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Back to the line of stability

Chasing mass accuracies below 10^{-9} using a Penning trap and highly charged ions

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Abstract. The Stockholm Penning trap has been connected to an electron beam ion source named CRYSIS located at the Manne Siegbahn Laboratory. It is combined to a high-resolution isotope separator that can provide singly charged mass selected ions of practically any element. These ions are fed into CRYSIS where it is subject to a very intense electron beam with an energy of 10–20 keV. The mass of the neutral atom is obtained by adding the masses of the missing electrons and subtracting their binding energies. The results on some 16 mass determinations made at an uncertainty from 3 to 0.3 ppb are commented on. In these measurements the mass number varies from 1 to 204 and the ion charges from 1+ to 52+. New mass values are obtained for the ^{3}H, ^{3}He and ^{4}He masses. We have confirmed the Manitoba measurements of the Q-value of the double beta-decay of ^{76}Ge and their mass measurements of the masses of ^{198}Hg and ^{204}Hg reaching the higher accuracy that traps offer. At present the mass uncertainty limit is about 3×10^{-10} which is demonstrated by comparing our results with the most accurately measured masses by other groups.

PACS. 32.10.Bi Atomic masses, mass spectra, abundances, and isotopes – 21.10.Dr Binding energies and masses – 07.75.+h Mass spectrometers

1 Comments on the use of highly charged ions

The cyclotron frequency of an ion with charge qe and rest mass m moving perpendicular to a magnetic field B is given by the well-known equation

$$\nu = \frac{1}{2\pi}\frac{qeB}{m}\,. \tag{1}$$

Let us assume that there are accurate methods of measuring ν. C. Scheidenberger, F. Herfurth, G. Bollen and K. Blaum have commented on such methods at this conference and we refer to their contributions for understanding the trap technology using time of flight for determining the cyclotron resonance frequency. By applying a ln and differentiation operation one obtains

$$\frac{\nu}{\Delta\nu} = \frac{m}{\Delta m}\,. \tag{2}$$

Furthermore, $\Delta\nu$ is related to Δt, the ion excitation time, in the equation

$$\Delta\nu \times \Delta t \sim 0.9\,. \tag{3}$$

$m/\Delta m = \nu/\Delta\nu$ is the mass resolving power, that increases linearly with the cyclotron frequency ν, a measure of the mass precision. It is obvious from eq. (1) that this quantity grows linearly with B and q. The last feature we wanted to explore with SMILETRAP. Thus, for example using Hg^{52+} ions for mass measurements in a trap gives a 52 times higher precision than using Hg^{1+} ions. For $B = 4.7$ T and ions with $q/A = 0.5$, ν becomes about 36 MHz and thus the mass resolving power is 0.36×10^8 for $\Delta\nu = 1$ Hz. It should be possible to collect statistics enough to measure a resonance at an accuracy of 1% of its half-width. Therefore, a statistical accuracy of a few parts in 10^{10} seems to be within reach. The deuteron, H_2^+ as well as bare nuclei up to ^{36}Ar also have $q/A = 0.5$ and evidently a gadget is required able to deliver highly charged ions. The procedure to produce these ions is described in [1]. For the very heaviest atoms like Hg we are limited in the value of q for natural as well as for technical reasons and we then loose a factor 2 in precision because the

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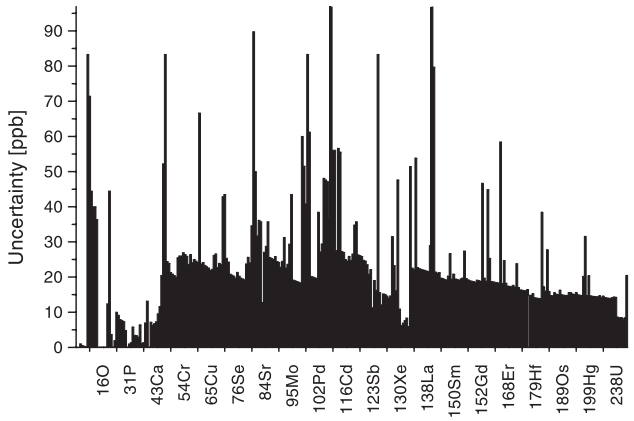

Fig. 1. The mass accuracy for stable isotopes taken from the tables of Audi and Wapstra [2]. As seen a Penning trap with a mass accuracy of 1 ppb can improve most of these mass values.

