Relativistic calculations of X-Ray transition energies and isotope shifts in heavy atoms

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Abstract

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 nonrelativistic configuration employing the Dirac-Fock-Sturm method. The obtained results are compared with other configuration-interaction theoretical calculations and with experimental data.
I. INTRODUCTION

Precision calculations of 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-,M- transition energies were tabulated in Ref. \[6\] and have been used in the NIST database \[7\]. As to the isotope shift in heavy neutral atoms, first measurements of the isotope shifts in X-ray K\(\alpha_1\) lines for neutral uranium isotopes have been performed by Brockmeier and co-authors \[8\] and for molybdenum isotopes by Sumbaev an Mezentsev \[9\]. In Ref. \[10\], the 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 in many-electron atoms can be calculated very accurately using the multiconfiguration Dirac-Fock method (MCDF) \[6, 12-14\] or configuration-interaction Dirac-Fock-Sturm (CI-DFS) method \[13, 16\]. But, as shown in Ref. \[6\], the MCDF method is not efficient enough for calculations of the inner-shell hole states. 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. 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 \[17, 18\]. 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 \[19, 21\]. As the result, the most pre-
cise theoretical predictions for the energies and isotope shifts of X-ray K and L lines are presented.

The 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 for the occupied atomic shells, we use the Dirac-Fock method \[22\] with the average of non-relativistic configuration. Then the DFS orbitals are obtained by solving the DFS equations for the vacant shells. At the last step, the relativistic CI+MBPT method is used to obtain the many-electron wave functions and the total energies.

*Average of nonrelativistic configuration. “LS-average”*

To evaluate the transition energies with vacancies in the inner shells we use the CI-DFS method in the approximation of the average of nonrelativistic configuration (for more details, see, the Ref. \[23\]). The choice of this approach for the case of an atom with open shells is caused by the following reason. The expression for the energy in one-configuration Dirac-Fock method for atoms with open nonrelativistic shells does not converge to the corresponding non-relativistic expression if the speed of light tends to infinity. In other words, the one-configuration Dirac-Fock method corresponds to the \( jj \)-scheme of coupling, which in its pure form is almost never realized in neutral atoms with open valence shells, and does not lead to the \( LS \)-coupling scheme (Russell-Saunders coupling) in the nonrelativistic limit. To remedy this shortcoming, it is necessary to consider the interaction of the relativistic configurations that correspond to the same nonrelativistic one. This corresponds to the intermediate type of coupling or the approximation of the barycenter of the nonrelativistic configuration.

The X-ray emission line widths 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 nonrelativistic
configuration average approximation.

The idea of the configuration average in the case of nonrelativistic Hartree-Fock method was treated in detail by Slater [24]. The formalism can easily be extended to include also the average of several relativistic configurations [18] corresponding to the same nonrelativistic one in the Dirac-Fock calculations. This configurational averaging technique was named as nonrelativistic “LS-average”.

Let the nonrelativistic shells are enumerated by indices \( A \) and \( B \) which incorporate the quantum numbers \( n_a l_a \) and \( n_b l_b \), respectively, and the relativistic shells are numbered by indices \( a \) and \( b \). In the approximation of the barycenter of nonrelativistic configuration the expression for the Dirac-Fock energy is given by

\[
E_{\text{nav}}^{\text{DF}} = \sum_a \bar{q}_a I_a + \frac{1}{2} \sum_{a,b} W_{A,B} \sum_{\mu_a=-j_a}^{j_a} \sum_{\mu_b=-j_b}^{j_b} \left[ \langle a \mu_a, b \mu_b | a \mu_a, b \mu_b \rangle - \langle a \mu_a, b \mu_b | b \mu_b, a \mu_a \rangle \right],
\]  

(1)

where \( q_A \) is the number of electrons (occupation number) in the nonrelativistic shell \( A \), \( \bar{q}_a \) is the average occupation number of the relativistic subshell \( a \),

\[
\bar{q}_a = \frac{2j_a + 1}{2l_A + 2} q_A,
\]  

