Magnetic Resonance of Trapped Ions by Spin-Dependent Cyclotron Acceleration

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1 Introduction

The frequencies of motion of ions trapped by static magnetic and electric fields may be detected through the charge induced on the trap plates. In a homogeneous magnetic field, these frequencies have long been used for high resolution measurements of the charge-to-mass ratio. The most important chemical application of this is mass spectroscopy via Fourier transform ion cyclotron resonance (ICR).[1,2,3] Single-ion sensitivity in the detection of the axial trapping frequency has also been demonstrated recently for masses of chemical interest by D. Pritchard.[4,5] We have recently proposed methods for transferring this exquisite sensitivity to the detection of the internal spectroscopy of ions, in particular the magnetic resonance spectra.[6,7] This presentation focuses on design issues for the most promising such method, in which spin-dependent cyclotron acceleration is imposed and the resulting change in ion orbit is detected as a change in the axial trapping frequency.

As in the electron g-factor measurement of H. Dehmelt,[8] the shift in axial trapping frequency is proportional to the strength of a static magnetic bottle field gradient. However, that direct effect of a spin flip is impractically small for nuclear spin flips of ions. In the present case, the transverse magnetic moment is coupled to a radiofrequency gradient to provide an accelerating force. A precedent is M. Bloom's deflection of neutral molecular beams by radiofrequency field gradients (the "transverse Stern-Gerlach effect").[9,10]

We have derived both semiclassically and quantum-mechanically the conditions under which a magnetic field gradient modulated at both the Larmor and cyclotron frequencies will lead to cyclotron acceleration proportional to the transverse magnetic moment of a coherent state of the particle and radiation field. In the presence of a magnetic bottle, the corresponding shift in the axial trapping frequency due to this spin-dependent work can be made much larger than the shift due directly to a spin flip.

This effect has been incorporated into a proposed experimental procedure in which the spin-flip probability, resulting from a period of high-resolution magnetic resonance, controls the presence or absence of a net axial frequency shift between two detection periods. A data reduction algorithm based on the fast Fourier transform allows rapid conversion of the "before" and "after" signals from one or many trapped ions into a point of the magnetic resonance spectrum or interferogram. Simulated signals, including the anticipated noise from both the detection circuit and intrinsic quantum fluctuations in the number of spins flipped, indicate the method is practical.

2 Ion Confinement in a Penning Trap and a Magnetic Bottle

An ion in a homogeneous static magnetic field $\vec{B}_0$, whose direction defines the z-axis, will circle in the transverse (x-y) plane at frequency $\omega_c = qB_0/m$. Axial (z-axis) trapping can be obtained by adding a static electric field $\vec{E} = \left(V_0/d^2\right)\left(x\hat{x}/2 + y\hat{y}/2 - z\hat{z}\right)$. Here V_0 is a DC trapping potential and d is a characteristic linear dimension dependent on the details of the electrode geometry (e.g., hyperbolic, cubic, cylindrical). An ion so trapped undergoes three different types of harmonic translational motion:[11] axial oscillation at frequency

$\omega_z = \sqrt{qV_0/md^2}$, rapid cyclotron motion in the transverse plane at frequency ω_+, and slower magnetron motion of frequency ω_-, with $\omega_\pm = \frac{1}{2}\left(\omega_c \pm \sqrt{\omega_c^2 - 2\omega_z^2}\right)$. In ICR, one monitors the radiofrequency voltage at ω_+ induced on a capacitor by the cyclotron orbit of a group of ions coherently excited by an oscillating electric field resonant with the cyclotron motion. Single ion sensitivity has been achieved for detection of both ω_z[4] and, indirectly, ω_+,[5] using axial detection. The charge-to-mass ratio is the only structural quantity measured on trapped ions by ICR to date.

In order to describe how other quantities, in particular the NMR spectrum, may be encoded into trapped ion signals, it is necessary to analyze the case of ion motion in the presence of a magnetic field gradient. In particular we consider the introduction of a magnetic bottle field of the form (in cylindrical coordinates, $\vec{r} = z\hat{z} + \rho\hat{\rho} + \phi\hat{\phi}$) $\Delta\vec{B} = B_2\left[\left(z^2 - \rho^2/2\right)\hat{z} - z\rho\hat{\rho}\right]$.[11,12] The presence of $\Delta\vec{B}$ couples the axial, cyclotron and magnetron motions to the spin. A classical analysis of the ion motion in a known spin state is adequate though the principal results can be confirmed with the trapping frequencies from first-order quantum perturbation theory.[11] To a very good approximation the axial amplitude is a simple one-dimensional sinusoid even in the presence of the magnetic bottle. The potential energy for the axial motion is

$$U_\pm = \pm\frac{|\gamma|\hbar B_0}{2} + \left(\frac{qV_0}{2d^2} + \mu_m B_2 \mp \frac{|\gamma|\hbar B_2}{2}\right)z^2 + \cdots. \quad (1)$$