Table 1. Atomic masses of atoms in the mass number region 1–204 determined with ions having charge $q = 1$–52 using SMILETRAP.

Isotope	Charge state	Atomic mass (u)	Ref.
^{1}H	1	1.007 276 466 72(16)(89)	[3]
^{3}H	1	3.016 049 278 4(29)	a)
^{3}He	2	3.016 029 323 5(28)	[4]
^{4}He	2	4.002 603 256 8(13)	[4]
^{20}Ne	9, 10	19.992 440 185(14)	[5]
^{22}Ne	9, 10	21.991 385 115(19)	[5]
^{28}Si	12, 13, 14	27.976 926 531 (14)	[6]
^{36}Ar	13, 14, 15, 16	35.967 545 105(15)	[5]
^{40}Ar	14, 16	39.962 383 122(40)	[5]
^{76}Ge	22, 23	75.921 402 758(96)	[7]
^{76}Se	24, 25	75.919 213 795(81)	[7]
^{86}Kr	26	85.910 610 729(110)	[5]
^{133}Cs	36, 37	132.905 45159(41)	[8]
^{198}Hg	52	197.966 768 4(6)	b)
^{204}Hg	52	203.973 494 2(6)	b)

a) Preliminary result.
b) Measured 3 weeks before ENAM2001. Uncertainties here 3 ppb; likely to be 2 ppb after final evaluation.

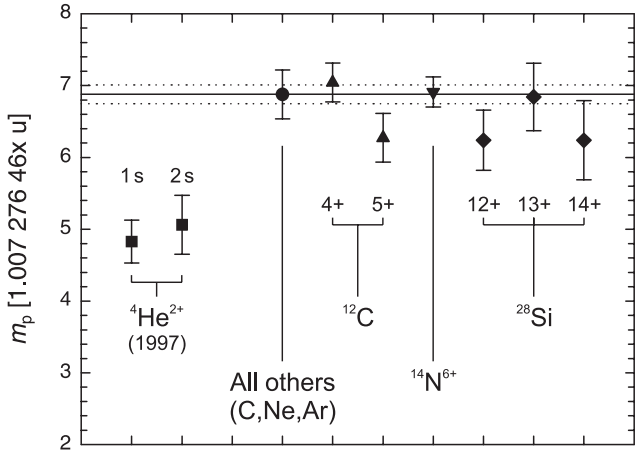

Fig. 2. In this figure we show the values of the proton mass obtained by comparing different charge states of ^{4}He, ^{12}C, ^{14}N, ^{20}Ne, ^{28}Si and ^{40}Ar [3]. Omitting ^{4}He we arrive at a mass value of 1.007 276 466 72(16) where 0.16 ppb only is due to statistics [3]. The accepted value of the proton mass is 1.007 276 466 89(13). This agreement indicates that our total systematic uncertainty is about 0.2 ppb.

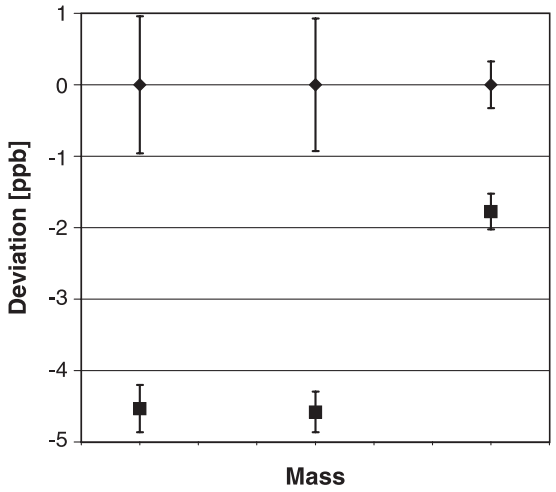

Fig. 3. From left to right comparison of our mass determination of ^{3}H, ^{3}He and ^{4}He [4] with the accepted values. These measurements were inspired by the fact that using the mass of ^{4}He as mass reference gave such an unreasonably low proton mass (fig. 2).

