Applications of Stochastic Process in the Quadrupole Ion traps

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Abstract: The Brownian motion or Wiener process, as the physical model of the stochastic procedure, is observed as an indexed collection random variables. Stochastic procedure are quite influential on the confinement potential fluctuation in the quadrupole ion trap (QIT). Such effect is investigated for a high fractional mass resolution Δm/m spectrometry. A stochastic procedure like the Wiener or Brownian processes are potentially used in quadrupole ion traps (QIT). Issue examined are the stability diagrams for noise coefficient, η = 0.07; 0.14; 0.28 as well as ion trajectories in real time for noise coefficient, η = 0.14.

The simulated results have been obtained with a high precision for the resolution of trapped ions. Furthermore, in the lower mass range, the impulse voltage including the stochastic potential can be considered quite suitable for the quadrupole ion trap with a higher mass resolution.

Keywords: Stochastic process, Quadrupole ion trap, Ion motion, Fractional mass resolution.

Introduction

There is the possibility that an ion trap mass spectrometer incorporates such traps as the Penning,1 Paul2 or Kingdon3 traps. In 2005, the Orbitrap was introduced according to the Kingdon trap.4 The two most popular kinds of ion traps are the Penning and the Paul traps (quadrupole ion trap).5,6 Of course, it is also possible that other kinds of mass spectrometers utilize a linear quadrupole ion trap selected as a mass filter. Interestingly, ion trap mass spectrometry has undergone many developmental stages in order to achieve its current condition with relatively high performance level and growing popularity. Paul and Steinwede7 invented Quadrupole ion trap (QIT) commonly used in mass spectrometry,5,8 ion cooling and spectroscopy,9,10 frequency standards,11 quantum computing12 and others. However, different geometries have also been suggested and utilized for QIT.13

Main properties of Wiener process

A Wiener process14,15 (notation W = (W)0,∞) is named in the honor of Prof. Norbert Wiener; other name is the Brownian motion (notation B = (B)0,∞). Wiener process is Gaussian process. As any Gaussian process, Wiener process is completely described by its expectation and correlation functions14,15

Main properties of W = (W)0,∞:

- W0 = 0
- Trajectories of Wiener process are continuous intervals of t ∈ [0, ∞] (see Figure (1)),
- expectation E[Wt] = 0,
- correlation function E[Wt,Ws] = min(t,s),
- for any t1,t2,...,tn the random vector (Wt1,Wt2,...,Wtn) is Gaussian,
- for any s,t
  - E[Wt] = t
  - E[Wt,Ws] = 0
  - E[(Wt+Ws)2] = t+s
- Increments of Wiener process on non overlapping intervals are independent, i.e. for (s1,t1) ∩ (s2,t2) = 0 the random variables Wt1-Ws1, Wt2-Ws2 are independent,
- paths of Wiener process are not differentiable functions,
- martingale property,
  - E[Wt|Ws] = Ws
  - E[(Wt-Ws)2|Ws] = t-s
- here Ws = {Ws:0 ≤ u ≤ s}.

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Wiener process as a scaled random walk

Consider a simple random walk on the lattice of integers $\mathbb{Z}$, where $\{\xi_k\}_{k \in \mathbb{Z}}$ is a collection of independent, identically distributed random variables with $P(\xi_k = \pm 1) = 1/2$. From the Central Limit Theorem\(^{16,17}\), we have,

$$\frac{X_n}{\sqrt{N}} \rightarrow N(0, 1),$$

in distribution as $N \rightarrow \infty$. Here $N(0, 1)$ is the Gaussian variable with mean 0 and variance 1. This suggests to define the piecewise constant random function $W^*_t$ on $t \in [0, \infty]$ by letting,

$$W^*_t = \sum_{n=1}^{\infty} X_{n+1} \xi_n,$$

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\( A = \Phi_0/4z_0^2 \), therefore \( r_0^2 = 2z_0^2 \). Consequently, electrodes shaped for the potential (4) can be obtained as follows,

\[
\Phi = \frac{\Phi_0}{2r_0^2} (r^2-2z^2) = \pm 1
\]  

Eq. (7) represents a hyperbolic equation for this potential. Also, the potential \( \Phi_0 \) used in hyperbolic electrodes is as follows,

\[
\Phi_0 = (U-V\cos(\Omega t))
\]  

thus, the stochastic potential, \( (\Phi_0)_{st} \), can be written as,

\[
(\Phi_0)_{st} = \Phi_0 + \text{random part},
\]

\[
\Phi_0 = \Phi_0 + \Phi_0(\eta dW_{1\Omega}/d\Omega)
\]

where \( W_1 \) is a Wiener procedure and \( \eta > 0 \) is the noise coefficient determining the size of the stochastic term.\(^3\)\(^4\)\(^5\) In this regard, the noise coefficient, \( \eta \), explains the amount of fluctuation potentially. For \( \eta = 0 \), the deterministic potential or normal potential can be stated as \( (\Phi_0)_{st} = \Phi_0 \). Here, the parameter is selected, therefore \( \sqrt{\text{Varinace}[\cos(\Omega t)]} \) is set to be about 14% as a common fluctuation in a potential. Also, the potential \( \Phi_{st} \) is usually written as follows,

\[
\Phi_{st} = \frac{1}{2r_0^2} (r^2-2z^2)(\Phi_0)_{st}
\]  

field elements in the trap therefore becomes,

\[
(E_x, E_z) = -\nabla \Phi(r,z)
\]  

