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Field imperfection induced axial secular frequency shifts in nonlinear ion traps

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Abstract

This article develops a simple analytical expression that relates ion axial secular frequency to field aberration in ion trap mass spectrometers. Hexapole and octopole aberrations have been considered in the present computations. The equation of motion of the ions in a pseudopotential well with these superpositions has the form of a Duffing-like equation and a perturbation method has been used to obtain the expression for ion secular frequency as a function of field imperfections. The expression indicates that the frequency shift is sensitive to the sign of the octopole superposition and insensitive to the sign of the hexapole superposition. Further, for weak multipole superposition of the same magnitude, octopole superposition causes a larger frequency shift in comparison to hexapole superposition. (Int J Mass Spectrom 189 (1999) 53–61) © 1999 Elsevier Science B.V.

Keywords: Nonlinear traps; Secular frequency; Multipoles; Frequency shift; Duffing equation

1. Introduction

The electric field distribution within an ideal Paul trap is designed to be linear (and the potential quadratic) by shaping the electrodes to a hyperboloid geometry [1]. The motion of ions within the pure quadrupolar potential are fully characterized by the Mathieu equation [2,3] and the ion secular frequency in the radial and axial directions, ω_u, is given by

$$\omega_u = \beta_u \Omega/2 \quad (1)$$

where Ω is the rf drive frequency applied to the central ring electrode and β_u is computed from the Mathieu parameters a_u and q_u by using the continuous fraction relationship between these terms [4,5]. When the value of q_u is less than 0.4, β_u may be computed from the adiabatic or Dehmelt approximation [6].

The electric field distribution in practical traps deviates from linearity because of constraints such as the truncation of electrodes, perforation in the electrodes for enabling entry of electrons and exit of destabilized ions, intentionally introduced distortions such as the “stretched” geometry [7], in addition to space charge [8], additional dipolar excitation potential [9,10], and collisions within the trap [8,11]. The consequence of nonlinear terms in the field distribution has been the theme of several simulation [12–14] and experimental studies [15–17]. Simulation studies of ion motion in nonlinear traps indicate that superposition of higher order terms in the electric field

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causes ion secular frequency to "shift" from the value computed in Eq. (1). It has been shown that positive octopole superposition results in an increase in the ion secular frequency, whereas negative octopole superposition has the opposite effect [8]. Hexapole superposition decreases the secular frequency but the effect is small compared to octopole superposition. Experimentally it has been known for several years [18] that the voltages at which ions are ejected from the trap are slightly different from the expected value when the field is not purely quadrupolar. In a recent article Nappi et al. [19] have provided experimental evidence for the shift in ion secular frequency using a nondestructive ion detection method. They have shown that the octopole and hexapole superposition resulted in a decrease in ion secular frequency.

Whereas estimation of shifts in secular frequency due to field nonlinearities have been reported in the literature using numerical integration techniques [8,9], no analytical expression exists that relates the shift of secular frequency to field aberrations. In this article we have attempted to derive an expression for the shift of secular frequency for a single ion motion in a nonlinear ion trap with hexapole and octopole superpositions. Our method follows suggestions for incorporating higher order terms in the field equations presented in recent publications [10,20,21]. The resulting equation of motion of the ion has the form of the Duffing equation and a perturbation method has been used to derive an expression for relating ion secular frequency shift to the nonlinearities. In the derivation below we have carried out computations when no ac supplementary voltage is applied. Furthermore, the field equations in this article do not incorporate anharmonicities due to space charge and collisions within the trap.

2. Theory

The potential within a nonlinear ion trap is represented by superposing weak higher order terms on the pure quadrupolar potential. In an ideal quadrupolar trap the potential distribution inside the trap has both spherical and rotational symmetry. When there are aberrations in the trap, a set of orthogonal functions is selected in such a way that it has the same symmetry as the system for representing the higher order terms. Legendre polynomials are preferred for expressing these nonlinearities [22,23].

