International Journal of Mass Spectrometry 279 (2009) 107–112

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

The true cyclotron frequency for particles and ions in a Penning trap

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ARTICLE INFO

Article history:
Received 7 July 2008
Received in revised form 17 October 2008
Accepted 17 October 2008
Available online 30 October 2008

PACS:
07.75.h.
21.10.Dr
32.10.Bi
82.80.Qx

Keywords:
Invariance theorem
Penning trap
Mass spectrometry
Radionuclides
Quadrupolar excitation

ABSTRACT

The true cyclotron frequency of a particle or ion, needed for mass spectrometry and other accurate measurements in a Penning trap, cannot be measured directly. It is not one of the oscillation frequencies of the trapped particle, and the three oscillation frequencies that can be measured vary with the misalignment and the harmonic distortion of the trap potential. Two methods to determine the cyclotron frequency are discussed. First, when all three eigenfrequencies of a trapped particle can be measured, the true cyclotron frequency is given by the prescription of the Brown–Gabrielse invariance theorem. This prescription makes possible a surprising number of the most accurate measurements in particle, nuclear and atomic physics because it accounts exactly for the lowest order electrostatic imperfections and magnetic misalignments. Second, when less accuracy is required, as when the masses of unstable nuclei are measured, a single sideband frequency is often measured instead—the frequency of a driving force that optimally couples two of the motions of the ion in the trap. A missing theoretical justification for this alternate method is provided using an expansion of the same invariance theorem. A remarkable suppression of systematic measurement errors is predicted, showing why these are not larger than reported measurement uncertainties, despite the contrary indication of simple estimates.

1. Introduction

A surprisingly large and varied number of the most precise measurements, and the most precise tests of fundamental symmetries (in particle, nuclear and atomic physics) are carried out with particles or ions in Penning traps. Many examples given below. These precise measurements have in common the need to determine and compare the cyclotron frequencies of charged particles suspended in the traps. All such measurements face two substantial challenges.

The first challenge is that the true cyclotron frequency can never be measured directly because it is not one of the three oscillation frequencies of the particle or ion in the trap. All such measurements thus deduce the true cyclotron frequency from one or more of the three oscillation frequencies that can be measured.

The second challenge is that each of the three oscillation frequencies that can be measured directly depends upon a misalignment angle and upon a distortion parameter. These are the unavoidable lowest order imperfections of a real Penning trap. The misalignment is between the axis of the trap's electrostatic quadrupole potential and the magnetic field direction. The distortion is the leading deviation from the perfect harmonic potential desired in a Penning trap.

Two different methods for determining cyclotron frequencies are frequently employed.

(1) For the most accurate measurements, all three of the oscillation frequencies of a trapped particle are measured. The prescription of the Brown–Gabrielse invariance theorem is used directly to deduce the desired cyclotron frequency from them.
(2) Where less accurate measurements suffice, as for the many measurements of the masses of unstable nuclei, only one frequency is typically measured. This single frequency is the sum of two of the three oscillation frequencies of an ion in a Penning trap. It is the frequency of the driving force that most efficiently couples these two motions.

The second method is treated in more detail to correct some misunderstandings, and to provide the missing theoretical justification for why a cyclotron frequency can be reliably deduced by this method. Simple estimates suggest that substantial systematic frequency shifts could be much larger than reported measurement uncertainties. An expansion of the Brown–Gabrielse invariance theorem predicts the remarkable suppression of such errors. This explains why the lack of careful attention paid to such shifts has not led to serious measurement errors, and why such errors have not shown up in the limited number of cases where more accurately

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doi:10.1016/j.ijms.2008.10.015

measured masses (e.g., made using the more accurate method listed above) are available for comparison.

