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Numerical analysis of segmented-electrode Orbitraps

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ABSTRACT

Simple geometries which are possible alternatives for the Orbitrap are studied in this paper. We have taken up for numerical investigation two segmented-electrode structures, ORB1 and ORB2, to mimic the electric field of the Orbitrap. In the ORB1, the inner spindle-like electrode and the outer barrel-like electrode of the Orbitrap have been replaced by 35 rings and 35 discs of fixed radii, respectively. In this structure two segmented end cap electrodes have been added. In this geometry, different potentials are applied to the different electrodes keeping top-bottom symmetry intact. In the second geometry, ORB2, the inner and outer electrodes of the Orbitrap were replaced by an approximate step structure which follows the profile of the Orbitrap electrodes. In the present study 45 steps have been used. In the ORB2, like the Orbitrap, the inner electrode is held at a negative potential and the outer electrode is at ground potential.

For the purpose of comparing the performance of ORB1 and ORB2 with that of the Orbitrap, the following studies have been undertaken: (1) variation of electric potential, (2) computation of ion trajectories, (3) simulation of image currents. These studies have been carried out using both 2D and 3D Boundary Element Method (BEM), the 3D BEM was developed specifically for this study. It has been seen in these investigations that ORB1 and ORB2 have performance similar to that of the Orbitrap, with the performance of the ORB1 being seen to be marginally superior to that of the ORB2.

It has been shown that with proper optimization, geometries containing far fewer electrodes can be used as mass analyzers. A novel technique of optimization of the electric field has been proposed with the objective of minimizing the dependence of axial frequency of ion motion on the initial position of an ion. The results on the optimization of 9 and 15 segmented-electrode traps having the same design as ORB1 show that it can provide accurate mass analysis.

1. Introduction

The Orbitrap is a relatively new mass analyzer based on the Kingdon trap [1]. The cylindrical outer electrode of the Kingdon trap was first modified to produce the harmonic axial potential by Knight [2]. Knight's Kingdon trap was further refined into the Orbitrap by Makarov [3–5]. The Orbitrap was subsequently incorporated in the mass spectrometer and its performance and applications were demonstrated [6–10]. The operation of the Orbitrap with axial ac dipolar excitation was also demonstrated [11] and simulated ion trajectories as well as image currents were computed [12,13].

The potential distribution inside the Orbitrap is 'hyper-logarithmic' in nature. To obtain this potential distribution, the Orbitrap uses a spindle-like inner electrode and a barrel-like outer electrode, both having axial symmetry around the central axis (z axis), as shown in Fig. 1. The curvature of the inner and the outer electrodes of the Orbitrap are defined by [4],

$$z=\sqrt{\frac{r^2}{2}-\frac{R_1^2}{2}+R_m^2\ln\left(\frac{R_1}{r}\right)} \quad (1)$$

and

$$z=\sqrt{\frac{r^2}{2}-\frac{R_2^2}{2}+R_m^2\ln\left(\frac{R_2}{r}\right)}, \quad (2)$$

respectively. Here R_1 and R_2 are the radii of the two electrodes at the center of the trap, and R_m is referred to as the characteristic radius, z and r are cylindrical coordinates. When a dc potential is applied between the inner electrode and (grounded) outer electrode, these electrodes create an electrostatic potential inside the Orbitrap such

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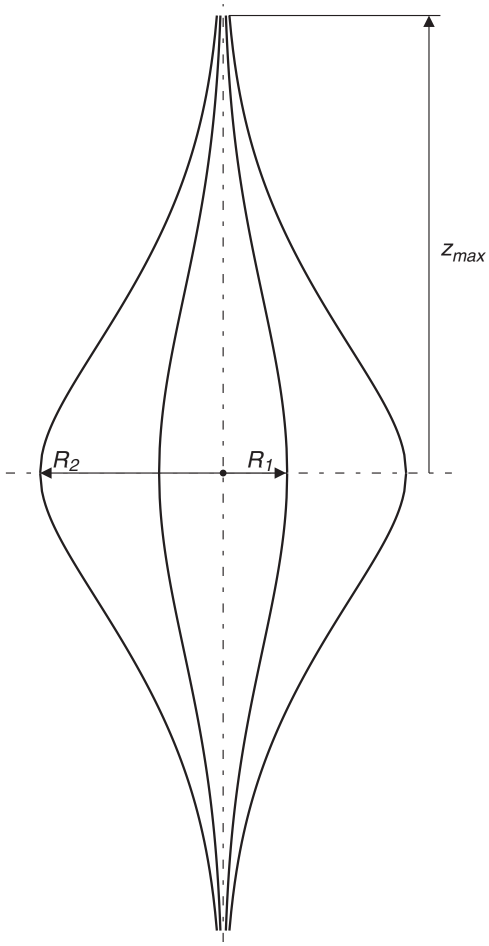

Fig. 1. Geometry of Orbitrap.

that the trapped ions have simple harmonic oscillations in the z direction. The frequency of this ion motion is inversely proportional to the mass-to-charge ratio of the ion and is independent of the ion motion in the x–y plane. The measurement of the frequency of the axial oscillations enables an accurate determination of mass-to-charge ratio of the trapped ions.

