Relativistic calculations of x-ray transition energies and isotope shifts in heavy atoms

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X-ray transition energies and isotope shifts in heavy atoms are evaluated. The energy levels with vacancies in the inner shells are calculated within the approximation of the average of a nonrelativistic configuration employing the Dirac-Fock-Sturm method. The obtained results are compared with other configuration-interaction theoretical calculations and with experimental data.

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I. INTRODUCTION

Precise calculations of the energies of the x-ray emission lines and the related isotope shifts in heavy atomic systems are required by experiments [1–6]. The most accurate to-date theoretical and experimental values of x-ray K-, L-, and M-transition energies were tabulated in Ref. [6] and have been used in the NIST database [7]. As for the isotope shift in heavy neutral atoms, the first measurements of the isotope shifts in x-ray $K\alpha_1$ lines for neutral uranium isotopes have been performed by Brockmeier and co-workers [8] and for molybdenum isotopes by Sumbaev and Mezentsev [9]. In Ref. [10], an experimental and theoretical study of the isotope shifts in x-ray L lines in neutral uranium was carried out. The isotope shifts of atomic x-ray K lines in mercury (Hg) were measured for different pairs of isotopes in Ref. [11].

From the theoretical side, the binding energies and the isotope shifts in heavy many-electron atoms can be calculated very accurately using various methods, including the multiconfiguration Dirac-Fock method (MCDF) [6,12–14], the configuration-interaction Dirac-Fock-Sturm (CI-DFS) method [15,16], the method combining the configuration interaction and many-body perturbation theory (CI+MBPT) [17], the relativistic coupled-cluster method [18], etc. But, as shown in Ref. [6], the MCDF method (as well as the other methods mentioned above) is not efficient enough for calculations of the autoionizing inner-shell hole states. Special methods, such as the complex scaling (CS) method or perturbation theory, should be used to calculate the Auger shifts of these states. The CS method was used in calculations of the Auger resonances of light atoms. For instance, the CS method in combination with the coupled-cluster method was used in nonrelativistic calculations of the hole ($1s^{-1}$) state of Be [19]. Unfortunately, this approach becomes too time consuming in the relativistic calculations of heavy neutral atoms. So, to take into account the correlation and Auger shift corrections to x-ray lines, in Refs. [6,12] the relativistic many-body perturbation theory (RMBPT) was employed. In the framework of the RMBPT method, the Auger shift can be estimated by a simpler and less accurate approach [20]. We note also that in Ref. [6] the quantum electrodynamics (QED) corrections have been determined using Welton's approximation.

In the present paper we use the assumption that the center of gravity of the x-ray emission line in heavy atoms can be calculated as the difference of the averages of nonrelativistic valence configurations with the different vacancies in the inner shells. This approximation is used in the Dirac-Fock and CI-DFS calculations in this work. In this approach the energy is averaged over all atomic terms of the nonrelativistic valence configuration. The idea of the nonrelativistic configurational average ("LS average") in the relativistic Dirac-Fock calculations was proposed in Refs. [21,22]. The validity of this approximation is demonstrated by our calculations of the binding energies of x-ray lines.

To calculate the Auger shifts we use the RMBPT method but, in contrast to Ref. [6], in the Brillouin-Wigner form. The obtained non-QED results are combined with the corresponding QED contributions, which have been evaluated by including the model Lamb-shift operator into the Dirac-Coulomb-Breit Hamiltonian [23–25]. As a result, the most precise theoretical predictions for the energies and isotope shifts of x-ray K and L lines are presented.

Atomic units ($\hbar = m = e = 1$) are used throughout the paper.

II. METHOD OF CALCULATION

In order to calculate the x-ray transition energies, we use the following three-step large-scale CI-DFS method [15,16]. At the first step, to obtain the one-electron wave functions φ_i for the occupied atomic shells, we use the Dirac-Fock method [26] with vacancies in the inner shells and the average of the nonrelativistic configuration for the group of valence electrons. Then the DFS orbitals are obtained by solving the DFS equations for the vacant shells. At the last step, the relativistic

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CI+MBPT method is used to obtain the many-electron wave functions and the total energies.

