CALCULATION OF STABILITY DIAGRAMS AND QUADRUPOLE MASS FILTER PERFORMANCE FOR GENERAL DIGITAL WAVEFORMS

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OVERVIEW

A matrix method solution of the Mathieu/Hill equation is applied to the harmonic case and a range of digital waveforms.

Stability diagrams, simulated mass spectral peaks and transmission/peak width curves are calculated for the various waveforms.

2D SIMION simulations are used to examine the effect of digital pulse period jitter.

INTRODUCTION

Digitally driven quadrupole mass filters offer a number of unique capabilities in comparison to conventional devices driven using analogue electronics. The flexibility inherent in the digital drive allows instantaneous changes in the duty cycle, frequency and even the form of the drive waveform. The ability to calculate and compare stability diagrams for differing digital pulse waveforms is critical to understanding these devices.

METHODS

We have implemented the matrix method approach to solving the Mathieu/Hill equation [1]. This allows fast calculation of ion trajectories and stability diagrams for any periodically repeating quadrupolar field. For a given set of conditions we need only solve for two ion trajectories over a single RF period. 1001 time points were used to model the waveform over the RF period.

To plot stability diagrams we use the parameters q and a as defined by equations (1) and (2):

$$q = \frac{4ze}{m\omega^2 r_0^2} V_{RF} = \frac{2ze}{m\omega^2 r_0^2}\left(U_1 - U_2\right) \qquad (1)$$

$$a = \frac{8ze}{m\omega^2 r_0^2} V_{DC} = \frac{4ze}{m\omega^2 r_0^2}\left(U_1 + U_2\right) \qquad (2)$$

Where V_{RF} and V_{DC} are the RF and DC voltages in the harmonic waveform, U_1 and U_2 are the maximum values for the two digital pulses. There are various possible definitions of *q* and *a* for digital waveforms, the advantage of this definition is that the pulse voltage values U_1 and U_2 are dependent only on *q* and *a*, not on the duty cycle or other details of the waveform.

Figure 1 shows the potentials for the digital waveforms compared in this work. These are plotted for *a*=0, hence U_1=-U_2. The rectangular signal shown has *d*=0.5 where d is the fraction of the period taken by the U_1 pulse. The two constant portions of the trapezoidal pulse used here are each equal to 1/6 of the total period. The middle of the W-wave is set to half the value of the corresponding voltage maxima. The rising/falling edges of the trapezoidal and triangular pulses have a constant gradient, while the points at zero potential for the M/W/U-waves are pinned to zero.

Simulated mass spectral peaks are obtained by running an ensemble of ions at a range of *q,a* values to scan across the peak. For the results in this poster we use an ion of m/z 556, initial RF phase is random, initial *x/y* position is Gaussian with σ=0.01r_0, initial *x/y* velocity is a thermal distribution T=1500K, 130mm quadrupole rod length, 5mm r_0, 1MHz RF frequency, 0.5eV axial energy. SIMION was used for simulation of peaks with temporal jitter in the waveform.

The resolution of the quadrupole is set by:

$$a = \eta\, q \frac{a_{tip}}{q_{tip}} \qquad (3)$$

Where η varies from 0-1, q_{tip} and a_{tip} are the *q,a* values for the tip of the first stability region. Calculation of peaks for a range of η values enables plotting of transmission vs peak width (FWHM) curves, where transmission is the percentage of ions transmitted at the top of the peak.

