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Spatial harmonics of linear multipoles with round electrodes

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ABSTRACT

The problem of creating hexapole, octopole, decapole and dodecapole electric fields with round-rod electrodes is considered. We propose a new numerical method to calculate the spatial harmonics and find the optimal electrode configurations. This configuration is characterized by the parameter $\gamma = r/r_0$, where r is the rod radius and r_0 is the radius of an inscribed circle between the electrode tips. We consider four different criteria for optimizing the field: (1) the value that makes the amplitude of the main multipole 1.0, (2) the value that makes the amplitude of the next higher harmonic after the main harmonic zero, (3) the ratio that gives the next two higher harmonics equal amplitudes but opposite signs and (4) the ratio that minimizes the deviation of the potential and electric field from the potential and electric field of an ideal multipole, averaged over the region within the multipole. Each gives slightly different values for the optimal value of γ. To minimize the field deviation from that of an ideal multipole the optimal values are $\gamma = 0.563$, 0.372, 0.278, 0.221 for hexapole, octopole, decapole, and dodecapole fields, respectively.

1. Introduction

Two-dimensional radio frequency (rf) electric fields are used for confinement of charge particles and as ion guides, and find widespread applications in mass spectrometry [1–8]. A two-dimensional electric field with a potential $\varphi(x, y)$ depends on the two Cartesian coordinates x and y, and is created by elongated parallel electrodes [4–6]. The potential can be written as sum of spatial harmonics (multipoles) as

$$\varphi(x, y) = U \ \mathrm{Re}\sum_{k=0}^{\infty} A_k z^k = U \,\mathrm{Re}\sum_{k=0}^{\infty} A_k (x + iy)^k \quad (1)$$

where A_k is the amplitude of the kth spatial harmonic, $i = \sqrt{-1}$, U is an applied voltage, and Re $f(z)$ is the real part of the complex function $f(z)$. The amplitude A_k is dimensionless if x and y are in units of r_0 (see below). The linear two-dimensional field with the complex potential $z^2 = (x + iy)^2$ is used for mass analysis in the quadrupole mass filter [4], where the electric fields are proportional to the coordinates ($E_x \propto x$ and $E_y \propto y$). Ion motion in the linear quadrupole field is described by Mathieu equations, which have solutions with sharp boundaries between stable and unstable regions. Quadrupole fields are created by four electrodes with hyperbolic cross sections $x^2 - y^2 = r_0^2$, where r_0 (the field radius) is the radius of an inscribed circle between the electrode tips. In practice, cylindrical (or round) electrodes are often used and the geometry of a quadrupole rod set is characterized by the parameter $\gamma = r/r_0$, where r is the rod radius and r_0 is the radius of an inscribed circle that touches the electrode tips. A quadrupole with four round rods generates harmonics with $k = 2$, 6, 10, 14, ... The dodecapole field component ($k = 6$) can be removed by choosing $\gamma = 1.14511$ [9–11]. However this does not optimize the peak shape, resolution and transmission of a quadrupole mass filter. The 20-pole harmonic ($k = 10$) with amplitude $A_{10} \approx -2 \times 10^{-3}$ influences the ion motion significantly [10,12]. In Ref. [10] it was proposed that $\gamma = 1.110$ should be chosen to remove nonlinear resonances which lead to peak splitting. Douglas and Konenkov showed [12] that the combined effects of the $k = 6$ and $k = 10$ harmonics on peak shape partially compensate each other because their amplitudes are similar but have opposite signs when $\gamma = 1.126$–1.130.

The analytical expressions for the spatial harmonics in Cartesian coordinates have been given by Szylagi [2]. The two-dimensional fields created by thin rods (wires), on which a symmetrical potential distribution is applied, have been studied analytically [3]. It was shown, for example, that it is possible to create a quadrupole field with 12 parallel electrodes that has a greater region of field linearity compared to the field of a round-rod set.

