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TWO-ELECTRODE DESIGN FOR ELECTROSTATIC ION TRAP INTEGRABLE IN POLAR COORDINATES

K.V. Solovyev[1,2], *M.V. Vinogradova*[1]

[1] Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russian Federation

[2]Institute for Analytical Instrumentation of the Russian Academy of Sciences, St. Petersburg, Russian Federation

An electrostatic field with a square additive dependence on one of coordinates, also providing integrability of charged particle motion equations has been studied in the paper. The conditions of ion-motion finiteness were found for this field and in doing so it was shown the ion trap constructability. Potential parameter values providing a presence of sufficient workspace between two field-defining electrodes were revealed. An algorithm of optimal matching in beam characteristics and electrodes' configuration was synthesized. To test the operability of the designed algorithm, three-dimensional equipotentials and a trajectory inside the ion-trap workspace were constructed. The ion trap designed in our studies can be put to experimental use as a mass spectrometer, extending the class of electrostatic ion traps presented by well-known Orbitrap and Cassini trap.

Keywords: mass spectrometry, ion trap, ideal focusing

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ДВУХЭЛЕКТРОДНАЯ РЕАЛИЗАЦИЯ ЭЛЕКТРОСТАТИЧЕСКОЙ ИОННОЙ ЛОВУШКИ, ИНТЕГРИРУЕМОЙ В ПОЛЯРНЫХ КООРДИНАТАХ

К.В. Соловьев[1,2], *М.В. Виноградова*[1]

[1] Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Российская Федерация;

[2]Институт аналитического приборостроения Российской академии наук, Санкт-Петербург, Российская Федерация

В работе исследовано квадратичное (по одной из координат) электростатическое поле, обеспечивающее интегрируемость уравнений движения заряженной частицы. Найдены условия финитности движения иона в этом поле и тем самым показана возможность построения ионной ловушки. Выявлены значения параметра поля, при которых структура эквипотенциалей поля обеспечивает наличие существенного рабочего пространства между двумя полезадающими электродами. Построен алгоритм оптимального согласования характеристик пучка и конфигурации электродов.

Ключевые слова: масс-спектрометрия, ионная ловушка, идеальная фокусировка

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Introduction

Electrostatic ion traps with perfect space and time focusing (PSTF) of the beam are becoming increasingly popular in mass spectrometry. The principle of perfect focusing of ions in an electrostatic field as a basis for designing mass spectrometry devices was patented by Golikov [1]; Makarov constructed the industrially produced OrbiTrap analyzer (see, for example, [5]) using this principle. The so-called Cassinian traps (also with PSTF) [3, 4–6], first proposed by Golikov and studied by Nikitina [7], have also been the center of much attention. Perfect focusing systems are an important area, with research ongoing in this direction.

This article continues a series of studies [8–11] considering a class of integrable electrostatic traps with PSTF. Perfect focusing along the z direction (for definiteness) in the trap is provided by including an additive term z^2 into the potential structure [8, 9]. We have earlier discussed in detail (see [9–11) the conditions for finite motion in traps that are integrable in parabolic and elliptic coordinates. In this case, we mean the coordinate systems separating the variables in the Hamilton–Jacobi equation after isolating oscillatory motion along z.

We have considered the case of integration in the polar coordinate system that we have briefly touched upon in [8]. Analysis was carried out in dimensionless variables that we have also used earlier [8–11].

Conditions for finite ion motion

An expression for the potential providing separation of variables was obtained in [8]:

$$\varphi(r,\gamma,z) = = z^2 - \frac{r^2}{2} + \mu\ln(r) + \varepsilon\frac{\cos 2\gamma}{r^2}, \qquad (1)$$

where μ, ε are the field parameters; $x = r\cos\gamma$, $y = r\sin\gamma$.

