International Journal of Mass Spectrometry 296 (2010) 43–46

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Comparison of calculated axial secular frequencies in nonlinear ion trap by homotopy method with the exact results and the results of Lindstedt–Poincare approximation

Alireza Doroudi*

Physics Department, Nuclear Science Research School, Nuclear Science and Technology Research Institute (NSTRI), P.O. Box 14395-836, Tehran, Iran

ARTICLE INFO

Article history:
Received 15 May 2010
Received in revised form 30 June 2010
Accepted 27 July 2010
Available online 6 August 2010

PACS:
05.45.−a
37.10.Ty

Keywords:
Homotopy perturbation method
Nonlinear ion trap
Secular frequency
Hexapole

ABSTRACT

In this paper the homotopy perturbation method is used for calculation of axial secular frequencies of a nonlinear ion trap with only hexapole superposition. The motion of the ion in a rapidly oscillating field is transformed to the motion in an effective potential. The equation of ion motion in the effective potential is the equation of an anharmonic oscillator with quadratic nonlinearity. The homotopy perturbation method is used for solving the resulted nonlinear equation and obtaining the expression for ion secular frequency as a function of nonlinear field parameter. The calculated secular frequencies are compared with the results of L.–P. method and the exact results.

1. Introduction

The ion trajectories in a trap with perfect rotational symmetry around the *Z*-axis can be derived analytically from the well-known Mathieu differential equation [1]. In an ideal ion trap the potential is pure quadrupole and the main properties of the movement of an ion are obtained by the solution of Mathieu equation.

In a practical ion trap, however, the electric field distribution deviates from linearity which is the characteristic of a pure quadrupolar trap geometry. This deviation is caused by misalignments, nonhyperbolic shapes, truncated electrodes, perforation in the electrodes, space charge potential of a large ion cloud [2], additional dipolar excitation potential [2,3] and collisions within the trap.

These nonlinear agents superimpose weak multipole fields (e.g., hexapole, octapole, and higher order fields) and the resulting nonlinear field ion traps exhibit some effects which differ considerably from those of the linear field traps.

The equation governing the motion of the ion in the nonlinear ion trap is the nonlinear Mathieu equation which can not be solved analytically. Many simulation studies [4–7] and experimental studies [8,9] have been done on the effects of nonlinear terms in the nonlinear equation of motion. The superposition of weak higher multipole fields changes the motions of ions compared to their motions in a pure quadrupole ion trap; thus, it is the nonlinear resonances which dramatically and qualitatively change the oscillation of ions in nonlinear traps.

Simulation studies have shown that the higher order terms in the electric field make the ion secular frequency to shift with respect to the value $\omega_u = \beta_u \Omega/2$ ($u = r$ or z). ω_u is the ion secular frequency in the radial and axial directions, Ω is the RF drive frequency applied to the central ring electrode and β_u is a function of Mathieu parameters a_u and q_u [10,11].

Simulation studies [12] have shown that hexapole superposition decreases the secular frequency, positive octopole superposition increases the ion secular frequency and the negative octopole superposition decreases the secular frequency. Experimentally, it has been shown that [13] the octopole and hexapole superposition resulted in a decrease in ion secular frequency.

Sevugarajan and Menon [14] have applied the Lindstedt–Poincare technique for solving the nonlinear equation of ion motion in nonlinear ion trap and have obtained the secular frequency shift as a function of the strength of hexapole

* Tel.: +98 2182063351; fax: +98 2188221074.
E-mail address: Adoroudi@aeoi.org.ir.

1387-3806/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2010.07.029

and octopole superposition. We use the results of this paper for comparison with the results of the present work.

The exact solution for nonlinear equation of an anharmonic oscillator with quadratic nonlinearity and the exact expression for its period have been studied by some authors [15,16]. They have found the exact expression for the period of nonlinear oscillator in terms of complete elliptic integrals. We have used the results of these papers and have calculated the exact frequencies of an anharmonic oscillator with quadratic nonlinearity. The mathematica software has been used for calculation of elliptic integrals.