Methods for and results of numerical calculations of the amplitudes A_k of potentials for the quadrupole mass filter have been given [5,6,9–11,13]. A detailed account of the numerical calculation of the potential in a linear quadrupole trap constructed with flat (planar) electrodes (rectilinear ion trap) is given in Ref. [5]. The surface of the electrodes is described mathematically by thin strips with given potential distributions. For given potentials on the strips,

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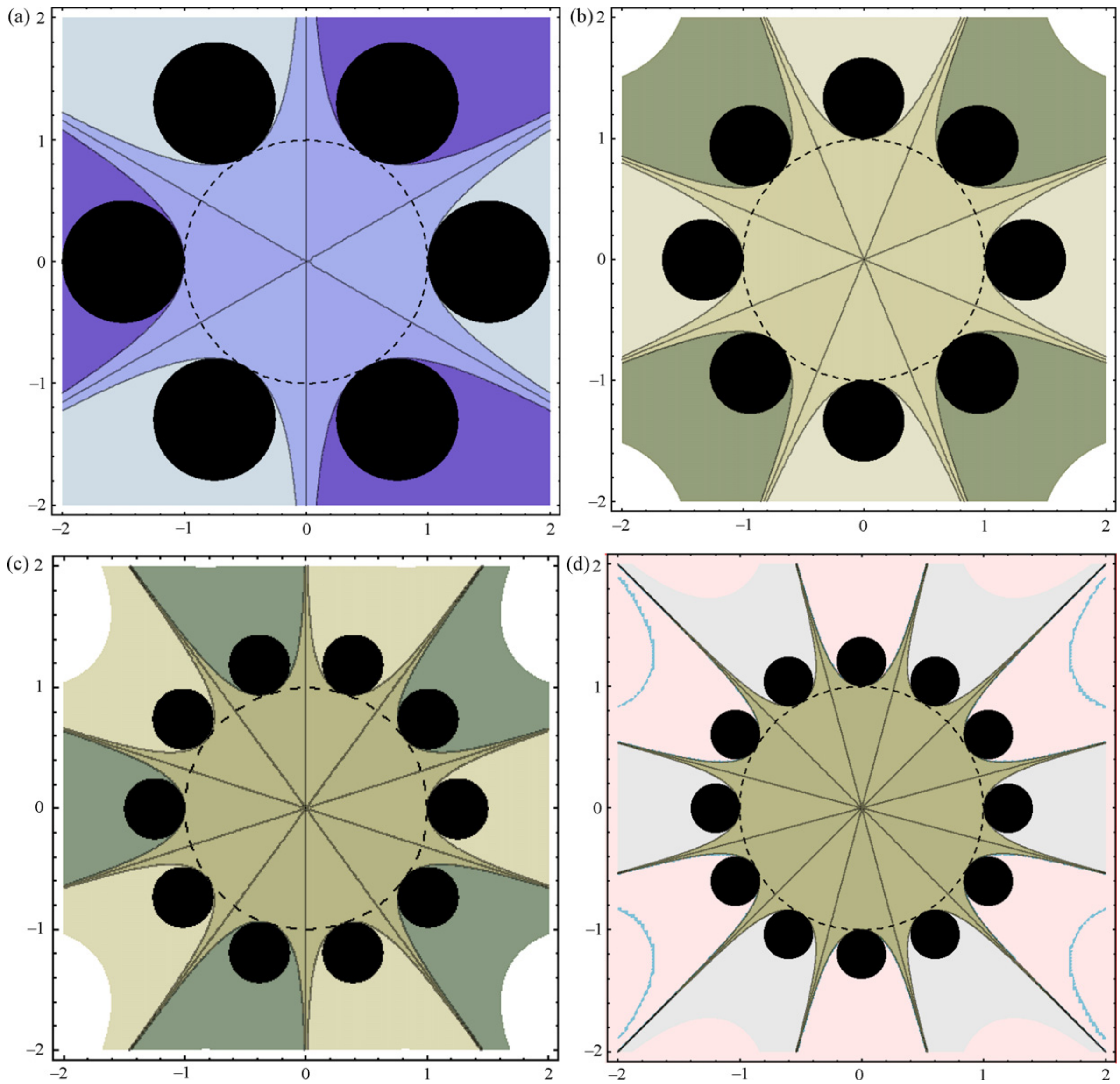

Fig. 1. Electrodes of multipoles. (a) Hexapole, (b) octopole, (c) decapole and (d) dodecapole. The radius of the circle marked by the dashed line is r_0. The radius of curvature r is equal to the radius of the cylinder shown in black.

the potential is calculated as a superposition of terms in a series. A similar numerical method has been used to calculate the harmonic amplitudes of a linear quadrupole constructed with round rods [11].

