Accurately accounting for effects on times-of-flight caused by finite field-transition times during the ejection of ions from a storage trap: A study for TOF and MRTOF mass spectrometry

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In applied forms of time-of-flight mass spectrometry utilizing ion storage devices prior to an analysis device, a non instantaneous electric ejection pulse appearing in the region of ion storage is applied for acceleration into the time-of-flight analyzer. Depending on the duration of the field transition time up to full field strength, the calculated mass value of the ion from the time-of-flight will be modified. For novel applications dedicated to precision measurements, as multi-reflection time-of-flight mass spectrometry of short-lived isotopes, it is aimed for to continuously decrease the measurement uncertainty while providing a mass accuracy in the same order. Even though dynamic-field models for time-of-flight mass spectrometry have been considered in the past for technological advances, it is important to study the accuracy of the measured mass in this context. Using a simplified linear model for the field transition, we provide a basic investigation of the scenario, and discuss the deviation from the classical “mass-over-charge” dependency of the ions’ flight, which becomes violated. Further, we provide numbers for the deviations of mass results for typical time-of-flight systems and also multi-reflection time-of-flight devices.

I. INTRODUCTION

Time-of-flight mass spectrometry (TOF MS) technology became one of today’s basic tools for particle identification and mass measurements in analytic chemistry, medicine, biology, and many fields of physics. Ions are created or stored at a chosen starting position and subsequently accelerated and guided by static electric fields (see also approaches using static magnetic fields) until their time of flight is detected by impact on a detection device at the end of the intended flight path. In many TOF MS systems used in science and industry, ions are created inside of an already existing static electric field, and are thus instantaneously accelerated towards an ion-TOF detector. However, in other applications as distance-of-flight mass spectrometry with constant-momentum acceleration or delayed ion extraction for MALDI TOF-MS, a purposely time-dependent acceleration scheme is applied to improve the performance and mass resolution. The ion motion using such acceleration schemes differs from that of the static case and the mass accuracy must be reconfirmed. Recent applications exploit the advantages of quadrupole ion traps as a preparatory stage for the ions, where an extraction field must be switched on to accelerate ions towards a mass spectrometer. In this case a time-dependent acceleration scheme is not intended, but unavoidable.

Especially in the growing community for precision mass measurements of unstable nuclei using multi-reflection time-of-flight (MRTOF) mass spectographs, the usage of ion traps is essential for accumulation and cooling of ions prior to the injection into an MRTOF system. However, in an ion trap the stored ions are first confined inside a certain volume by a trapping potential of typically a few volts depth realized by the principles of Paul traps or Penning traps, and only after a certain storage time the potential changes to a potential gradient of several tens to hundreds of volt per millimeter in order to extract the ions. In realistic systems, the duration of the extraction pulse can be in the order of 10 ns to 1 µs, which depends on the electronic components used. Masses are typically calculated using the assumption of a negligible switching time, i.e. using the static-field approach, where the TOF is proportional to the charge-over-mass ratio.

Nowadays TOF MS and in particular MRTOF MS aims to reach new levels of precision with relative uncertainties as low as \( \delta m/m = 1 \times 10^{-7} \) or even lower, as recently reported. In order to investigate the robustness of the electrostatic-field approach for high levels of precisions, we have performed a basic investigation of the time of flight for a single ion in a TOF MS system including a finite transition time of the ejection pulse from a trapping/starting region.

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We will point out the differences of the mass result obtained from the electrostatic theory and from the extended model. In addition, simulations of a reflectron \[4\] have been performed to benchmark the model under more realistic conditions, meaning a focusing of ions with approximate second-order corrections. The given number examples are adapted to masses of interest for the nuclear-physics community, where experiments are dominantly performed using singly-charged or doubly-charged ions up to mass number \(A \approx 250\). Further, the results and the impact on the obtained mass value will be regarded for the millisecond long flight times applied in multi-reflection time-of-flight mass spectrometry.

II. ACCELERATION REGION WITH A LINEAR FIELD INCREASE

We consider a simple scenario in which an ion is accelerated from an initially field-free region (initial trapping fields are not considered and regarded as switched off) with zero initial energy. We note that, except for the zero initial energy, this scenario is not necessarily hypothetical and can be approximately prepared in reality if intended. From the time \(t_0\) onwards (with \(t_0 = 0\) until explicitly mentioned again), an ejection field is increasing linearly in strength with the time \(t\) until the time \(t_T\), at which transition of the switch is completed and the full field-strength is present. In that way, the function of the electric field in one dimension is:

\[
E(t) = \begin{cases} 
E_0 \cdot \frac{t}{t_T} & \text{for } t \leq t_T \\
E_0 & \text{for } t > t_T 
\end{cases}
\]  \(1\)

The ion starts to travel and travels the distance \(x(t_T) = x_T\) when the field transition is complete. It further travels under the full field strength until reaching the position \(x(t_1) = x_1\), which is considered as the end of the acceleration region in which the electric field is considered to be constant (classical dipole field). Beyond the position \(x_1\), any type of TOF mass spectrometer can follow, meaning that the fields can be considered as unknown and will be treated in a general context later. The ion travels through this spectrometer until reaching the detector at position \(x_D\) at the detection time \(t_D\). The flow chart of this model is illustrated in Fig. 1.

In this study, the acceleration section of the device is as long or longer than the distance \(x_1\), so that \(x(t_T) \leq x_1\) (and \(t_T \leq t_1\)), which means that the transition is finished before the ion reaches the end of the acceleration section. Furthermore the ion starts at rest \((v_0 = v(0) = 0)\) at zero position \((x_0 = x(0) = 0)\), where \(t_0 = 0\).

