Title: Mapping the Pseudopotential Well for all values of the Mathieu Parameter q in Digital and Sinusoidal Ion Traps

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Abstract:

Previously our group developed spreadsheet based programs for facile production of stability diagrams because any change in the duty cycle of the rectangular waveforms changes their shape. In this publication, these programs have been extended to calculate the pseudopotential well depth of quadrupolar fields in each orthogonal direction for all values of the Mathieu parameter, q . These results were extended to 3D sinusoidal ion traps and the map of the pseudopotential well depth as a function of q was compared to the literature for validation. The duty cycle of digital ion trap waveforms were then varied to observe the change in the pseudopotential wells in each direction. Duty cycle was then manipulated with the goal of enhancing the capabilities and performance of the ion traps.

Keywords: Stability Diagrams, Digital Ion Traps and Guides, Spreadsheet Calculations

Introduction:

Sinusoidally driven traps and guides are mature technologies that work very well. However, digitally driven devices have significant advantages. The most obvious is extended mass range. The resonantly tuned circuits of sinusoidally driven devices fix their operational frequency and thus the mass range is limited by the maximum practical voltage. In contrast, digitally driven devices operate in the frequency domain which permits even singly-charged large proteins and complexes to be trapped by lowering the frequency of operation. More recently, our group demonstrated the advantage of manipulating digital waveform duty cycle and frequency to trap¹ and isolate ions² and subsequently perform collision induced dissociation.³ With this advance, MSⁿ can be performed in a single linear ion guide without any hardware beyond that required to operate simply as a digital ion guide.^{3,4} The duty cycle changes used to perform these operations also change the shape of the stability diagram. This complication is easily overcome by spreadsheets which recalculate stability diagrams for DITs and guides.⁵ These programs are available for download from our group website: <http://reilly.chem.wsu.edu/>.

Duty cycle manipulation permits the adjustment of the pseudopotential wells along each orthogonal axis of the quadrupole field as a function of the Mathieu parameter, q . To

demonstrate the manipulation of the pseudopotentials, the well depth has to be determined for all values of q . This is not a problem for DITs because the Hill equation can be solved exactly to determine the value of the stability parameter, β , which can be used to define the well depth. This manuscript defines and demonstrates the calculation of the pseudopotential well depth for all values of q for 3D DITs and guides and then extends it to sinusoidal ion traps. Finally, well depth vs q plots are used to demonstrate ion manipulation to yield better 3D trap performance.

Calculating the pseudopotential well depth for all values of q :

In our previous manuscript,⁵ matrix methods were used to create spreadsheet based solutions of the Hill equation and produce stability diagrams as a function of the Mathieu parameters a and q and as a function of ion mass to charge ratio and frequency. The stability of an ion at any value of a and q is defined by the following boundary condition:⁵

$$|Tr(M_u)| = |m_{11} + m_{22}| = 2\cos(\beta_u\pi) \quad (1)$$

Where $Tr(M_u)$ is the trace of the transfer matrix M_u describing ion motion along one of the trap's orthogonal axes. Solving for β yields this expression:

$$\beta_u = \pi^{-1} \cos^{-1} \left(\frac{|m_{11} + m_{22}|}{2} \right) \quad (2)$$

The criterion for stability comes out of the boundary values of the cosine function on the right side of the equation. If $|Tr(M_u)| < 2$, ion motion is stable.

When calculating pseudopotential well depth for SITs or DITs, the value of the Mathieu parameter a is generally set to zero. This means that there is no fixed DC potential, U , applied between the electrodes. Duty cycle manipulation of DITs and guides can achieve the same utility without applying DC a potential between the waveforms.³⁻⁵ A schematic diagram that defines all of the waveform parameters and the variables used in the calculation of the transfer matrix can be found in our previous publication.⁵

The trace of the transfer matrix for a waveform with 50/0/50 duty cycle was plotted as a function of q for each orthogonal direction in a 3D digital ion trap in Figure 1. The minimum of the trace in the z direction is located at $q_z = 0.5$. The stability boundaries in the z direction occurs at $q_z = 0$ and 0.7125 (where $|Tr(M_z)| = 2$). The minimum and boundaries in the r

Figure 1: The trace of the transfer matrix as a function of q used to define ion stability

direction occurs at $q_r = 1, 0$ and 1.425 , respectively. Upon observing these plots for the first time, it seemed intuitively obvious that the value of the trace tracked the well depth. Logically $|\text{Tr}(\mathbf{M}_u)|$ had to be related to the well depth. The pseudopotential approximation has long been used to define the well depth of ions trapped in oscillating electric fields.^{6, 7}

The pseudopotential treatment ignores the trajectory ripple resulting from higher order oscillations. Ignoring the higher order oscillations at high q is a serious oversight when attempting to model ion motion because the amplitude of those oscillations increases with increasing q . However, the pseudopotential approximation is not being used here to model ion motion at high values of q . Only the well depth is being calculated. Justification for ignoring the higher order oscillation will be made after using the pseudopotential to define the well depth in terms of $|\text{Tr}(\mathbf{M}_u)|$ and plotting the result.

