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Quasirelativistic Hartree-Fock equations consistent with Breit-Pauli approach

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The properties of the quasirelativistic Hartree-Fock equations are investigated. Different ways of forming the equations are discussed. The relativistic corrections employed in the traditional quasirelativistic Hartree-Fock equations are compared with the ones used within the Breit-Pauli approach. The two-electron contact interactions are revised and the new versions of the quasirelativistic Hartree-Fock equations are considered. The solutions of these equations are compared among themselves and also with those obtained within the Dirac-Fock and nonrelativistic Hartree-Fock approaches. Solution data are provided for some heliumlike, neonlike, and mercurylike ions.

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I. INTRODUCTION

Taking account of relativistic effects is important when investigating the highly charged ions, spectra of heavy atoms, x-ray spectra, and many other atomic objects. This can be done in different ways. The Breit-Pauli (BP) approximation [1,2] is among the simplest ones. Nonrelativistic radial orbitals obtained by solving Hartree-Fock (HF) [3,4] or analogous equations are used while applying this method. Relativistic effects are taken into account by calculating the energy corrections calculated with accuracy up to their second order in the fine structure constant. This approach allows one to obtain the energy spectra and wavelengths of electron transitions with high accuracy even for the ions with the ionization degree exceeding twenty, at the same time taking into account the correlation effects. However, this approach cannot provide results of high accuracy when calculating the probabilistic characteristics of transitions in heavy atoms. This is due to the fact that the inner shells of heavy atoms fall inside a very strong nuclear field and, as a consequence, the influence of relativistic effects on the wave functions of these electrons is great. Taking account of this influence while solving the corresponding equations leads to essential changes of the radial orbitals (ROs) of the inner shells. This affects the behavior of the electrons in the outer shells, although there the electron velocities are not high and consequently the direct relativistic corrections are small. Unfortunately, the described indirect relativistic effects can be accounted for neither within the BP approximation nor by the calculation of correlation effects. As a result, the obtained probabilistic characteristics are not reliable enough even for the neutral heavy atoms when one is applying BP approach with an extensive inclusion of correlation effects.

The employment of solutions of Dirac-Fock (DF) equations [5–7] when obtaining ROs is the most obvious choice for taking into account the relativistic effects. However, the application of this method leads to a considerable complication in calculations, such as the appearance of the large and the small components of ROs, the splitting of some shells into two subshells, the use of ***jj***-coupling even in the cases when it is not physically justified etc. A fortunate compromise is the creation of quasirelativistic HF equations [8] that do not depend on the total momentum of an electron [9]. When obtaining RO these equations allow us to take into account the main relativistic effects staying at the same time within the framework of the usual ***LS***-coupling and traditional methods of calculations corresponding to the BP approach when computing spectral characteristics. These benefits explain the wide popularity of the program for the solution of the quasirelativistic HF equations based on the methods described in monograph [10]. The mentioned program is quite successfully used for the semiempirical adjustment of the energy spectra and calculations of energy spectra using the empirical factors of Slater integrals. However our attempt to use the resulting ROs in *ab initio* calculations based on the configuration interaction approach within our methods [11,12] was not successful. The reason is the behavior of ROs in the vicinity of the nucleus, insufficient assurance of orthogonality of ROs while solving the equations, the complexity of computation of the integrals of energy operator matrix elements outside the initial program etc.

In this context we started the development of our own methods for solving the quasirelativistic HF equations (QRHF) in purely theoretical calculations within the BP approach with extensive inclusion of correlation effects. First we abandoned the pointlike nucleus model [13,14]. Taking into account the finite size of the nucleus provides us with the exact analytical expansion of quasirelativistic radial orbitals in the powers of radial variable at the origin. Examination of suitability of this approach in the case of hydrogenlike ions revealed that the accuracy of the obtained results increased especially for *s* electrons [14,15]. The analysis of quasirelativistic equations shows that it is possible to abandon the effective potential described by the statistical methods [16,10], and to use instead the conventional direct and exchange HF potentials in the equations. This allowed us to describe correctly the electron electrostatic interaction and to get a more specific description of the interelectron contact interactions in the equations. The present work is devoted to the investigation of these problems. As it is known [8], the presence of relativistic terms in the potential leads to a small nonorthogonality of ROs in the case of the closed shells unlike in the case of the usual HF equations. The problem of insuring the orthogonality of the resulting ROs while solving

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the quasirelativistic equations is not addressed here. In the open shell case the nonorthogonality problem is even more outstanding. Therefore all the examples investigated further include only the closed shell configurations.

In Sec. II the technique of forming the quasirelativistic equations from the DF equations is examined together with the main assumptions used for their derivation. In Sec. III the results of solution of the equations in the case of heliumlike ions are discussed along with the complications in taking account of two-electron contact interactions in the equations. In Sec IV the expressions enabling us to improve and simplify the description of electron contact and spin-contact interactions are obtained. In Sec. V the results of solving the obtained equations are presented. The main inferences are drawn in the conclusion.

II. DERIVATION OF QUASIRELATIVISTIC EQUATIONS FROM DIRAC-FOCK EQUATIONS

The quasirelativistic HF equations described in [10] were formed by simply adding the mass velocity and Darwin terms of the Pauli equations for one-electron atoms [1] to the usual nonrelativistic one-electron differential equations. The resulting equation is numbered (7.60) in the monograph [10] (all signs in the equation are reversed)

$$\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-U_{eff}(r)-\varepsilon_{nl}+\frac{\alpha^2}{4}[\varepsilon_{nl}+U_{eff}(r)]^2 + \delta(l,0)\frac{\alpha^2}{4}\left(1-\frac{\alpha^2}{4}[\varepsilon_{nl}+U_{eff}(r)]\right)^{-1}\frac{dU_{eff}(r)}{dr} \times\left(\frac{d}{dr}-\frac{1}{r}\right)\right]P(nl|r)=0. \tag{2.1}$$

Hereinafter, $P(nl|r)$ is the desired radial orbital; ε_{nl} denotes the absolute value of the single-electron energy in Rydbergs; α is the fine structure constant; $U_{eff}(r)$ is the central field potential incorporating the nuclear contribution $-2Z/r$ and the electron interaction. The exchange part of electron interaction is taken into account in $U_{eff}(r)$ effectively by statistical methods [16]. In Eq. (2.1) the term containing the squared sum of ε_{nl} and $U_{eff}(r)$ describes the relativistic correction to the potential arising from the dependence of electron mass on velocity. The term containing the δ symbol $\delta(l,0)$ describes a correction for the electron contact interactions with nucleus and among themselves.