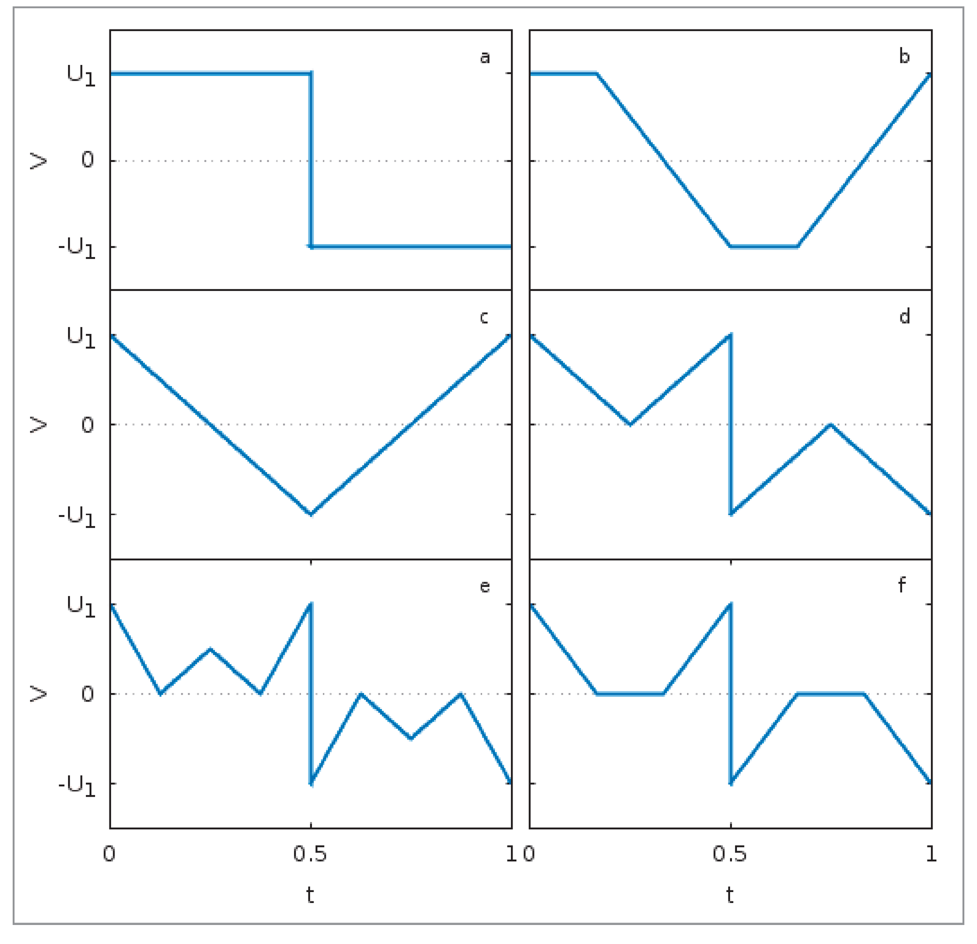

Figure 1. Plot of digital waveforms over one RF period T. a) Rectangular d=0.5, b) Trapezoidal, c) Triangular, d) M-wave, e) W-wave, f) U-wave.

RESULTS

Figure 2 shows the boundary of the first stability region for the harmonic, rectangular, trapezoidal and triangular waveforms. The stability diagrams for these systems are related by scaling in the *q*-axis alone. As might be expected the harmonic lies between the rectangular and triangular waveforms. The chosen trapezoidal waveform is close to the harmonic, while a general trapezoidal waveform can fall anywhere between a rectangular and triangular waveform. The lack of scaling in the *a*-axis is expected, since the quadrupolar DC voltage applied in all these waveforms is identical for the same *a*.

