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EFFECT OF ENTRY CONDITIONS ON ION TRANSMISSION IN A QUADRUPOLE FIELD

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ABSTRACT

Maximum amplitudes of ion trajectories in a two-dimensional quadrupole field have been computed by numerical integration of Mathieu's equation. The range of initial conditions, such as initial displacement of ions, phase at entry and radial velocity at entry, are those encountered in practical mass spectrometer operations. These computations have been carried out for a and q values along various mass scan lines in the range of $m/\Delta m = 70$–1000. The bounds on the initial displacement of ions and radial velocity at entry are calculated for 100% ion transmission through the field. It is found that the bounds on the initial displacement and radial velocity are higher when both of them are non-zero than when either of them is zero indicating that the interaction effects cause higher bounds than those predicted by individual effects.

INTRODUCTION

The development of the r.f. quadrupole mass spectrometer in recent times has caused considerable impact in the field of mass spectrometry. A quadrupole mass spectrometer is simple and compact in design, it is non-magnetic, it is strongly focusing and hence of relatively high transmission, and its resolution and transmission can both be controlled electronically. Because of its versatility, it has found extensive use in the laboratory for routine analytical work.

Quantitative aspects of spectra obtained in quadrupole mass spectrometers, however, deserve detailed study. Trajectory calculations have been carried out by several workers[1–6]. This involves calculation of the x and y amplitudes of ions as a function of initial displacements, radial velocities, r.f. phase, and the magnitude of the a and q parameters in the stability diagram. Even when a mass spectrometer is operated well inside the stability region, very often the stable ions have amplitudes larger than the r.f. field dimensions. As a result, even some intrinsically stable ions are lost to the analyzer because of high amplitudes. In such cases the trajectories of only those ions whose maximum amplitudes are well within the field boundaries are of practical significance. Paul et al.[1] have made maximum amplitude calculations with β values which are of interest in mass spectrometers. In this case the maximum amplitudes were calculated as a function of initial phase of entry for (a) zero radial velocity and non-zero initial displacement, and (b) axial entry with non-zero radial velocity. A calculation of the contours representing maximum permissible initial displacements for 100% ion transmission for zero radial velocity was also made. Fischer[2] has made analytical calculations on the range of permissible radial velocities and initial displacements for which the maximum amplitude is the field radius r_0 using $a = 0$ and a set of three q values. But these a and q values are not of mass spectrometric interest. Powell[3] has computed the maximum amplitudes of x and y trajectories for a and q values on a mass scan line corresponding to a resolution of 40, in addition to trajectory calculations for a few other resolutions. He has verified that the maximum amplitudes in the x and y directions, x_m and y_m, have approximately linear dependence upon $1/(1-\beta_x)$ and $1/\beta_y$.

One of the first things to attempt for a quantitative analysis of analyzer operation is to determine whether all the ions injected at the entrance of the quadrupole field reach the exit end, assuming that they execute stable oscillations. In this the ions not only have to be executing stable oscillations in terms of the solutions of Mathieu's equations, but also their maximum amplitudes in the trajectory must be less than the field dimensions. Theoretically, this means calculation of maximum amplitudes of trajectories as a function of the initial displacements x_0 and y_0, initial phase ωt_0, and initial velocities $\dot{x}_0$ and $\dot{y}_0$ with a and q values chosen in the mass spectrometer range. In the present work we have made these calculations for mass spectrometer resolutions in the range of 70–1000. We have obtained limiting values of initial radial velocities and initial displacements for unit efficiency of ion transmission through the quadrupole field.

ION TRAJECTORY COMPUTATIONS

The motion of ions in the two-dimensional quadrupole field are 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 $\xi = \omega t/2$.