Where \( \nabla \) is the gradient. From Eq. (11) we obtain,

\[
(E_x, E_z) = \left[ \begin{array}{c}
\frac{\rho}{2}(\Phi_0)_{st} \\
\frac{2z}{r_0}(\Phi_0)_{st} 
\end{array} \right]
\]  

The equations of motion for a singly charged positive ion in the QIT is represented thusly,

\[
\frac{d^2z}{d\xi^2} + (a_z-2q_2\cos2\xi)(1+\eta dW_{1\Omega}/d\Omega)z = 0
\]  

\[
\frac{d^2r}{d\xi^2} + (a_r-2q_2\cos2\xi)(1+\eta dW_{1\Omega}/d\Omega)r = 0
\]  

The \( a \) and \( q \) are for the \( z \) and \( r \) parts and the dimensionless parameter \( \xi \) are as follows,

\[
\xi = \frac{\Omega t}{2}, \quad a_z = -2a_r = \frac{4eU}{mz_0^2\Omega^2}, \quad q_z = -2q_r = \frac{2eV}{mz_0^2\Omega},
\]  

where \( m \) can be regarded as the ion mass and \( e \) as the electronic charge.

Thus, \( \Omega/2\pi \) is considered as the drive radio frequency (rf), \( z_0 \) as one-half the shortest separation of the end cap electrodes, \( r_0 = 2z_0 \) as the square of ring electrode radius and \( a_r \) and \( q_z \) as the trapping parameters. The standard Wiener procedure can be defined by a time step \( d\xi \) as follows,

\[
\frac{dW}{d\xi} = -\sqrt{2}\xi N(0,1)
\]

where, \( N(0,1) \) is seen as the standard normal distribution that is the normal distribution including mean \( \mu = 0 \) and variance \( \sigma^2 = 1 \) and density function given as,

\[
\phi(z) = \frac{1}{\sqrt{2\pi}} \frac{1}{z^2}
\]

In Matlab, the command “randn” was used to add the elements of distribution \( N(0,1) \).

Fig. (3) compares the periodic impulsional potential of the form \( \eta \cos(\Omega t)dW_{1\Omega}/d\Omega \), for \( \eta = 0.0, 0.7, 0.14, 0.28 \).

**Numerical results**

**Stability regions**

Two stability parameters monitor the ion motion for each dimension \( z (z = z) \) and \( z = z \) in the cases of the quadrupole ion trap for deterministic and stochastic cases respectively. The ion's stable and unstable motions, in the plane \( (a_z, q_z) \) and for the \( z \) axis, can be determined through making comparison between the amplitude of the movement and different values of \( a_z, q_z \). For calculating the precise elements of the motion equations for the stability diagrams, a numerical approach was used. The fifth order Runge-Kutta approach (using 0.001 stepwise increments) was used via the Matlab software as well as the scanning approach.

Fig. (4) displays the calculated first stability area for the quadrupole ion traps including and excluding the stochastic potential, red points (red color): QIT, blue circles (blue color): stochastic QIT, (a): \( \eta = 0.07 \), (b): \( \eta = 0.14 \) and (c): \( \eta = 0.28 \). Fig. (4) indicates that increasing noise coefficient \( \eta \), decreases the first stability area.

**Ion trajectories**

Fig. (5) indicates the ion trajectories in real time for stochastic as well as deterministic cases including \( a_z = -2a_r = 0 \) and \( q_z = -2q_r = 0.4 \). Indications are done by a solid line (green line): \( z-z \) for deterministic case, dash line (black line): \( z-z \) for stochastic case when \( \eta = 0.14 \). Here “st” stands for “stochastic”.

