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The Electrostatic Ion Beam Trap : a mass spectrometer of infinite mass range

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We study the ions dynamics inside an Electrostatic Ion Beam Trap (EIBT) and show that the stability of the trapping is ruled by a Hill's equation. This unexpectedly demonstrates that an EIBT works like a quadrupole trap. The parallelism between these two kinds of traps is illustrated by comparing experimental and theoretical stability diagrams of the EIBT. The main difference with quadrupole traps is that the stability depends only on the ratio of the acceleration and trapping electrostatic potentials, not on the mass nor the charge of the ions. Our model is confirmed by the experimental observation of parametric resonances in the EIBT, where ions excited to their oscillation frequency are ejected out of the trap. These frequencies are proportional to the square root of the charge/mass ratio of each trapped species, while the stability is independent of the mass and charge. The EIBT can thus be used as a mass spectrometer of infinite mass range.

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Electrostatic Ion Beam Trap (EIBT) [1] are taking an important place in between very low-energy charged-particles storage devices, such as quadrupole and Penning traps [2] and high energy storage rings [3]. With the ConeTrap [4], electrostatic rings [5] and the Mini-Ring [6], they form a new family of trap operating at energies of a few keV. They are used for atomic and molecular metastable-states studies, molecular fragmentation and photodissociation (see, e.g., [7] for a review). Beyond providing trapping of energetic particles in a well defined direction, these traps have many interesting features : they are small, relatively inexpensive, easy to setup and operate and have a field-free region where ions move freely and where measurements can easily be performed. They can even be used as Time Of Flight (TOF) mass spectrometers [8] or cooled at cryogenic temperatures [9].

Despite these interesting features, all the published theoretical models describing EIBT are based on one dimensional approximations, neglecting the radial motion. This leads to very inaccurate predictions of the trap stability and operating domain, and restrict severely their flexibility, as finding reasonable working points requires lengthy and tedious experimental exploration. This may partly be explained by the lack of an analytical formula for the electrostatic potential inside these traps leading to the dilemma of choosing between a simplistic analytical model and a heavy numerical treatment unsuited to explore the huge space of parameters. Usual beam simulation codes fail to produce good results as the numerical inaccuracies at the ion turning points lead to energy non conservation reaching a few 100eV over a few tens of oscillations, which render the simulations useless. Here we solve completely the problem, using methods developed for radio-frequency quadrupole traps. We show that the radial dynamic is ruled by a Hill's equation, a particular case of the Mathieu equation that describes quadrupole traps. This model yields very accurate predictions of the

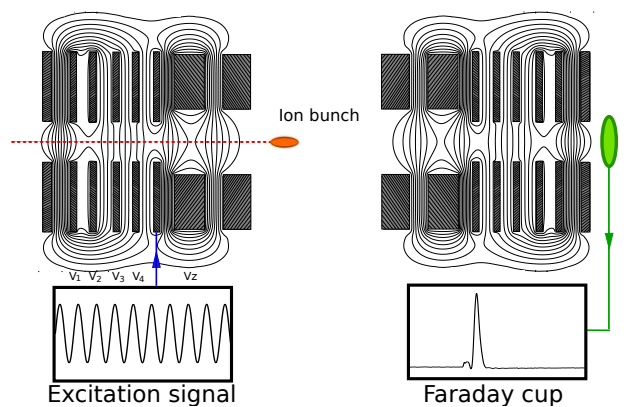


FIGURE 1. (Color online) Overview of the experimental setup. Five potentials are applied to the electrodes (represented by the striped rectangles), the other are grounded. The injection of the ion bunch (orange) is performed when all the electrodes on one side of the trap are grounded. The potentials are raised before the bunch has time to come back. The faraday cup (green) is linked to an oscilloscope via a charge amplifier. A sinusoidal voltage can be applied to an initially grounded electrode via a signal generator.

ions motion in the trap and of the stability region. We find Poincaré's sections corresponding to different stability areas and relate them to the observed beam dynamics.

The design and operation of the EIBT has been described previously in details [1] and a schematic drawing of the ion trap is shown in Fig. 1. The trap consists in a set of coaxial cylindrical electrodes roughly equivalent to two spherical mirrors, the electrostatic analog of a Fabry-Perot interferometer. The configuration of the trap is defined by the potentials of five of these electrodes $\{V_1, V_2, V_3, V_4, V_z\}$, the others being grounded. The length of the trap is 422mm and the inner radius of

the electrodes varies from 8mm to 13mm. An oscillating potential $V_{ex} \sin(\omega_{ex}t)$ can be applied to one of the grounded electrodes, where both V_{ex} (a few volts) and ω_{ex} (a few MHz) are adjustable.

