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Adjustment of the quasirelativistic equations for *p* electrons

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A development of the techniques for solving the quasirelativistic Hartree-Fock equations for quasirelativistic atomic calculations published earlier [Phys. Rev. A **74**, 052501 (2006)] is presented. Trial calculations using these techniques revealed that the one-electron characteristics and spin-orbit splitting are less precise in the case of *p* electrons. To overcome this problem, a different method of averaging the spin-orbit interaction within the quasirelativistic Hartree-Fock equation is proposed for *p* electrons. The specific account of the contact interaction in the case of *p* electrons is discussed. The technique for calculating the spin-orbit interaction constant while using the quasirelativistic radial orbitals is presented. Since the pecularities appear on the level of one-electron interactions, only hydrogenlike ions are investigated. Data revealing how the methods under discussion influence the results obtained are presented.

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I. INTRODUCTION

There are several well-known groups of computer codes for *ab initio* calculations of the spectral characteristics of atoms and ions, taking extensively into account the relativistic and correlation corrections. One of the widely used program systems [1] is based on the multiconfiguration Hartree-Fock approach on the basis of nonrelativistic radial orbitals within the Breit-Pauli (BP) approximation [2,3], taking into account relativistic corrections up to the second order in the fine-structure constant α. However, the Breit-Pauli approximation is insufficient for describing the properties of highly charged ions precisely enough. Moreover, within this approach it is impossible to take into account the indirect relativistic effects in heavy atoms. These effects are caused by the fact that the inner shells of such atoms are strongly relativistic, and they influence the radial orbitals of the outer shells, where electrons are comparatively slower, and where the BP approximation seems to be rather effective. Multiconfiguration calculations on the basis of Dirac-Fock (DF) functions taking complete account of relativistic effects are often performed by using the GRASP2 code [4–6]. This computer code is used to obtain data in the present work. Other relativistic multiconfiguration or configuration-interaction Dirac-Fock methods allowing one to determine the QED effects more precisely are also widely used and successfully applied for accurate calculations of various physical quantities; see, for example, [7–10]. However, the employment of double-component relativistic radial orbitals, causing the splitting of a shell of equivalent electrons into two subshells according to the total momentum of the electron, makes the computations slower and more difficult. A fortunate compromise in this case is the quasirelativistic approach, where the main relativistic effects are taken into account already in obtaining the radial orbitals. These orbitals remain one component and independent of j. The most popular computer program implementing this approach is Cowan's code described in [11]. However, this program was created a long time ago and has some drawbacks, which are quite compensated by the possibility of using different empirical corrections and semiempirical fitting. In this context, work was started to improve the quasirelativistic approach for determination of radial orbitals [12–14] and to create a code for solution of the quasirelativistic Hartree-Fock (QRHF) equations. The purpose of this project is to include this and some other programs into the program system [1], which is quite easy to implement due to its very convenient and flexible modular construction. As a result, the possibility of high-precision *ab initio* calculations of spectral characteristics of highly charged ions and heavy atoms will be created.

In [14], a new version of the QRHF equations was introduced. These equations are well consistent with the BP approach, where the solutions of such equations are used. The development of this method and the creation of the corresponding computer codes enabled us to perform real calculations of the spectra of atoms and ions. The great effectiveness of the used radial orbitals (ROs) was demonstrated, although some shortcomings became known, too. The main problem concerns the insufficiently precise spin-orbit splitting of the terms while calculating the spectra of *np* shells of highly charged ions. The same problem appears when using the quasirelativistic ROs within the AUTOSTRUCTURE package [15]. This fact indicates that the insufficient precision of the behavior of ROs of *p* electrons is not the feature of the QRHF equations proposed by the authors in [14], but rather their general peculiarity. Already, as in [13], devoted to the solution of quasirelativistic equations in the case of hydrogenlike ions, it was noted that the energy values obtained for electrons with an orbital quantum number equal to 1 were distinguished by their lower precision among the solutions for other electrons. Thus, there is the necessity to refine the quasirelativistic equations for *p* electrons so that the description of these electrons would be no less precise than that of electrons with lower or higher values of the orbital quantum number.