According to the method of group functions [27], the total many-electron wave function is presented in the form of an antisymmetric product of the wave functions of two groups of electrons. The first one is the group of "active" electrons, while the second one is the group of "frozen" electrons. In the formulation of our problem, the core electrons are active, and the valence electrons are frozen. Thus, the total electronic energy $E_{\rm tot}$ of the atom can be represented as a sum of two parts,

$$E_{\rm tot} = E_{vv} + E_{cv},$$

where E_{vv} is the energy of the valence electrons and E_{cv} is the total energy of the core electrons in the Coulomb and exchange field of the valence electrons.

The x-ray emission linewidths of heavy atoms are so large that they can exceed the value of the multiplet splitting of the atomic valence levels. In this case, to calculate the position of the center of gravity (or maximum) of the x-ray line observed in the experiment, it is sufficient to calculate the transition energies and isotope shifts in the approximation of the nonrelativistic configuration average of the group of valence electrons (for more details, see Ref. [28]).

A. Average of nonrelativistic valence configuration: *LS* average

The total energy of the valence electrons E_{vv} is calculated by the Dirac-Fock method in the configuration average approximation. The idea of the configuration average in the case of the nonrelativistic Hartree-Fock method was treated in detail by Slater [29]. The formalism can be easily extended to the case of the relativistic configuration [30]. The well-known procedure of the relativistic configurational average is meaningful only when j-j coupling dominates, which obviously is not the case for most neutral atoms. Furthermore, the use of a pure j-j coupling scheme leads to a wrong nonrelativistic limit. To remedy this shortcoming, it is necessary to consider the interaction of the relativistic configurations which correspond to the same nonrelativistic one. This corresponds to an intermediate type of coupling or approximation of the barycenter of the nonrelativistic configuration.

For these reasons it is reasonable to use the averaging over all the j-j configurations arising from a valence nonrelativistic configuration in the calculations of neutral atoms. As a result, one can derive the following energy expression in the nonrelativistic configurational LS average (see Ref. [22] for details),

$$\begin{aligned} E_{vv} = E^{\rm DF}_{\rm nav} = &\sum_a \widetilde{q}_a\, I_a + \frac{1}{2}\sum_a \widetilde{q}_a(\widetilde{q}_a - w_A)F^0(a,a) + \sum_{a<b} \widetilde{q}_a\widetilde{q}_b\,\omega_{AB}\,F^0(a,b) \\ &+ \sum_a \sum_{k>0} \widetilde{q}_a(\widetilde{q}_a - w_A) f^k_{aa} F^k(a,a) + \sum_{a<b}\sum_k \widetilde{q}_a\,\widetilde{q}_b\,\omega_{AB}\,g^k_{ab}\,G^k(a,b). \end{aligned} \tag{1}$$

Here, indices a and b enumerate relativistic shells, A and B denote nonrelativistic shells, q_a and q_b are the numbers of electrons (occupation numbers) in the shells a and b, and q_A and q_B are the numbers of electrons in the nonrelativistic shells A and B, respectively. I_a is the one-electron radial integral [30] and $F^k(a,b)$ and $G^k(a,b)$ are the standard Coulomb and exchange radial integrals [30], respectively. The parameters $\widetilde{q}_a$, w_a, and ω_{AB} in Eq. (1) are defined as

$$\widetilde{q}_a = \frac{2j_a+1}{4l_A+2} q_A, \quad w_a = \frac{q_A - \widetilde{q}_a + 2j_a}{4l_A+1}, \tag{2}$$

$$\omega_{AB} = \begin{cases} \dfrac{4l_a+2}{4l_a+1}\dfrac{q_A-1}{q_A}, & A = B, \\ 1, & A \neq B. \end{cases} \tag{3}$$

