Octupolar-Excitation Penning-Trap Mass Spectrometry for Q-Value Measurement of Double-Electron Capture in ^{164}Er

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The theory of octupolar-excitation ion-cyclotron-resonance mass spectrometry is presented which predicts an increase of up to several orders of magnitude in resolving power under certain conditions. The new method has been applied for a direct Penning-trap mass-ratio determination of the ^{164}Er-^{164}Dy mass doublet. ^{164}Er is a candidate for the search for neutrinoless double-electron capture. However, the measured $Q_{\epsilon\epsilon}$ value of 25.07(12) keV results in a half-life of 10^{30} years for a 1 eV Majorana-neutrino mass.

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Exciting progress in Penning-trap mass spectrometry in the past two decades has led to a variety of direct mass measurements of stable and radioactive nuclides with very high accuracy [1]. For the mass determination of short-lived nuclides, the time-of-flight (TOF) ion-cyclotron-resonance (ICR) technique [2] has become the method of choice.

A recent important step was the replacement of the quadrupolar excitation by an octupolar excitation of the ion motion [3,4]. This new technique provided an immediate gain in resolving power, thus giving hope for resolving TOF-ICR resonances of ions with close-lying masses, e.g., low-lying nuclear isomers. However, up to now, this has not been experimentally proven with a mass doublet. In addition, no theoretical description of the octupolar excitation has been available.

The present Letter fills these gaps. First, the line shape of octupolar TOF-ICR resonances is derived from an analytical calculation. Second, the octupolar-excitation technique is directly applied for a measurement of the mass difference of ^{164}Er and ^{164}Dy. In this experiment, a resolving power of about 2×10^7 has been achieved, exceeding the resolving power provided by the conventional technique for the same excitation time by more than an order of magnitude. This improvement allowed the resolution of the two TOF-ICR resonances of the pair of nuclear isobars differing in mass by only about 25 keV. The present mass doublet has been chosen due to its presumed importance for neutrino physics. ^{164}Er is a promising candidate for a search for neutrinoless double-electron capture [5]. The probability of this process is given by [6]

$$\lambda_{\epsilon\epsilon} = |V_{\epsilon\epsilon}|^2 \frac{\Gamma_{2h}}{(Q_{\epsilon\epsilon} - B_{2h})^2 + \Gamma_{2h}^2/4}, \quad (1)$$

where $V_{\epsilon\epsilon}$ is the transition amplitude between two atoms [5,7], $Q_{\epsilon\epsilon}$ is the difference between the initial and final atomic (ground-state) masses, and B_{2h} and Γ_{2h} are the energy and the width of the double-electron hole in the atomic shell of the daughter nuclide, respectively. An observation of this neutrinoless transition would prove that the neutrino is a Majorana particle. Furthermore, a measurement of the half-life of this process would allow a determination of the effective Majorana-neutrino mass. The measurement of its $Q_{\epsilon\epsilon}$ value with higher precision than to date is essential to draw a conclusion on ^{164}Er's suitability as a neutrinoless double-electron capture candidate.

In Penning-trap mass spectrometry [1,8], the charge-to-mass ratio q/m of an ion is obtained by a measurement of its cyclotron frequency $\omega_c = 2\pi\nu_c = qB/m$ in a strong homogeneous magnetic field B. This frequency is determined by observing the resonant interconversion of the ion's magnetron and cyclotron motional modes due to the action of an additional quadrupolar or octupolar azimuthal rf field. In the latter case, for example, the field

$$\Phi_{\mathrm{rf}} = C(x^4 - 6x^2y^2 + y^4)\cos(\omega_{\mathrm{rf}}t + \chi_{\mathrm{rf}}) \quad (2)$$

is introduced into the trap via an eightfold segmented ring electrode. The interconversion process due to quadrupolar rf fields has been described classically [9] as well as in a quantum mechanical framework [10,11].

Even though a classical treatment is sufficient, the quantum approach offers several advantages. A clear and intuitive picture of the basic physical interaction emerges: A photon of frequency $\omega_{\mathrm{rf}} \approx n\omega_c = n\omega_+ + n\omega_-$ is absorbed, while simultaneously n cyclotron oscillator quanta with energy $n\hbar\omega_+$ are created and n magnetron oscillator quanta with energy $-n\hbar\omega_-$ are annihilated (with $n = 1$ for quadrupolar and $n = 2$ for octupolar excitation). The inverse process also takes place. An important property of this interaction is the conservation of the sum of the numbers of cyclotron and magnetron quanta. Denoting the annihilation and creation operators for cyclotron oscillator quanta by $\hat{a}_+$ and $\hat{a}_+^\dagger$, respectively, and those for the magnetron oscillator by $\hat{a}_-$ and $\hat{a}_-^\dagger$, we obtain

$$\hat{N}_{\mathrm{tot}} = \hat{N}_+(t) + \hat{N}_-(t) = \hat{a}_+^\dagger(t)\hat{a}_+(t) + \hat{a}_-^\dagger(t)\hat{a}_-(t). \quad (3)$$

