$_2^+$ relative to several charge states of ^{12}C, but also of ^{28}Si, ^{14}N, ^{20}Ne, and ^{40}Ar, making use of measurements of these atoms at the 10^{-10} level by MIT [41]. The fourth is another measurement by the SMILETRAP group [38], but making use of the Ramsey variant of their TOF method, and measuring H$_2^+$ against D$^+$ as a reference. To obtain the proton mass they assumed an average vibrational excitation energy of 0.74(7) eV for H$_2^+$ and a value for $M[d]$ = 2.013 553 212 73(4) u, as provided in a private communication from the UW group. (Using the updated mass for D from the UW group, see Table 2, increases this value for $M[p]$ by only 7.5 ppt.)

The fifth is a recent and advanced measurement with a fractional uncertainty of 3.3×10^{-11} by the MPIK-Heidelberg/Mainz/GSI/RIKEN collaboration, using a purpose built, cylindrical, multi-Penning trap system for light ions, now called LIONTRAP [46]. Here the cyclotron frequencies of a proton and a ^{12}C^{6+} ion were measured, mainly using the PnA technique, but with checks by the double-dip technique, and by alternately shuttling the two ions into a "measurement" trap from reservoir traps on either side. A quadratic potential could be produced over a relatively large volume in the measurement trap by incorporating two sets of compensation electrodes. The equilibrium position shift was avoided by using two axial detectors, one resonant at about 525 kHz for ^{12}C^{6+} and the other at 740 kHz for the proton, so the measurements of f_c', f_z and f_m could be carried out at the same trap voltage. By using the PnA technique, and reducing the effective temperature of the axial motion using feedback cooling, a proton cyclotron radius as small as 9 μm could be used. Hence relativistic shifts to the

cyclotron frequency were reduced and the estimated systematic uncertainty due to special relativity on the CFR was 7 ppt. Overall, the largest uncertainty was from the finite axial motion, mainly of the proton, combined with the quadratic magnetic field inhomogeneity B_2, which gave 27 ppt. The model of systematics was also checked by comparing $^{12}C^{3+}$ to $^{12}C^{6+}$ and the proton to $^{16}O^{8+}$. As Table 1 shows, the MPIK* result is in a 2 standard-deviation disagreement with both the UW and the second SMILETRAP result and indicates a lighter proton. However, the SMILETRAP–MPIK* disagreement might also indicate that the deuteron is lighter than as measured by the UW group, see next section.

New measurements of H_2^+/D^+ using two simultaneously trapped ions are currently in progress at FSU [55]. Unlike the SMILETRAP TOF technique in which the measurements were carried out on H_2^+ within a few seconds after leaving the ion source, the H_2^+ is trapped for many days and can be Stark-quenched to the vibrational ground state [76]. This removes the uncertainty due to the vibrational distribution of the H_2^+ that had to be assumed in [38].

Table 2. Atomic mass values for the deuteron.

Source	Atomic Mass (u)
MIT 1993 [73]	2.013 553 212 6(6)
UW 2015 [77]	2.013 553 212 745(40)
SMILETRAP 2008 [38,46] [1]	2.013 553 212 00(36)
AME2016 [5]	2.013 553 212 80(12)

[1] Using the MPIK* result of Table 1 for $M[p]$ [46] as the reference.

3.2. Deuteron and Neutron

3.2.1. Deuteron

Table 2 shows the results for the mass of the deuteron. Similar to the proton mass, the MIT measurement [73] determined the ratio of $^{12}CD^{4+}$ to $^{12}C+$ using the Ramsey technique at constant trap voltage. The more precise UW result, with fractional uncertainty of 2×10^{-11} [77], is from the final analysis of data taken a decade earlier using similar techniques as for their proton measurement. A significant advantage compared to the proton is that D^+ was measured against $^{12}C^{6+}$, which has the same nominal m/q. The analysis used data from 10 runs, each taking about a month including tests for systematics. The error budget had comparable contributions from uncertainty in the axial amplitude combined with trap imperfections, the fits to the axial-frequency error signal versus drive frequency, the phase of the phase-locked-loop that is used to detect the shifts in axial frequency, and from image charge. The image charge shift was estimated at 245 ppt, but its uncertainty was estimated to be 10 ppt in the CFR. Only the uncertainty in the image charge was treated as a systematic error (that is, not reduced in the average). In the third row, we show the result of combining the D^+/H_2^+ ratio as measured by SMILETRAP (the fourth result for the proton in Table 1) [38] with the MPIK* 2017 proton mass [46], to give a mass for the deuteron. As can be seen, this results in a deuteron mass 0.75(36) nu smaller than the UW value.