As it is noticed in [10], one can derive the same equations out of the exact relativistic DF equations [in order to use the same definitions of ε_{nl} and potentials as in Eq. (2.1) and the usual HF equations, the additional multipliers $\frac{1}{2}$ are included]

$$\frac{dP(nlj|r)}{dr}=-\frac{\kappa}{r}P(nlj|r)+\alpha\left\{\left[\frac{2}{\alpha^2}-\frac{1}{2}\varepsilon_{nlj} -\frac{1}{2}V_{DF}(nlj|r)\right]Q(n\bar{l}j|r)-\frac{1}{2}\chi_{DF}(n\bar{l}j|r)\right\}, \tag{2.2}$$

$$\frac{dQ(n\bar{l}j|r)}{dr}=\frac{\kappa}{r}Q(n\bar{l}j|r)+\alpha\left\{\left[\frac{1}{2}\varepsilon_{nlj}+\frac{1}{2}V_{DF}(nlj|r)\right]P(nlj|r) +\frac{1}{2}\chi_{DF}(nlj|r)\right\}. \tag{2.3}$$

Here $P(nlj|r)$ and $Q(n\bar{l}j|r)$ are the large and small components of a radial wave function, respectively, ε_{nlj} denotes the relativistic single-electron energy, $V_{DF}(nlj|r)$ is a direct part of the potential including both the interaction with nucleus and the electron interaction, $\chi_{DF}(n\bar{l}j|r)$ and $\chi_{DF}(nlj|r)$ are the exchange parts of the potential, $\kappa=(2j+1)(l-j)$, $\bar{l}=2j-l$.

Within the relativistic Dirac-Fock approach the direct potential, being the same for the large and the small components, is (for simplicity let us consider the equations averaged over all the states of the investigated relativistic configurations)

$$V_{DF}(nlj|r)=-\frac{2Z}{r}+\frac{2}{r}\left\{\sum_{n'l'j'}[N_{n'l'j'} -\delta(nlj,n'l'j')]Y_0(n'l'j',n'l'j'|r) +\sum_{k>0}\frac{2}{N_{nlj}}f_k(j^{N_{nlj}})Y_k(nlj,nlj|r)\right\}. \tag{2.4}$$

The exchange potential for the large component can be written as follows:

$$\chi_{DF}(n\bar{l}j|r)=\frac{2}{r}\sum_{nlj\neq n'l'j'}\left\{\sum_k\frac{g_k(j^N,j'^{N'})}{N_{nlj}}Y_k(nlj,n'l'j'|r)\right\} \times Q(n'\bar{l}'j'|r) \tag{2.5}$$

and for the small component as

$$\chi_{DF}(nlj|r)=\frac{2}{r}\sum_{n'l'j'\neq nlj}\left\{\sum_k\frac{g_k(j^N,j'^{N'})}{N_{nlj}}Y_k(nlj,n'l'j'|r)\right\} \times P(n'l'j'|r). \tag{2.6}$$

$N_{n'l'j'}$ denotes the number of electrons in the subshell, f_k and g_k are the averaged angular coefficients. Here Y_k are potential functions appearing by variation of the radial integrals of electrostatic interaction of electrons

$$Y_k(nlj,n'l'j'|r)=r^{-k}\int_0^r x^k[P(nlj|x)P(n'l'j'|x) +Q(n\bar{l}j|x)Q(n'\bar{l}'j'|x)]dx +r^{k+1}\int_r^\infty\frac{1}{x^{k+1}}[P(nlj|x)P(n'l'j'|x) +Q(n\bar{l}j|x)Q(n'\bar{l}'j'|x)]dx. \tag{2.7}$$

Since the small component $Q(n\bar{l}j|r)$ contains a factor α, the potential function Y_k and all the potentials in conformity include the terms proportional to the square of the fine structure constant.

In order to proceed to the quasirelativistic approximation it is necessary to get rid of the small component of the radial wave function and to interpret the large component in terms of the usual radial orbital. Here in order to get the equations of the form (2.1) one must abandon the exchange interactions already in the Dirac-Fock equations and introduce instead the effective potentials (it is implied that the discontinuity at the nodes of radial orbitals is smoothed out)

$$U_P(nlj|r) = V_{DF}(nlj|r) + \frac{\chi_{DF}(n\bar{l}j|r)}{Q(n\bar{l}j|r)}, \tag{2.8}$$

$$U_Q(nlj|r) = V_{DF}(nlj|r) + \frac{\chi_{DF}(nlj|r)}{P(nlj|r)}. \tag{2.9}$$

Then it is necessary to substitute these potentials into Eqs. (2.3) and (2.4), respectively. For further transformations the following assumption is made:

$$U_P(nlj|r) = U_Q(nlj|r) \equiv U_{eff\ DF}(nlj|r). \tag{2.10}$$

Now one can obtain the following equation by expressing the small component from Eq. (2.2) through the large one and substituting it into Eq. (2.3)

$$\begin{aligned}\biggl[&\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U_{eff\ DF}(nlj|r) - \varepsilon_{nlj} + \frac{\alpha^2}{4}[\varepsilon_{nlj} \\ &+ U_{eff\ DF}(nlj|r)]^2 + \frac{\alpha^2}{4}\biggl(1 - \frac{\alpha^2}{4}[\varepsilon_{nlj} \\ &+ U_{eff\ DF}(nlj|r)]\biggr)^{-1}\frac{dU_{eff\ DF}(nlj|r)}{dr}\biggl(\frac{d}{dr} \\ &- \frac{X_{lj}+1}{r}\biggr)\biggr]P(nlj|r) = 0.\end{aligned} \tag{2.11}$$

Here $X_{lj} \equiv j(j+1) - l(l+1) - s(s+1) \equiv -\kappa - 1$. As it has been mentioned before, Y_k can be represented in the form of two terms, one of which is proportional to α^2 and is calculated by the integration of the small components. Then one can write down

$$U_{eff\ DF}(nlj|r) = U_{eff}(nlj|r) + \alpha^2 U_{eff,rel}(nlj|r). \tag{2.12}$$

After substitution of (2.12) into (2.11) and truncation of the terms containing the fourth power of α the resulting equation becomes

$$\begin{aligned}\biggl[&\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U_{eff}(nlj|r) - \frac{\alpha^2}{4}U_{eff,rel}(nlj|r) - \varepsilon_{nlj} \\ &+ \frac{\alpha^2}{4}[\varepsilon_{nlj} + U_{eff}(nlj|r)]^2 + \frac{\alpha^2}{4}\biggl(1 - \frac{\alpha^2}{4}[\varepsilon_{nlj} \\ &+ U_{eff}(nlj|r)]\biggr)^{-1}\frac{dU_{eff}(nlj|r)}{dr}\biggl(\frac{d}{dr} - \frac{X_{lj}+1}{r}\biggr)\biggr]P(nlj|r) \\ &= 0.\end{aligned} \tag{2.13}$$