2. Basic challenge of mass spectrometry in a Penning trap

The basic idea of any mass spectrometry in a Penning trap is to compare the cyclotron frequencies of charged particles or ions. In a magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$ (with no electric field present) the nonrelativistic, angular cyclotron frequency of a particle or ion with charge q and mass M is

$$\omega_c = \frac{qB}{M}. \tag{1}$$

Ideally two masses would be compared by comparing their respective cyclotron frequencies, ensuring that either the magnetic field does not change during the measurement time or that magnetic field drift is accurately corrected. For a magnetic moment measurement a cyclotron frequency is not compared to another cyclotron frequency, but to a spin precession frequency associated with the same particle or ion.

A significant challenge is that ω_c is not one of the oscillation eigenfrequencies of a charged particle suspended within a Penning trap. The electric and magnetic field of the Penning trap result in three oscillation eigenfrequencies [1],

$$\text{trap} - \text{modified cyc. frequency}: \quad \bar{\omega}_+ = \bar{\omega}_+[\theta, \phi, \epsilon] \tag{2a}$$

$$\text{axial frequency}: \quad \bar{\omega}_z = \bar{\omega}_z[\theta, \phi, \epsilon] \tag{2b}$$

$$\text{magnetron frequency}: \quad \bar{\omega}_- = \bar{\omega}_-[\theta, \phi, \epsilon], \tag{2c}$$

none of which is the desired ω_c. The true cyclotron frequency, ω_c, thus cannot be measured directly with a particle or ion in a Penning trap. It can only be deduced from one or more of the oscillation frequencies that can be measured directly, or from measurable combinations of these frequencies. Furthermore, the three oscillation frequencies that can be directly measured are unavoidably functions of two misalignment angles (θ and ϕ) and a harmonic distortion factor (ϵ), all of which are difficult to control or tune out.

The electrostatic potential at position $\mathbf{r} = (x, y, z)$ within the Penning trap is a function of ϵ already in the lowest order of an expansion in r/d,

$$V = \frac{V_0}{2d^2}\left[z^2 - \frac{1}{2}(x^2 + y^2) - \frac{1}{2}\epsilon(x^2 - y^2)\right] + \cdots. \tag{3}$$

The trap constant V_0/d^2 is a ratio of a trapping voltage divided by the square of a characteristic trap dimension. The first three terms describe the desired quadrupole. The right two terms are an unwanted and unavoidable harmonic distortion, described by the single parameter ϵ if a properly chosen principal axis coordinate system is used [2]. With respect to this principle axis coordinate system, the components

$$B_x = B\sin\theta\cos\phi \tag{4a}$$

$$B_y = B\sin\theta\sin\phi \tag{4b}$$

$$B_z = B\cos\theta, \tag{4c}$$

describe a spatially uniform magnetic field in terms of θ and ϕ.

There are significant shifts in the oscillation frequencies caused by the misalignment and distortion since θ, ϕ and ϵ are present already in the lowest order of a potential expansion in r/d. It is natural to expect that these leading terms will have a bigger effect upon measured oscillation frequencies than will potential terms of higher order in r/d (that are not written out explicitly in Eq. (3)).

Potential terms of higher order in r/d will make the oscillation frequencies of trapped particles or ions depend upon the oscillation amplitudes [1]. These anharmonicity terms will become important only if the imperfection factors θ and ϕ can be made extremely small, or their effect upon the measured frequencies is remarkably suppressed in some unexpected way. The electrode potentials can then be tuned to minimize the higher order shifts, and the particle oscillation amplitudes can be varied to make sure that measured frequencies are independent of amplitude and trap tuning.

What are typical sizes for the misalignment angle, θ, and the harmonic distortion parameter, ϵ? These will differ, of course, for different traps, depending upon how the trap is constructed, and how well it is aligned with respect to the magnetic field. Patch potentials upon the inner electrode surfaces, and charges introduced from outside the trap (e.g., as part of a loading process) that accumulate upon undesired insulating films on the electrodes, can be important, as may be changing liquid helium and nitrogen levels upon which the relative position of the solenoid and trap may depend.