3.2.2. Neutron

The mass of the neutron is obtained from the wavelength of the 2.2 MeV gamma ray emitted in the (non-resonant) neutron capture reaction $n + p \rightarrow d + \gamma$, combined with the masses of p and d. Using the Bragg-crystal diffraction wavelength result obtained by a National Institute of Standards and Technology (NIST) and Institut Laue-Langevin (ILL) collaboration [78], subsequently corrected following a re-evaluation of the crystal lattice spacing, and then for the conversion between wavelength and u, Huang et al. obtained an equivalent mass difference $p + n - d = 2\,388\,169.95(42)$ nu [4]. The result of combining this deuteron binding energy with the UW mass for d [77] and the 2017 MPIK* mass for p [46] is compared with the AME2016 result in Table 3. As can be seen, the reduced proton mass

results in a neutron mass increased by ~0.3 nu, but the change is less than the uncertainty due to the wavelength measurement.

Table 3. Atomic mass values for the neutron.

Source	Atomic Mass (u)
NIST/ILL + UW + MPIK* (see text)	1.008 664 916 11(42)
AME2016 [5]	1.008 664 915 80(50)

3.3. Tritium and Helium-3

In Table 4 we show values for the atomic masses of tritium and helium-3 as given in the respective publications. (The atomic mass of the triton can be obtained from the mass of the tritium atom by subtracting $5.485\,653\,052\,57(16) \times 10^{-4}$ u, and that of the helion from helium-3 by subtracting $1.097\,075\,006\,640(32) \times 10^{-3}$ u).

Table 4. Atomic masses of tritium and helium-3 as originally reported.

Source	Tritium (u)	Helium-3 (u)
SMILETRAP 2006 [79]	3.016 049 278 7(25)	3.016 029 321 7(26)
FSU 2015 [32]	3.016 049 281 78(19)	3.016 029 322 43(19)
UW 2015 [77]		3.016 029 321 675(43)

The first row gives the results of the SMILETRAP group from CFRs of ^{3}He$^+$, ^{3}He^{2+}, and T$^+$ measured against H$_2{}^+$ using the TOF technique [79]. Here the H$_2{}^+$ ions, allowing for vibrational excitation energy, were assumed to have an average mass of 2.015 101 497 03(27) u as given in reference [34].

The second row gives the results from the FSU group of CFR measurements of ^{3}He$^+$ and T$^+$ against HD$^+$ [32]. For both HD$^+$/^{3}He$^+$ and HD$^+$/T$^+$, both ions were simultaneously trapped, but alternated between large and small cyclotron radii, the cyclotron frequency measurement being carried out on the inner ion using the PnP technique. The results were obtained from 34 measurements of HD$^+$/^{3}He$^+$ and 31 of HD$^+$/T$^+$, each lasting 8 to 10 h, resulting in a statistical uncertainty of 17 ppt for each ratio. The HD$^+$ mass was calculated using the CODATA2010 masses for the proton and deuteron [80], and the very precise non-relativistic HD$^+$ binding energy given in reference [81]. In addition, the CFR was corrected by 9.4×10^{-11} to allow for the polarizability of the HD$^+$ molecular ion [58,81], with the assumption it remains in its ground rotational and vibrational level. Because the two CFRs differ from 1 by only 0.2%, most systematic errors were estimated to be negligible. However, a surprisingly large 3% imbalance was observed in the cyclotron radii, which was assumed to be due to a strong frequency dependence in the cyclotron drive transfer function. This led to a common systematic uncertainty of 45 ppt being assigned to both ratios.