(2)

\( I_a \) is the one-electron diagonal matrix element of the Dirac operator \( \hat{h}_D \), which is independent of the projection \( \mu \),

\[
I_a = \langle a \mu | \hat{h}_D | a \mu \rangle,
\]  

(3)

and

\[
W_{A,B} = \begin{cases} 
\frac{q_A q_B}{(4l_A + 2)(4l_B + 2)}, & A \neq B \\
\frac{q_A (q_A - 1)}{(4l_A + 2)(4l_A + 1)}, & A = B.
\end{cases}
\]  

(4)

The detailed formulas for the Dirac-Fock energy in the approximation of the average of nonrelativistic configuration are given in Appendix.

**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 \( \phi_a \) is used. These orbitals are obtained by solving the Dirac-Fock-Sturm equations [15, 16]. Various
excited configurations are obtained from the main configuration by single and double excitations of “active” electrons. According to the method of group functions [25], the wave functions are 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 “active” are the core electrons, and the “frozen” are the valence electrons. 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,

\[ \rho^{(\text{val})}(r, r') = \sum_a \frac{\tilde{q}_a}{2j_a + 1} \sum_{\mu = -j_a}^{j_a} \varphi_{a\mu}(r) \varphi_{a\mu}^+(r'), \]

where the summation runs over indices of the valence electrons and \( \tilde{q}_a \) is defined by Eq. (2).

**QED corrections**

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

\[ V^{\text{QED}} = V^{\text{SE}} + V^{\text{Uehl}} + V^{\text{WK}}, \]

where \( V^{\text{SE}} \) is so-called model self-energy operator, \( V^{\text{Uehl}} \) and \( V^{\text{WK}} \) are the Uehling and Wichmann-Kroll parts of the vacuum polarization, respectively. Both \( V^{\text{Uehl}} \) and \( V^{\text{WK}} \) are local potentials. The Uehling potential can be evaluated by a direct numerical integration of the well-known formula [26] or, more easily, by using the approximate formulas from Ref. [27]. A direct numerical evaluation of the Wichmann-Kroll potential \( V^{\text{WK}} \) is rather complicated. For the purpose of the present work, it is sufficient to use the approximate formulas for this potential from Ref. [28].

Following Refs. [19, 20] we represent the one-electron SE operator as the sum of local \( V^{\text{SE}}_{\text{loc}} \) and nonlocal \( V_{\text{nl}} \) parts,

\[ V^{\text{SE}} = V^{\text{SE}}_{\text{loc}} + V_{\text{nl}}, \]

where the nonlocal potential is given in a separable form,

\[ V_{\text{nl}} = \sum_{i,k=1}^n |\phi_i\rangle B_{ik} \langle \phi_k|. \]
Here $\phi_i$ are so-called projector functions. The choice of these functions is described in details in Ref. [19]. The constants $B_{ik}$ are chosen so that the matrix elements of the model operator $V_{ik}^{SE}$ calculated with hydrogenlike wave functions $\psi_i$ are equal to the matrix elements $Q_{ik}$ of the exact SE operator $\Sigma(\varepsilon)$ [29]:

$$
\langle \psi_i | V_{ik}^{SE} | \psi_k \rangle = Q_{ik} \equiv \frac{1}{2} \langle \psi_i | \left[ \Sigma(\varepsilon_i) + \Sigma(\varepsilon_k) \right] | \psi_k \rangle.
$$

(9)

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

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

(10)

The local part of the SE potential was taken in a simple form [19],

$$
V_{\text{loc,} \kappa}^{SE}(r) = A_\kappa \exp \left( -r/\lambda_C \right),
$$

(11)

where the constant $A_\kappa$ is chosen to reproduce the SE shift for the lowest energy level at the given $\kappa$ in the corresponding H-like ion and $\lambda_C = \hbar/(mc)$. The computation code based on this method is presented in Ref. [20].

