Why Is Sideband Mass Spectrometry Possible with Ions in a Penning Trap?

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Many masses, particularly the masses of unstable nuclei, are measured with ions in Penning traps by determining the frequency of a driving force that most efficiently couples two of the three motions of trapped ions. A missing explanation of why such sideband mass spectroscopy works, contrary to simple estimates, begins with the established Brown-Gabrielse invariance theorem.

Many masses are measured using ions in Penning traps, some by measuring only a single sideband frequency of a driving force that most efficiently couples two of the three oscillatory motions of the trapped ion [1,2]. This sideband method is useful for measuring a range of masses with unstable as well as stable nuclei since it is quick and requires no retuning of resonant detectors to change ion species. Examples include testing the isobaric-multiplet mass equation [3], comparing the ^{3}He and tritium masses to complement electron neutrino mass measurements [4], and precise mass measurements of Hg isotopes [5] and ^{7}Li [6]. Comparing ^{50}Mn and ^{54}Co masses determines a CKM matrix element $|V_{ud}|$, helping to demonstrate that a row of the CKM matrix is consistent with unitarity to 1 part in 10^3 [7]. Many masses of unstable nuclei have been measured to probe the boundaries of the nuclear valley of stability (see reviews [8–10]).

Fractional uncertainties of 10^{-7} to 10^{-9} are reported for such measurements. The small uncertainties are surprising insofar as simple estimates suggest that systematic frequency offset shifts could be much larger. Why are such shifts not observed in the few cases where more accurately measured masses of stable ions are available to check the method? This Letter explains why sideband mass spectrometry can work, providing the explanation that is missing from the measurement reports, reviews and discussions of accuracy [11–14]. The explanation starts from the well-known Brown-Gabrielse invariance theorem [15]. An expansion predicts a striking suppression of the leading systematic frequency shift offsets.

Mass spectrometry in a Penning trap seeks to compare cyclotron frequencies of charged particles or ions in a magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$. For a charge q and mass M,

$$\omega_c = qB/M. \qquad (1)$$

A mass ratio is thus a ratio of cyclotron frequencies times an integer ratio of charges.

A substantial challenge is that the true cyclotron frequency, ω_c, cannot be measured directly with a particle or ion in a Penning trap. A trapped particle has three oscillation frequencies [16], none of which is ω_c:

trap-modified cyc. freq.: $\bar{\omega}_+ = \bar{\omega}_+[\theta, \phi, \epsilon]$,   (2a)

axial freq.: $\bar{\omega}_z = \bar{\omega}_z[\theta, \phi, \epsilon]$,   (2b)

magnetron freq.: $\bar{\omega}_- = \bar{\omega}_-[\theta, \phi, \epsilon]$.   (2c)

All three are functions of two misalignment angles (θ and ϕ) and a harmonic distortion factor (ϵ).

The magnetic field and potential at $\mathbf{r} = (x, y, z)$ in all real Penning traps are given to lowest order in r/d by

$$\mathbf{B} = B\sin\theta\cos\phi\hat{\mathbf{x}} + B\sin\theta\sin\phi\hat{\mathbf{y}} + B\cos\theta\hat{\mathbf{z}}, \qquad (3)$$

$$V = \frac{V_0}{2d^2}\left[z^2 - \frac{1}{2}(x^2 + y^2) - \frac{1}{2}\epsilon(x^2 - y^2)\right] + \cdots. \qquad (4)$$

These trapping fields are characterized by the familiar field strength B and trap constant V_0/d^2 (the ratio of a trapping voltage and the square of a trap dimension). Also to lowest order in r/d, the fields are characterized by θ, ϕ, and ϵ. The first three terms in V are the desired electrostatic quadrupole. An unwanted and unavoidable harmonic distortion is described by the single parameter ϵ in a properly chosen coordinate system [15].

Typical sizes for θ and ϵ will differ, of course, for different traps—depending upon how the trap is constructed, and upon how it is aligned with respect to the magnetic field. Patch potentials on electrode surfaces, and charges accumulated upon unexpected insulating films on electrodes, can be important, as may be liquid helium and nitrogen levels that cause the direction of $\mathbf{B}$ to change.

With no reported values for θ and ϵ for the traps used for sideband mass spectrometry, we use the estimate $\theta \sim 10^{-2}$ and $\epsilon \sim 10^{-2}$ [11] (consistent with what is measured *in situ* in my lab before *in situ* optimization). It may be possible to make θ (but not ϵ) an order of magnitude smaller by careful alignment with an electron beam, but an *in situ* measurement (described later) may be needed.

