Editors' Suggestion

Nonlinear isotope-shift effects in Be-like, B-like, and C-like argon

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Violation of linearity of the King plot is investigated for a chain of partially stripped argon isotopes. The nonlinearity originates within the standard model from subtle contributions to the isotope shifts from next-to-leading order effects, which have never been systematically studied so far. In light atoms these nonlinear effects are dominated by the quadratic nuclear recoil ($\propto 1/M^2$, where M is the nuclear mass). Large-scale relativistic calculations of the linear and quadratic mass shift and the field shift are performed for the $2P$ fine-structure transitions in Be-like, B-like, and C-like argon ions. Nonlinearities of the King plots from 5 to 30 kHz are found, which is four orders of magnitude larger than previous estimates in comparable systems. Accurate calculations of these effects are vital for identification of possible nonlinearities originating from physics beyond the standard model.

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I. INTRODUCTION

Investigations of isotope-shift phenomena offer an excellent possibility to selectively probe nuclear effects and to extract nuclear parameters from the observed atomic spectra. On the theoretical side, the isotope shifts of atomic levels have the advantage that they can be calculated to a much higher absolute precision than the atomic energy levels. Depending on the nuclear charge Z, the isotope shifts are governed either by the nuclear mass (low-Z ions) or by the finite nuclear size (high-Z ions), thus yielding an opportunity for a detailed study of individual nuclear effects. On the experimental side, the isotope-shift phenomena offer a possibility for extracting information about the nucleus, by means of the so-called King-plot analysis [1,2].

Isotope-shift studies can also improve our understanding of fundamental physics. It has recently been demonstrated [3,4] that isotope-shift measurements can be used to constrain the coupling strength of hypothetical new-physics boson fields to electrons and neutrons. More specifically, the presence of a light boson particle would cause a nonlinearity of the King plot for the isotope shifts of two atomic transitions of several isotopes of the same element. The absence of the King-plot nonlinearities observed so far allowed the authors to draw constraints on the coupling strength of the hypothetical particles.

Experimentally, no King-plot nonlinearities were observed in the measurements [5,6] performed at the 100 kHz accuracy level. The present-day isotope-shift experiments, however, may improve the accuracy by several orders of magnitude. Specifically, measurements of optical-clock transitions were demonstrated on a few-Hertz precision level, by simultaneously exciting two Ca^+ isotopes in the same trap [7]. An even higher precision can be achieved by using correlated or even entangled states [8]. The coherent high-resolution optical spectroscopy [9] can provide access to isotope-shift measurements of highly charged ions, thus tremendously extending the choice of useful transitions.

As already pointed out in Ref. [4], some small nonlinearities of the King plot should appear within the standard model framework, but they have never been calculated. The only attempt to address this issue was made by Flambaum and coworkers [10], who derived approximate analytical formulas for the field shift in the mean-field approximation and calculated the King-plot nonlinearities for heavy and superheavy atoms. In the present work we perform relativistic calculations of the nonlinear isotope-shift effects for several fine-structure transitions in argon ions. We also analyze constraints on hypothetical boson fields that can be realistically derived from the King-plot analysis in these systems.

The isotope-dependent part of the energy of an electronic state of an atom is traditionally represented as a sum of the *mass shift* and the *field shift*,

$$E_{\rm is} = \frac{m}{M}K + \frac{R^2}{\lambda\!\!\!^{-2}_C}F, \tag{1}$$

where m is the electron mass, M is the nuclear mass, $R = \langle r^2\rangle^{1/2}$ is the root-mean-square (rms) radius of the nuclear charge distribution, and $\lambda\!\!\!^{-}_C$ is the Compton wavelength divided by 2π ($\lambda\!\!\!^{-}_C = 386.159$ fm and $\lambda\!\!\!^{-}_C = 1$ in relativistic units). K and F are usually called the mass-shift and the field-shift constant, respectively. Note that, in our formulation, the constants K and F have units of energy, since they are multiplied by dimensionless ratios in Eq. (1).

It is important that in the present work we require Eq. (1) to be *exact* in the standard model framework. In other words, we ascribe all higher-order effects to K and/or to F, which

thus acquire some dependence on nuclear parameters. In many practical situations, this weak dependence can be ignored and one can treat K and F as "constants" depending only on the electronic state of the atom but not on the nuclear properties of the isotope. As explained below, such an assumption leads to a King plot which is exactly linear. In the present work, however, we will address deviations from this linear form, caused by a tiny dependence of K and F on nuclear parameters.