The optimal values of $\gamma = r/r_0$ for hexapole and octopole fields created with round rods, have been calculated using SIMION 3D Version 6 [13] and are $\gamma_H = 0.5375$ and $\gamma_O = 0.355$ for hexapoles and octopoles, respectively. SIMION 3D is effective for three-dimensional problems. For two-dimensional fields there are more effective and simpler numerical methods [5,9–11].

In this work we develop methods for the calculation of the harmonic amplitudes A_N of two-dimensional hexapole, octopole, decapole and dodecapole potentials created with round rods and determine optimal values of γ. We consider four different criteria for optimizing the field: (1) the value that makes the amplitude of the main multipole 1.0, (2) the value that makes the amplitude of the next higher harmonic after the main harmonic zero, (3) the ratio that gives the next two higher harmonics equal amplitudes but opposite signs and (4) the ratio that minimizes the deviation of the potential and electric field from the potential and electric field of an ideal multipole, averaged over the region within the multipole. Each gives slightly different values for the optimal value of γ. The goal of this work is to study the spatial harmonics with a numerical method developed for round electrodes.

2. Methods

2.1. Multipole rod structure and equations of ion motion

The cross sections of the electrodes for producing ideal multipole fields are described by

$$\mathrm{Re}(x+iy)^N = r_0^N \tag{2}$$

where r_0 is the radius of an inscribed circle between the electrodes, and N is the order of the multipole. The expression with $N=2$ corresponds to a quadrupole, $N=3$ a hexapole, $N=4$ an octopole, $N=5$ a decapole and $N=6$ a dodecapole. Every multipole of order N has $2N$ electrodes. The shapes of the electrodes calculated from Eq. (2) have been shown by Szabo [14]. Manufacturing and precisely mounting electrodes with these exact shapes is difficult, and round rods are often used in practice. Rod structures for the multipoles with $N = 3$–6, constructed with round rods, are shown in Fig. 1. We choose the field radius as the unit of length i.e., $r_0 = 1$. The first geometrical approximation to the exact electrode geometry is a cylinder, inscribed in the cross section of the curve given by Eq. (2) with radius of curvature r given by [1]

$$r = \frac{r_0}{N-1} \tag{3}$$

These round rods are shown in black in Fig. 1. The exact electrode shapes are shown by curves touching the round (black) rods. When the multipoles are constructed with round rod electrodes, the field has many higher order spatial harmonics with diminishing amplitudes [2,3]. Due to the symmetries of the rod sets, we can write the potential for a $2N$ multipole as

$$\Phi_N(x,y) = \mathrm{Re}\sum_{k=0}^{\infty} A_{(2k+1)N} z^{(2k+1)N} \tag{4}$$

The main harmonic, N is given by

$$\varphi_N(x,y) = \mathrm{Re}\ A_N z^N \quad N = 3, 4, 5 \text{ or } 6. \tag{5}$$

For confinement of ions, RF fields with voltages $\pm V\cos\Omega t$ are applied between rod pairs [1]. As with a quadrupole mass filter, dc and rf voltages $\pm(U + V\cos\Omega t)$ can also be applied between rod pairs. Then equations of motion of an ion in perfect multipole fields ($A_N = 1, A_K = 0, k \neq N$) may be written in dimensionless variables as

$$\frac{d^2x}{d\xi^2} = -(a_N + 2q_N\ \cos 2\xi)\mathrm{Re}[(x+iy)^{N-1}] \tag{6}$$

$$\frac{d^2y}{d\xi^2} = -(a_N + 2q_N\ \cos 2\xi)\mathrm{Re}[i(x+iy)^{N-1}] \tag{7}$$

$$a_N = \frac{8(N-1)eU}{m\Omega^2 r_0^2};\quad q_N = \frac{4(N-1)eV}{m\Omega^2 r_0^2},\quad \xi = \frac{\Omega t}{2} \tag{8}$$

From Eqs. (6) and (7) one can see that the ion motions in the two directions x and y are coupled (for $N > 2$) and there are no stability regions like those of a quadrupole field ($N = 2$) [4]. Ion motion in multipole rf fields is usually described as motion in an effective potential [1].