In the present paper, we will confine ourselves to the investigation of one-electron ions, since the considered properties reveal themselves already in hydrogenlike ions, i.e., on the level of one-electron interactions. In the next section, the data showing the difference in precision of the results for *p*

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electrons and others are presented. In Sec. III a different method of averaging the spin-orbit interaction is described, and in the fourth section the method of taking into account the contact interaction in the case of *p* electrons is discussed. The data revealing how these methods influence the obtained ROs are also presented there. In Sec. V, we discuss the techniques of calculation of the spin-orbit interaction constant with the quasirelativistic ROs and the influence of the described approaches on its value. The main results of the paper are summarized in the Conclusion.

II. THE PECULIARITIES OF QUASIRELATIVISTIC RESULTS FOR *p* ELECTRONS

While solving the quasirelativistic equations for hydrogenlike ions [14], it was concluded that, in the case of *s* electrons, the one-electron energies and other characteristics of ROs are in good agreement with the solutions of the DF equations. The parameters of radial orbitals with $l \geqslant 2$ are also in relatively good coincidence with the values of *j*-averaged relativistic characteristics,

$$x(nl) = \frac{(2j_- + 1)x(nlj_-) + (2j_+ + 1)x(nlj_+)}{4l+2}, \tag{2.1}$$

where

$$j_\pm = l \pm 1/2. \tag{2.2}$$

At the same time, the good coincidence is absent in the case of the quasirelativistic orbitals of *p* electrons. This fact is demonstrated in Table I. The table contains the one-electron energies and the averaged distances from the origin obtained by solving the DF equations and quasirelativistic equations for hydrogenlike ions. Hereinafter, the solutions of the Dirac equations obtained using the computer code [6], taking into account the finite size of the nucleus, are treated as DF results. They are denoted in bold in the table for the convenience of comparison. The QR results are meant to be the solutions of the following equations (here and everywhere, atomic units are used):

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) - \varepsilon_{nl}\right)P(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl} + U(r)]^2 P(nl|r) + \delta(l,0)\frac{\alpha^2}{4}\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} + U(r)]\right)^{-1}\frac{dU(r)}{dr}\left(\frac{d}{dr} - \frac{1}{r}\right) \times P(nl|r) = 0, \tag{2.3}$$

i.e., equations averaged over the total momentum of the electrons and taking into account the contact interaction only in the case of *s* electrons. These equations conform to Eq. 3 from [16]. The only difference between these equations is that the finite-size nucleus is taken into account while solving Eq. (2.3):

$$U(r) = \begin{cases} \dfrac{1}{16}\dfrac{Z}{r_{nuc}}\left[-63 + 42\left(\dfrac{r}{r_{nuc}}\right)^2 - 18\left(\dfrac{r}{r_{nuc}}\right)^6 + 7\left(\dfrac{r}{r_{nuc}}\right)^8\right], & r < r_{nuc}, \\ -\dfrac{2Z}{r}, & r \geqslant r_{nuc}. \end{cases} \tag{2.4}$$

This potential of the finite-size nucleus was created in [12] especially for solving the QRHF equations. The methods developed for the numerical solution of the usual Hartree-Fock equations [17] and described in [18] were used to solve Eq. (2.3).

As is seen from Table I, the one-electron energies of *s* electrons are in very good coincidence with the DF values. The results for *d* and *f* electrons are a little less accurate; however, the coincidence is rather good even in the case of $Z=100$. The one-electron energies of *p* electrons are inferior to the other electrons in accuracy by one order of magnitude, or even more when the charge of the nucleus and principal quantum number are the same. A similar phenomenon also appears in the case of other characteristics of the ROs, as is seen from the averaged distances from the origin presented in Table I. For these characteristics, the differences in deviations are slightly smaller than those of one-electron energies. This indirectly indicates that the deviations appear because of an insufficiently precise account of the relativistic effects while solving the equations for *p* electrons. The one-electron energies obtained by solving the quasirelativistic equations with full account of the contact interaction (QR+C), i.e., without $\delta(l,0)$ in Eq. (2.3), are also presented in Table I to ensure that the above problems are not caused by neglecting the contact interaction for electrons with $l>0$. Nevertheless, it is clearly seen from Table I that such inclusion of the contact interaction substantially worsens the results for all electrons with $l>0$ when solving Eq. (2.3).