According to the pseudopotential approximation, the displacement resulting from secular oscillation along the z -axis is given by:^{7, 8}

$$\frac{d^2 Z}{dt^2} = -\omega_z^2 Z = -\frac{\beta_z^2 \Omega^2 Z}{4} \quad (3)$$

The force on an ion of mass m and charge e is given by:⁶

$$m \frac{d^2 Z}{dt^2} = -e \frac{d\bar{D}_z}{dZ} = -\frac{m\beta_z^2 \Omega^2 Z}{4} \quad (4)$$

Rearrangement and integration yield:

$$D_z = -\frac{m\beta_z^2 \Omega^2 z_0^2}{8e} = -\frac{\beta_z^2 V}{2q_z} \quad (5)$$

$$\text{Where: } q_z = \frac{4eV}{m\Omega^2 z_0^2} \text{ and } a_z = \frac{-8eU}{m\Omega^2 z_0^2} \quad (6)$$

are the normal expressions of the Mathieu parameters for a 3D ion trap. Substitution of equation (2) into equation (5) yields:

$$D_z = -\frac{V}{2\pi^2 q_z} \left[\cos^{-1} \left(\frac{|m_{11} + m_{22}|}{2} \right) \right]^2 \quad (7)$$

Similarly:

$$D_r = \frac{V}{2\pi^2 q_r} \left[\cos^{-1} \left(\frac{|m_{11} + m_{22}|}{2} \right) \right]^2 \quad (8)$$

$$q_z = -2q_r \quad (9)$$

These equations calculate the pseudopotential for all stable values of q_u . Here the $q_z < 0.3$ restriction typically applied the Dehmelt approximation⁹ may be ignored because β_z was exactly determined by a matrix solution to the Hill equation. Equations (7) and (8) were then used with the assumption of a 100 V_{0-p} potential to plot the pseudopotential well depth for a 3D DIT as a function of q for a 50 % duty cycle in Figure 2 (a). The blue curve depicts the well depth in the z direction and the red in the r direction. In this case ions remain trapped when the values of D_z and D_r are both less than zero.

Therefore the ions are stable in a DIT below $q = 0.7125$. The green line is a Dehmelt-like approximation of the well depth defined by $D_z = \frac{\pi^2 q_z V}{48}$ according to Ding et al.⁹ Note that the green line overlaps with the red matrix-derived D_r curve until approximately $q = 0.3$ whereupon it diverges. The equation $D_z = \frac{\pi^2 q_z V}{48}$ approximates the well depth of the trap in total up to $q = 0.3$ rather than the well along the z -axis. The total well depth of the trap defines the amount of energy required to detrap

the ion along any direction. It therefore occurs along the direction with the minimum trap potential. As Figure 2 (a) illustrates, the amount of energy required to detrap the ion along the z -axis (blue curve) is significantly greater than the amount of energy required to remove the ion along the r -axis until $q = 0.634$ above which the ion will now eject along the z -axis. These potential well segments define the overall trap well depth D as a function of q .

In a previous publication,⁸ our group showed that the results for digital ion traps may be extended to sinusoidal ion traps by creating a Fourier series to approximate 50% duty cycle square waves.

Figure 2: Calculation of the pseudopotential well depth along z and r as a function of q for (a) 3D digital ion trap (DIT) and (b) a 3D sinusoidal ion trap (SIT). (c) presents a close up of the SIT well depth between 0 and 0.908 for comparison with currently used approximations. The green lines represent the Dehmelt approximation for the well depth used at small values of q . An approximation at high q is in purple. When ion motion is unstable, the well depth is undefined and is given a value of 0.

$$f(x) = \frac{4}{\pi} \sum_{n=1,3,5,\dots}^{\infty} \frac{1}{n} \sin\left(\frac{n\pi x}{L}\right) \quad (10)$$

The series in equation 10 yields the coefficient $4/\pi$ which may be used to scale results for a DIT to a SIT. A plot of the pseudopotential well depth for a SIT as a function of q can easily be obtained by multiplying each factor of q on the right hand side of equations (7) and (8) and the range by $\pi/4$ as shown in Figure 2 (b).

To check the quality of the sinusoidal 3D ion trap well depth produced by matrix method solution of the Hill equation for a digital 3D ion trap and followed by transformation with the factor of $4/\pi$, the Dehmelt-pseudopotential well approximation, ($D=qV/8$ —green line) that is used to approximate the well depth at low q is included as well as the effective potential well depth approximation produce by Sudakov, ($D' = V(1-\beta^2)/2q$ —purple line), that permits approximation of the well depth at high values of q ¹⁰ were included in a close up of the SIT well depth over the range of q from 0 to 0.908 in Figure 2 (c). These approximations are in good agreement with matrix method calculations. Note that the well depth diminishes to zero as q approaches 0 and 0.908. It also reaches the deepest point at $q = \sim 0.8$. This same qualitative behavior is shown in March's ion trap mass spectrometry tutorial in Figure 11(b).¹¹ Consequently, there is very good agreement between our SIT calculations and the literature.