The spin magnetic moment operator has been replaced by its two high-field eigenvalues (upper and lower signs) assuming a single spin 1/2 nucleus with gyromagnetic ratio γ. The only coupling to the transverse motion is through the mechanical magnetic moment μ_m = (q/2)[x(dy/dt)-y(dx/dt)]. This quantity is however a constant of the motion,[13] so that the axial motion is separable with a parametric dependence on the ion's transverse orbit. The ellipsis denotes terms quadratic or higher in B_2/B_0. We have performed exact three-dimensional trajectory calculations to confirm that Eq. 1 suffices for the times and orbits of the numerical examples discussed later. The axial frequency for each ion, including corrections to ω_z due to the magnetic bottle, can be written from Eq. 1 as

$$\tilde{\omega}_z^\pm = \omega_z + \frac{B_2}{m\omega_z}\left(\mu_m \mp \frac{|\gamma|\hbar}{2}\right) + O\left(B_2^2\right). \quad (2)$$

A key illustration of this coupling was the use of the spin-dependent shift of the axial frequency to measure the g-factor of the electron[8,11] cooled at 4 K to the ground state of its cyclotron motion. The straightforward generalization of this to ions is not practical, since the shift is inversely proportional to mass at fixed observation frequency ω_z. Extending this shift to a 100 amu ion with a proton magnetic moment under conditions similar to those used in the single electron experiments yields an impractically small 4 μHz shift. A more difficult problem is that the three trapping frequencies and the Larmor frequency become inhomogeneously broadened due to the wide range of μ_m values present in a thermal ensemble. Minimizing this by ion cooling methods would be time-consuming and reducing this range to be less than the spin magnetic moment requires lower temperatures as mass increases, since this quantum decreases inversely with mass.

3 Spin-Dependent Cyclotron Acceleration: IRICE

Rather than attempt to measure the small spin-dependent term in the axial motion, we derive a form of spin-dependent cyclotron acceleration analogous to cyclotron excitation via ICR: this is *i*nternally *r*esonant *i*on *c*yclotron *e*xcitation (IRICE). The resonant electric field of ICR is replaced by an oscillating magnetic gradient with components at the cyclotron and Larmor (ω_0) frequencies. This field is constructed by arranging two orthogonal quadrupole coils: one is parallel to the x-axis with current proportional to $\cos(\omega_0 t+\pi/2)\cos(\omega_+ t)$, and the other is directed along the y-axis with current proportional to $\cos(\omega_0 t+\pi)\cos(\omega_+ t+\pi/2)$.[14] With gradient field strength G for each, the total magnetic field is

$$\vec{B} = \left\{B_0 + Gz\sin\left[\left(\omega_0 + \omega_+\right)t\right]\right\}\hat{k} - G\cos(\omega_0 t)\sin(\omega_+ t)\left(x\hat{i} + y\hat{j}\right). \quad (3)$$

A quantum-mechanical description of a spin-1/2 magnetic moment in this field shows that the eigenstates of spin lie in the transverse plane, aligned such that the spin-dependent force $\vec{F}_s = \left(\vec{\mu}\bullet\vec{\nabla}\right)\vec{B}$ resonant with the ion cyclotron motion is

$$\vec{F}_s = \mp\frac{|\gamma|\hbar G}{4}\left[\sin(\omega_+ t)\hat{i} + \cos(\omega_+ t)\hat{j}\right]. \quad (4)$$

Like the force in ICR excitation, this is resonant with the cyclotron motion, but with explicit spin dependence due to a gradient dipole force.[9,10,15]

Neglecting the magnetron mode, the transverse ion motion is described as a cyclotron oscillation of radius ρ_+ and phase ϕ_+ (the sense of rotation used here is appropriate for a positively charged ion):

$$\vec{x} = \rho_+\left[\cos(\omega_+ t + \phi_+)\hat{i} - \sin(\omega_+ t + \phi_+)\hat{j}\right]; \quad (5)$$

$$\frac{\partial \vec{x}}{\partial t} = -\omega_+ \rho_+ \left[\sin(\omega_+ t + \phi_+)\hat{i} + \cos(\omega_+ t + \phi_+)\hat{j} \right]. \quad (6)$$