III. ENERGIES OF X-RAY EMISSION LINES

In Table I, the natural widths taken from Ref. [30] 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 photoelectron spectrum as a multi-peak 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 II 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 II, III, IV, and V respectively. The calculations have been performed using the Dirac-Fock method [22] in the approximation of the barycenter of nonrelativistic configuration including the Breit, electron correlation, QED, and nuclear recoil (mass shift) contributions.
Table I: The comparison of the natural line widths and the widths of the multiplet splitting for uranium X-ray lines. \( \Delta M \) is the width of the multiplet splitting and \( \Gamma \) is the natural line width.

| Line   | Transition         | \( \Gamma \) (eV) | \( \Delta M \) (eV) |
|--------|--------------------|--------------------|--------------------|
| L\( \alpha_2 \) | \( 2p_{3/2} \rightarrow 3d_{3/2} \) | 11.7              | 16.8               |
| L\( \beta_1 \)  | \( 2p_{1/2} \rightarrow 3d_{3/2} \) | 13.5              | 16.55              |
| L\( \beta_3 \)  | \( 2s_{1/2} \rightarrow 3p_{3/2} \) | 23.9              | 28.4               |
| L\( \beta_4 \)  | \( 2s_{1/2} \rightarrow 3p_{1/2} \) | 30.1              | 27.7               |
| K\( \alpha_1 \) | \( 1s_{1/2} \rightarrow 2p_{3/2} \) | 104.5             | 27.7               |
| K\( \alpha_2 \) | \( 1s_{1/2} \rightarrow 2p_{1/2} \) | 106.3             | 27.6               |

The nuclear charge distribution was taken into account within the Fermi model with the root-mean-square nuclear radii taken from Ref. [31, 32]. The QED contributions are evaluated by including the model Lamb-shift operator into the Dirac-Coulomb-Breit Hamiltonian [19].

The nuclear recoil effect is calculated within the Breit approximation using the relativistic nuclear recoil Hamiltonian [15, 33–36],

\[
H_M = \frac{1}{2M} \sum_{i,k} \left[ p_i \cdot p_k - \frac{\alpha Z}{r_i} \left[ \alpha_i + \left( \frac{\alpha_i \cdot r_i}{r_i^2} \right) r_i \right] \cdot p_k \right].
\]  

(12)

The uncertainties of the total values of the X-ray lines in Tables II, III, IV, V are mainly due to the correlation and Auger shift contributions which depend on the way of the calculations. 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 case of uranium atom, the nuclear polarization and deformation corrections were taken from Refs. [37–39] and [31], respectively. The uncertainty of 50% was assumed for these corrections. For \(^{136}\text{Xe}\) and \(^{204}\text{Hg}\) atoms, the nuclear polarization and deformation corrections are negligible [40].

The comparison of the energies of the K\( \alpha \) lines for \(^{238}\text{U}\), \(^{136}\text{Xe}\), and \(^{204}\text{Hg}\) and the L lines for \(^{238}\text{U}\) 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.
Table II: Individual contributions to the energy of the Kα 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, 41].

| Transition                          | Kα₁         | Kα₂         |
|-------------------------------------|-------------|-------------|
|                                     | This work   | Theory [41] | This work   | Theory [41] |
| 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      | 0.0002      | 0.0002      |
| Nuclear deformation                 | 0.0001      | -           | 0.0001      | -           |
| Total                               | 98.4333(38) | 98.4359b    | 94.6508(30) | 94.6553b    |

| Theory [6]                          | 98.4336(36) | 94.6531(37) |
| Experiment [6, 7]                   | 98.43158(28)| 94.65084(56) |

$^a$ Corrected according to Refs. [37–39].

$^b$ Corrected for the updated value of the nuclear polarization.