The third row gives the result of a measurement of ^{3}He^{2+} against ^{12}C^{6+} and ^{12}C^{5+} by the UW group, which was reported in the same publication as the measurements on D$^+$ [77]. The data consisted of 4 runs of ^{3}He^{2+} versus ^{12}C^{6+}, of which two involved an extra contaminant ^{12}C^{6+} ion, and 3 of ^{3}He^{2+} versus ^{12}C^{5+}, all of which are non-doublets. The error budget contains similar contributions as for the measurements on the deuteron, with a common systematic uncertainty of 9 ppt on an estimated image charge shift of 220 ppt.

Since the SMILETRAP publication [79] and the FSU publication [32], improved values for the mass of the proton and deuteron have been published. In the case of the SMILETRAP result, it is possible to bypass uncertainty due to the mass of H$_2{}^+$, both due to the proton mass and the average excitation energy, by using their H$_2{}^+$/D$^+$ measurement in reference [38] to relate T$^+$ and ^{3}He$^+$ to D$^+$. Hence, the latest UW result for D$^+$ [77] can be used as the reference. Making these adjustments, the corrected T and ^{3}He masses are shown in the first row of Table 5. Further, and significantly, there has

been a re-measurement of $HD^+/^3He^+$ by the FSU group using a substantially rebuilt apparatus, with confirmation by taking the ratio of the two CFRs $^3He^+/H_3^+$ and HD^+/H_3^+ [61]. The result is in good agreement with the 2015 result [32], but a factor of two more precise. Because systematic errors in both the 2017 and 2015 measurements are likely to be common, the new $HD^+/^3He^+$ ratio supersedes the previous one. However, the 2015 result can still be used to relate the mass of T to the new mass of ^3He. Hence, using the new $HD^+/^3He^+$ ratio from reference [61], the $T^+/^3He^+$ ratio from reference [32], the deuteron mass from reference [77], and the proton mass from reference [46], we obtain the results given in the third row of Table 5. For ease of comparison, in the second row, we have copied the UW result for ^3He [77] from Table 4.

Table 5. Updated atomic masses of tritium and helium-3 (see text).

Source	Tritium (u)	Helium-3 (u)
SMILETRAP [38,79]	3.016 049 278 9(25)	3.016 029 321 9(26)
UW 2015 [77]		3.016 029 321 675(43)
FSU 2017 [32,61]	3.016 049 281 48(11)	3.016 029 322 14(9)
AME 2016 [5]	3.016 049 281 99(23)	3.016 029 322 65(22)

As can be seen from Tables 4 and 5, the FSU mass of ^3He, while being consistent with the lower precision SMILETRAP result, is significantly higher than the UW result. And, although allowing for the updated proton mass has reduced the discrepancy from 0.76(0.19) nu to 0.47(0.1) nu, because of the increased precision, the discrepancy is still 4 standard deviations. Additional evidence for a heavier ^3He than that reported in reference [77] is provided by referring the mass of ^3He to that of the proton only, using the H_3^+ ion [56]. In this case, because the H_3^+ may have significant stored rotational energy, only an upper limit to $3M[p] - M[h]$ can be given. However, if this is done, using the proton mass of reference [46] as a reference, the result is $M[^3He] > 3.016 029 322 00(14)$ u, which is inconsistent with the UW result [77] by (more than) $3.3(1.5) \times 10^{-10}$ u. We note that the discrepancy would be nearly removed if the FSU CFRs involving HD^+ were not corrected for the polarizability of the HD^+ ion, which would be appropriate if the HD^+ did not spend the majority of time in its ground-state during the measurement. However, this is inconsistent with the fact that the first excited rotational level of HD^+, which has a mean lifetime of 150 s, has an excitation energy corresponding to 63 K, while the trap electrodes are at 4.2 K. The AME2016 results are 0.5 nu higher than the updated FSU results because they were based on the 2015 FSU results and lacked the updated proton mass of reference [46].

