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Theory of peak coalescence in Fourier transform ion cyclotron resonance mass spectrometry

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Peak coalescence, i.e. the merging of two close peaks in a Fourier transform ion cyclotron resonance (FTICR) mass spectrum at a high number of ions, plays an important role in various FTICR experiments. In order to describe the coalescence phenomenon we would like to propose a new theory of motion for ion clouds with close mass-to-charge ratios, driven by a uniform magnetic field and Coulomb interactions between the clouds. We describe the motion of the ion clouds in terms of their averaged drift motion in crossed magnetic and electric fields. The ion clouds are considered to be of constant size and their motion is studied in two dimensions. The theory deals with the first-order approximation of the equations of motion in relation to *dm*/*m*, where *dm* is the mass difference and *m* is the mass of a single ion. The analysis was done for an arbitrary inter-cloud interaction potential, which makes it possible to analyze finite-size ion clouds of any shape. The final analytical expression for the condition of the onset of coalescence is found for the case of uniformly charged spheres. An algorithm for finding this condition for an arbitrary interaction potential is proposed. The critical number of ions for the peak coalescence to take place is shown to depend quadratically on the magnetic field strength and to be proportional to the cyclotron radius and inversely proportional to the ion masses. Copyright © 2009 John Wiley & Sons, Ltd.

The most accurate mass measurements for large biological and polymeric molecules are provided by Fourier transform ion cyclotron resonance mass spectrometry(FTICRMS).[1,2] In this technique ion masses are measured by exciting synchronous cyclotron motion of ions in high magnetic fields and measuring the frequencies of this motion which are connected to masses by the expression: $m_i/z_i = B/\Omega_i$, where m_i is the ion mass, z_i the ion charge, Ω_i the cyclotron frequency, and B the strength of the magnetic field.[3] In high-throughput experiments such as the analysis of complex mixtures like oil or a mixture of proteins in biological samples we deal with very high dynamic ranges of concentrations for individual components in the mixture, which sometimes exceed six orders of magnitude. If the FTICR signal detection limit corresponds to approximately 50 charges, at the high boundary of the dynamic range we are dealing with about 50 million charges. For this reason, ion–ion interactions play an essential role in this type of mass spectrometry experiments. At high numbers of ions in the FTICR cell, non-neutral plasma effects take place.[4] The best known effect caused by ion–ion interactions is the so-called peak coalescence.[5] Peak coalescence in the simplest form manifests itself by the merging of two adjacent peaks in the FTICR spectrum into one when the number of ions in the cell exceeds some critical number, which depends on the cell geometry, ion masses, magnetic field intensity and other experimental parameters. This phenomenon influences the performance of the mass spectrometer, making it impossible to resolve close peaks when there are large numbers of ions in the FTICR cell and thus decreasing the effective dynamic range of the mass spectrometer. In this work we have developed a theory to describe the coalescence phenomenon by analytically investigating ion cloud motion in a uniform magnetic field for the case of close mass-to-charge ratios of ions in the interacting clouds.

Previous attempts to investigate this problem theoretically, such as those by Naito and Inoue[6,7] and Mitchell and Smith,[8] were based either on point charge or on-line charge models, in which clouds of Coulombically interacting ions were substituted by point or lines of charges. This introduces the value of the initial distance between the clouds into the theories. However, in reality the initial separation of the clouds is often equal to zero if proper modes of cyclotron motion excitation are used. This case cannot be properly addressed by point or line charge theories, because the initial energy of interaction would be infinite. Moreover, in the work of Naito and Inoue[6,7] the problem of the occurrence of coalescence is investigated under the assumption of center-of-mass equations of motion being integrated independently from the coordinates of relative position. The motion of the center-of-mass can then be presented as a uniform rotary motion. Mitchell and Smith[8] used the same assumption to derive the coalescence criterion. However, as shown in this work, if the center-of-charge (for close mass-to-charge ratios

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the difference between center-of-mass and center-of charge is negligible) rotates at a constant velocity and at a steady radius, ions of different mass-to-charge ratios are already seen as one peak in the Fourier spectrum. The conditions of coalescence in the work of Mitchell and Smith, and Naito and Inoue, are also arguable. In the work of Mitchell and Smith[8] in order for coalescence to take place the frequency of the mutual revolving of the clouds should be higher than the difference between the cyclotron frequencies. In the work of Naito and Inoue[7] the complex of two coalescing clouds can be split only if the frequency of the mutual revolution resonates with the frequency of the force that makes the distance between the clouds oscillate. It is not obvious though, and it is not proved in the cited papers, why these conditions are necessary.

The current work deals with the arbitrary interaction potential, which makes it possible to analyze finite-sized clouds of any shape. The final analytical expression for the coalescence condition is found for the case of uniformly charged spheres.