Assuming $\mu \neq 0$, (we are going to confirm below that this condition holds true) and introducing a substitution of variables $r = r_1\sqrt{\mu}$, $r = r_2\sqrt{\mu}$, we obtain the following expression from equality (1)

$$\varphi_1 = z_1{}^2 - \frac{r_1^2}{2} + \ln r_1 + \varepsilon_1\frac{\cos 2\gamma}{r^2},$$

where $\varphi_1 = \frac{\varphi}{\mu} - \frac{1}{2}\ln\mu$, $\varepsilon_1 = \frac{\varepsilon}{\mu^2}$.

We can eliminate the parameter μ in expression (1) by means of this scaling, equating this parameter to unity and greatly simplifying further analysis.

The remaining parameter ε considerably affects the topology of field (1), determining both the number of its saddle points in the z = 0 plane and the form of equipotentials. The number of saddle points corresponds to the number of real values of the saddle radius r_s in eight pairs (r_s,γ_s) of polar coordinates

$$\left(\sqrt{1\pm\sqrt{1+8\varepsilon}}\Big/\sqrt{2},\pi/2\right),$$

$$\left(\sqrt{1\pm\sqrt{1+8\varepsilon}}\Big/\sqrt{2},-\pi/2\right),$$

$$\left(\sqrt{1\pm\sqrt{1-8\varepsilon}}\Big/\sqrt{2},0\right),$$

$$\left(\sqrt{1\pm\sqrt{1-8\varepsilon}}\Big/\sqrt{2},\pi\right)$$

and varies from 2 to 6 as ε in equality (1) takes critical values {–1/8, 0, 1/8}. The topology of field (1) is very important for choosing a system of field-defining electrodes bounding the working volume of the trap.

Ion motion in the $r\gamma$ plane orthogonal to the direction of perfect focusing z is determined by the first integrals

$$\frac{\dot{r}^2}{2} = E - \left(\ln r - \frac{r^2}{2} + \frac{C}{r^2}\right), \qquad (2)$$

$$\frac{r^4\dot{\gamma}^2}{2} = C - \varepsilon\cos 2\gamma, \qquad (3)$$

where E and C are variable separation constants.

$$E = \frac{\dot{r}_0^2 + r_0^2\dot{\gamma}_0^2}{2} + \ln r_0 - -\frac{r_0^2}{2} + \varepsilon\frac{\cos 2\gamma_0}{r_0^2}, \qquad (4)$$

$$C = \frac{r_0^4\dot{\gamma}_0^2}{2} + \varepsilon\cos 2\gamma_0.$$

As usual, we should now find the conditions for finite motion in the $r\gamma$ plane. Evidently, the nature of ion motion along r is determined by the profile of the effective potential

$$U_{eff}(r) = \ln r - \frac{r^2}{2} + \frac{C}{r^2}$$

and the transverse energy E.

Notice that the potential U_{eff} has a well (Fig. 1) in the range of values $0 < C < 1/8$, while the coordinates of the minimum and maximum of $U_{eff}(r)$ are defined as

$$r_{\min,\max} = \frac{\sqrt{1\mp\sqrt{1-8C}}}{2}, \qquad (5)$$

where the minus sign corresponds to the

minimum radius and the plus sign to the maximum radius.

The minimum and maximum values of the effective potential are expressed as

$$U_{eff\,\min,\max} = \pm\frac{\sqrt{1-8C}}{2} + \ln\frac{1\mp\sqrt{1-8C}}{2}.$$

If $C \to 0$, $U_{eff\,min} \to -\infty$, $U_{eff\,max} \to -1/2$;

if $C = 1/8$, the maximum and minimum of the potential U_{eff} coincide:

$$r_{min} = r_{max} = 1,\ U_{eff\,min} = U_{eff\,max} = -(\ln 2)/2,$$

and the well disappears.

The term that hinders particle motion towards the r singularity disappears in the expression of the effective potential with $C \leq 0$ (the same as for $\mu = 0$ in equality (1)); accordingly, the condition $C > 0$ should be satisfied.

