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Perturbation theory for ion motion in quadrupole radio frequency field

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ABSTRACT

Paper develops a perturbation theory for description of ion motion in quadrupole radio frequency (RF) field. First order corrections for the ion phase coordinates caused by field perturbations over one period of the RF field are derived. Transformation matrix of the phase coordinates over one RF period is obtained and stability parameter of the perturbed ion motion is defined in the first order approximation. Results are applied for investigation of stability diagram of ion motion in a quadrupole mass filter. Boundaries of stability are defined in linear approximation and resolving power dependence from the slope of the operating line is obtained. In contrast to previously known results current approach allows obtaining corresponding dependences in semi analytical form expressed in terms of unique solutions of Mathieu equation at the tip of stability.

1. Introduction

Over half century have passed since invention by Paul et al. [1] of mass filtering principles of quadrupole radio frequency fields. By now this technique found wide range of applications in mass spectrometry. Quadrupole mass filters are routinely used as stand alone mass analyzers and as a part of tandem instruments. Principles of quadrupole operation are well investigated theoretically and by means of computer simulations [2]. Experimental practice shows that reliable quadrupole operation sets rather high requirements on machining and assembling accuracy of electrode system [3]. Ideal quadrupole field, for which Mathieu equation theory applies, is only realized in a system of infinite rods of ideal hyperbolic shape. Apart from few exceptions quadrupoles are made of rods with circular cross section and contain field distortions. Even when hyperbolic rods are used, field inside quadrupole is inevitably distorted due to machining and assembling inaccuracies and by fringing fields. Influence of those distortions on quadrupole operation, although minimized in practical devices, is not completely clear as some recent experiments indicate [4]. Also comparatively small periodic perturbations of power supply result in considerable influence on quadrupole operation [5].

Influence of small field perturbation on operation of a quadrupole mass filters can be investigated by means of perturbation theory. Present paper is the first step in development of such theoretical approach and has a target to set up the basis of the method. Because of big volume of associated mathematics this paper deals with the simplest case of ion motion in a mass filter with pure quadrupole field, and perturbation is a shift of ion motion parameters from the tip of stability. Although this case was investigated previously numerically, the method which will be developed in this paper has general applicability and will be used later for description of other types of perturbations.

2. Ion motion equations. Principles of mass filtering

Electrode system of the quadrupole mass filter consists of four parallel rods of hyperbolic cross section arranged symmetrically around common axis (see Fig. 1). With appropriate power supply (positive phase to the pair of opposite rods in X direction, and negative at Y rods) a quadrupole field appears in the inner volume between the rods:

$$\Phi(x, y) = [U + V\cos\Omega(t - t_0)] \cdot \frac{x^2 - y^2}{r_0^2}. \quad (1)$$

Here U and V are constant (DC) part and amplitude of the variable radio frequency (RF) components of periodic power supply on the rods, Ω and t_0 are frequency and initial phase of the RF supply, and r_0 is so-called, "field radius", which is the radius of the inscribed circle between the rods. Equations of motion for ion of mass m and charge e in the field of Eq. (1) are Mathieu equations:

$$\frac{d^2x}{d\xi^2} + (a + 2q\cos 2\xi) \cdot x = 0, \quad (2.a)$$

$$\frac{d^2y}{d\xi^2} - (a + 2q\cos 2\xi) \cdot y = 0. \quad (2.b)$$

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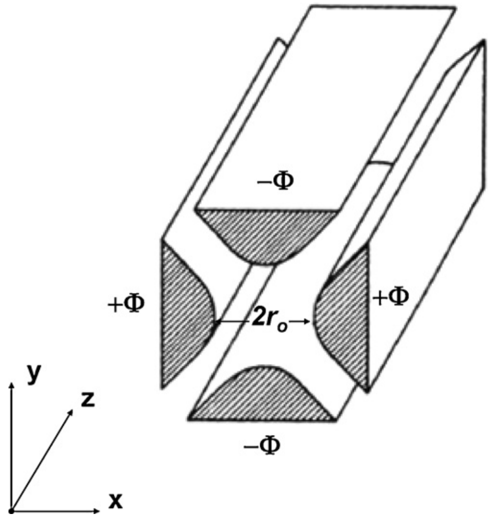

Fig. 1. Electrode system for a quadrupole mass filter with hyperbolic electrodes and potentials of electrodes for generating quadrupole field between rods.

Here dimensionless parameters are used

$$\xi = \frac{\Omega}{2}(t - t_0), \quad a = \frac{8eU}{m\Omega^2 r_0^2}, \quad q = \frac{4eV}{m\Omega^2 r_0^2}. \tag{3}$$

Except from regions of fringing field motion along the quadrupole axis in Z direction happens with constant velocity and is not considered here.

Mass filtering in such device takes place when parameters (3) lie near values, that correspond to the tip of the first stability region: $a_1 = 0.236993$ and $q = 0.705996$. This point is an intersection of two stability boundaries of motion along X and Y directions (see Fig. 2). For any fixed power supply voltages parameters (3) ions of different mass have parameters that appear on the same "operating line" defined by equation $a = 2\lambda q$. Selecting appropriate value of parameter $\lambda = U/V$ operating line can be located just below the tip of the first stability region (see Fig. 2). In this case only ions of particular mass range that falls between the boundaries of stability will pass the filter. Ions of different mass will be rejected to the rods either in X or Y direction due to increase of vibration amplitude.