The large number of parameters implied in the tuning of the EIBT makes changing setup difficult as it requires a lengthy trial and error procedure. In a previous article [10], we presented a method to obtain an analytical formula of the potential inside the EIBT. Using this method, we calculate the potential on the axis $V(z)$ as a function of the five potentials applied to the electrodes. The general solution of the Laplace equation in cylindrical symmetry, is a series of the form

$$V(r, z) = \sum_{n=0}^{+\infty} \frac{(-1)^n}{2^{2n}(n!)^2} r^{2n} V^{(2n)}(z). \quad (1)$$

If we limit ourselves to quadratic terms (we shall come back on this approximation below), the trajectory of an ion in the trap, without any external excitation, is described by the following set of equations :

$$\frac{d^2z}{dt^2} = \left(-\frac{dV(z)}{dz} + \frac{1}{4} r^2 \frac{d^3V(z)}{dz^3} \right) \quad (2a)$$

$$\frac{d^2r}{dt^2} = \frac{1}{2} r \frac{d^2V(z)}{dz^2}, \quad (2b)$$

where, in order to have dimensionless equations, we made the following substitutions : $z \rightarrow \frac{z}{L}$, $r \rightarrow \frac{r}{L}$, $t \rightarrow \frac{t}{\tau}$ and $V_i \rightarrow \frac{V_i}{E}$, where L is the half-length of the trap, $v_0 = \sqrt{\frac{2qE}{m}}$, E is the acceleration voltage and $\tau = \frac{L}{v_0}$.

With $z(0) = 0$, $r(0) = 0$, $\frac{dz}{dt}(t=0) = 1$, Eq. (2a) describes the motion $z(t)$ along the z -axis, which is periodic of period $T = 1/f_z$. Substituting in Eq. (2b), we obtain the following Hill's equation [11] :

$$\frac{d^2r}{dt^2} - \left(\frac{1}{2} \frac{d^2V(z(t))}{dz^2} \right) r = 0. \quad (3)$$

This corresponds to a change from the trap reference frame to the ion one. The longitudinal motion of the ion plays here the same role as the quadrupole traps radio-frequency. The principal matrix of (3) is

$$M(t) = \begin{pmatrix} \psi_1(t, t_0) & \psi_2(t, t_0) \\ \dot{\psi}_1(t, t_0) & \dot{\psi}_2(t, t_0) \end{pmatrix}, \quad (4)$$

where $\psi_1(t, t_0)$ is the solution of Eq. (3) with initial conditions $\psi_1(t_0, t_0) = 1$ and $\dot{\psi}_1(t_0, t_0) = 0$, and $\psi_2(t, t_0)$ with $\psi_2(t_0, t_0) = 0$ and $\dot{\psi}_2(t_0, t_0) = 1$ respectively. Liouville's formula [12] shows that $\det M(t, t_0) = 1$ and therefore the characteristic equation of the monodromy matrix $M(t_0 + T)$ is given by $x^2 - 2\Delta x + 1 = 0$ where :

$$\Delta = \text{Tr}(M(t_0+T)) = \frac{\psi_1(t_0 + T, t_0) + \dot{\psi}_2(t_0 + T, t_0)}{2}.$$

Applying Floquet's theorem [12], we know that if $\Delta^2 > 1$, one of the two solutions is unbound, while for $\Delta^2 < 1$ there are two bounded solutions :

$$r(t) = e^{\pm i \frac{\pi}{T} \beta t} p_{\pm}(t), \quad (5)$$

where $p_{\pm}(t+T) = p_{\pm}(t)$ and $\Delta = \cos(\pi\beta)$. β is often called the stability parameter [2]. Hill's equation is stable, and thus trapping can be observed, when $|\Delta| < 1$, which is equivalent to $0 + 2k\pi < \beta < 1 + 2k\pi \quad \forall k \in \mathbb{Z}$.

We performed experiments using ion beams produced by the SIMPA[13] 14.5GHz electron cyclotron resonance ion source (ECRIS), accelerated to $E = 5.2\text{keV}/\text{charge}$. A magnetic dipole enables us to select the ions by their mass/charge ratio. An ion beam is continuously injected into the trap, in a potential configuration corresponding to no entrance mirror and a closed output mirror. A sequencer is used to activate a set of fast high-voltage switches to close the entrance mirror, trapping the ions, which then oscillate between the two mirrors with a period of $\approx 2\mu\text{s}$. The number of ions remaining in the trap after a fixed time (typically $500\mu\text{s}$) can be measured by switching off the exit mirror : particles are ejected out of the trap and hit a faraday cup. The signal is processed by a charge pre-amplifier and a double delay line amplifier. After calibration, the uncertainty on the number of ions is $\approx 10\%$. In this article, we present experimental data that was observed with Ne^{5+} at $5.2\text{kV}/\text{charge}$. We varied only two of the five potentials, V_1 and V_z , the three others, V_2 , V_3 and V_4 being fixed at a constant value, respectively 5.85kV , 4.15kV and 1.65kV .