To ensure finite motion with $0 < C < 1/8$, the value of the constant E should satisfy the inequalities

$$U_{eff\,min}(C) \leq E < U_{eff\,max}(C).$$

On the other hand, there is an interval of values of the parameter C embedded in the interval $]0.1/8[$, which satisfies the condition for finite motion, for any $E < -(\ln 2)/2$. The upper limit of C is found from the condition $U_{eff\,min}(C) = E$, and there is also a lower limit of the interval for $E > -1/2$, calculated from the condition $U_{eff\,max}(C) = E$.

It is convenient to introduce the quantity

$$\Delta E = E - U_{eff\,min}(C),$$

characterizing the kinetic ion energy.

With constant ΔE, finiteness is observed for

$$0 < C < C_{\max} < 1/8,$$

where $C_{\max}$ is found from the solution of the equation

$$U_{eff\,max}(C_{max}) - U_{eff\,min}(C_{max}) = \Delta E.$$

Notably, the condition for radial stability completely coincides with the case of the classical orbitrap here.

Angular motion is determined by the cosine (with amplitude $|\varepsilon|$) profile of the potential γ well and the value of the C constant. As the oscillations are symmetrical with respect to $\gamma = 0$, it is convenient to choose a negative ε ($\varepsilon < 0$).

Further, the quantity $C \in [-|\varepsilon|,|\varepsilon|[$, mathematically sound in terms of constrained angular motion, limits particle motion in the sector

$$-\gamma_b \leq \gamma \leq \gamma_b,\ \gamma_b = \frac{\arccos(C|\varepsilon|)}{2}. \quad (6)$$

Motion along γ is not limited if $C > |\varepsilon|$, the trajectory of the ion (in case of r finiteness) is located in a ring. Conditions for radial confinement are satisfied provided that the inequalities $0 < C < 1/8$ hold true. Accordingly, the range

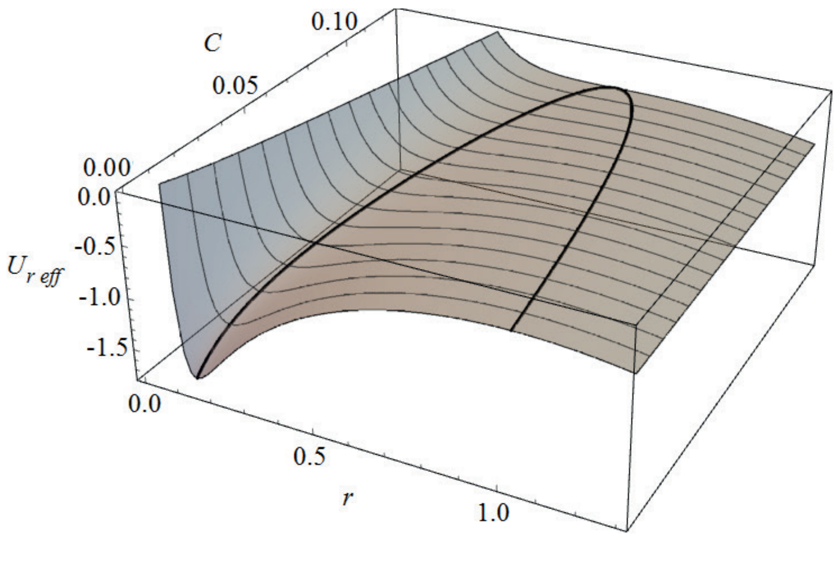

Fig. 1. Graphic representation of function of effective potential $U_{eff}(r, C)$.
Lines indicate the positions of maxima and minima for different C values.

of angular displacements is bounded from below by the segment

$$-\pi/4 \leq \gamma \leq \pi/4.$$

The range of γ oscillations is also bounded from above with $C < 1/8 < |\varepsilon|$. There are clearly no obstacles to both radial and angular finite motion if the appropriate initial data are chosen for the particle. The trajectory of ion motion in the $r\gamma$ plane lies within the region

$$\Omega = [r1,r2] \times [-\gamma b, \gamma b], \qquad (7)$$

where r_1, r_2 are solutions of the equation $U_{eff}(r, C) = E$.