The motion of the ion as a function of time can be derived in a very straight-forward way. We can calculate the velocity \(v_T\) at the time \(t = t_T\) by:

\[
v_T = \frac{E_0}{t_T} \int_0^{t_T} dt = \frac{qE_0}{m} \frac{t_T^2}{2},
\]  \(2\)

and the corresponding position \(x_T\) by:

\[
x_T = \int_0^{t_T} dt v(t) = \frac{qE_0}{m} \frac{t_T^2}{6},
\]  \(3\)

To reach the end of the acceleration section, the ion will travel from \(x_T\) to \(x_1\) under constant acceleration.

\[
x_1 = x_T + v_T \cdot (t_1 - t_T) + \frac{qE_0}{2m} \cdot (t_1 - t_T)^2.
\]  \(4\)

The time \(t_1\) which the ion needs to travel to \(x_1\) is obtained
by the quadratic equation:
\[ t_1^2 - t_T t_1 - \frac{2mx_1}{qE_0} + \frac{t_T^2}{3} = 0 \] (5)
with the positive solution:
\[ t_1 = \frac{t_T}{2} + \sqrt{\frac{2mx_1}{qE_0} - \frac{t_T^2}{12}} . \] (6)

The transition time \( t_T \) is now explicitly present in the time of flight \( t_1 \) at that position, and the relation used for mass calculations from the TOF of ions:
\[ \text{TOF} \propto \sqrt{\frac{m}{q}} \] (7)
is not exact anymore. The kinetic energy \( K(t_1) = K_1 \) at the position \( x_1 \) is:
\[ K_1 = \frac{q^2E_0^2}{2} \cdot \left( \frac{2x_1}{E_0q} - \frac{t_T^2}{12m} \right) , \] (8)
which contains a mass dependency scaling with the square of the transition time \( t_T \). The obtained energy loss with increasing \( t_T \) is intuitive as the ion already travels a fraction of the distance under a decreased acceleration field before the full field is present. This leads to a reduction of kinetic energy as compared to the case at which an instant field is present. The difference of kinetic energies between the case of the static field and that of the linearly increasing field is:
\[ \delta K_1 = K_1|_{t_T>0} - K_1|_{t_T=0} = -\frac{q^2E_0^2t_T^2}{24m} . \] (9)

For later usage, the static part of the kinetic energy \( K_1 \) for \( t_D = 0 \) and the dynamic contribution can be separated
\[ K_1 = qE_0x_1 + \delta K_1 . \] (10)

In order to justify the approximations in the following, a realistic number example for the decrease of kinetic energy \( K_1 \) at the position \( x_1 \) with increasing transition time of the ejection field is shown in Fig. 2.

III. MODIFIED TIME OF FLIGHT FOR A GENERAL 1D MASS SPECTROMETER

In order to apply the dynamic ion acceleration to any mass spectrometer that follows the acceleration region, the TOF \( t_D \) to reach the detector can be obtained from the TOF integral starting at the end of the acceleration section \( x_1 \) and ending at the detector \( x_D \):
\[ t_D = t_1 + \int_{x_1}^{x_D} dx \frac{1}{\sqrt{\frac{2E_0x'}{m}}} , \] (11)
where the kinetic energy measures the value that the ion has obtained in the acceleration section plus the integral over the charge times the electric fields \( E(x) \) experienced in the mass spectrometer up to the position \( x \):
\[ K(x) = K_1 + q \int_{x_1}^{x} E(x')dx' . \] (12)

As it will turn out useful to separate the charge \( q \) from the kinetic energy, this integral expression is used instead of \( K(x) \) as generic term.
\[ t_D = t_1 + \int_{x_1}^{x_D} dx \frac{1}{\sqrt{qE_0x_1 + q \int_{x_1}^{x} E(x')dx' + \delta K_1}} . \] (13)

Typical transition times of modern devices are below 200 ns and typical average kinetic energies for TOF MS are above 1 keV, which causes a deficit in kinetic energy well below one per cent, if the mass number is not too low. Thus, an expansion to the first order with respect to small differences of kinetic energy is sufficient for many realistic cases:
\[ t_D \approx t_1 + \int_{x_1}^{x_D} dx \frac{1}{\sqrt{q\delta K_{\text{stat}}(x)}} - \frac{1}{2} \int_{x_1}^{x_D} \frac{dx}{\sqrt{q\delta K_{\text{stat}}(x)}} , \] (14)
with
\[ \delta K_{\text{stat}}(x) = E_0x_1 + \int_{x_1}^{x} E(x')dx' \] (15)
as expression for a measure of kinetic energy (excluding the charge) at the position \( x \) in the spectrometer for the static case with \( t_T = 0 \). While the approximation in

![FIG. 2. Kinetic energy obtained during ion acceleration as a function of the duration of a linear field increase. The numbers are calculated assuming 200 V/cm as full ejection-field strength for a singly-charged \(^{133}\text{Cs}^+\) alkali ion traveling to the position \( x_1 = 1 \text{ cm} \) using transition times \( t_T \) up to 1000 ns.](image-url)
Eq. [13] is general (as long as valid), for the linear field increase we can express the time \( t_1 \) and the energy deficit \( \delta K_1 \) using Eq. [9] and Eq. [10]

\[
t_D = \frac{t_T}{2} + \sqrt{\frac{2m_1x_1}{qE_0} - \frac{t_T^2}{12}} + \frac{1}{2} \sqrt{2} \int_{x_1}^{x_D} \frac{dx}{\sqrt{K_{stat}(x)}} \cdot \sqrt{\frac{m}{q}} + \frac{1}{\sqrt{8}} \frac{E_0^2 t_T^2}{24} \int_{x_1}^{x_D} \frac{dx}{\sqrt{K_{stat}(x)}} \cdot \sqrt{\frac{q}{m}}
\]