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

Isotope shifts of atomic systems give a useful tool for determination of the nuclear charge radius differences (see, e.g., Refs. [4, 31, 42–44] and references therein). For the last years a significant progress was gained in calculations of the isotope shifts in highly charged ions [13, 15, 45–48]. 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
Table III: 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.

| Transition                        | $K\alpha_1$ | $K\alpha_2$ |
|-----------------------------------|-------------|-------------|
|                                   | 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) |

the spherically-symmetric Fermi model:

$$\rho(r, R) = \frac{N}{1 + \exp[(r - c)/a]},$$  \hspace{1cm} (13)

where the parameter $a$ is generally fixed to be $a = 2.3/(4\ln3)$ fm and the parameters $N$ and $c$ are determined using the given value of the root-mean-square nuclear charge radius $R = \langle r^2 \rangle^{1/2}$ and the normalization condition: $\int d\rho(r, R) = 1$. The potential induced by $\rho(r, R)$ is defined as

$$V_N(r, R) = -4\pi Z \int_0^\infty dr' r'^2 \rho(r', R) \frac{1}{r_>},$$  \hspace{1cm} (14)

where $r_> = \max(r, r')$. This potential is used in the Dirac-Coulomb-Breit Hamiltonian to obtain the relativistic wave functions. The related isotope shifts are evaluated by the formula:

$$\delta E_{FS} = \langle \psi | \sum_i \delta V_N(r_i, R) | \psi \rangle,$$  \hspace{1cm} (15)

where $\delta V_N(r, R) = V_N(r, R + \delta R) - V_N(r, R)$ and $\delta R$ is the difference of the rms radii for the isotopes under consideration.
Table IV: Individual contributions to the energy of the Kα-lines for $^{204}$Hg (in keV) with the nuclear charge radius R=5.4744 fm.

|                          | Kα1    | Kα2    |
|--------------------------|--------|--------|
| 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 V: Individual contributions to the energy of the L-lines for $^{238}$U (in keV) with the nuclear charge radius R=5.8569 fm.

|                          | Lα2   | Lβ1   | Lβ3   | Lβ4   |
|--------------------------|-------|-------|-------|-------|
| 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) |

In Tables VI and VII we present the contributions to the field shifts for the Kα-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. Expect 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. [47]. Namely, this was done by multiplying the s-state QED correction factor taken from Refs. [49, 50] 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 Kα lines were indistinguishable in those experiments and, therefore, the Kα₁ and Kα₂ transition values taken from Ref. [8] are assumed to be the same. The theoretical uncertainty is estimated as a doubled quadratic sum of the an uncertainty due to unknown nuclear polarization and deformation effects and a half of the QED contribution. In accordance with the results of Ref. [47], 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 VIII 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 Kα lines. The only difference is the neglecting the QED contributions for the Lα₂ and Lβ₁ lines. As one can see, there exists a rather large discrepancy between theory and experiment [10] for the Lβ₁ line. The reason of this discrepancy is unclear to us.

In Table IX the individual contributions to the total isotope shifts for the Kα lines in ²⁰⁴,²⁰²Hg 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 X. 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 configuration-interaction method in the Dirac-Fock-Sturm basis in approximation of the barycenter of valence nonrelativistic configuration. The obtained results are compared with the 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 case of the L lines, there exist some discrepancies
Table VI: Individual contributions to the isotope shift for the Kα lines in $^{235,238}$U (in meV) with given values of nuclear charge radii ($^{235} R = 5.8287 \text{ fm}$, $^{238} R = 5.8569 \text{ fm}$).

|                     | Kα1        | Kα2        |
|---------------------|------------|------------|
| 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 VII: Individual contributions to the isotope shift for the Kα lines in $^{233,238}$U (in meV) with given values of nuclear charge radii ($^{233} R = 5.8138 \text{ fm}$, $^{238} R = 5.8569 \text{ fm}$).

|                     | Kα1        | Kα2        |
|---------------------|------------|------------|
| 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)  |

between theory and experiment for the isotope shifts in uranium atoms. The discrepancy becomes especially large for the Lβ$_1$ lines. The reason of this discrepancy remains unclear to us.

