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) are taking an important place in between very low-energy charged-particles storage devices, such as quadrupole and Penning traps and high energy storage rings. With the ConeTrap, electrostatic rings and the Mini-Ring, 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., 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 or cooled at cryogenic temperatures.

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 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 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 \( \omega_{ex} \) (a few MHz) are adjustable.

The large number of parameters implied in the tuning of the EIBT makes changing setup difficult as it requires few MHz) are adjustable.

### Hill’s equation

The Hill’s equation is a series of the form

\[
V(r, z) = \sum_{n=0}^{\infty} \frac{(-1)^n}{2^{2n}(n!)^2} r^{2n} V^{(2n)}(z). \tag{1}
\]

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:

\[
\begin{align*}
\frac{d^2z}{dt^2} &= -\frac{dV(z)}{dz} + \frac{1}{2}\frac{dV}{dz} \frac{d^2V(z)}{dz^2}, \tag{2a} \\
\frac{d^2r}{dt^2} &= \frac{1}{2}\frac{dV}{dz} \frac{d^2V(z)}{dz^2}. \tag{2b}
\end{align*}
\]

where, in order to have dimensionless equations, we made the following substitutions: \( z \to \frac{z}{T}, r \to \frac{r}{L}, t \to \frac{t}{\tau} \) and \( V_\tau \to \frac{V}{E} \), where \( L \) is the half-length of the trap, \( v_0 = \sqrt{\frac{2Ze}{m}}, E \) is the acceleration voltage and \( \tau = \frac{L}{v_0} \).

With \( z(0) = 0, r(0) = 0, \frac{dy}{dx}(0) = 0 \), Eq. \( 2a \) describes the motion \( z(t) \) along the \( z \)-axis, which is periodic of period \( T = 1/f_z \). Substituting in Eq. \( 2a \), we obtain the following Hill’s equation:

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

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 radiofrequency. The principal matrix of \( 3 \) is

\[
M(t) = \begin{pmatrix}
\psi_1(t, t_0) & \psi_2(t, t_0) \\
\psi_1(t, t_0) & \psi_2(t, t_0)
\end{pmatrix}, \tag{4}
\]

where \( \psi_1(t, t_0) \) is the solution of Eq. \( 3 \) with initial conditions \( \psi_1(t_0, t_0) = 1 \) and \( \psi_1(t_0, t_0) = 0 \), and \( \psi_2(t, t_0) \) with \( \psi_2(t_0, t_0) = 0 \) and \( \psi_2(t_0, t_0) = 1 \) respectively. Liouville’s formula shows that det \( M(t, t_0) = 1 \) and therefore the characteristic equation of the monodromy matrix \( M(t_0 + T) \) is given by \( x^2 - 2ax + 1 = 0 \) where:

\[
\Delta = Tr(M(t_0 + T)) = \frac{\psi_1(t_0 + T, t_0) + \psi_2(t_0 + T, t_0)}{2}.
\]

Applying Floquet’s theorem, we know that if \( \Delta^2 > 1 \), one of the two solutions is unbound, while for \( \Delta^2 < 1 \) there are two bounded solutions:

\[
r(t) = e^{\frac{i}{2} \sqrt{2} \beta} p_\pm(t), \tag{5}
\]

where \( p_\pm(t + T) = p_\pm(t) \) and \( \Delta = \cos(\pi \beta) \). \( \beta \) is often called the stability parameter.

Hill’s equation is stable, and thus trapping can be observed, when \( |\Delta| < 1 \), which is equivalent to \( 0 < k \pi < \beta < 1 + 2k \pi \), \( \forall k \in Z \).

We performed experiments using ion beams produced by the SIMPA 14.5GHz electron cyclotron resonance ion source (ECRIS), accelerated to \( E = 5.2 \text{keV/charge} \). 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, and the trap, which then oscillate between the two mirrors with a period of \( \approx 2 \mu s \). 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 5.2kV/charge. We varied only two of the five potentials, \( V_1 \) and \( V_2 \), the three others, \( V_3 \), \( V_4 \) and \( V_5 \) 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 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...
The results above where obtained with no RF excitation ($V_{ex} = 0$). We now study the EIBT behavior when varying the frequency of the sinusoidal excitation signal for $V_{ex} = 10$V with a fixed set of electrode potentials ($V_{1} = 7.6$ kV, $V_{2} = 3.23$ 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 [17]. These resonances occur when

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

where $f_{ex} = \omega_{ex}/2\pi$, $f_r = \beta f_z$ is the modulation of the radial motion [see Eq. (5)]. Figure 3 shows that the resonances appears at the frequencies predicted theoretically by the calculation of $\beta$, 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 [10]. 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. (4), whose only parameters are the ratios of the trapping potentials to the accelerating potential $V_{1}/E$. This means that all the charged particles produced by ionization will be trapped independently of their mass and charge. This
are narrower when solution. For instance, we have noticed that the peaks
of EIBT. Finally we propose a new technique of mass
are governed by a Hill’s equation is to have ions moving

d be tuned or when the the radial

The resonances illustrated on Fig. 4 are broad and the resolution achieved (M/δM ≃ 100) cannot compete with
anharmonic potential but the lack of theoretical treatment and the

Finally, one should note that this model can be applied
directly to the ConeTrap and electrostatic rings 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 but the lack of theoretical treatment and the

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 paracellism 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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