In Table 6, we show the mass differences between atoms of tritium and helium-3 expressed in eV. It is important to note that several important systematic errors cancel for this difference, so the uncertainty is smaller than that obtained from the uncertainties in the individual masses. The first row gives this difference as measured by the UW group [82], using an earlier apparatus than that used for the other measurements discussed in this review. (The absolute masses for ^3He and T reported in reference [82] were found to be in error by several standard deviations by the SMILETRAP group, but the relevant systematic error at least partly cancels for the T-^3He difference.) The second row gives the result from the 2006 SMILETRAP measurements [79], and the third gives the more than a factor of 10 more precise result from the FSU group [32]. This result is higher than the SMILETRAP result by 2.2(1.2) eV and its uncertainty is slightly less than that of the absolute calibration of the retarding voltage in KATRIN, which is now 90 meV [70].

Table 6. Mass difference between atoms of tritium and helium-3, expressed in eV.

Source	$M[T] - M[^3He]$ eV
UW 1993 [82]	18 590.1(1.7)
SMILETRAP 2006 [79]	18 589.8(1.2)
FSU 2015 [32]	18 592.01(0.07)

3.4. Helium-4

The three most recent determinations of the atomic mass of ^{4}He are shown in Table 7. (The mass of the alpha-particle can be obtained by subtracting 1.097 075 002 640(32) $\times$ 10^{-3} u). The first two, from Mainz and SMILETRAP, respectively, used the TOF detection technique with H$_2^+$ and D$_2^+$ as references. The third is a much more precise (1.6 $\times$ 10^{-11} fractional precision) measurement of the CFR of ^{4}He^{2+} against ^{12}C^{6+} (and so a mass doublet) by the UW group [83], using their swept-cyclotron-drive axial-frequency-shift detection technique. The estimated systematic uncertainty was 9 ppt from image charges and 13.4 ppt from all other sources. The two TOF measurements disagree with each other by 7.9(2.6) nu, and the more precise TOF measurement disagrees with the cryogenic Penning trap result by 2.7(1.3) nu.

Table 7. Atomic mass values for ^{4}He.

Source	Atomic Mass (u)
Mainz 2001 [84]	4.002 603 248 9(22)
SMILETRAP 2001 [85]	4.002 603 256 8(13)
UW 2004 [83]	4.002 603 254 153(64)
AME 2016 [5]	4.002 603 254 13(6)

4. Atomic Masses of ^{87}Rb and ^{133}Cs for the Atom-Recoil Method for the Fine-Structure Constant

The fine-structure constant α ($=e^2/(2\varepsilon_0 hc)$) is the dimensionless constant that characterizes the strength of the electromagnetic interaction. In the new-SI, with e and h fixed, its measurement determines the permittivity of free space ε_0, which is no longer fixed. Currently, the two most precise methods for obtaining α are based on measurements of the anomaly of the g-factor of the free electron, i.e., its difference from the Dirac value of 2; and, the recoil velocity of atoms having absorbed a photon of light. In the former case, α is obtained by combining a complex Quantum Electrodynamics (QED) calculation of $g_e - 2$ in terms of α up to 10-th order [86], with a precise measurement using a single electron in a cryogenic Penning trap [87].

Regarding the second method, the atom-recoil measurements yield values for h/m_{atom}, where m_{atom} is the absolute mass of the particular atom. The most precise measurements have been performed with ^{87}Rb [88] and ^{133}Cs [89] using atom-interferometric techniques. These resulted in values for h/m_{atom} with fractional uncertainties of 1.2 $\times$ 10^{-9} and 4 $\times$ 10^{-10}, respectively. From these measurements, α is obtained using the relation (c.f. Equation (1) above)

$$\alpha^2 = (2R_\infty/c)(h/m_{atom})\,(M[atom]/M[e]) \tag{4}$$

Hence, to obtain α, in addition to the Rydberg constant, measured at 6 $\times$ 10^{-12} relative precision [2], and the atomic mass of the electron, measured to 2.9 $\times$ 10^{-11} (see the next section), it is also necessary to know the atomic mass of the particular atom.