II. KING PLOT

The King plot [1,2] is a widely used method that allows for a systematic study of the isotope shifts of two atomic transitions in a chain of isotopes. In order to construct a King plot, we consider two electronic transitions (which will be labeled as "a" and "b") for a chain of at least four isotopes of the same element with mass numbers $(A_0, A_1, A_2, \ldots)$. Note that the transitions a and b may belong to different charge states of the same element.

A. Standard formulation

Within the standard formulation, the mass-shift and field-shift constants in Eq. (1) are assumed to depend only on the electronic transition but not on the isotope. In this case, the isotope shift of the energy of the transition a between the isotopes i and j is

$$E_{aij} = \left(\frac{m}{M_i} - \frac{m}{M_j}\right)K_a + \left(\frac{R_i^2}{\lambda\!\!\!^{-2}_C} - \frac{R_j^2}{\lambda\!\!\!^{-2}_C}\right)F_a \equiv \mathcal{M}_{ij}K_a + \mathcal{R}_{ij}F_a. \tag{2}$$

Introducing the modified transition energies n_{aij},

$$n_{aij} = \frac{E_{aij}}{\mathcal{M}_{ij}}, \tag{3}$$

one rewrites Eq. (2) as

$$n_{aij} = K_a + \frac{\mathcal{R}_{ij}}{\mathcal{M}_{ij}}F_a. \tag{4}$$

Considering Eq. (4) for two transitions a and b, one can eliminate the isotope-dependent constant $\mathcal{R}_{ij}/\mathcal{M}_{ij}$, arriving at

$$n_{bij} = \left(K_b - \frac{F_b}{F_a}K_a\right) + \frac{F_b}{F_a}n_{aij}. \tag{5}$$

Fixing the index j and plotting n_{bij} $(= y_i)$ against n_{aij} $(= x_i)$ for different isotopes i, one gets the linear dependence of the form

$$y_i = \mathcal{A} + \mathcal{B}x_i, \tag{6}$$

where the coefficients $\mathcal{A}$ and $\mathcal{B}$ do not depend on the isotope parameters. The dependence of n_{bij} on n_{aij} is widely known as the King plot [1,2]. Measuring the modified frequencies n_{bij} and n_{aij}, one obtains the experimental values for the coefficients $\mathcal{A}$ and $\mathcal{B}$, i.e., for the ratio of the field-shift constants F_b/F_a and for the combination $K_b - (F_b/F_a)K_a$.

B. Extended formulation: Standard model

We now take into account that the constants K and F in Eq. (1) depend not only on the transition but also on the isotope, $K \equiv K_{ai} = K_a + \delta K_{ai}$, and the same for F. In this case, Eq. (4) becomes

$$n_{aij} = K_{aij} + \frac{\mathcal{R}_{ij}}{\mathcal{M}_{ij}}F_{aij}, \tag{7}$$

where

$$K_{aij} = \frac{\frac{m}{M_i}K_{ai} - \frac{m}{M_j}K_{aj}}{\mathcal{M}_{ij}} \equiv K_a + \delta K_{aij}, \tag{8}$$

$$F_{aij} = \frac{\frac{R_i^2}{\lambda\!\!\!^{-2}_C}F_{ai} - \frac{R_j^2}{\lambda\!\!\!^{-2}_C}F_{aj}}{\mathcal{R}_{ij}} \equiv F_a + \delta F_{aij}. \tag{9}$$

Equation (5) then becomes

$$n_{bij} = \left(K_{bij} - \frac{F_{bij}}{F_{aij}}K_{aij}\right) + \frac{F_{bij}}{F_{aij}}n_{aij}. \tag{10}$$

Considering the above equation as a functional dependence of n_{bij} $(= y_i)$ on n_{aij} $(= x_i)$ for different values of the isotope index i and a fixed $j = 0$, we get a set of equations

$$y_i = \mathcal{A}_i + \mathcal{B}_i x_i. \tag{11}$$

The coefficients $\mathcal{A}_i$ and $\mathcal{B}_i$ in the above equations depend (slightly) on the isotope index i and, therefore, the (three or more) points (y_i, x_i) no longer lie on a straight line.