The quasirelativistic equation (2.3) before averaging over *j* appears as

$$\left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U(r) - \varepsilon_{nlj}\right)P(nlj|r) + \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]^2 \times P(nlj|r) + \frac{\alpha^2}{4}\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nlj} + U(r)]\right)^{-1} \times \frac{dU(r)}{dr}\left(\frac{d}{dr} - \frac{X_{lj}+1}{r}\right)P(nlj|r) = 0. \tag{2.5}$$

The spin-orbit interaction parameter

TABLE I. One-electron energies and averaged distances from the origin for hydrogenlike ions (a.u.).

		ε			$\bar{r}$	
Z	*nl*	DF	QR	QR+C	DF	QR
50	1*s*	**1294.5535**	1294.5567		**0.028623**	0.028623
	2*s*	**326.4846**	326.4839		**0.114027**	0.114524
	2*p*	**318.9277**	318.7653	319.26	**0.097113**	0.097643
	3*s*	**143.8268**	143.8269		**0.259805**	0.260396
	3*p*	**141.5818**	141.5399	141.59	**0.244120**	0.245130
	3*d*	**139.8270**	139.8238	140.03	**0.207711**	0.208084
	4*s*	**80.3690**	80.3691		**0.465640**	0.466264
	4*p*	**79.4248**	79.4085	79.47	**0.451304**	0.452493
	4*d*	**78.6851**	78.6839	78.77	**0.415879**	0.416674
	4*f*	**78.3821**	78.3818	78.41	**0.357969**	0.358261
	5*p*	**50.7151**	50.7073	50.73	**0.718538**	0.719820
	5*d*	**50.3372**	50.3366	50.38	**0.684168**	0.685159
	5*f*	**50.1818**	50.1817	50.20	**0.626631**	0.627297
100	1*s*	**5923.1255**	5922.5997		**0.011879**	0.011877
	2*s*	**1545.3448**	1545.2371		**0.046869**	0.047844
	2*p*	**1379.1376**	1361.5083	1403.9	**0.043755**	0.045103
	3*s*	**656.9509**	656.9182		**0.112312**	0.113493
	3*p*	**607.3498**	602.6785	615.1	**0.112341**	0.114834
	3*d*	**571.2711**	571.0407	574.5	**0.100349**	0.101117
	4*s*	**357.5520**	357.5386		**0.207843**	0.209097
	4*p*	**336.9588**	335.1581	340.2	**0.211246**	0.214289
	4*d*	**321.8571**	321.7689	323.2	**0.201638**	0.203258
	4*f*	**316.6696**	316.6797	317.2	**0.175908**	0.176497
	5*p*	**213.2670**	212.4059	214.9	0.340248	0.343668
	5*d*	**205.6191**	205.5771	206.3	**0.333159**	0.335179
	5*f*	**202.9678**	202.9600	203.2	**0.308218**	0.309559

TABLE II. One-electron energies for particular values of j (a.u.).

		$j=1/2$		$j=3/2$	
Z	*nl*	DF	QR	DF	QR
50	2*p*	**326.4945**	326.4945	**315.1444**	315.1443
	3*p*	**143.8297**	143.8297	**140.4579**	140.4579
	4*p*	**80.3703**	80.3703	**78.9521**	78.9521
	5*p*	**51.1977**	51.1977	**50.4739**	50.4739
100	2*p*	**1548.1447**	1548.1441	**1294.6262**	1294.6261
	3*p*	**657.7659**	657.7657	**582.1391**	582.1390
	4*p*	**357.8845**	357.8844	**326.4948**	326.4945
	5*p*	**223.8153**	223.8152	**207.9967**	207.9967

$$X_{lj} = j(j+1) - l(l+1) - s(s+1) \tag{2.6}$$

depends only on total, orbital, and spin momenta of an electron, and ensures inclusion of the spin-orbit interaction in the equation. The solutions of these quasirelativistic equations for the states corresponding to particular values of the total momentum j of an electron are in very good agreement with the results of the solutions of DF equations even in the case of p electrons. This is clearly seen from Table II, where the one-electron energies obtained by solving Eqs. (2.5) are compared with the data of solutions of DF equations. There, perfect coincidence of the results is observed. This fact reveals that, in the case of p electrons, the traditional averaging of the equations over j, i.e., the conversion of Eq. (2.5) into Eq. (2.3), causes great deviations. The deviation is less meaningful for other electrons, as Eqs. (2.3) and (2.5) coincide in the case of s electrons, and the neglect of contact interaction is quite justified for electrons with $l \geqslant 2$, as follows from Table I.