If P_n is the Legendre polynomial of order n, then the potential distribution inside the trap in terms of spherical coordinates is given by

$$\phi(\rho,\theta,\varphi) = \phi_0 \sum_{n=0}^{\infty} A_n \frac{\rho^n}{r_0^n} P_n(\cos\theta) \tag{2}$$

where ϕ_o is a time dependent quantity in rf traps and is given by

$$\phi_0 = V_0 \cos \Omega t \tag{3}$$

where

V_0 = 0-peak voltage of the rf potential

Ω = frequency of the rf potential

A_n = dimensionless weight factors for different terms

r_0 = radius of the ion trap in radial direction

The various terms corresponding to $n = 0,1,2,3\ldots$etc. represent the multipole components of the potential.

In the present work two higher order multipoles, hexapole and octopole corresponding to terms when $n = 3$ and $n = 4$, are taken into account along with the quadrupole component for calculating the potential distribution inside the trap. Eq. (2) becomes simpler if we write the multipole components in terms of time dependent r and z cylindrical coordinates. The multipole component corresponding to $n = 2,3,4$ in terms of cylindrical coordinates [24] are given below

$$P_2(\cos\theta) = \frac{2z^2 - r^2}{2\rho^2} \tag{4}$$

$$P_3(\cos\theta) = \frac{2z^3 - 3zr^2}{2\rho^2} \tag{5}$$

$$P_4(\cos\theta) = \frac{8z^4 - 24z^2r^2 + 3r^4}{8\rho^4} \tag{6}$$

where $\rho^2 = z^2 + r^2$.

Expanding Eq. (2) and substituting Eq. (3), (4), (5), and (6) we get the final expression for the potential distribution inside the trap that is given by

$$\phi(r,z,t) = \frac{A_2}{r_0^2} V_0 \cos \omega t \left[z^2 - r^2 + \frac{h}{r_0}\left(z^3 - \frac{3}{2} r^2 z\right) + \frac{8f}{r_0^2}\left(z^4 - 3r^2z^2 + \frac{3}{8} r^4\right)\right] \quad (7)$$

where $h = A_3/A_2$ and $f = A_4/A_2$. Here A_2, A_3, and A_4 refer to the weight of the quadrupole, hexapole, and octopole superposition. The parameters f and h represent octopole and hexapole superposition relative to the quadrupole contribution.

From classical mechanics, the three-dimensional motion of an ion within a pseudopotential well [25] with no excitation potential applied to the endcap electrode is given by

$$m \frac{d^2\rho}{dt^2} + e\nabla U_{\mathrm{eff}}(r,z) = 0 \quad (8)$$

where ρ is the ion position vector and

$$U_{\mathrm{eff}}(r,z) = \frac{1}{2}\frac{e}{m}\left\langle \left| \int_t \nabla\phi \, dt \right|^2 \right\rangle \quad (9)$$

Substituting Eq. (7) in (9) and then Eq. (9) in Eq. (8) and writing the equation of motion in the axial (z) direction we get

$$\frac{d^2z}{dt^2} + \omega_0^2 z + \frac{9h}{2r_0}\,\omega_0^2 z^2 + \frac{8f}{r_0^2}\,\omega_0^2 z^3 = 0 \quad (10)$$

where

$$\omega_0 = \frac{q_z\Omega}{2\sqrt{2}} \quad (11)$$

$$q_z = \frac{4eA_2V}{mr_0^2\Omega^2} \quad (12)$$

The expression for secular frequency ω_0 as shown in Eq. (11) is similar to the expression for secular frequency obtained using the adiabatic or Dehmelt approximation [6] when $a_u = 0$ (that is, no dc potential is applied). In our present computations (because values of q_z larger than 0.4 will be encountered) the secular frequency is computed from Eq. (1) instead of Eq. (11).

Eq. (10) has the general form of the well-studied Duffing equation [26–28] except for the magnitudes of the coefficient of the nonlinear terms. In order to reduce the magnitude of these coefficients, we introduce a new dimensionless dependent variable x, with the substitution

$$z = \frac{xr_0}{8}\, 10^{-10} \quad (13)$$

Substituting (13) into Eq. (10) we get

$$\frac{d^2x}{dt^2} + \omega_0^2 x + \alpha_2 x^2 + \alpha_3 x^3 = 0 \quad (14)$$

where

$$\alpha_2 = \frac{9h\omega_0^2}{16}\, 10^{-10} \quad (15)$$

$$\alpha_3 = \frac{f\omega_0^2}{8}\, 10^{-20} \quad (16)$$

Eq. (14) represents the equation of motion of an ion inside a nonlinear ion trap and has the form of an undriven Duffing oscillator. Equations of motion of this form in nonlinear fields have been previously used by Yoda and Sugiyama [29] and Luo et al. [30]. After taking into account the effect of damping and external dipolar excitation they have shown that their equation of ion motion in the nonlinear ion trap is similar to the forced Duffing oscillator. Recently, Vedel et al. [21] have also used a similar expression for understanding coupled radial–axial ion motion.