When the three oscillation frequencies of a trapped particle or ion can be measured it is possible to measure and minimize the alignment and distortion as this is measured *in situ*, as discussed in Section 5 . Typically $|\theta| \sim |\epsilon| \sim 10^{-3}$ or slightly better is achieved.

No *in situ* measurement methods are available when only one measured sideband frequency is used for mass spectrometry. In the absence of reported values for θ and ϵ for this method, we use the estimate $\theta \sim 10^{-2}$ and $\epsilon \sim 10^{-2}$ [3]. This is consistent with what we have measured in my lab *in situ* before *in situ* optimization. It may be possible to do an order of magnitude better in θ by very carefully aligning with an electron beam, but the case will be much more convincing if an *in situ* measurement is carried out. Such a procedure will not reduce ϵ, of course. This would require segmenting electrodes and applying slightly different potentials to each electrodes, doing an *in situ* measurement to make the optimization.

In the following two sections we examine in more detail the two very different methods of dealing with the fact that the true cyclotron frequency cannot be measured directly in a Penning trap, and with the fact that the three oscillation frequencies that can be measured (and hence combinations of these frequencies) all depend on misalignment angles θ and ϕ, and upon a harmonic distortion factor ϵ.

3. When all three oscillation frequencies can be measured

The most accurate mass spectrometry and magnetic moment measurements are carried out by measuring the oscillation frequencies of one particle or ion confined in a Penning trap [1] (examples below). Sometimes a second ion is stored in the same trap but far enough away to avoid a reduction in the accuracy of the measurement [4,5], and sometimes with two ions in a coupled magnetron orbit [6].

When all three eigenfrequencies of a particle or ion in a Penning trap can be measured, the Brown–Gabrielse invariance theorem [2]

$$(\omega_c)^2 = (\bar{\omega}_+[\theta, \phi, \epsilon])^2 + (\bar{\omega}_z[\theta, \phi, \epsilon])^2 + (\bar{\omega}_-[\theta, \phi, \epsilon])^2. \tag{5}$$

gives the prescription that makes possible the most precise measurements of masses (to parts in 10^{11} and a bit better) and magnetic moments (to parts in 10^{13}). The theorem was derived by solving for the eigenfrequencies of the motion of a particle or ion in the magnetic and electric fields given in Eqs. (4) and (3). The true cyclotron frequency is thereby accurately determined, not only in the case of perfect trap, but also for all reasonable values of θ, ϕ and ϵ—the parameters that describe the leading and unavoidable distortions of a real Penning trap. For two particles in a trap, the invariance theorem also takes out the lowest order effects of particle–particle interactions [5].

For low-mass particles there is typically a hierarchy of oscillation frequencies

$$\bar{\omega}_+ \gg \bar{\omega}_z \gg \bar{\omega}_-. \tag{6}$$

In this limit, two measured oscillation frequencies will sometimes suffice to determine the true cyclotron frequency, using a prescription that comes from an expansion of the invariance theorem in powers essentially of $\bar{\omega}_z/\bar{\omega}_+$,

$$\omega_c = \bar{\omega}_+[\theta,\phi,\epsilon] + \frac{(\bar{\omega}_z[\theta,\phi,\epsilon])^2}{2\bar{\omega}_+[\theta,\phi,\epsilon]} + \cdots. \tag{7}$$

(See Eq. (14) of Ref. [2].) This approach suffices for the measurements of the magnetic moment of the free electron [7–9], for example, though small relativistic corrections that depend upon the resolved quantum state must be included as well for the most accurate measurements [8,9], owing to the extremely small uncertainties that are achieved. (See Eq. (2) of Ref. [9].)

