Research Article

Modelling mass analyzer performance with fields determined using the boundary element method

J. Raymond Gibson,* Kenneth G. Evans and Stephen Taylor

Computer modelling is widely used in the design of mass analysers to evaluate proposed designs and determine the effects of manufacturing imperfections. For quadrupole mass filters and ion traps, the models require accurate values of the electric field throughout the regions of the analyser in which ions travel. Most published results using models to predict mass analyser behaviour use electric fields computed with finite element (FE) or finite difference (FD) method. However, the boundary element method (BEM) is capable of achieving the same, or higher, accuracy with both computation times and memory requirements that are at least an order of magnitude less than those required by FE and FD methods. In this paper, electric field evaluation is performed using the BEM formulated in a manner described by previous workers; modifications to their method are described, which lead to higher accuracy field values. Simultaneous equation solution techniques are incorporated, which avoid solutions that are physically not realistic. The performance of linear quadrupole mass spectrometers with hyperbolic, circular and planar section electrodes has been determined using fields computed using these methods and compared with previous results obtained by alternative field computation techniques and with experiment. Behaviour of an ion trap mass spectrometer with circular symmetry has also been investigated. The results demonstrate that in each case using the BEM to determine the fields produces the observed behaviour. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: mass analyser; electric fields; BEM; QMS; ion trap

Introduction

When developing quadrupole mass filters (QMS filters) and ion traps for use as mass analyzers, both the cost and problems of precision reassembly make it difficult to compare the behaviour of different designs or to perform experiments to measure the effects of imperfections. Consequently, when designing advanced systems, for example high performance or unconventional devices, the simulation of instrument performance prior to construction is essential. Designers use computer models to predict the behaviour of proposed systems; the expected system response is obtained by tracing the individual paths of very large numbers of ions. The ion motion is determined by computing successive small changes, steps, in an ion's position and velocity as it moves in the electric field of the analyser. A comparison of some modelling techniques for ion traps is given by Forbes et al.,[1] while March and Todd[2] give a wide ranging review of all ion trap topics. Development of ion traps is a very active field; recent examples of the use of models to predict ion trap behaviour are in Ref. [3–5] and references therein. There are fewer recent descriptions of models predicting the performance of QMS filters; early ones are reviewed by Dawson[6] and recent examples are Gibson and Taylor,[7,8] Taylor and Gibson,[9] Douglas et al.[10] and Ding et al.[11]

For QMS filter and ion trap designs that match the ideal form, that is the electrodes have perfect hyperbolic cross sections and are positioned exactly, the particle equations of motion may be derived and exact analytical solutions obtained. In non-ideal cases, determination of particle motion requires very accurate values of the electric field at all points in the region in which the particles move. For some symmetrical designs, for example QMS filters with correctly positioned circular section electrodes, analytic

multipole expansions[10,11] allow the field to be determined. In most other cases electric field values are obtained by computing the potential distribution in the region of interest then computing the derivative of the potential. Determination of the potential distribution requires the solution of Laplace's equation with the boundary conditions set by the electrode geometry and the applied potentials. One computation technique, the boundary element method (BEM; Brebbia and Dominguez),[12] provides solutions of Laplace's equation and allows direct computation of the fields without first computing the potentials.

Difficulties Arising in Electric Field Computation

Some of the available packages for the solution of Laplace's equation were developed to investigate problems in stress analysis or fluid flow and later adapted for electrostatic applications; exceptions include SIMION[13] and Poisson Superfish.[14] Most, but not all, packages use finite element (FE) or finite difference (FD) methods. Generally the regions of interest in stress analysis and fluid flow investigations are those where rapid field changes occur. Packages developed for these applications are optimised to find the field to high accuracy and with high resolution in areas of

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rapid change. For electrostatic systems, rapid change occurs close to the electrodes but most ions in QMS filters and ion traps travel in regions that are at a significant distance from the electrodes. High field accuracy and resolution are required at the ion positions rather than in regions close to the electrodes. Even with this requirement the meshes used by FE and FD methods must not have so few points in regions of rapid change that the accuracy of the fields at the ion positions is affected.

Packages are further restricted by input mechanisms that only allow a limited range of electrode geometries to be specified; consequently, investigators often create their own packages to model their unique designs. The FE and FD methods, even with over relaxation techniques, require large computational time to obtain the accuracy required when designing QMS filters and ion traps. Also small systematic features sometimes appear in FE and FD results that have a large effect on particle motion. However, although these difficulties exist, recent publications describing models predicting the behaviour of QMS filters and ion traps and also most available field determination packages, except the package CPO,[15] use FE or FD techniques to determine the potentials that are the solution of Laplace's equation.

A package originally developed for electrostatic lens modelling that produces accurate field values is CPO.[15] This is based on the BEM although it differs from most common BEM descriptions, for example, that of Brebbia and Dominguez,[12] in the manner in which the solution is formulated. The commercially available CPO package places some limits on the electrode structures that can be input and has limited capability for the number of charged particles that can be traced. Hence, CPO is not always applicable for design studies of QMS filters and ion traps, although it has been used successfully in several cases, for example, by Brkic et al.[16,17] to model miniature QMS devices. CPO is based on the work by Read and co-workers[18–20] but this work appears to have been neglected in many recent studies (including our own). The technique was used by Beaty[21,22] and, more recently, Douglas et al.[10,23,24] use the technique, although they do not appear to know of Read's work, and use the term 'the method of equivalent charges'. The method is capable of determining the fields to high accuracy, and computation time is usually at least an order of magnitude less than for FE and FD methods for results of similar accuracy. The technique places almost no restriction on electrode geometry when users develop their own programs.