ions available have $q/A = 0.25$ (mass about 200, charge about 50). Thus, one has to know to what extent there is a frequency shift for ion species with different values of q/A. If eq. (1) is applied to two ion species 1 and 2 (the reference ion) these equations divided give the following expression provided that there is no change in B between the two frequency measurements:

$$R = \frac{\nu_1}{\nu_2} = \frac{q_1 m_2}{q_2 m_1}\,. \tag{4}$$

ν_1/ν_2 is thus the relevant observable in the mass measurements. It is therefore very important that the time between the two frequency measurements is small. In order to get the mass M of the neutral atom one has to add the mass of the q missing electrons and subtract their binding energies E_B:

$$M = \frac{1}{R}\frac{q_1}{q_2} m_2 + q_1 m_e - \frac{E_B}{c^2}\,. \tag{5}$$

E_B can be accurately calculated from experimentally measured ionization energies for lighter elements [9] while one has to rely upon relativistic calculations [10] for heavier atoms. These are, in particular, very accurate for filled electron shells and such shells plus or minus one electron. Uncertainties in the calculations are claimed to be as small as 20 eV. In addition to statistical limitation one has to

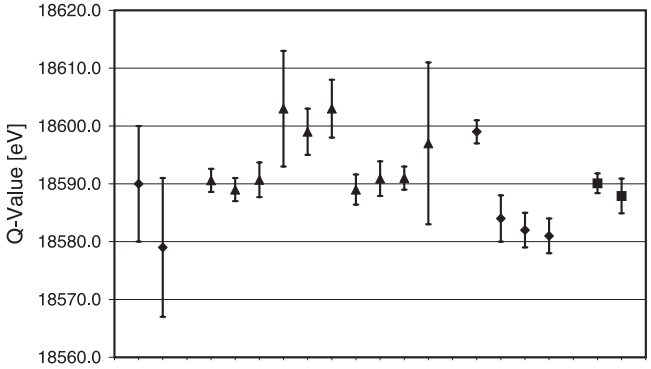

Fig. 4. All published values of the Q-value of the tritium beta-decay. To the very right the values obtained by the Seattle group and by us. The two values to the left are from classical spectrometers and the rest are obtained from the analysis of the tritium β-decay spectrum. As seen the trap measurements agree, the main reason being that, whoever of the two groups has unknown systematic uncertainties they cancel in the mass difference because the masses of ^{3}H and ^{3}He are likely to have been measured under similar conditions. There is a project suggested to be located in Karlsruhe to study the tritium beta-decay with a very strong source. It is not excluded that the Q-value determined in traps will be a useful parameter in future trials to set an even more conservative limit for the electron antineutrino mass. Very likely a tenfold Q-value improvement is then required.

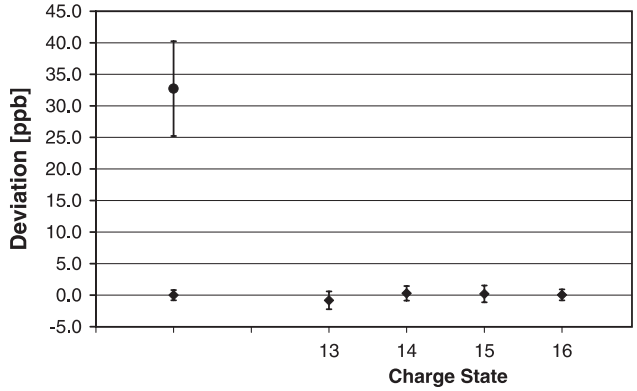

Fig. 5. To the left is the deviation between our mass value of ^{36}Ar (zero deviation) [5] and accepted value [2]. Our value is determined from four different charge states (to the right in the picture). Note the nice agreement for the four different charge states. The nucleus of this atom is a mirror nucleus with 18 neutrons and 18 protons but the accuracy of this mass value can never be used for testing nuclear models that are too crude by many orders of magnitude.