The wide applicability of the Brown–Gabrielse invariance theorem is illustrated by a list of some the measurements that use its prescription directly:

(1) The most accurate measurements of the magnetic moment of the free electron—both the measurement that stood for 20 years [7] and the recent 15 times more precise value with a precision of 3 parts in 10^{13} that supplanted it [8,9].
(2) The most accurate determination of the fine structure constant α, now determined to 3 parts in 10^{10} (about 20 times more precise than achieved by any other method) [9,10].
(3) The most precise measurement and comparison of the antiproton and proton charge-to-mass ratios to 9 parts in 10^{11} [4]—the most stringent test of CPT invariance with a baryon system.
(4) The most precise comparison of the positron and electron magnetic moments to 2 parts in 10^{12} [7]—the most stringent test of CPT invariance with a lepton system.
(5) The most precise measurements of the magnetic moment of bound electrons [11,12].
(6) The most precise determinations of the electron mass (in amu)—from measurements of the bound electron magnetic moments [13], and also from direct measurements alternating between one proton and one electron [14].
(7) The most accurate measurements of masses in atomic mass units, deduced from mass ratios measured with a precision as high as 7 ppt [6], where ppt stands for a part in 10^{12}. Examples include:

p (140 ppt) [15]	D (71 ppt) [16]	^{4}He (15 ppt) [17]
^{13}C (77 ppt) [18]	^{14}N (86 ppt) [18]	^{15}N (73 ppt) [18]
^{16}O (11 ppt) [16]	^{20}Ne (120 ppt) [18]	^{28}Si (21 ppt) [5]
^{31}P (29 ppt) [5]	^{40}Ar (82 ppt) [18]	^{136}Xe (80 ppt) [19].

(8) Measurements of the dipole moments of CO^+ [20] and PH^+ [5] molecules.

4. When only one sideband frequency is measured

A very different measurement method determines the true cyclotron frequency ω_c from a measurement of a single sideband frequency for a trapped ion [21,22]. Since one frequency can be measured more rapidly than three, this so-called "quadrupolar excitation" method is used to measure the mass of ions with unstable nuclei. In this section we examine the one-frequency method, estimate the systematic uncertainties that might be expected, and then use an expansion of the Brown–Gabrielse invariance theorem to evaluate the systematic frequency shifts that arise. We show that the one-frequency measurements could not achieve the uncertainties that have been reported without a remarkable suppression of systematic frequency shifts that is described and explained using the invariance theorem. Measurement examples include:

(9) The most stringent test of the isobaric-multiplet mass equation [23].
(10) The most accurate comparison of the ^{3}He and tritium masses [24] as needed for measurements of the electron antineutrino mass.
(11) Precise mass measurements of ^{50}Mn and ^{54}Co to make the most precise determination of the CKM matrix element $|V_{ud}|$, contributing to a demonstration that one row of the CKM matrix is consistent with unitarity to 1 part in 10^3 [25].
(12) Precise mass measurements of Hg isotopes [26] and ^{7}Li [27].
(13) Many measurements of the masses of unstable nuclei, measured to probe the boundaries of the nuclear valley of stability (see reviews in [28–30]).

The one frequency that is measured is the sum of two oscillation frequencies, $\bar{\omega}_+[\theta,\phi,\epsilon] + \bar{\omega}_-[\theta,\phi,\epsilon]$, which we shall call $\bar{\omega}_c[\theta,\phi,\epsilon]$:

$$\bar{\omega}_c[\theta,\phi,\epsilon] \equiv \bar{\omega}_+[\theta,\phi,\epsilon] + \bar{\omega}_-[\theta,\phi,\epsilon]. \tag{8}$$

This measured sideband frequency is the frequency at which a driving force with a radial quadrupole symmetry most efficiently couples the cyclotron and magnetron motions of the trapped ion [21,22]. The cyclotron motion is excited as the magnetron motion is cooled. The excitation takes place quickly, just what is needed to do measurements before an unstable nucleus decays. There is no need for resonant detectors which can detect the motion of image charges in the trap electrodes that are caused by ion motions. Sometimes the drive is applied using a Ramsey time sequence [35–37]. Here we neglect power broadening or other shifts that could arises from the application of the quadrupolar drive, etc. (See the treatment of such mode coupling in [38].)