(16)

Except for the first two terms, the equation can be separated in parts where charge and mass are extracted as \( \sqrt{m/q} \) and \( \sqrt{q/m} \), respectively. However, as \( t_T^2/12 \) is very small, the remaining square root can be expanded as

\[
\sqrt{\frac{2m_1x_1}{qE_0} - \frac{t_T^2}{12}} \approx \sqrt{\frac{2m_1x_1}{qE_0}} - \frac{1}{2} \sqrt{\frac{qE_0}{2m_1x_1}} \frac{t_T^2}{12},
\]

(17)

where charge and mass can be extracted in the same way as mentioned before. If, for completeness, also an additional non-zero offset time for the field transition \( t_0 \) is added to the TOF, we can finally rewrite Eq. [16] as

\[
t_D = t_0 + \frac{t_T}{2} + \alpha \sqrt{\frac{m}{q}} + \beta \sqrt{\frac{q}{m}}.
\]

(18)

The two parameters \( \alpha \) and \( \beta \) are device-specific functions depending on the electric fields in the spectrometer, but also on the initial condition of an ion (position, energy). Only if a high-quality TOF focus can be achieved at the detector, and the dependency on the initial conditions can be averaged resulting in a mean TOF of an ion distribution, \( \alpha \) and \( \beta \) can be regarded as true device constants. As both contributions to the value of \( \beta \) are proportional to \( t_T^2 \), we obtain the well-known static case for \( t_T \to 0 \):

\[
t_D = t_0 + \alpha \sqrt{\frac{m}{q}}.
\]

(19)

We note that the approximation made in Eq. [14] does not cover the case of ion reflections as performed in a reflectron or multi-reflection device. As the ions are slowed down to zero energy, the assumption that the influence of \( \delta K_1 \) on time of flight is small enough to justify the expansion is not valid in general. However, these systems are optimized to operate in a non-dispersive (isochronous) or low-dispersive mode, i.e. to achieve a very similar flight time at the detector for different ion energies. In that way the derivative \( \partial t_D / \partial \delta K_1 \) yields very small values, even if the ions are momentarily stopped.

IV. CALCULATION OF THE MASS FROM TIME-OF-FLIGHT DATA

Reviewing first the static case, masses can be calculated from the time of flight using a single reference mass \( m_1 \), two reference masses \( m_1, m_2 \), or even several masses if available during the measurement. In our study, we will investigate the calibration with a single reference or two references. When calibrating with a single reference species with well known mass (\( m_1 \) with the TOF \( t_{D1} \)), the device parameter \( \alpha \) from Eq. [19] can be eliminated by division \( t_D/t_{D1} \) (\( t_D \) for the analyte ion), and the solution for the mass of interest is:

\[
m = m_1 \cdot \left( \frac{t_D - t_0}{t_{D1} - t_0} \right)^2.
\]

(20)

The offset time \( t_0 \), denoting the real starting time of the ejection process as compared to the start time of the data acquisition system in the experiment, is unknown and must be determined with other methods. To overcome this problem, \( t_0 \) can either be measured or can be eliminated from the mass equation using the information of a second mass if available (see, e.g., [13]), referred to as double-reference calibration:

\[
m = \left( C_{TOP} \cdot \Delta_{1,2} + \frac{\Sigma_{1,2}}{2} \right)^2
\]

(21)

where \( \Delta_{1,2} = \sqrt{m_1} - \sqrt{m_2} \), \( \Sigma_{1,2} = \sqrt{m_1} + \sqrt{m_2} \), and

\[
C_{TOP} = \frac{(2t_D - t_{D1} - t_{D2})}{2(t_{D1} - t_{D2})}
\]

(22)

A mass calibration with the linear model for \( t_T > 0 \) faces similar issues, but with the difference that the additional unknown coefficient \( \beta \) is present. If we assume that the offset time \( t_0 \) can be determined by measurements other than using masses, two well-known references are required and the corresponding times of flight. Starting form Eq. [13] with \( t_0 \) already known, the constants \( \alpha \) and \( \beta \) can be found in a straightforward way by using two reference ions with mass and charge \( X_1 = \sqrt{m_1/q_1} \) and \( X_2 = \sqrt{m_2/q_2} \), and detection times \( t_{D1} \) and \( t_{D2} \), respectively:

\[
\alpha = \frac{t_{D1}X_1 - t_{D2}X_2}{X_1^2 - X_2^2}
\]

(23)

and

\[
\beta = \frac{t_{D2}X_1^2X_2 - t_{D1}X_1X_2^2}{X_1^2 - X_2^2},
\]

(24)

where the detection time can be reduced by the constant offset

\[
t_{\tilde{D}} = t_D - \frac{t_T}{2} - t_0.
\]

(25)

The equation for the reduced detection time of an unknown ion with \( X = \sqrt{m/q} \) is

\[
t_{\tilde{D}} = \alpha \cdot X + \beta \cdot X.
\]

(26)
giving a quadratic equation for the mass-to-charge ratio
\[ X^2 - \frac{t_D}{\alpha} X + \frac{\beta}{\alpha} = 0 \] (27)
with the positive solution
\[ X = \frac{t_D}{2\alpha} + \sqrt{\left(\frac{t_D}{2\alpha}\right)^2 - \frac{\beta}{\alpha}}. \] (28)
Finally, the mass is obtained by
\[ m = q \left( \frac{t_D}{2\alpha} + \sqrt{\left(\frac{t_D}{2\alpha}\right)^2 - \frac{\beta}{\alpha}} \right)^2. \] (29)
If the offset time \( t_0 \) is not known with sufficient precision, then three independent measurements are necessary. This case will be discussed later in the appendix (Sec. V.C).