GENERAL THEORY

Let us consider two ion clouds of two masses – m_1, m_2 and equal charges q (in order to simplify the theory we assume the total charges of the clouds to be equal). These ion clouds are considered to have 2 degrees of freedom each, i.e. their position in the XY plane described in terms of their Cartesian coordinates (the two-dimensional case). We also assume the ion clouds to be axially symmetric and of a constant shape; therefore, their interaction can be described by an interaction potential $\varphi(L)$, where L is the distance between the centers of the clouds. Since the clouds are axially symmetric, their spin-like rotation may not be taken into account. The equation of motion for the center of each cloud in the stationary frame of reference is then:

$$m\vec{a}_s = q\left[\vec{v}_s \times \vec{B}\right] + \vec{F}_C, \tag{1}$$

where F_C is the force created by the potential φ, $\vec{v}_s$ and $\vec{a}_s$ are the velocity and the acceleration vectors in the stationary frame of reference and $\vec{B}$ is the magnetic field vector. The magnetic field is uniform and is oriented perpendicular to the XY plane. We neglected the radial electric field caused by the potential at the trapping electrodes.

Since we plan to deal with ion clouds of close masses, we will therefore introduce an average mass $M = (m_1 + m_2)/2$ and $\Delta m = (m_2 - m_1)/2$, so that $m_1 = M - \Delta m$, $m_2 = M + \Delta m$. We can then consider the motion of the clouds in the frame of reference which rotates at a mean cyclotron frequency $\Omega = qB/M$. The law of transition to a non-inertial frame of reference is[9] as follows:

$$m\vec{a}^* = \vec{F} + m\Omega^2\vec{v}^* - 2m\left[\vec{\Omega} \times \vec{v}^*\right], \tag{2}$$

where $\vec{r}^*, \vec{v}^*, \vec{a}^*$ are the radius-vector, velocity and acceleration, respectively, of the center of the cloud in the rotating frame of reference and $\vec{F} = q\left[\vec{v}_s \times \vec{B}\right] + \vec{F}_C$.

In terms of $\vec{r}^*$ and $\vec{v}^*, \vec{F}$ is expressed as:

$$\begin{aligned}\vec{F} &= q\left[\left(\left[\vec{\Omega} \times \vec{r}^*\right] + \vec{v}^*\right) \times \vec{B}\right] + \vec{F}_C = q\left[\vec{v}^* \times \vec{B}\right] \\ &\quad + q\left[\left[\vec{\Omega} \times \vec{r}^*\right] \times \vec{B}\right] + \vec{F}_C \\ &= q\left[\vec{v}^* \times \vec{B}\right] - \vec{r}^* \cdot (qB\Omega) + \vec{F}_C.\end{aligned} \tag{3}$$

We have used the triple product expansion here (note that $\vec{B}$ is directed in the opposite way to $\vec{\Omega}$ for positive charges).

We can now obtain the equation of motion in the rotating frame of reference:

$$m\vec{a}^* = q\left[\vec{v}^* \times \vec{B}\right] - \vec{r}^* \cdot (qB\Omega) + m\Omega^2\vec{r}^* - 2m\left[\vec{\Omega} \times \vec{v}^*\right] + \vec{F}_C. \tag{4}$$

We will omit the asterisk mark on coordinates in the rotating frame of reference, because we only use these coordinates hereafter.

$$\vec{a} = \frac{q}{m}\left[\vec{v} \times \vec{B}\right] - \left(\Omega^2 - \frac{qB}{m}\Omega\right)\vec{r} - 2\left[\vec{\Omega} \times \vec{v}\right] + \frac{\vec{F}_C}{m}, \tag{5}$$

We then replace B with $M\Omega/q$:

$$\vec{a} = -\frac{M}{m}\left[\vec{v} \times \vec{\Omega}\right] - \Omega^2\left(1 - \frac{M}{m}\right)\vec{r} - 2\left[\vec{\Omega} \times \vec{v}\right] + \frac{\vec{F}_C}{m}. \tag{6}$$

$$\begin{aligned}\vec{a} &= \left[\vec{\Omega} \times \vec{v}\right]\left(\tfrac{M}{m} - 2\right) - \Omega^2\left(1 - \tfrac{M}{m}\right)\vec{r} + \tfrac{\vec{F}_C}{m} \\ &= -\left[\vec{\Omega} \times \vec{v}\right]\left(\tfrac{M \pm 2\Delta m}{M \pm \Delta m}\right) - \Omega^2\left(\tfrac{\pm\Delta m}{M \pm \Delta m}\right)\vec{r} \pm \tfrac{\vec{F}_C}{M \pm \Delta m},\end{aligned} \tag{7}$$

where '+' denotes the cloud of the larger mass and '−' is for the lower mass.

The coalescence takes place only for the clouds with close mass-to-charge ratios of the ions. Therefore, we will simplify the equation of motion on the basis of the assumption that $\Delta m << M$. To obtain a first-order approximation we should take into account that $v/\Omega r$ is of the order of $\Delta m/M$, because:

$$\begin{aligned}v &\sim v_s - \Omega r = \frac{qB}{m}r - \Omega r = \Omega r\frac{M}{m} - \Omega r \\ &= \Omega r\left(\frac{M}{M - \Delta m} - 1\right) \sim \Omega r\frac{\Delta m}{M}.\end{aligned} \tag{8}$$

We should then take a zero-order approximation for $\left(\frac{M \pm 2\Delta m}{M \pm \Delta m}\right)$ and a first-order approximation for $\left(\frac{\pm\Delta m}{M \pm \Delta m}\right)$. We should also take a zero-order approximation of the Coulomb force in relation to $\Delta m/M$, which gives us:

$$\vec{a} = -\left[\vec{\Omega} \times \vec{v}\right] - \Omega^2\left(\frac{\pm\Delta m}{M}\right)\vec{r} \pm \frac{\vec{F}_C}{M}. \tag{9}$$