III. SPIN-ORBIT INTERACTION AVERAGING FOR *p* ELECTRONS

The problem of p electrons was noted in [13], but it was not solved there. In that paper, it is mentioned that the effect might be related to inaccuracy of the averaging of the spin-orbit interaction for p electrons. Indeed, in the case of p electrons, the spin-orbit interaction, which is missing for s electrons, plays an important role, as the operator describing this interaction contains r^{-3}—the same as the operator of the contact interaction. This is clearly seen from Eq. (2.5).

In the case of s electrons, the parameter X_{lj} is equal to 0. The averaging of this parameter using the formula (2.1) for electrons with $l > 0$ also leads to zero value. As a result, Eq. (2.3) and its solutions become independent of the total momentum of an electron. But the employment of the expression (2.1) for averaging of the spin-orbit interaction implies that the radial orbitals $P(nlj|r)$ do not depend, or only slightly depend, on the total momentum j. Even though this is true for ROs with $l \geqslant 2$, it is not true for p electrons. Thus it is necessary to take into account the properties of the corresponding ROs while averaging the X_{lj}. In the present paper, it is proposed to take into account not only the statistical weight of the averaged state $2j+1$, but also the value of the radial integral $\langle nlj|r^{-3}|nlj\rangle$, while averaging the X_{lj}. In this case, the expression for the averaged value of the parameter under discussion appears as follows:

$$X_{nl} = \frac{(2j_- + 1)\langle nlj_-|r^{-3}|nlj_-\rangle X_{lj_-} + (2j_+ + 1)\langle nlj_+|r^{-3}|nlj_+\rangle X_{lj_+}}{(2j_- + 1)\langle nlj_-|r^{-3}|nlj_-\rangle + (2j_+ + 1)\langle nlj_+|r^{-3}|nlj_+\rangle}. \tag{3.1}$$

The analytical expression of the integrals $\langle nlj|r^{-3}|nlj\rangle$ might also be used to obtain the averaged parameter. The paper [19] might serve this purpose. There, the analytical expressions of all integrals calculated on the basis of Dirac functions are presented. However, as is noted in [19] and follows from the expressions proposed there, the corresponding integral is indeterminate in the case of pj_- electrons. Infinity appears already in the quadratic term of the series expansion of $\langle nlj|r^{-3}|nlj\rangle$ from [19] in powers of the fine-structure constant α. This is one additional factor sustaining the special matter of the spin-orbit interaction and the necessity of the correct averaging in the case of p electrons. Infinities do not appear in these integrals when solving Eq. (2.5), since the equations are solved with account of the finite size of the nucleus. This fact enables one to perform the averaging of X_{lj} using the numerical values of the integrals.

It is necessary to obtain the value of the averaged parameter accurate only up to second order of the fine-structure constant α. For this purpose the integral $\langle nlj|r^{-3}|nlj\rangle$ is expressed as a power series,

$$\langle nlj|r^{-3}|nlj\rangle = \langle nl|r^{-3}|nl\rangle_0 + \alpha^2\langle nlj|r^{-3}|nlj\rangle_2 + O(\alpha^4). \tag{3.2}$$

The first term represents an integral calculated on the basis of the usual nonrelativistic ROs. A simple analytical expression exists for this integral:

$$\langle nl|r^{-3}|nl\rangle_0 = \frac{Z^3}{n^3}\frac{2}{l(l+1)(2l+1)}. \tag{3.3}$$

Substitution of (3.2) into (3.1), taking into account (2.2) and the properties of X_{lj},

$$X_{lj_-} = -(l+1) \quad \text{and} \quad X_{lj_+} = l, \tag{3.4}$$

leads to the following expression:

$$X_{nl} = \alpha^2\frac{l(l+1)(\langle nlj_+|r^{-3}|nlj_+\rangle_2 - \langle nlj_-|r^{-3}|nlj_-\rangle_2)}{(2l+1)\langle nl|r^{-3}|nl\rangle_0} + O(\alpha^4). \tag{3.5}$$

