Practical Quadrupole Theory: Graphical Theory

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Traditional treatments of how quadrupoles work rely heavily on complex equations, both empirically and analytically derived. Newcomers to the field are often overwhelmed by the abstract nature of such purely theoretical treatments, often requiring in depth study to reach an intuitive understanding of how quadrupoles work, and more importantly, how to optimize performance in experiments involving quadrupoles.

This presentation focuses on the use of graphical tools to provide an intuitive understanding of how quadrupoles work. The correlation between the Mathieu stability diagram and peak width and mass calibration is illustrated. Voltage scan lines through the regions of stability for the stability diagram are correlated with mass peak widths. Changes in the intercept and slope of the scan line are demonstrated for use to control peak width, to approximate unit mass resolution across the mass range. Once the basic graphical concepts presented here are mastered, the reader is directed to review a more rigorous treatment of quadrupole theory such as the most excellent treatment found in the second chapter of March and Hughes' book "Quadrupole Storage Mass Spectrometry".(1) The second chapter is titled "Theory of Quadrupole Mass Spectrometry" and provides a quite approachable introduction to the equations and their derivations. Of course, the most rigorous treatment of quadrupole theory is present in Peter Dawson's classic "Quadrupole Mass Spectrometry and its Applications".(2) That book and subsequent papers by Dawson are thorough in their coverage, and are quite approachable once one has developed an intuitive understanding of the basic concepts.

This presentation approach is unique to any yet found in the literature, with its focus on practical implications of quadrupole theory, de-emphasizing the complex abstract equations typically utilized in traditional summaries of quadrupole theory.

I. INTRODUCTION

The purpose of this presentation is to de-mystify the theory associated with how quadrupoles operate.

This introduction is a collection of general background information intended to clarify the typical implementations of quadrupole systems.

A quadrupole mass filter consists of four mutually parallel, high mechanical precision, electrically isolated electrodes oriented such that the electric field between them is hyperbolic (quadrupolar).

While some manufacturers choose to fabricate high precision hyperbolic surfaced electrodes, a common way to manufacture a quadrupole is to orient four round poles such that their centers coincide with the corners of an imaginary square.

The round poles would be oriented such that the distance between the faces of opposite poles is nominally 1/1.148 times the rod diameter. This ratio is chosen such that the geometric center of the quadrupole approximates an ideal hyperbolic field.

Ions to be mass analyzed are focused down the center of the quadrupole, with a combination of precise DC and RF voltages applied to the quadrupole rods (typically a constant RF frequency, 700 kHz to a few MHz).

For a given system, the amplitude of the voltages determines which mass (or range of masses) will have stable trajectories through the quadrupole. Ions having unstable trajectories are neutralized by striking the quadrupole electrodes.

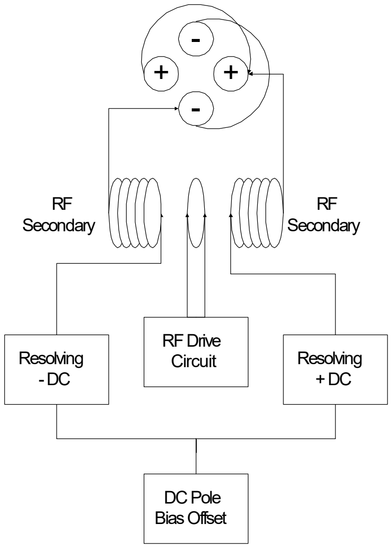

Figure 1. Schematic of typical quadrupole power supply connections.

Opposite pairs of quadrupole rods are typically electrically connected, yielding a requirement for two electrical connections to the quadrupole.

The quadrupole power supply can be schematically described to include:

- A DC pole bias supply which determines the centerline potential of the quadrupole (i.e. same potential and polarity added to both pairs of rods).
- Two Resolving DC supplies providing equal magnitude but opposite polarities to each pair of quadrupole rods. The potential for both of these DC supplies are biased from ground by the pole bias supply.
- A high voltage RF transformer circuit which has a single primary and two secondaries, which are 180 degrees out of phase with each other. The resolving DC supplies serve as inputs to the secondaries.