This equation is analogous to the equation of motion in crossed magnetic and electric fields.[10] Therefore, in this work we will try to describe the motion of the ion clouds in terms of their averaged drift motion. The drift motion is described by the equation:[10]

$$\vec{v}_d = \frac{1}{q}\frac{\left[\vec{F} \times \vec{B}\right]}{B^2}, \tag{10}$$

where $\vec{v}_d$ is the drift velocity. In our case:

$$\vec{v}_d = -\frac{\left[\vec{a}_e \times \vec{\Omega}\right]}{\Omega^2}, \tag{11}$$

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where $\vec{a}_e$ is the acceleration that would be imparted by the electric field if there were no magnetic field. When we apply this to Eqn. (9):

$$\vec{v}_d = -\left(\frac{\pm\Delta m}{M}\right)\left[\vec{r}\times\vec{\Omega}\right] \pm \frac{\left[\vec{F}_C\times\vec{\Omega}\right]}{M\Omega^2} \tag{12}$$

and for each cloud the equations of the drift motion are:

$$\begin{aligned}\vec{v}_1 &= -\left(\frac{\Delta m}{M}\right)\left[\vec{r}_1\times\vec{\Omega}\right] + \frac{\left[\vec{F}_C\times\vec{\Omega}\right]}{M\Omega^2}\\ \text{and } \vec{v}_2 &= \left(\frac{\Delta m}{M}\right)\left[\vec{r}_2\times\vec{\Omega}\right] - \frac{\left[\vec{F}_C\times\vec{\Omega}\right]}{M\Omega^2},\end{aligned} \tag{13}$$

where $\vec{r}_1$,$\vec{r}_2$ and $\vec{v}_1$,$\vec{v}_2$ are the radius vectors and velocities, which describe the drift motion of the centers of the ion clouds (in the rotating frame of reference).

Instead of the coordinates of each cloud $\vec{r}_1$ and $\vec{r}_2$ we will use the following:

$$\vec{r}_0 = \frac{\vec{r}_1+\vec{r}_2}{2} \text{ and } \vec{r}' = \frac{\vec{r}_2-\vec{r}_1}{2}. \tag{14}$$

The advantage of using $\vec{r}_0$ and $\vec{r}'$ coordinates is that in the linear approximation the charge induced on the detection electrodes is proportional to $(\vec{r}_1+\vec{r}_2)$, given that the charges of the ion clouds are equal.[3] Since the induced charge is the only value detected by the FTICR mass spectrometer, we only need to solve the equations of motion for $\vec{r}_0$ and this will be enough to find the form of the ICR signal and the FTICR spectrum. Thus, Eqns. (13) and (14) are transformed into:

$$\begin{aligned}\vec{v}_0 &= \left(\frac{\Delta m}{M}\right)\left[\vec{r}'\times\vec{\Omega}\right]\\ \text{and } \vec{v}' &= \left(\frac{\Delta m}{M}\right)\left[\vec{r}_0\times\vec{\Omega}\right] - \frac{\left[\vec{F}_C\times\vec{\Omega}\right]}{M\Omega^2},\end{aligned} \tag{15}$$

where $\vec{v}_0 = d\vec{r}_0/dt$ and $\vec{v}' = d\vec{r}'/dt$.

When we differentiate the first equation by time and substitute $\dot{\vec{r}}'$ with $\vec{v}'$ from the second equation, we can obtain an expression for $\vec{a}_0 = d\vec{v}_0/dt$:

$$\begin{aligned}\vec{a}_0 &= \left(\frac{\Delta m}{M}\right)\left[\left(\left(\frac{\Delta m}{M}\right)\left[\vec{r}_0\times\vec{\Omega}\right] - \frac{\left[\vec{F}_C\times\vec{\Omega}\right]}{M\Omega^2}\right)\times\vec{\Omega}\right]\\ &= -\left(\frac{\Delta m}{M}\right)^2\Omega^2\vec{r}_0 + \left(\frac{\Delta m}{M}\right)\frac{\vec{F}_C}{M}.\end{aligned} \tag{16}$$

Here $\vec{F}_C$ depends only on $\vec{r}'$ and these vectors are co-directional, i.e. $\vec{F}_C$ can be expressed as $\vec{F}_C = f(r')\cdot\vec{r}'$, and $\vec{r}'$ can be in turn expressed from Eqn. (15), taking into account that the vectors $\vec{r}'$ and $\vec{\Omega}$ are orthogonal:

$$\vec{r}' = -\left(\frac{M}{\Delta m}\right)\frac{1}{\Omega^2}\left[\vec{\Omega}\times\vec{v}_0\right], \tag{17}$$

for magnitudes:

$$|\vec{r}'| = \left(\frac{M}{\Delta m}\right)\frac{1}{\Omega}|\vec{v}_0|. \tag{18}$$

Now if we substitute $\vec{F}_C$ in Eqn. (16) with its expression:

$$\vec{a}_0 = -\left(\frac{\Delta m}{M}\right)^2\Omega^2\vec{r}_0 - f\left(\left(\frac{\Delta m}{M}\right)\frac{1}{\Omega}v_0\right)\frac{1}{\Omega^2}\frac{\left[\vec{\Omega}\times\vec{v}_0\right]}{M}. \tag{19}$$