For sideband mass spectrometry [1,2,17], the single measured frequency $\bar{\omega}_c[\theta, \phi, \epsilon]$ is that of the driving force that most efficiently couples ion cyclotron and magnetron motions—a frequency that is the sum of the actual oscillation frequencies for these two motions,

$$\bar{\omega}_c[\theta, \phi, \epsilon] = \bar{\omega}_+[\theta, \phi, \epsilon] + \bar{\omega}_-[\theta, \phi, \epsilon]. \quad (5)$$

The cyclotron motion is excited as the magnetron motion is cooled, and sometimes a Ramsey time sequence [18] is used. (We neglect additional frequency shifts related to the quadrupolar drive strength.)

The central question here is how big is the difference between the measured $\bar{\omega}_c[\theta, \phi, \epsilon]$ and the desired ω_c,

$$\Delta\bar{\omega}_c[\theta, \phi, \epsilon] = \bar{\omega}_c[\theta, \phi, \epsilon] - \omega_c. \quad (6)$$

In the following paragraphs we explore the consequences of $\Delta\bar{\omega}_c[\theta, \phi, \epsilon]$ for mass spectroscopy, estimate its size, and then calculate it more carefully.

The many measurement papers (e.g., [3–7]) tacitly assume $\Delta\bar{\omega}_c[\theta, \phi, \epsilon] = 0$. They quote the perfect-trap prescription that is true only when $\theta = \epsilon = 0$,

$$\omega_c = \omega_+ + \omega_-, \quad (7)$$

but then deduce a value of ω_c by substituting their measured $\bar{\omega}_+[\theta, \phi, \epsilon] + \bar{\omega}_-[\theta, \phi, \epsilon]$ on the right in this equation. The implicit approximation that $\Delta\bar{\omega}_c[\theta, \phi, \epsilon] = 0$ is not justified or even discussed.

How do such systematic frequency shifts affect deduced mass ratios? The mass ratio of two ions, one with mass M, atomic mass A, and charge $q = ne$, and the second a reference ion (with M_{ref}, A_{ref}, and n_{ref}), is

$$\frac{M}{M_{\text{ref}}} = \frac{n}{n_{\text{ref}}} \frac{\omega_c^{(\text{ref})}}{\omega_c} = \frac{n}{n_{\text{ref}}} \frac{\bar{\omega}_c^{(\text{ref})}[\theta, \phi, \epsilon]}{\bar{\omega}_c[\theta, \phi, \epsilon]}(1 + R). \quad (8)$$

The systematic error that arises from $\Delta\bar{\omega}_c[\theta, \phi, \epsilon]$ is

$$R = \frac{\Delta\bar{\omega}_c}{\bar{\omega}_c} - \frac{\Delta\bar{\omega}_c^{(\text{ref})}}{\bar{\omega}_c^{(\text{ref})}} + \cdots. \quad (9)$$

If reported measurement uncertainties of 10^{-7} to 10^{-9} are to be believed, R must be smaller than these factors. Some cancellation between the opposite sign terms in Eq. (9) can be expected; without a model or measurement it is hard to say how much. However, much of the needed suppression must come from very small $\Delta\bar{\omega}_c/\bar{\omega}_c$ and $\Delta\bar{\omega}_c^{(\text{ref})}/\bar{\omega}_c^{(\text{ref})}$.

Why should the systematic frequency offset error be so incredibly small? With no explanation provided in the nuclear mass measurement reports, reviews, and discussions of achievable accuracies, we start with simple estimates. These are then contrasted with a prediction based upon an expansion of an invariance theorem.

The fractional shift R should at least be suppressed by the size of the small parameters θ and ϵ since the systematic shift must vanish in the limit of perfect alignment ($\theta = 0$) and no distortion ($\epsilon = 0$)—a perfect-trap limit that is difficult to attain. However, a small-parameter suppression of $\theta \sim \epsilon \sim 10^{-2}$ is not nearly enough to account for the reported measurement uncertainties of 10^{-7} to 10^{-9}. We can strengthen the argument by adding a symmetry requirement of invariance under $\theta \to -\theta$ and $\epsilon \to -\epsilon$. This suppresses the systematic shift by a factor $\theta^2 \sim \epsilon^2 \sim$

10^{-4}, but still much less than needed to explain the reported uncertainties. If nearly equal masses are compared we would expect an additional suppression, but not the very large additional factor of 10^{-3} to 10^{-5} that is needed to justify the reported uncertainties.