Restricting to the minimal number of three points, the nonlinearity of a three-point curve (11) may be conveniently defined [10] as a shift of the ordinate of the third point from the straight line defined by the first two points,

$$\delta y = (y_3 - y_1) - \frac{y_2 - y_1}{x_2 - x_1}(x_3 - x_1). \tag{12}$$

Rewriting this definition for the King plot, we arrive at

$$\delta E_{b30} = \mathcal{M}_{30}\left[n_{b30} - n_{b10} - \frac{n_{b20} - n_{b10}}{n_{a20} - n_{a10}}(n_{a30} - n_{a10})\right]. \tag{13}$$

Note that δE_{b30} has the unit of energy. Physically, it is the difference of the (A_3, A_0) isotope shift of the transition b from the linearly predicted position based on the (A_2, A_0) and (A_1, A_0) isotope shifts of the transitions a and b.

δE_{b30} is the definition of the King-plot nonlinearity as used in Ref. [10]. It has, however, a drawback of being not symmetrical with respect to the transitions a and b. In other words, with just three points, there are two different nonlinearities, δE_{b30} and δE_{a30} (where δE_{a30} is obtained from δE_{b30} by $a \leftrightarrow b$). In the present work, we define the nonlinearity in a symmetric way, as a half-sum of these two absolute values,

$$\Delta_{\rm NL}(ab) = \Delta_{\rm NL}(ba) = \tfrac{1}{2}(|\delta E_{a30}| + |\delta E_{b30}|). \tag{14}$$

C. Extended formulation: New physics

We now consider the King-plot analysis in the presence of a hypothetical boson particle with mass m_ϕ. The interaction between the electrons and neutrons mediated by such a boson

can be effectively described [11] by a Yukawa-type potential,

$$V_\phi = -\alpha_{\rm NP}(A-Z)\frac{e^{-m_\phi r}}{r}, \tag{15}$$

where $A-Z$ is the number of neutrons in the nucleus and $\alpha_{\rm NP}$ is the coupling constant, $\alpha_{\rm NP} = q_n q_e$, where q_n and q_e are the strength of coupling to neutrons and electrons, respectively.

With a new particle, the isotope-dependent part of the energy of the reference state becomes [cf. Eq. (1)]

$$E_{\rm is} = \frac{m}{M}K + \frac{R^2}{\lambda\!\!\!^{-2}_C}F + \frac{\alpha_{\rm NP}}{\alpha}AX_\phi, \tag{16}$$

where A is the mass number of the isotope and α is the fine-structure constant. X_ϕ is the "new-physics" isotope-shift constant defined as

$$X_\phi = \left\langle -\sum_k \frac{\alpha\, e^{-m_\phi r_k}}{r_k} \right\rangle, \tag{17}$$

where k numerates the electrons in the atom and the matrix element is evaluated with the atomic reference-state wave function. The expression for the reduced frequency now becomes [cf. Eq. (7)]

$$n_{aij} = K_{aij} + \frac{\mathcal{R}_{ij}}{\mathcal{M}_{ij}}F_{aij} + \frac{\alpha_{\rm NP}}{\alpha}\frac{A_i - A_j}{\mathcal{M}_{ij}}X_{\phi,a}, \tag{18}$$

where we took into account that the isotope dependence of $X_{\phi,a}$ can be safely neglected.

III. THEORY OF THE ISOTOPE SHIFT

A. Leading effects

The mass shift of energy levels is induced by the nuclear recoil effect. Within the Breit approximation [i.e., up to the order $(Z\alpha)^4 m/M$], the recoil effect is induced by the relativistic recoil operator [12,13]

$$H_{\rm rec} \equiv \frac{m}{M}\widetilde{H}_{\rm rec} = \frac{m}{M}(\widetilde{H}_{\rm rnms} + \widetilde{H}_{\rm rsms}), \tag{19}$$

where $H_{\rm rnms}$ and $H_{\rm rsms}$ are the relativistic normal and specific mass shift operators, respectively,

$$\widetilde{H}_{\rm rnms} = \frac{1}{2}\sum_k \left[\boldsymbol{p}_k^2 - \frac{Z\alpha}{r_k}\left(\boldsymbol{\alpha}_k + \frac{(\boldsymbol{\alpha}_k\cdot\boldsymbol{r}_k)\boldsymbol{r}_k}{r_k^2}\right)\cdot\boldsymbol{p}_k\right], \tag{20}$$

$$\widetilde{H}_{\rm rsms} = \frac{1}{2}\sum_{k\neq l}\left[\boldsymbol{p}_k\cdot\boldsymbol{p}_l - \frac{Z\alpha}{r_k}\left(\boldsymbol{\alpha}_k + \frac{(\boldsymbol{\alpha}_k\cdot\boldsymbol{r}_k)\boldsymbol{r}_k}{r_k^2}\right)\cdot\boldsymbol{p}_l\right], \tag{21}$$

and summations over k and l run over all electrons. Fully relativistic calculations of the isotope-shift effects were performed over the past two decades by several groups [14–19].