For Cartesian coordinates, Eqn (19) appears as:

$$\ddot{x}_0 = -\omega^2 x_0 - \theta f(v_0/\omega)\dot{y}_0, \tag{20a}$$

$$\ddot{y}_0 = -\omega^2 y_0 + \theta f(v_0/\omega)\dot{x}_0, \tag{20b}$$

where:

$$\omega = \Omega\Delta m/M, \theta = 1/M\Omega. \tag{21}$$

x_0, y_0 are the components of the radius-vector $\vec{r}_0$. Simple transformations (multiplying Eqn. (20a) by $\dot{x}_0$ and Eqn. (20b) by $\dot{y}_0$ and then adding) will give the fist integral:

$$v_0{}^2 + \omega^2 r_0{}^2 = E, \tag{22}$$

where E is a constant to be found from the initial conditions. Another first integral (known as the angular momentum) may be found by multiplying Eqn. (20a) by y_0 and Eqn. (20b) by x_0, and then subtracting:

$$\ddot{y}_0 x_0 - \ddot{x}_0 y_0 = \theta f(v_0/\omega)(\dot{x}_0 x_0 + \dot{y}_0 y_0), \tag{23}$$

$$\frac{d}{dt}(\dot{y}_0 x_0 - \dot{x}_0 y_0) = \frac{1}{2}\theta f\left(\sqrt{E/\omega^2 - r_0{}^2}\right)\frac{d(r_0{}^2)}{dt}, \tag{24}$$

Here we have also replaced v_0 with its expression derived from Eqn. (22). Since

$$r' = v_0/\omega = \sqrt{E/\omega^2 - r_0{}^2}, \tag{25}$$

and then

$$d(r_0{}^2) = -d(r'^2), \tag{26}$$

we can show that integrating the right-hand side of Eqn. (24) gives us the potential of Coulomb interaction φ:

$$\begin{aligned}\int \theta f\left(\sqrt{E/\omega^2 - r_0{}^2}\right)d(r_0{}^2) &= -2\int \theta f(r')\cdot r' dr'\\ &= -2\int F_C(r')\cdot dr' = \Delta\varphi.\end{aligned} \tag{27}$$

Taking into account this result we can integrate Eqn. (24) and obtain:

$$\dot{y}_0 x_0 - \dot{x}_0 y_0 = \frac{1}{2}\theta\Delta\varphi. \tag{28}$$

Equations (28) and (22) form a system of equations for $\dot{x}_0$ and $\dot{y}_0$:

$$\dot{x}_0{}^2 + \dot{y}_0{}^2 + \omega^2 r_0{}^2 = E, \tag{29a}$$

$$\dot{y}_0 x_0 - \dot{x}_0 y_0 = \frac{1}{2}\theta\Delta\varphi. \tag{29b}$$

This allows us to express $\dot{x}_0$ and $\dot{y}_0$ in terms of x_0 and y_0:

$$\dot{x}_0 = -\frac{1}{2}\frac{\theta\Delta\varphi\cdot y_0}{r_0{}^2} \pm \frac{x_0}{r_0}\sqrt{E - \omega^2 r_0{}^2 - \frac{\theta^2\Delta\varphi^2}{4r_0{}^2}}, \tag{30a}$$

$$\dot{y}_0 = \frac{1}{2}\frac{\theta\Delta\varphi\cdot x_0}{r_0{}^2} \pm \frac{y_0}{r_0}\sqrt{E - \omega^2 r_0{}^2 - \frac{\theta^2\Delta\varphi^2}{4r_0{}^2}}, \tag{30b}$$

Finally we can use Eqn. (30) to find dr_0/dt:

$$\frac{dr_0}{dt} = \frac{x_0\dot{x}_0 + y_0\dot{y}_0}{r_0} = \sqrt{E - \omega^2 r_0{}^2 - \frac{\theta^2\Delta\varphi^2}{4r_0{}^2}}. \tag{31}$$

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If we introduce a function:

$$g(r_0) = E - \omega^2 {r_0}^2 - \frac{\theta^2 \Delta\varphi^2}{4{r_0}^2}, \quad (32)$$

$$\text{so that } \frac{dr_0}{dt} = \sqrt{g(r_0)}, \quad (33)$$

the $g(r_0)$ function can then be used as a characteristic function to study the coalescence phenomenon. Knowing this function one can find the range of variation of r_0, because the ion cloud motion can only proceed if r_0 is in the regions of positive $g(r_0)$, and never in the regions of negative $g(r_0)$, since dr_0/dt would be imaginary in this region, which is impossible.

If the Coulomb interaction is not taken into account and the clouds are initially fully overlapped, r_0 oscillates from its initial value (excitation radius) to zero since the $g(r_0)$ function is positive over this interval. This means that the rotation radius for the center-of-charge (observed from a stationary frame of reference) changes from maximum to zero periodically. The detected signal will appear as a sinusoidal oscillation with the amplitude alternating from maximum to zero. This effect is known as beats and results in two close peaks in a FTICR spectrum.