The coefficients $f^k_{a,a}$ and $g^k_{a,b}$ are given by

$$f^k_{a,a} = -\frac{1}{2}\frac{2j_a+1}{2j_a}\frac{\left(C^{k0}_{j_a-\frac{1}{2},j_a\frac{1}{2}}\right)^2}{2k+1} = -\frac{1}{4}\frac{2j_a+1}{2j_a}\Gamma^k_{j_a,j_a}, \quad g^k_{a,b} = -\frac{\left(C^{k0}_{j_a-\frac{1}{2},j_b\frac{1}{2}}\right)^2}{2k+1} = -\frac{1}{2}\Gamma^k_{j_a,j_b}, \tag{4}$$

where $\Gamma^k_{j_a,j_b}$ are the coefficients introduced in Ref. [30],

$$\Gamma^k_{j_a,j_b} = 2\begin{pmatrix} j_a & j_b & k \\ \frac{1}{2} & -\frac{1}{2} & 0 \end{pmatrix}^2. \tag{5}$$

The expression (1) can be rewritten in the same form as the nonrelativistic expression for the energy in the Hartree-Fock method [31],

$$\begin{aligned} E^{\rm DF}_{\rm nav} = &\sum_A q_A \overline{I}_A + \frac{1}{2}\sum_A q_A(q_A-1)\overline{F}^0(A,A) + \sum_{A<B} q_A\,q_B\,\overline{F}^0(A,B) \\ &+ \sum_A\sum_{k>0} q_A\,(q_A-1)\overline{f}^k_{A,A}\overline{F}^k(A,A) + \sum_{A<B}\sum_k q_A\,q_B\,\overline{g}^k_{A,B},\overline{G}^k(A,B), \end{aligned} \tag{6}$$

where $\overline{F}^k(A,B)$ and $\overline{G}^k(A,B)$ are effective mean values of the radial integrals defined as

$$\overline{F}^0(A,B)=\begin{cases}\displaystyle\sum_{j_a\in A}\sum_{j_b\in B}\frac{(2j_a+1-\delta_{j_a,j_b})(2j_b+1)}{(4l_A+2)(4l_A+1)}F^0(a,b), & A=B,\\[2ex] \displaystyle\sum_{j_a\in A}\sum_{j_b\in B}\frac{(2j_a+1)(2j_b+1)}{(4l_a+2)(4l_b+2)}F^0(a,b), & A\neq B,\end{cases} \tag{7}$$

for $k=0$, and

$$\overline{G}^k(A,B)=\frac{1}{2}\sum_{j_a\in A}\sum_{j_b\in B}(2j_a+1)(2j_b+1)\begin{Bmatrix} j_a & j_b & k\\ l_b & l_a & \frac{1}{2}\end{Bmatrix}^2 G^k(a,b),\quad \overline{F}^k(A,A)=\overline{G}^k(A,A), \tag{8}$$

for $k>0$.

In the nonrelativistic limit, the integrals $\overline{F}^k(A,B)$ and $\overline{G}^k(A,B)$ approach the corresponding nonrelativistic radial integrals defined in the nonrelativistic Hartree-Fock method [31].

The coefficients $\overline{f}^k_{A,A}$ and $\overline{g}^k_{a,b}$ coincide with the corresponding coefficients defined in the nonrelativistic Hartree-Fock method in the approximation of the center of gravity,

$$\overline{f}^k_{A,A}=-\frac{1}{4}\frac{4l_A+2}{4l_A+1}\frac{\left(C^{k0}_{l_A0,l_A0}\right)^2}{2k+1},$$
$$\overline{g}^k_{a,b}=-\frac{1}{2}\frac{1}{2k+1}\left(C^{k0}_{l_A0,l_B0}\right)^2. \tag{9}$$

B. CI-DFS method with average of nonrelativistic configuration

To take into account the electron correlations, the large-scale configuration-interaction (CI) method in the basis of four-component Dirac-Fock-Sturm (DFS) orbitals φ_a is used. These orbitals are obtained by solving the Dirac-Fock-Sturm equations [15,16].

The wave function of a group of active electrons was obtained by the CI+MBPT method. Various excited configurations are obtained from the main configuration by single and double excitations of "active" electrons. In addition, the contribution of the so-called Auger configurations was obtained by the RMBPT method using a simple pole integration approach suggested in Ref. [20]. This approach made our method more stable.