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Table VIII: 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 IX: 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)    |

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Table X: Total isotope shifts for the $K\alpha$ lines in $^{204,202}\text{Hg}$, $^{204,201}\text{Hg}$, $^{204,200}\text{Hg}$, $^{204,199}\text{Hg}$, and $^{204,198}\text{Hg}$ (in meV) with given values of nuclear charge radii taken from Ref. [32].

| Isotope | Theory | Experiment $^{[1]1}$ | K$\alpha_1$ | K$\alpha_2$ |
|---------|--------|----------------------|--------------|--------------|
| $^{204,202}\text{Hg}$ | Theory | -148(3) | -147(3) |
| | Experiment $^{[11]}$ | -156(44) | -156(44) |
| $^{204,201}\text{Hg}$ | Theory | -246(6) | -246(6) |
| | Experiment $^{[11]}$ | -286(36) | -286(36) |
| $^{204,200}\text{Hg}$ | Theory | -291(7) | -292(7) |
| | Experiment $^{[11]}$ | -305(30) | -305(30) |
| $^{204,199}\text{Hg}$ | Theory | -408(9) | -408(9) |
| | Experiment $^{[11]}$ | -425(40) | -425(40) |
| $^{204,198}\text{Hg}$ | Theory | -424(10) | -424(10) |
| | Experiment $^{[11]}$ | -468(44) | -468(44) |
Appendix A: Dirac-Fock method with the approximation of the average of relativistic configuration (jj-average) and the average of nonrelativistic configuration (LS-average)

Let 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. Thus \( A = (n_A l_A) \), \( a = (n_A l_A j_a) = (A j_a) \), and

\[
q_A = \sum_{a \in A} q_a, \quad q_B = \sum_{b \in B} q_b.
\]

First we consider the relativistic average configuration (jj-average). In this approximation the energy is expressed as

\[
E_{DF}^{\text{rav}} = \sum_a q_a I_a + \frac{1}{2} \sum_a q_a (q_a - 1) F^0(a, a) + \sum_{a < b} q_a q_b F^0(a, b) + \sum_a \sum_{k > 0} q_a (q_a - 1) f_{aa}^k F^k(a, a) + \sum_{a < b} \sum_k q_a q_b g_{ab}^k G^k(a, b),
\]

where \( q_a \) and \( q_b \) are the numbers of electrons in the shells \( a \) and \( b \), \( I_a \) is the one-electron radial integral [51], and \( F^k(a, b) \) and \( G^k(a, b) \) are the standard Coulomb and exchange radial integrals [51], respectively. The coefficients \( f_{aa}^k \) and \( g_{ab}^k \) are given by

\[
f_{aa}^k = -\frac{1}{2} \frac{2j_a + 1}{2j_a} \left( \frac{C_{j_a - j_a - k}^{00}}{2k + 1} \right)^2 = -\frac{1}{4} \frac{2j_a + 1}{2j_a} \Gamma_{j_a, j_a}^k, \tag{A2}
\]

\[
g_{ab}^k = -\frac{\left( C_{j_a - j_b - k}^{00} \right)^2}{2k + 1} = -\frac{1}{2} \Gamma_{j_a, j_b}^k.
\]

Where \( \Gamma_{j_a, j_b}^k \) are the coefficients introduced in Ref. [51],

\[
\Gamma_{j_a, j_b}^k = 2 \left( \frac{j_a j_b k}{\frac{1}{2} - \frac{1}{2} - \frac{1}{2}} \right)^2. \tag{A3}
\]