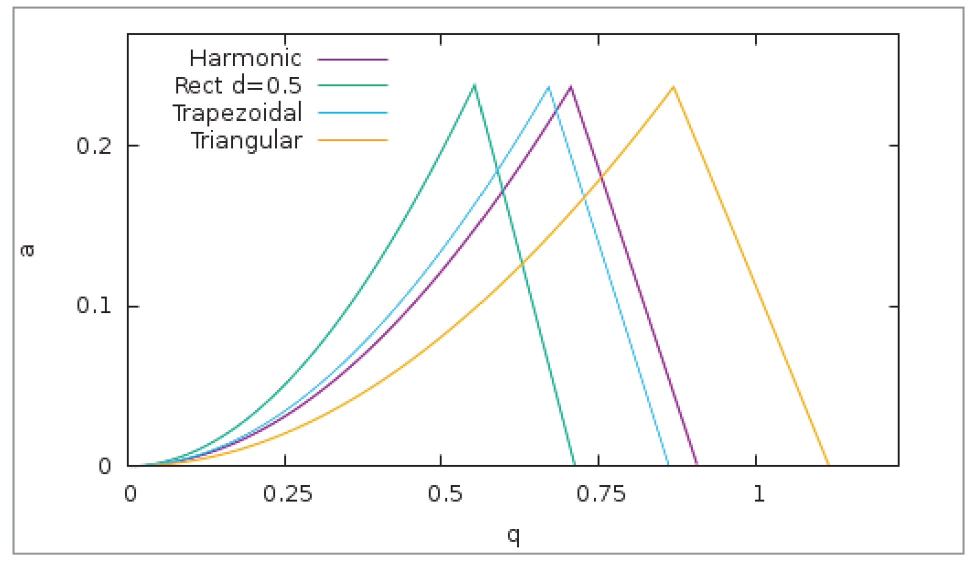

Figure 2. Boundaries of the first stability region for the harmonic, rectangular (d=0.5), trapezoidal and triangular waveforms.

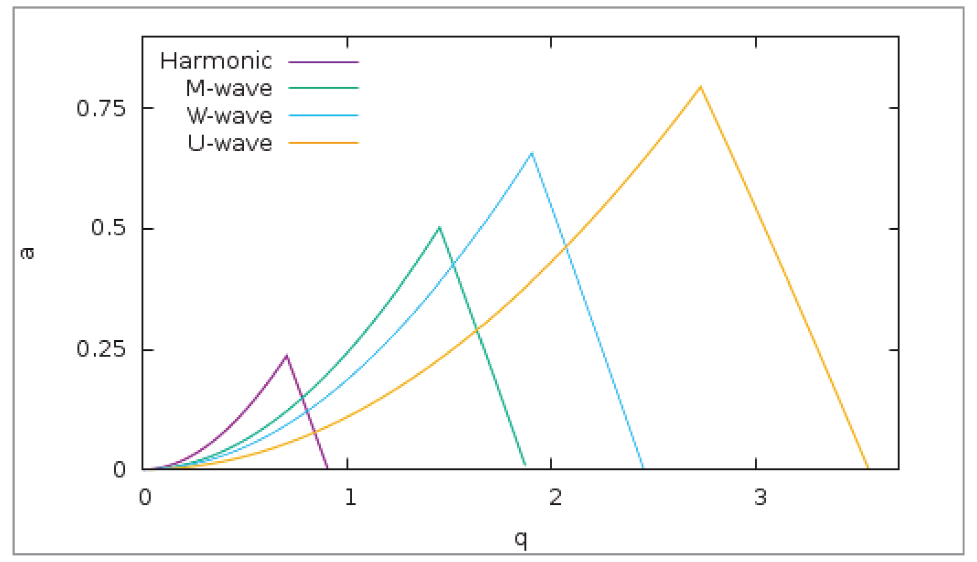

Figure 3. Boundaries of the first stability region for the harmonic, M-wave, W-wave and U-wave waveforms.

Figure 3 shows the boundary of the first stability region for the harmonic, M-wave, W-wave and U-wave waveforms. These three waveforms behave quite differently to those of **figure 2** in that the stability diagrams are scaled in both *q* and *a*.

The reason for this becomes clear when we consider the effect of non-zero *a*-values on these waveforms. **Figure 4** shows the rectangular and M-wave waveforms for *q*=1, *a*=1, hence U_1=-3U_2. Since the centres of the two "M" pulses are pinned to zero the M-wave potential is not simply shifted when *a* is non-zero. This means that for a given *a*-value the effective quadrupolar DC is significantly lower for M/W/U-waveforms. For example the quadrupolar DC is halved for the M-wave, this is clear from inspection of the M-wave and the rectangular potentials.

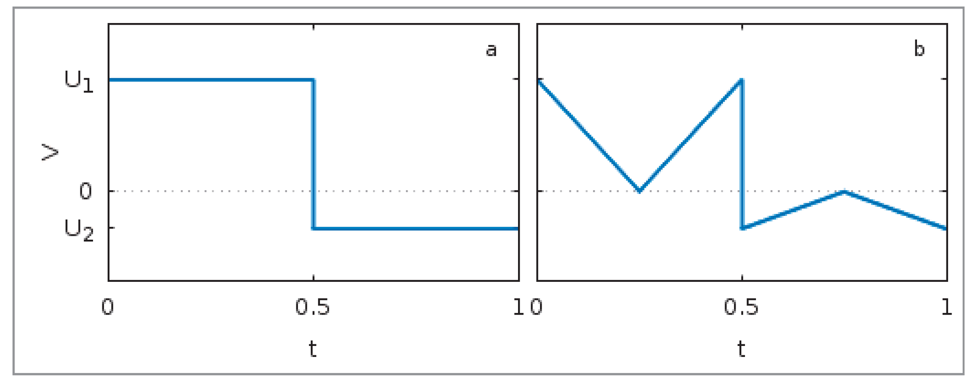

Figure 4. Plot of digital waveforms over one period for q=1, a=1. a) Rectangular d=0.5, b) M-wave.