For illustration of the deviation of the calculated mass from the true mass value when the raising time of the extraction field is not included, a simple example for a single-stage TOF spectrometer has been calculated. Positively charged ions are accelerated in an ideal dipole field of 200 V/cm strength over a distance of \( x_1 = 5 \) cm. After the travel through this distance, the ions move without any force through a drift tube of length \( L = x_D - x_1 \).

The first-order TOF focus in the electrostatic case will occur at \( L = 2x_1 = 10 \) cm (see [2]) and a TOF detector is assumed at this position. In order to include the raising time of the field, Eq. 14 has been used, where the integral on the right side becomes trivial due to the constant velocity. The time of flight for a mass \( A = 100 \) ion of this system yields about 4.6 \( \mu \)s. The recalculated of the mass from the TOF has then been performed with Eq. 20 and Eq. 21 to investigate the relative difference of the measured mass from the real mass \( (m_{\text{meas}} - m_{\text{real}})/m_{\text{real}} \). The mass of an \( A = 85 \) ion (close to the alkali \( 85^{\text{Rb}} \)) will be considered as reference mass for calibration using Eq. 20 and the mass \( A = 133 \) (like \( 133^{\text{Cs}} \)) is additionally used as a second reference when Eq. 21 is applied for two reference ions. The result for both methods of mass calibration is shown in Figure 3.

In the case where a single reference mass is used and no further corrections are done as in Fig. 3a), deviations in the order of a few parts per thousand up to a few percent are obtained from this example, where the latter could result in a mismatch of one mass number or even more. This seems to be large deviation at glance, but the resolution achieved with such type of mass spectrometer is typically low and the purposes of such devices (e.g., analysis of gases etc.) are mostly not harmed as some components are known before. It is also important to note that the transition time in this number example is already a large fraction of the total time of flight (see Sec. VI.A for more details). In Fig. 3b), the constant term \( t_T/2 \) from Eq. 13 has been subtracted and the residual deviations are orders of magnitude lower, which proves its large contribution to the inaccuracies. It can be further seen that the masses cross the zero line at the calibration mass as expected. The calibration method with two masses in Fig. 3c) performs as good as the single-mass calibration in part b), but even though the offset time can be eliminated by this method, the effect of finite transition times does not vanish.

V. NUMERICAL STUDIES

In the following, a finite transition time will be studied by calculating the ions’ time of flight within a model of a classical reflectron \( \text{I} \) in one dimension. The device functions \( \alpha \) and \( \beta \) will be discussed and the masses of ions calculated using a simulation without additional offset time \( (t_0 = 0) \).

For a study with a numerical example, the model of an ideal reflector in one dimension has been chosen. The reason for the choice is that we cover the situation where a reflection of ions takes place and hence probe the robustness of the approximations in Eq. 14 for such scenarios. The reflectron consists of five discrete separated regions, where in each of them a constant electric...
field of certain strength is present. Although such a system can be calculated in an analytical way, a numerical solution has been chosen to keep more flexibility (as adding/removing field regions) during the optimization.

A description of the reflectron model including the applied electric potentials is shown in Fig. 4. The field transition between each two regions is instantaneous, which is an approximation referring to the usage of conductive meshes or wire grids. The ions are accelerated using two different dipole fields, which is a linearly increasing field (in time) in the starting region followed by a constant field for post acceleration. They pass through a field-free drift region of 80 cm length, and are later decelerated using two other regions with dipole fields directed against the ions’ motion: a strong field over a short distance followed by a weak field over a longer distance, until a reflection is achieved. After the reflection, the ions return to the origin and are focusing in TOF at the detection plane position of 10 cm where their time of flight is recorded.

The voltages have been chosen to match realistic conditions, so that comparable values can be found in a laboratory. Further, at the detection plane position an approximate TOF focus takes place, for which the presence of two deceleration regions allow corrections to the second order (of the time of flight as a function of the ions’ starting position). A satisfying focus has been found using the commercial software SIMION, i.e. by varying the rightmost two voltages and investigating the kinetic energy as a function of the ions’ position around the focus point.

In order to analyze the focal conditions, the ions have been initialized using a Gaussian probability distribution with a width parameter of 1 mm centered around the position 0.5 cm (i.e. the center of the starting region). One of the ions was initialized exactly at that position and serves as test ion. If the test ion crosses the detection plane on the way back from the ion mirror, the positions and energies for all other ions are recorded at that time step and hence the position-energy distribution can be analyzed. The focal distribution used for further calculations is shown in Fig. 5. The s-shape of the curve shows mainly the uncorrected third-order components of the position-energy distribution remaining after the optimization. For the data-analysis of TOF spectra, it was necessary to limit the spatial region for the initialization of ions. Although the full shape could be analyzed in principle, the representation in time of flight is challenging as it differs by far from a well-known shape such as a Gaussian distribution. To this end, the linear region of the position-energy distribution at the focal point is used to map the initial Gaussian distribution (width parameter of 250 µm) in space approximately to a final Gaussian.
distribution in TOF (see the bottom of Fig. 5). This linear region contains an energy spread of about 50 eV obtained by the starting position of the ions.