Figure 2 shows a comparison between the theory outlined above and experiment. The contours show constant values $|\Delta| - 1$ and the stability region is defined by $|\Delta| - 1 < 0$. The shaded map represents the number of ions remaining after $500\mu\text{s}$ of trapping in a given configuration of (V_z, V_1) . For each point, we made several trapping cycles to obtain the average number of ions trapped in this configuration. The resolution of the experimental map is 10V along V_z and 50V along V_1 .

Configurations where trapping can be observed experimentally are contained in the stability region defined by Floquet's theory. However, as we can see on Fig. 2, some settings (e.g., in the region marked C) are predicted theoretically to be stable, which is not observed experimentally. Complementary to our analytical approach, we have developed a 3D C++ code based on the GSL [14] library, able to simulate individual particle motions in the trap, with accurate conservation of the energy and momentum. Since the potential is derived from an analytical formula, these simulations are two order of magnitude faster than what can be achieved with commercial software and energy conservation can be guaranteed over trapping times of milliseconds.

The Poincaré sections corresponding to the three points denoted A , B and C on Fig. 2, evaluated with our code, are plotted on Fig. 3. We have taken into account

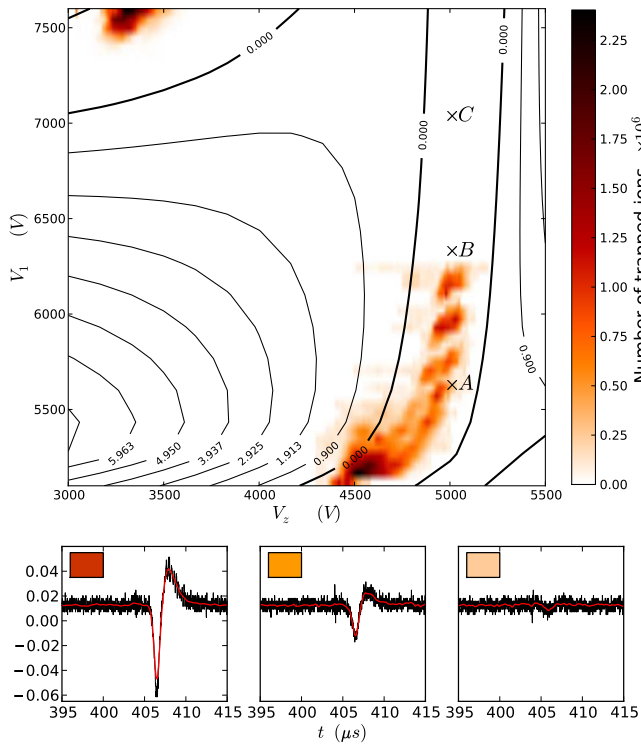


FIGURE 2. (Color online) Comparison between theory and experiment : contour lines represent constant values of the stability coefficient $|\Delta| - 1$ and the shaded map represents number of ions remaining after $500\mu\text{s}$ of trapping in this configuration. Signals recorded from the charge amplifier connected to the faraday cup are presented in the lower part of the figure, together with the color code used in the upper part.

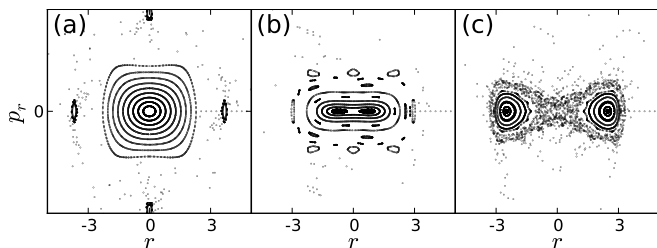


FIGURE 3. Three Poincaré sections corresponding respectively to point A, B and C on Fig. 2. The abscissa represents the radial position while the ordinate is the radial momentum of the particles (dimensionless). We observe a transition from a mode centered on $r = 0$ to a mode centered on $r \neq 0$.

the quadratic radial term in Eq. (2a), which leads to a system of coupled non-linear equations. We observe that point B is located at the transition between a case where trapping is concentrated at the center of the trap and a case where trapping is centered on a given radius, which grows as V_1 increases and where chaotic motion occurs. This proves that trapping is possible in all the predicted areas even if the chaotic region is more difficult to observe.