In a strict sense this equation implicitly contains high powers of the fine structure constant because of the denominator of the contact term. However, the neglect of the denominator leads to the absurd results when solving the equations [10]. The equation still depends on the electron total momentum j. In order to abandon this dependence it is necessary to perform averaging using the conventional expression

$$x_{nl} = \frac{1}{4l+2}\sum_{j=l-1/2}^{l+1/2}(2j+1)x_{nlj} \equiv \frac{2lx_{nlj_-} + (2l+2)x_{nlj_+}}{4l+2}, \tag{2.14}$$

where x_{nl} denotes any physical characteristic. After such averaging, Eq. (2.13) becomes

$$\begin{aligned}\biggl[&\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - U_{eff}(nl|r) - \frac{\alpha^2}{4}U_{eff,rel}(nl|r) - \varepsilon_{nl} \\ &+ \frac{\alpha^2}{4}[\varepsilon_{nl} + U_{eff}(nl|r)]^2 + \frac{\alpha^2}{4}\biggl(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} \\ &+ U_{eff}(nl|r)]\biggr)^{-1}\frac{dU_{eff}(nl|r)}{dr}\biggl(\frac{d}{dr} - \frac{1}{r}\biggr)\biggr]P(nl|r) = 0.\end{aligned} \tag{2.15}$$

Now none of the characteristics in (2.15) do depend on j, and the parameter X_{lj} sums to zero and meets the well-known property of the spin-orbit interaction.

It is necessary to compare Eq. (2.15) with the quasirelativistic equation (2.1) in order to understand what other simplifications are needed. First, it is necessary to omit the relativistic term in the potential

$$U_{eff,rel}(nl|r) = 0, \tag{2.16}$$

which is defined through the small component of the wave function, therefore it is impossible to evaluate it. Second, one must include the delta symbol $\delta(l,0)$ into the term describing the contact interactions that correspond with the BP approximation for the electron interaction with the nucleus.

Thus in order to obtain the quasirelativistic equations (2.1) from relativistic DF equations it is necessary to assume the following:

(1) possibility of describing the interactions using the effective potentials (2.8) and (2.9);

(2) equality of the effective potentials of the large and the small components (2.10);

(3) possibility of rejecting the account of some parts of relativistic effects (2.16);

(4) possibility of attributing the delta symbol $\delta(l,0)$ to all contact interactions taken into account.

Statistical methods are used to describe the electron exchange interaction potential rather often while solving equations [10]. However, the possibility of existence of the equality

$$\frac{\chi_{DF}(n\bar{l}j|r)}{Q(n\bar{l}j|r)} = \frac{\chi_{DF}(nlj|r)}{P(nlj|r)}, \tag{2.17}$$

following from (2.10), seems to be not quite justified. It becomes especially obvious when taking into consideration that large and small components contain different numbers of nodes and their locations do not coincide. At the same time there is no necessity of introducing effective potentials [17]. It is possible to get rid of the direct presence of the small component in the equation for the large component by substituting the expression for $Q(n\bar{l}j|r)$ from (2.2) into Eq. (2.3) without employing (2.8)–(2.10). As a result one obtains

$$\begin{aligned}&\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-V_{DF}(nlj|r)-\varepsilon_{nlj}\right\}P(nlj|r)-\chi_{DF}(nlj|r)\\ &\quad+\frac{\alpha^2}{4}[\varepsilon_{nlj}+V_{DF}(nlj|r)]^2P(nlj|r)+\frac{\alpha^2}{4}[\varepsilon_{nlj}\\ &\quad+V_{DF}(nlj|r)]\chi_{DF}(nlj|r)+\frac{\alpha^2}{4}\Bigg(1-\frac{\alpha^2}{4}[\varepsilon_{nlj}\\ &\quad+V_{DF}(nlj|r)]\Bigg)^{-1}\frac{dV_{DF}(nlj|r)}{dr}\left(\frac{d}{dr}-\frac{X_{lj}+1}{r}\right)P(nlj|r)\\ &\quad+\frac{\alpha}{2}\left(\frac{d}{dr}+\frac{X_{lj}+1}{r}\right)\chi_{DF}(n\bar{l}j|r)\\ &\quad-\frac{\alpha^2}{4}\left(1-\frac{\alpha^2}{4}(\varepsilon_{nlj}+V_{DF}(nlj|r))\right)^{-1}\\ &\quad\times\frac{dV_{DF}(nlj|r)}{dr}\frac{\alpha}{2}\chi_{DF}(n\bar{l}j|r)=0.\end{aligned}\tag{2.18}$$

Furthermore, the same as in deriving of Eq. (2.15), it is necessary to explicitly express the dependence of relativistic potentials on α

$$V_{DF}(nlj|r)=V(nlj|r)+\alpha^2V_{rel}(nlj|r),\tag{2.19}$$

$$\chi_{DF}(nlj|r)=\chi(nlj|r)+\alpha^2\chi_{rel}(nlj|r),\tag{2.20}$$

and to keep only the terms containing α in the power not higher than the second one. Then it is necessary to perform the averaging over the possible values of the electron total momentum (2.14). The resulting equation appears as follows:

$$\begin{aligned}&\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-V(nl|r)-\varepsilon_{nl}\right\}P(nl|r)-\chi(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}\\ &\quad+V(nl|r)]^2P(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}+V(nl|r)]\chi(nl|r)+\frac{\alpha^2}{4}\Bigg(1\\ &\quad-\frac{\alpha^2}{4}[\varepsilon_{nl}+V(nl|r)]\Bigg)^{-1}\frac{dV(nl|r)}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)P(nl|r)\\ &\quad-\alpha^2V_{rel}(nl|r)P(nl|r)-\alpha^2\chi_{rel}(nl|r)+\frac{\alpha}{2}\left(\frac{d}{dr}+\frac{1}{r}\right)\chi(n\bar{l}|r)\\ &=0.\end{aligned}\tag{2.21}$$