The procedure of the relativistic configurational average is meaningful only when the jj-coupling dominates, that obviously is not true for most of neutral atoms. Furthermore, the use of the pure jj-coupling scheme leads to a wrong nonrelativistic limit. For this reason it is reasonable to use the averaging over all the jj-configurations arising from a valence
nonrelativistic configuration in the calculations of neutral atoms. Starting with equation (1) we obtain the following energy expression in the nonrelativistic configurational average (LS-average)

\[ E_{\text{nav}}^{\text{DF}} = \sum_a \tilde{q}_a I_a + \frac{1}{2} \sum_a \tilde{q}_a (\tilde{q}_a - w_A) F^0(a, a) + \sum_{a<b} \tilde{q}_a \tilde{q}_b \omega_{AB} F^0(a, b) \]

\[ + \sum_a \sum_{k>0} \tilde{q}_a (\tilde{q}_a - w_A) f_{aa}^k F^k(a, a) + \sum_{a<b} \sum_k \tilde{q}_a \tilde{q}_b \omega_{AB} g_{ab}^k G^k(a, b), \]

where the parameters \( \tilde{q}_a \), \( w_a \), and \( \omega_{AB} \) are defined as

\[ \tilde{q}_a = \frac{2j_a + 1}{4l_A + 2} q_A, \quad w_a = \frac{q_A - \tilde{q}_a + 2j_a}{4l_A + 1}, \]

\[ \omega_{AB} = \begin{cases} \frac{4L_a + 2}{4L_a + 1} \frac{q_A - 1}{q_A}, & A = B, \\ 1, & A \neq B. \end{cases} \]

Here \( q_A \) is the total number of electrons in the nonrelativistic shell \( A = n_a l_a \).

The expression \( (A4) \) can be rewritten in the same form as the nonrelativistic expression for the energy in the Hartree-Fock method \[52\],

\[ E_{\text{nav}}^{\text{DF}} = \sum_A q_A T_A + \frac{1}{2} \sum_A q_A (q_A - 1) \mathcal{F}^0(A, A) + \sum_{A<B} q_A q_B \mathcal{F}^0(A, B) \]

\[ + \sum_A \sum_{k>0} q_A (q_A - 1) f_{A,A}^k \mathcal{F}^k(A, A) + \sum_{A<B} \sum_k q_A q_B g_{A,B}^k \mathcal{G}^k(A, B), \]

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

\[ \mathcal{F}^0(A, B) = \begin{cases} \sum_{j_a \in A, j_b \in B} \frac{(2j_a + 1 - \delta_{j_a, j_b})(2j_b + 1)}{(4L_A + 2)(4L_A + 1)} F^0(a, b), & A = B, \\ \sum_{j_a \in A, j_b \in B} \frac{(2j_a + 1)(2j_b + 1)}{(4L_A + 2)(4L_B + 2)} F^0(a, b) & A \neq B. \end{cases} \]

for \( k = 0 \) and

\[ \mathcal{G}^k(A, B) = \frac{1}{2} \sum_{j_a \in A, j_b \in B} (2j_a + 1)(2j_b + 1) \left\{ \frac{j_a}{l_a} \frac{j_b}{l_b} \frac{k}{l} \right\}^2 G^k(a, b), \quad \mathcal{F}^k(A, A) = \mathcal{G}^k(A, A) \]

for \( k > 0 \).

In the nonrelativistic limit, the integrals \( \mathcal{F}^k(A, B) \) and \( \mathcal{G}^k(A, B) \) tend to the corresponding nonrelativistic radial integrals defined in the nonrelativistic Hartree-Fock method \[52\].
The coefficients $f_{A,A}^k$ and $g_{a,b}^k$ coincide with the corresponding coefficients defined in the nonrelativistic Hartree-Fock method in the approximation of the center of gravity,

$$f_{A,A}^k = -\frac{1}{4} \frac{4l_A + 2}{4l_A + 1} \frac{(C_{lA0,lA0}^{k0})^2}{2k + 1},$$

$$g_{a,b}^k = -\frac{1}{2} \frac{1}{2k + 1} \left( C_{l_A0,l_B0}^{k0} \right)^2 .$$

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