The high resolution and the high mass accuracy of the Orbitrap mass spectrometer requires precisely manufactured shapes of the electrodes. The imperfections in manufacturing the complex shapes of the electrodes of the Orbitrap will result in the compromised quality of the electric field and will manifest itself in the performance degradation of the Orbitrap. As indicated by Makarov [14], the mass production of such electrode shapes is challenging. Therefore Makarov suggested the use of different arrangements of segmented-electrode structures to approximate the electric field of the Orbitrap [14].

Although the segmented-electrode geometries for Orbitrap were suggested in 2010 [14], no analyses of these structures have been presented in the mass spectrometry literature. It is perhaps the absence of such analyses that has prevented these structures, although simpler to manufacture compared to the original Orbitrap, from being widely adopted by researchers in university laboratories. This is in contrast to the widely used geometries such as the Cylindrical Ion trap (CIT) and Rectilinear Ion Trap (RIT) that are suggested as simplifications of hyperbolic geometries such as the Paul trap (QIT) and Linear Ion Trap (LIT) [15–21].

Motivated by the earlier studies on the CIT and the RIT, we take up for analysis two segmented-electrode Orbitrap geometries in the present study. It will be shown that even the geometries having very few segments in their electrodes can be made to perform reasonably well as mass analyzers with proper optimization of their fields.

Table 1
Geometry parameters and dimensions of Orbitrap, ORB1 and ORB2. All dimensions are in millimeters.

Parameter	Orbitrap	ORB1	ORB2
R_1	7.0	3.5	7.0
R_2	20.0	20.0	20.0
z_{max}	50.0	50.0	50.0
h		1.857	2.222
w		2.625	
t		3.0	
g		1.0	0.5

The two structures that have been taken up for investigation have been motivated by suggestions in Makarov [14]. We call these structures ORB1 and ORB2. In one of these geometries, ORB1, the inner spindle-like electrode was replaced by 35 disc shaped electrodes and the outer barrel-like electrode of the Orbitrap was replaced by another set of 35 ring shaped electrodes. Both the inner and outer electrodes have fixed radii. Additionally, end cap electrodes consisting of concentric rings were also used in this structure. In the second geometry, ORB2, the inner and outer electrodes of the Orbitrap were replaced by an approximate step structure which follows the profile of the Orbitrap electrodes. The geometry of ORB1 and ORB2 is presented in Fig. 2a and b, respectively.

Our numerical analysis, carried out on a single ion, will consist of comparing the following parameters in the simplified geometry structures with the Orbitrap, (1) electric potential, (2) trajectories of the ion, (3) image currents. The 2D Boundary Element Method (BEM) was used for computation of the potential and ion trajectories in a given geometry. The induced image current computation was done by using 3D BEM which was developed for this study.

When the number of segments in the electrodes becomes small, the axial frequency of ion motion starts varying with the initial position of the ion. This could potentially lead to loss of resolution in mass analyzer. A novel optimization procedure to correct the field is proposed. When this optimization is carried out, the variation of axial frequency with initial position is greatly reduced. Then these geometries can be used as mass analyzers. This optimization has been demonstrated on a 9 and 15 segment ORB1 geometries.

Section 2 presents the geometries of the ion traps used in this work. Section 3 presents different computational methods used in this work. Section 4 discusses the results obtained in this study. Finally some concluding remarks are presented in Section 5.

2. Geometries considered

2.1. Orbitrap

Geometry of the Orbitrap used in this study is shown in Fig. 1. The maximum radius of its inner electrode is denoted by R_1 while that of the outer electrode is denoted by R_2. The length at which the Orbitrap is truncated is denoted by Z_{max}. The total length of the Orbitrap is $2Z_{max}$. Values of R_1 and R_2 have been fixed at 7 mm and 20 mm, respectively, as given in Makarov [4] and Z_{max} has been arbitrarily fixed at 50 mm. The values of these geometry parameters are also tabulated in Table 1. A dc potential of −50 V is applied on the inner electrode of the Orbitrap whereas the outer electrode is kept at ground potential (0 V).

In the geometries discussed below, the number of segments that the inner and outer electrodes have been divided is within the range of 20–80 suggested by Makarov [14].