In order to investigate the accuracy of the calculated mass corrections with a finite field-transition time, mass calculations with relative accuracies of $\delta m/m \approx 10^{-7}$ are desired. For the calculation of very precise times of flight, a separate code has been written. As the equations of motion do not solve for the time of flight but for the position of the particle, the uncertainty for the TOF is on the order of the time step itself. In the cases discussed here, this would require a time step of about $10^{-14}$ s to reach the required precision, even though the propagation in the regions of constant fields is trivial. One way to solve for the time of flight more effectively while keeping the simulation flexible, and without rewriting the equations of motion to solve for the time, is the use adaptive time steps when an ion is approaching a chosen position where the electric field changes (and also the final plane for detection). When an ion crosses a plane, the time step is turned back and the crossing procedure is repeated with half time steps. The step is reduced further by such bisecition down to $10^{-20}$ s. After crossing the test plane at minimum time step, it is increased back to a default value (we note that SIMION also provides a similar library).

The times of flight have been fitted using the binned maximum-likelihood estimator provided by the ROOT package [24] developed at CERN. From the extracted center of the distribution the characteristic device functions, the masses, and the mass uncertainties have been calculated (in the order of $10^{-7}$ µs for 50000 ions). The study has been performed once for the static approach, i.e. without transition time of ion extraction, and once for $t_T = 100$ ns.

The characteristic device functions $\alpha(x_0)$ and $\beta(x_0)$ written as constants in Eq. [18] describe the time of flight as a function of the ions’ mass and charge, but depend on the initial conditions of the ions. In the simple case of zero initial velocity as regarded in this study, the initial position of the ion is the only parameter. Note that the voltages and position of the detection plane modify the entire function and are regarded as fixed. To extract the device functions using Eq. [24] and Eq. [24] the time of flight of two single ions have been simulated for different initial positions. As alkali ions like $^{85}$Rb$^+$ and $^{133}$Cs$^+$ are often used as reference ions, the chosen mass numbers for this study are 85.0 and 133.0, both assumed as positive and singly-charged ions. The result of the device functions for the voltages and focus position discussed above is shown in Fig. 6. For the static case shown in Fig. 6 a) and b), the function $\alpha(x_0)$ has an offset and a small variation according to the focal conditions, which is five orders of magnitude smaller than the offset (see y-axis). The function $\beta(x_0)$ results in values equal to zero within the precision of the simulation. If a transition time of 100 ns is included as in c) and d), the function $\alpha(x_0)$ changes slightly and now also non-zero values for $\beta(x_0)$ are obtained. Note that value of $\beta(x_0)$ is to be multiplied by the reciprocal $\sqrt{q/m}$ being about six orders of magnitude larger than $\sqrt{m/q}$ for a singly-charged ion with $A = 100$. In a mass measurement using TOF spectra by summing many ions from a spatial distribution into a histogram, the average result of the entire initial distribution reduces these functions to the coefficients in Eq. [18].

As a next step, the relative mass accuracy using the dynamic model has been calculated using a TOF fit for a set of 50000 ions, where the time of flight of ions with mass numbers between $A = 20$ and $A = 250$ has been simulated using a transition time of $t_T = 100$ ns. The calculation of the mass from the obtained data has been performed using TOF spectra of two ion species, again with mass number $A = 85$ and $A = 133$, for the calculation of the device constants $\alpha$ and $\beta$, and ion mass 85 has further been used as reference mass for the calculation of masses of all other species. For comparison also the calibration using Eq. [20] and Eq. [21] has been performed, i.e. without inclusion of the transition time, where both chosen reference masses have been used for the latter case. The result is shown in Fig. 7.

The results approximately reflect the numbers ob-

![Diagram](image-url)
obtained for Fig. 3 except for the new case including the full correction. Regarding first the uncorrected case in Fig. 7a) with the single reference $A = 85$, the deviation of the calculated mass values increases to the per cent level for light masses. When masses very close to the reference mass are calculated, the deviation becomes very small and the mismatch in timing uncritical. In Fig. 7b) the full correction within the model studied has been applied by first calculating the two coefficients $\alpha$ and $\beta$ using the times of flight for $A = 85$ and $A = 133$, and subsequently the mass according to Eq. 29 using $A = 85$ as reference ion. The relative accuracy achieved is below $5 \times 10^{-8}$ for the full investigated mass scale. The significant deviation of some of the points with smallest error bars is due to the slight mismatch of the Gaussian fitting function and the real data shape (single-ion simulation is always exact). The slight increase of the mass deviation towards light ions reflects the accuracy limit of the approximations made in Eq. 14 (magnitude of $\delta K_1$) and Eq. 17 (mass value), which provide better accuracy for heavier masses. However, also the uncertainties derived from the derivatives (Sec. 5A) increase strongly for lighter masses. The usage of a two-reference calibration according to Eq. 21 shows satisfying results as well, but the relative deviation increases above $10^{-7}$ for masses significantly lighter than that of the lighter reference ion.

The uncertainties of the mass values have been calculated with the assumption that the mass values of the references are exactly known. Each case in Fig. 7 has been treated separately using the corresponding derivatives, while we will only provide the new derivatives for the corrected case in Fig. 7b) in the appendix.