In a previous paper [17] we have applied the homotopy perturbation method for solving the axial nonlinear equation of ion motion by considering the hexapole and octopole fields superposition and have calculated the ion secular frequencies as a function of nonlinear field parameters. In Ref. [17] for comparison purposes we have ignored the hexapole superposition and have considered only the octopole field. With only octopole field superposition the resulting nonlinear equation has a cubic nonlinearity and the equation is a Duffing-like equation. In this paper we consider only the hexapole field superposition and the resulting nonlinear equation has a quadratic nonlinearity. We apply the same homotopy perturbation method for solving the nonlinear differential equation of ion motion with quadratic nonlinearity and calculate the ion secular frequencies. We compare the results of this paper with those obtained using Lindstedt–Poincare technique [14] and with the exact results.

The outline of the paper is as follows: In Section 2 the homotopy method is briefly introduced. In Section 3 the axial equation of ion motion in a nonlinear ion trap is derived. In Section 4 the homotopy method is applied to solve the nonlinear differential equation of ion motion in nonlinear ion trap. The results are also given in this section. Finally, the concluding remarks are given in Section 5.

2. Homotopy method

The standard Lindstedt–Poincare method [18,19] is applicable to equations like $\ddot{x} + \omega_0^2 x + \varepsilon f(x) = 0$ which has a linear term ($\omega_0^2 x$) and a small perturbation parameter (ε). This method cannot be applied to a system with a nonlinear differential equation unless the nonlinear differential equation has both a linear term and a small parameter. In the homotopy perturbation method [20–25], the nonlinear differential equation does not need to have either a linear term or a small parameter. The homotopy perturbation method can solve various nonlinear equations. For illustration of the basic idea of this method, we consider the following nonlinear differential equation:

$$A(u) - f(\vec{r}) = 0 \qquad \vec{r} \in \Omega \tag{1}$$

with boundary conditions:

$$B\left(u, \frac{\partial u}{\partial n}\right) = 0 \qquad \vec{r} \in \Gamma \tag{2}$$

where A is a general differential operator, B is a boundary operator, $f(\vec{r})$ is a known analytic function, and Γ is the boundary of the domain Ω. We believe that the operator A can be divided into two parts, a linear part (L) and a nonlinear part (N). Then the Eq. (1) can be written as:

$$L(u) + N(u) - f(\vec{r}) = 0 \tag{3}$$

By the homotopy technique, we construct a homotopy $v(\vec{r}, p) : \Omega \times [0, 1] \to \Re$ which satisfies:

$$H(v, p) = (1 - p)[L(u) - L(u_0)] + p(A(v) - f(\vec{r})) = 0 \tag{4a}$$

or

$$H(v, p) = L(v) - L(u_0) + pL(u_0) + p(N(v) - f(\vec{r})) = 0 \tag{4b}$$

where $p \in [0,1]$ is an embedding parameter, u_0 is an initial approximation of Eq. (1) which satisfies the boundary conditions.

From Eq. (4a) or (4b) we have:

$$H(v, 0) = L(v) - L(u_0) = 0 \tag{5}$$

and

$$H(v, 1) = A(v) - f(\vec{r}) = 0 \tag{6}$$

It is clear that when $p = 0$, Eq. (4a) or (4b) becomes a linear equation; and when $p = 1$ the equation transforms to the original nonlinear equation. So the changing of p from 0 to 1 is just that of $L(v) - L(u_0) = 0$ to $A(v) - f(\vec{r}) = 0$.