The leading, linear in m/M mass-shift constant is given by the expectation value of the nuclear recoil operator with the (nonrecoil) atomic wave function of the reference state,

$$K^{(1)} = \langle \widetilde{H}_{\rm rec}\rangle. \tag{22}$$

The field shift of energy levels is induced by the effect of the finite nuclear size (fns). The leading field-shift constant can be obtained as an expectation value of the derivative of the nuclear binding potential $V_{\rm nuc}$ over the square of the nuclear rms charge radius R^2 [20]

$$F = \langle V_{\rm FS}\rangle, \tag{23}$$

where

$$V_{\rm FS} = \sum_k \frac{\partial V_{\rm nuc}(r_k)}{\partial(R/\lambda\!\!\!^{-}_C)^2}, \tag{24}$$

and the summation over k runs over all electrons.

B. Quadratic mass shift

The leading isotope dependence of the mass-shift constant K comes from the quadratic [$\propto (m/M)^2$] nuclear recoil effect,

$$K = K^{(1)} + \frac{m}{M}K^{(2)}. \tag{25}$$

Within the Breit approximation, the quadratic mass shift is induced by the second-order perturbation of the operator $H_{\rm rec}$. It is known [21] that, for a spin-zero nucleus, there is no additional recoil operator $\propto (m/M)^2$ within the Breit approximation.

We calculate the quadratic mass-shift constant $K^{(2)}$ in two steps. First, we construct the nuclear-recoil-corrected many-electron wave function by including the recoil operator (19) into the Dirac-Coulomb-Breit Hamiltonian and diagonalizing the Hamiltonian matrix. Second, we determine $K^{(2)}$, neglecting higher-order $\propto (m/M)^3$ effects, by taking the difference

$$\frac{m}{M}K^{(2)} = \tfrac{1}{2}[\langle\widetilde{H}_{\rm rec}\rangle_M - \langle\widetilde{H}_{\rm rec}\rangle], \tag{26}$$

where $\langle . \rangle_M$ indicates the matrix element calculated with the nuclear-recoil-corrected wave function and $\langle\widetilde{H}_{\rm rec}\rangle = K^{(1)}$ does not depend on M. The factor of $1/2$ removes the double counting coming from the presence of the recoil terms both in the operator and in the wave function.

The quadratic recoil correction is known analytically for the hydrogenlike ions and numerically for the helium atom [21]. For a hydrogenlike system, the nonrelativistic contribution to $K^{(2)}$ is induced by the reduced mass and is just opposite to the corresponding contribution to $K^{(1)}$,

$$K^{(2)}_{\rm nr}({\rm hydr}) = -K^{(1)}_{\rm nr}({\rm hydr}). \tag{27}$$

This can also be used as a reasonable approximation for the *nonrelativistic* contribution to $K^{(2)}$ in few-electron systems (since the two-electron part of the nuclear recoil is usually smaller than the one-electron part). However, the relativistic effects can cause significant deviations from this simple formula. In particular, it was shown in Ref. [21] that for helium the relativistic correction to $K^{(2)}$ is much larger that the corresponding correction to $K^{(1)}$. It is, therefore, not surprising that the numerical calculations of $K^{(2)}$ performed in this work for the relativistic fine-structure transitions show significant deviations from the simple nonrelativistic estimate (27).

C. Other nonlinear effects

It was pointed out in Ref. [10] that for light atoms, such as argon considered here, the quadratic nuclear recoil is the main source of nonlinearity of the King plot within the

standard model framework. We now confirm this statement by examining other possible sources of a nonlinearity.