If $r \to 0$, equipotentials of field (1) have asymptotes $\gamma = \pm\pi/4$ theoretically limiting the angular size of the electrode near the singularity point by $\pi/2$. At the same time, the variation range for angles of γ oscillations of ions cannot be less than $[-\pi/4, \pi/4]$. This calls in question whether a trap using a two-electrode field-defining structure is feasible at all, or in other words, whether particle trajectory (at least with $z = 0$) may lie within the region of a constructively acceptable family of equipotentials. This region (position *1*) is shaded in gray in Fig. 2. This region is bounded by a separatrix passing through a saddle point of the field, asymptotically approaching the z axis at angles $\gamma = \pm\pi/4$. (By "constructively acceptable" we mean that a pair of nested equipotentials (from region *1* in Fig. 2, *b*) of the family (electrodes in an actual device) can bound the working volume, i.e., the region of beam motion (region *5* in Fig. 2, *b*). If it turns out that the beam penetrates through the outer electrode of the given pair at any values of the parameters and initial data, more field-defining fragments are to be included in the device's design, which should be avoided.

To answer the question we have formulated above, let us first consider beams that are infinitely thin with respect to r, formed by trajectories of ions propagating with zero radial velocity along the well of the effective potential $U_{eff}(r)$. Projecting these trajectories onto the $r\gamma$ plane yields arcs symmetrical relative to the angle $\gamma = 0$; the radius of each arc is $r_{\min}(C)$, its angular span is $-2\gamma_b(C)$. The arcs are described by formulae (5), (6) and depend on the parameter C associated with the initial data of the motion. Accordingly, the coordinates of the boundary points of the arcs form the following parametrically defined curves for a set of admissible values of C:

$$x_b(C) = r_{\min}(C)\cos(\gamma_b(C)),$$
$$y_b(C) = \pm\, r_{\min}(C)\sin(\gamma_b(C)), \qquad (8)$$

whose position (see Fig. 2, curves *3*) relative to the separatrix equipotential is what interests us.

Theoretically, it is possible to create a

a) *b*)