One reason that the BEM is efficient is that the number of unknown quantities (simultaneous equations that must be solved) is greatly reduced compared with FE and FD approaches, although evaluation of the equation coefficients is often more complicated. Typically, for the so-called two-dimensional (2D) problem, the number of unknowns is approximately the square root of the number required by FE and FD methods to achieve similar accuracy. This reduction in the number of equations arises because the BEM reduces the numerical dimensionality of the problem to be solved by one order; that is determination of a 2D field requires solution of a one-dimensional problem and three-dimensional (3D) field determination requires solution of a 2D problem. The BEM also has the advantage that no fixed potential boundary is required around the electrode structure although one may be included if appropriate.

Here, we outline methods for the computation of the electric fields for 2D systems and for cylindrically symmetrical 3D systems for which any electrode structure may be defined. The methods follow the BEM approach introduced by Read et al.,[18,19,20] but
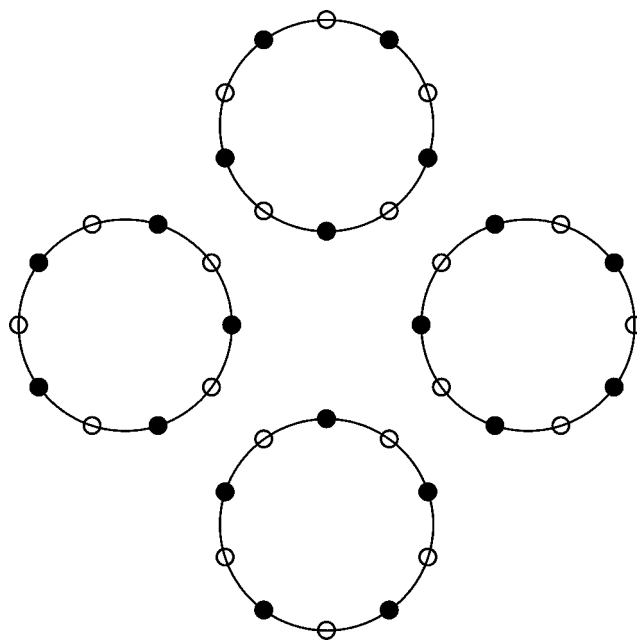

Figure 1. An example of typical positions selected for line charges (solid points) and defined points (open circles).

we introduce modifications that improve the accuracy of the field values.

All fields are 3D; the solution may be reduced to one in 2D for electrode systems whose cross section is independent of position in the third dimension. That is, for field computation, the electrode system is of infinite length in the third dimension; when the fields are used for predicting QMS filter behaviour, this is equivalent to ignoring end effects. A 2D solution is chosen when possible because it usually reduces the computation time and memory requirements by at least an order of magnitude for all methods of field determination.

2D Field Determination Using the BEM

The approach by Read et al. is to replace the electrodes by a number of charges at the surfaces of the electrodes. These charges are selected to require that the potentials at selected points on the surfaces of all electrodes equal the potentials applied to the electrodes; here, we call the points on the electrodes defined points. That is, the set of charges produces the same potential at any defined point as is produced by the electrode structure. For the 2D solution, a wide range of charge systems can be devised, for example, narrow rectangular sheet charges of infinite length. The most simple charge system for computational evaluation is a set of infinite length line charges of infinitesimal diameter as used by Douglas et al.[23]

Figure 1 illustrates the selection of charge and defined point positions for an electrostatic quadrupole with circular electrodes; the numbers of charges and defined points illustrated are almost two orders of magnitude less than the number required for an accurate solution. In Fig. 1, there are equal numbers of charges and defined points; later, we show that use of additional defined points improves the field values.

The potential difference $V_a - V_b$ between two points distances r_a and r_b from an infinite line charge of σ_k Coulombs per unit

length is

$$V_a - V_b = -\frac{\sigma_k}{2\pi\varepsilon_0} \ln\left(\frac{r_a}{r_b}\right) \quad (1)$$

Solutions of many electrostatic problems involve equations similar to Eqn 1 and it is conventional to define the zero of potential to be the value at an infinite distance from the charges, that is, with r_b infinite. However, it is not possible to use this definition to devise a simple formula for the potential at any distance from an infinite length line charge because it requires evaluation of either $\ln(1/r_b)$ or $-\ln(r_b)$ as r_b tends to an infinite value.