With appropriate initial conditions ωt_0, x_0 and $\dot{x}_0 = (dx/d\xi)_0 = (2/\omega)$

$(dx/dt)_0$, these equations were solved using an IBM 7044 computer adopting the fourth order Runge–Kutta method. Various operating lines were chosen such as $m/\Delta m = 70, 100, 200, 500, 1000$. The corresponding a/q values were determined using the equation[1]

$$m/\Delta m = 0.357/(0.23699 - a_{0.706}).$$

Along these operating lines the extremes of the ion oscillations were calculated for a number of operating points. The computation was carried out for about 160 cycles of ion motion. Computations with parameters given by Paul et al.[1] were also carried out and the results were compared with the present calculations.

RESULTS

x_m/x_0, y_m/y_0 values for the parameters $\dot{x}_0 = \dot{y}_0 = 0$, $\beta_x = 0.98, 0.96, 0.92$, $\beta_y = 0.02, 0.04, 0.08$ and x_m, y_m values for the parameters $x_0 = y_0 = 0$, $(dx/dt)_0 = (dy/dt)_0 = \omega$, $\beta_x = 0.98, 0.96, 0.92$, $\beta_y = 0.02, 0.04, 0.08$ as given by Paul et al.[1] differ less than 1 % from our computed values for the corresponding parameters.

Maximum amplitudes of ion oscillations have been computed along a range of mass scan lines for $m/\Delta m = 70$–1000, for operating points varying over $0.69 < q < 0.71$. Initial conditions of entry such as initial displacement of ions, radial velocity of ions and initial phase at entry were varied, and the maximum amplitudes of oscillations have been computed over a range of these parameters.

For resolutions of 100, 200, 500 and 1000 the maximum amplitudes plotted against different operating points are shown in Fig. 1. The initial position of ion entry is 0.01 inch (the amplitudes, however, can be arbitrarily scaled), and the radial velocity at entry is 0.005 inch/radian of applied field. The phase at ion entry, ωt_0, is zero. The maximum amplitudes have been plotted as x_m/x_0 and y_m/y_0 against different q values. The a values are those corresponding to the given resolutions.

For a mass scan line corresponding to a resolution of 200 the changes in maximum amplitude due to changes in radial velocity at entry of ions are plotted in Fig. 2. The initial displacement of ions is 0.005 inch and the phase at entry is zero. The radial velocities are 0.005, 0.0075 and 0.010 inch/radian. The maximum amplitudes are shown as x_m/x_0 and y_m/y_0. For a mass scan line corresponding to a resolution of 500 the effect of change in radial velocity is plotted in Fig. 3. The initial displacement of ions is 0.010 inch and the phase at entry is zero. x_m/x_0, y_m/y_0 have been plotted for radial velocities of 0.01, 0.005, 0.0025 inch/radian.

For a scan line with resolution 70, the changes in maximum amplitude due to changes in the initial displacement of ions is plotted in Fig. 4. The radial velocity of ions is 0.01 inch/radian and the initial phase at entry is zero.