In the quantum approach, the position operators $\hat{x}$ and $\hat{y}$ of the ion can be expressed in terms of the creation and annihilation operators of the cyclotron and magnetron motional modes: $\hat{x} + i\hat{y} = \sqrt{2\hbar/m\omega_1}(\hat{a}_+ + \hat{a}_-^\dagger)$, with $\omega_1 = \sqrt{\omega_c^2 - 2\omega_z^2}$, where ω_z is the frequency of the axial motion. Expansion of Φ_{rf} in terms of $\hat{a}_\pm$ and $\hat{a}_\pm^\dagger$ yields a decomposition into the various interactions induced by Φ_{rf}. Choosing $\omega_{\mathrm{rf}} = 2\pi\nu_{\mathrm{rf}} \approx n\omega_c$, and selecting the slowly varying terms (rotating wave approximation), we can isolate the interaction responsible for the interconversion of the motional modes ($n = 1$ for quadrupolar and $n = 2$ for octupolar excitation):

$$\hat{H}_{\mathrm{rf}}(t) = \hbar g\{e^{-i(\omega_{\mathrm{rf}}t+\chi_{\mathrm{rf}})}[\hat{a}_+^\dagger(t)\hat{a}_-(t)]^n + \mathrm{H.c.}\}. \quad (4)$$

Here "H.c." denotes the Hermitian conjugate of the first term, and the coupling parameter g is proportional to the applied rf voltage.

The transition to a classical description is made by taking expectation values with respect to quasiclassical coherent states $|\alpha\rangle$. The conservation law for the total number of oscillator quanta in the motional state of the ion can then be translated into a relation for the cyclotron and magnetron radii of the ion motion [11]:

$$R_+^2(t) + R_-^2(t) = R_+^2(0) + R_-^2(0) = 2\hbar/(m\omega_1)\langle\hat{N}_{\mathrm{tot}}\rangle. \quad (5)$$

The expectation value of the fraction of cyclotron oscillator quanta

$$n_+(\tau, \delta) = \frac{\langle\hat{N}_+(\tau, \delta)\rangle}{\langle\hat{N}_{\mathrm{tot}}\rangle} = \frac{R_+^2(\tau, \delta)}{R_+^2(0) + R_-^2(0)} \quad (6)$$

represents the conversion profile for the cyclotron motional mode after initially preparing a motional state with radii $R_\pm(0)$ and then applying a pulse of the octupolar rf field of duration τ with detuning $\delta = \nu_{\mathrm{rf}} - 2\nu_c$. n_+ depends on τ and δ, on the initial phase $\chi = \chi_{\mathrm{rf}} - 2(\chi_+ + \chi_-)$, and on the initial magnetron and cyclotron radii $R_\pm(0)$ of the ions.

The further analysis is based on the concept of the Bloch vector operator [10,11], which is a 3-component Hilbert space operator $\hat{\mathbf{T}}$ with angular momentum commutation rules. In connection with the Ramsey method, this concept was instrumental in establishing the analogy between nuclear magnetic resonance and the interconversion of motional modes in a Penning trap [11–13]: The Bloch vector operator is the analog of the nuclear spin, the cyclotron frequency ω_c takes the place of the Larmor frequency ω_L, and the electric rf field plays the role of the high-frequency magnetic field. In the context of Penning traps, the third component of the Bloch vector operator $\hat{T}_3$ immediately provides the desired interconversion profiles [see Eq. (7)]. In the case of octupolar excitation, it lowers the degree of nonlinearity of the equations of motion and thus makes a treatment in terms of known mathematical functions possible. The components of the Bloch vector operator are $\hat{T}_1 = \frac{\hbar}{2}(\hat{a}_+^\dagger\hat{a}_- + \hat{a}_-^\dagger\hat{a}_+)$, $\hat{T}_2 = \frac{\hbar}{2i}(\hat{a}_+^\dagger\hat{a}_- - \hat{a}_-^\dagger\hat{a}_+)$, and $\hat{T}_3 = \frac{\hbar}{2}(\hat{a}_+^\dagger\hat{a}_+ - \hat{a}_-^\dagger\hat{a}_-)$. One also defines $\hat{T}_\pm = \hat{T}_1 \pm i\hat{T}_2$ and the scalar operator $\hat{T}_0 = \frac{\hbar}{2}(\hat{a}_+^\dagger\hat{a}_+ + \hat{a}_-^\dagger\hat{a}_-) = \frac{\hbar}{2}\hat{N}_{\mathrm{tot}}$. The "length" of the Bloch vector follows from $\hat{T}_1^2 + \hat{T}_2^2 + \hat{T}_3^2 = \hat{T}_0(\hat{T}_0 + \hbar\hat{\mathbf{1}})$. Conversion profiles can now be expressed as