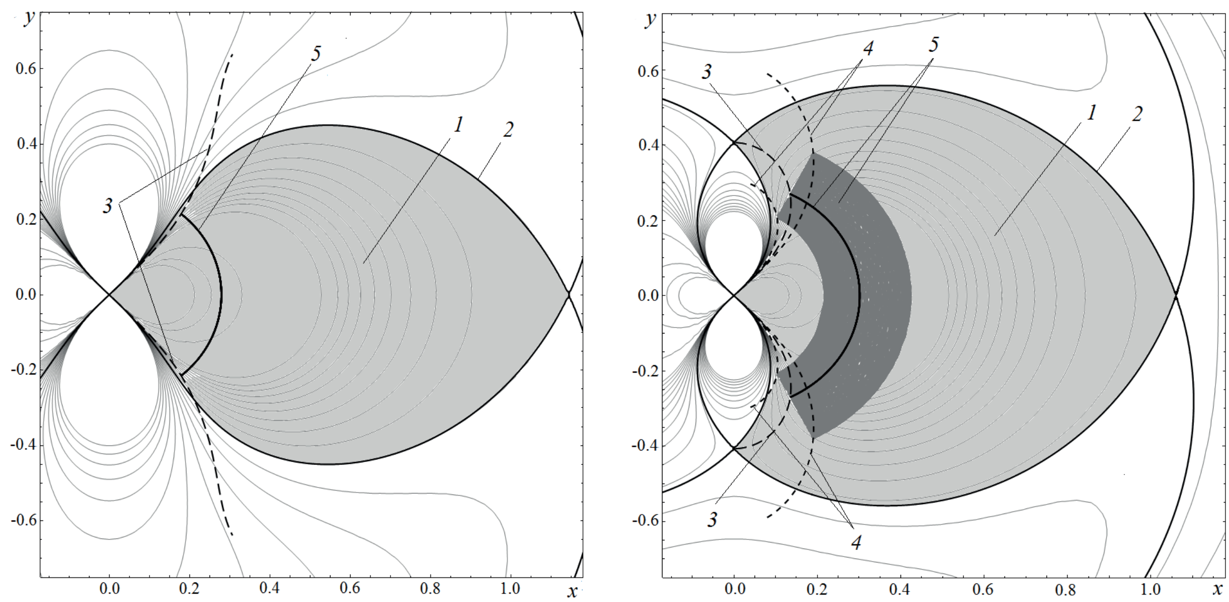

Fig. 2. Ion trajectories and equipotential field structure (1) with $\varepsilon = -0.2$ (*a*) and $\varepsilon = \varepsilon_c$ (*b*): region *1* of constructively acceptable equipotentials; separatrix equipotential *2*; parametrically defined curves (8) *3*; boundaries *4* of beam with non-zero radial velocity; projections *5* of beam trajectories with zero (*a*, *b*) and non-zero (*b*) radial velocities onto plane $r\gamma$

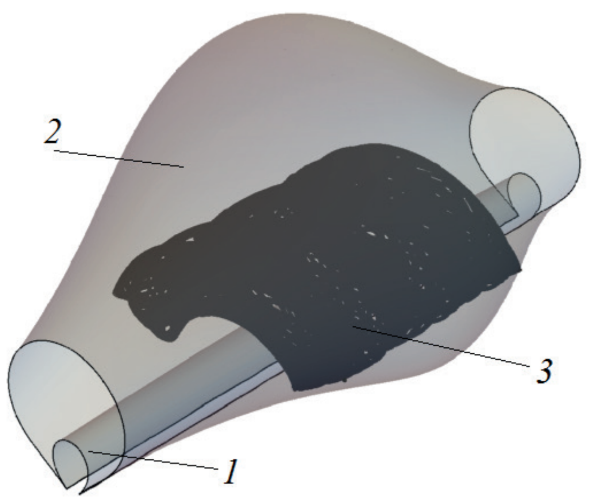

Fig. 3. Example of ion trap based on field (1) with $\varepsilon = \varepsilon_c$. The contours of the inner (*1*) and outer (*2*) electrodes and the ion trajectory (*3*) embedded in the working volume of the trap are shown

two-electrode trap if there is a non-empty interval of C values, such that the points $(x_b(C), y_b(C))$ are located in the region of admissible equipotentials. Notably, non-zero amplitudes of z and r oscillations mean that a gap should exist between the separatrix equipotential and the boundary point of γ oscillations (8). The larger this gap, the greater the phase volume of the ions stored by the trap. Both the position of the separatrix and the form of boundary curve (8) essentially depend on the values of the parameter ε. Equipotential structures with two saddles ($|\varepsilon| > 1/8$) do not allow for sufficient working volume within the separatrix equipotential. For example, the configuration corresponding to

$$\varepsilon = -0.2 < -1/8$$

(see Fig. 2, *a*) is clearly not feasible.

Field configurations with six saddles ($-1/8 < \varepsilon < 0$) offer better options. The range of values $\varepsilon_c < \varepsilon < 0$, where $\varepsilon_c \approx -0.06904$ corresponds to a separatrix that passes simultaneously through the lateral and vertical saddles of field (1), nearest to the center (see Fig. 2, *b*), seems the most attractive. To find ε_c, we use the condition of equal potential (1) at the locations of the given saddle points:

$$\varphi_c = \varphi\left(\sqrt{\frac{1-\sqrt{1+8\varepsilon_c}}{2}}, \frac{\pi}{2}, 0\right) = \varphi\left(\sqrt{\frac{1+\sqrt{1-8\varepsilon_c}}{2}}, 0, 0\right),$$

or

$$\sqrt{1-8\varepsilon_c} + \sqrt{1+8\varepsilon_c} + \ln\frac{1-\sqrt{1+8\varepsilon_c}}{1+\sqrt{1-8\varepsilon_c}} = 0.$$