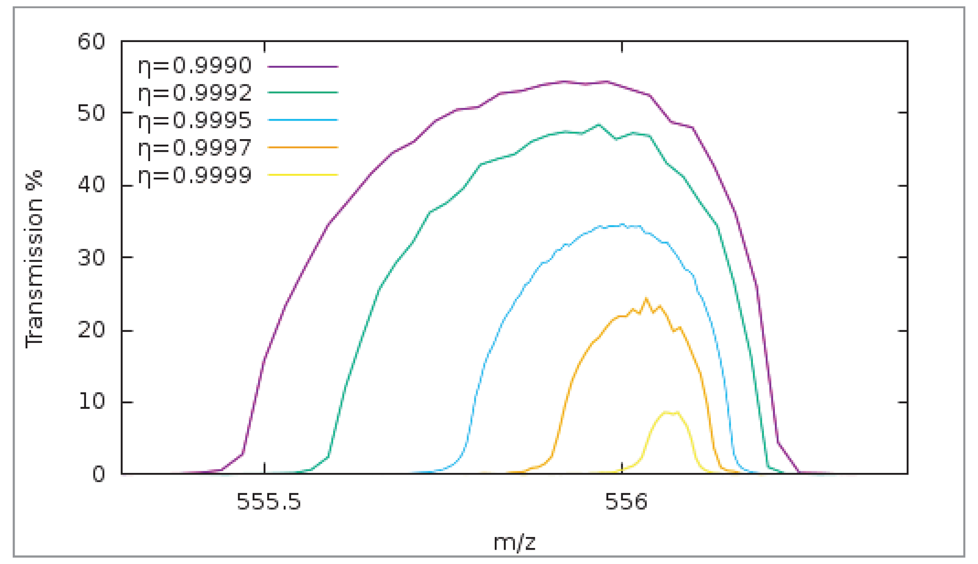

Figure 5. Simulated peaks for the harmonic waveform at a range of resolution settings.

We now consider results from simulated mass spectral peaks. As an example **Figure 5** shows simulated peaks for the harmonic waveform at a range of η values. As the scan line moves closer to the tip of the stability region the transmission window narrows, increasing resolution at the cost of transmission.

Figure 6 plots transmission vs peak width for the harmonic, rectangular, trapezoidal and triangular waveforms. The behavior of these waveforms is almost identical, at a given peak width we see a slight increase in transmission for the rectangular waveform and a slight decrease for the triangular.