For general cases (without symmetry), Douglas et al.[23] overcome the problem of evaluating the potential due to an infinite length line, as the distance tends to infinity by requiring a housing at zero potential around the electrode system and using the method of images. The following method overcomes the problem without the need to introduce a zero potential housing. P is a point at a very large finite distance from all the line charges and the potential at P is chosen to be the reference value from which all potential differences are determined. Denote the potential difference between any point M_i and P as V_i, the distance from any line charge σ_k to M_i as r_{ki}, and the distance from σ_k to P as r_{kP}. The contribution of a single line charge σ_k to V_i is

$$V_{ik} = \frac{\sigma_k}{2\pi\varepsilon_0} \times \ln\left(\frac{r_{kP}}{r_{ki}}\right) = c \times \sigma_k \times \ln\left(\frac{r_{kP}}{r_{ki}}\right) \quad (2)$$

Therefore, the total potential difference between M_i and P is

$$V_i = \sum_k c \times \sigma_k \times \ln\left(\frac{r_{kP}}{r_{ki}}\right) = c \times \sum_k \sigma_k \times (\ln(r_{kP}) - \ln(r_{ki})) \quad (3)$$

where $\sum_k$ indicates the sum over all the line charges used to replace all the electrodes. Note that if the r_{ki} values are obtained using Pythagoras' Theorem evaluation of the square root with the associated increase in computation time and rounding error is avoided by rewriting Eqn 3 as

$$V_i = c \times 0.5 \times \sum_k \sigma_k \times (\ln(r_{kP}^2) - \ln(r_{ki}^2)) \quad (4)$$

If there are equal numbers of line charges σ_k and defined points M_i, a set of equations with the form of Eqns 3 or 4 may be developed and solved for the values of the line charges. For simplicity, only the use of Eqn 3 is described; the derivation using Eqn 4 is almost identical. Once determined, the line charges and Eqn 3 may be used to find the potential or the field at any position of interest.

Using all the defined points, a set of equations, each one of the form of Eqn 3, is obtained and may be expressed in matrix notation as

$$\mathbf{V}^T = (\mathbf{A} + \mathbf{B})\,\sigma^T \quad (5)$$

with $\mathbf{A}$ the matrix of the terms $-c \times \ln(r_{ki})$ and $\mathbf{B}$ that of terms $c \times \ln(r_{kP})$; $\mathbf{V}^T$ is a column vector representing the potential differences at all points M_i and σ^T is a column vector representing the line charges. The expected solution for σ^T when point P is at an infinite distance is one with the sum of all charges (sum of all the elements of σ^T) equal to zero. This zero value can be deduced

by letting P become very large, so that all the values of r_{kP} tend to the same value r_P and writing Eqn 3 as

$$V_i = c \times \ln(r_P) \times \sum_k \sigma_k - c \times \sum_k \sigma_k \times \ln(r_{ki}) \quad (6)$$

As P tends towards infinity $\ln(r_P)$ also tends to infinity; since V_i is finite and all the σ_k are assumed finite, the expression $c \times \ln(r_P) \times \sum_k \sigma_k$ must be finite which can only be true if $\sum_k \sigma_k$ tends to zero as P tends to infinity. That is, an essential condition of any solution to Eqn (5) is that the sum of all the line charges must be zero within the limits of computational accuracy.

When P is at a great but not infinite distance, the sum of the charges will be small but not zero and Eqn 5 may be re-arranged as

$$\sigma^T = \mathbf{A}^{-1}(\mathbf{V}^T - \mathbf{B}\,\sigma^T) \quad (7)$$

As the position of reference point P is changed, the value of the terms of $\mathbf{B}\,\sigma^T$ will change. However, all the terms in any column of $\mathbf{B}$ are identical allowing $\mathbf{B}\,\sigma^T$ to be written as $V_P\,\mathbf{X}^T$, where $\mathbf{X}^T$ is the column matrix whose terms are all unity and V_P is a scalar quantity; Eqn 7 becomes

$$\sigma^T = \mathbf{A}^{-1}(\mathbf{V}^T - V_P\,\mathbf{X}^T) \quad (8)$$

Let $\sigma_1^T = \mathbf{A}^{-1}\mathbf{V}^T$ and $\sigma_2^T = \mathbf{A}^{-1}\mathbf{X}^T$, then for any position P the solution σ^T to Eqn 5 is

$$\sigma^T = \sigma_1 - V_P\sigma_2^T \quad (9)$$

so that

$$\sum_k \sigma_k = \sum_k \sigma_{1,k} - V_P \sum_k \sigma_{2,k} \quad (10)$$

The solution of the sum of all charges zero is the one that meets the requirement that the potential tends to zero as P tends to an infinite distance and $\sum_k \sigma_k = 0$ when

$$V_P = \sum_k \sigma_{1,k} \Big/ \sum_k \sigma_{2,k} \quad (11)$$

Standard simultaneous equation solution methods enable $\mathbf{A}^{-1}$ and hence σ_1^T to be determined by solving $\sigma_1^T = \mathbf{A}^{-1}\mathbf{V}^T$. As $\sigma_2^T = \mathbf{A}^{-1}\mathbf{X}^T$ with $\mathbf{X}^T$ a column of unit values, the values of the elements of matrix σ_2^T are easily determined. Equation 11 is then used to compute V_P and Eqn 9 provides the values of σ^T, the required set of line charges whose sum is zero.