Any one of the several techniques available in the literature [31] can be used to solve Eq. (14) and in this article we have used the Linsdedt–Poincare technique. The basic proposition of the Lindstedt–Poincare approach to the solution of the differential equation is to assume that the nonlinear terms in Eq. (14) change the secular frequency of the system from its ideal value of ω_0 to an altered secular frequency ω. It may be seen from Eq. (14) that the perturbed frequency ω does not

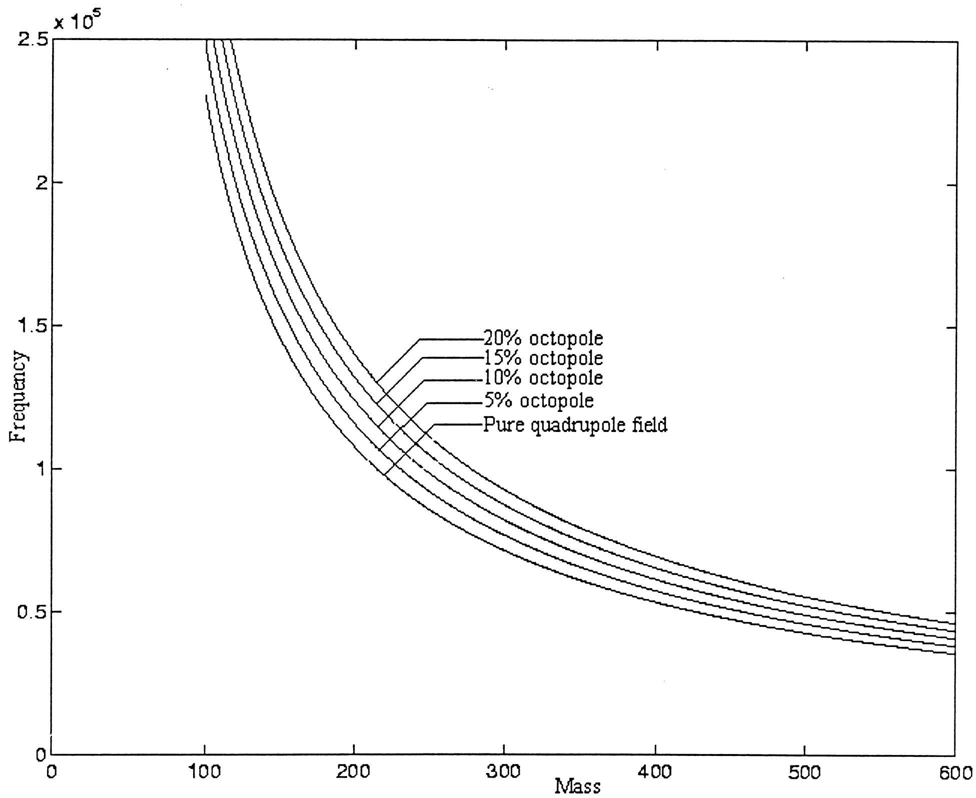

Fig. 1. Shift in the secular frequency for different values of positive octopole superposition.

appear explicitly in the differential Eq. (14). Consequently, a transformation is carried out on Eq. (14) by introducing a dimensionless term τ given by

$$\tau = \omega t \tag{17}$$

Upon introducing this dimensionless term τ, Eq. (14) is transformed to

$$\omega^2 \frac{d^2x}{d\tau^2} + \omega_0^2 x + \alpha_2 x^2 + \alpha_3 x^3 = 0 \tag{18}$$

and the differential equation has an explicit reference to the altered secular frequency ω.