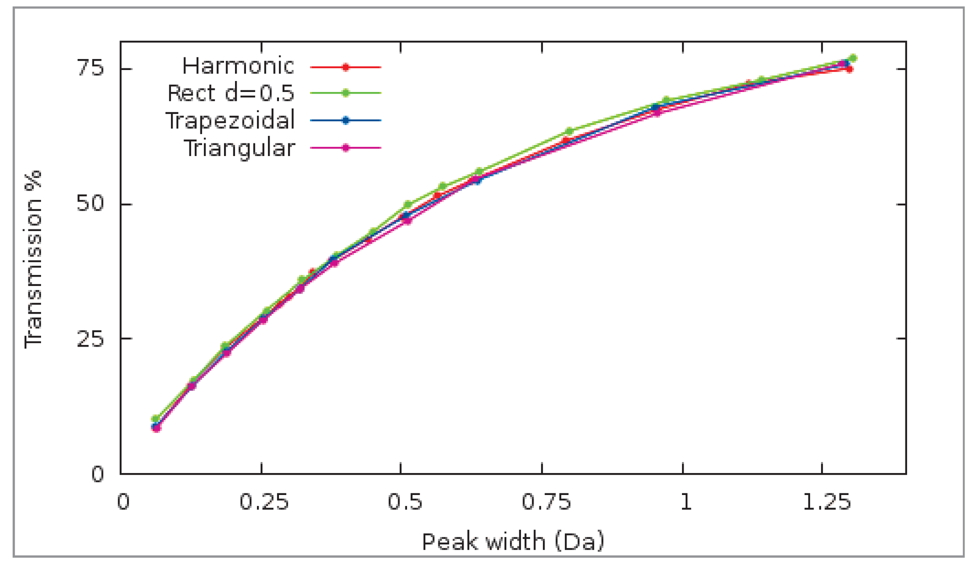

Figure 6. Transmission vs peak width for harmonic, rectangular, trapezoidal and triangular waveforms.

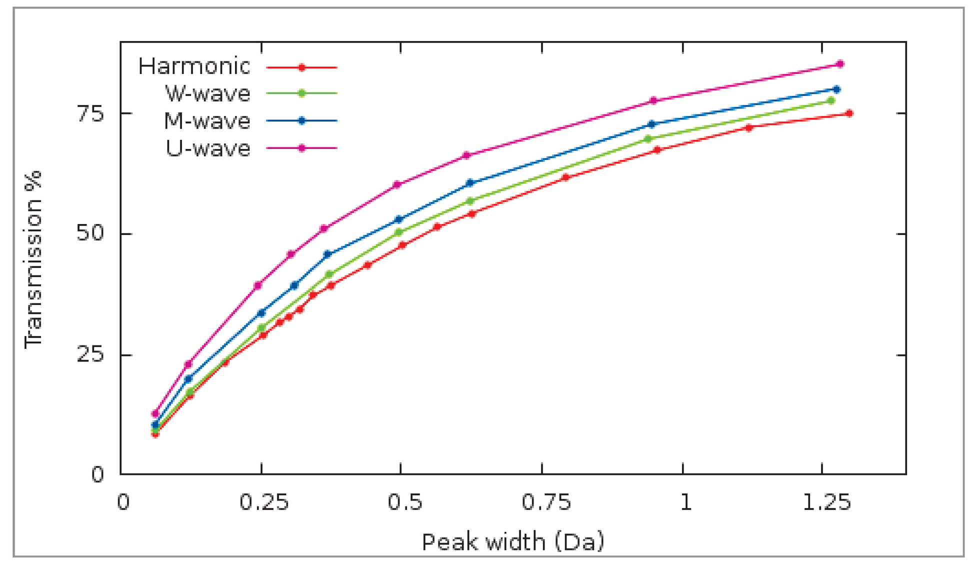

Figure 7. Transmission vs peak width for harmonic, M-wave, W-wave and U-wave waveforms

Figure 7 shows transmission vs peak width for the harmonic, W-wave, M-wave and U-wave waveforms. All three waveforms give increased transmission at a given peak width compared to the harmonic case, the increase is smallest for the W-wave and largest for the U-wave. If we consider the 0.25 Da wide peak results (η = 0.9996), transmission is 29.0% for the harmonic, 30.5% for W, 33.7% for M and 39.5% for U. So for this peak width we see about 1/3rd more transmission for the U-wave compared to the harmonic. Note that the tip of the stability diagram is higher in *q,a* for these waveforms so larger pulse voltages are required.

The rectangular waveform results presented so far all use a 50/50 duty cycle (*d*=0.5). In this mode we effectively apply resolving DC to obtain resolution. An alternative mode of operation is to adjust the duty cycle while keeping the pulse amplitudes identical, this gives a mass filter window when scanning along the *a*=0 line. As an example **Figure 8** shows the first stable region for the rectangular waveform with *d*=0.6. Resolution is controlled by adjusting the duty cycle, with *d*=0.6121 corresponding to η=1.