The results above were obtained with no RF excitation ($V_{ex} = 0$). We now study the EIBT behavior when varying the frequency of the sinusoidal excitation signal for $V_{ex} = 10\text{V}$ with a fixed set of electrode potentials ($V_1 = 7.6\text{kV}$, $V_z = 3.23\text{kV}$). When the excitation frequency is resonant with the ions motion frequency, ions gain energy at each oscillation and their trajectory becomes unstable as shown in [15]. These resonances occur when

$$nf_z + mf_r = f_{ex}, \quad \forall(n, m, k) \in \mathbb{Z}^3 \quad (6)$$

where $f_{ex} = \omega_{ex}/2\pi$, $f_r = \frac{\pi}{T}\beta f_z$ is the modulation of the radial motion [see Eq. (5)]. Figure 4 shows that the resonances appears at the frequencies predicted theoretically by the calculation of β , providing another confirmation of this approach. Note that only one species (Ne^{5+}) is trapped. This kind of resonance can not only be used to monitor the number of ions in the trap, but also leads to a new mass spectrometry method.

The EIBT has already been used as TOF mass spectrometer [8]. This technique can be compared to what is achieved with Penning traps, where ions oscillations are recorded to be analyzed by Fourier transform, giving a mass spectrum [16]. This is only possible if the potentials are chosen in order to be in the “synchronization-mode” [17], where the ions stay bunched, resisting the coulomb repulsion. This counterintuitive phenomenon is explained in [8] and requires a minimum number of trapped ions (few millions).

Synchronization restricts the use of the EIBT as a mass spectrometer in two ways. First, the unavoidable ion losses during trapping limit the time of synchronization and thus of observation, leading to a reduced upper bound of the mass spectrum’s resolution. Second, as mentioned in Ref. [8], synchronization tends to aggregate in the same bunch species whose charge/mass ratio are close. This is known in mass spectrometry as “peak-coalescence” and limits the resolving power.

The results presented above suggest that an EIBT can be used for mass spectrometry in the same way as quadrupole traps, where each ion species is successively ejected from the trap with a parametric excitation [16]. Usual methods (e.g., electrospray) could be used to ionize samples and send the resulting ions into an EIBT. Since the oscillation frequency is proportional to the square root of the charge/mass ratio, sweeping the excitation frequency f_{ex} will provide a mass spectrum of the desired range. Besides the simplicity of the setup, this technique has two fundamental advantages. First it is independent of synchronization and thus is limited neither by synchronization time nor by peak-coalescence. Second, the stability diagram shown on Fig. 2 is computed only with Eq. (3), whose only parameters are the ratios of the trapping potentials to the accelerating potential V_i/E . This means that all the charged particles produced by ionization will be trapped independently of their mass and charge. This

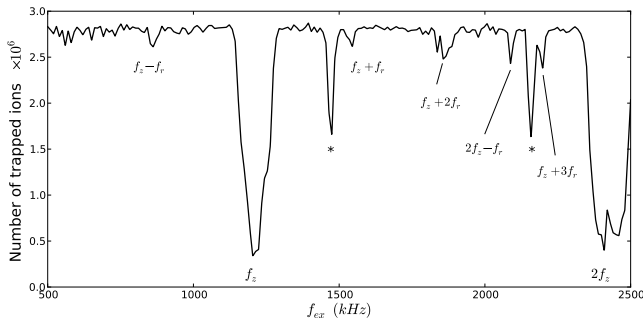


FIGURE 4. Experimental observation of the parametric resonances when $f_{ex} = n f_z + m f_r$ with n and m integers for $N e^{5+}$ at 5.2keV/charge. As on Fig. 2, each point represents the average of the ion signal on the faraday cup over several trapping cycles of $500\mu s$ for each frequency. The peak marked with * are not yet understood.

is very different from quadrupole traps where the stability of the trapping depends on the charge/mass ratio, limiting the range of the species that can be trapped and analyzed.

The resonances illustrated on Fig. 4 are broad and the resolution achieved ($M/\delta M \simeq 100$) cannot compete with advanced techniques. However, many parameters can be optimized and all the techniques dedicated to the quadrupole mass filters could be applied to enhance the resolution. For instance, we have noticed that the peaks are narrower when V_z is tuned or when the radial extent of the injected beam is reduced by closing a set of upstream vertical slits.