As before, σ^T is used to calculate the potentials at any location relative to the potential at some reference location. Since the reference location is now at infinite distance from the electrodes, Eqn 4 cannot be used with σ^T to calculate the potential because the terms $c \times \ln(r_P) \times \sum_k \sigma_k$ are infinite. However, although the individual terms are infinite, the value of the sum is finite and equal to V_P. Hence, the new equation for calculating potential at any position becomes

$$V_i = V_P + \mathbf{a} \times \sigma^T \quad (12)$$

where $\mathbf{a}$ is the vector with elements $-c \times \ln(r_{ki})$.

Practical Considerations and Improvements

Solution for the charges is straightforward. Typically, about 40–80 equispaced line charges are used to replace each electrode of a mass analyser for rapid initial checking of the behaviour of proposed systems. Those designs that appear to offer the required performance are investigated further using 100–300 charges in place of each electrode; very complicated electrode shapes may require more line charges.

When the charges were obtained using standard numerically efficient methods, for example Gaussian elimination, it was frequently found that the equations were ill conditioned. The values of the charge vector σ^T calculated satisfied the original equations to high precision. However, expected solutions are ones with the charges varying in a simple slowly changing manner with movement over an electrode's surface. Ill-conditioning often led to solutions where the charges oscillated by very large amounts, alternate charges were almost equally above and below the expected values. Some solutions produced charges about two orders of magnitude larger than the expected values. Even with these physically unreasonable charge values, the potential distributions matched the expected ones for systems for which there is an analytical solution at distances several times the charge separation from the conductors.

The effect of ill-conditioning is that the simultaneous equations are either effectively or actually under-determined; consequently, there are multiple solutions for the charge vector σ^T that will satisfy Eqn 9. Under these circumstances, it is beneficial to use the singular value decomposition, SVD, method[25] to solve the equations. SVD factors matrix **A** into the product of three matrices $\mathbf{A} = \mathbf{USW}^T$, in which **U** and **W** are square orthonormal matrices and **S** is a diagonal matrix containing the singular values. The pseudo-inverse of **A** is readily found from this factorisation as $\mathbf{A}^{-1} = \mathbf{WS}^{-1}\mathbf{U}^T$. **S** is a diagonal matrix; its inverse is found by replacing non-zero elements by their reciprocals and then transposing the result. The SVD method produces a useful result even for poorly conditioned equations. The SVD solution is the one, selected from all possible solutions, that is best in a 'least squares sense'. Our solutions by this method are always checked and so far all have a smoothly varying charge distribution except for electrodes of complex shape when some oscillations occur very close to discontinuities in electrode curvature. However, the effects of such oscillations on the fields at a distance equal to that of a few charge separations are negligible. Similar effects occur with other methods of field determination at discontinuities, because Laplace's equation defines a field with the second differential zero. That is, Laplace's equation is not valid in the infinitely small region at a discontinuity; numerical computation methods require finite size intervals and lead to incorrect results in regions close to discontinuities.

The SVD method is powerful and can be applied to sets of simultaneous equations with more equations than unknowns, a property we use later. The disadvantages of the method are that it is slower than simple methods and requires memory for the three additional large matrices, although there are techniques that allow some reduction in memory requirements. Computation time is variable but is approximately proportional to the cube of the number of equations; simple methods usually have a time proportional to the square of this number.

Using the SVD solution method, the potential distribution was determined for two identical parallel cylindrical conductors with potentials of equal magnitude but opposite sign. There is an
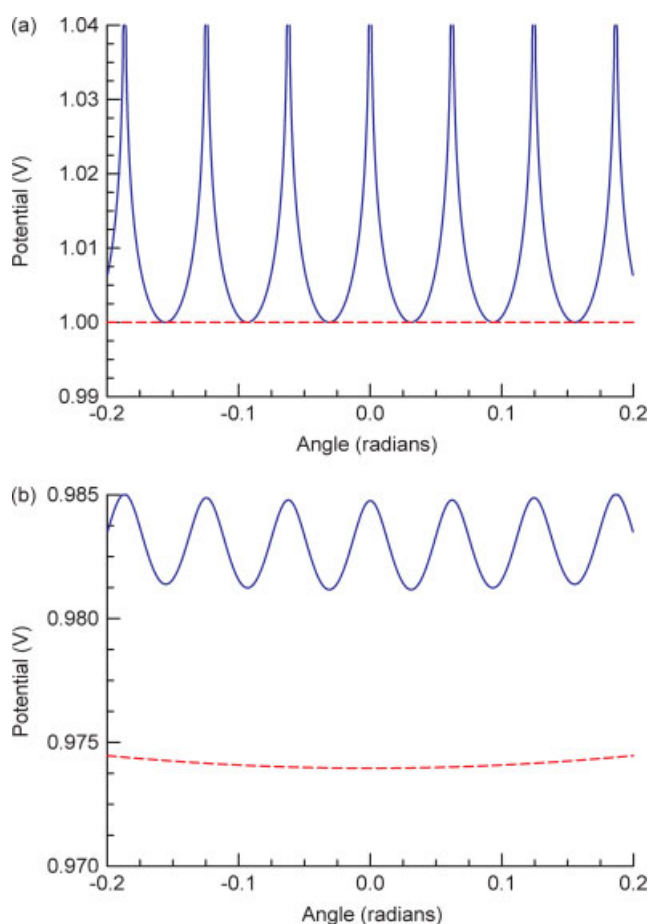