Table 8 shows the three most precise values for the fine-structure constant as obtained from $g_e - 2$, ^{87}Rb, and ^{133}Cs, respectively. The ^{87}Rb result [88] has been updated using the latest value for $M[e]$ (the fourth entry in Table 10), and the AME2016 [2] value for $M[^{87}$Rb]. As can be seen, while the two atom-recoil results agree, there is a 2.4 sigma tension between the $g_e - 2$ result and the ^{133}Cs result. As noted in reference [89], this level of (dis)-agreement provides information on physics beyond the Standard model and thus strongly motivates further related measurements.

The most recent measurements of the atomic masses of ^{87}Rb and ^{133}Cs are shown in Table 9. The SMILETRAP result [90] made use of high-charge states of ^{133}Cs (36+ to 42+) measured against ^{12}C^{4+} and H$_2^+$ using their TOF technique. The uncertainty in the binding energy corrections for these highly-charged ions was estimated to be ~10 eV, corresponding to ~10^{-10} of the Cs mass. The result was presented as a mass ratio with respect to the proton and has been converted here into $M[^{133}$Cs] using the new proton mass of reference [46]. Both the MIT [91] and the FSU results [31] used the

PnP method in the same Penning trap, but with several differences of technique. In particular, MIT, using the make-and-remake technique mentioned in Section 2.3.1, measured the CFRs $^{87}Rb^{2+}/C_3H_7^+$, $^{87}Rb^{2+}/C_3H_8^+$, $^{133}Cs^{2+}/C_5H_6^+$, and $^{133}Cs^{3+}/CO_2^+$. For reasons that were not understood, run-to-run scatter exceeded the estimated statistical error based on the data fit for each run. One might also be concerned about polarizability shifts for the hydrocarbon molecular reference ions. However, when averaged over all rotational sub-states, the only remaining contribution to polarizability from the body-frame dipole moment (i.e., "orientation polarizability") is from the ground-state [58], which has a small probability of occupation for these ions.

Table 8. Recent results for the inverse fine-structure constant.

Source	$1/\alpha$
$g_e - 2$ 2018 [86,87]	137.035 999 149(33)
^{87}Rb 2011 [88] [1]	137.035 998 995(85)
^{133}Cs 2018 [89]	137.035 999 046(27)
CODATA 2014 [2]	137.035 999 139(31)

[1] With updated value for $M[e]$.

Table 9. Atomic mass values for ^{87}Rb and ^{133}Cs.

Source	Rubidium-87	Cesium-133
SMILETRAP 1999 [90]		132.905 451 88(28)
MIT 1999 [91]	86.909 180 520(15)	132.905 451 931(27)
FSU 2010 [31]	86.909 180 535(10)	132.905 451 963(13)
AME 2016 [5]	86.909 180 531(6)	132.905 451 961(9)

In the case of the FSU results [30], the masses of ^{87}Rb and ^{133}Cs were related, robustly, to those of ^{86}Kr and $^{129,132}Xe$ by measuring $^{87}Rb^{2+}/^{86}Kr^{2+}$, $^{133}Cs^{3+}/^{132}Xe^{3+}$ and $^{133}Cs^{3+}/^{129}Xe^{3+}$ using the technique of two simultaneously trapped ions, and alternating between large and small cyclotron orbits. The masses of ^{86}Kr and $^{129,132}Xe$ had previously been obtained from extensive measurements using the make-and-remake technique of $^{84,86}Kr$ and $^{129,132}Xe$, in several charge states, against $^{12}C^{16}O_2^+$, $^{12}C_2H_2^+$ and $^{14}N_2^+$ [30]. Here, the mass of ^{16}O was taken from the AME2003 value [92], which was mostly based on the UW result [40] (see Table 11), while that of ^{14}N was also referenced to ^{16}O, using the ultra-precise MIT simultaneous measurement result for $^{14}N_2^+/CO^+$ [57]. The FSU and MIT results are in good agreement, and the fractional uncertainties of the FSU results, 1.2×10^{-10} and 1.0×10^{-10}, are a modest improvement for ^{87}Rb and a factor of 2 improvement for ^{133}Cs, respectively. We note that if one were to explain the above 2.4 sigma discrepancy between the $g_e - 2$ and ^{133}Cs values for α as due to an error in the ^{133}Cs mass, this error would need to be ~1.5×10^{-9}. Atom-interferometric techniques for measuring h/m_{atom} are being developed for various isotopes of other atoms including Li [93], Sr [94], and Yb [95], motivating measurements of the relevant atomic masses [31,96].