The interaction with the valence electrons is taken into account by the introduction of a single-particle potential, which is the sum of the Coulomb and exchange potentials. The Coulomb and exchange potentials of the valence electrons are constructed in the standard way using the first-order reduced density matrix taken in the approximation of the average of nonrelativistic valence configuration,

$$\rho^{(\mathrm{val})}(r,r')=\sum_a^{(\mathrm{val})}\frac{\widetilde{q}_a}{2j_a+1}\sum_{\mu=-j_a}^{j_a}\varphi_{a\mu}(r)\varphi^+_{a\mu}(r'), \tag{10}$$

where the summation runs over indices of the valence electrons and $\widetilde{q}_a$ is defined by Eq. (3).

C. QED corrections

In this paper we approximate the QED potential by the following sum,

$$V^{\mathrm{QED}}=V^{\mathrm{SE}}+V^{\mathrm{Uehl}}+V^{\mathrm{WK}}, \tag{11}$$

where V^{SE} is the so-called model self-energy operator, and V^{Uehl} and V^{WK} are the Uehling and Wichmann-Kroll parts of the vacuum polarization, respectively. Both V^{Uehl} and V^{WK} are local potentials. The Uehling potential can be evaluated by a direct numerical integration of the well-known formula [32] or, more easily, by using the approximate formulas from Ref. [33]. A direct numerical evaluation of the Wichmann-Kroll potential V^{WK} is rather complicated. For the purpose of the present work, it is sufficient to use the approximate formulas for this potential from Ref. [34].

Following Refs. [23,24], we represent the one-electron SE operator as the sum of local $V^{\mathrm{SE}}_{\mathrm{loc}}$ and nonlocal V_{nl} parts,

$$V^{\mathrm{SE}}=V^{\mathrm{SE}}_{\mathrm{loc}}+V_{\mathrm{nl}}, \tag{12}$$

where the nonlocal potential is given in a separable form,

$$V_{\mathrm{nl}}=\sum_{i,k=1}^{n}|\phi_i\rangle B_{ik}\langle\phi_k|. \tag{13}$$

Here, ϕ_i are so-called projector functions. The choice of these functions is described in detail in Ref. [23]. The constants B_{ik} are chosen so that the matrix elements of the model operator V^{SE}_{ik} calculated with hydrogenlike wave functions ψ_i are equal to the matrix elements Q_{ik} of the exact SE operator $\Sigma(\varepsilon)$ [35],

$$\langle\psi_i|V^{\mathrm{SE}}|\psi_k\rangle=Q_{ik}\equiv\frac{1}{2}\langle\psi_i|[\Sigma(\varepsilon_i)+\Sigma(\varepsilon_k)]|\psi_k\rangle. \tag{14}$$

Introducing two matrices, $\Delta Q_{ik}=Q_{ik}-\langle\psi_i|V^{\mathrm{SE}}_{\mathrm{loc}}|\psi_k\rangle$ and $D_{ik}=\langle\phi_i|\psi_k\rangle$, we find that

$$B_{ik}=\sum_{j,l=1}^{n}(D^{-1})_{ji}\langle\psi_j|\Delta Q_{jl}|\psi_l\rangle(D^{-1})_{lk}. \tag{15}$$

The local part of the SE potential was taken in a simple form [23],

$$V^{\mathrm{SE}}_{\mathrm{loc},\kappa}(r)=A_\kappa\exp(-r/\bar{\lambda}_C), \tag{16}$$

where the constant A_κ is chosen to reproduce the SE shift for the lowest-energy level at the given κ in the corresponding

TABLE I. The comparison of the natural linewidths and the widths of the multiplet splitting for uranium x-ray lines. ΔM is the width of the multiplet splitting and Γ is the natural linewidth.

Line	Transition	Γ (eV)	ΔM (eV)
$L\alpha_2$	$2p_{3/2}^{-1} \to 3d_{3/2}^{-1}$	11.7	16.8
$L\beta_1$	$2p_{1/2}^{-1} \to 3d_{3/2}^{-1}$	13.5	16.55
$L\beta_3$	$2s_{1/2}^{-1} \to 3p_{3/2}^{-1}$	23.9	28.4
$L\beta_4$	$2s_{1/2}^{-1} \to 3p_{1/2}^{-1}$	30.1	27.7
$K\alpha_1$	$1s_{1/2}^{-1} \to 2p_{3/2}^{-1}$	104.5	27.7
$K\alpha_2$	$1s_{1/2}^{-1} \to 2p_{1/2}^{-1}$	106.3	27.6

H-like ion and $\bar{\lambda}_C = \hbar/(mc)$. The computation code based on this method is presented in Ref. [24].