The frequency needed for mass measurements is the true cyclotron frequency ω_c of Eq. (1), not the measured sideband frequency $\bar{\omega}_c[\theta,\phi,\epsilon]$ of Eq. (8). Confusion arises insofar as most of the measurement papers (e.g., [23–27]) implicitly assume, with no theoretical justification, that these two frequencies are equal. In fact, they differ by a frequency shift $\Delta\bar{\omega}_c[\theta,\phi,\epsilon]$ that explicitly depends upon the misalignments and distortion, θ, ϕ and ϵ:

$$\bar{\omega}_c[\theta,\phi,\epsilon] \equiv \omega_c + \Delta\bar{\omega}_c[\theta,\phi,\epsilon]. \tag{9}$$

The assumption is made implicitly, without discussion, typically by quoting the formula

$$\omega_c = \omega_+ + \omega_-. \tag{10}$$

This formula is only correct when the ω_+ and ω_- are taken to be the unmeasurable frequencies $\bar{\omega}_+[0,0,0]$ and $\bar{\omega}_-[0,0,0]$. Surprisingly, most of the measurement papers incorrectly take ω_+ and ω_- in Eq. (10) to be the actual oscillation frequencies $\bar{\omega}_+[\theta,\phi,\epsilon]$ and $\bar{\omega}_-[\theta,\phi,\epsilon]$. This is an implicit assumption that $\Delta\bar{\omega}_c[\theta,\phi,\epsilon] = 0$ in Eq. (9).

How bad could this implicit assumption be? In other words, how big might we reasonably expect the frequency shift $\Delta\bar{\omega}_c[\theta,\phi,\epsilon]$ to be? We would expect that $\Delta\bar{\omega}_c[\theta,\phi,\epsilon]/\omega_c$ be at least suppressed by the small parameters θ and ϵ since the systematic shift must vanish in the unattainable limit of perfect alignment ($\theta = 0$) and no distortion ($\epsilon = 0$). However, a suppression by the small-angle factor $\theta \sim \epsilon \sim 10^{-2}$ is not nearly enough to account for measurement uncertainties reported to be as small as 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 the suppression factor is still much less than needed to explain the reported uncertainties.

If masses that are approximately equal are being compared we would expect an additional suppression, but still not nearly enough to justify the reported experimental uncertainties. The mass ratio of two ions, one with mass M, atomic mass A, and charge $q = ne$, and the second a reference ion (with $M_{\rm ref}$, $A_{\rm ref}$ and $n_{\rm ref}$), is

$$\frac{M}{M_{\rm ref}} = \frac{n}{n_{\rm ref}}\frac{\omega_c^{(\rm ref)}}{\omega_c} = \frac{n}{n_{\rm ref}}\frac{\bar{\omega}_c^{(\rm ref)}[\theta,\phi,\epsilon]}{\bar{\omega}_c[\theta,\phi,\epsilon]}(1+R). \tag{11}$$

The systematic error that arises is

$$R = \frac{\Delta\bar{\omega}_c}{\bar{\omega}_c} - \frac{\Delta\bar{\omega}_c^{(\rm ref)}}{\bar{\omega}_c^{(\rm ref)}} + \cdots. \tag{12}$$

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. (12) can be expected, in addition to the suppressions estimated in the previous paragraph. Without a model it is hard to say how much, but there should be more cancellation for ions with similar sideband frequencies. However, a large additional factor of 10^{-3} to 10^{-5} is still required if the claimed measurement uncertainties are to be correct.

How then can much smaller experimental uncertainties be claimed, given that no plausible explanation is offered in the measurement papers? The only answer so far is that the one-frequency method seems to give the right answer in the cases where it can be checked. "Calibrations" of the one-frequency method are possible in some cases by remeasuring the masses of ions that have been more accurately determined by measuring all three oscillation frequencies, and using the invariance theorem to eliminate any dependence upon θ, ϕ and ϵ. Different charge states of the same ions [31] can sometimes be measured to check the one-frequency method, and sometimes cluster ions that differ in the number of building block nuclei in the ion [32,33,39] can be used. There are also comparisons of one-frequency mass measurements and reaction based measurements [40].