Figure 2. Potentials (a) at the surface of and (b) on a circle radius 1·02 concentric with one of two parallel circular conductors. The solid line is the BEM solution and the broken line is the exact analytical value.

analytical solution for the potential distribution of this system that can be compared with that computed from the set of line charges. Conductors with radius 1 unit, centres separated by 4 units and with potentials of +1 V and −1 V were used; initially, each rod was replaced by 101 equispaced charges. Figure 2(a) shows the computed potential (solid line) and the exact value (broken line) moving along the surface of the conductor at a potential of +1 V. The potential is shown over a distance of three charge separations either side of the line joining the conductor centres; the position scale is labelled in terms of the angle between the line joining the charges and the radial line to the conductor surface.

An obvious feature in Fig. 2(a) is the presence of large ripples or spikes close to the charge positions where the potential derived from line charges tends to an infinite value. If the potential is computed on circles outside and concentric with the conductor, the spikes change to smooth oscillations that decrease in amplitude as the radius of the concentric circle is increased. The spikes also decrease in width as the number of charges is increased.

The computed potential only equals the conductor potential of +1 V at the defined points and is greater at all other positions on the conductor surface. Therefore, the mean conductor potential predicted is higher than the true value. Hence, when the charges are on the conductor surface and the values at points M_i are forced to the conductor potential, the computed fields have values as if the electrode sizes are slightly larger than their actual sizes. The

magnitude of this error decreases as the number of charges is increased. Similar problems can occur with FE and FD methods because the meshes used replace the electrodes by polygons that are usually totally external or internal to an electrode, and hence the polygons are slightly larger or smaller than the electrode.

Figure 2(b) is similar to Fig. 2(a) but shows the potential on the circle concentric with the conductor at a radius of 1·02 times the conductor radius; note that the scale of the potential axis has been expanded in Fig. 2(b). The fluctuations in the potential are already small, their amplitude is less than ±0·005 of the potential, but the mean potential is still higher than the analytical result.

Results of the form of Fig. 2 indicate that this initial approach with line charges at the electrode surface introduces an apparent overestimate of the electrode size. One alternative is to place charges within the electrodes instead of at the surface. If a set of charges can be found, which causes the potentials to be correct at all points on the electrodes, then, by the Laplace equation Uniqueness Theorem, these charges would also predict the correct potential at all locations bounded by the electrodes and the electric field would also be correctly predicted within the same region. In practice, computational techniques only allow the potential to be defined at a finite number of points on the electrode surfaces; the potential cannot be fixed at other locations on the electrodes. Care must be taken to ensure that a sufficient number of line charges are used so that the predicted variation of potential on the electrode surface is within acceptable limits.

These considerations led to investigations of the effects of moving the line charges into the conductor in the direction of the normal to the surface in the manner adopted by Douglas et al.,[10,23,24] but with much smaller movements. Figure 3 shows potentials determined at the same positions as in Fig. 2, but the method of computation has been modified. The chain lines in Fig. 3 are the potentials using the same defined points as used for Fig. 2, but the charges have been moved radially inward by an amount approximately equal to the charge separation. Moving the line charges inward reduces the amplitude of the oscillations and the mean potential is closer to, but still greater than, the correct value.

A simple shift of the charge positions still produces values for the potentials corresponding to electrodes larger than the true size, although the error is smaller. The method was further modified using the feature that simultaneous equation solution using SVD allows the use of more equations than unknown quantities (over specification); the shift of charge positions was combined with the use of additional points M_i. A range of systems may be envisaged and several were investigated; most produced similar improvements. The following arrangement is one of the most simple and allows programmes to be devised to automatically determine the coordinates for charge positions and the defined points M_i for many conductor shapes. The number of points M_i was doubled, that is, there were twice as many defined points as charges. For circular electrodes, defined points M_i were placed as before at the conductor surface on radial lines half way between the radial lines on which the charges were placed. Additional defined points M_i were placed at the conductor surface on the same radial lines as the charges (this is possible because the charges are now inside the electrodes). Adding the extra defined points produces potential values shown by the solid lines in Fig. 3. The use of extra points has almost no effect on the amplitude of the oscillations, but more importantly the mean potential is now very close to the analytical value. Figure 3b shows a reduced angular range because some differences are so small that a greatly
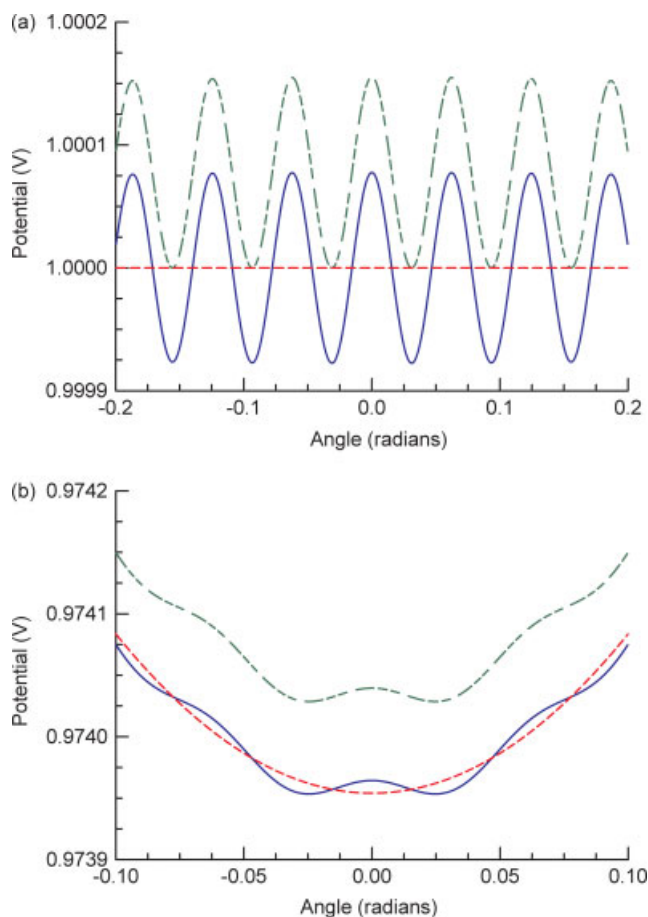