The embedding parameter p monotonically increases from 0 to 1 as the trivial problem $L(v) - L(u_0) = 0$ is continuously deformed to the problem $A(v) - f(\vec{r}) = 0$

The basic idea of the homotopy method is that continuously deform a simple problem easy to solve into the difficult problem to be solved. The basic assumption is that the solution of Eq. (4a) or (4b) can be written as a power series in p:

$$v = v_0 + pv_1 + p^2 v_2 + \cdots\cdots \tag{7}$$

Setting $p = 1$ results in the approximate solution of Eq. (1):

$$u = \lim_{p \to 1} v = v_0 + v_1 + v_2 + \cdots\cdots\cdot\cdot \tag{8}$$

This method has eliminated the limitations of the traditional perturbation methods; it can take full advantages of the traditional perturbation techniques and can be used for solving various strongly nonlinear equations.

3. The axial equation of ion motion in a nonlinear ion trap

A solution of Laplace's equation in spherical polar coordinates (ρ,ϑ,φ) for a system with axial symmetry can be written in the following general form [26]:

$$\phi(\rho, \vartheta, \varphi) = \phi_0 \sum_{n=0}^{\infty} A_n \frac{\rho^n}{r_0^n} P_n(\cos\vartheta) \tag{9}$$

where $\phi_0 = U + V\cos\Omega t$ is the potential applied to the trap (U is a direct current voltage and V is the zero to peak amplitude of the sinusoidal RF voltage), A_ns are arbitrary dimensionless coefficients, $P_n(\cos\vartheta)$ denotes a Legendre polynomial of order n, and r_0 is a scaling factor (i.e., the internal radius of the ring electrode).

When $\rho^n P_n(\cos\vartheta)$ is expressed in cylindrical polar coordinates (r,z) and the one higher order multipole, hexapole corresponding to $n = 3$, along with the quadrupole component corresponding to $n = 2$ are taken into account, the time dependent potential distribution inside the trap takes the form:

$$\phi(r, z, t) = \frac{A_2}{r_0^2} V\cos\Omega t \left[\frac{2z^2 - r^2}{2} + \frac{f_1}{r_0}\left(\frac{2z^3 - 3r^2 z}{2}\right)\right] \tag{10}$$

where $f_1 = A_3/A_2$. Here we have assumed the operation of the trap along the $a_u = 0$ axis in the Mathieu stability plot, that is, the DC component of ϕ_0 is equal to 0. The coefficients A_2 and A_3 refer to the weight of the quadrupole and hexapole superposition, respectively.

According to classical mechanics [27], the motion of an ion in a rapidly oscillating field such as $\phi(r,z,t)$ (due to the largeness of Ω) can be averaged and transformed to the motion in an effective potential, $U_{\text{eff}}(r,z)$, related to $\phi(r,z,t)$ through the following relation:

$$U_{\text{eff}}(r, z) = \frac{e}{2m}\left\langle \left| \int \vec{\nabla}\phi(r, z, t)dt \right|^2 \right\rangle \tag{11}$$

Insertion of Eq. (10) for $\phi(r,z,t)$ in Eq. (11) and averaging with respect to time gives the following relation for $U_{\text{eff}}(r,z)$,

$$U_{\text{eff}}(r,z) = \frac{1}{\lambda}\omega_{0u}^2\left(\frac{m}{e}\right)\left[r^2 + 4z^2 + \frac{{f_1}^2}{r_0^2}\left(9z^4 + \frac{9}{4}r^4\right) + \frac{12f_1}{r_0}z^3\right] \tag{12}$$

where $\lambda = 2$ for $u = r$ (radial direction) and $\lambda = 8$ for $u = z$ (axial direction).

By ignoring the term proportional to ${f_1}^2$ compared with the term proportional to f_1 (because $f_1 = A_3/A_2$ is small in comparison to 1), the final form of $U_{\text{eff}}(r,z)$ reduces to the following form,

$$U_{\text{eff}}(r,z) = \frac{1}{\lambda}\omega_{0u}^2\left(\frac{m}{e}\right)\left[r^2 + 4z^2 + \frac{12f_1}{r_0}z^3\right] \tag{13}$$