The next step in the Lindstedt–Poincare technique to evaluate the extent of the change in the secular frequency is to expand the dependent variable x and the frequency ω as an asymptotic series in powers of a perturbation parameter. The perturbation parameter may be any one among the coefficients of the nonlinear terms, and the nonlinear parameter α_2 is chosen as the perturbation parameter in our present computations. Because a cubic term is also present in Eq. (14), α_3 is expressed in terms of α_2; that is $\alpha_3 = b\alpha_2$, where b is a constant. These expansions take the form indicated below

$$x = (x_0 + \alpha_2 x_1 + \alpha_2^2 x_2 + \ldots) \tag{19}$$

$$\omega = (\omega_0 + \alpha_2 \omega_1 + \alpha_2^2 \omega_2 + \ldots) \tag{20}$$

Eqs. (19) and (20) are then substituted into the transformed Eq. (18), and the coefficients of like powers of α_2 are equated. By doing this we get a set of equations that can be successively solved for x_n and ω_n. When the values of ω_1, ω_2, ω_3. . .etc. are extracted and inserted into Eq. (20), we get the perturbed frequency, ω, that is given by [32]

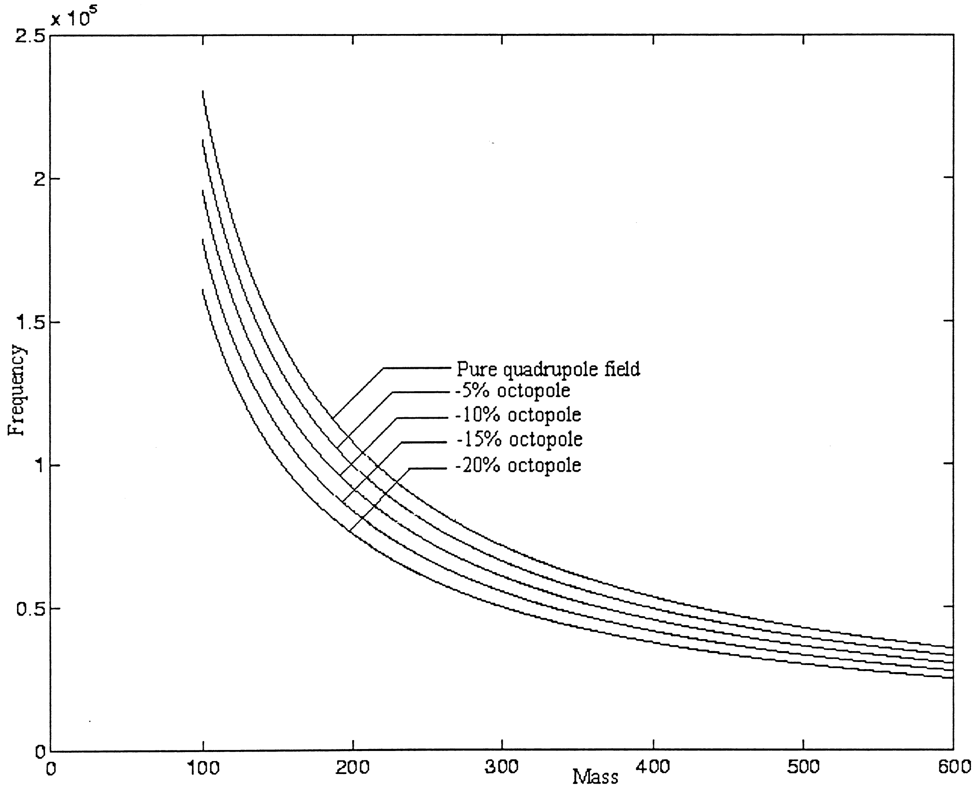

Fig. 2. Shift in the secular frequency for different values of negative octopole superposition.

$$\omega = \omega_0 \left[1 + \left(\frac{9\alpha_3 \omega_0^2 - 10\alpha_2^2}{24\omega_0^4} \right) A_0^2 \right] \quad (21)$$

where A_0 corresponds to the maximum value that x can have. The value for x_{max} is obtained by inserting z_0 for z in Eq. (13) for a specific trap design. Upon introducing the values for α_2 and α_3 into Eq. (21) we get the final expression for the perturbed frequency in terms of h and f, the strength of hexapole and octopole superposition, respectively, that is given by

$$\omega = \omega_0 \left[1 + \left(\frac{144f - 405h^2}{48} \right) \frac{z_0^2}{r_0^2} \right] \quad (22)$$

3. Results and discussion

Eq. (22) is an expression that relates the secular frequency of an ion to field aberrations (h and f). One fact that will be evident from this expression is that ion secular frequency will be dependent on the sign (positive or negative) of the octopole superposition whereas it will be insensitive to the sign of the hexapole superposition. For a given geometry of the trap the frequency shift is independent of the trap size. For instance, in our present computations we have assumed $r_0^2 = 2z_0^2$. Consequently, the fraction z_0^2/r_0^2 in Eq. (22) can be replaced by a constant 0.5.