II. SOLVING THE EQUATIONS

Don't read this section! It is obligatory that any presentation about quadrupole theory has to at least mention the Mathieu equation. **Skip over to the section entitled "Graphing the Solution…".**

The traditional treatment of quadrupole theory starts with a derivation of the Mathieu equation from 'F=ma' all the way through to the final parameterized form, with the following parametric substitutions:

$$\frac{d^2u}{d\xi^2} + (a_u - 2q_u \cos 2\xi)u = 0 \qquad a_u = \frac{8eU}{mr_0^{\,2}\Omega^2} \qquad q_u = \frac{4eV}{mr_0^{\,2}\Omega^2}$$

The *u* in the above equations represents position along the coordinate axes (x or y), x is a parameter representing Wt/2, *t* is time, *e* is the charge on an electron, *U* is applied DC voltage, *V* is the applied zero-to-peak RF voltage, *m* is the mass of the ion, *r* is the effective radius between electrodes, and W is the applied RF frequency.

The rigorous analytical solution to this second order linear differential equation is:

$$u(\xi) = \Gamma \sum_{n=-\infty}^{\infty} C_{2n} \exp(2n+\beta)i\xi + \Gamma' \sum_{n=-\infty}^{\infty} c_{2n} \exp-(2n+\beta)i\xi$$

Which, intuitively obvious to any person skilled in the art, reduces to a similar infinite sum of sine and cosine functions. But for our purposes, it is acceptable to simply consider ion trajectories to be infinite sums of sine and cosine functions, with each successive term having smaller amplitude and higher frequency.

Which really means that motion in each of the x and y directions is sinusoidal, consisting of macromotion at the fundamental frequency (ω_0), with micromotion at the harmonic frequencies added in, (or if the fundamental and the first harmonic are close in frequency, a beat pattern of the fundamental and the first harmonic, with micromotion of the rest of the harmonic frequencies added in).

III. GRAPHING THE SOLUTION...

But what really matters rather than the exact solutions of the Mathieu equation is: **Does the ion have a stable trajectory at the voltages applied? (i.e. Will the ion go through the quadrupole?)**

The answer to this question can be readily treated graphically. Simply plot the families of solutions to the Mathieu equation that have stable trajectories, and look to see if the voltages in question lie inside or outside one of the stability regions defined by the Mathieu equation solution boundaries.

Figure 2 (adapted from Figure 2.7 of Reference 1) shows the families of solution boundaries for the Mathieu equation that lie near the origin, showing four distinct regions of stable trajectories (with boundaries for both the x and y directions plotted) for ions moving through the quadrupole, using the Mathieu *a* and *q* parameters.

Region A from Figure 2 represents the traditional operating region for quadrupole mass filters. Figure 3 is an amplified view of this *First Stability Region,* with

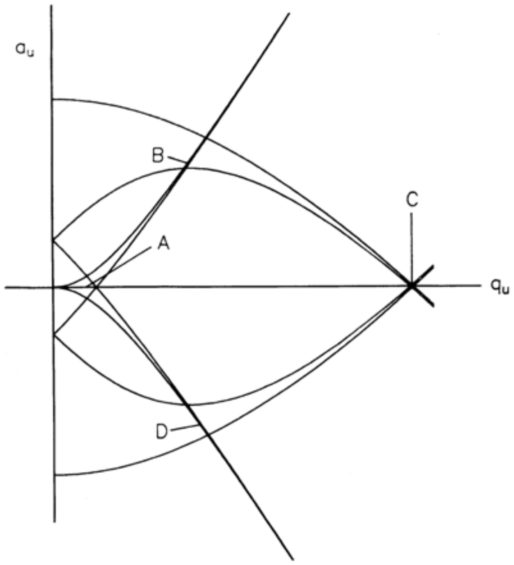

Figure 2. The Mathieu stability diagram in two dimensions (*x* and *y*). Regions of simultaneous overlap are labeled *A, B, C,* and *D*. [1]

suitable substitutions for the Mathieu parameters *a* and *q* to convert the axes into RF-DC voltage space for m/z 219, with r_0 calculated based on a 9.5 mm round quadrupole rod diameter, and an operating frequency Ω of 1.2 MHz.