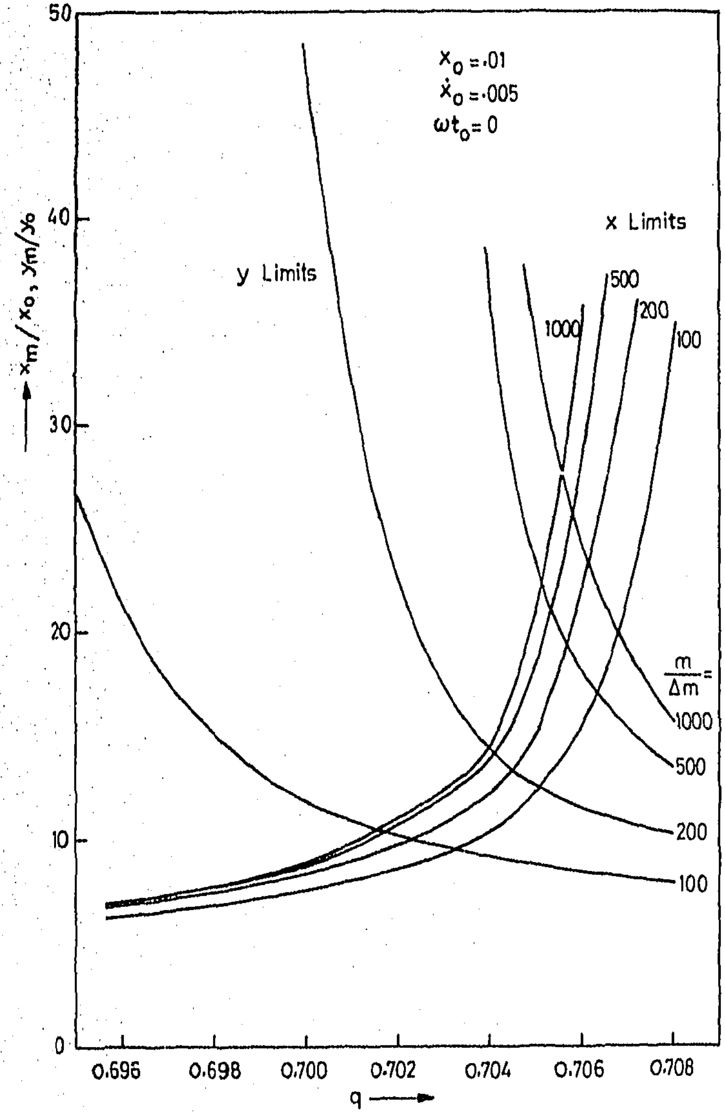

Fig. 1. Maximum amplitudes at various resolutions.

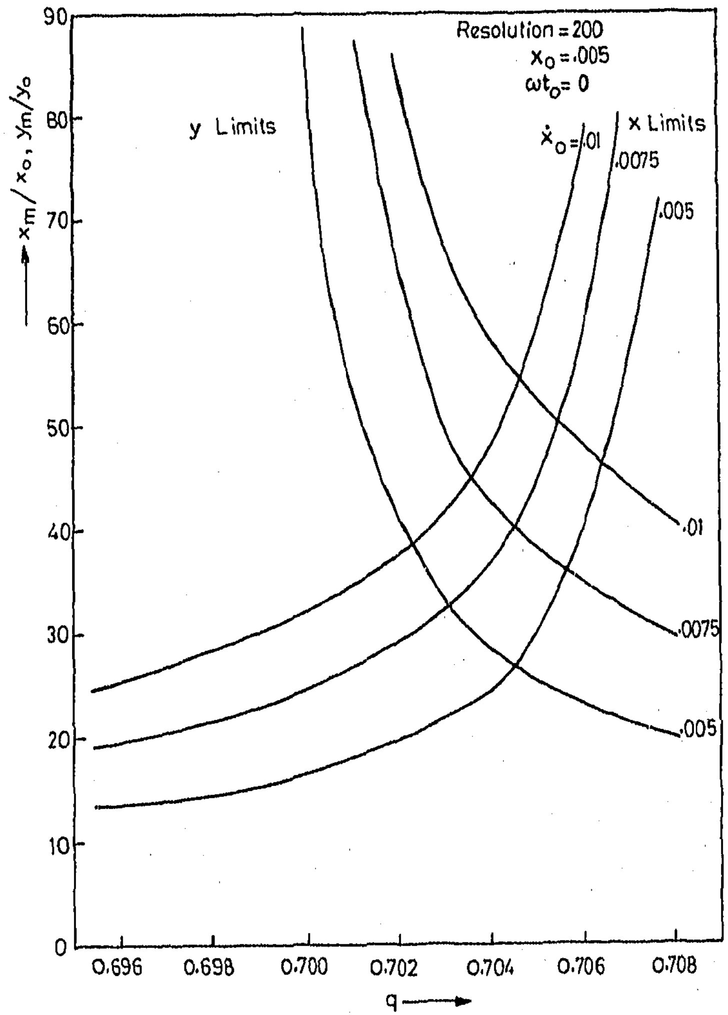

Fig. 2. Variation of maximum amplitude with radial velocity at resolution 200.

