EFFECT OF ION ENTRY PHASE, RADIAL VELOCITY AND POSITION ON QUADRUPOLE MASS FILTER OPERATION

P. K. GHOSH, ABHA JAIN AND R. NAGARAJAN*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016 (India)

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ABSTRACT

The effect of the ion entry conditions on quadrupole mass filter operation in terms of resolution–ion transmission characteristics has been studied by numerical calculations of ion trajectories for various sets of ion injection velocity, position and phase. The conventional “stability diagram” on the a–q plane describing the parametric region of stable solutions of Mathieu’s equation is contrasted with “practical stability diagrams” describing the parametric regions of “bounded” solutions of Mathieu’s equation. It is shown that if the initial radial velocity–position–phase injection conditions are specified, the mass filter can be operated at high resolution using constant a/q lines other than that required for the apex region of the conventional stability diagram. An extension of the definition of resolution has been proposed to apply to specific initial ion injection conditions.

INTRODUCTION

The stability diagram obtained from the qualitative (i.e., without explicit calculations of x(t) and y(t)) solution of Mathieu’s equation is generally used [1] to understand the operation of the quadrupole mass filter using hyperbolic electrode surfaces. The innate stability or instability of ions described by the stable and unstable regions in the a–q parameter space is independent of the initial conditions of entry of the ions and is solely determined by the values of the parameters a and q. But whether or not an injected ion will be transmitted through a field of finite dimensions is determined by the initial conditions of ion entry. Two cases arise: (1) where the ion is inherently unstable but is transmitted through the field

* Present address: Department of Chemical Engineering, State University of New York at Buffalo, N.Y., U.S.A.
as its amplitude of oscillation remains bounded and is less than the field dimension for the finite number of r.f. cycles it experiences, and (2) when the inherently stable ion is lost to the electrode surface because the amplitude of its oscillations, though finite, exceeds the bound imposed by the finite field dimension. So, for practical mass spectrometer operations, it is necessary to locate the parametric region corresponding to bounded ion trajectories for given initial conditions of radial velocity, position and phase of injection. Such “practical stability diagrams” representing regions of bounded ion oscillations, have the potential to explain the transmission behaviour of a sample of ions where the entry conditions are of a particular distribution.

To realize this objective, ion trajectories first need to be studied for a wide range of initial conditions of position and velocity as well as of phase. In preliminary work [2], we studied ion trajectories for several combinations of position and radial velocities at zero initial phase and attempted to relate empirically the location of practical stability diagram peaks to the initial conditions through resolution, as commonly defined [1, 3]. In a practical instrument, however, injection ordinarily takes place continuously for all phases, and trajectory information is needed accordingly. Such information, when available, can be used, with appropriate averaging, to predict resolution and peak shape in an actual spectrum. In the present paper we report the results of our investigation of the effect of varying the initial phase on resolution–ion transmission characteristics and discuss the effects of a constant $a/q$ ratio line on mass filter resolution for specific initial conditions of ion injection.

ION Trajectory Computations

The motion of ions in a two-dimensional quadrupole field is described by the differential equations

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

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

where $a = 8eU/mr_0^2\omega^2$, $q = 4eV/mr_0^2\omega^2$ and $\xi = \omega t/2$; $m$ and $e$ are respectively the ionic mass and the charge, $U$ the d.c. component and $V$ the peak r.f. (angular frequency $\omega$) amplitude of the potential on the electrodes, the closest distance between the opposite electrodes being $2r_0$. The method of ion trajectory computation using numerical integration of Mathieu's equation with specific initial conditions has already been described [2]. Various $a, q$ operation points in the range $q = 0.699–0.708$ were chosen along mass scan lines with resolutions
$m_0\Delta m = 100-1000$ (as defined in refs. 1, 3) and ion trajectories were computed for about 160 cycles of ion motion. From the maxima of the trajectories, limiting lines were obtained on the $a, q$ diagram which show the domain of $a, q$ values for which the ion amplitudes remain bounded, i.e., both $x$ and $y$ remain less than $r_0$. Since the $x$ and $y$ equations of motion are independent of one another, various practical stability diagrams were obtained for different combinations of $x_0, x'_0$, $y_0, y'_0$ and $\xi_0$.

The present computations involve eight sets of initial position–velocity conditions, $x_0$ (or $y_0$), $x'_0$ (or $y'_0$) being (in length and length/radian respectively) 0.015, 0.012; 0.010, 0.015; 0.012, 0.010; 0.010, 0.010; 0.015, 0.005; 0.005, 0.010; 0.008, 0.008; 0.010, 0.005; and each such condition for a set of 8 initial phases at entry in the range of $\xi_0 = 0$ to $\pi$, in steps of $\pi/8$.