For any set of RF and DC voltages, one could read directly from this figure whether ions of m/z 219 would have stable trajectories through a 9.5 mm quadrupole operated at 1.2 MHz. The area inside the boundaries represent voltages with stable trajectories, and the area outside the boundaries represent unstable trajectories for that stability region.

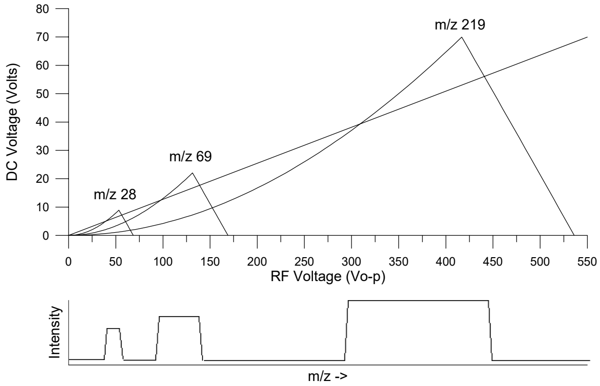

Figure 4. Stability diagrams for m/z 28, 69 and 219 plotted in RF-DC space, showing a straight scan line through the origin. The lower portion of the figure represents the mass peak widths resulting from the scan line passing into and out of the stability regions for each of the masses.

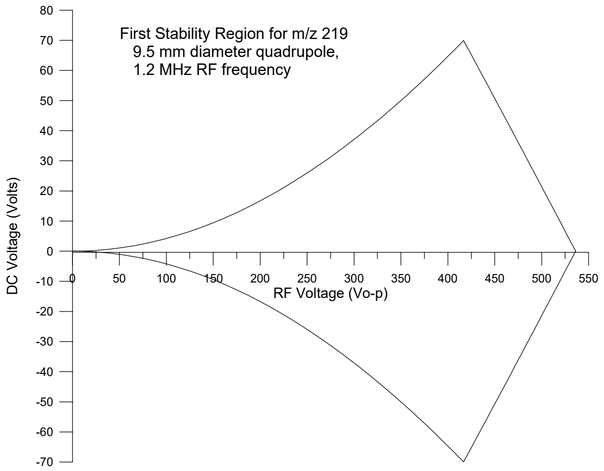

Figure 3. Expanded view of region *A* from Figure 2 (the '*First Stability Region'*) with suitable substitutions for *a* and *q* to convert into RF and DC space for mass 219 for a 9.5 mm quadrupole operated at 1.2 MHz.

IV. CONSTANT RESOLUTION SCANS

Note that the stability diagram shown in Figure 3 is symmetric around the DC voltage = 0 axis. In practice, when one assigns positive DC voltages to one rod pair, and negative DC voltages to the other pair, only the top half of this diagram is considered, with the bottom half of the diagram accessible by simply swapping the electrical connections to the quadrupole.

Figure 4 represents the stability diagrams for multiple masses plotted in the same RF-DC space. A linear scan line is drawn from the origin through the stability regions, passing from instability to stability back to instability for each of the masses. The bottom portion of Figure 4 represents the ion current that would be measured if RF and DC voltages are scanned through the values along this scan line as a function of time. If ions of various masses are directed into the quadrupole entrance, only certain ions will pass through the quadrupole to a detector at the exit, depending on whether the voltages yield stable trajectories. The various mass peak widths and positions correlate to the boundaries of their associated stability diagrams.

With a linear scan line through the origin, peak widths increase geometrically with increasing mass! (constant resolution)

If the slope of the mass scan line is decreased (dotted scan line in Figure 5), the scan line passes through a wider portion of the stability diagram, effectively widening the mass peak.