The ion optical properties for ideal electrodes, with shapes given by Eq. (2) have been studied in detail in Ref. [14]. Numerical solutions of the coupled equations (6) and (7) showed that there are not well defined the stability regions. In contrast to ion motion in a quadrupole field, the stability of an ion trajectory in a higher multipole depends on the initial conditions. For this reason the higher multipoles have not been used as mass filters.

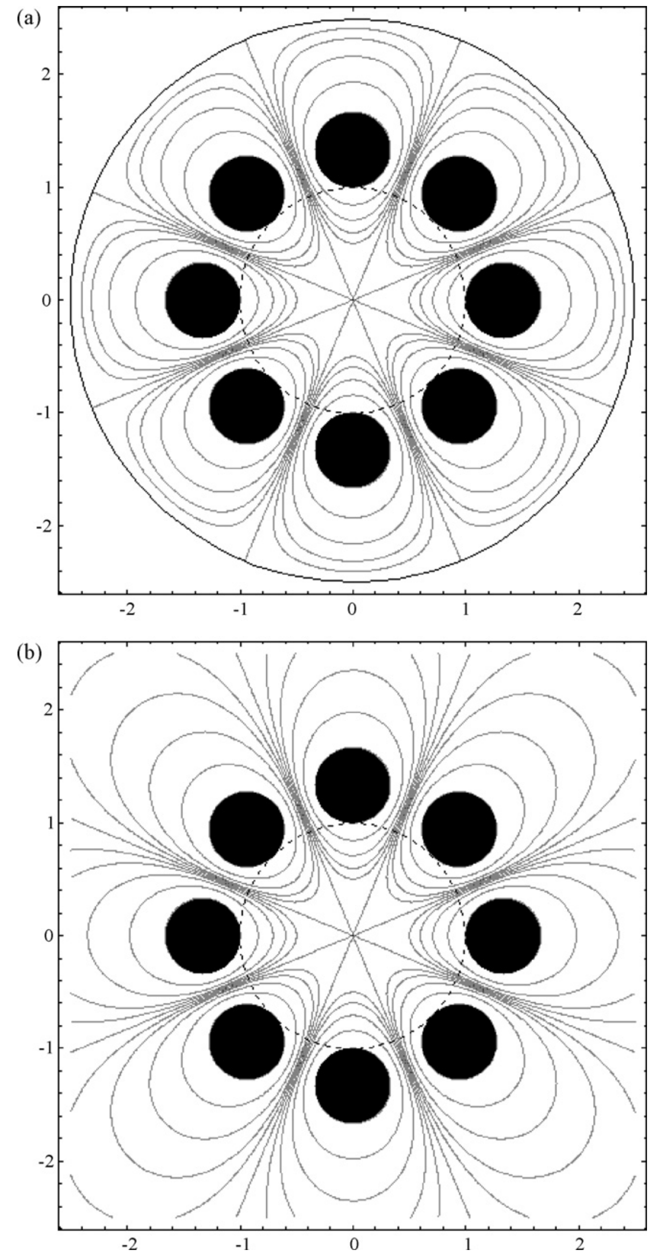

Fig. 2. (a) Potential distribution in an octopole with $r/r_0 = 0.3615$ with a grounded cylindrical case and (b) with no case.

2.2. Field calculations

Representation of the potential generated by a long symmetrical rod set by Eq. (1) allows an analytical description of the ion motion. Here we choose the applied potential $U = \pm 1$ V without limitations because the RF field is quasi-stationary (wavelength $\lambda = 2\pi c/\Omega \gg L$, where L is the electrode length and c is the velocity of light). We consider an external symmetrically arranged grounded metal casing with radius R_c.