The last three terms of Eq, (2.21) can be calculated using only the small component of the radial orbital therefore one must exclude them from the equation. The abandonment of the first two terms of these fully agrees with (2.16). Exclusion of the last term of the equation, which is also proportional to α^2 due to presence of the small component in description of $\chi(n\bar{l}|r)$ (2.5), leads to elimination of the exchange contact interaction accounted for in (2.1) for s electrons through the effective potential. The direct $V(nl|r)$ and exchange $\chi(nl|r)$ potentials obtained in the equation coincide with corresponding potentials of the usual HF equations. Finally the sought equation appears as

$$\begin{aligned}&\left\{\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}-V(nl|r)-\varepsilon_{nl}\right\}P(nl|r)-\chi(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}\\ &\quad+V(nl|r)]^2P(nl|r)+\frac{\alpha^2}{4}[\varepsilon_{nl}+V(nl|r)]\chi(nl|r)+\frac{\alpha^2}{4}\Bigg(1\\ &\quad-\frac{\alpha^2}{4}[\varepsilon_{nl}+V(nl|r)]\Bigg)^{-1}\frac{dV(nl|r)}{dr}\left(\frac{d}{dr}-\frac{1}{r}\right)P(nl|r)=0.\end{aligned}\tag{2.22}$$

A comparison of the derived equation with the quasirelativistic equation (2.1) reveals, that here a nonrelativistic potential appears. It is also possible to get the same potential in Eq. (2.1) by rejecting the use of effective potential in the nonrelativistic term of the equation. An interesting fact is that in the relativistic part of the equation the potential describing dependence of mass on velocity splits into the direct and exchange parts and the contact term contains the exchange potential neither within the derivative nor in the denominator.

While solving the equation, as in previous papers [14,15,17], the following nucleus charge density distribution was used [13]

$$\rho(x)=\frac{3Z}{4\pi r_{nuc}^3}\left[\frac{21}{8}-\frac{63}{8}\left(\frac{r}{r_{nuc}}\right)^4+\frac{21}{4}\left(\frac{r}{r_{nuc}}\right)^6\right],\quad r<r_{nuc}.\tag{2.23}$$

The radius r_{nuc} of a boundary of nucleus is defined so that at the center of nucleus the charge density is approximately equal to the density obtained by using the Fermi distribution. This is the distribution usually used for solving DF equations [18,19]. In our case r_{nuc} exceeds the radius of nucleus being used in the model of a uniformly charged ball by approximately 20%.

The charge density distribution (2.23) leads to the following expression for the potential:

$$\begin{aligned}V(x)=\frac{1}{16}\frac{Z}{r_{nuc}}\Bigg[&-63+42\left(\frac{r}{r_{nuc}}\right)^2-18\left(\frac{r}{r_{nuc}}\right)^6\\ &+7\left(\frac{r}{r_{nuc}}\right)^8\Bigg],\quad r<r_{nuc}.\end{aligned}\tag{2.24}$$

This potential is used both for description of the electrostatic interaction with the nucleus and for description of all the relativistic effects inside the nucleus. The expression (2.24) is also used to calculate the integrals inside the nucleus. The use of the potential (2.24) provides for simple expansion of ROs in powers of the radial variable in the nucleus region [14] and ensures a correct behavior of ROs when solving the equations in the outer region. For solving Eq. (2.22) and the equations below the same method as in the case of hydrogenlike ions described in [14,15] is used. This method is similar to the one used for solving conventional HF equations [4].

III. CALCULATIONS FOR HELIUMLIKE IONS

As it is seen by comparing Eqs. (2.1) and (2.22), the main differences appear while taking into account the exchange interaction between electrons. In order to neutralize the differences the calculation of the ground state of heliumlike ions is discussed in this section. Since the exchange potentials do not appear and $\delta(l,0)$ is equal to 1 for the configuration $1s^2$, the differences between the results of solutions of Eq. (2.1) obtained using the code [10] (hereinafter these results are denoted by CW) and the solutions of Eq. (2.22) provided by our own code can arise only from the account of the finite size of the nucleus in our program. The obtained results are also compared with the results of solving the DF equations by using the code [20], where the finite size of nucleus is taken into account as well, and with the results of solving the conventional HF equations [21] (these results are named HF after the type of the used Ros: if the energies are calculated in the Breit-Pauli approximation they are marked BP).

In the code based on [10] the energy of an atomic configuration in quasirelativistic approximation is determined through the sum of the generalized one-electron integrals and the usual Slater integrals. In the case of heliumlike ions under consideration the energy is written down as follows

$$E(1s^2) = 2I_{QR}(1s) + F_0(1s,1s). \tag{3.1}$$

Here $F_0(1s,1s)$ is Slater integral. $I_{QR}(1s)$ represents a generalized integral which contains both all the one-electron interactions and all the relativistic corrections, as it follows from description of the method [10] and the obtained results. The integral can be expressed as

$$I_{QR}(nl) = I(nl) + \frac{\alpha^2}{4}I_{mv}(nl) + \frac{\alpha^2}{4}I_c(nl), \tag{3.2}$$

where $I(nl)$ is a usual integral of the electron kinetic energy and the interaction energy with nucleus; $I_{mv}(nl)$ denotes the relativistic energy correction due to dependence of electron mass on velocity. When solving Eq. (2.22) this integral is determined as

$$\begin{aligned} I_{mv}(nl) = -\frac{1}{2}\int_0^\infty & P(nl|r)\{[\varepsilon_{nl} + V(nl|r)]^2 P(nl|r) \\ & + [\varepsilon_{nl} + V(nl|r)]\chi(nl|r)\}dr. \end{aligned} \tag{3.3}$$

$I_c(nl)$ is assigned to the contact interaction correction and is expressed from (2.22) as follows:

$$\begin{aligned} I_c(nl) = -\frac{1}{2}\int_0^\infty & P(nl|r)\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\right)^{-1}\frac{dV(nl|r)}{dr} \\ & \times\left(\frac{d}{dr} - \frac{1}{r}\right)P(nl|r)dr. \end{aligned} \tag{3.4}$$

The energy definition (3.1) is used to calculate the data presented in Table I. In this table the energy values are compared with the energies obtained within the DF approach. For completeness of comparison this table also contains the energy values calculated within the conventional nonrelativistic HF approximation and in BP approach using the same HF functions. The comparison of the last two values allows us to evaluate the influence of relativistic corrections on the total energy of configuration.

TABLE I. Total energies of heliumlike ions (a.u.).