RESULTS

The results of trajectory computations, in the form of the $a, q$ value of apex points of the practical stability diagrams, are given in Table 1 for the eight sets of initial radial velocity–position and eight initial phases. A set of typical practical stability diagrams is shown in Fig. 1 describing the parametric space of bounded oscillations for the initial phase $\xi_0 = 3\pi/8$. The effect of initial phase variation.
TABLE 1

PRACTICAL STABILITY DIAGRAM APEX POINTS

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a The $a$, $q$ values of the apex points are reported (estimated error ± 0.0001) as a function of the initial conditions. Each section of the Table is for a specific $\xi_o$, wherein the rows and columns represent $(x_0, y_0)$ and $(x_0^*, y_0^*)$ respectively. For numerical values of $x_0, x_0^*$ or $y_0, y_0^*$, the following notations are used: (1) 0.015, 0.012; (2) 0.010, 0.015; (3) 0.012, 0.010; (4) 0.010, 0.010; (5) 0.015, 0.005; (6) 0.005, 0.010; (7) 0.008, 0.008; (8) 0.010, 0.005. Several $x$, $y$ limit lines could not be plotted as the corresponding $x$ ($y$) amplitudes are either too small or too large for intersection with the $r_0/x_0, y_0$ limiting line. $\pi/8 : 0.010, 0.005$; $y$ amplitudes are too small. $\pi/2 : 0.010, 0.015$ and 0.015, 0.012 $y$ amplitudes are too large. $3\pi/8 : 0.010, 0.015$ and 0.015, 0.012 $y$ amplitudes are too large. $3\pi/4 : 0.010, 0.015$ $x$ amplitudes are too small and $y$ amplitudes are too large; also, for 0.015, 0.012; 0.012, 0.010; 0.010, 0.010 $y$ amplitudes are too large.
on the location of the apex point for a given set of initial velocity-position conditions is illustrated in Fig. 2 using the initial conditions \( x_0, x'_0, y_0, y'_0 \) of 0.008, 0.008, 0.008, 0.008 and 0.010, 0.010, 0.008, 0.008 respectively and about sixteen \( \xi_0 \) values.

Fig. 2. Practical stability diagram apex point loci due to initial phase \( \xi_0 \) variation. The circles represent apex points from actual computation for specific initial phases; the \( \xi_0 \) values are shown next to the circles in units of \( \pi/16 \). The locus between the open circles for \( \xi_0 = 12(\pi/16) \) and \( \xi_0 = 14(\pi/16) \), in the absence of information on \( 13(\pi/16) \), is somewhat uncertain.

Errors arise in finding the intersection of the \( x_m/x_0, y_m/y_0 \) versus \( q \) curves with the \( r_0/x_0, y_0 \) limiting line (\( r_0 \) is taken as 0.350) as well as in drawing the \( x, y \) limiting lines of practical stability diagrams. We estimate the overall error in the reported \( a, q \) points at the \( x-y \) limit intersections as less than \( \pm 0.0001 \) for both \( a \) and \( q \). Within this error margin the \( x, y \) limit lines of the practical stability diagrams are essentially parallel to the \( x, y \) limit lines of the conventional stability diagram. In plotting the limit lines of the former, more weight was given to those \( x_m/x_0, y_m/y_0 \) curves wherein actually computed values of maxima occur close to the \( r_0/x_0, y_0 \) limiting line. This reduces any extrapolation or interpolation error. The dispersion of apex point \( a, q \) values for \( \xi_0 = 0 \) and \( \xi_0 = \pi \) in Table 1 shows, for cases which are identical insofar as the mass spectrometer operation is concerned, the extent of computational as well as data processing error for two initial phases differing by \( 2\pi \) radians.
DISCUSSION

There exists no a priori reason to expect that the practical stability diagrams will remain confined within the conventional stability diagram. That this is indeed realized in practice, is shown by the practical stability diagrams occurring beyond the confines of the stability diagram representing the qualitative solution of Mathieu's equation. The shift pattern of the apex points on the $a, q$ plane as a function of the initial velocity–position–phase conditions is complex. While a detailed qualitative correlation involving all the initial conditions is difficult, an explanation of movement of the limit lines with entry phase seems possible. It can be seen from Fig. 2 as well as from the results given in Table 1 that the $x$ limit lines move out farthest around $\zeta_0 = 3\pi/4$ and move in closest around $\zeta_0 = \pi/4$ while for the $y$ limit lines the opposite is true. This correlates reasonably to the entry phase electrode potential and its immediate trend of change with $\zeta$, since, in the $x$ direction the potential is expected to be most strongly focusing for ions around $\zeta_0 = 3\pi/4$ and most weakly focusing around $\zeta_0 = \pi/4$; in the $y$ direction, the potential is expected to be most strongly defocusing around $\zeta_0 = 3\pi/4$ and most weakly defocusing around $\zeta_0 = \pi/4$.