The classical equation of ion motion in the effective potential $U_{\text{eff}}(r,z)$, and with no excitation potential applied to the endcap electrodes is given by:

$$\frac{d^2\vec{r}}{dt^2} + \frac{e}{m}\vec{\nabla}U_{\text{eff}}(r,z) = 0 \tag{14}$$

where $\vec{r}$ is the position vector of the ion. From the above equations we get the equation of motion in the axial (z) direction as:

$$\frac{d^2z}{dt^2} + \omega_{0z}^2 z + \alpha_2' z^2 = 0 \tag{15}$$

where

$$\omega_{0z} = \frac{q_z\Omega}{2\sqrt{2}} \tag{16}$$

$$q_z = \frac{4eV}{mr_0^2\Omega^2} \tag{17}$$

$$\alpha_2' = \frac{9f_1\omega_{0z}^2}{2r_0} \tag{18}$$

In the resulted equation by introducing the dimensionless variable x through the relation $x = z/r_0$, and omission of index z from ω_{0z} (for simplicity) we get the equation,

$$\frac{d^2x}{dt^2} + \omega_0^2 x + \alpha_2 x^2 = 0 \tag{19}$$

where $\alpha_2 = (9/2)f_1\omega_0^2$.

There are several methods [19,28] that can be used for solution of the nonlinear Eq. (19). In the next section of this article we have used the homotopy perturbation method for solving the nonlinear differential equation of motion.

4. Application of homotopy method for solution of the equation of motion and the results

For solving the nonlinear equation $\ddot{x} + \omega_0^2 x + \alpha_2 x^2 = 0$ with initial conditions $x(0) = A$, and $\dot{x}(0) = 0$, we construct the following homotopy:

$$\ddot{x} + \omega^2 x + p[(\omega_0^2 - \omega^2)x + \alpha_2 x^2] = 0 \qquad p \in [0,1] \tag{20}$$

When $p = 0$, the equation becomes the linearized equation, $\ddot{x} + \omega^2 x = 0$, and when $p = 1$, it turns out to be the original nonlinear problem. We assume that the periodic solution to Eq. (20) can be written as a power series in p, similar to the power series in Eq. (7):

$$x = x_0 + px_1 + p^2x_2 + \cdots\cdots \tag{21}$$

Substitution of this equation into Eq. (20), and collecting terms of the same power of p, gives the following set of equations:

$$\begin{cases} \ddot{x}_0 + \omega^2 x_0 = 0, & x_0(0) = A, \quad \dot{x}_0(0) = 0 \\ \ddot{x}_1 + \omega^2 x_1 + (\omega_0^2 - \omega^2)x_0 + \alpha_2 x_0^2 = 0, & x_1(0) = 0, \quad \dot{x}_1(0) = 0 \end{cases} \tag{22}$$

The first equation of this set can be solved easily, giving the solution $x_0(t) = A\cos\omega t$.

Substitution of $x_0(t)$ into the second equation and after doing some algebra, having no secular term, implies:

$$\omega = \omega_0 \tag{23}$$

This is the approximate amplitude independent secular frequency in first order. For going to higher order approximation, the parameter-expanding method (the modified Lindstedt–Poincare method) [29] is applied. For this purpose, we construct the following homotopy,

$$\ddot{x} + \omega_0^2 x + p\alpha_2 x^2 = 0 \tag{24}$$

Now, we expand the coefficient of the linear term (ω_0^2) and the solution ($x(t)$) into power series of p:

$$\omega_0^2 = \omega^2 + p\omega_1 + p^2\omega_2 + \cdots\cdots \tag{25}$$

$$x = x_0 + px_1 + p^2x_2 + \cdots\cdots \tag{26}$$

Substitution of these power series into equation (24), and collecting terms of the same power of p, results in the following set of equations:

$$\begin{cases} \ddot{x}_0 + \omega^2 x_0 = 0 \\ \ddot{x}_1 + \omega^2 x_1 + \omega_1 x_0 + \alpha_2 x_0^2 = 0 \\ \ddot{x}_2 + \omega^2 x_2 + \omega_1 x_1 + \omega_2 x_0 + 2\alpha_2 x_0 x_1 = 0 \end{cases} \tag{27}$$