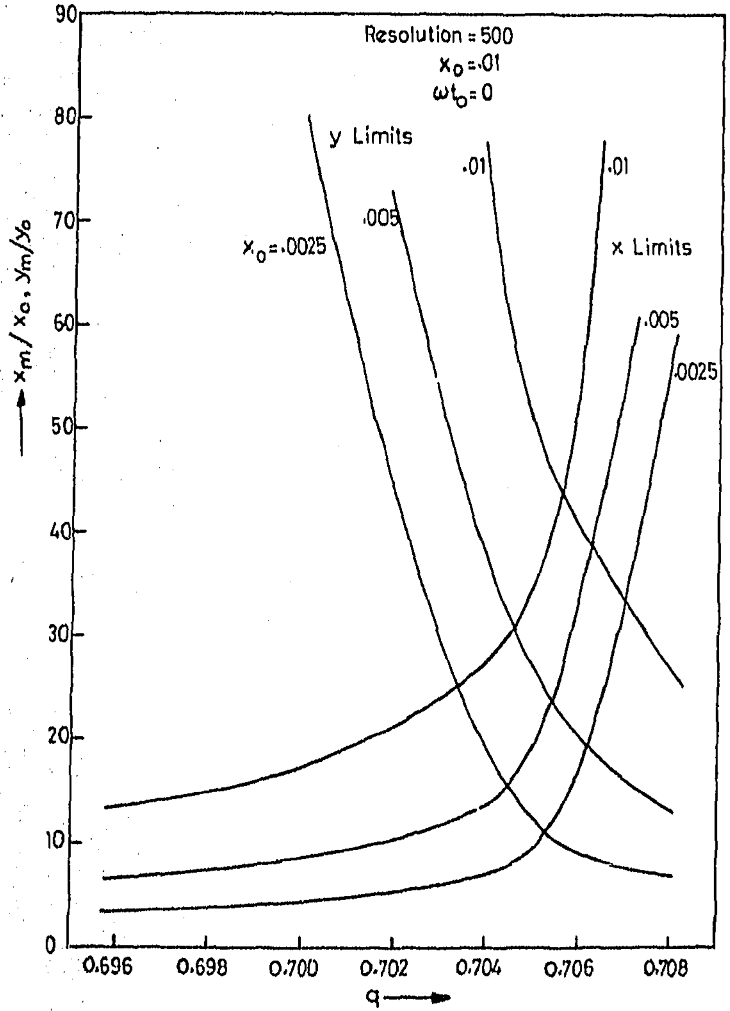

Fig. 3. Variation of maximum amplitude with radial velocity at resolution 500.