Z	E_{DF}	$E_{(2.22)}$	E_{CW}	E_{BP}	E_{HF}
4	−13.61400	−13.61400	−13.61404	−13.61333	−13.61130
10	−93.98276	−93.98277	−93.98346	−93.97039	−93.86111
30	−892.0663	−892.0671	−891.8018	−891.4699	−881.3610
50	−2556.309	−2556.316	−2552.701	−2548.914	−2468.861

As it is seen in Table I, both E_{CW} and $E_{(2.22)}$ are in very good agreement with the DF results, essentially exceeding the accuracy obtained in BP approach for high ionization degrees. At the same time, for a small nuclear charge CW gives energies slightly lower than DF and for large values of $\boldsymbol{Z}$ it is somewhat inferior in the accuracy than our results. Most likely this is related to the features of calculations of $\boldsymbol{ns}$-radial orbitals in the vicinity of the origin that are implemented in [10]. As it is shown in [14], while solving Eq. (2.1) for hydrogenlike ions, in the case of the small charge nuclei the usage of program [10] for the s electrons yields the values of one-electron energies that fall below both the corresponding values given by the solutions of Dirac equations [1] and the solutions of DF equations that take into account the finite size of nucleus [20]. In the case of s electrons in hydrogenlike ions [14] the differences between the solutions of (2.22) and the solutions of DF equations are rather small and most likely they are related to the different models of the nucleus used. In the case of heliumlike ions under consideration the difference between DF results and our ones is slightly larger. At the same time the obtained energy values are little lower than the E_{DF} over the entire range of $\boldsymbol{Z}$. Most likely the discussed differences depend on the insufficiently correct account of the two-electron contact interaction.

Within the BP approach three types of contact interactions are considered. These imply the one-electron contact interaction with nucleus and two electron interactions: electron-contact and spin-contact ones. One can obtain the integral of contact interaction with the nucleus from (3.4) substituting the derivative of the full direct potential with a derivative of the potential created only by a nucleus:

$$\begin{aligned} I_{Zc}(nl) = \int_0^\infty & P(nl|r)\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\right)^{-1}\frac{d(Z/r)}{dr} \\ & \times\left(\frac{d}{dr} - \frac{1}{r}\right)P(nl|r)dr. \end{aligned} \tag{3.5}$$

It is necessary to mention, that the denominator is usually omitted while calculating the integral using the conventional

TABLE II. Integrals R_c and differences of contact integrals ΔI_c of heliumlike ions (a.u.).

Z	R_c	ΔI_c
4	0.000333	−0.000333
10	0.006088	−0.006079
30	0.186187	−0.183506
50	0.994034	−0.965157

HF functions, and this results in the possibility of integrating (3.5) by parts

$$I_{Zc}^{HF}(nl) = \delta(l,0)\frac{1}{2}Za_0^2(nl). \tag{3.6}$$

Here $a_0(nl)$ determines the slope of the HF radial orbital at the origin. Within our approach the absence of denominator in (3.5) leads to obviously incorrect results. Furthermore, even by neglecting the denominator it is impossible to obtain a simple expression, since in the region of nucleus the potential is not of a Coulomb type but is estimated by formula (2.24) both while calculating the integral (3.5) and solving the equation.

As is known, within the conventional BP approximation [2] there is a relation between the diagonal matrix elements of the spin-contact (sc) and the electron-contact (ec) terms

$$\langle K\upsilon LS \| H_{sc} \| K\upsilon LS\rangle = -2\langle K\upsilon LS \| H_{ec} \| K\upsilon LS\rangle. \tag{3.7}$$

Here K and υ denote the configuration and additional quantum numbers. It means that the spin-contact interaction is twice as large as the electron-contact one and is of opposite sign. Within the conventional BP approximation these two interactions are taken into account simultaneously through the correction of Slater integrals expressed as follows:

$$R_c(nl,n'l') = \int_0^\infty \frac{1}{r^2}P^2(nl|r)P^2(n'l'|r)dr. \tag{3.8}$$

Thus the energy of the ions under consideration within the BP approximation should be written in the form

$$E_{BP}(1s^2) = 2\left(I(1s) + \frac{\alpha^2}{4}I_{mv}(1s) + \frac{\alpha^2}{4}I_{Zc}(1s)\right) + F_0(1s,1s) + \frac{\alpha^2}{4}R_c(1s,1s). \tag{3.9}$$

In order to evaluate the influence of conversion of the energy definition (3.1) into (3.9) on the energy value, the values of integrals R_c and the doubled values of differences of integrals I_c and I_{Zc}

$$\Delta I_c(1s) = 2[I_c(1s) - I_{Zc}(1s)] \tag{3.10}$$

are given in Table II. If the energy definition (3.1), derived from Eqs. (2.22), is in good agreement with the BP approach, the values of quantities presented in the table must be sufficiently close. Indeed, their absolute values coincide to a high degree, especially keeping in mind that the denominator, which exists in the definitions of integrals (3.4) and (3.5), is absent in (3.8). However, R_c and ΔI_c have opposite signs. Consequently, the energy values must be increased by a quantity approximately equal to two R_c integrals while changing the definition of energy from (3.1) to (3.9) in agreement with the BP approximation. Since the relation (3.7) holds, therefore the spin-contact interaction, which raises the configuration energy value, is not taken into account in expression (3.1).

From the statement above it follows that the good coincidence of the energy values E_{CW} and $E_{(2.22)}$ in Table I is caused not by a high accuracy of Eq. (2.22) but rather by a quite random compensation of the unaccounted relativistic corrections both of the order of α^2 and of higher orders. It is clearly seen from Table II that the spin-contact electron interaction correction raises the configuration energy by almost two atomic units when $Z=50$.

It is necessary to mention that the values of integrals $F_0(1s,1s)$ calculated using the solutions of Eq. (2.22) are in good agreement with the corresponding integrals obtained when solving (2.1) for all the nuclear charge values. Thus it comes out that both Eqs. (2.1) and (2.22) do not take into account the spin-contact electron interaction, while the twice smaller electron-contact interaction is taken into account correctly. It becomes clear that the spin-contact interaction potentials have been lost when rejecting the term $U_{eff,rel}(nl|r)$ at developing (2.1) and the terms $V_{rel}(nl|r)$ and $\chi_{rel}(nl|r)$ at constructing of (2.22) due to impossibility of evaluating them within the quasirelativistic approach. In (2.22) the term describing the exchange part of an electron-contact interaction has also disappeared when omitting $\frac{\alpha}{2}(\frac{d}{dr}+\frac{1}{r})\chi(nl|r)$. It seems illogical to take into account the weaker electron-contact relativistic interactions in Eqs. (2.1) and (2.22) at the same time reject the twice-stronger spin-contact ones. The presence of the δ symbol $\delta(l,0)$ in the contact term of Eq. (2.1) reveals that even the electron-contact interactions are taken into account only for s electrons in the equation.