Let z_l be the distance from a point to the centers of the lth rod, $l = 1, 2, \ldots, 2N$. We will write the complex potential $F(z)$ of the field generated by $2N$ parallel electrodes in the form

$$F(z) = \sum_{l=1}^{2N} F_l(z), \quad \text{where } F_l(z) = C_{l0}\ln(z - z_l) + \sum_{j=1}^{\infty} C_{lj}(z - z_l)^{-j} \tag{9}$$

The coefficients C_{lj} are determined from the boundary conditions

$$\mathrm{Re}\ F(z)|_{S_l} = (-1)^{l+1};\quad l = 1, 2, \ldots, 2N \tag{10}$$

where S_l is the edge of the lth rod. For numerical calculation of the amplitudes A_k from the series of $F_l(z)$ of Eq. (9) we need to limit the sum to a finite number m

$$F_l^m(z) = C_{l0}\ \ln(z - z_l) + \sum_{j=1}^{m} C_{lj}(z - z_l)^{-j} \tag{11}$$

On the boundary S_l take $m + 1$ equidistant points z_{lj} equal to the number of unknown coefficients C_{lj} in the series of Eq. (11). Substituting the complex coordinates z_{lj} in the boundary condition Eq. (10) gives a system of linear equations for the values of C_{lj}. The complex function $F_l^m(z)$ is then expanded in a Taylor series about $z = 0$ (the multipole center). This gives the harmonic amplitudes A_k.

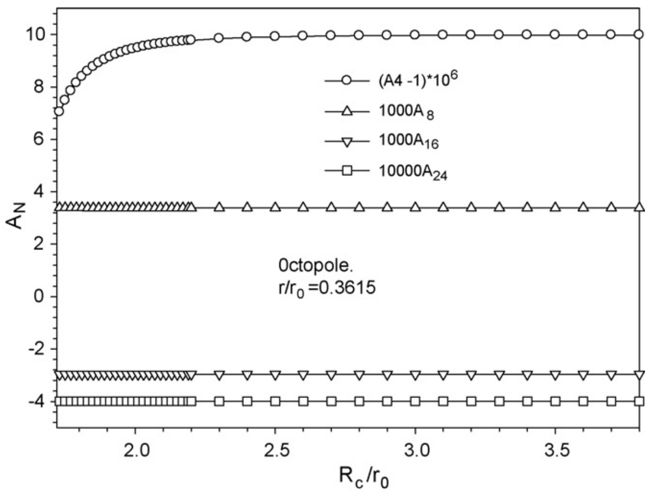

Fig. 3. Influence of the external case radius on the main spatial harmonics of an octopole.

Taking into account a grounded cylindrical casing (Fig. 2) the boundary condition Eq. (10) can be rewritten as [11].

$$\text{Re}\left[F(z)-F\left(\frac{R^2}{z^*}\right)\right]\Bigg|_{S_l}=(-1)^l;\quad l=1,2,\ldots,2N \tag{12}$$

where $z^*=(x-iy)$ is the complex conjugate of $z=x+iy$. The calculation procedure for the amplitudes A_l remains the same.

The potential distributions for an octopole ($N=4$) with a cylindrical housing with radius $R=2.5r_0$ and without a housing ($R=\infty$) are shown in Fig. 2a and b, respectively. The equipotential lines from a positive rod tip to the center have values 1/2, 1/4, 1/8, 1/16, 0. The +1 V equipotential line is the electrode surface. Visually it is not possible distinguish differences in the potential distributions within the unit circle marked by the dashed line. In numerical calculations high precision arithmetic was used. The high precision arithmetic represents digits as 1/4 instead of 0.25 and 224/1000 instead of 0.224 and so on. The number $m+1$ points on a circular rod S_l, and number m of terms in the series of Eq. (11) was typically $m=40$–100. With $m=50$ the difference in last significant digits is 10^{-12}, compared to when $m=100$. Thus the calculation is precise to a value 10^{-10} or better.

2.3. Criteria for rod set optimization

As a measure ε_φ of the deviation of the potential distribution $\Phi_N(x,y)$ (Eq. (4)) of a multipole with $2N$ round rods from the ideal field $\varphi_N(x,y)$ (Eq. (5)) we use the square root of the mean square deviation, averaged over the circular region with radius $r_0=1$ (Fig. 2), given by

$$\varepsilon_\varphi=\frac{\left[\int_{x^2+y^2<1}(\Phi_N(x,y)-\varphi_N(x,y))^2dx\ dy\right]^{1/2}}{\left[\int_{x^2+y^2<1}\varphi_N^2(x,y)dx\ dy\right]^{1/2}} \tag{13}$$

The value of ε_φ can be expressed in explicit form when the potentials Φ_N (Eq. (4)) and φ_N (Eq. (5)) are represented in the polar