The validity of the pseudopotential approximation for calculating well depths

Defining the well depth as a function of β is a standard practice that has been around since the inception of ion traps. It is still standardly used today. For each value of q , β is used to scale the well depth of a quadratic potential in which the ion oscillates. Approximation of the trapping of ions in a quadratic potential is the pseudopotential approximation. It is also known as an effective potential.¹² It is used to simplify complex physics—in this case the complex motion of ions trapped in an oscillating electric field. β is generally approximated by a simple function of the Mathieu parameters, a and q ; the most famous is the Dehmelt approximation:

$$\beta_u \simeq \sqrt{a_u + \frac{q_u^2}{2}} \quad (11)$$

Dehmelt took this approximation farther and defined the secular frequency of the trapped ions at low values of q where higher order oscillations are not significant. While the Dehmelt approximation does a satisfactory job of modelling β_u at low q , this function is recognized to be a poor fit above $q = 0.4$. Other approximations have been employed to generate better agreement between theory and experiment. When Sudakov¹⁰ produced an “effective potential” to account for the higher order oscillations at high q , it was an approximate potential that was only effective at high values of q . This was a quadratic potential that he then used to calculate to calculate β_u and then the well depth as a function of β_u and q , $D' = V(1-\beta_u^2)/2q_u$.¹⁰ This function diverges significantly as q decreases (see Figure 2 (c)).

The method presented in this paper makes these approximations obsolete. The matrix method of solving the Hill equation provides an exact value of $|\text{Tr}(\mathbf{M}_u)|$ at each and every point in a, q space. The trace was used to exactly define the stability parameter β at each point. It already accounts for the higher order oscillations without using a series expansion such as the continued fraction expression (equation 28 of March's ion trap tutorial).¹¹ The calculation presented here works at all points in a, q space—not just the first stability region—because it can exactly calculate $|\text{Tr}(\mathbf{M}_u)|$ and β_u at any point on the a, q plane.

Recognize that modeling the well depth of an ion trapped in an oscillating electric field with a static voltage and a couple of derived parameters is by definition an approximation. However, matrix method calculation of the well depth is as valid as any approximation can be. This method agrees with literature results at low and high values of q (see Figure 2 (c)) and provides a continuous description of the well depth at all values of q and a —no other calculation of the well depth does this.

Duty cycle based ion manipulation in 3D digital ion traps

Matrix solutions to the Hill equation can also be used to predict well depth for any rectangular driving waveform. The position of the minima of the pseudopotential well depth along each orthogonal axis can be manipulated with waveform duty cycle. In Figure 3 (a), a 53/0/47 duty cycle (where the ring high voltage waveform is high for 53% and low for 47 % of the waveform cycle) places the minimum of the D_z well below the position defined by the green dot where boundary excitation along the ring axis occurs. Because the pseudopotential well is deep along z and shallow along r , ion motion along z should be very well confined while secular excitation along r should occur.

Alternatively, excitation along the z -axis can occur while excitation along r is kept to a minimum. Figure 3 (b) depicts the well depth profiles generated by a 44/0/56 duty cycle waveform. The green dot in this plot reveals the value of q where secular excitation along z is high while along r it is minimal. Axial specific excitation at each of the green points in Figure 3 (a) and (b) was demonstrated by simulated ion trajectories in Figure 3 (c) and (d) respectively.

Figure 3: Duty cycle induced preferential excitation along the r and z axes in a 3D ion trap.

The strategies depicted here illustrate the possibility of increasing the resolution of boundary ejection. Figure 3 (b) reveals significant deepening of the well in the r direction while increasing dD_z/dq_z . This combination should increase the resolving power of mass selected boundary ejection.

The duty cycle can also be manipulated to align the pseudopotential well minima. This was accomplished using a 41.5/0/58.5 duty cycle as depicted in Figure 4. Alignment narrows the stable mass range somewhat, but it also increases the maximum trap well depth by approximately a factor of 3 in comparison with the 50% duty cycle case (Compare Figures 2 and 4). Increasing the well depth narrows the spread of secular frequencies of the ions and thereby increases the resolving power.

This strategy also makes the well in the z direction more symmetric and allows ion ejection along the z axis in both the low mass and high mass directions. The symmetry of the slopes on either side of the well suggests similar mass selected instability resolution can be achieved in either direction. It should consequently lead to better ion isolation using mass selected instability.

Figure 4: Duty cycle manipulation of the pseudopotential well minima for better resonant ejection

Conclusions:

The pseudopotential well depth has been calculated for all values of the Mathieu parameter q using spreadsheet generated values of the trace of the transfer matrix. The generated well depth curves have great potential for defining ion motion as a function of duty cycle and q . Manipulation of the duty cycle of digital waveforms was shown to have great potential for improving resolution and sensitivity in digital ion traps.

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