III. ENERGIES OF X-RAY EMISSION LINES

In Table I, the natural widths taken from Ref. [36] are compared with the widths of the multiplet splitting for x-ray lines in uranium. The multiplet splitting arises if the atom contains open valence shells. When a core electron vacancy is created, an unpaired electron in the core can couple with electrons in the outer shells. This creates a number of states which can be seen in the photoelectron spectrum as a multipeak envelope.

The comparison of the widths gives an indication of the right application of the approximation of the barycenter of nonrelativistic configuration. It is expected that the approximation of the barycenter configuration is applicable in the case when the natural linewidth is bigger than or at least comparable to the multiplet splitting magnitude. The data in Table I demonstrate that the required conditions are fulfill.

The results of the calculations of the $K\alpha$ lines for uranium, xenon, and mercury and the L lines for uranium are presented in Tables III–VI, respectively. The calculations have been performed using the Dirac-Fock method [26] in the approximation of the barycenter of nonrelativistic configuration (1). The Breit, electron correlation, QED, and nuclear recoil (mass shift) contributions are evaluated using the CI-DFS method. The nuclear charge distribution was taken into account within the Fermi model with the root-mean-square nuclear radii taken from Refs. [37,38]. The QED contributions are evaluated by including the model Lamb-shift operator into the Dirac-Coulomb-Breit Hamiltonian [23].

The nuclear recoil effect is calculated within the Breit approximation using the relativistic nuclear recoil Hamiltonian [15,39–42],

$$H_M = \frac{1}{2M}\sum_{i,k}\left[\boldsymbol{p}_i\cdot\boldsymbol{p}_k - \frac{\alpha Z}{r_i}\left[\boldsymbol{\alpha}_i + \frac{(\boldsymbol{\alpha}_i\cdot\boldsymbol{r}_i)\,\boldsymbol{r}_i}{r_i^2}\right]\cdot\boldsymbol{p}_k\right]. \tag{17}$$

The results of the calculations of the individual contributions to the recoil effect (mass shift) for $K\alpha$ lines in xenon and uranium are collected in Table II. We note that the separation of the mass shift into the individual mass shift contributions is the same as in Ref. [43].

TABLE II. The values of the normal mass shift (NMS), the relativistic normal mass shift (RNMS), the specific mass shift (SMS), and the relativistic specific mass shift (RSMS) contributions to the total value of the mass shift (Total MS) for xenon and uranium $K\alpha$ lines (in eV).

	Line	NMS	RNMS	SMS	RSMS	Total MS
^{136}Xe	$K\alpha_1$	−0.172	0.059	0.044	−0.010	−0.080
	$K\alpha_2$	−0.167	0.055	0.040	−0.005	−0.078
^{238}U	$K\alpha_1$	−0.708	0.548	0.116	−0.088	−0.133
	$K\alpha_2$	−0.661	0.508	0.083	−0.039	−0.109

The uncertainties of the total values of the x-ray lines in Tables III–VI are mainly due to the correlation and Auger shift contributions which depend on the way of the calculations. They are determined by studying the stability of the results with respect to a variation of the basis size. For uranium, for instance, we use the basis set which includes all orbitals with the excitations up to $(13s\ 12p\ 10d\ 8f)$ shells. The results of these calculations are unstable within 1 eV, so the conservative estimates of the uncertainty of the order of 2–3 eV are used. In the case of the uranium atom, the nuclear polarization and deformation corrections were taken from Refs. [44–46] and [37], respectively. The uncertainty of 50% was assumed for these corrections. For ^{136}Xe and ^{204}Hg atoms the nuclear polarization and deformation corrections are negligible [47].

A comparison of the energies of the $K\alpha$ lines for ^{238}U, ^{136}Xe, and ^{204}Hg and the L lines for ^{238}U with other theoretical results and experimental data demonstrates very good agreement. This allows us to conclude that the approximation of the barycenter of the nonrelativistic configuration in the calculations of the x-ray transition energies is applicable for heavy atoms with open valence shells.