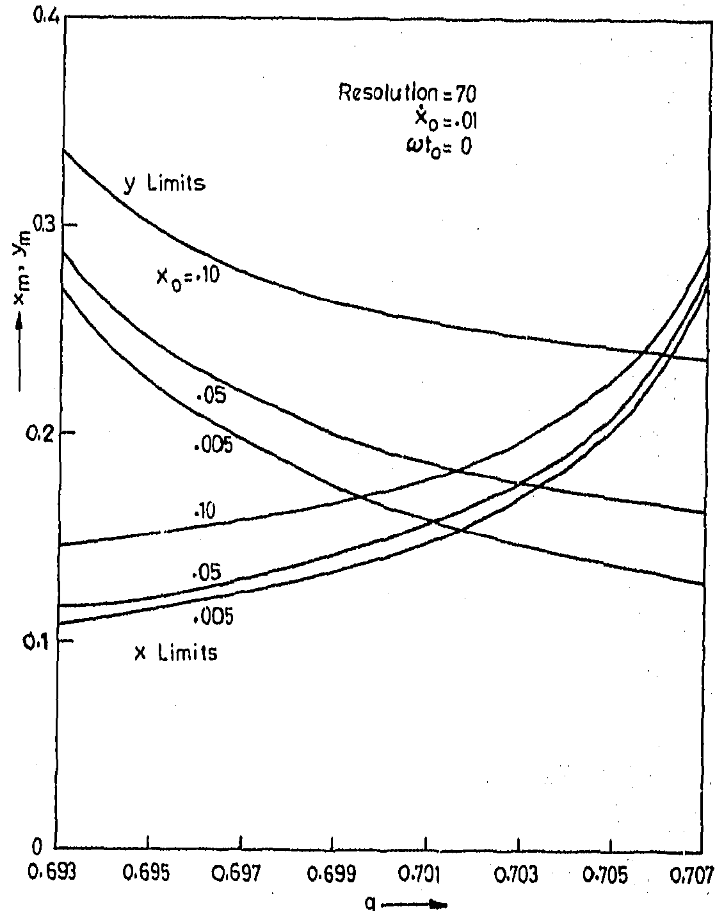

Fig. 4. Variation of maximum amplitude with initial displacement at a resolution of 70.

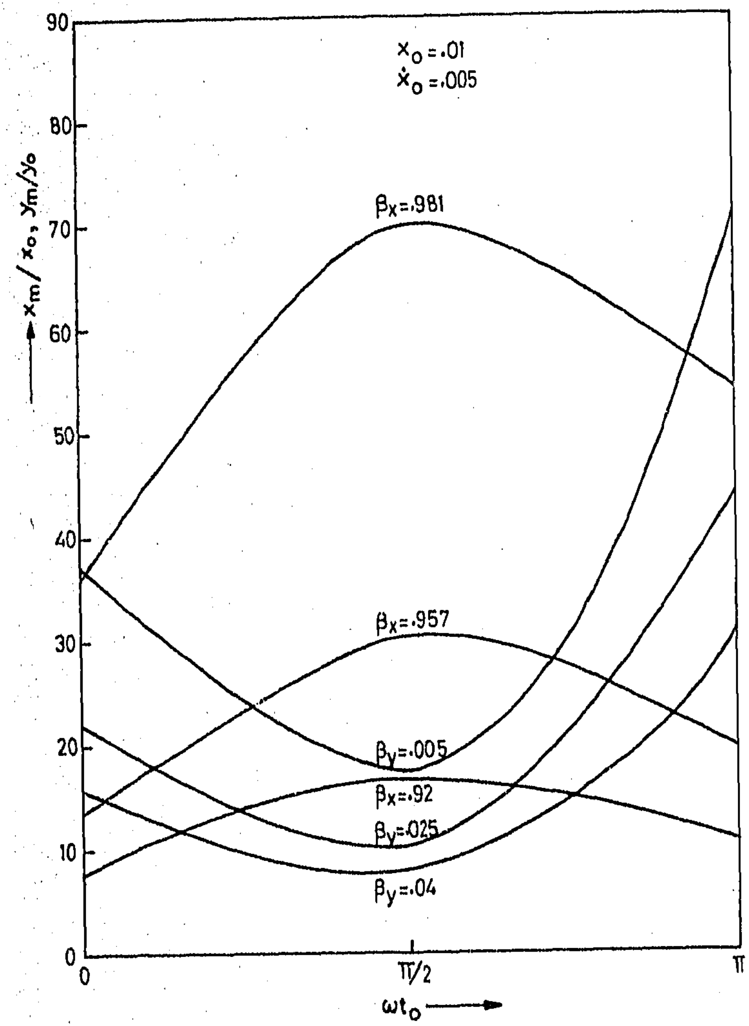

Fig. 5. Variation of maximum amplitude with initial phase for different β values.