$$n_+(\tau, \delta) = \langle\hat{T}_0 + \hat{T}_3(\tau, \delta)\rangle/\hbar\langle\hat{N}_{\mathrm{tot}}\rangle. \quad (7)$$

The Hamiltonian for the ion motion in the Penning trap with an octupolar rf field can be reformulated in terms of the Bloch vector operator $\hat{\mathbf{T}}$ as

$$\hat{H}(t) = \omega_1\hat{T}_0 + \omega_c\hat{T}_3(t) + g\hbar^{-1}[e^{-i(\omega_{\mathrm{rf}}t+\chi_{\mathrm{rf}})}\hat{T}_+^2(t)] + g\hbar^{-1}[e^{+i(\omega_{\mathrm{rf}}t+\chi_{\mathrm{rf}})}\hat{T}_-^2(t)]. \quad (8)$$

The resulting Heisenberg equations of motion for the Bloch vector operator are nonlinear of second degree with time-dependent coefficients. This explicit time dependence is eliminated by a time-dependent unitary transformation ($\hat{T}_i \rightarrow \hat{T}_i'$). By taking expectation values, a normalized Bloch vector $X_i = \langle\alpha|\hat{T}_i'|\alpha\rangle/\langle\alpha|\hat{T}_0|\alpha\rangle$ is defined. It describes the motional state of the ion by a point on the unit sphere. With the dimensionless variables $\theta = 2g\langle\hat{N}_{\mathrm{tot}}\rangle\tau$ and $\eta = \pi\delta/(2g\langle\hat{N}_{\mathrm{tot}}\rangle)$, the Heisenberg equations of motion are translated into the following system:

$$\begin{aligned} \dot{X}_1(\theta) &= +\eta X_2(\theta) - X_2(\theta)X_3(\theta), \\ \dot{X}_2(\theta) &= -\eta X_1(\theta) - X_1(\theta)X_3(\theta), \\ \dot{X}_3(\theta) &= 2X_1(\theta)X_2(\theta). \end{aligned} \quad (9)$$

Equations of this type are known as Volterra-Zhukovsky gyrostat equations [14] and can be solved in terms of linear rational functions of Jacobi elliptic functions $\mathrm{sn}(z; k^2)$, for example,

$$X_3(\theta) = \frac{a_{11} + a_{12}\mathrm{sn}(w(\theta - \theta_0); k^2))}{a_{21} + a_{22}\mathrm{sn}(w(\theta - \theta_0); k^2))}. \quad (10)$$

The timelike variable θ describes the development of the system, either by changing the pulse duration τ while keeping the "amplitude" $2g\langle\hat{N}_{\mathrm{tot}}\rangle$ fixed, or vice versa. The amplitude itself can be changed by varying the coupling via the applied octupole voltage, or $\langle\hat{N}_{\mathrm{tot}}\rangle$ via the initial magnetron radius $R_-(0)$. The coefficients a_{ik}, the scale function w, the delay θ_0, and the parameter k^2 of the elliptic function all depend in a complicated fashion on the detuning parameter η, the phase χ, and the other initial data.

The profile function n_+ is now simply given by $n_+(\theta, \eta) = 0.5[1 + X_3(\theta, \eta)]$. Figure 1 and all other conversion profiles have been calculated by use of this relation. The knife-edged ridge arising at the resonance frequency ($\delta = 0$) reflects the fact that at the resonance the period of the Jacobi elliptic functions grows rapidly to rather large values, which gives rise to the remarkable resolving power of octupolar excitation. It is limited only by our lack of complete control of the ion motion, which requires us to take averages over the initial distributions of the cyclotron and magnetron radii and phases and also by the indeterminacy resulting from the finite duration of the octupolar radiation pulse. Full details will be available in a separate publication [15].