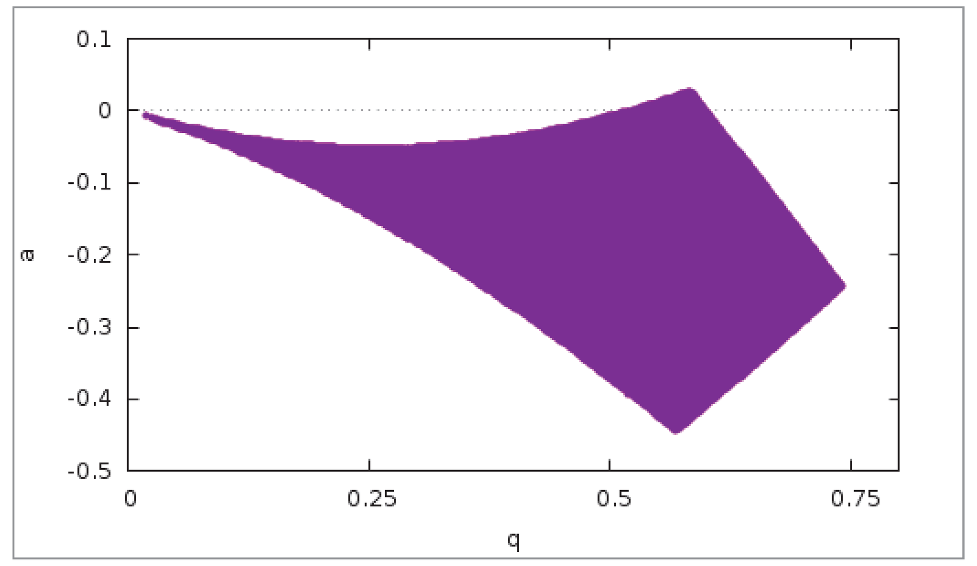

Figure 8. First stability region for the rectangular waveform with d=0.6.

Operation in this mode is attractive as it requires only one pulse voltage amplitude, simplifying the practical requirements of pulse generation. **Figure 9** compares the transmission vs peak width for the rectangular waveform with *d*=0.5 operated in the conventional manner, and the rectangular waveform with *a*=0 and resolution set by varying *d*. We see in general that the *a*=0 mode of operation gives a slight increase in transmission at a given peak width. One caveat of this mode of operation is that if we wish to use a pre-filter we require two additional phase locked pulse voltages.

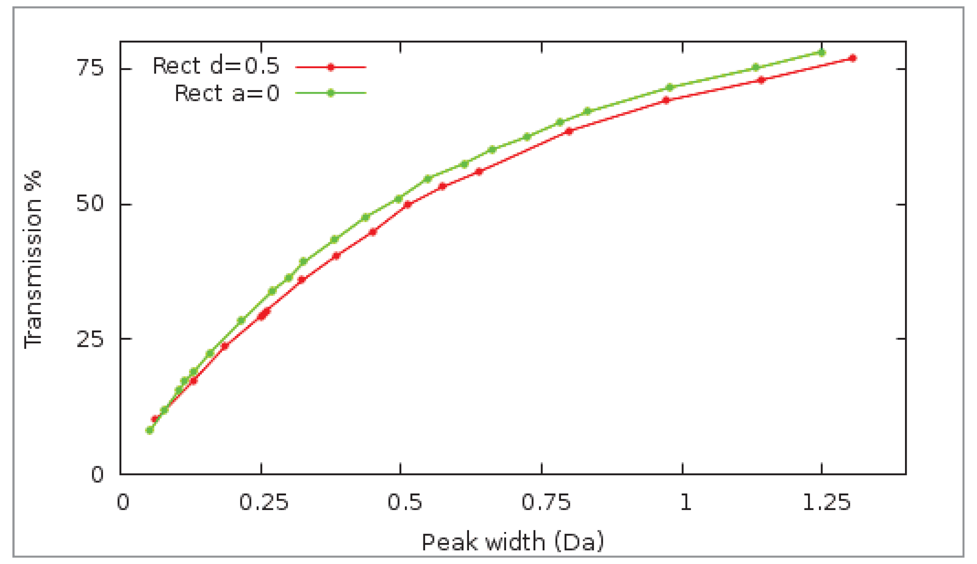

Figure 9. Transmission vs peak width for the rectangular d=0.5 and variable d, a=0 modes of operation.