First, we consider the energy correction that depends both on the nuclear mass M and the nuclear size R. The underlying physical effect is the fns correction to the nuclear recoil ("fns recoil"). Strictly speaking, this is neither mass shift nor field shift, but we can formally enforce the form of Eq. (1) by ascribing the corresponding correction either to K or to F. It is tempting to try to calculate this effect numerically, e.g., by varying the nuclear radius in the numerical code for the relativistic recoil correction. This would lead, however, to a completely incorrect result. It was shown in Ref. [22] that the numerically dominant fns recoil contribution coming from the relativistic operator (19) is spurious and is exactly canceled by the corresponding part of the QED fns recoil effect. Therefore, any meaningful calculation of the fns recoil effect can be performed only within the framework of QED, which is beyond the scope of the present paper.

In the present study, we estimate the fns recoil effect within the nonrelativistic independent-electron approximation. In this limit, the fns recoil effect is induced just by the reduced-mass correction to the leading fns contribution; see, e.g., Ref. [23]. Therefore, within this approximation the leading field-shift constant should be multiplied by the reduced-mass prefactor,

$$F \to F\left(1 - 3\frac{m}{M}\right). \tag{28}$$

We expect that this estimation gives the correct order of magnitude of the effect, even though we are considering the fine-structure transitions, for which the nonrelativistic approximation does not work well.

Another effect that may contribute to the nonlinearity of the King plot is the relativistic correction to the field shift. For a light hydrogenlike atom, the numerically dominant relativistic fns correction is delivered by the leading logarithmic approximation and is given by (see, e.g., Ref. [23])

$$\delta E_{\rm fns} = \delta E_{\rm fns,nr}\left[1 - (Z\alpha)^2 \ln\left(Z\alpha\frac{R}{\lambda\!\!\!^{-}_C}\right)\right], \tag{29}$$

where $\delta E_{\rm fns,nr}$ is the nonrelativistic fns energy shift. Note that this relativistic correction appears also in the fully relativistic approach [10,24], originating through a modification of the exponent of the R dependence of the fns energy shift,

$$\left(Z\alpha\frac{R}{\lambda\!\!\!^{-}_C}\right)^2 \to \left(Z\alpha\frac{R}{\lambda\!\!\!^{-}_C}\right)^{2\gamma}, \tag{30}$$

where $\gamma = \sqrt{1-(Z\alpha)^2}$.

Only the R-dependent part of the relativistic fns correction contributes to the nonlinearity of the King plot. As an estimation, we assume it to have the same form as for the hydrogenic atoms,

$$F \to F\left[1 - (Z\alpha)^2 \ln\left(\frac{R}{\lambda\!\!\!^{-}_C}\right)\right]. \tag{31}$$

Finally, we consider the nuclear polarization, which is obviously isotope dependent and thus contributes to the nonlinearity of the King plot. Reference [25] reported the following estimate for the nuclear-polarization energy shift $\delta E_{\rm npol}$, which is based on available calculations for medium- and high-Z ions,

$$\delta E_{\rm npol} \approx -\frac{1}{1000}\delta E_{\rm fns} \pm 100\%. \tag{32}$$

This estimate gives a reasonable Z scaling of the nuclear polarization but can significantly underestimate the effect for the isotope shift. In order to correct for this, we introduce an additional dependence on the mass number A,

$$\delta E_{\rm npol} \approx -\frac{1}{1000}\delta E_{\rm fns}\left(\frac{A}{A_0}\right)^n \pm 100\%, \tag{33}$$

where A_0 is the mass number of a selected isotope in the isotope chain and n is an empirical parameter. The giant resonance model of the nuclear polarizability by Migdal [26] (see also Ref. [10]) yields $\delta E_{\rm npol} \propto R^2 A$, and thus $n = 1$. Numerical calculations of the nuclear-polarization energy shifts for isotope chains of heavy H-like ions [27] suggest even larger values of n. For our estimates in the present work we will use $n = 3$ and assume that it yields the expected order of magnitude of the effect. So, we estimate the influence of the nuclear polarization on the nonlinearity of the King plot by applying the following multiplicative factor to the field-shift constant:

$$F \to F\left[1 - \frac{1}{1000}\left(\frac{A}{A_0}\right)^3\right]. \tag{34}$$

IV. CALCULATIONS

In the present work we investigate the $2P$ fine-structure transitions in Be-like, B-like, and C-like argon, specifically, the $(1s)^2 2s2p\ {}^3P_2 - {}^3P_1$ transition in Ar^{14+} (labeled as "a"), the $(1s)^2(2s)^2 2p\ {}^2P_{3/2} - {}^2P_{1/2}$ transition in Ar^{13+} (labeled as "b"), and the $(1s)^2(2s)^2(2p)^2\ {}^3P_1 - {}^3P_0$ transition in Ar^{12+} (labeled as "c"). We perform relativistic calculations of the mass-shift and field-shift constants $K^{(1)}$, $K^{(2)}$, and F. The calculations are performed by the relativistic configuration-interaction (CI) method with configuration-state wave functions (CSFs) constructed with B-splines. Our implementation of the method is described in Refs. [28,29].