map all possible systematic errors. Here we would like to strongly emphasize that the observable $\frac{\nu_1}{\nu_2}$ can be considered as a directly observed quantity only if the two frequency measurements are close in time. Therefore, with an excitation time of 1 s we scan 21 frequencies for one of the two ion species twice that takes about 50 seconds. Then after a time of only a few seconds we switch to the mass reference ion (H_2^+) repeating the procedure. Thus, the cycle time is less than 2 minutes. There is a set of uncertainties in the frequency measurements of each ion. The relevant observable can therefore be written

$$R = \frac{\nu_1 + \Delta^1\nu_1 + \Delta^2\nu_1 + \Delta^3\nu_1 + ...}{\nu_2 + \Delta^1\nu_2 + \Delta^2\nu_2 + \Delta^3\nu_2 + ...}\,. \qquad (6)$$

Most of these frequency uncertainties, known or not, are about 0.1 or less. The frequency uncertainties cancel to a large extent if the two frequency measurements are done under similar conditions. This is the case for the relativistic mass increase during excitation for q/A doublets. The mass uncertainties are analyzed in detail in a forthcoming paper [11]. It is concluded that mass uncertainties of 1 ppb can be obtained in routine measurements lasting for less than 20 hours while it is possible to reach a few times 10^{-10} with running times of 1-2 weeks, when the two ions are q/A doublets. A strong support for these accuracy claims, is the fact that we agree with the MIT group [12] within 1 ppb (mainly statistics in our case) for the masses (table 1) of ^{20}Ne and ^{40}Ar determined in what we consider as routine measurements. Furthermore, in a measurement of the mass of ^{28}Si with a statistical uncertainty of 0.15 ppb we are only 0.3 ppb off the more accurate MIT data. In addition, we have used different

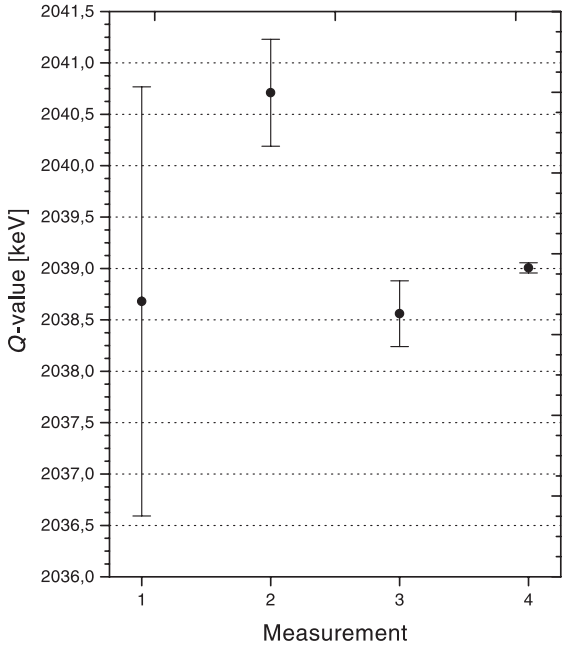

Fig. 6. The Q-values of the double beta-decay of ^{76}Ge. To the left the value derived from the mass tables [2]. The next two values have been reported by the Manitoba group [13,14] and to the right the value measured by us [7]. The double beta-decay without the emission of neutrinos is a decay mode violating the standard model for weak interaction. In the search for this peak or a limit for its appearance the position of the monochromatic electron peak is given by the Q-value. If the last measurement of the Manitoba group would be correct the quoted accuracy would be enough. The main result is that we have confirmed the last value of the Manitoba group. The use of our higher accuracy is only justified if the resolution of future detectors can be considerably improved.