IV. ISOTOPE SHIFTS OF X-RAY LINES IN NEUTRAL URANIUM AND MERCURY

Isotope shifts of atomic systems give a useful tool for the determination of the nuclear charge radius differences (see, e.g., Refs. [4,37,49–51] and references therein). For the last years significant progress was gained in the calculations of the isotope shifts in highly charged ions [13,15,43,52–54]. Here, with the methods developed for highly charged ions, we calculate the isotope shifts of the x-ray lines in neutral atoms. As is known, the isotope shifts of the energy levels are mainly determined by the finite nuclear size (field shift) and nuclear recoil (mass shift).

The field shift is caused by the difference in the nuclear charge distribution of the isotopes. The main contribution to the field shift can be calculated in the framework of the Dirac-Coulomb-Breit Hamiltonian. The nuclear charge distribution is usually approximated by the spherically symmetric Fermi model,

$$\rho(r, R) = \frac{N}{1+\exp[(r-c)/a]}, \tag{18}$$

where the parameter a is generally fixed to be $a = 2.3/(4\ln 3)$ fm and the parameters N and c are determined using the given value of the root-mean-square (rms) nuclear charge radius

TABLE III. Individual contributions to the energy of the $K\alpha$ lines for ^{238}U (in keV) with the nuclear charge radius $R = 5.8569$ fm in this work and $R = 5.8625$ fm in Refs. [6,48].

	$K\alpha_1$		$K\alpha_2$	
Transition	This work	Theory [48]	This work	Theory [48]
Dirac-Fock	99.1031	99.1016	95.2777	95.2763
Breit	−0.4339	−0.4319	−0.3940	−0.3923
Frequency-dependent Breit	0.0067	0.0066	0.0126	0.0125
QED	−0.2466	−0.2436	−0.2486	−0.2460
Electron correlations + Auger shift	0.0038	0.0030	0.0030	0.0046
Mass shift	−0.0001		−0.0001	
Nuclear polarization	0.0002	0.0002[a]	0.0002	0.0002[a]
Nuclear deformation	0.0001		0.0001	
Total	98.4333(38)	98.4359[b]	94.6508(30)	94.6553[b]
Theory [6]	98.4336(36)		94.6531(37)	
Experiment [6,7]	98.43158(28)		94.65084(56)	

[a]Corrected according to Refs. [44–46].
[b]Corrected for the updated value of the nuclear polarization.

TABLE IV. Individual contributions to the energy of the $K\alpha$ lines for ^{136}Xe (in keV) with the nuclear charge radius equal to $R = 4.7964$ fm.

	$K\alpha_1$		$K\alpha_2$	
Transition	This work	Theory [3]	This work	Theory [3]
Dirac-Fock	29.8909	29.8908	29.5665	29.5660
Breit	−0.0736	−0.0733	−0.0693	−0.0691
Frequency-dependent Breit	0.0004	0.0004	0.0008	0.0008
QED	−0.0410	−0.0410	−0.0416	−0.0416
Electron correlations + Auger shift	0.0021	0.0017	0.0020	0.0022
Mass shift	−0.0001		−0.0001	
Total	29.7788(21)	29.7787	29.4582(20)	29.4584
Theory [6]	29.7783(29)		29.4584(30)	
Experiment [6,7]	29.77878(10)		29.458250(50)	

TABLE V. Individual contributions to the energy of the $K\alpha$ lines for ^{204}Hg (in keV) with the nuclear charge radius $R = 5.4744$ fm.

	$K\alpha_1$	$K\alpha_2$
Dirac-Fock	71.2322	69.2850
Breit	−0.2674	−0.2465
Frequency-dependent Breit	0.0034	0.0061
QED	−0.1519	−0.1540
Electron correlations + Auger shift	0.0029	0.0035
Mass shift	−0.0001	−0.0001
Theory (this work)	70.8191(18)	68.8942 (19)
Theory [6]	70.8190(22)	68.8943 (23)
Experiment [6]	70.8195(18)	68.8951 (17)

TABLE VI. Individual contributions to the energy of the L lines for ^{238}U (in keV) with the nuclear charge radius $R = 5.8569$ fm.