For excitation small compared to the initial energy, the change in cyclotron energy due to IRICE over a period τ is

$$\Delta E_+ = -\int_{\vec{x}(0)}^{\vec{x}(\tau)} \vec{F} \bullet d\vec{x} = \int_0^\tau \vec{F} \bullet \left(\frac{\partial \vec{x}}{\partial t} \right) dt = \mp \frac{|\gamma| \hbar G \omega_+ \rho_+ \tau}{4} \cos\phi_+ . \quad (7)$$

The corresponding change in cyclotron radius is

$$\Delta\rho_+ = \mp \frac{|\gamma| \hbar G \tau}{4 m \omega_+} \cos\phi_+ . \quad (8)$$

An illustration of this effect is presented in Fig. 1. This can then be monitored as a change in the axial frequency in the presence of a magnetic bottle; this change is $\delta = \tilde{\omega}_z(\rho_+ + \Delta\rho_+) - \tilde{\omega}_z(\rho_+)$. For a 100 amu ion with a proton magnetic moment in B_0 = 1 T, with B_2 = 1000 T/m^2, $\tilde{\omega}_z / 2\pi$ = 26253.9 Hz, ρ_+ = 5 mm, ϕ_+ = 0, G = 200 G/cm, and τ = 1 sec, the IRICE change in the cyclotron radius is $\Delta\rho_+$ = 1.4 μm, with the corresponding axial frequency shift $\delta/2\pi$ = 0.4 Hz. This represents an improvement of five orders of magnitude when compared to the 4 μHz direct spin shift quoted in Section 2.

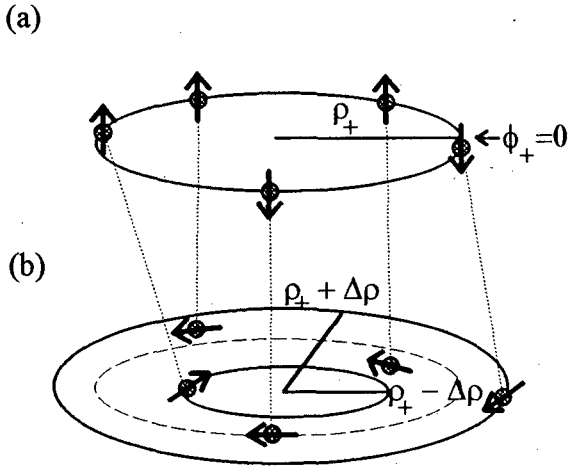

Fig. 1. Illustration of the IRICE effect. The circles represent ions; the arrows represent the orientation of each spin eigenvector. (a) Prior to IRICE, the spin axis of quantization is the z-axis. Ions excited to the cyclotron radius ρ_+ by coherent ICR excitation have been dephased by B_2 during an initial axial detection period. (b) IRICE quantizes the spins transversely and accelerates the ions to new orbits. The effect scales with $\cos\phi_+$, as seen in Eq. 8., and is thus maximized with $\phi_+ = 0$ or π.

4 Proposed Experimental Procedure

IRICE may be incorporated as the central feature in a proposed experimental magnetic resonance procedure by inserting it between two periods of axial frequency detection. Cyclotron radius changes due to IRICE are then monitored as axial frequency differences between the two detection periods, each carried out in the presence of a magnetic bottle; the bottle converts radius changes into frequency changes via Eq. 2. The NMR information is encoded by introducing a period of spin evolution within the IRICE period. (Inhomogeneity of the NMR spectrum is avoided by switching off the magnetic bottle during the spin evolution and the IRICE period.) The spin evolution results in a certain probability of flipping the transverse orientation of the spin; this probability can then be modulated by varying the timing or frequency conditions of an NMR experiment. For example, IRICE could be split into two periods separated by spin evolution in B_0 during the variable time t_1; Fourier transformation of the resulting interferogram would yield the NMR spectrum. Alternately, a simpler implementation could involve the sweeping of the Larmor frequency term in the IRICE field, yielding a continuous wave experiment. NMR lines would then be detected as peaks in the magnitude of the axial frequency shifts detected.

Our approach to overcome the inhomogeneous distribution of the axial frequency and to extract the axial frequency shifts involves convolving spectra taken before and after the IRICE/NMR period. The multiplication of the signal from the "before" axial detection period by the signal from the "after" period, with the "after" time axis reversed, produces a signal whose Fourier transform includes a peak at the difference between the "before" and "after" frequencies.

The technique proposed extends the applicability of NMR to gas phase trapped ions by circumventing the insensitive method of detection through Faraday law methods, substituting the single ion sensitivity of trapped ion detection. Since the observation time can be seconds, the potential frequency resolution is many orders of magnitude better than that of ion beam spectroscopy, which is transit-time limited.

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