The present calculation of the isotope-shift constants encounters several difficulties. The first one comes from the fact that we are considering the fine-structure transitions, for which all relativistic effects are very much enhanced. The second one comes from strong mixing of the reference state with the closely lying levels. In order to take this into account, we perform the CI expansions from multiple reference states, including the dominant mixing configurations as additional reference states. In particular, we use the $1s^2 2s^2 + 1s^2 2p^2$ reference state for the Be-like argon, the $1s^2 2s^2 2p + 1s^2 2p^3$ reference state for the B-like argon, and $1s^2 2s^2 2p^2 + 1s^2 2p^4$ for C-like argon. In the CI expansion we include the single (S), double (D), and the dominant part of triple (T) and quadruple (Q) excitations from the multiple reference states specified above. The CI expansions in this work include up to 1.6 million CSFs.

Table I illustrates relative contributions of individual excitations in our CI calculations of the mass-shift constants $K^{(1)}$ and $K^{(2)}$. It can be seen that the contribution of the

TABLE I. Results of the relativistic configuration-interaction calculation of the mass-shift constants $K^{(1)}$ and $K^{(2)}$ with inclusion of single (S), double (D), triple (T), and quadruple (Q) excitations for Be-like, B-like, and C-like argon, in a.u.

Label	Transition	Ion		$K^{(1)}$	$K^{(2)}$
a	$(1s)^2 2s2p\ ^3P_2 - {}^3P_1$	Ar^{14+}	SD	−0.107 23	0.289 1
			SDT	−0.107 22	0.289 5
			SDTQ	−0.107 22	0.289 5
			Final	−0.107 2 (3)	0.289 (3)
b	$(1s)^2(2s)^2 2p\ ^2P_{3/2} - {}^2P_{1/2}$	Ar^{13+}	SD	−0.189 99	−0.324 8
			SDT	−0.189 57	−0.217 8
			SDTQ	−0.190 01	−0.201 7
			Final	−0.190 0 (3)	−0.202 (35)
c	$(1s)^2(2s)^2(2p)^2\ ^3P_1 - {}^3P_0$	Ar^{12+}	SD	−0.071 9	−2.202
			SDT	−0.066 2	0.120
			SDTQ	−0.074 0	0.310
			Final	−0.074 0 (16)	0.310 (68)

TQ excitations is quite small for the Be-like charge state but becomes much more significant for B-like and especially for C-like ions. We also observe that the relative contribution of the TQ excitations is much more important for $K^{(2)}$ than for $K^{(1)}$. Most spectacularly, the inclusion of the TQ excitations for C-like argon reduces the result for $K^{(2)}$ by an order of magnitude. The quintuple excitations (for B- and C-like ions) are partly included in our calculations through the usage of multiple reference states. However, a systematic study of such excitations is presently not possible due to technical limitations for the size of the CSFs expansion. The numerical uncertainty of the obtained results was estimated by varying the choice of the one-electron basis, which changes the relative contributions of the individual excitations.

V. RESULTS AND DISCUSSION

Numerical results of our relativistic calculations of the isotope-shift constants $K^{(1)}$, $K^{(2)}$, and F are presented in Tables I and II. The definition of the isotope-shift constants is given by Eqs. (1) and (25). We note that our results for $K^{(1)}$ do not include the QED part of the nuclear recoil, which was accounted for Be-like and B-like argon in Refs. [19,30]. The QED correction to $K^{(1)}$ does not cause a nonlinearity in the King plot, so it is not considered in the present work. The results of our CI calculation for the linear isotope-shift constants are in good agreement with previous relativistic calculations [17,19,30].

TABLE II. Comparison of the present calculation of the linear mass-shift constant $K^{(1)}$ and the field-shift constant F for Be-like, B-like, and C-like argon with the literature values, in a.u.