From a mathematical viewpoint, stochastic as well as theoretical results are closely related. Thus, employing stochastic procedure in quadrupole ion trap potential makes us able to simulate and obtain the numerical outcomes including high accuracy (see Figs. (5)). Table (1) reveals the
values of $q_z$ for QIT including and excluding the stochastic potentials for the equivalent points. Thus, two operating points observed in their corresponding stability diagram have the same $\beta_z$: $\beta_z = 0.3; 0.6; 0.9$. For the computations, the following equations can be used,

$$\frac{a_z - \beta^2}{q_z} = \frac{1}{q_z} \left( \frac{a_z - \beta^2}{q_z} \right) - \frac{1}{q_z} \left( \frac{a_z - (2 + \beta)^2}{q_z} \right) - \frac{1}{q_z} \left( \frac{a_z - (4 + \beta)^2}{q_z} \right) - \ldots$$

Figure 3. Shape of potential function for the impulsional potentials of the form $\eta \cos(\Omega t) dW_\Omega / d\Omega$; blue color: $\eta = 0$ and red color: $\eta = 0.07; 0.14; 0.28$ for (a), (b) and (c), respectively.

Figure 4. The first stability regions, red points: QIT, blue circles: stochastic QIT, (a): $\eta = 0.07$, (b): $\eta = 0.14$ and (c): $\eta = 0.28$; with initial conditions, $z(0) = 0.01$, $2(0) = 0$, $r(0) = 0.01$ and $\eta(0) = 0$. 
and

\[
\frac{a_2 - \beta^2}{dW}{\frac{d\xi}{d^2}} = \frac{1}{q_{(1 + \eta dW)}} 
\]

(17)

Now, we use Eq. (19) to calculate \( V_{\text{max}} \) for \( ^{131}\text{Xe} \) with \( \Omega = 2\pi \times 1.05 \times 10^6 \) rad/s and \( z_0 = 0.783 \) cm when \( \eta = 0.14 \) as follows,

\[
V_{\text{max}} = \frac{(131/(6.022 \times 10^{20}) \times (0.783 \times 10^{-2})^2}{2 \times 1.602 \times 10^{-19}} 
\times (2 \pi \times 1.05 \times 10^6)^2 \times (1 + 0) = 5455 
\]

\[
V_{\text{max}} = \frac{(131/(6.022 \times 10^{20}) \times (0.783 \times 10^{-2})^2}{2 \times 1.602 \times 10^{-19}} 
\times (2 \pi \times 1.05 \times 10^6)^2 \times (1 + 0.014) = 6983 
\]

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\times (2 \pi \times 1.05 \times 10^6)^2 \times (1 + 0.014) = 6983 
\]

Fig. (6A) shows the behavior of function \( q_{(\eta)} \) for \( \beta_2 = 0.3; 0.6; 0.9 \) when \( a_x = 0 \). As \( \beta_2 \) increase, the difference \( q_{(0.07)} - q_{(0.28)} \) will also increase.

Fig. (6B) shows \( q_{(\eta)} \) and \( V_{\text{max}} \) as a function of \( \eta \) in a QIT determined for the first stability area as \( 0 \leq \eta < 0.28 \) in parts (a) and (b), respectively. To plot Fig. (6B), we have to use Table and Table when \( \eta = 0.07; 0.14; 0.28 \). Fig. (6B,a) shows that when all factors increase, there is an outcome decrease and Fig. (6B,b) shows that with increasing parameter \( \eta \); the values of \( q_{(\eta)} \) increases also. Higher \( V_{\text{rf}} \) is shown to have better mass separation particularly for the lower ion mass range.

The effect of stochastic potential form on the mass resolution

Generally, the resolution of a quadrupole ion trap mass spectrometry\textsuperscript{21} can be regarded as a function of the mechanical precision of the hyperboloid of the QIT \( \Delta r_0 \), and the stability performances of electronics tools like, variations in voltage amplitude \( \Delta V \) and the rf frequency \( \Delta \Omega \textsuperscript{21} \) which tells us how precise the type of voltage signal

\[
\text{(a)}
\]

\[
\text{(b)}
\]

Figure 5. The ion trajectories in real time with \( a_x = -a_x = 0 \) and \( q_x = -q_x = 0.4 \), solid line (green line); \( \xi-z \) for deterministic case, dash line (black line): \( \xi-z \) for stochastic case when \( \eta = 0.14 \); with initial conditions, \( z(0) = 0.01 \) and \( \xi(0) = 0 \).

Figure 6. (A): The behavior of function \( q_{(\eta)} \) for \( \beta_2 = 0.3; 0.6; 0.9 \) when \( a_x = 0 \), (B): The behavior of \( q_{(\eta)} \) and \( V_{\text{max}} \) in the first stability region when \( a_x = 0 \), (a):\( q_{(\eta)} \) and (b): \( V_{\text{max}} \) for \( ^{131}\text{Xe} \) with \( \Omega = 2\pi \times 1.05 \times 10^6 \) rad/s, \( U = 0 \) V, \( z_0 = 0.783 \) cm.
used. The present study considers the resolution of a quadrupole ion trap including and excluding stochastic potential. The factor \( \eta \partial \Delta V / \partial z \) is very important in plotting stability diagrams and potential for the goal of the mass resolution.