Note that the leading edge of the stability diagram comes up three times more slowly than the trailing edge goes down. The net result of this characteristic shape

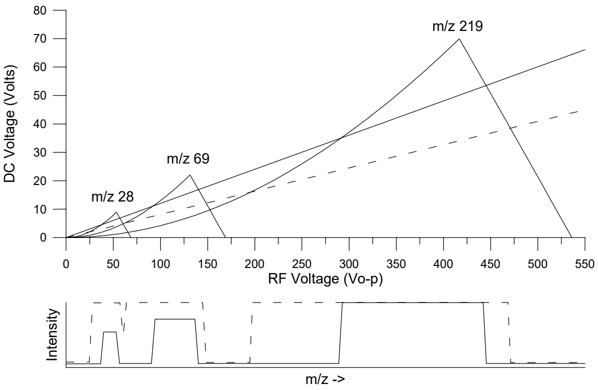

Figure 5. When the slope of the scan line is reduced (dotted scan line through the stability diagrams), the mass peaks widen, with the center of mass position moving to lower apparent mass.

of the stability diagram is that as the resolution is decreased (making the peak wider) the location of the leading edge of the mass peak moves to lower apparent mass three times faster than the trailing edge of the mass peak moves to higher apparent mass, yielding a shift of the center of the mass peak to lower apparent mass.

Changes to Mass Resolution result in predictable changes in Mass Calibration!

V. UNIT MASS RESOLUTION SCANS

Traditional treatments of quadrupole theory, including references 1 and 2 generally suggest that the typical quadrupole scan line is one with a constant *a/q* ratio (i.e. scan line drawn through the origin with constant slope in RF-DC space yielding constant mass resolution).

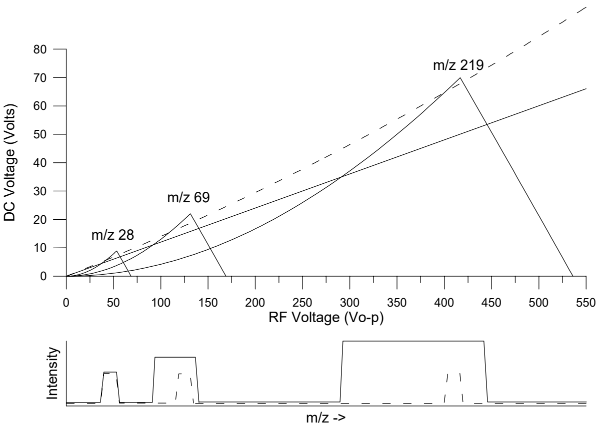

Figure 7. In order to achieve constant peak width across the mass range, a scan line that goes through the origin must be a curve with an increase in the DC to RF voltage ratio with increasing mass (dotted line in figure above).

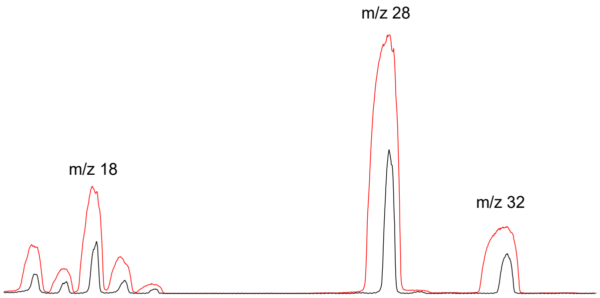

Figure 6. Experimental mass scan from m/z 15 to 35 demonstrating two different mass resolutions. Note that the scan showing wider peaks (red line) demonstrate lower apparent mass positions than the narrower mass peaks, as predicted by theory. These spectra were acquired using the Extrel Merlin Automation data system, and were gathered using a 19 mm tri-filter quadrupole operated at 1.2 MHz.

Commercial quadrupoles are almost **never** operated in this constant resolution mode, rather they are generally operated with a mass resolution that increases linearly with increasing mass (i.e. constant peak width, or Unit Mass Resolution).

To achieve unit mass resolution across the mass range, a scan line that goes through the origin must be a curve with an increase in the DC to RF voltage ratio with increasing mass. (See Figure 7.)

Historically, this curved ideal scan line has been approximated using a straight line in analog hardware by raising the slope of the scan line and lowering its intercept so as to not go through the origin. (See Figure 8). The intercept and slope are generally set empirically by simultaneously optimizing light and heavy calibration masses to unit mass resolution. Unfortunately, masses between these endpoint masses will not have constant peak width using a straight scan line.

In Extrel systems, the intercept, which primarily affects low mass resolution, is called delta-M, and the slope of the scan line, which primarily effects high mass resolution, is called delta-Res. This nomenclature is rumored to be taken from a paper or report published in the early 1960's by someone at MIT???