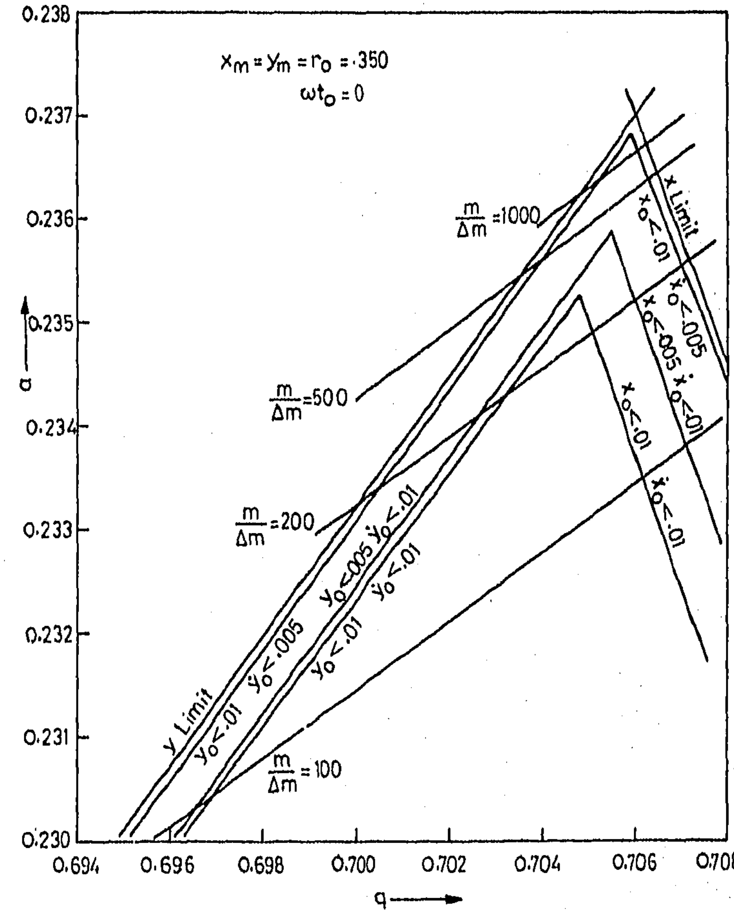

Fig. 6. Permissible entry conditions for 100 % ion transmission.

Figure 5 shows the effect of initial phase at entry on the maximum amplitude of ion motion. The β values are computed using the expressions given by Paul et al.[1],

$$(1-\beta_x)^2 = (0.23699-a_{0.706})/1.9375$$

$$\beta_y^2 = (0.23699-a_{0.706})/0.79375$$

The maximum amplitudes are shown for different β values. The initial displacement of ions is 0.01 inch and the radial velocity at entry is 0.005 inch/radian.

Figure 6 shows the contours representing regions of the operating parameters a and q for which 100 % ion transmission in the quadrupole field takes place for the given conditions of entry of ions. The radius of the field is taken to be 0.350 inch. These contours are obtained by determining the x and y limits along various mass scan lines for given entry conditions of ions.

DISCUSSION

The computations of Paul et al.[1] led to the following empirical equations:

$$D = 2\,x_0 \approx r_0\,(\Delta m/m)^{\frac{1}{2}}$$

$$\dot{x}_m, \dot{y}_m < 0.16\,\omega r_0\,(\Delta m/m)^{\frac{1}{2}}$$

for 100 % transmission of ions. These were arrived at considering the effects of initial displacement of ions and radial velocity at entry independently. In our calculations the effects of initial displacement and radial velocity at entry are simultaneously studied. It is found that the bounds given by Fig. 6 are higher than the bounds obtained from the equations of Paul et al.[1]. This presumably is due to the fact that the above empirical equations are derived for zero initial displacement and non-zero initial radial velocity or vice versa, and thus are not valid for non-zero values of both. Brubaker[7] has observed experimentally that off-axis entry of ions with non-zero radial velocity at entry results in higher ion transmission than entry at axis. The bounds given in Fig. 6 for the entry conditions of ions should be valuable to the mass spectrometer designer.

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