The effect of the magnitude and sign of the field aberration are graphically plotted in Figs. 1–4. In all these plots, a trap with $r_0 = 7$ mm ($r_0^2 = 2z_0^2$) and rf drive frequency of 1 MHz have been considered. The value of the rf potential is fixed at 300 V_{0-p}. Figs. 1–3 plot the secular frequency of mass between 100 and 600 u whereas in Fig. 4 the mass range is 100–500 u. In all plots, a curve corresponding to pure quadrupolar field secular frequency [obtained from Eq. (1)] has also been included for the purpose of comparison.

Fig. 1 plots the secular frequency of ions in a

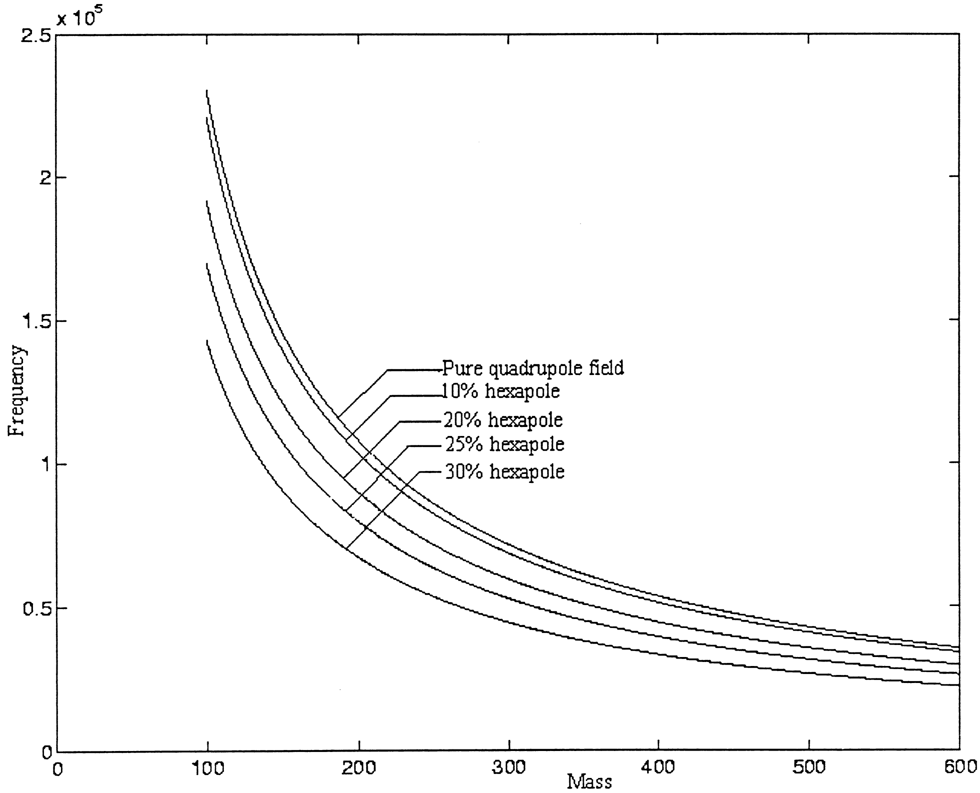

Fig. 3. Shift in the secular frequency for different values of hexapole superposition.

quadrupolar field with only a positive octopole superposition. From Fig. 1 it can be seen that a positive octopole superposition shifts the secular frequency to higher values compared to the pure quadrupolar field. As the octopole superposition increases, the shift in the secular frequency also increases. In this plot, positive octopole superpositions of 5–20% have been considered. On the other hand, when we have a negative octopole superposition the situation becomes reversed, that is, the secular frequency decreases as the negative octopole superposition increases. This effect can be seen from Fig. 2, which is a plot of negative octopole superpositions of −5 to −20%.