The 'error function' that represents the difference between the straight line approximation and the 'ideal' curved scan function (see Figure 9) has been implemented in commercial systems both in analog electronic circuitry and in software.

Extrel traditionally calls such an analog correction circuit the 'linearizer' circuit. Other manufacturers are rumored to have similar circuits in their designs.

VI. CONCLUSIONS

The purpose of this presentation is to de-mystify the theory associated with how quadrupoles operate.

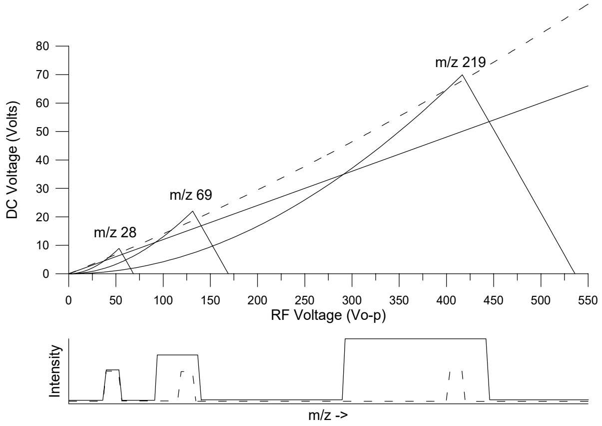

Figure 8. In order to achieve constant peak width across the mass range, a scan line that goes through the origin must be a curve with an increase in the DC to RF voltage ratio with increasing mass (dotted line in figure above).

Using this graphical approach, quadrupole operation can be understood intuitively without extensive study of the equations of motion.

A quadrupole operates as a band-pass filter with stable transmission dictated for a given ion by its mass-to-charge ratio and whether the applied RF and DC voltages fall within the stability diagram for that mass-to-charge.

The mass resolution for a quadrupole is controlled via the application of a certain ratio of DC and RF voltages. Increasing the DC to RF voltage ratio will increase mass resolution to the extreme that the DC-RF operating points lie outside the stability diagrams. (i.e. above the apex of the stability diagram, with the apex representing infinite resolution).

With a linear scan line through the origin, peak widths increase geometrically with increasing mass! (constant resolution)

Changes to Mass Resolution result in predictable changes in Mass Calibration. Decrease resolution to make the mass peaks wider and the center of the mass peaks will move to lower apparent mass.

Traditional summaries of quadrupole theory mislead the reader into believing that quadrupoles are operated with constant *a/q* ratios (Constant DC to RF voltage ratios), and hence constant resolution.

Commercial quadrupoles generally use some electronic or software implementation to approximate the curved scan function defined by physics to yield unit mass resolution.

VII. REFERENCES

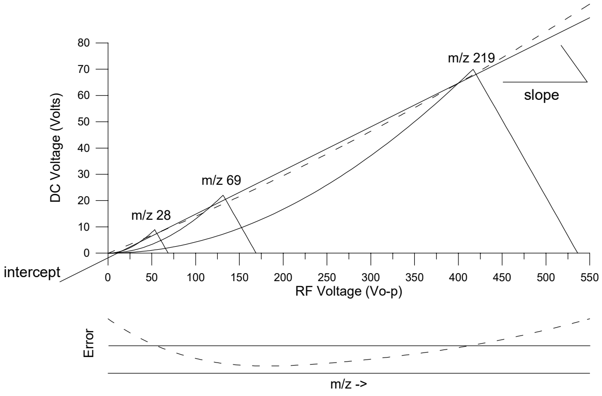

Figure 9. The 'error function' that represents the difference between the straight line approximation and the 'ideal' curved scan function has been implemented in commercial systems both in analog electronic circuitry and in software.

1. March, R.E., and Hughes, R.J. *Quadrupole Storage Mass Spectrometry*, Wiley Interscience, New York, 1989. Chapter 2: "Theory of Quadrupole Mass Spectrometry", Pages 31-110.
2. Dawson, P.H. *Quadrupole Mass Spectrometry and its Applications,* Elsevier, Amsterdam, 1976.