Transition	Ion	$K^{(1)}$	F
a	Ar^{14+}	−0.1072(3)	−0.000 326(1)
		−0.107[a]	−0.000 3[a]
		−0.1072[c]	−0.000 33[c]
b	Ar^{13+}	−0.1900(3)	−0.001 43(1)
		−0.1913[b]	−0.001 4(1)[b]
		−0.1908[c]	−0.001 45[c]
c	Ar^{12+}	−0.0740(16)	−0.000 118(5)
		−0.0735[c]	−0.000 13[c]

[a]CI-DFS [30], without QED.
[b]CI-DFS [19], without QED.
[c]MCDF [17].

Table III presents numerical results of our calculations of the "new-physics" isotope-shift constant X_ϕ defined by Eq. (17), for different values of masses of the hypothetical boson m_ϕ. Predictably, for small values of the boson mass m_ϕ, $\exp(-m_\phi r)/r \approx 1/r$, so that X_ϕ does not depend on m_ϕ.

Knowing the isotope-shift constants $K^{(1)}$, $K^{(2)}$, and F for several transitions of the same element, we can now calculate the modified isotope shifts n_{xij} according to Eq. (7) and then the nonlinearity of the King plot according to Eq. (14). We consider the King plots constructed for three pairs of transitions, (a, b), (b, c), and (a, c), and the chain of four isotopes of Ar with the mass numbers $(A_0, A_1, A_2, A_3) = (36, 38, 40, 42)$.

Using the values of the isotope-shift constants summarized in Table II, we obtain the following results for the King-plot nonlinearities caused by the quadratic recoil effect:

$$\Delta_{\rm NL}(ab) = 12.2(3)\ \text{kHz}, \tag{35}$$

$$\Delta_{\rm NL}(bc) = 29.(7)\ \text{kHz}, \tag{36}$$

$$\Delta_{\rm NL}(ac) = 5.3(1.7)\ \text{kHz}. \tag{37}$$

We checked that other nonlinear effects discussed in Sec. III C induce very small contributions to $\Delta_{\rm NL}$. The largest of the subleading effects is the nuclear polarization, whose contributions to $\Delta_{\rm NL}$ for the transitions under consideration were found to be ∼0.1–0.2 kHz.

It is interesting that the King-plot nonlinearities calculated in this work are by 3–4 orders of magnitude larger than the previous estimate (3 Hz) obtained for Ca^+ in Ref. [10]. The reason for such a difference is not clear to us. It might be pointed out that no actual calculations were performed in Ref. [10]; only the expected order of magnitude of the effect was estimated.

TABLE III. "New-physics" isotope-shift constant X_ϕ, in a.u., for different values of masses of the hypothetical boson m_ϕ.

Transition	$m_\phi = 10$ eV	$m_\phi = 10^2$ eV	$m_\phi = 10^3$ eV	$m_\phi = 10^4$ eV	$m_\phi = 10^5$ eV	$m_\phi = 10^6$ eV	$m_\phi = 10^7$ eV
a	0.020	0.020	0.020	0.018	0.0029	3.1×10^{-5}	2.8×10^{-7}
b	0.027	0.027	0.027	0.024	0.0050	1.1×10^{-4}	1.3×10^{-6}
c	0.014	0.014	0.014	0.013	0.0019	1.3×10^{-5}	$1.\times10^{-7}$

Our calculations demonstrate that isotope-shift measurements accurate at the Hertz level, like the one reported for Ca^+ in Ref. [7], could no longer ignore nonlinearities appearing in the standard model framework in the King-plot analysis. It is clear that such effects should become observable in the near future. Specifically for argon isotopes, an experimental identification of the nonlinear effects calculated in the present work is feasible by applying the quantum-logic technique, as recently demonstrated for boronlike Ar^{13+} [9]. With the same technique, the ground-state $(1s)^2(2s)^2(2p)^2\ {}^3P_1 - {}^3P_0$ transition in carbonlike Ar^{12+} at about 1015 nm could be resolved with a comparable level of precision (of a few Hertz). The argon isotopes ^{36}Ar, ^{38}Ar, and ^{40}Ar are stable and affordable for such experimental studies. ^{42}Ar is a β emitter with a lifetime of 33 years and is in principle also accessible for this kind of experiment, arguably with some efforts regarding procurement and safety requirements. More stable isotopes are available for calcium. The same transitions in boron- and carbon-like Ca are still in the laser-accessible range for studying the King-plot nonlinearities with even five isotopes, corresponding to four data points in the King plot.