It is clear from Figs. 1 and 2 that the practical stability diagrams will shift, depending on the initial conditions of velocity and position as well as on the phase at injection. Since the mass filter resolution depends on the interval $\Delta q$ in the region of stability on the constant $a/q$ line, the resolution for specific initial ion injection conditions will depend on the location of the practical stability diagram apex point on the $a, q$ plane and hence on the specific initial condition used. The resolution therefore will not be uniquely specified by the $a/q$ ratio but will vary, depending on the initial conditions, and thus the same constant $a/q$ line will correspond to low resolutions for some initial conditions and at the same time that of infinite resolution (i.e., if it goes through the peak of any practical stability diagram) for some other set of initial conditions. It is also obvious from Fig. 1 that at constant $a$, increase in the $q$ of the apex point implies higher resolution, and for constant $q$, an increase in $a$ of the apex point implies lower resolution, both for a constant $a/q$ line of operation. The definition of resolution used by Paul et al. [1, 3] makes use of $a, q$ values of the apex of the conventional stability diagram. Since the $x, y$ limit lines of the practical stability diagrams are parallel to the corresponding limit lines of the conventional stability diagram, one can, on the basis of the slopes of these lines, write

$$\frac{m}{\Delta m} = \frac{q_{\text{apex}}}{\Delta q} = \frac{(0.623 q_{\text{apex}} - a_{q_{\text{apex}}})(1.246 q_{\text{apex}} + a_{q_{\text{apex}}})}{1.869 q_{\text{apex}}(a_{q_{\text{apex}}} - a_{q_{\text{apex}}})}$$

where $q_{\text{apex}}$ and $a_{\text{apex}}$ define the apex point of a practical stability diagram, and $a_{q_{\text{apex}}}$ represents the $a$ value a constant $a/q$ line takes at $q_{\text{apex}}$. The variation of $q_{\text{apex}}$ and $a_{q_{\text{apex}}}$ in the $a, q$ region investigated has little effect on $m/\Delta m$ owing to
the terms in the numerator. Thus, on the basis of an assumption of average values of $q_{apex}$ and $a_{apex}$, one obtains $m/\Delta m = 0.178/(a_{apex}-a_{apex})$ for an expression of resolution which can be applied to individual practical diagrams. For a set of specific values of $x_0, x'_0, y_0, y'_0$ and $\xi_0$, the ions can only be either bounded or beyond the bounds, corresponding to a hundred or zero percent transmission respectively. As a consequence, the resulting mass peaks should be rectangular in such a mode of injection.

The general feature of the locus of practical stability diagram apex points, as shown in Fig. 2, is a closed cycle from $2\xi_0 = 0$ to $2\xi_0 = 2\pi$. The pattern remains essentially the same for all the initial conditions investigated. The observation that, for the beginning of the phase cycle, the $q$ values are relatively smaller is of a general nature. It should be pointed out that, for a given constant $a/q$ line cutting across the practical stability diagram apex point locus, all those phases for which the peak points fall below the intersecting line imply that the ion will be lost when entry at the corresponding phases takes place. Those entry phases for which the peak points are above the line contribute to transmission trajectories. Also, the larger the total $\Delta q$ intercept of the peak point locus, the poorer will be the resolution for a given radial velocity-position injection. In fact, in such cases there seems to be merit in operating the filter part of the phase cycle so as to keep only a small portion of the apex locus above the constant $a/q$ line. The overall effect, when $x_0, x'_0, y_0, y'_0$ also vary, will depend on the energy distribution and injection points of the initial ion sample. The parallelism of the practical stability diagram limit lines with the limit lines of the conventional stability diagrams indicates a relationship of $\beta_z$ (or $\beta_y$) with $x_0/r_0, x'_0/r_0$ (or $y_0/r_0, y'_0/r_0$) and $\xi_0$. In

![Fig. 3. Criterion used for upper bound of trajectories.](image-url)
principle, these two quantitative relationships can evolve from Table 1, from which any practical stability diagram, and the apex point locus for the entire phase cycle, can be generated.

One of the limitations of the present set of calculations is the criterion used for arriving at parameter limits for bounded oscillations by considering only those trajectories which go beyond the bound of field dimension in either the $x$ or $y$ direction independently, and no attempt has been made to consider both amplitudes simultaneously (Fig. 3). This should have been done, as those ions, which have both $x$ and $y$ values higher than the imposed bound, i.e., between the hyperbolic rods near the zero potential lines, are not fully taken into account. However, calculations show that the conditions for which the $x$ amplitudes are very large, the $y$ amplitudes are very small, and vice versa [2]. This means that if the ion has an amplitude too high in one direction, it is also close to the same axis, and the criterion used for arriving at the parameter limits for bounded oscillations has inherently negligible error.

**NOTE ADDED IN PROOF**

Since submission of this paper, there have been comments in the literature (Int. J. Mass Spectrom. Ion Phys., 14 (1974) 317) about the limiting values reported in our earlier work. Recently, Arvind Arora of this laboratory checked our results using an entirely different computer program calculating up to 160–200 cycles of ion motion. A check of the results for injection conditions $\xi = 0.01, 0.01; 0.008, 0.008$ using all the $\xi_0$ values and also those for $\xi_0 = 3\pi/8$ using all the initial conditions, show that most of the apex points reported here are within the specified error limits.

**REFERENCES**