The first equation of this set is easily solved and we get the solution $x_0(t) = A\cos\omega t$. Insertion of this solution in the second equation of the set (27) and implication for no secular term in $x_1(t)$, gives the result,

$$\omega_1 = 0 \tag{28}$$

The second equation of the set is solved for this value of ω_1 and the final solution for $x_1(t)$, along with the solution for $x_0(t)$ are inserted in third equation of the set. No secular term for $x_2(t)$ implies that:

$$\omega_2 = \frac{5}{6}\frac{\alpha_2^2A^2}{\omega^2} \tag{29}$$

Combining these results with $p = 1$ gives rise to the result:

$$\omega_0^2 = \omega^2 + \omega_1 + \omega_2 = \omega^2 + \frac{5}{6}\frac{\alpha_2^2A^2}{\omega^2} \tag{30}$$

By rearranging this equation, we get the following equation:

$$\omega^4 - \omega_0^2\omega^2 + \frac{5}{6}\alpha_2^2A^2 = 0 \tag{31}$$

This equation can be easily solved for ω^2 and the final result is:

$$\omega = \sqrt{\frac{\omega_0^2 + \sqrt{\omega_0^4 - \frac{10}{3}\alpha_2^2A^2}}{2}} \tag{32}$$

In this relation A is the maximum value for x and $x_{\max}$ can be obtained by using the relation $z_0/r_0 = 1/\sqrt{2}$ for ion trap and inserting z_0 for z in equation $x = z/r_0$. Insertion of the expressions for A and α_2 in Eq. (32) gives the final result:

$$\frac{\omega}{\omega_0} = \sqrt{\frac{1 + \sqrt{1 - \frac{135}{4}f_1^2}}{2}} \tag{33}$$

The perturbed frequencies can be calculated through the relation (33) as a function of field aberration (parameter f_1). It is clear from the relation that ion secular frequency is independent of the sign of the hexapole superposition.

The values of ω/ω_0 for different values of f_1 are given in Table 1 and for comparison purposes the values of ω/ω_0 in

Table 1
Comparison of the calculated values of ω/ω_0 in this paper with the values of the Lindstedt–Poincare approximation and the exact values.

f_1	Lindstedt–Poincare	Homotopy method (this paper)	Exact results
0.01	0.99958	0.99958	0.99957
0.05	0.98945	0.98945	0.98793
0.10	0.9578	0.95235	0.93919
0.11	0.94895	0.94052	0.92122
0.12	0.93925	0.92654	0.89820
0.13	0.92870	0.90979	0.86757
0.14	0.91731	0.88933	0.82342
0.15	0.90508	0.86329	0.74569
0.155	0.8986	0.84703	0.65559
0.157	0.89601	0.83964	0.50997
0.1571	0.89588	0.83925	0.45955

Lindstedt–Poincare approximation which can be calculated [14] by the relation:

$$\frac{\omega}{\omega_0} = 1 - \frac{405 f_1^2}{96} \tag{34}$$

are also given in the table.

For a nonlinear oscillator with only a quadraic term as a nonlinearity ($\alpha_2 \neq 0$), the exact values of frequencies are available in the literature [15,16] and are given in terms of complete elliptic integrals (relation No. (46) of Ref. [16]). Mathematica software has been used for calculation of numerical values of elliptic integrals and finding the roots of cubic polynomial equations.

In Table 1, the exact values of secular frequencies for different values of f_1 are compared with the results of this paper and the results of Lindstedt–Poincare approximation. As is seen in the table, the results of this paper are closer to the exact values than those of the Lindstedt–Poincare method. There is no bounded motion for the values of $f_1 \rangle 0.1571$ and the homotopy method has reasonable solution for f_1 values up to 0.172.