The simplest way out of this situation is the rejection of all relativistic two-electron interactions in the quasirelativistic equation (2.22). This results in the following equation:

$$\left\{\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(nl|r) - \varepsilon_{nl}\right\}P(nl|r) - \chi(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]^2P(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\chi(nl|r) + \delta(l,0)\frac{\alpha^2}{4} \times\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\right)^{-1}\frac{d(-2Z/r)}{dr}\left(\frac{d}{dr} - \frac{1}{r}\right)P(nl|r) = 0, \tag{3.11}$$

where only the nuclear potential is accounted in the contact term. In this context the inclusion of $\delta(l,0)$ into the equation becomes more valid. However there is a possibility of taking into account all two-electron contact interactions in the equation.

IV. TAKING INTO ACCOUNT THE TWO-ELECTRON PART OF CONTACT INTERACTION

As it is well known, within the BP approach the summary electron-contact and spin-contact interaction are taken into account through the relativistic corrections of Slater integrals [2]

$$F_k^{rel}(nl,n'l') = F_k(nl,n'l') + \frac{\alpha^2}{4}(2k+1)R_c(nl,n'l'), \qquad (4.1)$$

$$G_k^{rel}(nl,n'l') = G_k(nl,n'l') + \frac{\alpha^2}{4}(2k+1)R_c(nl,n'l'). \qquad (4.2)$$

The variation of integral $R_c(nl,n'l')$ with regard to radial orbital $P(nl|r)$ results in the formation of the function

$$Y_c(nl,n'l') = \frac{1}{r^2}P(nl|r)P^2(n'l'|r). \qquad (4.3)$$

The additional factor 2 appears when considering the interaction of non-equivalent electrons, and the factor 4 when the interactions inside a shell are investigated. In order to take into account the two-electron contact interaction it is sufficient to add up a function Y_c with a multiplier $\frac{\alpha^2}{4}(2k+1)$ to all the usual potential functions Y_k included into the direct and exchange potentials of Eq. (3.11). However, this implies a certain complication of the calculation and the necessity of obtaining two types of potentials, since the potentials describing the dependence of mass on velocity and the contact interaction with nucleus should not contain relativistic corrections to avoid the appearance of terms of a higher order of the fine structure constant.

There is another option. As it is clear from (4.1) and (4.2) the integrals R_c do not depend on the range k and coincide for the direct and exchange interactions. In this case the energy of the equivalent electron contact interaction can be expressed as

$$\Delta E_c(nl^N) = \frac{\alpha^2}{4}R_c(nl,nl)\sum_{k=0}^{2l}(2k+1)f_k(l^N,l^N). \qquad (4.4)$$

The energy of the inter-shell contact interaction is

$$\Delta E_c(nl^N,n'l'^{N'}) = \frac{\alpha^2}{4}R_c(nl,n'l')\left\{\sum_{k=0}^{2\,\min(l,l')}(2k+1)f_k(l^N,l'^{N'}) + \sum_{k=|l-l'|}^{l+l'}(2k+1)g_k(l^N,l'^{N'})\right\}. \qquad (4.5)$$

Here f_k and g_k denote the angular coefficients of the matrix elements of the electron electrostatic interaction energy operator. In the general case, they depend on the orbit and spin momenta of the considered term. However, the coefficients averaged over all the terms of the considered configuration are usually used while solving HF and analogous equations. This is particularly suitable for the two-electron contact interaction correction. The coefficients averaged over all terms of a configuration and, consequently, correctly describing the interaction of the closed shells have simple analytical expressions:

$$f_0(l^N,l^N) = \frac{N(N-1)}{2}, \qquad (4.6)$$

$$f_k(l^N,l^N) = -\frac{N(N-1)}{2(2l+1)(4l+1)}(l\|C^{(k)}\|l)^2, \quad k>0, \qquad (4.7)$$

$$f_k(l^N,l'^{N'}) = \delta(k,0)NN', \qquad (4.8)$$

$$g_k(l^N,l'^{N'}) = -\frac{NN'}{2(2l+1)(2l'+1)}(l\|C^{(k)}\|l')^2. \qquad (4.9)$$

Hereinafter $(l\|C^{(k)}\|l')$ denotes a submatrix element of the spherical function. Substituting (4.6) and (4.7) into the sum of the expression (4.4) and using the relation

$$\sum_{k=0}^{2l}(2k+1)(l\|C^{(k)}\|l)^2 = (2l+1)^2 \qquad (4.10)$$

one obtains the simple expression

$$\Delta E_c(nl^N) = \frac{\alpha^2}{4}\frac{N(N-1)(2l+1)}{2(4l+1)}R_c(nl,nl), \qquad (4.11)$$

which describes the averaged contact interaction inside a shell. Substituting (4.8) and (4.9) into (4.5) and using the relation

$$\sum_{k=|l-l'|}^{l+l'}(2k+1)(l\|C^{(k)}\|l')^2 = (2l+1)(2l'+1) \qquad (4.12)$$

one obtains an expression for the averaged contact interaction between shells

$$\Delta E_c(nl^N,n'l'^{N'}) = \frac{\alpha^2}{4}\frac{NN'}{2}R_c(nl,n'l'). \qquad (4.13)$$

An interesting fact becomes clear when forming (4.13): the averaged exchange part of the contact interactions is exactly half as small as the direct part and has an opposite sign. As a consequence, the total interaction (4.13) is twice smaller than the corresponding direct one.

The expressions (4.11) and (4.13) allow us to take into account the two-electron contact interactions by adding just one term to the direct potential of the quasirelativistic equation (3.11)

$$\left\{\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} - V(nl|r) - \frac{\alpha^2}{4}V_c(nl|r) - \varepsilon_{nl}\right\}P(nl|r) - \chi(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]^2P(nl|r) + \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\chi(nl|r) + \delta(l,0)\frac{\alpha^2}{4}\left(1 - \frac{\alpha^2}{4}[\varepsilon_{nl} + V(nl|r)]\right)^{-1}\frac{d(-2Z/r)}{dr}\left(\frac{d}{dr} - \frac{1}{r}\right)P(nl|r) = 0. \qquad (4.14)$$

This additional term is expressed as follows

$$V_c(nl|r) = \frac{2}{r^2}\left\{\frac{N(N-1)(2l+1)}{(4l+1)}P^2(nl|r) + \sum_{n'l'}\frac{NN'}{2}\frac{1}{r^2}P^2(n'l'|r)\right\} \quad (4.15)$$

and allows us to take into account all contact interactions between electrons.

As it is known, besides the considered two-electron contact interactions there are a whole series of other interactions ("spin-orbit," "orbit-orbit," "spin-spin") within the BP approach. These interactions appear only within and between the open shells. Because of this reason the averaging of them over all the states of the configuration results in the disappearance of such interactions in the averaged energy. Correspondingly, these interactions need not be included when solving QRHF equations.