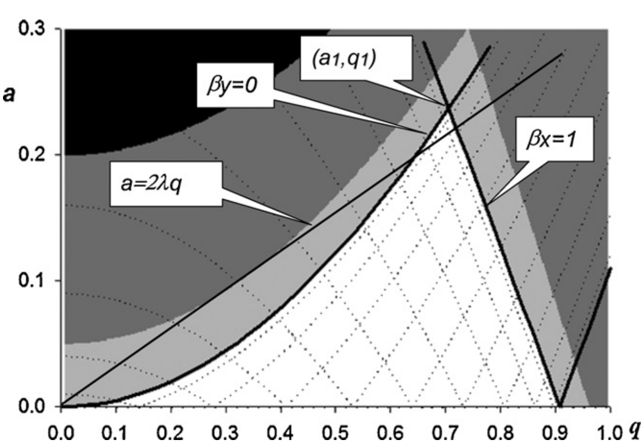

Fig. 2. First region of stability of ion motion in a quadrupole mass filter. Regions of unstable motions are shown by grey color. Dotted lines are curves of equal stability parameter β with step 0.1. Solid lines are boundaries of stability.

3. Matrix method for ion motion description

Solutions of Eqs. (2.a) and (2.b) can be obtained by means of Mathieu equation theory, which is well developed [6]. But for our purposes matrix method [7–9] appears to be most convenient. In particular this method applies also in cases when periodic power supply is not sinusoidal. In this method ion motion is characterized by coordinated of ion at particular phase of the RF supply at each period (stroboscopic coordinates). Let us consider first of Eqs. (2.a) and (2.b), i.e. equation of motion along X direction. Stroboscopic coordinates at the beginning of each RF cycle are defined as follows:

$$x_n = x(n\pi), \quad v_n = x'(n\pi) \tag{4}$$

Here x' stands for derivative of coordinate over dimensionless time variable ξ, π is the RF period in dimensionless units and $n = 0, 1, 2 \ldots$ – is the period number. For a linear equation (2.a) solution at other values of the RF phase τ can be expressed in terms of two independent solutions $u_1(\tau)$ and $u_2(\tau)$ as follows

$$x(n\pi + \tau) = x_n \cdot u_1(\tau) + v_n \cdot u_2(\tau). \tag{5}$$

Here we introduced a new variable τ according with $\xi = n\pi + \tau$ so that new variable spans over a single RF cycle $0 \le \tau \le \pi$. Derivatives over variable τ are equal to corresponding derivatives over ξ so that Eqs. (2.a) and (2.b) are the same when using new variable. "Special" solutions are defined by the following initial conditions

$$u_1(0) = 1; \quad u_1'(0) = 0 \quad \text{and} \quad u_2(0) = 0; \quad u_2'(0) = 1. \tag{6}$$

Coefficients of motion Eqs. (2.a) and (2.b) are periodic and independent of the cycle number n. That is why special solutions are the same when computed from the beginning of each cycle. Thus Eq. (5) applies to any RF cycle, which is advantage of this representation of ion trajectory. Velocity of ion is defined from Eq. (5) as follows

$$v(n\pi + \tau) = x_n \cdot u_1'(\tau) + v_n \cdot u_2'(\tau). \tag{7}$$

From Eqs. (5) and (7) one can derive recurrence relations between ion phase coordinates at the beginning and end of each RF cycle in the form of matrix equation

$$\begin{pmatrix} x_{n+1} \\ v_{n+1} \end{pmatrix} = \begin{pmatrix} m_{11}x_n + m_{12}v_n \\ m_{21}x_n + m_{22}v_n \end{pmatrix} = \mathbf{M} \cdot \begin{pmatrix} x_n \\ v_n \end{pmatrix}, \tag{8}$$

where "monodromy" matrix $\mathbf{M}$ is calculated from values of special solutions at the very end of the RF cycle:

$$\mathbf{M} = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = \begin{bmatrix} u_1(\pi) & u_2(\pi) \\ u_1'(\pi) & u_2'(\pi) \end{bmatrix}. \tag{9}$$

It follows from recurrence relation (8) that phase coordinates at the beginning of each RF cycle can be expressed in terms of initial phase coordinates at the beginning of the first cycle using powers of monodromy matrix:

$$\begin{pmatrix} x_n \\ v_n \end{pmatrix} = \mathbf{M}^n \cdot \begin{pmatrix} x_0 \\ v_0 \end{pmatrix}. \tag{10}$$

For matrices of size 2×2 powers are calculated analytically [9] as follows

$$\mathbf{M}^n = \begin{vmatrix} \cos \pi\beta n + A \sin \pi\beta n & B \sin \pi\beta n \\ -\Gamma \sin \pi\beta n & \cos \pi\beta n - A \sin \pi\beta n \end{vmatrix}, \tag{11}$$

where

$$A = \frac{m_{11} - m_{22}}{2 \sin \pi\beta}, \quad B = \frac{m_{12}}{\sin \pi\beta}, \quad \Gamma = \frac{-m_{21}}{\sin \pi\beta}. \tag{12}$$