When we consider the hexapole superposition in the absence of the octopole superposition, the secular frequency decreases and the change is insensitive to the sign of the hexapole superposition. The reason is evident in Eq. (22), where the parameter h, which represents the hexapole superposition, has a power of 2. Fig. 3 plots hexapole superpositions of 10%, 20%, 25%, and 30%. Fig. 4 is a plot of combined hexapole and octopole superposition on the pure quadrupole field. In this plot the curves are plotted for (a) 10% octopole and 10% hexapole, (b) 5% octopole and 5% hexapole, (c) −5% octopole and 5% hexapole and (d) −5% octopole and 10% hexapole. When both the octopole and hexapole superpositions are present, the shift may be either positive or negative depending on the magnitude and sign of the superpositions. This is evident from the fact that the contribution of these two terms appears independently in Eq. (21) and they are summed to obtain the resultant frequency shift.

Finally, in Fig. 5 we plot the magnitude of the frequency shift $\Delta\omega$ as a function of nonlinearities. The

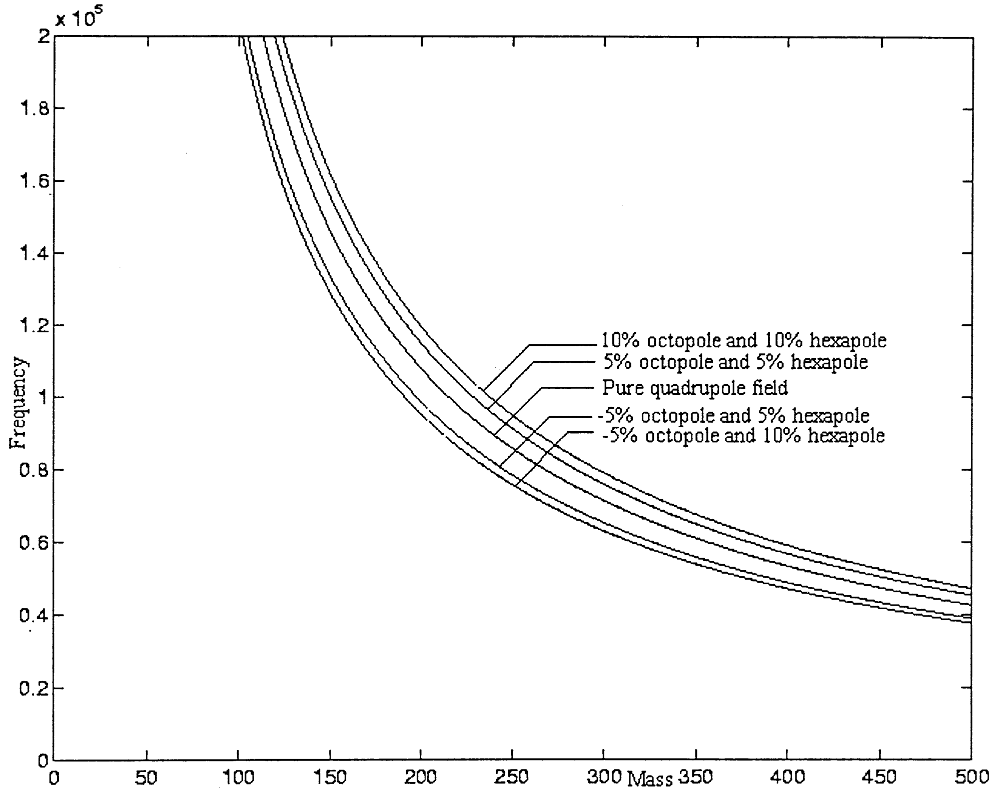

Fig. 4. Shift in the secular frequency for different values of both hexapole and octopole superposition.

frequency shift $\Delta\omega$ can be obtained from Eq. (22) and is given by

$$\Delta\omega = \omega_0\left[\left(\frac{144f - 405h^2}{48}\right)\frac{z_0^2}{r_0^2}\right] \quad (23)$$

Eq. (23), which incorporates the weight factors of the nonlinearities, will give the frequency shift for different conditions of field aberrations. This equation suggests that octopole aberrations will cause a linear shift in the secular frequency and the shift will depend on the sign of the octopole superposition, whereas the shift due to hexapole nonlinearities will not only be sign insensitive but also have low magnitudes relative to the octopole superposition when its nonlinear contribution is small. For higher values of hexapole superposition (above 35%) the frequency shift will be higher than that of the shift caused by the octopole superposition (Fig. 5). Note that when the hexapole and octopole contributions are 35.56% each, the effect of frequency shift due to one will be nullified by the other, and this point is independent of mass and the drive potential.