V. COMPARISON OF THE RESULTS OBTAINED USING DIFFERENT APPROXIMATIONS

In this section the results of solving Eqs. (3.11), where the contact interaction between electrons is not taken into account at all, and Eqs. (4.14) with a complete account of these interactions are examined. The output from the solutions of DF equations [20] is considered as the precise data. In the tables, for simplicity of comparison, only these values are presented in full whereas others are shown in the form of deviations from DF values computed as

$$\Delta x = x - x_{DF}. \quad (5.1)$$

The one-electron values dependent on the total momentum j within DF approach are averaged according to the formula (2.14). In order to ascertain the role of relativistic corrections the results obtained using the solutions of HF equations are also presented. These results allow us to evaluate the influence of transition from the nonrelativistic ROs to the quasirelativistic ones on the characteristics under consideration. The deviations obtained with the CW results are presented only for one-electron values. It is done so because in this case the authors do not have the possibility of calculating the configuration energies within BP approach with taking the contact interactions correctly into account, in the same way as it has been done in all other cases. As it is known and as it follows from expressions (4.11) and (4.13), the complete inclusion of the contact interactions between electrons raises the total energy, whereas the inclusion of the spin-contact interaction only lowers it. The same as before, the configurations with closed shells are considered as an example that avoids the necessity of performing energy averaging over all configuration states.

As it is mentioned in the introduction, the nonorthogonality of ROs appearing because of the presence of relativistic terms in the potential is disregarded while solving the equations, the same as in [10]. However, after the completion of self-consistency the ROs with higher values of the principal quantum number n are orthogonalized to the ROs with the lower values of n through the Schmidt procedure. Then the overlap integrals were of the orders from 10^{-3} for inner shells to 10^{-5} for outer shells practically in all cases. Only for Z=90 the overlap integral is $\langle 1s|2s\rangle \approx 0.05$ and other overlap integrals of deepest inner shells are a little smaller. It is necessary to emphasize, that in all cases the orthogonalization procedure improved the coincidence with the DF results of both the total energies and the averaged values of the orders of the radial variable.

TABLE III. Deviations of the total energies of heliumlike ions (a.u.).

Z	$\Delta E_{(3.11)}$	$\Delta E_{(4.14)}$	ΔE_{BP}	$\Delta E_{(2.22)}$
4	0.00067	0.00067	0.00067	0.00067
10	0.01214	0.01208	0.01237	0.01216
30	0.36413	0.34678	0.59641	0.36891
50	1.86882	1.61823	7.39523	1.95219

As a first example, the data for the same heliumlike ions as in Sec. III are presented in Table III. This table contains only the deviations themselves, since the values E_{DF} are presented in Table I. In the last column of the table the deviations obtained using the solutions of Eqs. (2.22) and the energy expression (3.9) are presented. As it is seen from the table, all the approaches under consideration provide good coincidence with E_{DF} and practically coincide among themselves when the ionization degree is small. At the same time, the advantage of the solutions of Eqs. (4.14) becomes more clear after comparing these to the solutions of (3.11) and especially to the (2.22) as the charge of nucleus grows. In this case the obtained energy values are higher than those obtained using the solutions of Eqs. (2.22) with the energy expression (3.1).

The simplest configuration containing a close shell of electrons with $l>0$ is the neon one. The results of energy calculation of this configuration for different $\boldsymbol{Z}$ values are presented in Table IV. The results of the calculations for the ions with a high number of shells, mercurylike (Z=80,85,90), are presented in Table V. It is seen from these tables, that in all cases the use of the solutions of Eqs. (4.14) within the BP approach allows one to obtain the energy values in the best agreement with E_{DF}. It is pretty natural, since the relativistic corrections consistent with BP approach are taken into account most completely in Eqs. (4.14).

As it is seen from Tables III–V, the BP approach allows one to obtain the energy values in a relatively good agreement with the solutions of DF equations even in the cases of highly charged ions. This explains the wide popularity of the

TABLE IV. Deviations of the total energies of neonlike ions (a.u.).

Z	E_{DF}	$\Delta E_{(3.11)}$	$\Delta E_{(4.14)}$	ΔE_{BP}
20	−643.255	0.168	0.166	0.167
30	−1568.582	0.645	0.623	0.870
40	−2918.745	1.679	1.580	3.445
50	−4715.832	3.573	3.243	11.405

BP approach for calculations of the energy spectra of ions, including the highly charged ones. However, the initial HF orbitals themselves do not possess this property. Let us consider the one-electron energies ε_{nl} obtained by solving different equations in order to compare the properties of ROs. Such data are presented in Table VI for Hg I ($Z=80$). As it is seen from the table, the solutions of the three types of quasirelativistic equations give the results with comparatively small deviations. The ratio errors amount to a tenth or even hundredth fractions of a percent for all electrons when using Eqs. (3.11) and (4.14). This is a very good result especially in comparison to the HF functions. It is interesting that in some cases Eq. (3.11) gives better results, but in other cases Eq. (4.14) provides better agreement with the purely relativistic results. The same picture is observed when comparing the results obtained using the methods investigated in this work with the ones obtained while solving the equations with the help of the program [10]. Here and in all trial calculations the values ε_{1s} obtained by our methods are noticeably closer to the DF results than the CW output. Most likely this is due to the correct behavior of the RO in the vicinity of the origin, ensured by the account of the finite size of nucleus in the methods we develop. A comparison of deviations with those from the last column of the table shows that the use of the quasirelativistic ROs instead of the conventional HF ones enables us to obtain the tenth or even the hundredth times more accurate one-electron energies.

Other important one-electron characteristics are the averaged electron distances from the origin of coordinates

$$\bar{r}=\int_0^\infty P(nl|r)rP(nl|r)dr. \tag{5.2}$$

These data for neutral mercury are presented in Table VII. As is seen from the table all three quasirelativistic equations under consideration give quite similar deviations from the DF results in this case, too. Unfortunately, it seems that the correct taking into account of the two-electron contact interactions in (4.14) slightly worsens the value of the considered integral compared to the output of (3.11). Nevertheless, this deterioration is insignificant. The equations considered in this work provide better agreement with the DF compared to CW equations practically in all cases. It is very important that the compliance with the solutions of DF equations rises by a factor of ten compared to the data for HF functions especially in the case of the outer shells electrons. The major differences between HF and DF results appear in the cases of s electrons. The differences increase with the growth of the orbital quantum number l while the principal quantum number remains the same. In the cases of $4f$ and $5d$ shells the differences even change their sign. The quasirelativistic functions are in much better agreement with the relativistic ones and do not exhibit such simple tendency. This fact is very significant. The non-diagonal integral of the (5.2) type is used for calculations of the electric dipole transitions. The improvement of the integral caused by the switch from the usual HF equations to the quasirelativistic ones is very important since it is impossible to achieve the same response by taking into account the correlation effects.