However, if we take the Coulomb interactions into account, it turns out that for some kinds of interaction potentials (e.g. the interaction of uniformly charged spheres) under certain conditions the value of r_0 may be locked in a narrow interval near its initial value, denoted here as R. If the ion clouds start in the same position, R will be equal to the excitation radius. The alteration range of the amplitude for the detected signal is then defined by the width of the interval in which r_0 is locked. The beats then do not appear, and the transient has the form of a modulated signal. Such a transient is known to give a major peak and two side peaks in a FTICR spectrum, which is to say that the peaks of the two masses are unresolved. The intensities of the side peaks are proportional to the depth of modulation, i.e. to the width of the interval of r_0 alternation. Let us consider the transition from non-coalescent to coalescent motion for the example of ion clouds in the form of uniformly charged spheres.

The case of uniformly charged spheres

The interaction potential between two uniformly charged spheres (of radius ρ and charge q each) is:[11]

$$\varphi(L) = kq^2 \frac{192\rho^5 - 80L^2\rho^3 + 30L^3\rho^2 - L^5}{160\rho^6} \text{ for } L < 2\rho \quad (34)$$

and

$$\varphi(L) = \frac{kq^2}{L} \text{ for } L \geq 2\rho, \quad (35)$$

where L is the distance between the centers of the clouds, and k is Coulomb's constant. From Eqn. (25):

$$L = 2|\vec{r}'| = 2\sqrt{E/\omega^2 - {r_0}^2}. \quad (36)$$

We assume that the clouds are initially fully overlapped, i.e. $L(t=0) = 0$, then:

$$\Delta\varphi(L) = \varphi(L) - \varphi(0) = kq^2 \frac{-80L^2\rho^3 + 30L^3\rho^2 - L^5}{160\rho^6} \text{ for } L < 2\rho \quad (37)$$

and

$$\Delta\varphi(L) = \varphi(L) - \varphi(0) = kq^2\left(\frac{1}{L} - \frac{6}{5\rho}\right) \text{ for } L \geq 2\rho. \quad (38)$$

If we identify the initial cyclotron radius of both clouds by R, and since $L(t=0) = 0$, from Eqn. (36) we get $E = \omega^2 R^2$, and thus $L = 2\sqrt{R^2 - {r_0}^2}$.

Thus it turns out that in the case of uniformly charged spheres the interval of r_0 alternation experiences an abrupt change at a certain critical value of charge that each cloud bears (i.e. number of ions in each cloud). Figure 1 shows (a) the $g(r)$ functions, (b) the center-of-charge trajectories and (c) the resulting FTICR spectra for three values of $kq^2\theta$. The trajectories and spectra are obtained by a numerical solution of the system of differential Eqns. (30) with the interaction potential defined by Eqns. (34) and (35). For numerical computations we chose the unit of length so that $R = 1$, and the unit of time so that $\Omega = 1$. These units will be referred to as l.u. and t.u., respectively. $\rho = 0.4$ l.u. The numerical solution was based on MATLAB 7.5 (The Math Works, Natick, MA, USA) ordinary differential equation solver ODE45. The values of $kq^2\theta$ (in (l.u.)^3/(t.u.)) shown in Fig. 1 are: slightly lower (0.003) than the critical value (left row), near (0.042) the critical value (middle row) and slightly higher (0.05) than the critical value (right row).

In the case of $kq^2\theta = 0.003$ the interval of r_0 alternation spans from $0.4R$ to R, but for $kq^2\theta = 0.005$ this interval shrinks to about $0.98R$, R. This transition happens at a certain value of $kq^2\theta$ when the flexure of the graph becomes tangential to the axis of the abscissa (Fig. 1(a), center). At this point the lower boundary of the interval of r_0 alternation jumps from $0.65R$ to $0.95R$. We will consider this value of $kq^2\theta$ as minimal for the onset of the coalescent motion regime. The trajectories (Fig. 1(b)) and the spectra (Fig. 1(c)) also demonstrate that the motion switches from separate to coalescent at this point. The same condition can be used for an arbitrary potential, if the effect of abrupt reduction of the range of r_0 alternation takes place.

The condition of coalescent motion described above can be formalized as: $dg/dr_0 = 0$ and $g = 0$ at certain r_0. It is convenient to introduce a new variable $\xi = \sqrt{R^2 - {r_0}^2}$ and to replace r_0 with $\sqrt{R^2 - \xi^2}$. The physical meaning of ξ is (according to Eqn. (36), and taking into account that $E = \omega^2 R^2$) half of the distance between the centers of the ion clouds. The condition, which is fulfilled at the threshold of coalescent and normal motion, remains the same: $dg/d\xi = 0$ and $g = 0$ at certain ξ. Using the expression for $g(r_0)$ (Eqn. (32)) (taking into account that $E = \omega^2 R^2$) this condition is transformed into:

$$\omega^2\xi^2 - \frac{\theta^2\Delta\varphi^2}{4\left(R^2 - \xi^2\right)} = 0, \quad (39)$$

$$\frac{d}{d\xi}\left(\omega^2\xi^2 - \frac{\theta^2\Delta\varphi^2}{4\left(R^2 - \xi^2\right)}\right) = 0. \quad (40)$$