4. Conclusion

The motion of ions in a trap with a superposed field aberration may be computed from a Duffing-like equation. The field aberrations included in the present computations are the octopole and hexapole superposition. In this article a perturbation method has been used to derive an analytical relationship to describe the dependence of ion secular frequency on octopole and hexapole superposition. The frequency shift due to octopole superposition is seen to be linearly depen-

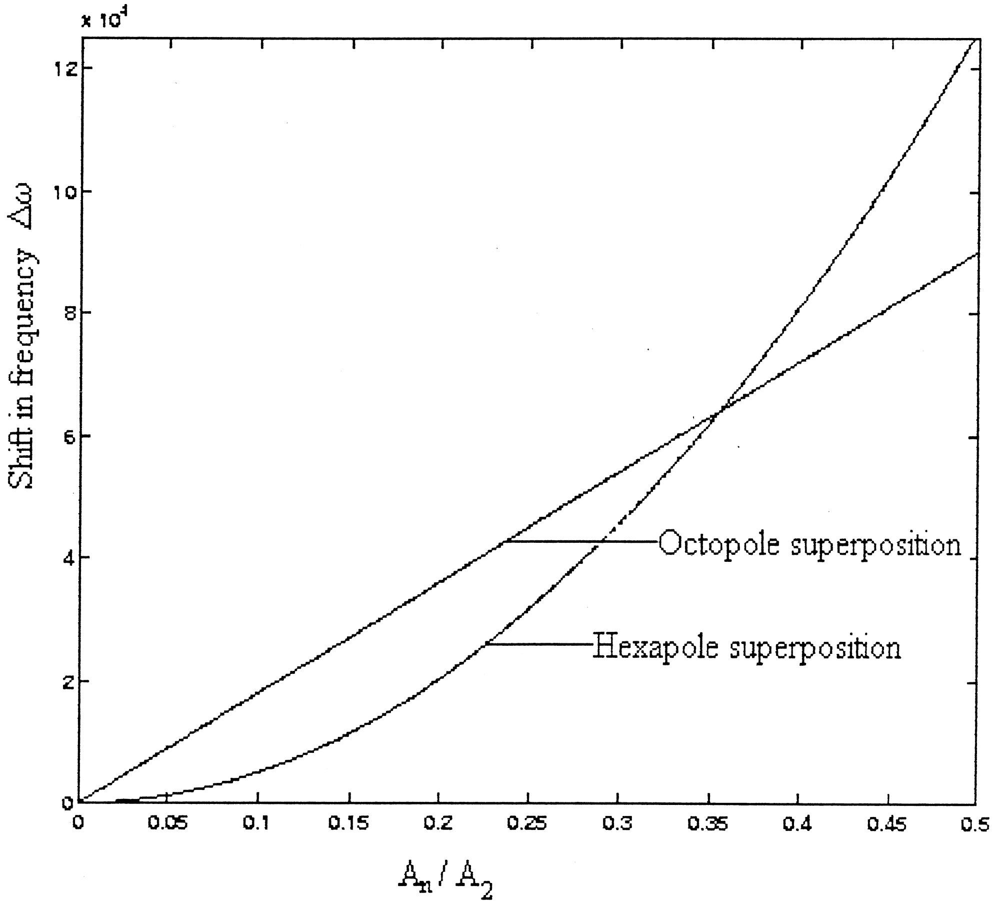

Fig. 5. Frequency shift $\Delta\omega$ for different values of hexapole and octopole superpositions.

dent on the octopole weight factor. This results in the secular frequency shift being dependent on the sign of the octopole superposition. On the other hand, because the hexapole weight factor appears as a quadratic term, the ion secular frequency is independent of the sign of the hexapole superposition.

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