Figure 3. Improvement in the computed potentials shown in Fig. 2. The chain line shows the effect of moving the line charges inside the conductors; the solid line shows the effect of the further change of doubling the number of defined points; and the broken line is the exact analytical value.

enlarged potential scale is required for illustration purposes. For the two conductor system, the agreement between the analytical solution and computations using line charges was best when the charges were moved inward by a distance of about 0·6 to 0·8 times the charge separation. For potentials at a radius of about 1·1 times or greater the conductor radius the difference between model and analytical case is close to the limit of computational accuracy when 101 line charges were used.

Comparison of results for the behaviour of QMS models using fields determined by other methods confirmed that movement of approximately 0·8 times the charge separation usually provided the best agreement; however, results do not depend strongly on the value selected. For a range of electrode shapes, it was found that movement should be in the direction of the normal to the surface. The value of 0·8 times charge separation and movement in the normal direction were selected for use when adapting the method for more complex electrode systems for which the solution is unknown. Note that as the charges are moved further inward it becomes increasingly difficult to accurately represent electrodes whose shapes change rapidly.

Thus, when optimum line charge density values have been found equipotential surfaces computed using the values closely match correct ones. However, the computed values do exhibit a series of small fluctuations (corrugations) running parallel to the axis of the electrode system. The amplitudes of the fluctuations

depend on the number and spacing of the line charges and their positions relative to the surface of the electrodes. The amplitude of the fluctuations decreases rapidly with movement away from an electrode; with about 300 line charges representing each conductor for the two conductor example the amplitude is less than computational accuracy at a distance of about 0·05 times the electrode radius.

Application of 2D Field Results to Predict QMS Filter Behaviour

The BEM using line charges was used to repeat our past computations of QMS behaviour for which fields were obtained using FD methods. Results were almost identical but field computations for similar precision were completed in times more than an order of magnitude less than using Poisson Superfish and several orders less than using simple relaxation; the computations also required less memory. Computation times are affected by actions of the computer's operating system, but typically on a single processor 3 GHz machine for a round rod QMS simple FD methods required over one hundred hours, Poisson Superfish (an FD solution that includes over relaxation) took about 8 h, whereas the 2D BEM took about 40 min.

Furthermore, it is simple to adapt the present approach to any electrode geometry and we have modelled the behaviour of QMS systems with hyperbolic sections on the side of the electrodes facing the QMS axis, circular section electrodes, elliptical section electrodes and rectangular section electrodes in various orientations. The method also allows investigation of electrode displacement, incorrect potentials, any number of electrodes and any geometry. The only requirement of our field calculation programs is input files giving the coordinate positions for each of the line charges and every point M_i plus the electrode potential at each point M_i. When the electrode shape changes in a discontinuous manner, for example, at the corner of a square electrode, smaller separation of the charges and points M_i is necessary in the region of the sudden change. The method adopted in such cases is to set the charge separation to a very small value close to a discontinuity or a region where the curvature is higher than elsewhere and smoothly increase the separation moving away from these regions. The inward normal charge displacement of 0·8 of the local value of the charge separation is retained resulting in the magnitude of the displacement varying. For most electrode forms, it is trivial to devise a computer program that will produce all the required data; even when a program is not easily prepared manual creation of an input file with the aid of a calculator and text editor is tedious but not impossible as the number of values required is usually <1000.