Finally, one should note that this model can be applied directly to the ConeTrap [4] and electrostatic rings [5, 6] since the only requirement for the radial motion to be governed by a Hill's equation is to have ions moving periodically in an electrostatic field. An analog method has recently been proposed with an anharmonic potential [18] but the lack of theoretical treatment and the over simplified setup left the advantages of the technique undisclosed.

In this work, we have shown both theoretically and experimentally that the radial motion of ions in a EIBT is ruled by Hill's equation, in the same way as quadrupole traps are. Using this similarity, we were able to predict stability regions, which is of the utmost importance for the use of this kind of traps. This formalism also allowed us to unveil some fundamental phenomena like the existence of parametric resonances when the motion is excited by a radiofrequency. This parallelism is easy to pursue and provides reliable tools to explore the physics of EIBT. Finally we propose a new technique of mass spectrometry using the EIBT, which reveals its ability to perform mass analysis over an unbound mass range.

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- [1] D. Zajfman, O. Heber, L. Vejby-Christensen, I. Ben-Itzhak, M. Rappaport, R. Fishman, and M. Dahan, *Phys. Rev. A*, **55**, R1577 (1997).
- [2] F. G. Major, V. N. Gheorghe, and G. Werth, *Charged Particle Traps* (Springer, 2005) ISBN 978-3-540-22043-5, pp. 17–49.
- [3] M. Larsson, *Reports on Progress in Physics*, **58**, 1267 (1995).
- [4] H. T. Schmidt, H. Cederquist, J. Jensen, and A. Fardi, *Nucl. Instrum. Meth. B*, **173**, 523 (2001).
- [5] S. P. Møller, *Nucl. Instrum. Meth. A*, **394**, 281 (1997).
- [6] J. Bernard, G. Montagne, R. Brédy, B. Terpend-Ordaciere, A. Bourgey, M. Kerleroux, L. Chen, H. T. Schmidt, H. Cederquist, and S. Martin, *Rev. Sci. Instrum.*, **79**, 075109 (2008).
- [7] L. H. Andersen, O. Heber, and D. Zajfman, *J. Phys. B : At. Mol. Opt. Phys.*, **37**, R57 (2004).
- [8] D. Strasser, T. Geyer, H. B. Pedersen, O. Heber, S. Goldberg, B. Amarant, A. Diner, Y. Rudich, I. Sagi, M. Rappaport, D. J. Tannor, and D. Zajfman, *Phys. Rev. Lett.*, **89**, 283204 (2002).
- [9] M. Lange, M. Froese, S. Menk, J. Varju, R. Bastert, K. Blaum, J. R. C. López-Urrutia, F. Fellenberger, M. Grieser, R. von Hahn, O. Heber, K.-U. Kühnel, F. Laux, D. A. Orlov, M. L. Rappaport, R. Repnow, C. D. Schröter, D. Schwalm, A. Shornikov, T. Sieber, Y. Toker, J. Ullrich, A. Wolf, and D. Zajfman, *Review of Scientific Instruments*, **81**, 055105 (2010).
- [10] A. Vallette and P. Indelicato, *Phys. Rev. ST Accel. Beams*, **13**, 114001 (2010).
- [11] G. Hill, *Acta Mathematica*, **8**, 1 (1886/12/13/).
- [12] J. K. Hale and H. Kocak, *Dynamics and bifurcations*, Vol. 3 (Springer, 1991).
- [13] A. Gumberidze, M. Trassinelli, N. Adrouche, C. I. Szabo, P. Indelicato, F. Haranger, J.-M. Isac, E. Lamour, E.-O. L. Bigot, J. Merot, C. Prigent, J.-P. Rozet, and D. Vernhet, *Rev. Sci. Instrum.*, **81**, 033303 (2010).
- [14] M. Galassi and al, *GNU Scientific Library Reference Manual (3rd Ed.)* (2008) ISBN ISBN 0954612078.
- [15] X. Z. Chu, M. Holzki, R. Alheit, and G. Weitha, *International Journal of Mass Spectrometry and Ion Processes*, **173**, 107 (1998), ISSN 0168-1176.
- [16] F. G. Major, V. N. Gheorghe, and G. Werth, *Charged Particle Traps II, Applications* (Springer, 2009) ISBN 978-3-540-92260-5, pp. 38–80.
- [17] H. B. Pedersen, D. Strasser, B. Amarant, O. Heber, M. L. Rappaport, and D. Zajfman, *Phys. Rev. A*, **65**, 042704 (2002).
- [18] A. V. Ermakov and B. J. Hinch, *Review of Scientific Ins-*

truments, **81**, 013107 (2010).