Successful calibrations, where these are possible, are encouraging for one-frequency mass spectrometry in a Penning trap. However, as long as the remarkable suppression of the misalignment and distortion shifts is not understood it is not possible to identify and prevent the circumstances that could change the suppression of these shifts. Moreover, some measurements which reported high accuracy were carried out in apparatus for which no calibration at all was done. Even for apparatus where a careful calibration was once carried out, there is still cause for concern in the absence of an understanding of why the method works. Whenever the apparatus is adjusted or repaired it seems possible that the small values of θ, ϕ and ϵ might well change, requiring a new set of calibration measurements. Also, as the level of liquid nitrogen and liquid helium change in the dewar for the superconducting solenoid that typically provides the magnetic field for the trap, it is certainly possible that the alignment between the magnetic field and the trap will change, requiring that calibration measurements be done as a function of cryogen levels. Finally, calibrations generally cannot be carried out for exactly the masses that are being measured. An interpolation of the calibration is required, and a sensible interpolation requires a justified model of the shifts being interpolated.

Fortunately, an expansion of the Brown–Gabrielse invariance theorem predicts the needed suppression of the systematic frequency shift errors, and thus provides the missing explanation and justification. The normal hierarchy of frequencies for an ion in a Penning trap is used, Eq. (6), along with a small-angle expansion ($|\theta| \ll 1$ and $|\epsilon| \ll 1$), to obtain

$$\frac{\omega_c}{\bar{\omega}_+[\theta,\phi,\epsilon]} = 1 + \frac{1}{2}\left(\frac{\bar{\omega}_z[\theta,\phi,\epsilon]}{\bar{\omega}_+[\theta,\phi,\epsilon]}\right)^2 + \cdots \tag{13}$$

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

(See Eqs. (16) and (17) of Ref. [2].)

The key result comes from substituting these two expressions into Eq. (9) to determine the systematic offset of the measured sideband frequency from ω_c,

$$\Delta\bar{\omega}_c[\theta,\phi,\epsilon] \approx \bar{\omega}_-\left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2\right). \tag{15}$$

The shift is of order of the magnetron frequency, itself the shift of the cyclotron frequency caused by the addition of a perfect quadrupole potential. The systematic shift is thus very small compared to the cyclotron frequency, given the hierarchy in Eq. (6). It is also independent of charge and mass to lowest order. The systematic frequency shift is quadratic in θ and ϵ, as anticipated. The resulting systematic shift of a measured mass ratio is

$$R = \left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2\right)\left(\frac{n_{\rm ref}A}{nA_{\rm ref}} - 1\right)\frac{\bar{\omega}_-}{\bar{\omega}_+^{(ref)}} + \cdots \tag{16a}$$

$$= \left(\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2\right)\left(\frac{\bar{\omega}_+^{(ref)} - \bar{\omega}_+}{\bar{\omega}_+}\right)\frac{\bar{\omega}_-}{\bar{\omega}_+^{(ref)}} + \cdots. \tag{16b}$$

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, the small ratio $\bar{\omega}_-/\bar{\omega}_+$, 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 [25]. The second factor is 10^{-4} in this example, much smaller than usual. Nonetheless, the suppression of the systematic 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 that was reported. Fortunately the expanded invariance theorem has been playing the role of an unrecognized guardian angel. The three factors together make R smaller than the reported uncertainty for this example measurement, for the other measurements listed above, and for the sideband mass spectroscopy of unstable and stable nuclei in Penning traps in general.