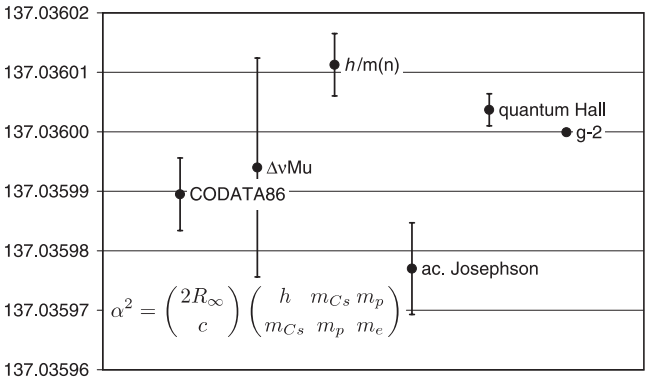

Fig. 7. Scattered values of the fine structure constant determined in different ways. The most accurate value is obtained by combining the value of the experimental determination of $g-2$ [15] for the free electron and a QED calculation [16]. By using the ratios in the equation in the lower part of the picture α can be determined independently of QED. With the three ratios determined to an uncertainty of 2 ppb α would be twice as accurate as before. We measured the mass ratio $\frac{m_p}{m_{Cs}}$ at ~ 2 ppb [8]. The mass of ^{133}Cs was measured by the MIT group [17] with an uncertainty of 0.2 ppb. The bottleneck today is in $\frac{h}{m_{Cs}}$ that still has an uncertainty 7×10^{-9} [18,19].

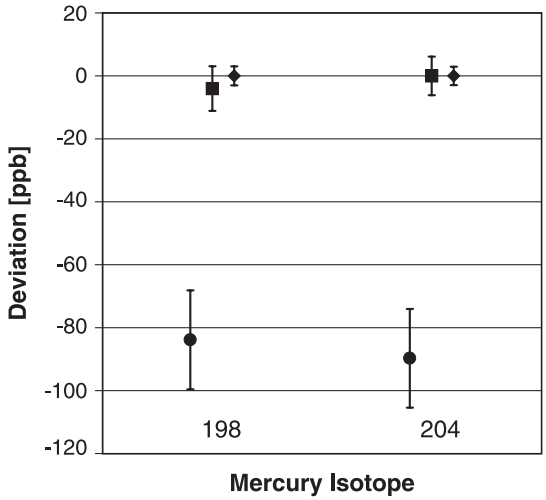

Fig. 8. The deviation between the mass determinations of the ^{198}Hg and ^{204}Hg mass by us (diamonds: zero deviation), the Manitoba group (squares) [21], and the accepted values (circles) [2]. Although we and the Manitoba group use entirely different methods the agreement is excellent. In Stockholm 52+ ions were used, because the electrons correspond to a closed Nickel-like electron shell for which the binding energies can be accurately calculated. The source to our progress was cooling of the Hg ions in the electron beam ion source with He gas (alpha-particles). A more detailed description of the experiment will appear in a paper submitted to Nuclear Physics [22].

charge states of ^{12}C, ^{14}N, ^{20}Ne, ^{28}Si and ^{40}Ar (all these masses are known to about 0.1 ppb [12]) to determine the mass of the proton [3] using H_2^+ as a carrier for the proton (the ratio of this mass and that of the proton is known to an uncertainty less than 0.1 ppb [11]). The total statistical uncertainty in our measurements is 0.16 ppb. Our proton mass value not including systematic uncertainties is only 0.17 ppb below the accurate value 1.007 276 466 89(13) of the Seattle group [20].

It should finally be added that the accuracy level recently achieved with selected rather than cooled ions could not have been achieved without stabilizing the trap temperature and the pressure of the helium in the dewar of the superconducting coil. The connection of the frequency synthesizer was done in order to avoid frequency changes of the order of 0.5 ppb.

2 Results

Some relevant results are summarized in table 1. Due to limited space we comment some of the results in the figure captions (see figs. 1-8). In fig. 1 the mass uncertainties taken from the mass tables [2] for the stable isotopes are indicated. It is evident, that with a mass spectrometer where 1 ppb can be achieved relatively easy, it would be rather dull and meaningless to improve all these masses only to make the mass tables more precise and attractive. Therefore, our measurements have been colored by needs of testing the trap properties, and more often, to measure masses that are related to current interesting problems in physics, for example the Q-values of the double beta-decay of ^{76}Ge, and the beta-decay of ^{3}H. The mass of ^{133}Cs is related to a new way of determining the fine structure constant.

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