	$L\alpha_2$	$L\beta_1$	$L\beta_3$	$L\beta_4$
Dirac-Fock	13.4869	17.3123	17.5446	16.6560
Breit	−0.0496	−0.0895	−0.0474	−0.0391
Frequency-dependent Breit	0.0056	−0.0003	−0.0022	−0.0006
QED	−0.0058	−0.0037	−0.0401	−0.0404
Electron correlations + Auger shift	0.0007	0.0010	0.0003	0.0002
Mass shift	−0.0000	−0.0000	−0.0000	−0.0000
Theory (this work)	13.4379(17)	17.2198(20)	17.4552(16)	16.5762(16)
Theory [6]	13.4382(14)	17.2187(16)	17.4565(36)	16.5762(34)
Experiment [6,7]	13.43897(19)	17.22015(28)	17.45517(73)	16.57551(30)

TABLE VII. Individual contributions to the isotope shift for the $K\alpha$ lines in ^{235,238}U (in meV) with given values of nuclear charge radii ($^{235}R = 5.8287$ fm, $^{238}R = 5.8569$ fm).

	$K\alpha_1$	$K\alpha_2$
Dirac-Fock	1346.35	1323.88
Breit	−12.34	−12.06
Frequency-dependent Breit	0.07	0.12
QED	−13.89	−13.89
Electron correlations + Auger shift	−0.17	−0.18
Mass shift	−1.70	−1.39
Total theory	1318(30)	1296(30)

TABLE VIII. Individual contributions to the isotope shift for the $K\alpha$ lines in ^{233,238}U (in meV) with given values of nuclear charge radii ($^{233}R = 5.8138$ fm, $^{238}R = 5.8569$ fm).

	$K\alpha_1$	$K\alpha_2$
Dirac-Fock	2056.57	2022.24
Breit	−18.86	−18.42
Frequency-dependent Breit	0.11	0.19
QED	−21.20	−21.21
Electron correlations + Auger shift	−0.25	−0.26
Mass shift	−2.86	−2.34
Total theory	2014(46)	1980(45)
Experiment [8]	1800(200)	1800(200)

$R = \langle r^2\rangle^{1/2}$ and the normalization condition $\int d\,r\rho(r, R) = 1$. The potential induced by $\rho(r, R)$ is defined as

$$V_N(r, R) = -4\pi Z \int_0^\infty dr' r'^2 \rho(r', R)\frac{1}{r_>}, \qquad (19)$$

where $r_> = \max(r, r')$. The explicit formulas for $V_N(r, R)$ in the case of the Fermi model can be found, e.g., in Ref. [55]. This potential is used in the Dirac-Coulomb-Breit Hamiltonian to obtain the relativistic wave functions and the total energies. The related isotope shifts are evaluated by the formula

$$\delta E_{FS} = E_{\rm tot}(R_A) - E_{\rm tot}(R_B), \qquad (20)$$

where R_A and R_B are the rms radii of the isotopes A and B and $E_{\rm tot}(R_A)$ and $E_{\rm tot}(R_B)$ are the total electronic energies.

In Tables VII and VIII we present the contributions to the field shifts for the $K\alpha$ lines in ^{235,238}U and ^{233,238}U, respectively. The total theoretical values are given by a sum of the Dirac-Fock, Breit, frequency-dependent Breit, QED, mass shift, and electron-correlation contributions. Except for the QED correction, all other terms are evaluated in the same way as the x-ray line energies. The QED corrections are determined employing the approach presented in Ref. [43]. Namely, this was done by multiplying the s-state QED correction factor taken from Refs. [56,57] with the nuclear size effect on the total transition energy.

The obtained theoretical results are compared with the related experimental data from Ref. [8]. We note that the $K\alpha$ lines were indistinguishable in those experiments and, therefore, the $K\alpha_1$ and $K\alpha_2$ transition values taken from Ref. [8] are assumed to be the same. The theoretical uncertainty is estimated as a doubled quadratic sum of the uncertainty due to an unknown nuclear polarization and deformation effects and a half of the QED contribution. In accordance with the results of Ref. [43], we have assumed that the uncertainty caused by uncalculated nuclear polarization and deformation effects should be on the level of 1% of the corresponding field shift contribution.