The numerical computations of integrals $\langle nlj|r^{-3}|nlj\rangle$ on the basis of the quasirelativistic functions obtained by solving Eq. (2.5) for different values of the nucleus charge and for a series of values of the principal quantum number enabled us to obtain the following approximate numerical formula:

$$X_{np} = \alpha^2 Z^2\left(-\frac{37}{30} - \frac{5}{9n} + \frac{2}{3n^2}\right). \tag{3.6}$$

This formula entirely coincides in its structure and dependence on Z, α, and n with the expressions obtained for $l \geqslant 2$ by substituting the analytical expression of the $\langle nlj|r^{-3}|nlj\rangle$ integrals from [19] into (3.1).

Expression (3.6) needs to be introduced into Eq. (2.5) instead of X_{lj}. Thus, a quasirelativistic equation containing more precise averaging by j appears (for the case of p electrons). At the same time, the correction obtained can no longer be related to the spin-orbit interaction, as it does not depend on j, i.e., it does not satisfy the main property of this interaction. This correction must be interpreted as a correction to the contact interaction, which arises from the spin-orbit interaction in the same manner as the contact interaction itself originates from the electrostatic interaction with a nucleus.

As the parameter X_{np} contains α^2, the fourth order of the fine-structure constant correction appears within the equation. This should not result in an excess of accuracy for the following reasons. First, Eq. (2.5) is obtained from the Dirac equations without elimination of the terms of higher order in α. (The terms of α^4 and higher orders are omitted only when obtaining the QRHF equations, i.e., only the terms containing two-electron relativistic interactions are omitted when obtaining the equations.) Second, Eq. (2.5) includes α^2 in the denominator, and that conforms to the presence of all powers of α when the corresponding power expansion is applied. Third, the concept of an expansion in powers of α is not fully justified when considering Eq. (2.5), since the terms containing high powers of the fine-structure constant might strongly influence the total potential and consequently the behavior of radial orbitals in the vicinity of the origin. This radically distinguishes the properties of the one-electron relativistic corrections from the properties of the two-electron ones where the potentials near the origin are small.

IV. CONTACT INTERACTION ADJUSTMENT FOR *p* ELECTRONS

In the previous section, the term specifying the contact interaction for p electrons was obtained. However, it is known that the one-electron contact interaction is taken into account only for s electrons within the BP approach, whereas it is considered negligible for other electrons. In this connection, the delta symbol $\delta(l,0)$ is included in the contact term of the QRHF equations [11,14], as in Eq. (2.3). This property of the contact interaction is quite correct if nonrelativistic radial orbitals are used. But in a relativistic approach one must talk about electrons with $j=1/2$ and not about s electrons. Some of the p electrons belong to the same group. The distinctive feature of electrons with $j=1/2$ is rather high density of the probability in the vicinity of the origin, and a strong influence of the relativistic effects correspondingly. The solutions of Eq. (2.5) for particular values of j possess the same properties.

Let us consider the influence of the contact interaction within (2.5) in the case of $j_\pm = l \pm 1/2$. For this purpose, the radial orbital and its derivative in the vicinity of the origin must be presented as an expansion in a series of powers of the radial variable,

$$P(nl|r) = a_0 r^{l+1}[1+O(r)], \qquad \frac{dP(nl|r)}{dr} = (l+1)a_0 r^l[1+O(r)]. \tag{4.1}$$

The derivative of the potential $U(r)$ (2.4) outside the nucleus is proportional to r^{-2}. Substituting (4.1) into the numerator of the contact and spin-orbit potential, one may obtain the following dependence:

TABLE III. One-electron energies and averaged distances from the origin for p electrons (a.u.).

Z	nl	ε		$\bar{r}$	
		A	B	A	B
50	$2p$	318.9422	319.9489	0.097469	0.097100
	$3p$	141.5913	141.8906	0.244863	0.244306
	$4p$	79.4297	79.5559	0.452175	0.451427
	$5p$	50.7179	50.7825	0.719462	0.718523
100	$2p$	1375.7769	1382.8277	0.044324	0.044051
	$3p$	606.9138	609.0367	0.113640	0.113213
	$4p$	336.8957	337.8046	0.212765	0.212170
	$5p$	213.2727	213.7429	0.341842	0.341071

$$\frac{d(-2Z/r)}{dr}\left(\frac{d}{dr}-\frac{X_{lj}+1}{r}\right)P(nlj|r)=br^{l-2}(l-X_{lj})+O(r^{l-1}). \tag{4.2}$$

