Comment on "Why is Sideband Mass Spectrometry Possible with Ions in a Penning Trap?"

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The 2009 Letter by Gabrielse [1] elevates an incomplete 3D force-balance expression [Eq. (3a)] to the status of an "invariance theorem"; and deprecates the 2D relation [Eq. (5c)] which describes both sideband mass spectrometry [2] and the modern spectroscopy devices pervading chemistry and biology [3]. Unfortunately, Eq. (3a) "builds in" systematic errors in dynamical frequencies.

The Letter describes a charged particle (q, m) moving in a hyperbolic Penning trap with $\mathbf{B} = B\hat{z}$, with "bare" cyclotron frequency $\Omega \equiv qB/m$. The vacuum potential $\phi(\rho, \theta, z)$ of Eq. (1a) is generated by hyperbolic electrodes (i.e. Dirichlet b.c.), and the force is calculated from the (fundamentally incomplete) Eq. (2a), as

$$\phi \;\equiv\; (m/2q)\omega_z^2\,[z^2 - {}^1\!/_2\,\rho^2] \qquad (1a)$$

$$\widehat{\phi} \;=\; (m/2q)[\widehat{\omega}_z^2\,z^2 - \widehat{\omega}_\rho^2\,\rho^2]\,, \qquad (1b)$$

with

$$F \;=\; -q\nabla\phi \quad \text{(wrong)} \qquad (2a)$$

$$\;=\; -q\,\nabla\widehat{\phi}\,. \qquad (2b)$$

The correct force of Eqs. (1b) and (2b) is properly derived from an effective potential $\widehat{\phi}$ which includes mobile boundary (image) charges from q itself [4–7], and space-charge from other particles [5] (if any). Both effects make $\nabla^2\widehat{\phi} \neq 0$, i.e. $\widehat{\omega}_z^2 \neq 2\widehat{\omega}_\rho^2$ in Eq. (1b), precluding the deceptively simple form of Eq. (1a). As example, a grounded metal shell (Dirichlet b.c.) gives $\phi(\mathbf{x}) = 0$ everywhere inside; but a charge q experiences a non-zero image force, $F_i \propto q^2$. Ignoring F_i is analogous to ignoring m/M "reduced mass" effects with a mobile force center of mass $M \gg m$.

The "invariance theorem" following from Eqs. (1a) and (2a) relates the observable cyclotron, magnetron, and z-bounce frequencies $\{\omega_c, \omega_m, \omega_z\}$ by Eq. (3a),

$$\omega_c^2 + \omega_m^2 + \omega_z^2 \;=\; \Omega^2 \quad \text{(wrong)} \qquad (3a)$$

$$\;=\; \Omega^2 + \widehat{\omega}_z^2 - 2\widehat{\omega}_\rho^2 \qquad (3b)$$

whereas the proper force law gives (3b).

In hyperbolic traps with size $d_0 \sim 0.5$ cm, an applied potential $V_0 \sim 1$ Volt establishes mobile boundary charges of magnitude $Q \sim (4\pi\varepsilon_0)\,d_0 V_0 \sim 3 \times 10^6 e$, giving $F_0 \propto qQ$. Image-charge and space-charge effects then give force corrections $F_i/F_0 \sim q/Q$, i.e.

$$(\widehat{\omega}_z^2 - 2\widehat{w}_\rho^2)/\widehat{\omega}_z^2 \;\sim\; q/Q \;\sim\; O(10^{-6} \to 10^{-1})\,, \qquad (4)$$

where 10^{-1} represents q in a space-charge-dominated trap. These effects can be subtle: image charges generally increase $\widehat{\omega}_\rho$; whereas they decrease $\widehat{\omega}_z$ in hyperbolic traps but *not* in cylindrical traps [5, 6].

The gist of Ref. 1 is that both tilt mis-alignment (with angle τ) and non-circularity of ϕ (with eccentricity ε) leave $\nabla^2\phi = 0$; that is, vary $\widehat{\omega}_z^2$ and $\widehat{\omega}_\rho^2$ by factors of τ^2 and ε^2. For optimized traps [1], one may have $\tau^2 \sim \varepsilon^2 \sim 10^{-6}$, similar in magnitude to the ignored systematic error of Eq. (4). Of course, Ref. 1 correctly notes that these systematic errors can be reduced by *relative* frequency measurements using known masses.

A more broadly applicable 2D θ-symmetric perspective notes that the cyclotron and magnetron dynamics is *independent* of the z-dynamics, even though ω_z may be used for axial cooling or cyclotron orbit detection [8]. Then, 2D force-balance for a kinetic or drift orbit at radius ρ in field $E_\rho = -\partial\widehat{\phi}/\partial\rho \equiv (q/m)\,\widehat{\omega}_\rho^2\rho$ gives frequencies $\omega = \{\omega_c, \omega_m\}$ satisfying

$$(q/m)\,E_\rho/\rho - \omega\Omega + \omega^2 \;=\; 0\,, \qquad (5a)$$

$$\omega_c^2 + \omega_m^2 \;=\; \Omega^2 - 2\widehat{\omega}_\rho^2\,, \qquad (5b)$$

$$\omega_c + \omega_m \;=\; \Omega\,. \qquad (5c)$$

Equation (5b) is simpler than (3b), and can be used to *determine* $E(\rho)$. Tilt gives weak z-dependence to $\widehat{\omega}_\rho$, mitigated in effect by the smallness of $\omega_m \sim \omega_\rho^2/\Omega$. Equation (5c) probably has the broadest utility: Ω is obtained directly as the optimal frequency for nonlinear sideband coupling of ω_m and ω_c [2].

Overall, image- and space-charge effects are important for precision spectroscopy, for multipole particles or multiple species, for axially-elongated traps, and for micron-sized traps. Modern devices utilize relative mass information and even "walking calibration" [3] to attain ppb accuracy. None of these techniques are well served by an invariance estimate which ignores image forces and confusingly conflates axial and radial dynamics.

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