Table IX displays the results of the calculations of the L-line isotope shifts, which are carried out for uranium isotopes with $A = 238, 235$. The isotope shifts of these lines are generally determined in the same way as for the $K\alpha$ lines. The only difference is in neglecting the QED contributions for the $L\alpha_2$ and $L\beta_1$ lines. As one can see, there exists a rather large discrepancy between theory and experiment [10] for the $L\beta_1$ line. The reason for this discrepancy is unclear to us.

In Table X the individual contributions to the total isotope shifts for the $K\alpha$ lines in ^{204,202}Hg are presented. It can be seen that the total theoretical results are in good agreement with the experimental ones [11]. The total values of the isotope shifts for different pairs of mercury isotopes are selected in Table XI. The main theoretical uncertainty comes from the nuclear polarization contribution. It is worth noting that for all isotopes of mercury the theoretical predictions agree with the experimental ones [11].

V. CONCLUSION

In this paper we have evaluated the energies and the isotope shifts of the x-ray lines in neutral atoms using the

TABLE IX. Individual contributions to the isotope shift for the L lines in ^{235,238}U (in meV) with given values of nuclear charge radii ($^{235}R = 5.8287$ fm, $^{238}R = 5.8569$ fm).

	$L\alpha_2$	$L\beta_1$	$L\beta_3$	$L\beta_4$
Dirac-Fock	−5.608	16.863	228.750	222.565
Breit	0.084	−0.200	−1.444	−1.372
Frequency-dependent Breit	0.046	−0.003	−0.041	−0.025
QED			−2.203	−2.194
Electron correlations + Auger shift	−0.002	−0.004	0.013	0.012
Mass shift	−0.079	−0.229	−0.454	−0.394
Total theory	−5.56(11)	16.43(35)	225(5)	219(5)
Experiment [10]	−6(2)	30(2)	253(8)	241(10)

TABLE X. Individual contributions to the isotope shift for the $K\alpha$ lines in ^{204,202}Hg (in meV) with given values of nuclear charge radii ($^{204}R = 5.4744$ fm, $^{202}R = 5.4648$ fm).

	$K\alpha_1$	$K\alpha_2$
Dirac-Fock	−149.116	−149.118
Breit	1.227	1.229
Frequency-dependent Breit	−0.007	−0.007
QED	−1.614	−1.619
Electron correlations + Auger shift	0.098	0.102
Mass shift	1.199	1.079
Total theory	−148(3)	−147(3)
Experiment [11]	−156(44)	−156(44)

configuration-interaction method in the Dirac-Fock-Sturm basis in approximation of the barycenter of the valence nonrelativistic configuration. The obtained results are compared with previous calculations and experiments. The comparison demonstrates good agreement of the obtained theoretical results for the K lines and the related isotope shifts in uranium and mercury atoms. In the case of the L lines, there exist some discrepancies between theory and experiment for the isotope shifts in uranium atoms. The discrepancy becomes especially large for the $L\beta_1$ lines. The reason for this discrepancy remains unclear to us.

TABLE XI. Total isotope shifts for the $K\alpha$ lines in ^{204,202}Hg, ^{204,201}Hg, ^{204,200}Hg, ^{204,199}Hg, and ^{204,198}Hg (in meV) with given values of nuclear charge radii taken from Ref. [38].

		$K\alpha_1$	$K\alpha_2$
^{204,202}Hg	Theory	−148(3)	−147(3)
	Experiment [11]	−156(44)	−156(44)
^{204,201}Hg	Theory	−246(6)	−246(6)
	Experiment [11]	−286(36)	−286(36)
^{204,200}Hg	Theory	−291(7)	−292(7)
	Experiment [11]	−305(30)	−305(30)
^{204,199}Hg	Theory	−408(9)	−408(9)
	Experiment [11]	−425(40)	−425(40)
^{204,198}Hg	Theory	−424(10)	−424(10)
	Experiment [11]	−468(44)	−468(44)

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