In the case of $j=l+1/2$, by taking into account the corresponding value of X_{lj} from (3.4), one might obtain that the first term of (4.2) disappears, and the contact potential in the equation cannot contain negative powers of a radial variable for all electrons with $l>0$. The first term does not disappear when $j=l-1/2$. In this case, for p electrons the negative power of a radial variable appears in (4.2), which leads to high values of the contact potential in the vicinity of the nucleus. In the case of s electrons, where $X_{sj}=0$, the first term of (4.2) also disappears, but the main term of the contact potential remains r^{-1}—the same as in the case of p electrons with $j=l-1/2$. Thus, it is clear that one must take into account the contact interaction for pj_{-} electrons, just as for s electrons.

Hence, besides the delta symbol $\delta(l,0)$ in the equation for s electrons, it is necessary to find a way to take into account the contact interaction for p electrons. The statistical weight of the p electrons with $j=l-1/2$, when account of the contact interaction is essential, is equal to 2. The statistical weight of nonrelativistic p electrons is equal to 6. Thus, the coefficient allowing one to average the contact interaction for electrons with $l=1$ appears to be equal to $1/3$. Now the adjusted quasirelativistic equation (2.3), independent of the total momentum of an electron, is written down as follows for any type of electron:

$$\begin{aligned}&\left(\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-U(r)-\varepsilon_{nl}\right)P(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]^2P(nl|r)\\&\quad+\left(\delta(l,0)+\frac{1}{3}\delta(l,1)\right)\frac{\alpha^2}{4}\left(1-\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]\right)^{-1}\\&\quad\times\frac{dU(r)}{dr}\left(\frac{d}{dr}-\frac{\delta(l,1)X_{np}+1}{r}\right)P(nl|r)=0.\end{aligned} \tag{4.3}$$

In this way, the equation remains the same both for s electrons and for electrons with $l\geqslant 2$. The results of solving this equation are presented in Table III. The table contains the one-electron energies and the averaged distances from the origin for p electrons. The data of two kinds of calculations are presented: Set A are the results of solving Eq. (4.3); set B are the results of solving Eq. (4.3) without the spin-orbit correction of the contact term, i.e., when $X_{np}=0$. Comparison of data presented in Table III with the corresponding data of DF calculations from Table I reveals that the solutions of Eq. (4.3) provide more accurate energy values (set A) than those of Eq. (2.3) without the contact interaction for p electrons. At the same time, the rejection of spin-orbit correction (set B) causes noticeable deviations in determining the one-electron energies. The deviations of the averaged distances are similar to those for the energies. The improvement of other RO parameters is also observed, including the spin-orbit interaction constant discussed in the next section.

V. CALCULATION OF SPIN-ORBIT INTERACTION ON THE BASIS OF QUASIRELATIVISTIC RADIAL ORBITALS

Before investigating the influence of the proposed approach on the accuracy of calculations of the mentioned correction, it is worthwhile to discuss the methods of calculation of the spin-orbit interaction in the case of quasirelativistic ROs. In the case of nonrelativistic ROs, the one-electron part of the spin-orbit interaction is defined in terms of a radial integral as follows:

$$\eta_{nr}(nl)=\frac{\alpha^2}{8}\int_0^\infty P(nl|r)\frac{1}{r}\frac{d(-2Z/r)}{dr}P(nl|r)dr. \tag{5.1}$$

Since the finite-size nucleus potential is used while solving the quasirelativistic equations, it is necessary to replace the pointlike nucleus potential $-2Z/r$ by the potential $U(r)$ (2.4) when applying the quasirelativistic ROs:

$$\eta_0(nl)=\frac{\alpha^2}{8}\int_0^\infty P(nl|r)\frac{1}{r}\frac{dU(r)}{dr}P(nl|r)dr. \tag{5.2}$$

That is not all, though. In Eq. (2.5), the term describing the spin-orbit interaction (X_{lj}) contains the same denominator as does the contact interaction. Thus, there is the possibility of presenting an alternative expression of the integral under investigation,

$$\eta_1(nl)=\frac{\alpha^2}{8}\int_0^\infty\frac{P(nl|r)\frac{1}{r}\frac{dU(r)}{dr}P(nl|r)}{\left(1-\frac{\alpha^2}{4}[\varepsilon_{nl}+U(r)]\right)}dr. \tag{5.3}$$

In this form (5.3) is in better agreement with the contact interaction integral calculated on the basis of quasirelativistic orbitals.