Recently, there was a suggestion put forward [3,4] to use (the absence of) the observed nonlinearity of the King plot in the isotope-shift measurements in order to constrain the hypothetical new long-range forces between the electron and the nucleus. Reference [4] analyzed perspectives of such constraints for a (rather optimistic) variant of the experimental accuracy of 1 Hz and the absence of King-plot nonlinearities on this level. Our calculations show that the typical King-plot nonlinearities originating within the standard model are much larger than 1 Hz; it is clear that we could constrain the new-physics effects only to the level on which we are able to control the accuracy of the nonlinear effects within the standard model.

In order to predict which constraints on the new-physics coupling constant $\alpha_{\rm NP}$ in Eq. (15) one could expect from isotope-shift measurements of the transitions considered in this work, we list in Table IV the ratios $\alpha_{\rm NP}/\alpha$ that induce a 1 kHz King-plot nonlinearity $\Delta_{\rm NL}$, for different masses of the hypotetical boson m_ϕ. We conclude that the perspective constraints are on a much more modest scale than was anticipated in Ref. [4]. In order to obtain better constraints, one would need to search for elements and/or transitions for which the standard-model King-plot nonlinearities are as small as possible. In particular, investigations of heavier elements might be advantageous since for them the nuclear recoil effects are suppressed due to a larger nuclear mass.

VI. CONCLUSION

In this work we performed relativistic calculations of the isotope-shift constants for the $2P$ fine-structure transitions in Be-like, B-like, and C-like argon. In particular, the quadratic recoil constant $K^{(2)}$ in these systems was calculated. Because of significant contributions from triple and quadruple excitations, large-scale configuration-interaction calculations with more than a million configuration-state functions were employed, in order to obtain reliable predictions for the quadratic mass-shift constant.

We studied nonlinear effects in the King plot for a chain of argon isotopes. It was demonstrated that, for such light atoms, the nonlinear effects in the King plot are dominated by the quadratic recoil effect. For the considered fine-structure transitions, nonlinearities from 5 to 30 kHz were found. Such effects should be clearly visible in the forthcoming isotope-shift experiments at the Hertz accuracy level.

The nonlinear effects in the King plot arising within the standard model and the accuracy of their theoretical description put a limitation on possible constraints on hypothetical new long-range forces between the electron and the nucleus, which can be derived from the isotope-shift investigations. We performed calculations demonstrating to which level the new-physics coupling constant can be realistically constrained for the considered transitions.

In the present study we addressed isotopes with even number of nucleons and zero nuclear spin. For odd isotopes, additional complications may arise due to the presence of the hyperfine structure of the energy levels. In particular, a measurement of the isotope shift of the $6s5d\ {}^3D_{1,2} - 6s6p\ {}^1P^o_1$

TABLE IV. Ratios of the "new-physics" coupling constant $\alpha_{\rm NP}$ to the fine-structure constant α, which would cause a nonlinearity of the King plot of 1 kHz, for different values of masses of the hypothetical boson m_ϕ.

	Transitions	$m_\phi = 10$ eV	$m_\phi = 10^2$ eV	$m_\phi = 10^3$ eV	$m_\phi = 10^4$ eV	$m_\phi = 10^5$ eV	$m_\phi = 10^6$ eV	$m_\phi = 10^7$ eV
$\alpha_{\rm NP}/\alpha$	(a, b)	1×10^{-11}	1×10^{-11}	1×10^{-11}	1×10^{-11}	8×10^{-11}	2×10^{-8}	2×10^{-5}
	(b, c)	5×10^{-12}	5×10^{-12}	5×10^{-12}	6×10^{-12}	4×10^{-11}	1×10^{-8}	6×10^{-6}
	(a, c)	1.5×10^{-11}	1.5×10^{-11}	1.5×10^{-11}	1.6×10^{-11}	1×10^{-10}	2×10^{-8}	3×10^{-5}

transitions in barium isotopes [31] reported results in disagreement with the King-plot behavior predicted by theory [17] for odd isotopes.

Recently, we learned about a measurement of the $^1S_0 - {}^3P_{0,1}$ isotope shifts in strontium with a 10 kHz accuracy [32]. The authors observe a possible nonlinearity of the King plot and conclude that "Future theoretical and experimental studies should help to explain our observations...".

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