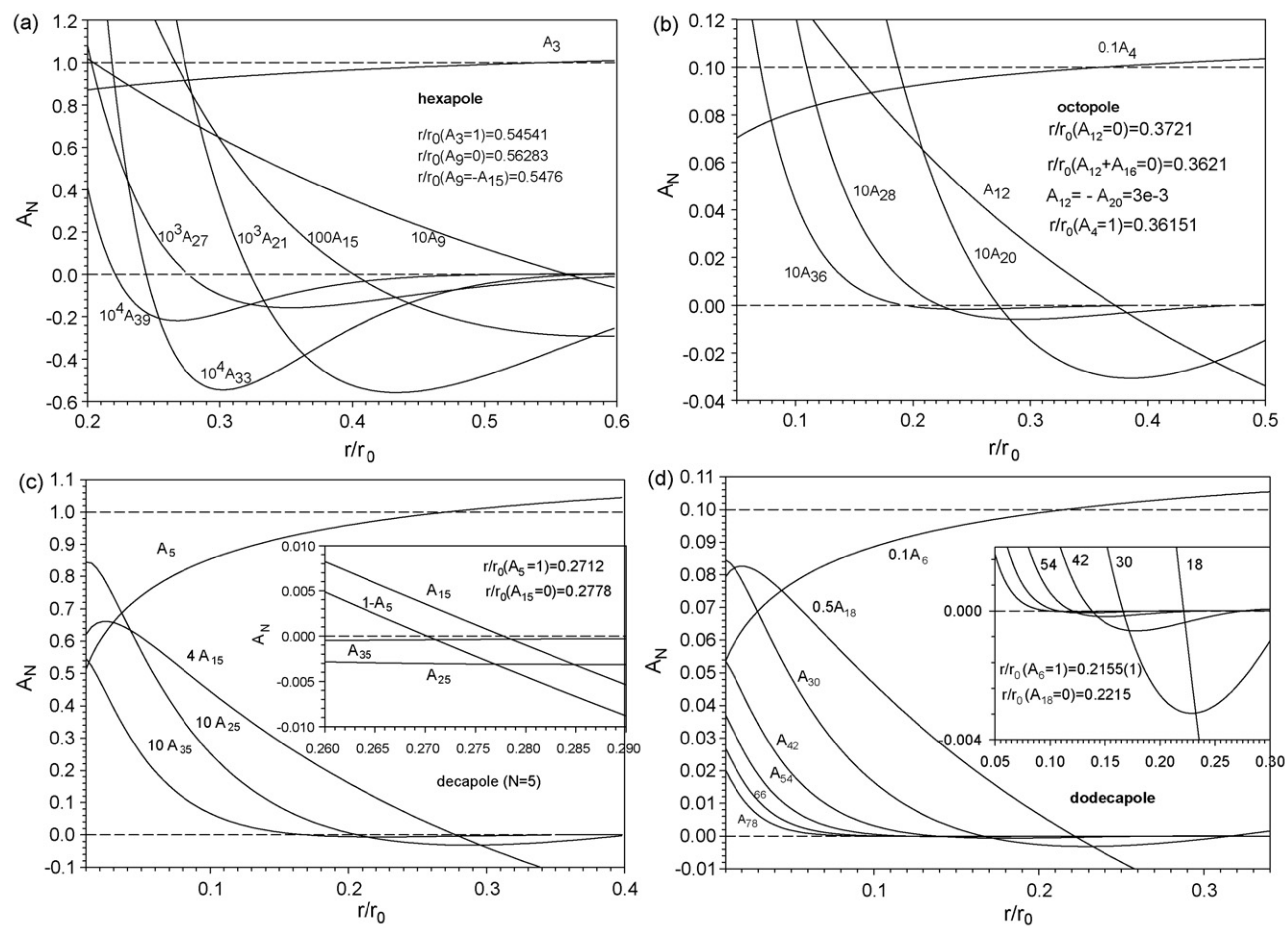

Fig. 4. Amplitudes $A_{(2k+1)N}$ vs. r/r_0 for (a) hexapole (b) octopole (c) decapole and (d) dodecapole fields, with no external case.

Table 1
Optimal parameters r/r_0.