5. Atomic Mass of the Electron from the *g*-Factor of Hydrogen-Like Ions and Future Possibilities for Measuring the Fine-Structure Constant

5.1. Atomic Mass of the Electron

The atomic mass of the electron has been obtained by the UW group, who compared the cyclotron frequencies of small clouds (5 to 13) of electrons and a $^{12}C^{6+}$ ion in a Penning trap [97], see the first row of Table 10.

Table 10. Atomic mass values for the electron.

Source	Atomic Mass (u)
UW 1995 [97]	0.000 548 579 911 1(12)
Mainz 2002 ^{12}C^{5+} [98]	0.000 548 579 909 2(4)
Mainz 2004 ^{16}O^{7+} [99]	0.000 548 579 909 6(4)
MPIK* 2014 ^{12}C^{5+} [100,101]	0.000 548 579 909 065(16)
CODATA 2014 [2]	0.000 548 579 909 070(16)

Here, the precision was limited by the line shape in the swept-cyclotron drive method and by the large relativistic shift to the cyclotron frequency of the electron due to its small mass. Using quantum-jump techniques with a single electron in a trap cooled by a dilution refrigerator, as applied to the latest measurements of $g_e - 2$ [87], a greatly improved measurement of the CFR of an electron relative to a negative ion such as H$^-$ or C$^-$ should be possible.

However, as initially developed at Mainz, the uncertainty due to SR has instead been overcome by extracting the electron mass from precise measurements of the *g*-factor of the electron bound in hydrogen-like ions such as ^{12}C^{5+} and ^{16}O^{7+} [98–100] combined with bound-state QED theory, (e.g., references [101,102]). In the measurements, which have been recently reviewed in this journal [103], the microwave frequency that flips the ion's electron spin in a magnetic field is determined at the same time as the ion's cyclotron frequency. Since the electron spin-flip frequency f_{sf} can be written in terms of the electronic *g*-factor of the hydrogen-like ion g_{ion} as $f_{sf} = (g_{ion}\mu_B/h)B$, where $\mu_B = eh/(4\pi m_e)$ is the Bohr magneton, and the cyclotron frequency is given by $f_c = (1/2\pi)(q_{ion}/m_{ion})B$, it follows that

$$m_e/m_{ion} = (g_{ion}/2)(e/q_{ion})(f_c/f_{sf}). \tag{5}$$

Hence, if g_{ion} can be accurately calculated, as is the case for lower-*Z* hydrogen-like ions [101], m_e/m_{ion} can be determined from a measurement of f_{sf}/f_c. If the ion is ^{12}C^{5+}, after allowance for ionization energies, this gives the atomic mass of the electron. Otherwise, the atomic mass of the atom must be measured separately. Results of early experiments at Mainz on C^{5+} and O^{7+} are shown in the second and third rows of Table 10. These values change slightly if the updated theory for the g-factor is used [101]. Using refinements such as the PnA method to measure the cyclotron frequency, a second and considerably more precise measurement of the *g*-factor of C^{5+} has been carried out by Sturm et al. [100]. Here, the largest contribution to uncertainty was 25 ppt from statistics, and the dominant systematic error was the 14 ppt uncertainty in the image charge correction of 282 ppt. In future work, this could be reduced by using a larger Penning trap. When combined with the updated theory for the *g*-factor [101], this gives the result for the electron mass at 3×10^{-11} relative precision shown in the last row of Table 10. This result is a fraction $3.6(2.0) \times 10^{-9}$ lower than the UW result based on the CFR measurement.