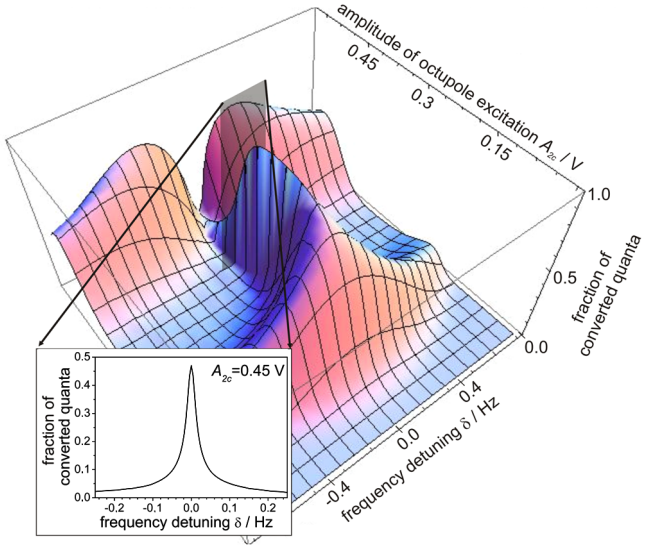

FIG. 1 (color online). Conversion landscape for a pulse duration of the octupolar rf field $\tau = 2$ s. The ratio of the initial cyclotron and magnetron radii is assumed to be 0.03; an average over the initial phase $\chi = \chi_{\mathrm{rf}} - 2(\chi_+ + \chi_-)$ has been performed. Cuts through the figure for a constant amplitude represent conversion profiles $n_+(\delta)$ vs the frequency detuning $\delta = \nu_{rf} - 2\nu_c$. The inset represents a cut at the experimentally used amplitude A_{2c} of 0.45 V.

The octupolar and quadrupolar techniques were used in comparison to determine the $Q_{\epsilon\epsilon}$ value of double-electron capture in ^{164}Er by a measurement of the cyclotron-frequency ratio of singly charged ions of ^{164}Er and ^{164}Dy with SHIPTRAP [16]. The setup and experimental procedures are described in Ref. [17]. For the present measurement, a laser ablation ion source [18] was used to create ions by irradiation of erbium- and dysprosium-oxide samples deposited onto stainless steel plates. After cooling and centering in the preparation trap, the ion cyclotron frequency ν_c was determined in the measurement trap by monitoring the conversion of magnetron motion into cyclotron motion either at ν_c for quadrupolar or at $2\nu_c$ for octupolar excitation. The data were taken in two measurement periods. In one period, the cyclotron frequencies were measured alternately with a pulse duration of 2 s and an amplitude of the octupolar rf field of 0.45 V. In the other period, the excitation was replaced by the quadrupolar two-pulse (Ramsey) technique (two 250-ms pulses separated by a waiting time of 1.5 s) [12].

The measurements with the Ramsey technique were used as a reference for the octupolar measurements and, therefore, were performed with substantially higher statistics to match the precision. Each of the 20 frequency measurements of the octupolar period and of the 110 frequency measurements of the Ramsey period lasted approximately 10 and 20 min and contained in total between 250–350 ions and 500–700 ions per resonance, respectively.

Moreover, in order to experimentally confirm the superiority of the octupolar to the conventional quadrupolar excitation technique with respect to the resolving power, the octupolar technique was used to perform a simultaneous measurement of both frequencies. In Fig. 2, typical quadrupolar one-pulse (a) and octupolar (b) TOF-ICR resonances are shown. The quadrupolar TOF-ICR resonance was fitted with the theoretical function from Ref. [9]. Because of the extreme resolving power of the octupolar technique, even the small residual fluctuations of the pressure- and temperature-stabilized magnetic field [19] led to a non-negligible resonance broadening and, thus, to a Gaussian line shape.

Care was taken to provide equal starting conditions for Er and Dy ions in the measurement trap in order to minimize a possible systematic shift of the frequency ratio due to imperfections [20]. For a study of ion-ion interactions in the measurement trap, the data were analyzed following the procedure given in Ref. [21] and divided into five sets according to the number of detected ions per cycle. There was no indication for any correlation between the frequency ratios and the number of ions. The final