Main field	r/r_0 ($A_N = 1$)	r/r_0 ($A_{3N} = 0$)	r/r_0 ($A_{3N} = -A_{5N}$)	$\gamma_\varphi = r/r_0$	$\gamma = r/r_0$ [13]
Hexapole, $N = 3$	0.5454	0.5628	0.5476	0.563	0.5375
Octopole, $N = 4$	0.3615	0.3721	0.3621	0.372	0.355
Decapole, $N = 5$	0.2717	0.2778	0.2711	0.278	
Dodecapole, $N = 6$	0.2155	0.2215	0.2162	0.221	

coordinate system ρ, ϑ:

$$\Phi_N(\rho, \vartheta) = \sum_{k=0}^{\infty} A_{(2k+1)N} \rho^{(2k+1)N} \cos[(2k+1)N\vartheta] \tag{14}$$

$$\varphi_N(\rho, \vartheta) = A_N \rho^N \cos N\vartheta \tag{15}$$

so that, for example

$$\int_{x^2+y^2<1} \varphi_N^2(x, y)dx\ dy$$
$$= A_N^2 \int_0^{2\pi} \cos^2(N\vartheta)d\vartheta \int_0^1 \rho^{2N}\rho\ d\rho = \frac{\pi A_N^2}{2(2N+1)} \tag{16}$$

For a given multipole, from Eq. (12) it follows that the potential deviation, ε_φ, is

$$\varepsilon_\varphi = \frac{\sqrt{N+1}}{A_N}\left(\sum_{k=1}^{\infty} \frac{A_{(2k+1)N}^2}{2(2k+1)N+1}\right)^{1/2} \tag{17}$$

In the same way, we obtain a measure ε_E of the deviation of the electric field strength in the form

$$\varepsilon_E = \frac{\left[\int_{x^2+y^2<1} |\vec{\nabla}\Phi_N(x, y) - \vec{\nabla}\varphi_N(x, y)|^2 dx\ dy\right]^{1/2}}{\left[\int_{x^2+y^2<1} |\vec{\nabla}\varphi_N(x, y)|^2\right]^{1/2}}$$
$$= \frac{1}{A_N}\left[\sum_{k=1}^{\infty}(2k+1)A_{(2k+1)N}^2\right]^{1/2} \tag{18}$$

3. Results and discussion

These calculations show that an external metal casing has a very weak influence on the potential distribution within the multipoles as is the case with a quadrupole field [9–11], and as discussed by Gerlich [1]. As an example, the variation of the amplitudes A_4, A_8, A_{16} and A_{24} with the casing radius R_c for an octopole is shown in Fig. 3. Here the ratio $r/r_0 = 0.36151$ is used. This gives $A_4 = 1.0 + 1 \times 10^{-5}$ when there is no external case ($R_c = \infty$). The change in A_4 from the case touching the rods, $R_c/r_0 = 1.723$, to $R_c/r_0 = 3.8$ is about 3×10^{-6}. The amplitudes of the other higher multipoles, A_8, A_{16} and A_{24} show no practical changes. Thus to determine the optimal value of r/r_0 the external metal casing need not be included.

The variation of the amplitudes A_N with the ratio r/r_0 for hexapole, octopole, decapole and dodecapole are shown in Fig. 4(a–d) for a metal casing of radius $R_c = \infty$. At small rod radius r, all multipoles have large amplitude higher order harmonics. Every multipole set has a parameter r/r_0 at which amplitude of the main harmonic $A_N = 1.00$. For $N = 3, 4, 5, 6$ these values are $r/r_0 = 0.5454$, 0.3615, 0.2712 and 0.2155, respectively. When $A_N = 1$ the higher harmonics have amplitudes with opposite signs and the sum of the amplitudes is zero. Indeed, if $A_N = 1$ it follows from Eq. (3) that

$$\Phi_N(x, y) = \text{Re}\ z^N + \text{Re}\sum_{k=1}^{\infty} A_{(2k+1)N} z^{(2k+1)N} \tag{19}$$

The potential Φ_N of the positive rod at the point $x = 1$ and $y = 0$ ($z = 1$) equals 1.0 V. We have

$$1 = 1 + \sum_{k=1}^{\infty} A_{(2k+1)N}, \quad \text{so that} \sum_{k=1}^{\infty} A_{(2k+1)N} = 0 \tag{20}$$

The next harmonic after the main multipole with amplitude A_N ($N = 3, 4, 5, 6$) can be removed by using $r/r_0 = 0.5628$ ($A_9 = 0$) for the hexapole, $r/r_0 = 0.3721$ ($A_{12} = 0$) for the octopole, $r/r_0 = 0.2778$ ($A_{15} = 0$) for the decapole and $r/r_0 = 0.2215$ ($A_{18} = 0$) for the dodecapole. Only one of next two higher harmonics $3N$ and $5N$ can be removed by adjusting r/r_0 (Fig. 4).