An unusual situation arises for a large suppression of the alignment and distortion shifts, from order $(r/d)^2$ terms in the potential. These low order shifts can then be much smaller than anharmonicity shifts that arise from the higher order, $(r/d)^4$ terms in the potential, making the latter the limit to the measurement accuracy that can be attained. 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 calibrations, where these have been possible, can be regarded as confirming the prediction of the remarkable suppression of the alignment and distortion shifts, 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. (16). Still, without the invariance theorem explaining the very substantial suppression of shifts there would be

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 systematic shifts depends upon the alignment and distortion, etc.

The role of the Brown–Gabrielse invariance theorem for explaining why one-frequency sideband mass spectrometry is possible has not been appreciated, so far. The measurement papers (e.g., examples above) never mention the theorem. When the theorem is briefly referred to in nuclear mass review papers (e.g., [28–30]), and in discussions of accuracy (e.g., [22,3,31–34]), it is treated as essentially irrelevant because it predicts shifts smaller than reported measurement uncertainties. In fact, the invariance theorem is crucial for justifying and explaining why this method can work at current measurement accuracies, just because it predicts that such systematic shifts should be orders of magnitude smaller than what might be expected or otherwise explained. Except for this remarkable suppression of leading order alignment and distortion shifts, the one-frequency mass spectrometry of an ion or particle in a Penning trap would not be possible at the current level of precision.

5. *In situ* measurements of the alignment and the harmonic distortion

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. (14) gives the prescription

$$\frac{9}{4}\theta^2 - \frac{1}{2}\epsilon^2 \approx \frac{2\tilde{\omega}_-[\theta,\phi,\epsilon]\tilde{\omega}_+[\theta,\phi,\epsilon]}{(\tilde{\omega}_z[\theta,\phi,\epsilon])^2} - 1. \quad (17)$$

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,

$$\tilde{\omega}_z^2 \propto 1 - \frac{3}{2}\theta^2 + \cdots, \quad (18)$$

comes from Eq. (15) of Ref. [2]. Maximizing the observed axial frequency by adjusting θ is thus an *in situ* way to locate $\theta = 0$. There is no report of using these methods to calibrate Penning traps for sideband mass spectrometry, on radionuclides, for example. However, this has been done for high precision measurements on stable particle and ions in a number of labs, including ours. For example, the prescription of Eq. (18) and mechanical adjustments produced $|\theta| < 10^{-3}$, and Eq. (17) revealed a persistent negative contribution that indicated $|\epsilon| \leq 10^{-3}$ for several high precision hyperbolic traps (Van Dyck, private communication).

6. Conclusions

In conclusion, precise measurement of masses and magnetic moments can be carried out with particles and ions in a Penning trap if their true cyclotron frequency can be determined. Because this frequency is not an oscillation frequency of the trapped particles and ions that can be measured directly, two very different methods are used to determine its value. First, the most accurate mass spectroscopy and measurements of magnetic moments takes place when the three oscillation frequencies for a stable particle or ion in a trap are all measured. The Brown–Gabrielse invariance theorem provides the measurement prescription that determines the true cyclotron frequency from the three eigenfrequencies, independent of most important and unavoidable misalignments and distortion of the trapping potential. Second, the masses of many unstable and stable nuclei are determined by measuring a single cyclotron sideband frequency of ions in Penning traps—actually the frequency of a driving force that most effectively couples the magnetron and cyclotron motion of ions in the trap. Systematic shifts must be smaller than the measurement uncertainties that are reported. An expansion of the Brown–Gabrielse invariance theorem supplies the missing explanation of why this is possible, by describing the remarkable suppression of the lowest order systematic frequency shifts that is needed.

Acknowledgements

This work was supported by the NSF, by the AFOSR and by a Humboldt Research Award. Helpful comments from J. Äystö, K. Blaum, G. Bollen, L.S. Brown, J. DiSciacca, N. Guise, J. Hardy, E. Myers, W. Quint, R. Schuch, G. Savard and R.S. Van Dyck, Jr. are gratefully acknowledged.

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