VI. A TIME RESCALING TECHNIQUE FOR ON-LINE MASS MEASUREMENTS OF RADIOACTIVE IONS WITH A SINGLE REFERENCE MASS

The research topic concentrating mainly on precision and accuracy of time-of-flight measurements is dedicated to precision mass measurements of unknown exotic nuclei produced at radioactive ion beam facilities (called also on-line facilities). Ionic masses of previously barely known nuclei are measured with high accuracy and precision to provide new data of nuclides far from stability. In facilities using the ISOL technique (see, e.g. 24, 25), several species with similar mass-to-charge ratio are produced and delivered simultaneously, which provides ease for the calibration of the mass spectrometer as one or several species in the ensemble are typically well known. In other experiments as for example performed at in-flight facilities with beam-fragment separators (see, e.g. 27, 28), this is not always the case and a separate ion source has to be used. Although ion-sources providing molecular ions at many mass numbers are available in principle, for practical reasons mainly alkali sources are used. We have investigated the feasibility of measuring the device constants $\alpha$ and $\beta$ in an independent calibration measurement and using only one reference ion species in an experiment at a later time (on-line experiment) when TOF drifts have been caused by altering electric fields and thermal expansion of the apparatus.

To this end the simulation performed in Sec. V has been repeated for the two masses $A = 85$ and $A = 133$ to obtain the times of flight $t_{D1}$ and $t_{D2}$ for the given electric field. Afterwards, the electric field strength in the reflection section (see Fig. 4) has been multiplied by a factor of $1 + 10^{-8}$ to simulate a later state of the setup at which the power supplies for the electrodes yield slightly different voltages. The device constants from the first simulation have been used to calculate the masses as done before in Sec. V and the reference ion with $A = 85$ of the second simulation with altered field, yielding $\overline{t}_{D1}$ (all time values from second run marked with prime), was used to scale all times of flight from other ions according to

$$\text{corrected } \overline{t}_{D} = \overline{t}_{D} \frac{\overline{t}_{D1}}{t_{D1}},$$

(30)

to match the newly measured times with the previously measured times for $\alpha$ and $\beta$. Also in this study we assume that the start time of the ion ejection and the transition time are already measured with sufficient accuracy. The extended equation for the mass in this scenario is given...
\[ m = q \left( \frac{\tilde{t}_p \tilde{t}_{D1}}{2\alpha \tilde{t}'_{D1}} + \left( \frac{\tilde{t}_p \tilde{t}_{D1}}{2\alpha \tilde{t}'_{D1}} \right)^2 - \frac{\beta}{\alpha} \right)^2. \] (31)

The comparison of the relative mass deviation obtained in the experiment when such a recalibration is used (or not used) is shown in Fig. 8. The deviation without compensating for the altered electric field acts as an offset for the mass scale (Fig. 8a), and yields about \(4 \times 10^{-5}\) for our reflectron example. This is expected as all flight times are equally scaled by the altered field. Similarly, a rescaling is expected to serve as a recalibration to the correct mass value. However, the non-trivial contribution of the recalibration can be seen in Fig. 8b). Towards masses significantly lighter than the reference mass, deviations larger than the \(10^{-7}\) level are obtained due to the reuse of \(\alpha\) and \(\beta\) without modification.

From our example, we obtain the information that an on-line recalibration using a simple rescaling is meaningful also when the finite transition for ion ejection is included. Hence, a single-reference measurement can provide accurate mass results if the measured mass is not excessively less than that of the reference ions. Especially for MRTOF mass measurements, such a calibration is meaningful, as the number of ion reflections can be varied during an experiment. The newly obtained time of flight can then be adapted to the originally measured device constants \(\alpha\) and \(\beta\) by scaling.

For simplicity of the studies above, an offset time \(t_0 = 0\) was assumed, or equally a well known offset time which can be subtracted from all TOF values. In reality the knowledge of the moment of ion ejection versus that of the start of the data acquisition can be a challenge, and can have significant effects on the resulting mass values. Especially for experiments with MRTOF devices in which the mass value and its uncertainty is the goal of the measurement, error estimations dedicated to \(t_0\) are important. To this end the sum \(t_0 + t_T/2 = \tilde{t}_0\) can be regarded as the same source of uncertainty as both of them add up directly. If the total time of flight for the ions increases, as in the order of tens of milliseconds for MRTOF MS, a constant mismatch of the knowledge of \(t_0\) will have a small influence. It is worthwhile to look at experimental parameters including those for typical MRTOF MS operation applied to the corrected approach of Eq. 29.

We assume again two reference measurements of the same measurement set (other than in Sec. VII) to determine \(\alpha\), \(\beta\), and the mass \(m\) of an \(A = 100\) ion regarded as an unknown analyte. The relative mass deviation with a constant mismatch \(\Delta t_0 = 5\) ns has been investigated for different total flight times. This number for the mismatch has been chosen since an accuracy a few nanoseconds can realistically be achieved using modern oscilloscopes for signal measurements. As it has been demonstrated that the full correction for \(t_T > 0\) (see Fig. 4) yields accurate results, and to be able to compare with the static approach from Eq. 20 in a simple way, no explicit transition time for the ion ejection has been applied. The correct
flight times can then directly be calculated by scaling the TOF obtained for \( A = 100 \) and no separate simulation is necessary to obtain longer TOF values. Subsequently, the constant offset time is added and \( \alpha, \beta, \) and the masses are recalculated yielding a deviation of calculated mass from the real value as shown in Fig. 9. For typical flight times of several milliseconds and the chosen analyte mass and references, the deviations for the corrected approach drop quickly below the \( 10^{-7} \) level in this example, which matches the accuracy limits of state-of-the-art devices. The new corrected method allows to perform a single-reference measurement at the moment of the experiment, but the compensation of the mismatch is significantly better. As this is only one number example, i.e. for one combination of reference masses, case-by-case studies are necessary if required after an experiment.