5. Conclusion

In this paper we have derived the equation of ion motion in axial direction of a nonlinear ion trap. The nonlinear ion trap is generated by superposition of weak multipole fields on the pure quadrupole field. Only hexapole field superposition is considered. The computed axial equation of ion motion is a nonlinear equation with quadratic nonlinearity. We have used the homotopy perturbation method for solution of the resulted equation and calculation of the axial secular frequencies of the ions in the trap. The results of this paper are compared with the exact results and the results of the Lindstedt–Poincare method.

References

[1] N.W. McLachlan, Ordinary Non-linear Differential Equations in Engineering and Physical Sciences, Oxford University Press, UK, 1958.
[2] F. Vedel, M. Vedel, in: R.E. March, J.F.J. Todd (Eds.), Practical Aspects of Ion Trap Mass Spectrometry, CRC, New York, 1995.
[3] A.A. Makarov, Anal. Chem. 68 (1996) 4257.
[4] F.L. Londy, R.L. Alfred, R.E. March, J. Am. Soc. Mass Spectrom. 4 (1993) 687.
[5] R.E. March, A.W. McMahon, F.A. Londry, R.F. Alfred, J.F.J. Todd, F. Vedel, Int. J. Mass Spectrom. Ion Process. 95 (1989) 119.
[6] R.E. March, A.W. McMahon, E.T. Allinson, F.A. Londry, R.F. Alfred, J.F.J. Todd, F. Vedel, Int. J. Mass Spectrom. Ion Process. 99 (1990) 109.
[7] H.A. Bui, R.G. Cooks, J. Mass spectrom. 33 (1998) 297.
[8] X.Z. Chu, M. Holzki, R. Alheit, G. Weitha, Int. J. Mass Spectrom. Ion Process. 173 (1998) 107.
[9] M. Vedel, J.U. Rocher, M. Knoop, F. Vedel, Appl. Phys. B 66 (1998) 191.
[10] R.E. March, J.F.J. Todd, Quadrupole Ion Trap Mass Spectrometry, John Wiley & Sons, Inc, Amsterdam, 2005.
[11] P.H. Dawson, Quadrupole Mass Spectrometry and It's Application, Elsevier, Amsterdam, 1976.
[12] J. Franzen, Int. J. Mass spectrom. Ion Process. 125 (1993) 165.
[13] M. Nappi, V. Frankevich, M. Soni, R.G. Cooks, Int. J. Mass Spectrom. Ion Process. 177 (1998) 91.
[14] S. Sevugarajan, A.G. Menon, Int. J. Mass Spectrom. 189 (1999) 53.
[15] B.F. Apostol, J. Theor. Phys. 86 (2003) 1.
[16] P. Amore, F.M. Fernandez, Eur. J. Phys. 26 (2005) 589.
[17] A. Doroudi, Phys. Rev. E 80 (2009) 056603–56611.
[18] J.B. Marion, Classical Dynamics of Particles and Systems, San Diego, 1970.
[19] A.H. Nayfeh, Problems in Perturbations, Wiley, New York, 1985.
[20] J.H. He, Phys. Lett. A 350 (2006) 87.
[21] J.H. He, Phys. Lett. A 347 (2005) 228.
[22] J.H. He, Chaos Soliton Fractals 26 (2005) 695.
[23] J.H. He, Appl. Math. Comput. 156 (2004) 591.
[24] J.H. He, Int. J. Mod. Phys. B 20 (2006) 1141.
[25] J.H. He, Topological Methods Nonlinear Anal. J. Juliusz Schauder Center 31 (2008) 205.
[26] J.D. Jackson, Classical Electrodynamics, John Wiley & Sons, Inc. (1999).
[27] L.D. Landau, E.M. Lifshitz, Mechanics, Reed Publishing Ltd., 1981.
[28] A.H. Nayfeh, D.T. Mook, Non-linear Oscillations, John Wiley and Sons, Inc., New York, 1995.
[29] J.H. He, Int. J. Non Linear Mech. 37 (2002) 315.