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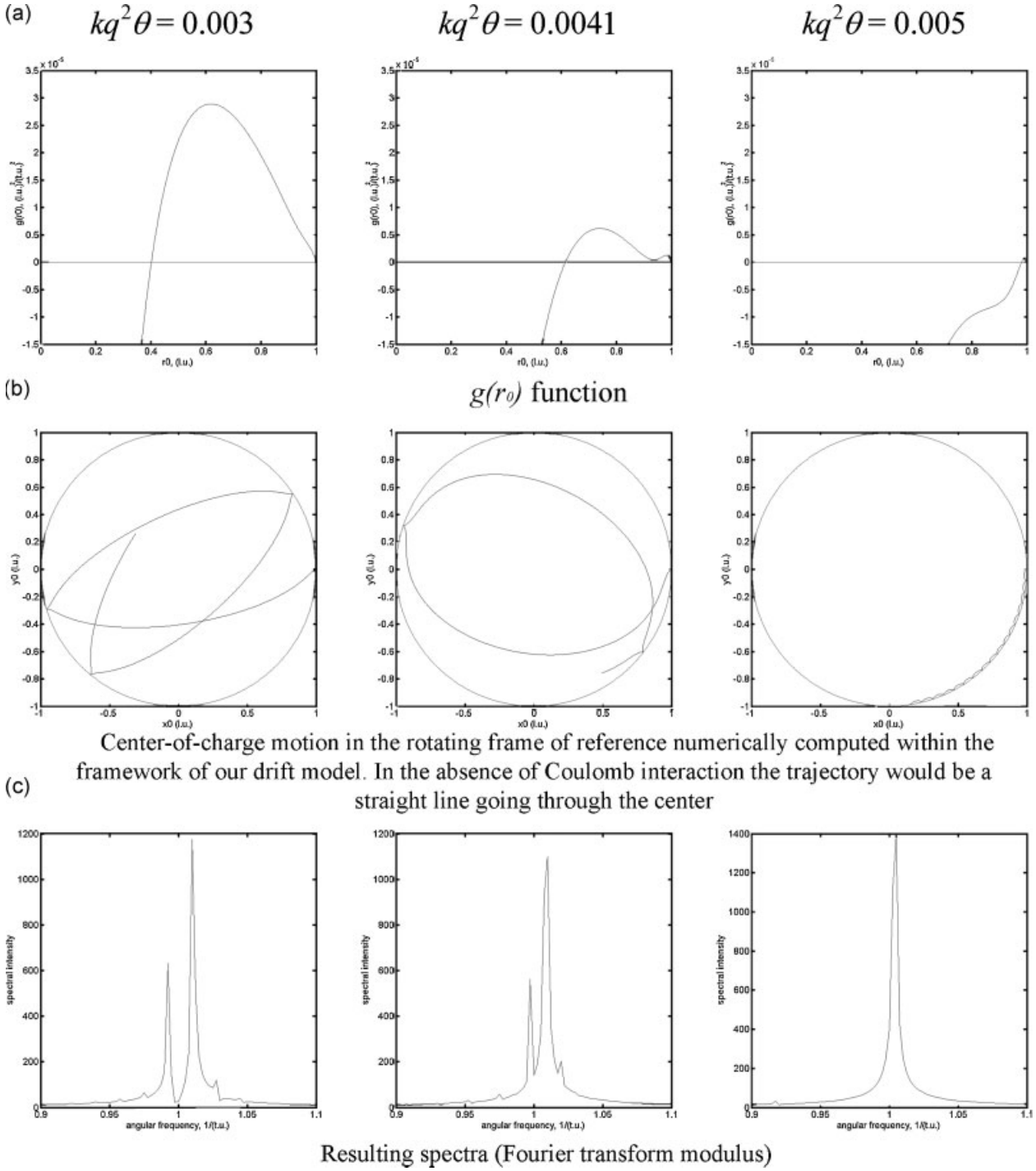

Figure 1. The $g(r_0)$ functions, center-of-charge trajectories and the resulting spectra for different values of $kq^2\theta$.

Since $\Delta\varphi < 0$ for equally charged clouds, Eqn. (39) is equivalent to:

$$\Delta\varphi = -\frac{2\omega\xi}{\theta}\sqrt{R^2 - \xi^2}. \tag{41}$$

Using Eqn. (41), Eqn. (40) can thus be transformed into:

$$\frac{d}{d\xi}\Delta\varphi = \frac{d}{d\xi}\left(-\frac{2\omega\xi}{\theta}\sqrt{R^2 - \xi^2}\right). \tag{42}$$

Equations (41) and (42) are equivalent to the statement that function $\Delta\varphi(\xi)$ is tangential to the function:

$$h(\xi) = -\frac{2\omega\xi}{\theta}\sqrt{R^2 - \xi^2}. \tag{43}$$

As can be seen from Fig. 2, in order to evaluate the coalescence threshold one may use the point-charge-like $\Delta\varphi(r_0)$ function with the appropriate initial energy:

$$\Delta\varphi(\xi) = kq^2\left(\frac{1}{2\xi} - \frac{6}{5\rho}\right). \tag{44}$$