VIII. SUMMARY AND CONCLUSION

A new time-of-flight model including a linear increase in field strength for the ejection of ions towards a TOF mass spectrometer has been investigated. Using first-order approximations, a general form for the flight time of ions in this scenario has been derived resulting in the opportunity to correct for the emerging distortions of calculated masses from TOF data. This correction covers all usual time-of-flight mass spectrometers and also multi-reflection devices. The magnitude of the effects have been investigated using dedicated numerical examples.

The results show effects being of significance for general purpose mass spectrometry as it can lead to a misidentification in the order of a mass number if the trap-ejection switches are not state-of-the-art. The corrections also play a role for high-precision mass measurements with MRTTOF MS using a single mass reference. If the reference mass is not in the same mass region of the ions in question, these deviations can eventually have significant impact on measurement results as obtained from this study. Hereby, the by far largest contribution of impact is an additional constant time offset of half the duration of the ejection-field transition. This adds directly as a delay to the start time of the measurement.

So far, the field-transition times have not been recognized as remarkable error source for the measurements of nuclear masses. The reason is that in many cases ions of a similar mass to that of the analyte are used as a reference, and also that the transition times of state-of-the-are switches are very short as in the order of tens of nanoseconds, whereas the total flight times are on the order of milliseconds.

Cases where the effect of such imperfections may increase to significant levels concern mass measurements of heavy ions or superheavy elements with medium-mass alkali ions used as reference. Test measurements for confirmation of this study are to be performed in an upcoming experiment under realistic conditions, where also the robustness of the approach for deviations of the transition from a linear shape can be investigated. So far, conclusive experimental data is not present and requires measurements including a larger mass region and a dedicated setup with adjustable field transition.

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X. APPENDIX

A. Derivatives for uncertainty calculation for the case of an externally measured offset time $t_0$

(according to Sec. [V])

We consider the case where the offset time and the transition time is measured with methods other than using further reference ions. In the case of using the same data to obtain $\alpha$ and $\beta$ and performing the mass calculation, Eq. [29] was used (Fig. 7b). For the calculation of the uncertainty considering the input masses and the inner derivatives for $\alpha$ and $\beta$, please see the next subsection.

\[
\frac{\partial m}{\partial t_D} = 2\sqrt{qm} \left( \frac{1}{2\alpha} + \frac{1}{4\alpha^2} \frac{\tilde{t}_D}{\sqrt{\left(\frac{\partial \alpha}{\partial t_D}\right)^2 - \frac{\beta}{\alpha}}} \right)
\]

\[
\frac{\partial m}{\partial t_{D1}} = 2\sqrt{qm} \left( -\frac{\tilde{t}_D}{2\alpha^2} \frac{\partial \alpha}{\partial t_{D1}} - \frac{\tilde{t}_{D1}^2}{4\alpha^2} \frac{\partial \alpha}{\partial t_{D1}} + \frac{\beta \frac{\partial \alpha}{\partial t_{D1}} - \beta \frac{\partial \alpha}{\partial t_{D2}}}{2\alpha^2} \right) \frac{1}{\sqrt{\left(\frac{t_0}{2\alpha}\right)^2 - \frac{\beta}{\alpha}}}
\]

\[
\frac{\partial m}{\partial t_{D2}} = 2\sqrt{qm} \left( -\frac{\tilde{t}_D}{2\alpha^2} \frac{\partial \alpha}{\partial t_{D2}} - \frac{\tilde{t}_{D2}^2}{4\alpha^2} \frac{\partial \alpha}{\partial t_{D2}} + \frac{\beta \frac{\partial \alpha}{\partial t_{D2}} - \beta \frac{\partial \alpha}{\partial t_{D1}}}{2\alpha^2} \right) \frac{1}{\sqrt{\left(\frac{t_0}{2\alpha}\right)^2 - \frac{\beta}{\alpha}}}
\]
(according to Sec. VI)

We consider the case where the offset time and the transition time is measured with methods other than using further reference ions. Furthermore, the possibility of rescaling the time of flight as performed in Sec. VI will be included. This means that Eq. 31 is used, where \(\alpha\) and \(\beta\) are measured using \(t_{D1}\) and \(t_{D2}\), whereas \(t'_{D1}\) and \(t'_{D1}\) are obtained from an independent measurement at a later time and the ratio of \(t'_{D1}/t_{D1}\) is then used for the correction of the analyte ion’s flight time. For the calculation of the mass uncertainty, we will list first the outer derivatives of Eq. 31 and then the inner derivatives for \(\alpha\) and \(\beta\).

\[
\frac{\partial m}{\partial t'_{D1}} = 2\sqrt{qm} \left[ \frac{\tilde{t}_{D1}}{2\alpha^2 t'_{D1}} \left( \alpha - \tilde{t}_{D1} \frac{\partial \alpha}{\partial t_{D1}} \right) + \frac{\tilde{t}_{D1}^2}{4\alpha^2 t'_{D1}} \left( \alpha - \tilde{t}_{D1} \frac{\partial \alpha}{\partial t_{D1}} \right) \right] \left( \alpha - \tilde{t}_{D1} \frac{\partial \alpha}{\partial t_{D1}} \right) \frac{1}{\sqrt{\left( \frac{\tilde{t}_{D1}}{2\alpha t'_{D1}} \right)^2 - \frac{\beta}{\alpha}}} \tag{35}
\]

\[
\frac{\partial m}{\partial t'_{D2}} = 2\sqrt{qm} \left[ \frac{\tilde{t}_{D1}}{2\alpha^2 t'_{D2}} \frac{\partial \alpha}{\partial t_{D2}} - \frac{\tilde{t}_{D1}^2}{4\alpha^3 t'_{D2}} \frac{\partial \alpha}{\partial t_{D2}} + \frac{\tilde{t}_{D1}^2}{4\alpha^3 t'_{D2}} \frac{\partial \alpha}{\partial t_{D2}} \right] \frac{1}{\sqrt{\left( \frac{\tilde{t}_{D1}}{2\alpha t'_{D1}} \right)^2 - \frac{\beta}{\alpha}}} \tag{36}
\]