For deriving an influential theoretical formula for fractional resolution, we should consider the stability parameters of the impulse excitation for the QIT including and excluding stochastic potential as follows,

\[
q_c = \frac{4eV}{m} \frac{1}{r_0^2 \Omega^2}
\]

(19)

\[
q_{cs} = \frac{4eV}{m} \left( 1 + \frac{\partial W}{\partial z} \right) \frac{1}{r_0^2 \Omega^2}
\]

(20)

By taking the partial derivatives associated with the variables of the stability parameters \( q_c \) for Eq. (20) and \( q_{cs} \) for Eq. (21), the expression of the resolution \( \Delta m \) of the QIT including and excluding stochastic potential are as follows,

\[
\Delta m = \left( \frac{8eV}{r_0^2 \Omega^2} \right) |\Delta r_c| + \left( \frac{4eV}{r_0^2 \Omega^2} \right) |\Delta V_c| + \left( \frac{8eV}{r_0^2 \Omega^2} \right) |\Delta \Omega_c| \]

(21)

\[
(\Delta m)_{st} = \left( \frac{8eV}{r_0^2 \Omega^2} \right) |\Delta r_{cs}| + \left( \frac{4eV}{r_0^2 \Omega^2} \right) |\Delta V_{cs}| + \left( \frac{8eV}{r_0^2 \Omega^2} \right) |\Delta \Omega_{cs}| \]

(22)

Figure 7. The fractional resolution as a function of the noise coefficient \( \eta \), (a) resolution of \( \Delta m \) as function of ion mass \( m \), dash dot line (red line): deterministic case \( (\eta = 0) \) and dash line (green line): stochastic case \( (\eta = 0.14) \).

Now, in order to find the fractional resolution, we have,

\[
\frac{m}{\Delta m} = \left( \frac{\Delta V_c}{V_c} + 2 \Delta \Omega_c / \Omega + 2 \Delta r_c / r_0 \right)^{-1}
\]

(23)

\[
\left( \frac{m}{\Delta m} \right)_{st} = \left( \frac{\Delta V_{cs}}{V_{cs}} + 2 \Delta \Omega_{cs} / \Omega + 2 \Delta r_{cs} / r_0 + \frac{\Delta \Omega_{cs} \partial \Delta W / \partial \Omega}{1 + \eta \partial \Delta V / \partial z} \right)^{-1}
\]

(24)

Here Eq. (24) and Eq. (25) are the fractional resolutions for QIT with and without stochastic potential, respectively.

Fig. (7a) indicates the fractional resolution that is a function of the noise coefficient \( \eta \) and Fig. (7b) displays the resolution of \( \Delta m \) that is a function of ion mass \( m \), where a dash dot line (red line); represents deterministic cases \( (\eta = 0) \) and dash lines (green line) represent stochastic case \( (\eta = 0.14) \).

Regarding the fractional mass resolution, the following uncertainties were used for the voltage, rf frequency and the geometry; \( \Delta V/V = 10^{-5}, \Delta \Omega/\Omega = 10^{-7}, \Delta r_0/r_0 = 3 \times 10^{-4} \), for \( \eta = 0.007,0.14,0.28 \) we have assumed arbitrarily the noise coefficient \( \Delta \eta = 10^{-7} \). The fractional resolutions obtained are \( (m/\Delta m)_{st} = 298,812,1113,1448 \) for \( \eta = 0.007,0.14,0.28 \), respectively. When stochastic potential is applied \( (\eta = 0.14) \), the limited voltage of rf increases by a factor of approximately 1.14; thus, the voltage uncertainties were taken as \( \Delta V/V = 1.14 \times 10^{-5} \). Once these fractional resolutions were considered for the tritium isotope mass \( m = 3.202348 \), then, \( \Delta m = 0.001954 \) and 0.001959 with and without stochastic potential, the values for \( \eta = 0 \) and \( \eta = 0.14 \) were achieved, respectively.

Theoretically, we have,
stochastic process has higher resolution during mass separation. It has been shown that \( (m/\Delta m)_{\eta=0} \leq m/\Delta m \), this means that, with increase in \( \eta \) the value of \( m/\Delta m \) also increases and therefore the power of resolution increases too due to a reduction in \( \Delta m \). Empirically, the width of the mass signal spectra seems to be better separated. Anyway, at least in the lower mass range, the impulse voltage including the stochastic potential is clearly quite suitable for the quadrupole ion trap with higher mass resolution. The fractional resolutions obtained are \( (m/\Delta m)_{\eta=0} = 298 \) and \( (m/\Delta m)_{\eta=0.14} = 1113 \); therefore, \( \Delta m < (\Delta m)_{\eta=0.14} \) and this indicates that \( \eta = 0.14 \) when higher resolution in mass separation is involved.

Author’s contributions

All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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