There is a value r/r_0 between the ratio where $A_N = 1$ and the ratio where $A_{3N} = 0$ at which the next two largest amplitude harmonics after the main harmonic (N) have opposite signs $A_{3N} = -A_{5N}$ and their effects on ion motion may partially compensate each other. This was the reason for choosing $r/r_0 = 1.126$–1.130 for the quadrupole [12]. For the hexapole, the $N = 9$ and $N = 15$ harmonics have amplitudes $A_9 = -A_{15} \approx 2.8 \times 10^{-3}$ at $r/r_0 = 0.5476$; for the octopole the $N = 12$ and $N = 20$ harmonics have amplitudes $A_{12} = -A_{20} \approx 3.0 \times 10^{-3}$ at $r/r_0 = 0.3621$. The data for the other multipoles are given in Table 1. The other high order harmonics have amplitudes an order of magnitude lower.

The ratio r/r_0 is optimized by minimizing ε_φ and ε_E, given by Eqs. (17) and (18). The variation of ε_φ with r/r_0 is shown in Fig. 5 for octopole, hexapole, decapole and dodecapole fields. The calculations include the first six harmonics: N, $3N$, $5N$, $7N$, $9N$ and $11N$ (Eqs. (17) and (18)). The values of ε_φ are a minimized at $\eta = r/r_0 = 0.565$, 0.372, 0.278 and 0.221 for the hexapole, octopole, decapole and dodecapole fields, respectively, where the main spatial harmonic dominates. The variations of ε_E have minima at the same r/r_0.

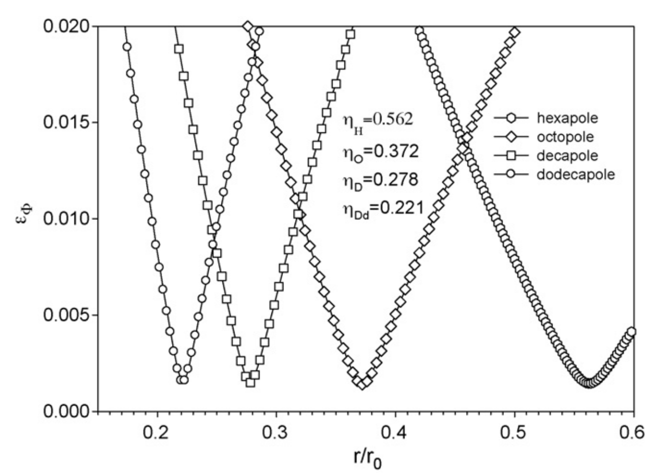

Fig. 5. Mean deviation ε_φ of potential fields from ideal fields vs. the ratio r/r_0 for four multipoles.

Table 1 summarizes the optimal values of r/r_0 for all the cases discussed here. From Table 1 it is apparent that the minima of ε_φ and ε_E occur for the geometry where $A_{3N} = 0$; that is when the main higher harmonic is zero. The amplitude of this harmonic is much larger than the others on the interval of r/r_0 considered here and so this harmonic dominates the contributions to ε_φ and ε_E. For a quadrupole, ε_φ also has a minimum at $\gamma = 1.1451$ where $A_6 = 0$. The values of γ for the hexapole and octopole in Ref. [13] are slightly different from the present data due to the different fitting procedure used. A reviewer has pointed out that from data of Table 1, it follows that a good approximation for the value of γ that makes $A_{3N} = 0$ is $\gamma = 1.11/(N - 1)$.

4. Conclusions

Round rods allow construction of multipole fields with an average deviation ε_φ of 0.2% from an ideal field. These data may be useful for the design of multipole ion guides, and other devices based on multipoles.

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