5.2. Atomic Masses for g-Factor Measurements for the Electron Mass

Equation (5) applied to ions other than ^{12}C^{5+} requires precise measurements of the atomic masses of the ions. In addition to the measurement on ^{16}O^{7+} for *M*[*e*] [99], a measurement of f_{sf}/f_c on ^{28}Si^{13+} [104] with a fractional uncertainty of 5×10^{-11} was carried out to provide information on the difficult to calculate, higher-order terms in in the QED theory of the *g*-factor that scale with high powers of Z. In Table 11, we show some of the recent measurements of the atomic masses of ^{16}O and ^{28}Si. (^{16}O is also important as a reference for FSU and MIT measurements of ^{87}Rb and ^{133}Cs for the fine-structure constant, see Section 4.)

Table 11. Atomic mass values for ^{16}O and ^{28}Si.

Source	Oxygen-16 (u)	Silicon-28 (u)
MIT 1995 [41]	15.994 914 619 5(21)	27.976 926 532 4(20)
UW [40]	15.994 914 619 46(16)	
FSU [15]		27.976 926 535 0(6)
AME2016 [5]	15.994 914 619 60(17)	27.976 926 535 0(5)

As can be seen, the MIT and UW results for ^{16}O are in good agreement and both are adequately precise for the ^{16}O^{7+} g-factor measurement [99]. The MIT result [41] was obtained from a set of interlocking ratios using the make-and-remake technique, of which ^{12}CH$_4^+$/^{16}O$^+$, ^{12}C$_2$H$_4^+$/^{12}C^{16}O$^+$, and C$_3$H$_8^+$/CO$_2^+$ had the most influence [21]. The UW result, at 1.0×10^{-11} fractional precision, involved comparisons of ^{16}O^{6+} against ^{12}C^{4+} and ^{12}C^{6+} using the swept cyclotron frequency scheme. For ^{28}Si, the FSU and MIT results, both using the PnP technique, are in reasonable agreement. The MIT result was based on the doublet CFRs ^{12}C$_2$D$_2$H$_2^+$/^{28}SiH$_2^+$ and ^{15}N$_2^+$/^{28}SiH$_2^+$ (with ^{12}CH$_3^+$/^{15}N$^+$ and ^{12}C$_2$D$_2$H$_2^+$/^{15}N$_2^+$). The more precise (2.2×10^{-11} fractional precision) FSU measurement made use of simultaneously trapped ions, alternating between large and small cyclotron radii, and obtained $M[^{28}$Si] from the doublet CFRs ^{12}C$_2$H$_4^+$/^{28}Si$^+$, ^{13}C$_2^+$H$_2^+$/^{28}Si$^+$, ^{28}SiH$_3^+$/^{31}P$^+$, and ^{16}O$_2^+$/^{31}PH$^+$ [15]. Hence, the FSU ^{28}Si result has sensitivity to the UW result for ^{16}O, both directly, and also through the ultra-precise MIT results for ^{13}C$_2$H$_2^+$/^{14}N$_2^+$ [43] and ^{12}C^{16}O$^+$/^{14}N$_2^+$ [57], which link ^{13}C to ^{16}O.

We also note that the theory for the g-factor of ^{4}He$^+$, due to its low Z, has smaller theoretical uncertainties and also smaller uncertainties due to nuclear size than ^{12}C^{5+}. This motivates measurements of f_{sf}/f_c and additional measurements of $M[^4$He].