The actual value of the separatrix potential corresponding to the parameter ε_c is

$$\varphi_c = -\frac{\sqrt{1-8\varepsilon_c}}{2} + \frac{1}{2}\ln\frac{1+\sqrt{1-8\varepsilon_c}}{2} \approx -0.564977.$$

Calculating the dimensions along z of a trap containing ions starting with a nonzero velocity $\dot{z}_0$ from the $z = 0$ plane, we should bear in mind that the three-dimensional equipotential surface of field (1) is pressed against the z axis with distance from the $z = 0$ plane (Fig. 3).

The section of the three-dimensional equipotential

$$f(x, y) + z^2 = d$$

by the plane $z = Z$ has the form

$$f(x, y) = d - Z^2,$$

i.e., it is contained among the equipotentials of the two-dimensional field $f(x,y)$ that is a section of a three-dimensional field by the plane $z = 0$ [8].

Notably, a decrease in the potential with increasing Z corresponds to transition from the separatrix equipotential to internal equipotentials of a region for the given field regions. Accordingly, a cylinder filled with particle trajectories (its base is a region Ω (see formula (7)), and its generator is parallel to the z axis) should be embedded into the surface, which collapses to the z axis with distance from the $z = 0$ plane. Therefore, if we can locate points (8) within a certain equipotential that is internal with respect to the separatrix, we can estimate the admissible dimensions of the beam and the trap along the z coordinate and determine the maximum velocities $\dot{z}_0$ of the ion starting from the symmetry plane. Clearly, taking into account non-zero radial velocities determining the radial size of the region Ω, also requires some space in placing the beam within the interelectrode region.

Notice that if we use trajectories with $\Delta E =$ const, the energy

$$E = \Delta E + U_{eff\,min}(C)$$

turns out to be greater than $U_{eff\,max}(C)$ for a certain C and, therefore, the upper admissible value of C is less than 1/8, since the trajectory leaves the well even before it disappears with decreasing well depth (with increasing C). Meanwhile, the actual position of the boundaries of the region Ω depends on two parameters: C and E (or ΔE). Each C is assigned to two values of $r_{min}(C)$ instead of one: $r_1(C, \Delta E)$, $r_2(C, \Delta E)$ (see formula (7)). As a result, expressions (8) are replaced by pairs of similar parametrically given boundaries (indicated by a short dashed line in Fig. 2, *b*).

Selecting trap parameters

Let us formulate an algorithm for selecting the parameters of the field of a two-electrode ion trap and the initial conditions for the ions confined in this trap.

Step 1. We select the value of the parameter ε in the interval $\varepsilon_c \le \varepsilon < 0$. We select the value of the parameter C allowing for the beam to be located within the working volume with boundaries (8) with zero radial spread. Let the potential of the separatrix surrounding the working volume be equal to φ_0.

Step 2. We assume that the length of the trap along z is equal to $2Z$; we find the potential

$$\varphi_1 = \varphi_0 - Z^2 - \delta,$$

where δ provides the necessary technological gap between the surface of the electrode and the region where the ions from the beam are concentrated.

Step 3. We solve the problem of embedding the beam in an external equipotential $\varphi(x,y,z) = \varphi_1$. We run a test search for the distance between points with a potential φ_1 along a straight line passing through the origin and point $(x_d(C), y_d(C))$ for each boundary point (8). In this case, we take into account the configuration of equipotentials on the $r\gamma$ plane.