With \(X_1 = \sqrt{m_1/q_1}\) and \(X_2 = \sqrt{m_2/q_2}\) for the two input masses used only implicitly in \(\alpha\) and \(\beta\), the outer derivatives for \(X_1\) and \(X_2\) equally yield:

\[
\frac{\partial m}{\partial X_{1,2}} = 2\sqrt{qm} \left[ \frac{\tilde{t}_{D1}}{2\alpha^2 t'_{D1}} \frac{\partial \alpha}{\partial t_{D1}} - \frac{\tilde{t}_{D1}^2}{4\alpha^3 t'_{D1}} \frac{\partial \alpha}{\partial t_{D1}} + \frac{\tilde{t}_{D1}^2}{4\alpha^3 t'_{D1}} \frac{\partial \alpha}{\partial t_{D1}} \right] \frac{1}{\sqrt{\left( \frac{\tilde{t}_{D1}}{2\alpha t'_{D1}} \right)^2 - \frac{\beta}{\alpha}}} \tag{37}
\]

The inner derivatives for \(\alpha\) and \(\beta\) are:

\[
\frac{\partial \alpha}{\partial t_{D1}} = \frac{X_1}{X_1^2 - X_2^2} \tag{40}
\]

\[
\frac{\partial \alpha}{\partial t_{D2}} = -\frac{X_2}{X_1^2 - X_2^2} \tag{41}
\]

\[
\frac{\partial \alpha}{\partial X_1} = -\tilde{t}_{D1} \frac{X_1^2 + X_2^2}{(X_1^2 - X_2^2)^2} + \frac{2\tilde{t}_{D2}X_1X_2}{(X_1^2 - X_2^2)^2} \tag{42}
\]

\[
\frac{\partial \alpha}{\partial X_2} = -\tilde{t}_{D2} \frac{X_1^2 + X_2^2}{(X_1^2 - X_2^2)^2} + \frac{2\tilde{t}_{D1}X_1X_2}{(X_1^2 - X_2^2)^2} \tag{43}
\]

\[
\frac{\partial \beta}{\partial t_{D1}} = -\frac{X_2^2 X_1}{X_1^2 - X_2^2} \tag{44}
\]
as the uncertainty of the charge is negligible, it is sufficient to use only the measurement uncertainty of the input masses if necessary.

\[
\frac{\partial \beta}{\partial m_{1,2}} = \frac{1}{2\sqrt{q_{1,2}m_{1,2}}}
\]

Finally, with \( \tilde{t}_{D,1,D2} = t_{D,1,D2} - t_T/2 - t_0 \), the contribution of the offset time \( t_0 \) and the transition time \( t_T \) is:

\[
\frac{\partial \tilde{t}}{\partial t_T} = \frac{1}{2} \left( \frac{\partial m}{\partial t_T} + \frac{\partial m}{\partial t_{D1}} + \frac{\partial m}{\partial t_{D2}} \right)
\]

\[
\frac{\partial \tilde{t}}{\partial t_0} = - \left( \frac{\partial m}{\partial t_T} + \frac{\partial m}{\partial t_{D1}} + \frac{\partial m}{\partial t_{D2}} \right)
\]

C. Calculation \( \alpha, \beta, \) and the mass \( m \) when a third reference with \( m_3 \) is used to obtain \( t_0 \) without external measurement

In the case when a third reference is available, the offset time can be directly obtained from a time-of-flight measurement. Three times of flight are then available for the charge-to-mass ratios \( X_{1,2,3} = \sqrt{q_{1,2,3}/m_{1,2,3}} \). The linear system

\[
\begin{align*}
t_{D1} &= t_0 + \frac{t_T}{2} + \alpha X_1 + \beta X_1^2 \\
t_{D2} &= t_0 + \frac{t_T}{2} + \alpha X_2 + \beta X_2^2 \\
t_{D3} &= t_0 + \frac{t_T}{2} + \alpha X_3 + \beta X_3^2
\end{align*}
\]

can then be solved in a straight forward way, yielding:

\[
t_0 + \frac{t_T}{2} = \frac{t_{D1}X_1(X_2^2 - X_3^2) + t_{D2}X_2(X_3^2 - X_1^2) + t_{D3}X_3(X_1^2 - X_2^2)}{(X_1 - X_2)(X_2 - X_3)(X_3 - X_1)}
\]

\[
\alpha = \frac{t_{D1}X_1(X_3 - X_2) + t_{D2}X_2(X_1 - X_3) + t_{D3}X_3(X_2 - X_1)}{(X_1 - X_2)(X_2 - X_3)(X_3 - X_1)}
\]

\[
\beta = \frac{X_1X_2X_3\{t_{D1}(X_3 - X_2) + t_{D2}(X_1 - X_3) + t_{D3}(X_2 - X_1)\}}{(X_1 - X_2)(X_2 - X_3)(X_3 - X_1)}
\]

to obtain the device constants and also the combined offset time \( t_0 + t_T/2 \) from reference masses.