The only criterion in selecting the type of the integral is a comparison of the corresponding quantities with the value of the spin-orbit interaction constant that is obtained using the solutions of the Dirac equations, taking into account the finite size of a nucleus. This value is determined using the corresponding one-electron energies as follows:

TABLE IV. Spin-orbit interaction constant for *d* and *f* electrons (a.u.).

Z	nl	η_{nr}	η_0	η_1	η_{DF}
50	$3d$	0.2054	0.2133	0.2110	**0.2103**
	$4d$	0.0867	0.0903	0.0890	**0.0890**
	$5d$	0.0444	0.0462	0.0455	**0.0456**
	$4f$	0.0310	0.0315	0.0314	**0.0313**
	$5f$	0.0158	0.0162	0.0161	**0.0160**
100	$3d$	3.287	3.841	3.668	**3.623**
	$4d$	1.387	1.641	1.545	**1.546**
	$5d$	0.710	0.842	0.787	**0.793**
	$4f$	0.495	0.534	0.524	**0.517**
	$5f$	0.254	0.275	0.268	**0.267**

TABLE V. Spin-orbit interaction constant for *p* electrons (a.u.).

		Eq. (2.3)		Eq. (4.3)		DF
Z	nl	η_0	η_1	η_0	η_1	η_{DF}
50	$2p$	3.89	3.69	3.97	*3.75*	**3.78**
	$3p$	1.16	1.09	1.19	*1.11*	**1.12**
	$4p$	0.489	0.456	0.502	*0.467*	**0.473**
	$5p$	0.250	0.233	0.257	*0.238*	**0.241**
100	$2p$	92.94	74.60	107.95	*83.78*	**84.51**
	$3p$	28.23	21.62	33.50	*24.72*	**25.21**
	$4p$	11.83	8.92	14.11	*10.24*	**10.46**
	$5p$	6.00	4.49	7.17	*5.16*	**5.27**

$$\eta_{DF}(nl) = \frac{\varepsilon_{nlj_+} - \varepsilon_{nlj_-}}{2l+1} \tag{5.4}$$

These results for *d* and *f* electrons are presented in Table IV. The table contains the values of nonrelativistic integrals η_{nr} calculated by applying the formula (5.1) together with the expression (3.3), the results of calculations using formulas (5.2) and (5.3), based on the quasirelativistic functions, and an "exact" value η_{DF}. As is seen from the table, employment of the spin-orbit interaction integral containing a denominator enables one to obtain appreciably more accurate values while integrating the quasirelativistic ROs. At the same time, the employment of expression (5.2) often results in deviations, the absolute values of which are comparable with those obtained using the nonrelativistic ROs.

The effect of a transfer from the solutions of Eq. (2.3) to the solutions of Eq. (4.3) is obvious from Table V. There are given the values of the integrals η_0 and η_1 calculated by employing two types of quasirelativistic RO: the solution of Eq. (2.3) and that of (4.3). The data presented in Table V clearly show that, in the case of *p* electrons, the complete corrected Eq. (4.3) and the calculation of the integral with the denominator (5.3) (these values are in italics) enable one to obtain results that are in good agreement with the solutions of the DF equations in all cases examined.

VI. CONCLUSION

The results presented in this paper unambiguously show that it is necessary to take into account the contact interaction with the nucleus in a specific way while solving the quasirelativistic equations for *p* electrons. This is because the contact interaction is essentially important for electrons with $j=1/2$. It is better to eliminate this interaction for electrons with $j>1/2$. The correct averaging of the spin-orbit potential over the total momenta of the *p* electrons when taking into account the contact interaction is also required. Only such an approach enables one to obtain quasirelativistic equations with solutions in good coincidence for different parameters with the data obtained by employing the exact relativistic equations. Employment of a spin-orbit interaction integral containing a denominator enables one to obtain appreciably more accurate values when integrating the quasirelativistic radial orbitals.

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