The missing explanation and justification is based upon the Brown-Gabrielse invariance theorem [15],

$$(\omega_c)^2 = (\bar{\omega}_+[\theta, \phi, \epsilon])^2 + (\bar{\omega}_z[\theta, \phi, \epsilon])^2$$
$$+ (\bar{\omega}_-[\theta, \phi, \epsilon])^2. \quad (10)$$

This theorem is exact for the realistic trapping fields of Eqs. (3) and (4) (for which θ, ϕ and ϵ are never zero), not just to unattainable perfect traps [to which Eq. (7) applies]. It relates the square of the desired cyclotron frequency to the sum of the squares of the three real-trap eigenfrequencies.

The theorem is used directly for some of the most accurate measurements in particle, nuclear and atomic physics. Either all three oscillation frequencies are measured to determine ω_c, or two are used with an expansion of the theorem. Enabled measurements include the most accurate magnetic moment of the free electron to 3 parts in 10^{13} [19], the most accurate fine structure constant to 3 parts in 10^{10} [19], and the most accurate magnetic moments of bound electrons [20,21]. The most stringent tests of *CPT* invariance with baryons [22] and leptons [23] use the theorem, as does the most accurate determination of the electron mass [24]. The theorem is used for the most accurate measurements of the masses of stable ions in atomic mass units [25–30], deduced from mass ratios measured with an uncertainty as low as 7 parts in 10^{12} [31]. The theorem allows molecular masses to be measured accurately enough to determine the dipole moments of CO^+ [32] and PH^+ [29].

Sideband mass spectroscopy measurements cannot use the theorem directly. Only one frequency is measured and it is not one of the three oscillation frequencies. Instead, we use expansions to determine the needed frequency shift error, $\Delta\bar{\omega}_c[\theta, \phi, \epsilon]$. For the normal frequency hierarchy

$$\bar{\omega}_+ \gg \bar{\omega}_z \gg \bar{\omega}_- \quad (11)$$

and small angles ($|\theta| \ll 1$ and $|\epsilon| \ll 1$),

$$\frac{\omega_c}{\bar{\omega}_+[\theta, \phi, \epsilon]} \approx 1 + \frac{1}{2}\left(\frac{\bar{\omega}_z[\theta, \phi, \epsilon]}{\bar{\omega}_+[\theta, \phi, \epsilon]}\right)^2, \quad (12)$$

$$\bar{\omega}_-[\theta, \phi, \epsilon] \approx \frac{\bar{\omega}_z[\theta, \phi, \epsilon]^2}{2\bar{\omega}_+[\theta, \phi, \epsilon]}\left(1 + \frac{9\theta^2}{4} - \frac{\epsilon^2}{2}\right). \quad (13)$$

More details are near Eqs. (16) and (17) of Ref. [15].

The key result comes from substituting these two expressions into Eq. (6) to determine the systematic offset of the measured sideband frequency from ω_c,

$$\Delta \bar{\omega}_c[\theta, \phi, \epsilon] = \bar{\omega}_- \left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2 \right) + \cdots. \qquad (14)$$

The shift is very small since it goes as the magnetron frequency, itself the shift of ω_c due to the electrostatic quadrupole, and small compared to the cyclotron frequency given the hierarchy in Eq. (11). The shift is thus also independent of charge and mass to lowest order, and is quadratic in θ and ϵ, as anticipated. The resulting systematic shift of a measured mass ratio is

$$R = \left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2 \right) \left(\frac{n_{\text{ref}}A}{nA_{\text{ref}}} - 1 \right) \frac{\bar{\omega}_-}{\bar{\omega}_+^{(\text{ref})}} + \cdots, \qquad (15a)$$

$$= \left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2 \right) \left(\frac{\bar{\omega}_+^{(\text{ref})} - \bar{\omega}_+}{\bar{\omega}_+} \right) \frac{\bar{\omega}_-}{\bar{\omega}_+^{(\text{ref})}} + \cdots \qquad (15b)$$

with the second line giving a useful alternate version of the second factor.

This prediction of the fractional shift error in a mass ratio measurement is thus the product of three factors. The first factor describes how R is suppressed for small alignment and distortion angles, by a factor of perhaps 10^{-4} as we have seen. The second factor predicts that R depends linearly upon A with a slope that is also predicted. Equivalently, the second factor is a suppression by the difference in cyclotron frequencies divided by the cyclotron frequency of the first ion. The third factor is the small ratio $\bar{\omega}_-/\bar{\omega}_+$ that suppresses the frequency offset error by additional orders of magnitude.