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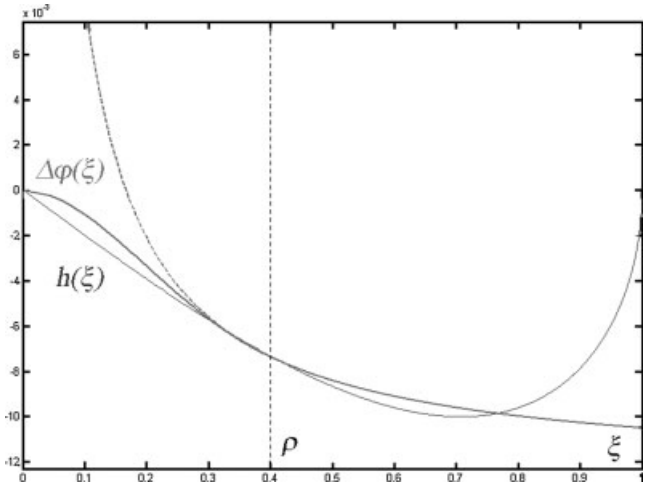

Figure 2. *h(ξ)* (thin line) and *Δφ(ξ)* (thick line) at a critical value of $kq^2\theta$ for the case of uniformly charged spheres (dashed line is point charge approximation).

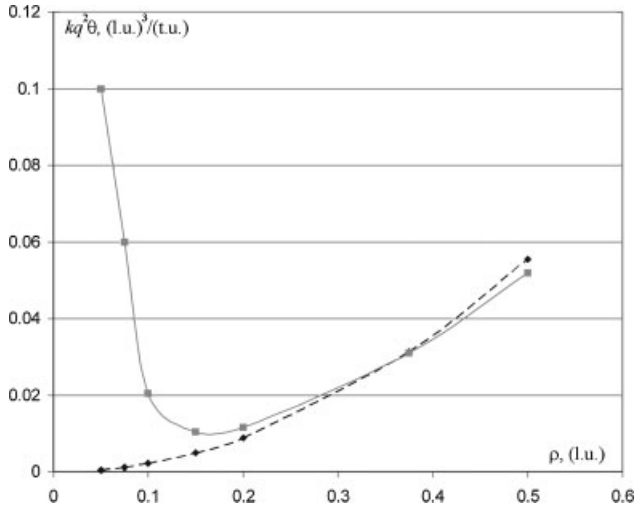

Figure 3. Threshold value of $kq^2\theta$ depending on the radius of the cloud ρ: computed numerically (solid line) and given by formula (48) (dashed line). ρ is expressed in fractions of *R*, i.e. in (l.u.).

Figure 2 also shows that the $h(\xi)$ function may be approximated by a linear function in a wide range of ξ. One may see that the ξ coordinate of the point of tangency is of the order of the radius of ion cloud, and that the ion cloud radius is usually a few times smaller than R. That means that it would be reasonable to replace $h(\xi)$ with a linear function in order to simplify the determination of the coalescence criteria. The linear approximation of $h(\xi)$ is:

$$h_1 = -\frac{2\omega R}{\theta}\xi. \tag{45}$$

Considering this, Eqns. (41) and (42) are simplified to:

$$\Delta\varphi = -\frac{2\omega R}{\theta}\xi, \tag{46}$$

$$\frac{d}{d\xi}\Delta\varphi = \frac{2\omega R}{\theta}. \tag{47}$$

For the case of spherical ion clouds, i.e. with the interaction potential defined by Eqn. (44), Eqns. (46) and (47) result in:

$$-kq^2\frac{1}{2\xi^2} = -\frac{2\omega R}{\theta}, \tag{48}$$

$$kq^2\left(\frac{1}{2\xi} - \frac{6}{5\rho}\right) = -\frac{2\omega R}{\theta}\xi. \tag{49}$$

This system of equations is easily resolved by substituting ξ from Eqn. (48) into Eqn. (49). The solution for $kq^2\theta$ is then:

$$kq^2\theta = \frac{25}{9}\rho^2 R\omega. \tag{50}$$

In order to verify the results of our analysis we computed the trajectories of interacting ion clouds by solving the equations of motion (1) (with the interaction potential defined by Eqns. (34)and (35)) numerically using the MATLAB 7.5 differential equation solver ODE45. For different values of ρ we picked out the threshold value of $kq^2\theta$, while the other parameters were: $R = 1$, $\Delta m/M = 0.01$, and $\Omega = 1$. The threshold value of $kq^2\theta$ was then compared with Eqn. (50) (Fig. 3). For values of ρ greater then $R/2$ the coalescence does not appear as a jump-like process, but as a gradual shift of the detected frequencies towards each other. Therefore, that region is not shown on the diagram. The comparison shows good agreement in the region where our model is valid. For small values of ρ the drift model is probably not applicable because the distance between the cloud centers undergoes considerable change throughout a single drift oscillation due to the strong repulsion.

In order to obtain the direct expression for the number of particles needed for the onset of coalescence we should substitute θ and ω with their expressions in Eqn. (21). Then:

$$kq^2\frac{1}{M\Omega} = \frac{25}{9}\rho^2 R\frac{\Omega\Delta m}{M}. \tag{51}$$

If the cloud consists of N particles then $M = N\mu$, $q = Ne$, where μ and e are the mass and charge of a single ion. When we substitute M, q and Ω in Eqn. (51) with their values, N is expressed as:

$$N = \frac{25}{9}\frac{\rho^2 R(\Delta\mu/\mu)B^2}{k\mu}, \tag{52}$$

where $\Delta\mu$ is half of the mass difference between ions in different clouds.