A common method of illustrating the results of a computer model of QMS performance is to examine the detailed shape of a mass peak. Figure 4 shows model results for one mass peak for a QMS constructed with circular section electrodes and the manufacturing defect of one y-electrode moved inward by an amount $0·005 \times r_0$. The broken line is our previously published result using Poisson Superfish to obtain the fields and the solid line is the result using the BEM approach with discrete infinite length line charges. The results using Poisson Superfish appear as if the QMS is constructed with a slightly larger ratio $r : r_0$ than the results using the BEM. We previously found a similar discrepancy[9] with Poisson Superfish again behaving as if $r : r_0$ is slightly larger
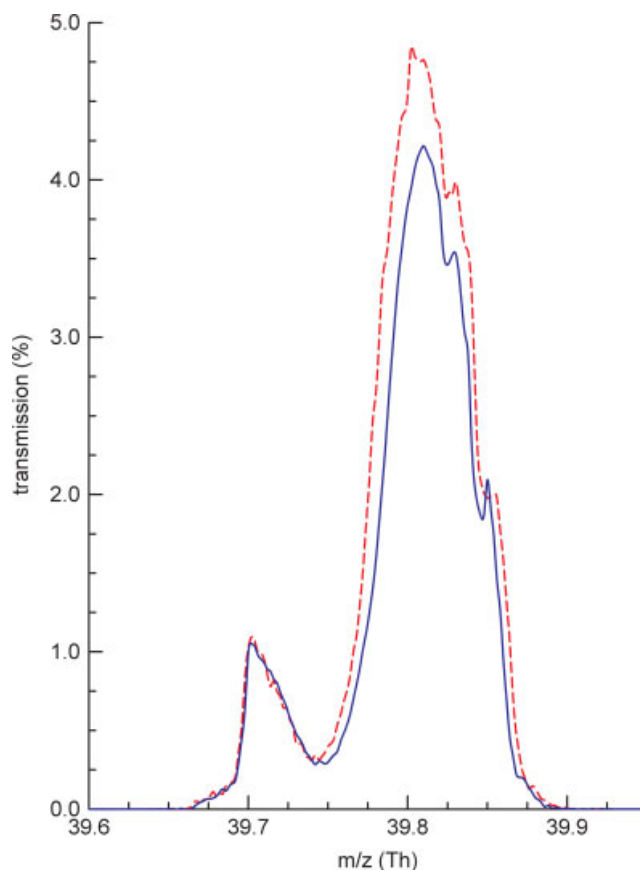

Figure 4. Computed QMS filter mass peak showing the effect of a displaced electrode with fields computed using Poisson Superfish (broken) and the BEM (solid).

when compared with results using fields from a simple, but very accurate, relaxation method.

A more extreme case is that of a QMS built with flat plate electrodes, for example, the one described by Pearce and Halsall.[26] A comparison of our prediction of behaviour with a digitised version of their results for air with water vapour present is shown in Fig. 5. To produce Fig. 5 it was necessary to make assumptions regarding the diameter of the ion source, the proportions of each species, and the spread in ion energies used by Pearce and Halsall as these are not stated. However, agreement is good considering that the fields differ greatly from the conventional form. Experimental peaks are less well defined than the theoretical ones; in part, this may be due to response time effects often observed using a chart recorder to obtain QMS data.

Cylindrically Symmetrical 3D Systems

The technique, including modification of the number and positions of charges, is readily adapted for systems where the electrode system has cylindrical symmetry around a central axis as, for example, in several designs of ion trap. In this case, each electrode is replaced by a number of circular line charges coaxial with the system axis. There is no longer a problem computing the potential at any position due to each charge as the equation for the potential at any point due to a circular line charge with the position of zero potential defined as infinity can be evaluated. However, the derivation of the potential is more complicated than
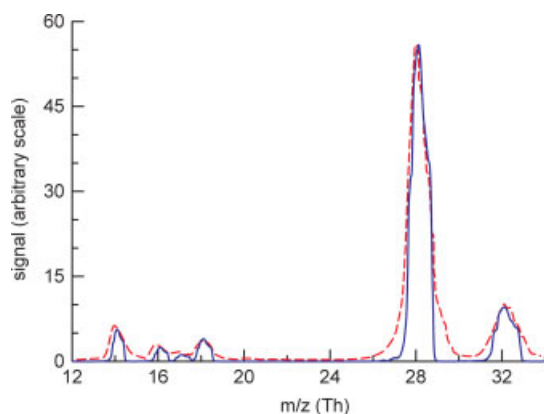
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Figure 5. Experimental results of Pearce and Halsall (broken) and computed (solid) mass spectra for a QMS filter constructed with flat plate electrodes.

might be expected; the potential at any point at a distance r from the axis and distance z from the plane of an infinitesimal thickness charge ring with a total charge Q and radius R is[27]

$$V = \frac{Q}{4\pi\varepsilon_0} \frac{2}{\pi} \left[(r+R)^2 + z^2 \right]^{-1/2} \int_0^{\frac{\pi}{2}} [1 - k^2 \sin^2 \beta]^{-1/2} d\beta \quad (13)$$

Equation 13 uses cylindrical coordinates and the azimuthal coordinate φ has been replaced using the substitution

$$\cos\varphi = 2\sin^2\beta - 1 \quad (14)$$

Also, Eqn 13 includes an elliptic integral of the first kind with modulus $k^2 = \frac{4rR}{(r+R)^2 + z^2}$; this may be evaluated rapidly using any of the many published routines, for example, Press *et al*.[25]

Evaluation of the coefficients of the simultaneous equations similar to those developed for the 2D case is slower than for the line charge system and the production of final potential values is also slower. However, potential distribution computation times are very short compared with alternative techniques which require a full 3D mesh.