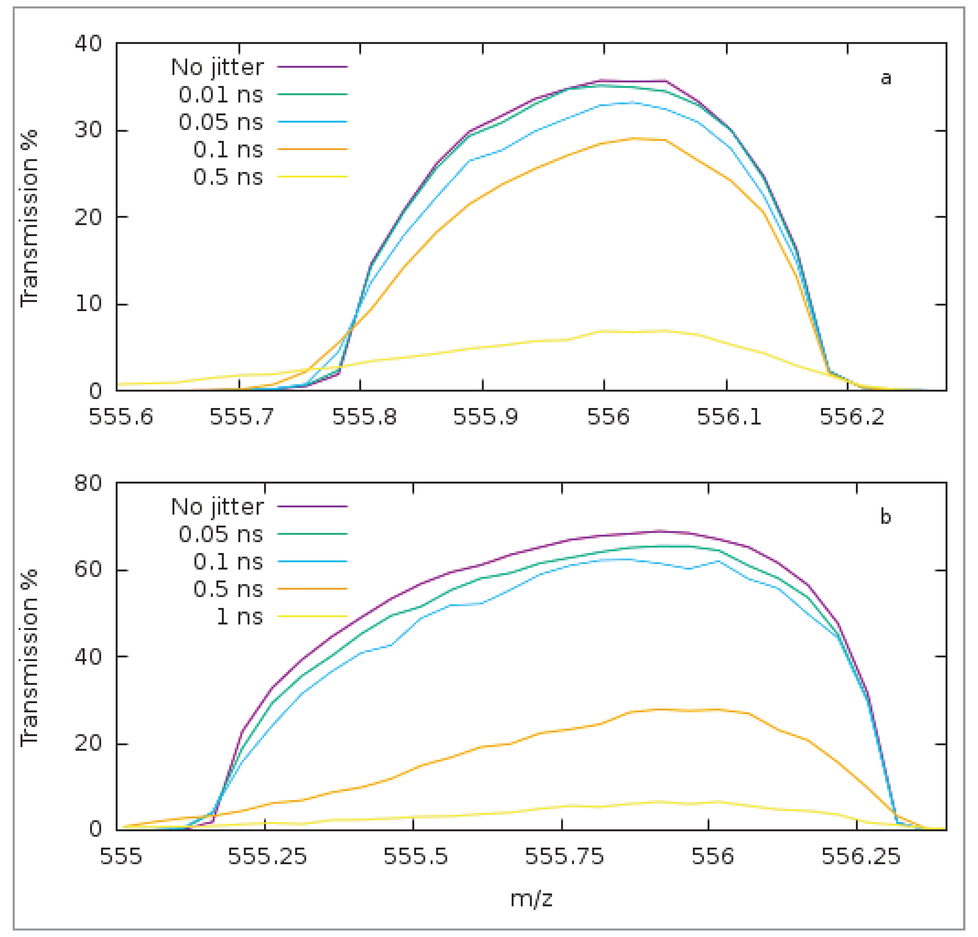

Figure 10. Effect of jitter for the rectangular d=0.5 waveform for two resolution settings. a) η=0.9995 b) η=0.9985

Figure 10 shows simulated peaks examining the effect of temporal jitter on the pulse period for the rectangular *d*=0.5 waveform at resolution settings for 0.3Da and 1Da peak widths. The jitter is applied as a +/- uniform spread about each pulse voltage change.

For the 0.3Da peak width case we see minor effects at a jitter of 0.05ns. At 0.1ns jitter we see 78% relative transmission, while at 0.5ns we are down to 19% with a significant low mass tail. At 1Da peak width the system is slightly more tolerant, for 0.1ns jitter we see 90% relative transmission, 40% at 0.5ns and 10% at 1ns. Both the 0.5ns and 1ns peaks have low mass tails.

These results suggest a minimum requirement of less than 1ns jitter for analytical performance to be maintained. In terms of the RF period this corresponds to < 1e-3 T.

CONCLUSION

- **The matrix method allows for fast calculation of stability diagrams and simulated peaks for any repeating waveform.**
- **No significant difference seen in the transmission/peak width behaviour between the harmonic case and the more conventional digital waveforms.**
- **M/W/U waveforms exhibit an increase in transmission at a given peak width.**
- **Duty cycle based operation of a rectangular waveform mass filter gives slightly improved transmission vs conventional operation at *d*=0.5.**
- **Temporal jitter of the digital pulse above 1e-3 T leads to transmission loss and peak distortion.**

References

1. Pipes, L.A.: Matrix solution of equations of the Mathieu-Hill type. J. Appl. Phys. **24**, 902–910 (1953)

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