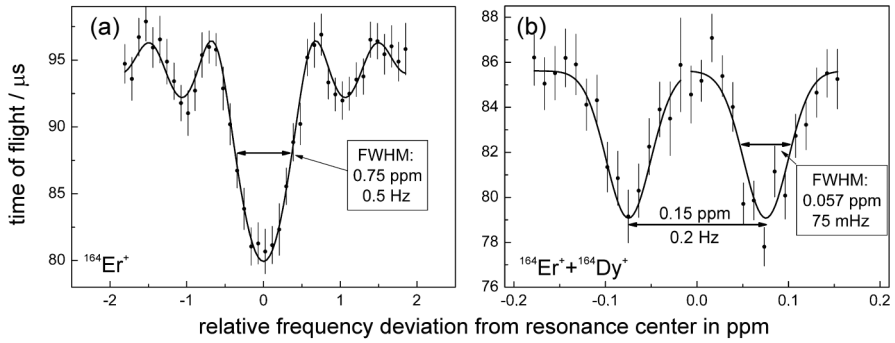

FIG. 2. (a) An experimental one-pulse quadrupolar TOF-ICR resonance of $^{164}Er^+$ in comparison with (b) octupolar TOF-ICR resonances of $^{164}Er^+$ and $^{164}Dy^+$. The pulse duration of the rf fields was 2 s.

frequency ratio is $R - 1 = \nu_c(^{164}Dy^+)/\nu_c(^{164}Er^+) - 1 = 1.6421(76) \times 10^{-7}$.

With the octupolar technique, we obtained a resolving power of about 2×10^7 [see Fig. 2(b)], which exceeds that of the quadrupolar technique by more than a factor of 10. This allowed the resolution of the TOF-ICR resonances of Er^+ and Dy^+. With the quadrupolar technique, such a resolving power would require an excitation time of 30 s, which is beyond the present capability. Moreover, such a long excitation time imposes a severe restriction on the half-lives of the accessible nuclides. Furthermore, the mass measurements would last substantially longer to acquire comparable statistics.

The $Q_{\epsilon\epsilon}$ value of ^{164}Er, determined by

$$Q_{\epsilon\epsilon} = [M(^{164}\mathrm{Dy}) - m_e][R - 1], \tag{11}$$

where $M(^{164}\mathrm{Dy})$ and m_e are masses of neutral ^{164}Dy and the electron, respectively, is equal to 25.07(12) keV.

To determine the probability of neutrinoless double-electron capture in ^{164}Er, an accurate calculation of the double-electron hole binding energy B_{2h} and of the nuclear matrix element $M(^{164}\mathrm{Er})$, which enters into the transition amplitude $V_{\epsilon\epsilon}$, was performed. $B_{2h} = 18.259(8)$ keV was calculated by use of the Dirac-Fock method [22] with the Breit, electron-correlation, and quantum electrodynamics corrections. The width of the autoionizing state of ^{164}Dy with two $2s$ holes is taken as twice the width of the L_1 level and is equal to 8.0(2.0) eV [23]. The nuclear matrix element $M(^{164}\mathrm{Er})$ was calculated within the quasi-random-phase approximation approach in which pairing, ground-state correlations, and the short-range correlations originate from the same realistic nucleon-nucleon interaction, namely, from the CD-Bonn potential [24]. The particle-particle strength parameter of the nuclear Hamiltonian was fixed by the assumption that the nuclear matrix element of two-neutrino double-electron capture is within the range between 0 and 0.1 MeV^{-1} and the unquenched axial vector coupling constant was used ($g_A = 1.25$). Thus, the values of $M(^{164}\mathrm{Er})$ range from 5.9 to 6.3. For the calculation of the half-life, the value of 6.0 was used.

With these input values for Eq. (1), the half-life of the neutrinoless double-electron capture in ^{164}Er becomes

$$T^{0\nu}_{1/2} = \frac{\ln 2}{\lambda_{\epsilon\epsilon}} \approx 10^{30} \left| \frac{1\ \mathrm{eV}}{m_{\beta\beta}} \right|^2 \text{years}, \tag{12}$$

where the effective neutrino mass $m_{\beta\beta}$ is taken in eV. For a count rate of one transition event a year, 300 tons of enriched Er are required, thus making this nuclide unfavorable for the search for neutrinoless double-electron capture.

In conclusion, for the first time the novel octupolar technique has been described analytically and employed to determine the small $Q_{\epsilon\epsilon}$ value of the double-electron ground-to-ground $0^+ \rightarrow 0^+$ transition in ^{164}Er by direct measurements of the mass ratio of $^{164}Dy^+$ and $^{164}Er^+$. This technique has provided an increase in resolving power by more than an order of magnitude and, thus, allowed a simultaneous measurement of the cyclotron frequencies of $^{164}Dy^+$ and $^{164}Er^+$. With such a superior resolution, the octupolar technique opens the door for ultrahigh-resolution Penning-trap mass spectrometry even for short-lived nuclides allowing the investigation of low-lying (< 10 keV) isomeric states. The $Q_{\epsilon\epsilon}$ value of 25.07(12) keV for ^{164}Er results in a half-life of 10^{30} years for a 1 eV mass of a Majorana neutrino.

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