5.3. Obtaining the Fine-Structure Constant from g-Factors of Highly-Charged Ions

It has been proposed by several authors, (e.g., see reference [105]), that since the theoretical expression for g_{ion} in Equation (5) is a function of α and $Z\alpha$, measurements of the g-factors of hydrogen-like ions of different Z can be combined to provide values for α as well as $M[e]$, provided the theoretical difficulties can be overcome. Fortuitously, due to cancellations in the theory, the g-factor for ^{12}C^{5+} is only weakly dependent on α, and the current uncertainty in α contributes to the theoretical uncertainty in the g-factor at only the $\sim 10^{-13}$ level, see Figure 5 of reference [72] (but note that the uncertainty in the current value of α is a factor of 14 times smaller than that used in reference [72]). At a higher Z, there is a much greater sensitivity to α, but also to uncertainty in the nuclear charge distribution. One strategy to overcome this is to make measurements on additional charge-states, such as lithium-like and boron-like, which enables much of the uncertainty due to nuclear size to be cancelled. Here too, precise atomic masses will be required. It was also noted in reference [72] that the nuclear size correction for the g-factor of ^{4}He$^+$, uniquely, results in a smaller uncertainty in g, about 10^{-13}, than that due to α, which is currently $\sim 5 \times 10^{-13}$. So, at least in principle, a measurement of f_{sf}/f_c on ^{4}He$^+$ at the (extreme) 10^{-13} level could produce a competitive value for α, provided there is an equally precise value for $M[e]/M[^4$He].

6. Atomic Mass of Si for the XRCD Technique and of He and Ar for the Boltzmann Constant

The X-ray-crystal-density (XRCD) method mentioned in the introduction, that formerly measured N_A and which can now be used to realize the kg, requires the atomic mass of ^{28}Si, and also of ^{29,30}Si if an isotopically impure sample is used. Acoustic gas thermometry (AGT) [2], which formerly measured the Boltzmann constant k_B and which now realizes the kelvin, generally uses either ^{4}He or ^{40}Ar, which may have fractions of ^{36,38}Ar, requiring atomic masses for these too. However, since all these masses have uncertainties in the AME 2016 less than 10^{-9}, except ^{38}Ar which has 5.5×10^{-9}, and the precision of the XRCD technique is at the 10^{-8} level, and of AGT is at the 10^{-6} level, the uncertainties in these atomic masses are not an issue.

7. Conclusions and Outlook

In general, thanks to the high precision of single-ion Penning trap techniques, atomic mass measurements do not currently limit the determination of other fundamental constants. However, one can foresee instances where improvement will be needed for this to remain true. For light ions, if it becomes clear that muonic lamb-shift measurements are a valid method for measuring the proton and deuteron charge radii, atomic masses of the proton and deuteron relative to the electron at the sub-10^{-11} level will be needed to match the precision of current 1s-2s hydrogen spectroscopy. They will also be necessary for interpreting the results of precision ro-vibrational laser spectroscopy of H_2^+ and HD^+ [65]. Regarding the mass of ^{3}He, despite the 4-sigma disagreement, which should be resolved, the precision measurements of FSU [32,61] and UW [77] have reduced its uncertainty to the 1×10^{-10} level, which should be adequate for an initial determination of the nuclear g-factor of ^{3}He [71]. Because of the importance of the T-^{3}He mass difference for neutrino mass, more measurements of this difference are desirable. And, if a measurement of the g-factor of ^{4}He were to be used to obtain a value for the electron mass at the sub-10^{-11} level of precision, a correspondingly precise value for M[^{4}He] will be required. And of course, because of the possibility of unknown or underestimated systematic errors, it is always metrologically useful for the most precise measurements to be tested by another measurement of comparable precision.

Likewise, although the atomic masses of ^{87}Rb and ^{133}Cs are not yet a limit for obtaining the fine-structure constant using the atom-recoil method, this could change in the future. It would also be preferable for their masses to be referenced more directly to that of ^{12}C than is the case at present. In fact, to reduce the atomic mass uncertainty of a heavy atom like ^{133}Cs to the 10^{-11} level is challenging since forming an m/q doublet would involve a large hydro-carbon molecule—with uncertain binding energy and polarizability corrections—or else a highly-charged Cs ion, also with uncertainty in the ionization energies. It is also worth noting that for obtaining α using Equation (4), it is not necessary for ^{12}C to be used as an intermediary. For example, an electronic g-factor measurement on ^{4}He$^+$, say, could be combined with a measurement of the mass ratio of ^{4}He and ^{133}Cs. And, as has been noted, high precision atom-recoil measurements are being developed in other systems such as ^{7}Li and isotopes of Yb. Therefore, more precise mass measurements may become motivated for these atoms.

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