Results for a Cylindrical Ion Trap

The method has been used to obtain the fields to model the behaviour of cylindrical ion traps. As for the QMS filter, we first produced fields for the ideal hyperbolic system originally described by Paul *et al*.[28] and compared the behaviour of the trap with these results with the behaviour using fields computed from the analytical expression. Provided enough charge rings were used, the results were almost identical. We also computed the fields for a trap that differs significantly from the ideal, we chose the design by Chaudhary *et al*.[3] and Fig. 6 shows the results we obtained for the spectrum of $CHCl_3^+$ assuming that the ions were initially distributed uniformly throughout the ion trap before the trapping period. Figure 6 is almost identical with Fig. 11 in Chaudhary *et al*.[3]; slight modifications can be produced by adjusting the assumed ion energy (temperature) and the positions in the trap at which ions are created. Such modifications are small, the largest effect is the rate of the extraction process.
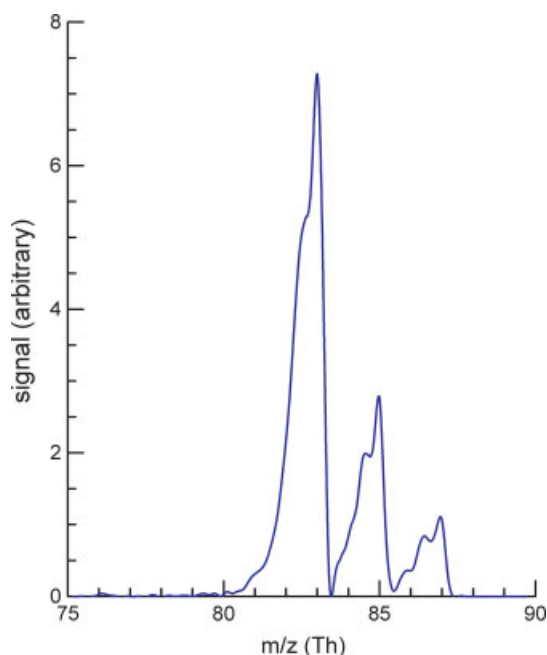

Figure 6. Computed QMS filter mass peak showing the effect of a displaced electrode with fields computed using Poisson Superfish (broken line) and the BEM (solid line).

Discussion and Conclusions

Once the charges have been determined, they may be used in several ways by programmes that trace charged particle motion. Unfortunately, the ideal method of using the charges to compute the field components directly at each point while tracing each particle requires excessive computation time. Should extremely high accuracy be required this method may be used if a high performance computing service is available.

For linear QMS systems and ion traps of the form used by Chaudhary *et al*.,[3] only a single evaluation of the field components is required as the potential differences between all electrodes are always in the same fixed ratios. For some more complex ion traps, it is necessary to compute the fields for the different charge ratios that occur during operation.

A feature of the solution using the BEM method to determine a set of charges is that it is possible to compute the electric field components at any position directly from the charges. For FE and FD methods, the computation result is the potential distribution and this must be differentiated to give the field components that decreases computational accuracy. To avoid computing the field values at each ion position when tracing its path, we first compute a grid of values of the electric field components, which is stored as a data file then read by the program that simulates QMS or ion trap behaviour. Using a finite difference solution to model round rod QMS systems,[7] we showed that a square grid in the region between electrodes with sides of about 1000 equispaced intervals was adequate provided that this was combined with separate bilinear interpolations between the grid points each time field values were required. To ensure accuracy, a grid with slightly more points was used. For hyperbolic section rods positioned at the ideal points, linear interpolation of the field components is exact (the field can also be determined exactly by analytical methods). For other section electrodes, the interpolation is approximate and higher order interpolation allows the grid spacing to be increased

at the expense of higher computation times. We also determined[7] that for circular section rods the grid should have at least four times as many points, and probably more, to achieve similar accuracy if nearest grid point is used instead of interpolation.

We have found that the BEM techniques developed by Read et al.[18–20] provide a very efficient method of determining electrostatic fields for use when modelling the behaviour of QMS filters and ion traps. By placing the charges used to model the conductors at points at a small distance inside the conductors, it is possible to achieve accuracy that matches other computational techniques. When the number of points at which the conductor potential was specified was larger than the number of charges and the position of the points was carefully chosen, almost exact mean potential values were obtained for the case of two parallel conductors. Representing each conductor by 101 line charges gave almost exact potential values at distances greater than 1·1 times the conductor radius; agreement in regions closer to the conductors is achieved by increasing the number of charges.

For QMS systems, we were able to reproduce our previous results obtained using FD techniques for QMS behaviour with more than an order of magnitude reduction in computation time and a reduction in the amount of memory required.

For the over specified case of more defined points than charges, a solution method is required that will find the best solution using some specified criterion. We found that SVD which provides a best solution in a least squares sense was successful for all the cases examined.

The technique may be extended to a full 3D form by replacing the electrodes by a series of point charges, or areas of surface charge, or line segments; the form selected is that most appropriate for the electrode geometry. Our previous results indicate that to achieve accurate results when modelling QMS filters and ion traps, a very large set of simultaneous equations must be solved. However, the size of the set is significantly less than the number required to achieve similar accuracy using FD or FE methods. At present, this probably requires computer facilities not available to many workers but this will not be the case in the future.

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