To solve the problem, we construct the field distribution along the given straight line, using expressions (1) and (6):

$$U(r,C) = \varphi(r, \gamma_b(C), 0) = -\frac{r^2}{2} + \mu\ln(r) + \varepsilon\frac{\cos\,(\arccos(C/\varepsilon))}{r^2} = U_{eff}(r,C).$$

The field distribution along the limiting ray $\gamma = \gamma_b(C)$ coincides with the effective potential, which means that the coordinates of the intersection points of the beam with the equipotential φ_1 and their positions relative to $r_{min}(C)$ coincide with the coordinates and the positions of the radial boundaries of the beam with the section Ω (7) for the energy $E = \varphi_1$. The critical values of the parameter C limiting the range of its admissible values are determined by the equation

$$\varphi(r_{min}(C), \gamma_b(C), 0) = \varphi_1,$$

giving the tangent point of the equipotential φ_1 and the limiting ray $\varphi(r_{min}(C), \gamma_b(C), 0) = \varphi_1$. The beam has an arc trajectory (in projection onto the $r\gamma$ plane) with critical values of C. For other values of C from the interval of admissible values, the motion occurs in the region Ω. The initial data for the motion is found by the values given for the parameters E and C using expressions (4). The beam fits perfectly into the dimensions of the external working equipotential. The relationship of admissible values of C and φ_1 is similar to that of C and E.

We should point out that this consideration only determines the boundary ions of the beam in the configuration space; to reduce the effect of space charge on the operation of the trap, it is advisable to increase the area

$$S_\Omega = 2\pi(r_2^2(C) - r_1^2(C))\gamma_b(C)$$

of the region Ω (see Eq. (7)) by selecting an appropriate C.

Note. Choosing an internal equipotential, it should be borne in mind that its maximum size (maximum radius of distance from the center) lies in the plane $r\gamma$ for $\gamma = 0$. Accordingly, if the internal radius of the beam is equal to r_1, it is sufficient to choose the following equipotential surface as the internal boundary of the system:

$$\varphi(r,\gamma,z) = \varphi_2,$$

where $\varphi_2 = \varphi(r_1 - \delta r, 0, 0)$ (δr is the necessary technological gap, see *Step 2*).

An example of a trap constructed according to this procedure and filled with a characteristic ion trajectory is shown in Fig. 3.

Conclusion

We have considered the nature of ion motion in an integrable electrostatic trap with variable separation in polar coordinates.

We have found the conditions for finite motion, analyzed the field of the trap and confirmed that only one of the parameters of the potential is significant.

We have established the effect of this parameter on field topology, finding the range of parameter values for a potential structure that can be used for designing a viable ion trap.

We have confirmed that the effective volume of the trap can be bounded by just two electrodes, which simplifies the design of the device.

We have formulated a method for selecting a coordinated configuration of the electrodes and the beam.

The algorithm proposed essentially formulates the constraints for subsequently solving a problem of conditional optimization. The next steps should include maximizing the phase volume of the beam over all phase coordinates and additional one-dimensional optimization of the system with respect to the parameter ε.

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THE AUTHORS

Solovyev Konstantin V.
Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation
k-solovyev@mail.ru

Vinogradova Maria V.
Peter the Great St. Petersburg Polytechnic University
29 Politechnicheskaya St., St. Petersburg, 195251, Russian Federation vinogradova_39@mail.ru

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СВЕДЕНИЯ ОБ АВТОРАХ

СОЛОВЬЕВ Константин Вячеславович – кандидат физико-математических наук, доцент кафедры физической электроники Санкт-Петербургского политехнического университета Петра Великого, младший научный сотрудник Института аналитического приборостроения РАН.

195251, Российская Федерация, г. Санкт-Петербург, Политехническая ул., 29
k-solovyev@mail.ru

ВИНОГРАДОВА Мария Валерьевна – студентка Института физики, нанотехнологий и телекоммуникаций Санкт-Петербургского политехнического университета Петра Великого.

195251, Российская Федерация, г. Санкт-Петербург, Политехническая ул., 29
vinogradova_39@mail.ru