All three factors are required to explain why the lowest order alignment and distortion shifts are smaller than the reported measurement uncertainties. This is even true when ions of the same mass number are compared, as illustrated in the recent determination of a CKM matrix element [7]. The second factor is 10^{-4}, much smaller than the usual case in this example. Nonetheless, the suppression of the frequency shift that is the product of the first two factors is only 10^{-8}, not enough to reduce the systematic shift below the 2×10^{-9} uncertainty reported. Fortunately the expanded invariance theorem plays the role of an unrecognized guardian angel. The three factors together make R smaller than the reported uncertainty for this measurement, for the measurements listed in the introduction, and for the sideband mass spectroscopy of unstable and stable nuclei in Penning traps, in general.

That the predicted suppression of the alignment and distortion shifts is very large turns out to be more important for sideband mass spectrometry, so far, than is the precise small size of the predicted shifts. There are naturally other sources of systematic shifts. For example, potential terms of order $(r/d)^4$ cause anharmonic oscillations of a trapped ion, with oscillation frequencies that depend upon amplitudes [16]. These anharmonicity shifts (along with shifts from contaminant ions in the trap, etc.) must be carefully studied and minimized, of course; the invariance theorem provides no protection from them. The unusual situation

that arises is that the predicted suppression of the alignment and distortion shifts is so great that these low order shifts can be smaller than the higher order anharmonicity shifts, which could then be the limit to the measurement accuracy that can be attained.

Systematic frequency shifts, due to low order alignment and distortion shifts and any other sources, should show up when well-known masses are remeasured with the sideband method under discussion. Some known masses are available, from accurately measured stable nuclei (measured with ions in Penning traps, making direct use of the invariance theorem). Some known mass ratios come from different charge states of the same ions [12], and from using clusters that differ in the number of building block nuclei in the ion [13,14,33]. There are also comparisons of Penning trap mass measurements and reaction based measurements [34]. The good agreement obtained where test masses and reactions are available (with some traps, solenoids and relative alignments of these) is encouraging for sideband mass spectroscopy of stable and unstable nuclei in a Penning trap, and begs for explanation.

The prediction based upon the invariance theorem provides the missing explanation of why these calibration measurements work as well as they do, without being limited by the much larger frequency shifts of the simple estimates. The calibrations thus confirm the prediction, though no calibration has yet been carried out accurately enough, and with other systematic errors minimized enough, to confirm the functional form and size predicted in Eq. (15a). Still, without the invariance theorem explaining the very substantial suppression of shifts, there would be more lingering questions about how well the calibrations should extrapolate to masses for which no test mass is available, whether the systematic shifts might be larger for some masses and charge states, how sensitively the shifts depends upon the alignment and distortion, whether the latter change in time, etc.

The frequency shift between the measured sideband frequency and the desired cyclotron frequency is predicted to be mostly independent of charge and mass, since the magnetron frequency is independent of both to lowest order. The invariance theorem thus offers a way to use stable ions to measure the alignment and distortion shifts that pertain when unstable nuclei are studied within the same trap with the same alignment. Rearranging Eq. (13) gives the prescription

$$\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2 \approx \frac{2\bar{\omega}_-[\theta, \phi, \epsilon]\bar{\omega}_+[\theta, \phi, \epsilon]}{(\bar{\omega}_z[\theta, \phi, \epsilon])^2} - 1. \qquad (16)$$

Just the needed combination of alignment and distortion angles for a particular trap, solenoid and alignment can be determined and minimized if all three eigenfrequencies can be measured with a stable particle or ion (or with an unstable ion if this becomes possible). In addition,

$$\bar{\omega}_z^{\,2} \propto 1 - \frac{3}{2}\theta^2 + \cdots \qquad (17)$$

comes from Eq. (15) of Ref. [15]. Adjusting θ to maximize the observed axial frequency will make $\theta = 0$. There is no report of using these methods to calibrate Penning traps used for sideband mass spectrometry of ions with stable or unstable nuclei. However, this has been done for higher precision measurements on stable particle and ions in a number of labs, including ours. For example, the prescription of Eq. (17) and mechanical adjustments produced $|\theta| < 10^{-3}$, and Eq. (16) revealed a persistent negative contribution that indicated $|\epsilon| \le 10^{-3}$ for several high precision hyperbolic traps [35].

In conclusion, the masses of many unstable and stable nuclei are determined by measuring a cyclotron sideband frequency of ions in Penning traps. Why are the systematic shifts smaller than the measurement uncertainties of 10^{-7} to 10^{-9} that are now being reported? A new application of the established Brown-Gabrielse invariance theorem provides the missing explanation, predicting a remarkable suppression of the lowest order frequency shifts.

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