In the last two tables only one ion is investigated. However, the same results are observed for different ionization degrees as well as a large number of other investigated configurations. In all cases the use of solutions of Eq. (4.14) enables us to obtain not only the total energy, but also the other RO characteristics with higher precision of the results.

TABLE V. Deviations of the total energies of mercurylike ions (a.u.).

Z	E_{DF}	$\Delta E_{(3.11)}$	$\Delta E_{(4.14)}$	ΔE_{BP}
80	−19648.87	22.23	16.66	215.67
85	−22904.64	25.73	17.37	320.37
90	−26488.16	27.65	15.16	468.22

TABLE VI. Deviations of the one-electron energies of the neutral mercury (a.u.).

nl	ε_{DF}	$\Delta\varepsilon_{(3.11)}$	$\Delta\varepsilon_{(4.14)}$	$\Delta\varepsilon_{CW}$	$\Delta\varepsilon_{HF}$
$1s$	3074.23228	3.48081	−1.34899	−8.32168	−295.55216
$2s$	550.25180	0.86044	0.23576	−0.09153	−79.51684
$2p$	479.05588	−1.20471	−1.54803	−1.00026	−26.87567
$3s$	133.11323	0.18411	0.05359	−0.09659	−19.97671
$3p$	111.90965	−0.26558	−0.33060	−0.18636	−7.56897
$3d$	87.38675	0.34171	0.31841	0.36116	0.75851
$4s$	30.64829	0.02356	−0.00653	−0.02901	−5.07496
$4p$	23.50038	−0.09205	−0.10484	−0.07198	−1.80149
$4d$	14.35022	0.04412	0.04215	0.04904	0.25936
$4f$	4.38080	0.01219	0.01516	0.00800	0.63156
$5s$	5.10305	−0.00224	−0.00731	−0.01258	−0.92104
$5p$	3.07396	−0.02435	−0.02568	−0.02095	−0.22309
$5d$	0.60482	0.00035	0.00080	0.00099	0.10938
$6s$	0.32803	−0.00179	−0.00217	−0.00270	−0.06699

TABLE VII. Deviations of $\bar{r}$ of the neutral mercury (a.u.).

nl	$\bar{r}_{DF}$	$\Delta\bar{r}_{(3.11)}$	$\Delta\bar{r}_{(4.14)}$	$\Delta\bar{r}_{CW}$	$\Delta\bar{r}_{HF}$
$1s$	0.01659	0.00001	0.00002	0.00008	0.00233
$2s$	0.06922	0.00026	0.00031	0.00088	0.01039
$2p$	0.06275	0.00087	0.00090	0.00084	0.00459
$3s$	0.17979	0.00013	0.00023	0.00101	0.02062
$3p$	0.18088	0.00060	0.00066	0.00122	0.01021
$3d$	0.16513	0.00022	0.00026	0.00017	0.00188
$4s$	0.39904	−0.00007	0.00014	0.00076	0.04025
$4p$	0.42317	0.00034	0.00047	0.00083	0.02015
$4d$	0.44812	−0.00042	−0.00036	−0.00012	0.00222
$4f$	0.48040	−0.00046	−0.00048	−0.00040	−0.01119
$5s$	0.91518	0.00008	0.00055	0.00112	0.09502
$5p$	1.04848	0.00014	0.00044	−0.00048	0.04693
$5d$	1.47172	−0.00273	−0.00281	−0.00272	−0.03904
$6s$	2.84340	0.00750	0.00969	0.01260	0.48501

VI. CONCLUSION

It is possible to form the quasirelativistic HF equations from the Dirac-Fock equations without employing the effective potential. In order to improve the equations it is necessary to introduce an additional potential describing the contact and the spin-contact electron interactions at the same time. After that the equations appear in the closest fit for the Breit-Pauli approach, within which the radial orbitals obtained using these equations should be used. Taking into account the finite size of nucleus is necessary for solving the equations. This enables us to obtain the correct expansions of radial orbitals at the origin and increases the accuracy of calculations. Both the total energies and the characteristics of radial integrals calculated using the obtained equations are in the best agreement with the solutions of the Dirac-Fock equations.

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[1] H. A. Bethe and E. E. Salpeter, *Quantum mechanics of one- and two- electron atoms* (Springer-Verlag, Berlin-Götingen-Heilderberg, 1957).
[2] Z. Rudzikas, *Theoretical atomic spectroscopy* (Cambridge University Press, 1997).
[3] V. Fock, Z. Physik **61**, 126 (1930).
[4] Ch. Froese-Fischer, *The Hartree-Fock method for atoms* (New York, John Wiley and Sons. 1977).
[5] B. Swirles, Proc. R. Soc. London **A152**, 625 (1935).
[6] J. P. Grant, Proc. Phys. Soc. London **86**, 523 (1965).
[7] J. P. Grant, Adv. Phys. **19**, 747 (1970).
[8] R. D. Cowan and D. G. Griffin, J. Opt. Soc. Am. **66**, 1010 (1976).
[9] D. D. Koeling and B. N. Harmon, J. Phys. C **10**, 3107 (1977).
[10] R. D. Cowan, *The theory of atomic structure and spectra* (University of California Press, 1981).
[11] P. Bogdanovich, Lith. J. Phys. **44**, 135 (2000).
[12] P. Bogdanovich, Nucl. Instrum. Methods Phys. Res. B **235**, 92 (2005).
[13] P. Bogdanovich and O. Rancova, Lith. J. Phys. **42**, 257 (2002).
[14] P. Bogdanovich and O. Rancova, Lith. J. Phys. **43**, 177 (2003).
[15] P. Bogdanovich, V. Jonauskas, and O. Rancova, Nucl. Instrum. Methods Phys. Res. B **235**, 145 (2005).
[16] R. D. Cowan, Phys. Rev. **163**, 54 (1967).
[17] P. Bogdanovich and O. Rancova, Lith. J. Phys. **46**, 153 (2006).
[18] J. P. Desclaux, Comput. Phys. Commun. **9**, 31 (1975).
[19] T. W. R. Johnson and K. T. Cheng, in *Atomic inner-shell physics*, edited by B. Craserman (Plenum Press, New York and London, 1985).
[20] K. G. Dyall *et al.*, Comput. Phys. Commun. **55**, 425 (1989).
[21] C. F. Fischer, Comput. Phys. Commun. **43**, 355 (1987).