Arbitrary interaction potential

The method described for the case of uniformly charged spherical clouds can be generalized for an arbitrary interaction potential. If an abrupt reduction in the range of r_0 alternation at a certain value of $kq^2\theta$ (which is proportional to the number of ions) takes place, all the mathematics leading to Eqns. (41) and (42) (or their simplified versions Eqns. (46) and (47)) remain valid. As an example, the $g(r)$ function for elliptical, uniformly charged ion clouds (semi-axes related as 3:1:1) has this feature (Fig. 4). Equations (46) and (47) make it possible to formulate a simple algorithm for finding the necessary number of ions for the coalescence to occur. Say we have an arbitrary interaction potential between two ion clouds of the same charge and a slightly different mass, measured from the point of zero distance between ion

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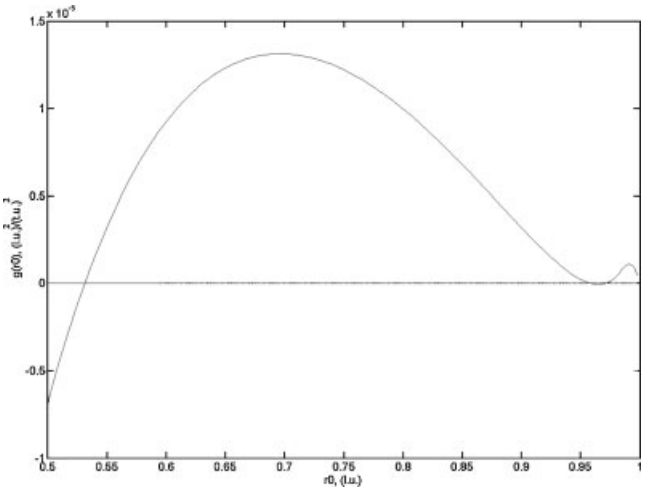

Figure 4. *g(r)* function for the interaction potential of two elliptical uniformly charged ion clouds at a threshold value of number of ions.

cloud centers. Let it be defined as follows:

$$\Delta\varphi = kq^2 \cdot \psi(\xi). \tag{53}$$

Again ξ is half of the distance between the centers of the ion clouds, and all the notation is the same as before. Any potential can be expressed in the form of Eqn. (53), because any interaction potential varies as the square of the electric charge. For $\psi(\xi)$, Eqns. (46) and (47) appear as:

$$\psi(\xi) = -\frac{2\omega R}{kq^2\theta}, \tag{54}$$

$$\frac{d}{d\xi}\psi(\xi) = -\frac{2\omega R}{kq^2\theta}\xi. \tag{55}$$

These equations mean that in order to find the threshold value of $kq^2\theta$ one needs to draw a tangent to $\psi(\xi)$ passing through the origin. Knowing the slope of this line is enough to find $kq^2\theta$. Let us designate the slope of the tangent line as ν, then, as follows from Eqns. (54) and (55), $kq^2\theta$ can be found as:

$$kq^2\theta = -\frac{2\omega R}{\nu}. \tag{56}$$

In order to pass on to the expression for the threshold value of the number of ions in each cloud, N, we should substitute θ and ω just as we did for the case of spherical clouds. The result is:

$$N = \frac{2}{\nu}\frac{R(\Delta\mu/\mu)B^2}{k\mu}. \tag{57}$$

CONCLUSIONS

A new theory of ion cloud interactions in the magnetic fields of a Fourier transform ion cyclotron resonance mass spectrometer was developed. The theory can predict the onset of synchronous cyclotron motion of clouds in the case of close mass-to-charge ratios of the ions in these clouds when the number of ions in the clouds increases. This theory can be used to study the coalescent motion phenomenon for arbitrary inter-cloud potential and hence arbitrary cloud shape. The critical number of ions for the phase synchronization or peak coalescence to take place depends quadratically on the magnetic field strength and is proportional to the cyclotron radius and inversely proportional to the ion masses.

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REFERENCES

1. Comisarow MB, Marshall AG. *Chem. Phys. Lett.* 1974; **25**: 282.
2. Comisarow MB, Marshall AG. *Chem. Phys. Lett.* 1974; **26**: 489.
3. Marshall AG, Hendrickson CL, Jackson GS. *Mass Spectrom. Rev.* 1998; **17**: 1.
4. Nikolaev EN, Heeren RM, Popov AM, Pozdneev AV, Chingin KS. *Rapid Commun. Mass Spectrom.* 2007; **21**: 3527.
5. Pasa-Tolic L, Huang Y, Guan S, Kim HS, Marhsall AG. *J. Mass Spectrom.* 1995; **30**: 825.
6. Naito Y, Inoue M. *J. Mass Spectrom. Soc. Jpn.* 1994; **42**: 1.
7. Naito Y, Inoue M. *Int. J. Mass Spectrom. Ion Processes* 1996; **157/158**: 85.
8. Mitchell DW, Smith RD. *Phys. Rev. E* 1995; **52**: 4366.
9. Landau LD, Lifshitz EM. *Mechanics*, (3rd edn). Pergamon Press: Oxford, 1976.
10. Landau LD, Lifshitz EM. *The Classical Theory of Fields*, (4th edn). Pergamon Press: Oxford, 1984.
11. Kermode MW, Mustafa MM, Rowley N. *J. Phys. G: Nucl. Part. Phys.* 1990; **16**: L299.

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